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Journal of Composites and Compounds

A review of carbon nanotube/TiO₂ composite prepared via sol-gel method

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ABSTRACT

A R T I C L E I N F O R M A T I O N

A substantial review is performed in this work about the development and design of Carbon Nanotubes/Titanium Article history: Oxide nanocomposites. The fundamental method of sol-gel synthesis of Carbon Nanotubes is also reported here. Received 11 Second Single-Walled and Multi-Walled Carbon Nanotubes are reviewed here as well. Finally, different applications for Accepted 25 Or Coll 9 jource. All rights reserved. Peer review under responsibility of jource Keywords:

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1. Introduction

Carbon and its compounds are an important part of nature [4-6]. Familiarity with diamond and graphite, which are infinite periodic networks of solid carbon, gets back to ancient times. Recently, the discovery of the nanotubes, fullerenes, and graphene have attracted the attention of researchers [7-10]. Meanwhile, there are many research concentrating on carbon nanotubes (CNT), which can be considered as a cylinder created by curling a graphene sheet having a regular hexagon structure. CNT diameter can be several times smaller than its length [11].

A carbon nanotube was discovered by Iijima (1991) [12]. An ideal carbon nanotube has a hollow, seamless, tube-like structure and it consists of a hexagon carbon atom which is rolled by a slice layer of graphite surfaces [13]. Based on the number of graphite surface layers, they can be categorized as (I) single-walled carbon nanotube (SWCNT) and (II) multi-walled carbon nanotube (MWCNT) [14]. CNTs can be considered as ideal catalyst carriers due to nanoscale hollow tube property, significant specific surface area, unique electronic structure, good absorbability, and remarkable chemical stability [15, 16]. In addition, it

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is reported that carbon nanotubes can be used as a support to disperse functional materials to improve their additional properties such as conductivity, structure, activity, and surface area [17].

Besides, CNTs exhibit a micro-range electric connection with a lower amount of additives due to their high aspect ratio making them a promising additive for LIB electrodes. In this regard, numerous reports have implied that the rate and cycling performance of composite electrode materials with CNT additives have been enhanced [18-20]. Note that the surface chemistry of CNTs allows them to be functionalized for especial applications.

Due to the abovementioned properties, CNTs have generated considerable interest in various applications such as polymer reinforcements, electronics, sensors, catalysis gas storage, and energy storage materials [21]. There are also many publications reporting the synthesis process, characterization, and their usage in various applications [22].

2. SWNTs and MWNTs

As mentioned, CNTs can be divided into two main categories: SWNTs (one graphene sheet) and MWNTs (several graphene sheets). Both are similar, but MWCNTs consist of several concentric tubes, in which they are fitted inside each other. Generally, SWNTs and MWNTs have diameters of 0.7–2 nm and 2–100 nm, respectively, while their length can be several millimetres to micrometres [23].

As MWCNTs possess large surface area and mesoporous characteristics as well as chemical stability, they may be a good alternative for catalyst and photocatalyst materials [2–5].

The usage of MWCNTs is based on the combination of advantageous properties of individual SWCNTs including their mechanical, thermal, optical, and electrical characteristics. It is noteworthy that the differences between the structural features of SWCNTs and MWCNTs influence dispersion and solubility in the solutions [24]. In addition, SWNTs are better fillers than MWNTs due to 1) Higher surface area and aspect ratio of SWNTs that provides more interfacial bonding over MWNTs and 2) The diameter of MWNTs outer shells can bond with the matrix and the inner shells diameter can slide and rotate freely, which is held only by Vander Waals forces. However, the drawback is that MWNTs are easiest to synthesize and process in large scale. Fig.1 and Table 1 illustrate the properties and structure of SWCNTs and MWCNTs, respectively.

Recently, nanocomposites based on MWCNTs have attracted much attention due to their one-dimensional ideal molecular structure, strong adsorption capacities, high surface areas (>150 m² g⁻¹), good mechanical properties, chemical, and thermal stability as well as a dispersant of catalysts effectively [25, 26], enhanced electronic properties and a large capacity of electron-storage [27]. They are conductive with almost no resistance at room temperature [28].

In nanocomposites, TiO₂/MWCNTs for instance, MWCNTs would accept photon-excited electrons or mixtures as the reservoir of electrons



Fig. 1. Structures of SWCNTs and DWCNTs (2 wall).

Properties of SWCNTs and MWCNT

Properties	SWCNTs	MWCNTs
Specific Area (m ² /g)	400-900	200-400
Specific gravity (g/cm3)	0.8-1.3	1.8-2.6
Tensile Strength (Pa)	(3-50)×1010	(1-15)×10 ¹⁰
Young's modulus (Pa)	1000	1000
Electrical conductivity (S/cm)	102-106	10 ³ -10 ⁵
Thermal stability (°C)	550-650	550-650
Thermal conductivity (W/m*K)	3000-6000	2000-3000

and then transfer electrons rapidly that result in the prevention of the recombination of electron-hole pairs to produce more oxidants and radicals [29]. Considering all these, MWCNTs show the potential of increasing the activity of photocatalysis [30, 31].

3. Methods of preparation

Composites based on CNTs/TiO₂ have been synthesized by various methods such as sol-gel [11], mechanical combination of TiO₂, and CNTs [32], electrophoretic deposition [33], chemical vapor deposition [34] and electro-spinning [35]. However, some of these routes take a lot of time and are costly, and need higher pressure and temperature or multiple steps during the synthesis process [36, 37]. The electro-spinning and chemical vapor deposition techniques are almost hard to perform and need specific instrument so that quantifying the ratio between composite and compounds may get hard. Based on the preparation method, different physical properties and uniformity of the oxide coating would be obtained in the composite materials [3].

Compared with the other techniques, the sol-gel method is a lowcost [38-40] and facile strategy [41] to prepare various corresponding hybrid semiconductors. The sol-gel methods have been well developed, and various extended sol-gel techniques have been presented due to the controllability of the synthesis conditions and simplicity of this method [42, 43].

4. Sol-gel processing

Due to various advantages of sol-gel method, it can be used to prepare nanocomposites such as CNT/TiO_2 [44]. In order to produce a highly crystalline anatase structure of oxide from its amorphous form, a high-temperature thermal treatment is needed. The high temperature leads to serious changes in the surface structure and particle size that can lead to a collapse of the mesoporous structure [45]. Thus mild conditions are required to synthesize TiO₂/CNT nanocomposites.

The sol-gel process could be divided into two major steps, namely, organic and inorganic. The organic route is used for functionalization of CNTs while the other is used for known surfactants to disperse CNTs [46].

During the sol-gel method, a suspension of the CNTs and precursors is provided, which leads to effective dispersion and molecular interaction between them. Furthermore, during the gelification process, the composite materials are formed at 25 °C, which inhibits the initial dispersed state of CNTs. In addition, the sol-gel matrix contains many pores that are capable of encapsulating the metal nanoparticles [47], carbon nanotubes [48-53], and guest molecules [46, 54-56].

Sol-gel method provides the possibility of adding carbon nanotubes into the precursor carbide during the synthesis process that causes better connections between the carbon and nanotubes. Also, it provides a more uniform mesoporosity throughout the material [57].



Fig. 2. Schematic of preparation of TiO2-MWCNTs.

5. TiO₂

Titanium dioxide (TiO_2) is a photocatalyst known as an environmental-friendly component because of its great thermal and chemical stability, catalytic activity, strong oxidizing power, nontoxicity, low cost, and other outstanding properties [58, 59]. In addition, due to high redox potential, wide bandgap semiconductor, this photocatalyst has been studied during the past few years. The most important application of TiO_2 is in the decontamination of polluted waters with dyes from industries such as cosmetics and textile [60-62]. However, the activity of this material is low that limited its application. In addition, because of its high recombination ability and low quantum yield of photo-generated electron-hole pairs, it is poorly efficient [3, 17, 63, 64].

Therefore, in order to enhance its photocatalytic efficiency, various techniques have been proposed. Meanwhile, nano-architectured TiO_2 provides superior characteristics namely large specific surface area, excellent biocompatibility, and high uniformity [65, 66], and it has been applied in various fields like fuel cells [67, 68], hydrogen sensor [69-72], biosensors [73-77], and highly efficient photocatalysis [78-80].

According to previous research, MWCNTs have the potential of enhancing the TiO_2 photocatalytic efficiency because they act as a photosensitizer and expand the absorption band of photocatalysts to the range of visible spectrum [81, 82]. Studies on MWCNTs /TiO₂ composites have revealed that they can enhance the photocatalytic degradation activities of organic-based contaminants as well as dyes [17, 83] and NO_x oxidation [84] under UV irradiation [30].

6. TiO,-CNT nanocomposites

As mentioned above, the nanocomposites of TiO2 have attracted great attention due to their superiority concerning physical, thermal, chemical, mechanical, optical, and electrical applications [85, 86]. Fig. 2 shows the procedure of CNT/TiO₂ preparation [3].

The production of CNTs/TiO₂ nanocomposite enables the utilization of the advantages of both materials including adsorption capacities of CNT with the surface area of 200–400 m²/g, reduction of E_g after doping of TiO₂ with CNT, as well as photocatalytic activity of TiO₂. The synthesis of CNTs with TiO₂ leads to easier control of morphology. Thus, these materials are activated via visible light radiation, yet the corresponding mechanism of activity in visible light is implicit. Two mechanisms have been proved to play a role in the addition of CNT to TiO₂ particles. One is the change of the sensitization and bandgap energy of TiO₂ while the other corresponds to the action of CNT as the photosensitizer, which is related to the permission of a reduction process and transferring electrons into the conduction band of TiO₂. The combination of nano-scale TiO_2 with CNTs may improve the electron-hole charges separation due to irradiation [87].

Moreover, the resultant CNT with positive charge eliminates an electron from the TiO_2 valence band, and subsequently, the TiO_2 with a positive charge can participate in oxidation procedure as water in the formation of hydroxyl [12]. The carbon nanotube, coupled with TiO_2 , can improve the overall performance of the photocatalytic process through a synergistic effect. Studies on CNTs/TiO_2 nanocomposites have been carried out by researchers in the field of the treatment of contaminated air and water using heterogeneous photocatalysis [88-90], photo-reduction of CO_2 [91, 92], hydrogen evolution [93, 94], sensors devices [95] and dye-sensitized solar cells [96-98].

The TiO₂-MWCNTs nanocomposite with hetero-junction microstructure (NCs) exhibits a great capability in conducting electrons and adsorption of organic pollutants [99, 100]. Additionally, due to the unique morphology of MWCNTs, which are composed of multiple overlaid graphite layers, form a tubular-shaped conductive structure through which the separation of electron-hole pairs on the surface of TiO₂-MWCNTs NCs is facilitated [64].

The mass ratio of CNTs/TiO₂ and the temperature of calcination are considered to be among the most effective parameters on the activity of CNT/TiO₂ composites. In this regard, the mass ratio in the range of 1.5–20 % is reported optimum for CNT/TiO₂, which is based on the value of treated pollutants.

Carbon nanotubes are considered as a good additive to TiO_2 photocatalysts because of their unique physical and chemical characteristics, particularly high surface area, and electronic conductivity. The high electronic conductivity of the carbon halts hole-electron annihilation on the surface of titanium dioxide crystals, resulting in the increment of the catalysis effectiveness [11].

The synthesis of CNT/TiO₂ nanocomposite has attracted much attention in the studies due to its high potential application in fields such as renewable energy and enhanced photo-activated catalysis being used in solar cells, sensor devices photocatalysis, CO_2 photoreduction, hydrogen evolution, and photo-electro-catalysis [93, 96, 101].

TiO₂/CNT composites are synthesized using sol-gel, chemical vapor deposition, and hydrothermal method. Scientists prefer sol-gel methods even though the methods can cause random agglomeration of TiO₂ onto the surface of nanotubes, a heterogeneous of CNTs by TiO₂, non-uniform coating, showing pure carbon nanotube surfaces. The photocatalytic activity of CNT/TiO₂ composites synthesized by the hydrothermal method is lower than the ones synthesized by sol-gel methods [87].

7. CNT/TiO₂ preparation method

 CNT/TiO_2 nanocomposite has attracted the attention of researchers due to the decontamination of water and air by hydrogen evolution, heterogeneous photo-catalysis, dye-sensitized solar cells, and CO_2 photo-reduction. These composites have been prepared by various methods that uniformity of the physical properties and oxide coating of the composite materials are different based on the process of preparation. Sol-gel route usually results in the formation of a non-uniform coating and heterogeneous of CNT/TiO_2 nanocomposite that is showing random aggregation of TiO₂ onto the CNT surface due to bare carbon nanotube surfaces [102].

8. Applications

8.1. Photocatalysis

Nowadays, the depletion of fossil resources and serious water pollution are among worldwide concerns yet to be solved. The most favour-



Fig. 3. The schematic process of the elimination of pollution in water with photocatalyst.

able approaches for the remediation of wastewater are solar energy driving semiconductor photocatalysis; however, their practical use is limited because of the relatively low photocatalytic efficiency. To tackle this limitation, a variety of techniques have been proposed to produce advanced photocatalysts including the preparation of a composite catalyst consisting of semiconductors with various functional components such as atoms, individual semiconductors or metals that can lead to designing high-efficiency catalysts through a facile approach [103]. The schematic of pollution removal with photocatalyst is shown in Fig. 3.

Carbon nanotubes have many distinctive properties and are vastly used as a support material for many catalysts [103]. The applications of CNTs/TiO₂ photocatalysts have been studied by several researchers [84, 104]. Mechanism of photocatalytic degradation illustrated in Fig. 4.

Abd Hamid et al. [3] synthesized a MWCNT/TiO₂ with the modified sol-gel method. They studied the photocatalytic activity by photodegradation of reactive black 5 dye with ultraviolet light irradiation. Their result showed that the photocatalytic performance was improved significantly due to the high surface area of MWCNTs. This prevented electron-hole pair recombination.

Tseng et al. [105] investigated $\text{TiO}_2/\text{MWCNT}$ nanocomposite with the aim of the relation between acid pretreated and photocatalytic activity. Their results indicated that the photodegradation efficiency increases 10% with increasing acid pretreatment time. In addition, they reported that the optimal acid pretreatments time was 4h that proved the important role of acid pretreatment time on physicochemical properties.

In other work, Chen et al. [17] studied the MWCNT/TiO₂ composite. They observed that the removal of methylene blue by composite under UV irradiation is not only due to photocatalytic degradation of TiO₂ and MWCNT absorption property. The electron transfer between TiO₂ and MWCNTs affected removal efficiency.

Yang et al. [106] prepared a TiO_2/CNT with different CNT content by sol-gel process and hydrothermal treatment and investigated the photocatalytic performance of the composite. An et al. [30] characterized the TiO_2 -MWCNTs nanocomposites photocatalyst prepared with the solgel method. Their research aimed to find the degradation efficiency of plastic (polyethylene) by the composite. They observed that composite had an absorption band covering the wide UV-vis range that resulted in increasing the absorption property. Their results show that changing the MWCNTs amount could optimize the degradation efficiency.

Recently, Miandoab et al. investigated the photocatalytic activity of MWCNT/TiO₂ and pseudo-tube TiO₂ degradation of acetaldehyde under visible light and UV-visible. Their results showed that under visible irradiation, the optimum (highest activity) fraction for MWCNT in anatase TiO₂ is 30 wt. %. Quanjie Wang et al. investigated the morphological structures of MWCNT/TiO₂ nanocomposite. They observed that nanocomposite has good absorption in the ultraviolet and visible light regions. Their results proved the efficiency of 83% under ultraviolet ir-



Fig. 4. Photocatalytic mechanism of degradation over the MWCNTs/TiO2 nanocomposite.



Fig. 5. Schematic diagram of the difference between CNTs with and without acid treatment after a complete ALD cycle.

radiation and stability that can be used for wastewater treatment [107].

Huang et al. studied the effect of oxygen contacting functional on the surface of CNT and the rate of growth. They investigated the effect of shell thickness of CNT as a prominent factor to determine the degradation efficiency of methylene blue. The CNT with 22 nm thickness has higher degradation efficiency compared to others after UV irradiation [2]. The schematic of their experimental work is shown in Fig. 5.

Ashkaran et al. [108] studied the CNT/TiO₂ with several methods (simple, heat treatment, and UV illumination). They found that CNT–TiO₂ nanocomposites enhanced the visible light absorption and significantly improved the efficiency of photocatalytic under visible irradiation.

In other research conducted by Akhavan et al. [109], CNT-doped TiO_2 thin films with different TiO_2 contents were prepared, and the results showed the photo-inactivation of Escherichia coli (E. coli) bacteria. The preparation approach was the sol-gel method in the presence of nitric acid, followed by dip coating to obtain films. The attractive advantages of this method include inexpensive synthesis of TiO_2 -CNT hybrids, preventing the addition of extra linker molecules, oxidizing agents, expensive equipment, extended reaction times, and preserving the intrinsic properties of both TiO₂ and the CNTs.

Wang et al. [110] studied the photoactivity of these materials synthesized by the sol-gel method via the conversion of phenol from model aqueous solutions as a probe reaction. A synergistic effect was observed resulting from a strong interaction between TiO_2 nanoparticles and MWCNT. Yen et al. [84] compared the photocatalytic activity for NO oxidation for MWCNT– TiO_2 nanocomposite, which was obtained by sol-gel and the hydrothermal method. The results showed that the former had better photocatalytic activity than that of the latter method.

Nguyen et al. [11] studied SWCNT with TiO_2 nanoparticle. They report that the TiO_2 clusters are coalescence and flexible into larger clusters. Also, they suggested the enhancement of photocatalytic is due to a decrease of recombination ability of electron-hole pairs and an increase in photocatalytic activity of composite because of CNTs presence under



Fig. 6. Schematic of (a) TiO2-DWCNTs nanocomposites and (b) flexible DSSC synthetic process.

visible light.

A modified sol-gel route was used by Gao et al. [17] to deposit a uniform TiO_2 film on CNTs to produce a composite structure for enhanced photocatalytic activity. The films were formed through atomic layer deposition (ALD) that were highly conformal films with the capability of atomic-scale thickness control in comparison with sol-gel and other traditional processes such as physical vapor deposition, hydrothermal method, and chemical vapor deposition (CVD) [36].

Dalt et al. [111] designed a TiO₂/MWCNT for photocatalytic degradation of organic dye (methyl orange dye). They determined an optical characterization by diffuse reflectance and photoluminescence spectroscopies. The heat-treated sample at 500 °C has the highest photocatalytic activity under UV radiation.

Most efforts in the field of CNTs deal with aligned nanotube whiskers and single nanotube arrangements [63]. On the other hand, the high potential of TiO₂ as anode material for a new generation of lithium-ion batteries has attracted much attention. Li et al. [87] observed that electron-hole charges of TiO₂ improved by combining with CNT depend on the quality of TiO₂ and CNT interfacial content. Their results show that the thinner TiO₂ layer provides a lower distance for electron transfer to the core of CNT.

Fan et al. [112] investigated the photosynthesis performance of mesoporous TiO₂-CNT nanocomposite. Their result showed a 3 wt. % CNT nanocomposite at 700C has the best photoelectric property. Photocurrent density was equal to 0.88 mA cm2 on TiO₂/CNTs, which is higher than that for the sample without CNTs. Qing et al. [18] studied the electrochemical performance of TiO₂/CNT in lithium-ion batteries. The CNT/ TiO₂ exhibited 1.5 times greater conductivity than bare TiO₂ nanofiber and 1.6-3 times higher lithium diffusivity. Table 2 lists the recent works about the photocatalytic performance of TiO₂/CNT nanocomposite.

8.2. Biosensor

Shen et al. [113] used CNT/TiO_2 for electrochemical biosensing of cancer cells. They reported the significant increase in electrochemical signals on the electrode modified with cancer cells compared to bare carbon nanomaterial. Based on their results, the nanocomposite could accelerate the electron transfer rate and increase detection sensitivity.

8.3. Solar cells

A new generation of solar cells that has attracted much attention is dye-sensitized solar cells (DSCs) due to simple fabrication and high efficiency. Yen et al. [114] synthesized MWCNT-TiO, nanocomposites via a sol-gel method and studied the DSSC performance of the composite. They realized the importance of optimum CNT loading to obtain 4.62% efficiency. Cheng et al. [1] studied the application of $\text{TiO}_2/\text{MWCNT}$ in flexible dye-sensitized solar cells. They found that a certain value of composite could decrease the resistance in charge transport that results in an improvement in adsorption of dye. They also suggested that flexible DSSC contains 0.5 wt. % TiO_2/MWCNT obtain an energy conversion efficiency of 3.89%.

In other work, Abdullah et al. [115] used CNT/TiO₂ nanocomposite for the fabrication of thin-film at different annealing temperatures. The result showed that the particle was anatase and DSSC with photoanodes annealed at a higher temperature (550 °C) had the highest carrier efficiency (95%). Also, the lifetime of photoanodes with higher temperature was increased, and the effective recombination rate was decreased. Moreover, Tettey et al. [116] employed a layer-by-layer assembly using an amphiphilic surfactant for preparation of MWCNT–TiO₂ nanoparticles thin films and reported that the photocatalytic activity of the thin films produced by this method made them suitable for the production of a highly efficient dye-synthesized solar cell. The schematic of TiO₂-DWCNTs nanocomposites is illustrated in Fig. 6.

8.4. Antibacterial

Abbas et al. [117] investigated the antibacterial synthesize TiO_2 -CNT material. They reported the strong activity of TiO_2 -CNT in the absence of light. They compared different CNT contacting samples for antibacterial activity and some other properties. Their results show that by increasing CNT content, the antibacterial activity increase significantly.

Also, Koli et al. [64] studied the antibacterial activity of CNT/TiO_2 . They observed that nanocomposites have efficient antibacterial activity under visible light irradiation, whereas TiO_2 nanoparticles did not have any repressive influence on bacteria under visible light. The cytotoxicity study shows that the viability of bare TiO_2 nanoparticles was improved by CNT.

8.5. Other applications

Sanchez et al. investigated the difference of two deposition method, dip coating, and screen printing to obtain a $TiO_2/MWCNT$ sensor. Their results show that the dip-coated films have no oriented rutile and anatase planes in comparison to screen-printing [118]. Rodroguez et al. [119] investigated the effect of TiO_2 in order to improve the thermal stability of MWCNT in the oxidizing environment. Their results showed that the structure was a changed from anatase to rutile by increasing the tem-

Table 2.

с · с	1 4 4 1 4 6	CTO CONT	5 54	1 1 4 1
Summarize of some r	photocataivtic performanc	$e \text{ of } 110_2/\text{CNT}$ na	anocomposite with	sol-gel method

Light Source	Degraded Component	CNT Content (wt. %)	Performance	Ref.
UV irradiation	methylene blue	19	~2 times higher	[102]
UV light.	NO	-	1.67 times higher	[105]
UV-A irradiation	methylene blue	16	~ 2 times higher	[87]
UV–vis	polyethylene (PE) plastic	20	~ 1.3 times higher	[106]
UV- vis	polyethylene (PE) plastic	20	\sim 1.4 times higher	[30]
UV-visible light	Reactive Black 5 dye	20	\sim 3 times higher	[3]
UV-visible light and visible light	Acetaldehyde	30	~ 1.8 times higher	[107]
UV- vis	NO oxidation	0-8	~ 1.5 times higher	[84]
UV	MB	0.2	~ 1.5 times higher	[17]
UV- vis	Methyl orange	-	~ 1.83 times higher	[110]
UV and vis	-	50	~ 1.1 and 1.5 times higher	[11]
UV-visible	MB	-	\sim 5 times higher	[2]
visible light	Escherichia coli bacteria	-	~ 2.5 times higher	[108]
visible light	Escherichia coli bacteria	20	\sim 3 times higher	[109]
UV	dye	-	\sim 4 times higher	[111]
UV	Methyl orange	-	~ 1.38 times higher	[112]

perature of calcination. The specimens calcined at a higher temperature (1000 °C) have a higher resistance to oxidation.

9. Conclusions and future insights

This article aimed to review some of the significant works performed about CNT/TiO₂ nanocomposites synthesized via the sol-gel method for various applications. The preparation processes of CNTs were initially presented. In the following, two major types of CNTs, namely SWCNTs and MWCNTs, were studied. CNT/TiO₂ nanocomposite and its preparation processes, especially sol-gel, were reviewed in the next step. Ultimately, the authors introduced several of the major applications about this nanocomposite.

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Effect of Cu-substitution on the microstructure and magnetic properties of Fe-15%Ni alloy prepared by mechanical alloying

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A B S T R A C T	ARTICLEINFORMATION
In this study, nanostructured ($Fe_{85}Ni_{15}$) _{100-x} Cu _x (x = 0, 0.5, 1.5, 3 and 5) powders were synthesized via mechani-	Article history:
cal alloying process. The obtained phases, microstructure, and magnetic properties of these alloys were studied	Received 13 October 2019
by X-ray diffraction analysis (XRD), scanning electron microscopy (SEM), and vibration sample magnetometer	Received in revised form 25 October 2019
(VSM). XRD results indicated that after a suitable time of milling, Ni and Cu were homogeneously distributed in	Accepted 3 November 2019
the Fe matrix, and (bcc) α -(Fe(Ni-Cu)) solid solution was obtained. It was found that by increasing Cu content in	
the alloy, work hardening increased, and thus the size of grains decreased while the internal micro-strain increased.	Keywords:
Also, morphological observations indicated that the addition of Cu led to the formation of finer particles. Also,	Nano-crystalline alloys
VSM analysis showed that the addition of Cu into Fe-Ni alloys lowered Ms. On the other hand, the coercivity	Mechanical alloying
increased by increasing copper content up to 1.5 at. %.	Ball mill
	E. M. C. II.

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1. Introduction

Recently, nanostructured materials have attracted great attention due to their excellent and unique electrical, magnetic, optical, catalytic, mechanical, and biological properties for various applications [1-11]. Several techniques including electrodeposition, rapid solidification [12-14], gas condensation, solid-state processing like friction stir welding (FSW) and mechanical alloying (MA) have been utilized to make nanostructured materials [15].

Among various techniques for fabricating such materials [16-19], it has been found that the solid state processing have some advantages in comparison with the convectional casting or rapid solidification methods [20-23]. This method, as a solid-state and non-equilibrium technique, is capable of producing a wide range of microstructures containing nano-crystalline supersaturated solid solutions, quasi-crystalline intermediates and amorphous phases [15, 20, 21, 24]. Also, in contrast to other new techniques such as liquid quenching (or melt-spinning), the MA process is a controllable process and operates at low temperatures as well as having the capability of large scale production [25-30].

During the first stages of the MA process, the impression force of the balls can deform the powder particles plastically and create new surfaces allowing the particles to bond together and thus results in an increment in the size of the particle [31]. For hard powders like nanosilica, the FSW method could be used for the production of composite-based nanostructures [32], but for ductile powders that tend to agglomerate, the ball mill acts better than FSW. Therefore, a wide range of particle sizes

develops and the composite particles have a layered structure containing blends of the starting constituents. Further deformation, leads to strain hardening and hence fracture of particles by a fragmentation of fragile flakes and/or fatigue failure [33-36]. It is estimated that in the first few minutes up to an hour, the lamellar spaces typically become small and the crystallite size becomes nano-sized. After milling for a while, steady-state balance is obtained, between the rates of the welding and fracturing, at the same time because of the accumulation of strain energy, the particles reach a maximum hardness [20, 37]. As a result of the increased amount of cold working, the number of crystal defects (dislocation, vacancies, grain boundaries, stacking faults, etc.) increases with time and thus diffusivity of solute elements increases [38]. This leads to an increment in the defects and dislocations density which reduces the activation energy for diffusion. Hence, cold weld and fracture recurrence of powders in MA process make diffusion easier [39].

Iron is a good ferromagnetic material with a low resistivity that leads to large eddy current loss [40]. In addition, Fe-based nano-crystalline materials exhibit very suitable soft magnetic properties [41, 42], as well as high magnetization and low coercivity [43]. This makes them good candidates for several applications like magnetic sensors, magnetic clutches, magnetic shielding, etc. [44].

Magnetic iron-nickel alloys, generally called permalloys, are of excessive attention due to their magnetic properties, which makes them good candidates for use in automotive and nano-magnetic sensors [45-47].

Also, it is reported that a small amount of copper to Fe-Co alloys,

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Fe-Ni-Cu alloy Magnetic properties



Fig. 1. X-ray diffraction pattern of (a) powder mixture before milling and after 72 h milling (b) FNC (c) FNC0.5 (d) FNC1.5 (d) FNC3 (e) FNC5.



Fig. 2. Crystallite size as a function of copper content after milling for 72 h.

leads to the grain size decrease and recovers some of the most important soft magnetic properties. Although there are several studies about the addition of various elements to Fe-Ni alloys, there is no report about the addition of Cu to this system. Accordingly, the aim of the present work is to investigate the effect of Cu doping on the microstructural and magnetic properties of nanocrystalline Fe₈₅Ni₁₅ alloys.

2. Materials and methods

In this study, Fe, Ni, and Cu powders with an average particle size of 15 μ m, 10 μ m and 63 μ m, respectively, were supplied from Merck Co. The purity of Fe, Ni and Cu powders was 99.5%, 99.9% and 99.9%, respectively.

Firstly, the steel vials of the ball mill were loaded with special amounts of powders, in which the ball to powder weight ratio was about 20:1. Two kinds of stainless steel balls with a diameter of 20 and 10 mm were used to increase the welding and fracturing processes [48] and prevent the formation of the close-packed array [20].

The powders were mechanically alloyed in an inert (argon) atmosphere through a planetary ball mill (Fritsch, Pulverisette 4). Common milling speed of 350 rpm and milling time of 72 h was employed. Five samples of $(Fe_{85}Ni_{15})_{100-x}Cu_x$ (x = 0, 0.5, 1.5, 3 and 5) system were prepared with different copper contents (Table 1).

The milled powders were characterized by X-ray diffraction analysis (XRD), which was carried out by a Philips X'pert High Score diffractometer (Brukers D8 System Germany) using Cu k α ($\lambda = 0.1542$ nm). For all the XRD investigations, an angular range (2 θ) of 20° – 90° was used. The crystallite size and the internal strain were determined by the Williamson- Hall method (Eq. 1) as below [49, 50]:

$$\beta \cos\theta = 2\varepsilon \sin\theta + 0.9 \frac{\lambda}{p} \tag{1}$$

where is the full-width at half-maximum (FWHM) of a diffraction peak, θ is the Bragg angle, D is the grain size, ε is the lattice strain, and λ is the X-ray wavelength [51, 52]. The XRD peaks were fitted by four-variable Gaussian functions using the sigma plot V.12.0 software. β can be determined as follows (Eq. 2):

$$\beta^2 = \beta_m^2 - \beta_c^2 \tag{2}$$

where β_{c} is the instrument broadening and β_{m} is the measured half-



Fig. 3. Lattice strain change after 72 h milling for the samples with different contents of Cu.

width broadening.

The morphology, microstructure and particles size of the powder were obtained by scanning electron microscopy (SEM) test via a Philips XL30 instrument. The mean particle size of about 350 particles was calculated by image analyzer software of Clemex version V 3.5. The magnetic properties of the milled powder were measured at room temperature by using vibrating sample magnetometer (VSM) at the maximum field of 10 kOe.

3. Results and discussion

3.1. Microstructure

Fig. 1 shows the X-ray diffraction patterns of the mixture of initial powders and mechanically alloyed samples after milling for 72 h. It can be seen that the XRD patterns of the samples before milling have only the peaks corresponded to Fe, Ni, and Cu elements. On the other hand, after 72 h milling, there was no trace of Ni and Cu peaks in the XRD patterns. Reactions finished in the vial before milling completion and the final product was 100% solid solution of α -Fe(Ni-Cu). Since the atomic diffusion is time-dependent, sufficient milling time is required to obtain the final products. By increasing the Cu content, the diffraction peaks became broader and less intense. This represents the continuous decrease in the crystallite size and the introduction of lattice strain.

This broadening is due to the second-order internal stress that affects the crystals at the macroscopic level and leads to the broadening of diffraction peaks [53, 54]. Also, the decrease in peak intensity can be attributed to different lattice parameters of Ni and Cu, i.e., the solid solution is formed [55] and induced strain is caused by the plastic deformation [56]. After milling for 72 hours and subsequent increase in the Cu content, it was observed that the peak corresponding to the (110) phase alpha-Fe bcc, has been shifted towards lower angles. The reason is that by increasing the amount of copper, more copper is dissolved in the iron structure that leads to the change in lattice parameters. Also, the iron peaks are shifted toward lower angles which is due to the entrance of Ni and Cu atoms to the Fe structure that leads to formation of solid solutions of (Ni)-Fe and bcc Fe-(Ni, Cu). Kaloshkin et al. [57] showed that the milled alloy powder of Fe-10% Ni showed only the bcc phase. In addition, the slight shift may be caused by first-order internal stress at a macroscopic level by changing the lattice parameter [54, 58].

Repeated fracture and welding of particles having large contact surfaces are reduced at ambient temperature, which leads to the formation of solid-solution during the mechanical alloying [56]. Moreover, the

Table 1.

-	5 15 100 A A	
Sample	Cu content	Code
1	0	FNC
2	0.5	FNC0.5
3	1.5	FNC1.5
4	3	FNC3
5	5	FNC5



Fig. 4. Variation of lattice parameter after 72 h milling of samples with different contents of Cu.

density of defects increased during the severe deformation while the diffusion distance decreased which provides suitable diffusion paths for Ni and Cu atoms in the iron lattice [20, 59].

Fig. 2 represents the effect of copper content on the crystallite size of milled alloys. It can be noticed that by increasing Cu content, the crystallite size of alloys decreased from 18 to 8 nm. This can be related to the solubility of Cu atoms in the iron structure and its hardening effect. Smaller crystallite size would lead to higher strength and hardness [60].

It can also reduce the grain size of powders that occurs during severe plastic deformation that results in strain hardening [61, 62] [63]. Hamzaoui et al. [64] showed that by adding 10% nickel to iron, its crystallite size decreased to 10.4 nm after milling for 96 h. At the first stages of MA, a great amount of crystal defects e.g. dislocations are created. At longer milling time, higher dislocation density is formed which might lead to the formation of new boundaries inside nanoscale crystals [65].

Fig. 3 demonstrates the internal strain variation of Fe-(Ni, Cu) structure for different Cu contents after 72 h milling. As it is illustrated, by increasing the amount of copper content, a great increase was observed in the rate of internal strain at first but, at 1.5 at. % Cu, the amount of internal strain became a plateau.

Generally, the increase in micro-strain value might be due to the severely cold working and plastic deformation of powders. Commonly, during mechanical alloying defects are formed in the interface of grains [60, 66-69]. The increase in strain level has corresponded to high dislocations' density [70].

The volume fraction of grain boundaries (f_{gb}) in polycrystalline materials can be estimated as below:

$$f_{gb}^{-} = 1 - f_{g}$$
(3)
where f_{g} is the grain volume fraction given by:
$$f_{g}^{-} = \frac{(D-d)^{3}}{D^{3}}$$
(4)

where D represents crystallite size and d is the effective thickness of the grain boundary [65, 71, 72].

Table 2 lists the changes in grain boundaries' volume fraction versus

Table 2.

The volume fraction of grain boundaries for the samples with various contents of copper.

Sample	D (nm)	F _{gb} (%)
FNC	18	12
FNC0.5	15	14
FNC1.5	12	18
FNC3	10	21
FNC5	8	26

Cu content after 72 h milling. From table 2, it is obvious that as the copper content increased, the crystallite size decreased while f_{gb} increased. This is because of the grain boundaries' effect on the movement of dislocations.

Fig. 4 shows the variation of the lattice parameter (ao) with different copper contents after 72 h milling. According to the figure, the lattice parameter increased by increasing Cu content and reached a plateau at 5 %. This can be due to the saturation of Cu atoms in the Fe structure. Furthermore, the lattice expansion could be attributed to the dissolution of copper with a higher radius into the interstitial sites [73]. However, it could be due to the severe plastic deformation of the powders during MA [74], in which the dislocations are formed as well as sub-boundaries. This leads to faster diffusion of Cu into the Fe structure. Accordingly, during the mechanical alloying operation, lattice parameter difference, and concentration of defects such as dislocations and vacancies, result in an increment in the lattice parameter [68].

3.2. Morphology and Particle Size

Fig. 5 depicts the SEM micrographs of powder of all samples after 72 h milling. The relating average particle size of the powders is shown in Fig. 6. Accordingly, by increasing the content of copper, the average particle size decreased. The minimum average particle size was obtained about 3 μ m for 5 at. % of Cu. Powders became finer and particle size distribution was uniform with spherical and equal size shapes. It can be seen that the MA processing time was high enough to decrease the particle size distribution. Also, the powder had an almost spherical shape and the addition of Cu makes the particles more brittle which may cause higher grinding of powder and finer particles.

3.3. Magnetic properties

3.3.1. Saturation Magnetization

Fig. 7 depicts the variations of saturation magnetization after 72 h,



Fig. 5. SEM images of powders milled for 72 h containing (a) 0, (b) 1.5, (c) 3, and (d) 5 at.% Cu.



Fig. 6. Average particle size of the powders for samples with different amounts of Cu after 72 h milling.



Fig. 7. Saturation magnetization changes after 72 h milling for the samples with different contents of Cu.

for the milled samples with different contents of copper. It can be seen that the magnetization decreases slightly with increasing the Cu content that can be attributed to the diamagnetic nature of Cu in the structure [65, 75]. The introduction of diamagnetic moments into the specimens leads to the decrease in magnetic properties during the milling process [76] that would be due to the movement of domain walls [75] which can be affected by the defects induced by milling and can greatly hinder the wall movement through the defects. The decrease of crystallite size during the microstructure refinement leads to an increment in grain boundary volume fraction which, in turn, causes an increase in the amount of the atoms present in the grain boundary.

This is because of the low density of grain boundaries structure and higher interatomic distances between neighbor atoms that can decrease the effective magnetic moment by variation of the magnetic exchange interaction of the nearest atoms [77, 78]. On the other hand, due to the change in lattice parameter, the addition of copper leads to a remarkable expansion in the Fe lattice, i.e., the expansion of the lattice has a significant effect on the distance between atoms that are associated with a severe decrease in the saturation magnetization [79]. Slight increase of M_s can be due to the dominance of nanostructure effect over the negative effect of copper. Also, it can be attributed to the presence of surrounding Ni on Fe atoms. Furthermore, this can be corresponded to increment in contamination level due to long milling time [49] as well as the formation of defects that may negatively affect the ferromagnetic ordering [68].

3.3.2. Coercivity

Fig. 8 shows the variation of coercivity with different contents of copper after milling for 72 h. According to the figure, the coercivity first increased by increasing the Cu content, up to 1.5% (61.28 Oe), and then decreased to 32.26 Oe. The initial increment of the coercivity could be due to several factors such as higher residual stress and dislocation density as a result of the severe plastic deformation through milling.

During the milling process, impurities and contaminations such as oxides are transferred from container to the powder. These non-magnetic impurities can increase the H_e since they are the main factor in closing the magnetic domain walls [80].

Accordingly, it was observed that by increasing the percentage of copper up to 3%, the coercivity rapidly reduced. The relationship between H_e , M_s , and grain size is as follows [25, 65]:



Fig. 8. Variation of coercivity for samples with different contents of Cu.

$$H_c \approx 3\sqrt{\frac{kT_cK_1}{aM_s}}\frac{1}{D}$$
⁽⁵⁾

in which, D, K_1 , $T_{c'}$ and k are the crystallite size, magnetic-crystalline anisotropy, Corie temperature, respectively, and k is constant [81].

According to obtained results, at lower contents of 3% Cu, the grains size (12 nm) is more than the exchange length (L_{ex}). When the grains size is more than L_{ex} , the grains boundary hinders the field wall, since volume fraction of grain boundaries increases as a result of grains fining. When crystallite size (10 nm) is less than exchange length, effect of the field walls decreases and each grain acts as a separate filed. In this case, there is no grain boundary, therefore, magnetic walls move easier and H_e decreases.

4. Conclusions

The nanocrystalline (Fe₈₅Ni₁₅)_{100-x}Cu_x (x=0, 0.5, 1.5, 3, and 5) system was successfully prepared through the mechanical alloying method. Increasing copper content enhanced the rate of hard-working which leads to an increment in defects especially dislocations. This led to the reduction of crystallite size as well as the increment of internal strain. The X-ray diffraction peaks were broadened with increasing copper content, which mainly was due to decreased crystallite size and increased lattice strain. The crystallite size varied in the range of 18 to 8 nm in copper-free Fe-Ni up to 5% Cu content. Also, the lattice parameter was higher in copper-containing samples. The addition of Cu into Fe-Ni alloys lowered the M_{s^3} which was due to its diamagnetic effect. On the other hand, the coercivity increased by increasing copper content up to 1.5%. This was due to the increment in crystal defects and finer grain size.

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Effect of MgF₂ Addition on the Mechanical Properties of Hydroxyapatite Synthesized via Powder Metallurgy

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ABSTRACT

Hydroxyapatite, a type of bioceramics, is mainly used as an implant for hard tissues due to its similarity to the structure of hard tissues. The aim of this study is to improve the mechanical properties of hydroxyapatite for biological uses. For this purpose the effect of magnesium fluoride (MgF,) addition with different weight percentages (0, 5, 7.5 and 10 wt. %) on the mechanical properties of pure hydroxyapatite sintered at various temperatures (900, 1000 and 1100 °C) for 1 hour was investigated. XRD analysis was performed to study the decomposition of hydroxyapatite and the transformed phases. The density, Vickers microhardness and fracture toughness of the Keywords: specimens were measured. The SEM analysis was performed to investigate the microstructure of samples. The results showed that the decomposition of hydroxyapatite to tri-calcium phosphate (TCP) decreased with increasing MgF2. Also, an increment in density and mechanical properties of the specimens were observed with increasing Tri-Calcium Phosphate (TCP) the amount of hydroxyapatite. The fracture toughness of sintered pure hydroxyapatite increased from 2.3 to 1.3 MPa.m^{1/2}. The specimen containing 10 wt. % MgF₂ sintered at 1100 °C showed the best mechanical properties. ©2019 jource. All rights reserved.

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Hydroxyapatite Magnesium Fluoride (MgF₂) Sinter

1. Introduction

Hydroxyapatite (HA), with the chemical composition of $Ca_{10}(PO_4)_{\epsilon}(OH)_{\gamma}[1, 2]$, due to its similarity to inorganic sections of bone and biocompatibility, is an important material in bone replacement as well as implants for hard tissues. HA is used in various fields such as biomedical applications [3-8]. Due to poor mechanical properties of HA, especially low flexural strength and fracture toughness, its uses are limited to applications with no mechanical stress or low stress [9-14]. Therefore, efforts have been made to improve the mechanical properties of HA-based implants [15-24].

During the sintering process of HA, it decomposes to TCP or tetra-calcium phosphate phases (reactions (1) and (2)) [10, 25].

$$Ca_{10}(PO_{*})_{6}(OH)_{2} \rightarrow 2Ca_{3}(PO_{*})_{2} + Ca_{4}P_{2}O_{9} + H_{2}O$$
(1)
$$Ca_{10}(PO_{*})_{6}(OH)_{2} \rightarrow 3Ca_{3}(PO_{*})_{2} + CaO + H_{2}O$$
(2)

These decomposition reactions may negatively affect the density and consequently the mechanical properties of HA, which is due to the formation of secondary phases and production of H₂O. Also, the formed secondary phases increase the tendency for crack growth and biodegradation of HA ceramics. Meanwhile, TCP formation due to its high solubility, reduces the properties of HA composites [26].

Moreover, the addition of additives during the sintering process leads to the prevention of the HA to TCP degradation, as well as improvement in its mechanical properties. Several researches have been performed to investigate the effect of various additives such as MgF₂ [9, 10, 13], AlF₃ [27], NH₄F [28], MgO [29], AgNO₃ [30], LiNO₃ [26], CaF₂ [31] and etc. [32-36]. On the other hand, recently, attentions have been paid to the effect of different parameters e.g. temperature on HA properties [3, 37, 38]. In this regard, fluoride ion is known to be an important additive for HA. This is due to the substitution (or doping) of the F⁻ with OH⁻ presented in HA, which prevents the degradation of the HA or reduces the level of the decomposition to TCP. This results in the improvement of the mechanical properites. On the other hand, with entrance of F into the HA network, fluorapatite is formed which has higher thermal and chemical stability than that of HA that also prevents tooth and bone decay [9, 10, 13, 25, 39].

Mechanical alloying is known to have various advantages such as low time consumption [40-45], facility of process, and effective prop-

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Fig. 2. X-ray diffraction spectra for specimens containing different percentages of MgF2 sintered for 1 hour at (a) 900 °C, (b) 1000 °C, and (c) 1100 °C.

erties [46] that can be a good candidate to produce HA [47]. Although several research has been conducted to study the effect of adding MgF₂ to HA and its composites, further studies are required to investigate the effect MgF₂ addition to HA. Therefore, the aim of this study is to elucidate the effect of adding different amounts of the MgF₂ at different sintering temperatures on the mechanical properties and stability of HA as well as determining the optimum percentage of MgF₂ for preparing a biomaterial with desirable properties. For this purpose, MgF₂ with weight percentages of 5, 7.5 and 10 were added to HA and sintered at 900 to 1100 °C. Finally, the density, microstructure, hardness and fracture toughness of the specimens were evaluated.

2. Materials and methods

High purity HA powder (99.99%), the product of Aldrich Company, and MgF₂ powder of 97% purity from Analytical Fluka Company were provided. Fig. 1 shows the image of the purchased primary powders. Different weight percentages (5, 7.5 and 10 wt. %) of MgF₂ were added to HA. The mixtures containing HA and various amounts of MgF₂ were milled for 24 hours using alumina pellets. After the milling process, the mixtures were subjected to the cold isostatic press at 130 MPa. Then, they were sintered at temperatures of 900 to 1100 °C under airflow for 1 h without pressure.

The density of specimens was measured by the Archimedes method. The formed phases were evaluated after the sintering process using XRD analysis (INEL Equinox 3000). The test was performed by a diffractometry method using Cu-K_a irradiation (λ =1.54056 Å) under a voltage of 40 kV and a current of 30 mA. The specimens were evaluated at angles between 20 of 15 and 65 degrees. In order to investigate the microstructure, the sections of the specimens were polished using diamond paste and etched. Finally, the microstructure of the specimens was examined by scanning electron microscopy (SEM, AIS 2300-seron Tech) with an accelerating voltage of 20 kV. The hardness of the specimens was measured by Vickers microhardness test method (MHV1000Z), which was performed under 200 g load on the polished surfaces of the specimens for 10 sec. The values of fracture toughness (K_{IC}) were calculated using the results obtained from the microhardness test based on Eq. (3) [48].

$$K_{IC} = 0.016 \left(\frac{E}{H_V}\right)^{0.5} \left(\frac{P}{C^{1.5}}\right) \tag{3}$$

Here, HV is Vickers hardness (GPa), P is the applied force (N), E is the modulus of elasticity (GPa) and C is the crack length (m). The crack length was measured immediately by a calibrated optical microscope.

3. Results and Discussion

3.1. Phase Analysis

XRD analysis was used to evaluate the degradation of HA as well as determining the formed phases. Fig. 2 shows the X-ray diffraction for different percentages of MgF_2 at different sintering times.

Fig. 2 shows that HA and TCP are the main phases in the structure,



Fig. 3. Density variations of the specimens as percentage of MgF₂ at different temperatures of sintering.

while MgF_2 does not exist in the structure after the sintering process. This indicates that the decomposition of HA to TCP occurs due to sintering process.

The XRD spectra depicts that by the addition of MgF₂ to HA, the fluorapatite phase is also formed in the structure and after the sintering process, the phases of HA, TCP, fluorapatite and MgO are presented in the structure. The formation of the fluorapatite phase is because of F⁻ substitution instead of OH⁻ ions in the HA structure according to reaction (4). $Ca_{10}(PO_{4})_{6}(OH)_{2} + MgF_{2} \rightarrow Ca_{10}(PO_{4})_{6}F_{2} + MgO + H_{2}O$ (4)

Also, in order to evaluate the degradation rate of HA, it is necessary to check the intensity of HA and TCP peaks. To determine the HA decomposition into TCP, the relative values of the phases can be determined from the most extreme HA and TCP peaks. In fact, it is assumed that the concentrations of the HA and TCP phases are proportional to the height of their peaks in the mixture [10]. The rate of TCP formation in structures containing HA and TCP can be calculated using Eq. (5) [32].

the fraction of decomposed $HA = I_{TCP}/(I_{TCP}+I_{H,d})$ (5) where I_{TCP} is the peak intensity of the plane (0210) of the TCP phase and I_{HA} is the peak intensity of the plane (211) of HA. Using this equation, the percentage of HA decomposed into calcium phosphate can be determined. Clearly, the greater the value obtained from this relationship, the greater the decomposition. These values were calculated for different specimens and listed in Table 1.

According to calculations based on Eq. 5, the most appropriate sintering temperature for 5 and 7.5 wt. % MgF, was 900 °C, while for the specimen with 10 wt.% MgF2, sintering temperature of 1100 °C was suitable, in which, the lowest decomposition of 1.82 was observed. It should be noted that as the sintering temperature increased, the decomposition of pure HA significantly increased. The main reason for the decrease in the amount of degradation in the presence of fluorides is decomposition of MgF₂. As a result of this decomposition, F⁻ is released and replaced in the HA structure by the OH⁻ [9]. As a result of MgF, decomposition and reaction (4), a more stable phase of fluorapatite is formed and thus the decomposition of HA to TCP is reduced. Fluoride ions enhance the stability of the HA crystalline structure [13], and HA doped with F (fluorapatite) is more resistant to decomposition during sintering at high temperature than pure HA. According to Table 1, the higher the percentage of MgF, in the structure, the lower the degradation of HA to TCP and the more stable HA. As can be seen, the specimen containing 10 wt. % MgF, has only ~2 % of the decomposed-HA to TCP, and hence, HA stability is significantly increased. The main reason for this could be higher F- ions due to presence of higher MgF, content presented in the HA structure and consequently the reaction (4) occurs more, and higher fluorapatite is formed, thus the decomposition of HA to TCP is more prevented.

It should be noted that for samples from 7.5 to 10 wt. %, the degradation is increased. The reason for the negative effect of adding more than specific amount of MgF_2 on the stability of HA is that the excess MgF_2 does not participate in the formation of fluorapatite and is not visible in the X-ray diffraction (XRD) pattern because of its low content. This



Fig. 4. SEM images of sintered specimens at 900 °C: (a) 0 wt. % MgF₂; b) 5 wt. % MgF2; c) 7.5 wt. % MgF₂; d) 10 wt. % MgF₂.

excess MgF_2 forms eutectic melt at the reaction temperatures with HA or TCP. In fact, the relative coarsening of the grains and porosities with the addition of higher amounts of MgF_2 indicates the possibility of eutectic melt formation. This has been observed in other works [13, 49].

3.2. Density

The density values obtained for the specimens at different temperatures are presented in Fig. 3. Accordingly, the MgF2-free specimen has the lowest density compared to other specimens. It can be noted that in the presence of MgF₂, the phase decomposition of HA into secondary phases i.e. TCP is reduced that leads to higher density. The reason for the higher density due to lower HA degradation is the production of H₂O by decomposition of HA to TCP (reactions (1) and (2)). The produced H₂O results in porosity. On the other hand, by decreasing the amount of HA decomposition in the presence of MgF,, less H₂O and porosity in the structure is produced and hence the density increases [9, 10]. It was also observed that by increasing the MgF, content, the density increases. According to Table 1, HA decomposition decreases with an increasing percentage of MgF,. Additionally, the reduction of HA decomposition during sintering, reduces the amount of H₂O formed by HA decomposition and thus reduces the porosity of the sintered specimens. As a result, when HA decomposition becomes lower, the removal of porosity in the final sintering stages becomes easier, which results in a highly dense structure [10].

The TCP phase resulted from the decomposition of HA has a lower density. As a result, specimens with higher TCP phase have lower density [13]. Also, substitution of OH[•] with F[•] (reaction (4)) results in H₂O production. Replacement occurs below sintering temperature (below 1100 ° C). The H₂O produced in this reaction vaporizes and discharges from the powder mixture and fluorapatite is formed $(Ca_{10} (PO_4) {}_6F_2)$ [9].

Table 1.

Percentage of HA decomposed to TCP

Percentage of decomposed HA (%)	MgF ₂ (wt. %)
86.31	0
58.97	5
33.24	7.5
1.82	10



Fig. 5. SEM images of sintered specimens at 1000 °C: (a) 0 wt.% MgF₂; b) 5 wt.% MgF₂; c) 7.5 wt.% MgF₂; d) 10 wt.% MgF₂.



Fig. 7. Micro hardness values by weight percent of MgF2 at different temperatures.

At two temperatures of 900 °C and 1000 °C, the density decreased with increasing MgF₂ from 7.5 to 10 wt% (Fig. 3). Given that the variations in density with MgF₂ percentage depend on the variations in the decomposition rate of HA, the cause of the decrease in the density of these specimens can be attributed to the increase in HA decomposition. However, H₂O is also produced by the replacement of F⁻ with OH⁻ (reaction 3-4). But this replacement occurs at lower temperatures. Thus, the H₂O produced in this reaction vaporizes and discharges from the powder mixture and leads to the fluorapatite (Ca₁₀(PO₄)₆F₂) formation [10].

By increasing the sintering temperature from 900 to 1100 °C, the density increases. The reason for this is that as the sintering temperature increases, the surface melting of the powder particles increases, which leads to higher density of the material [50]. It should be noted that although the increase in sintering temperature facilitates sintering due to improved surface melting and allowing more densification during sintering, this increase in temperature also facilitates phase decomposition of HA and leads to a higher rate of HA decomposition. According to abovementioned points, HA decomposition has a negative effect on the density and properties of HA-containing materials. Therefore, a temperature should be chosen for sintering at which the density is not reduced. It was observed that by increasing the temperature from 900 °C to 1100 °C, although the rate of HA decomposition increased (Fig. 3), the condensation is also increased. It can be implied that with increasing temperature, the improvement of sintering has been dominant over the increase in the decomposition rate and resulting in higher density. Increasing the density of HA specimens due to increment of sintering temperature has also been reported by Z. Evis et al. [10].



Fig. 6. SEM images of sintered specimens at 1100 °C: (a) 0 wt.% MgF2; b) 5 wt.% MgF2; c) 7.5 wt.% MgF2; d) 10 wt.% MgF2.



Fig. 8. Fracture toughness variations as a function of MgF₂ content at different temperatures.

3.3. Microstructure

SEM images of the specimens at different temperatures are presented in Figs. 4-6. Accordingly, the amount of porosity in the specimens decreased with increasing MgF₂ and the pores became smaller. As stated, the decomposition of HA to TCP decreases with increasing MgF₂ and thus the H₂O produced by this phase decomposition also decreases. This reduces the porosity of the sintered specimens, that has been reported by other researchers [9, 10]. In fact, SEM images confirm the trend obtained for density variations.

According to Figs. 4-6, the increase in sintering temperature leads to a decrease in porosity in the structure. The reason is that sintering process improves with increasing temperature. Comparing the figures, it can be said that more surface melting at sintering temperatures of 1000 °C and 1100 °C is occurred compared to 900 °C. At temperatures of 1000 °C and 1100 °C, the particles and the grains are more difficult to separate and are more interconnected. However, it should be considered that in the specimens that have been sintered at higher temperatures (1000 °C and 1100 °C), porosities are relatively coarser. These are due to the higher phase decomposition of HA at these temperatures. As mentioned, increasing the temperature on one hand increases the phase decomposition and on the other hand, allows for higher densities to facilitate sintering. Although sintering improvement was dominant at this temperature range and resulted in a decrease in the overall porosity as well as increasing the density, due to more H₂O production during the HA decomposition, the size of porosities in the MgF₂-free specimens was larger than that of 900 °C. However, as can be seen in Fig. 4 to 6, this did not occur at higher MgF2 percentages. Generally, these results

confirm the trend for density variations in the specimens and other researches [51, 52].

3.4. Hardness and Fracture Toughness

As stated, the most important reason for the use of additives such as MgF_2 in HA materials is their effect on improving the mechanical properties of HA, which improves its usability in fields requiring mechanical load bearings. Both hardness and fracture toughness are two important mechanical properties that should be studied. The variation of microhardness as a function of MgF₂ percentage is shown in Fig. 7.

The fracture toughness of the specimens was calculated using Eq. 3 and its variation in terms of MgF_2 content is shown in Fig. 8. The obtained results of the hardness and fracture toughness show that by the addition of MgF_2 to HA, the hardness and fracture toughness increase. The fracture toughness of MgF_2 -free HA sample is approximately 1.3 MPa.m^{1/2}, while by addition of MgF_2 it was increased to 2.3 MPa.m^{1/2}, which is significantly high.

The higher the amount of MgF₂, the greater the hardness and fracture toughness, especially at 7.5% and 10 wt. %. The reason for this increase can be attributed to the improvement in the density of the specimen by increasing the amount of MgF₂. The higher density or the lower porosity leads to the higher structural connection and the greater resistance to mechanical loading. Fracture toughness indicates the material resistance to the formation and growth of cracks. When there is a greater potential for crack growth in the material, less fracture toughness or energy absorption is obtained in the sample before fracture. Therefore, the presence of porosity in the material results in reduced fracture toughness.

Generally, the hardness and fracture toughness of HA specimens are depended on the density and porosity. Higher density due to lower phase decomposition of HA or improving the sintering by optimizing the effective parameters such as temperature is achieved. The dependence of hardness and fracture toughness on porosity has also been reported by other researchers [9, 10, 13].

4. Conclusions

In the present study, MgF_2 with values of 5, 7.5 and 10 wt % was added to HA. The powders were milled and sintered at various temperatures for one hour after cold pressing. The most important results of this study are as follows:

- The addition of MgF₂, due to the substitution of F⁻ with OH⁻ in the structure of HA, resulted in the formation of a more stable fluorapatite phase, thus reducing the phase decomposition of HA to TCP.
- Increasing the amount of MgF₂ led to lower phase decomposition resulted in an increase in density, and consequently an increase in hardness and fracture toughness.
- 3. Increasing the sintering temperature resulted in an increase in the amount of HA phase decomposition, while the structure became denser i.e. better mechanical properties.
- 4. The best amount of MgF₂ to reduce the phase decomposition and achieve the desired density and properties, depends on the sintering temperature. The optimum amount of MgF₂ is 10 wt% for the temperature of 1100°C and 7.5 wt% for the temperatures of 900 °C and 1000 °C.
- Fracture toughness values increased from 1.3 MPa.m^{1/2} for pure sintered HA to 2.3 MPa.m^{1/2}, respectively.
- Maximum density, hardness and fracture toughness were obtained for sintering temperature of 1100 °C at 10 wt.% MgF,.

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Preparation of graphene nanolayers through surfactant-assisted pure shear milling method

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ABSTRACT

In this study, graphite powder was used to prepare few-layer graphene sheets through shear milling. During the Article history: process, graphite was well dispersed in double distilled water as a lubricant and sodium dodecylsulfate (SDS), Received 10 December 2019 followed by shaking and milling under low energy. The exerted sheer force led to the continuous delamination Received in revised form 21 December 2019 of graphene flakes. The microstructural investigation was performed by SEM. In addition, the energy-dispersive Accepted 27 December 2019 X-ray spectroscopy (EDS) analysis was performed to determine distinct levels of carbon in different fragments of graphite. The ultrathin multilayer structure of graphite was successfully obtained using the surfactant of SDS, Keywords: which can lead to the production of molecularly thin sheets by mechanical peeling. Moreover, it was found that this synthesis method has some advantages, including cost-effectiveness and ease in performance for producing many graphene nanolayers.

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1. Introduction

These days, nanomaterials, due to their highly attractive properties, have been broadly used in various types of applications, such as life sciences, the environment, information technology, etc. [1-5]. There are various methods to produce nano-sized materials, including sol-gel [6-9], ball-mill [10-13], co-precipitation [5], self-propagating high-temperature synthesis [14, 15], electrospinning [4, 16], etc.

Recently, the application of graphene has been gained increasing attention by researchers because of its unique properties [17-21]. Graphene, a single layer of graphite, is a basic block of sp2-bonded carbon for graphitic materials such as graphite [22-25], fullerene [26-28] and carbon nanotubes [29-38], which has both unique mechanical and physical properties making it a promising material for applications in nanotechnology [39-44]. A stable graphene sheet was discovered by Novoselov and Geim (2004) for the first time [45].

The value of the thermal conductivity of graphene is even more than diamond, and it has a high potential in increasing the convective heat transferring ability of a nanofluid [46-48]. The usage of graphene into the lubricant improves its potential for heat removal from a system, because of the significant role of graphene in increasing the amount of thermal conductivity. Recently, graphene has been introduced as the thinnest solid lubricant by some researchers with a mechanism of superlubricating, which could be confirmed by atomic force microscopy (AFM) [49, 50]. Graphene has been introduced by Bermen et al. [51], as a promising candidate for using in steel lubricants. The tribological properties of graphene have been investigated, and the results have shown excellent properties of graphene compared to the nanoparticle of graphite or carbon nanotube (CNT) [52].

It can be used in many applications such as solar cells [53, 54], hydrogen storage [7, 55], sensors [56-58], detectors [59], transistors [60] and other electronic devices in many applications due to its good electrical property [19, 21, 61-68], which makes it a good candidate to be used in lots of composites [69, 70]. Therefore, recently, many investigations have been focused on graphene and graphene nanolayer by numerous physicists, chemists, and material scientists [71].

Producing graphene at a large scale with uniform thickness has been one of the most important subjects for many researchers and scientists [72, 73]. Many controlled synthesis routes, viz. chemical vapor deposition (CVD), laser reduction, and wet chemical routes have been proposed to prepare a large amount of graphene [63, 74-78], with suitable physicochemical properties [79-81]. However, these processes should

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ARTICLE INFORMATION

Ultrathin Multilayer Structure Graphene nanolayer Sodium-dodecylsulfate



Fig. 1. Optical microscopy images of graphite particles after 60 hours of shear milling (a) with SDS and (b) without SDS.



Fig. 2. SEM micrographs of graphite particles after 60 hours milling (a) without SDS and (b) with SDS.

be low cost and simple e.g. mechanical exfoliation of graphite, producing a large area graphene sheet.

Several methods have been used for producing layered materials, like graphene, with no unwanted defect or functionalization. Meanwhile, mechanical exfoliation is the best option among these methods that is very simple procedure.

The delamination occurs via applied shear and compressive forces on the particles, in which the shear force should overcome the van der walls force existing between the sheets. Accordingly, there are several reports for preparing graphite nano-sheets or graphene by graphite exfoliation through three roll milling or shear ball milling [77, 82, 83].

However, all these studies have used graphene powders in the form of solid additive, in which the obtained suspension had low stability. Meanwhile, commercial fluids require high stability for a long time [84]. To overcome this limitation, functionalized graphene sheets were prepared e.g., aromatic or long alkyl chain functionalized graphene sheets dispersed in non-polar oil medium [85, 86]. Zhang et al. [87] used polyalphaolefin-9 (PAO) and dispersed oleic acid-modified graphene sheets in it. Although long-term storage stability is not achieved, graphene showed good wear resistance.

One of the major challenges in the graphene research field is how to count the number of atomic layers. Although optical microscopy can show graphene with certain layers on a silicon substrate, it is difficult to identify the number of layers of graphene accurately [62]. Therefore, although there are many reports about graphene nanolayers, insufficient reports have been issued about the preparation of the nanolayers via shear milling procedure.

In order to apply effective exfoliation, the stirred-media bead milling system can be utilized that has more shear forces other than impact one. Peukert et al. [75] used this method to prepare scalable graphene in a water medium along with an ionic surfactant.

Thus, in this paper, the synthesis of nanolayers via shear milling procedure is presented instead of the ball milling process to achieve nanolayer graphene flakes and stable dispersion of graphene in the medium. Scanning electron microscope (SEM) and optical microscopy (OM) were also used to characterize thin flakes on Si substrate. To provide well-dispersed graphite in water, sodium dodecyl sulfate (SDS) was used as the surfactant.

2. Experiment Procedure

High purity graphite powder with an average particle size of 200 μ m and SDS were purchased from Merck Co. (Germany). Two SDS-containing and SDS-free mixtures with 0.25 gr graphite and 200 ml deionized water were separately prepared and a flat alumina disc with 2cm diameter and 4mm thickness was put in the flask of each mixture. The flasks were shaken with orbital flask shaker for 60 hours at a speed of 380 rpm to keep the disc flat. Then, the samples were spin-coated on the Si substrate and dried at 80 °C for 2 h.

Raman spectra analysis was done with SEKI 750 Raman analyzer to investigate the sample in argon ion laser (514.5 nm line). The JEOL 2100 electron microscope was used for TEM analysis of samples on a carbon-coated copper grid. The optical microscopy (OM) and SEM (model: LEO 1450 VP) images of the samples were captured, and data of energy-dispersive EDX (model X-MAX) for different areas were collected.

3. Results and Discussion

Since graphite and graphene flakes are hydrophobic and tend to agglomerate in water, an ionic surfactant like SDS can hinder the coagulation and restacking of particles. The resulting suspension of graphite with SDS is stable in water to carry out the rest of the process. During delamination in the stirring media mill, the transferred energy from the grinding media causes sheets to be fractured, and mostly small fragments of graphite can be present in the ultimate suspension. During milling, SDS is adsorbed on the surface of the particles and creates a strong repulsive force that prevents the agglomeration and restacking of delaminated sheets. The optical microscopy results, which are presented in Fig. 1, show that the particle size of graphite flakes decreased to less than 50 µm in both mixtures, after mechanical treatment for 60 h. Fig. 2 represents the SEM images of graphite fragments on the surface of the silicon substrate. The presence of SDS leads to a significant change in the shape of particles after shear milling for 60 h (Fig. 2). It is worth noting that water allows the graphene planes to slip easily and SDS prevents the agglomeration of the particles and keeps the layers apart from each other. Applying low energy through shear milling of the graphite particles induces shear on graphene layers without causing high crystal defects [63].

As can be seen in Fig. 2(b), the particles obtained after 60 hours of milling have flak-like shape. Fig. 3 illustrates the SEM micrographs of thin flaky graphite. The accurate thicknesses of the thin sheets are difficult to estimate. Three areas are highlighted via arrows on in Fig. 3(a).

Energy-dispersive X-ray analysis (EDX) of point 2 is shown in Fig. 3(b), which contains C, O, and Si as well as a negligible amount of Na element. This proves the presence of carbon and silicon existing in the graphene and substrate, respectively. Fig. 4 shows various intensities of carbon at mentioned areas (Fig. 3(a)) after deposition on a silicon substrate. It is evident that the minimum intensity of C level corresponds to the layer with a minimum contrast (point 1), which refers to the very thin layers of graphene.

The transmission electron microscope (TEM) image of nanolayers is shown in Fig. 4. It can be seen that several dark layers are superimposed on each other. This denotes that several graphene nanolayers are stacked.

In order to distinguish the graphene from graphite and determine the number of layers, Raman spectroscopy was performed. D-band about



Fig. 3. (a) SEM micrographs of thin flaky graphite, (b) EDX spectrum of point 2, and (c) carbon intensity at each point .



Fig. 4. TEM micrograph of graphene nanolayers.

1350 cm⁻¹, G-band about 1580 cm⁻¹ and 2D-band about 2700 cm⁻¹ correspond to graphitic materials. Fig. 4 illustrates the Raman spectra of the materials. The G-band at 1581 and 1573 cm⁻¹, and D-band at 1356 and 1352 cm⁻¹ for graphite and graphene samples, respectively, prove almost the graphitic nature of the samples. In addition, the ordered and increased density of sp2 carbon is clear for the milled sample. It is reported that the 2D symmetry, as well as its full width at half maximum (FWHM), can distinguish the graphene and bulk graphite [88]. Furthermore, the 2720 cm⁻¹ is ascribed to a 2D peak for graphite that depicts the formation of few layers as well as the delamination of a few layers or monolayered graphene.

Besides, a single 2D peak was found in many places in the diluted film. On the other hand, the graphitic nature of the peak was also found in some places. Thus, it can be concluded that both multilayers and single-layered graphene sheets are formed.

4. Conclusions

Multilayer graphene sheets were synthesized by simple surfactant-assisted pure shear milling at ambient temperature. Water and SDS would accelerate the peeling-off process, and the SDS ionic surfactant hinders the agglomeration of graphite flakes. Optical microscopy showed the size reduction caused by mechanical energy. In addition, SEM and TEM images showed that the grinding media transferred enough energy to overcome the Van der Waals forces among the graphene sheets. The thickness of the achieved multilayer graphene sheet was estimated to be nano-sized.



Fig. 5. Raman spectra of dispersion after being processed.

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Determination of Hg²⁺ by diphenylcarbazone compound in polymer film

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ABSTRACT

ARTICLEINFORMATION

A sensitive optical sensor for determining Hg²⁺ concentration has been prepared by incorporating the indicator Article history: dye, diphenylcarbazone compound, into cellulose acetate polymer film. To prepare the sensor, a cellulose acetate Received 25 November 2019 film was hydrolyzed with base and then the diphenylcarbazone compound bonded to the film. This method is easy to perform and uses acetyl cellulose as a carrier. According to the results, the prepared sensor was able to deter- Accepted 22 December 2019 mine the Hg²⁺ concentration with a $\pm 6\%$ error. Also, the adsorption capacity was 3.41×10^{-3} mmol/g. ©2019 jource. All rights reserved. Peer review under responsibility of jource

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1. Introduction

One of the most popular poisonous elements in aquatic ecosystems is mercury (Hg2+) in a way that even a low amount of this element can significantly affect human health [1-8]. This is due to the Hg²⁺ accumulation in the human body from the food chain which causes serious damages to the brain, lungs, central nervous system, kidney, and the development of the fetus [9-14]. Unfortunately, the emission of mercury by humans is increasing [15, 16]. This increasing trend in environmental pollution is considered a global concern. For addressing this issue, a reliable and rapid method is needed to determine the mercury trace [17].

In this respect, a variety of sensitive analytical methods can be used to determine Hg2+ selectively such as inductively coupled plasma-atomic emission spectrometry (ICP-AES), inductively coupled plasma mass spectrometry (ICP-MS) [18, 19], cold-vapor atomic fluorescence spectroscopy (CVAFS) [20], and cold-vapor atomic absorption spectroscopy (CVAAS) [21-23]. Although these traditional techniques are sensitive with high accuracy, the measurement instruments are sophisticated, expensive, with high costs of operation, and the sample preparation process is complicated. These factors make these methods time-consuming for a large number of samples and are not unsuitable for routine monitoring in the field. Besides, during the collection, samples may be altered. Consequently, the design of an inexpensive, fast technique for the detection of Hg2+ is desired. Currently, some techniques are employed for field application and miniaturization including fluorimetry and colorimetry [24-31]. However, their application is still limited due to the interference of other metal ions and sophisticated synthesis of probe materials [32, 33]. Voltammetric methods which are electrochemical techniques have a high potential for the determination of Hg2+ in the field compared to other methods [34, 35]. This is because of possessing some inherent characteristics, including selectivity and sensitivity, miniaturization, cost-effectiveness, and rapid analysis time [36].

So far, in spite of the increasing interest in the development of a time-saving, easy-to-operate, low-cost, and reliable technique for the determination of Hg2+ in the field, only a few numbers of studies have addressed the optical sensors (fluorescent and colorimetric) [25, 37, 38]. Some studies have been worked on the determination of Hg2+ through voltammetric methods, but they are fragmentary and incompletely [39-41]. To the best knowledge of the authors, none of the previous studies have focused particularly on the determination of Hg2+ through voltammetric techniques. Moreover, the application of nanomaterials in these methods has been recently gained increasing attention. This research focuses on the preparation of a highly sensitive sensor for determining Hg²⁺ concentration by incorporating the indicator dye, diphenylcarbazone compound, into a polymer film.

2. Experiment Procedure

2.1. Materials

To prepare a standard solution of mercury chloride (HgCl,, 0.1 M), 2.715 g of HgCl, dissolved in 100 ml distilled water in a standard flask. Diphenylcarbazone compound 0.02% solution was prepared by dissolving the C,H,OH dye solution with a 2.00% concentration in a 100 ml

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Fig. 1. The possible reaction between the activated membrane and diphenylcarbazone compound.



Fig. 3. Adsorption of Hg2+ in different pH values.

volumetric flask. 2.264 g NH₄Cl was dissolved in 100 ml distilled water to prepare NH₄Cl solution with 0.4 M concentration and 2.14 g NaBrO₃ was dissolved in distilled water in a volumetric flask (250 ml) to obtain NaBrO₃ solution with 0.06 M concentration. For the preparation of polyvinyl alcohol and Thiourea solutions, 0.7 g and 1g of the reagents were dissolved in 100 ml of distilled water, respectively.

2.2. Methods

2.2.1. Sensor Preparation

For de-esterification of the acetyl group and the increase in the membrane porosity, the hydrolysis of acetyl cellulose was carried out. The transparent films were immersed in KOH (0.1 mol.1⁻¹) for 24 hours. Subsequently, the specimens were washed with distilled water followed by the treatment with a mixture of polyvinyl alcohol (0.70 % (w/v)) and thiourea (1.00 % (w/v)) solution for 48 hours at room temperature. Then, the polymer membrane was treated with a solution of diphenylcarbazone compound (0.020 % (w/v)) at room temperature and stirred for about 20 hours. At the next step, the film was washed by rinsing with distilled water to the extent that no absorbance was observed at the dye wavelength. The drying process of the film was carried out at 45 °C for 15 minutes.

2.2.2. Spectrophotometric Measurements

Shimadzu 2100 ultraviolet-visible (UV-Vis) spectrophotometer and a thermostated cell were used to measure the UV-Vis spectra at the controlled temperature of 25 °C \pm 0.1.

Table 1.

Determination of Hg2+ concentration

The standard amount of Hg ²⁺ (ng)	The measured amount of Hg ²⁺ by the proposed method (ng)		Mean ± SD	
10	9	12	11	10.6 ± 0.1
20	22	18	23	21 ± 0.1
25	23	26	27	25.3 ± 0.1



Fig. 2. UV-Vis spectrum of the polymer film functionalized with diphenylcarbazone compound.

3. Results and Discussion

The reaction between the activated cellulose film and the diphenylcarbazone compound is illustrated in Fig. 1. There is an amino group in the structure of the diphenylcarbazone compound, therefore, by special treatments, the molecules of the dye can be linked to cellulose acetate. According to Kostov et al. [42], just the dyes that have amino groups in their structure are able to be linked to cellulose acetate. With the help of thiourea, it is possible to link dyes with or without amino groups in their structure to cellulose acetate polymer.

As a result of the high activity of the carrier, the interaction of the carrier compounds having the low molecular weight and a free para-position in their structure is possible.

Therefore, indicators with a free para-position or hydroxyl group in their molecule can be employed. In addition, to link the molecules of dye to the cellulose acetate membrane, thiourea acts as a bridge. This results in the covalent bonding between the indicator and the polymer film [43]. BrO³⁻ can oxidize diphenylcarbazone compound in the presence of Hg²⁺ in an acidic environment (pH ~ 4.5) [44].

3.1. UV-Vis Spectrum of Functionalized Cellulose Acetate

The UV-Vis spectrum of the treated cellulose acetate was obtained by measuring the intensity at a different wavelength and plotted against wavelength. The UV-Vis spectrum of the diphenylcarbazone-functionalized film obtained is shown in Fig. 2. As illustrated, the maximum absorption appeared at 480 nm. Thus, the spectrophotometric measurements were carried out at 480 nm.

3.2. The Effect of pH on the Adsorption of Hg^{2+}

The acidity of the solution affects the Hg^{2+} determination sensitivity of the diphenylcarbazone compound. The adsorption plot versus pH for the functionalized polymer film is shown in Fig. 3. The pH value was adjusted with sodium hydroxide or hydrochloric acid at an Hg^{2+} concentration of 1.0×10^{-5} mol/mL and the amount of adsorbed Hg was measured by spectroscopy. The adsorption of Hg^{2+} decreases for a pH value of lower than 5. Decreasing the pH of the solution reduces the adsorption of the diphenylcarbazone compound. However, in neutral solutions, the interfering of other heavy ions increases and they produce colored compositions with diphenylcarbazone compound. When acidity increases, the diphenylcarbazone-mercury complex formed on the polymer film gradually decomposes and decolorizes [45, 46]. Therefore the determination measurement was carried out at pH = 5.

3.3. Determination of Micro-amounts of Hg²⁺ by UV-Vis Spectroscopy

(1)



Fig. 4. Calibration curve for Hg at the wavelength of 480 nm.

vestigated at 480 nm for different Hg2+ concentrations in the range of 0 to 25 ng/mL to obtain the calibration curve. The calibration curve obtained is linear from 0 to 25 ng as shown in Fig. 4. Three measurements for each absorption value for each solution were carried out and the mean value was reported. By employing the plotted calibration curve, the determination of unknown concentrations of mercury was performed. The results of measurements with the prepared sample are summarized in Table 1. The error of the measurements was within $\pm 6\%$ for samples 10 to 25 ng.

3.4. Adsorption Isotherm of Hg²⁺ on the Functionalized Cellulose Acetate Film

Fig. 5 illustrates the optical characteristics of the immobilized diphenylcarbazone compound on the cellulose acetate film for different concentrations of Hg2+. To evaluate the binding capacity of the functionalized polymer film, a rebinding experiment was carried out by using 0.2 g of the polymer film in 25 mL phosphate buffer solution of $HgCl_2$ (pH \sim 4). The suspension was stirred at 25 °C for 30 minutes and the absorption amount in the range of 0 to 200 µg/25mL was measured. After the exposure to the solution, the polymer film was removed from the solution and the concentration of remaining Hg2+ was analyzed. The mercury amount adsorbed on the surface of the functionalized polymer was calculated by Eq. (1): Q =

$$C_i - C_e$$

where C₂ and C₁ denote the equilibrium and initial concentrations of Hg²⁺ (25 µg/mL), respectively [47]. Fig. 4 shows the obtained results of the adsorbed Hg2+. It is evident that with increasing the concentration of Hg^{2+} in solutions from 0 to 150 μ g/25mL, the amount of Hg^{2+} adsorbed by the functionalized cellulose acetate increased linearly. According to the adsorption curve, the functionalized cellulose acetate film has the maximum adsorption capacity of Hg^{2+} equal to 3.41×10^{-3} mmol/g.

4. Conclusions

One of the most popular poisonous elements in aquatic ecosystems is mercury and the design of a reliable and rapid method for determination of mercury is needed. In this research, an optical sensor was prepared by the functionalization of hydrolyzed cellulose acetate by diphenylcarbazone.

The UV-Vis spectra of the polymer film showed a peak at 480 nm. The maximum adsorption was achieved at pH = 5 and by the decrease in pH, the adsorption decreased. Using the calibration curve, the error in determining the concentration of Hg2+ was around 6 %. The film exhibited the capability of the adsorption capacity in a wide range of Hg2+ concentration.



Fig. 5. Hg adsorption of the functionalized cellulose acetate film.

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ADTICLE INFORMATION

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A review of clinical applications of graphene quantum dot-based composites

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ABSTRACT	ARTICLEINFORMATION
This review represents an overview of the graphene quantum dots (GQDs) synthesis and their applications as	Article history: Pageived 28 December 2010
ments in the GQDs for therapy and their potential toxicity for both in vitro and in vivo are reviewed. The recent	Received in revised form 30 December 2019
findings and issues for GQDs and their composites with respect to stability and optimal size and toxicity at various applications are presented.	Accepted 31 December 2019
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1. Introduction

Quantum dots (QDs) are semiconductor fluorescent inorganic nanocrystals. Their size ranges from 1 to 10 nm. Their small size has made them unique in comparison with macrocrystalline materials. GDs with unique properties have been used in many branches of science; for example, their use in pharmaceutical and medical technology is evolving [4, 5]. The notable features of quantum dots are their rich surface area and optical properties that have led to their applications as probes for targeted drug delivery as well as treatment fields. In fact, by combining with ligands, QDs can target intended cells or tissues. Recently, with advances in the production of biocompatible quantum dots, their use for in vivo applications has become more prominent [7].

QDs can be also in the form of a semiconductor core, with a coating (as a shell), and a cap that results in good solubility in various solvents such as aqueous buffers. The unique optical and semiconducting characteristics of QDs are derived from the inorganic core [9]. The QDs are luminescent nanocrystals that are used for carriers or probes in medical applications such as drug delivery [10-13], imaging, and therapy due to their rich surface chemistry [15]. Ligands are used as functionalizing groups in QDs for specific target applications in cells or tissues [7]. In addition, ligands have the main role in the stability of colloids, distribution of particle size, solubility, the morphology of particles, and limiting the agglomeration and excessive particle growth [19]. Indeed, ligands result in electrostatic or hydrophobic interactions and covalent coupling of QDs to carbohydrates, DNA fragments, peptides, viruses, and other products [21]. The structure of QDs coupled with ligands is illustrated in Fig. 1. During the synthesis of QDs, organic materials such as carboxylic acids, primary amines, alcohols, long-chain carbon, and thiols, can be used as ligands [9]. Recently, the preparation of biocompatible QD has resulted in providing suitable nanocrystals with potential applications for in vivo utilization [2].

2. Physicochemical properties of quantum dots

Due to the nanocrystals grain boundary and electron hole pairs (excitons) of QDs, they have unique optical properties. In addition, photophysical properties of QDs include photochemical robustness, broad absorption and size-tunable spectra, high yields of fluorescent quantum, significant coefficients of absorption extinction, resistance to the effect of photobleach and fluorescence intermittency reduction. The above-mentioned photo-physical features make QDs suitable to be applied in different biomedical fields such as diagnosis, drug delivery, gene therapy, etc. [9, 22].

2.1. Size-tunable absorption and emission

Another feature of QDs is the size-tunable light emission properties (Fig. 2). As mentioned above, the QDs diameter ranges from 2 to 10 nm. The size adjusting of QDs results in the tuned fluorescence at an extensive wavelength (WL) from 400 to 4000 nm that enables the determination along with the visible light, ultraviolet (UV), and infrared spectra. The confinement degree increases by the decrease in QDs diameter, results in an increase in the energy of bandgap, and finally generates a higher energy exciton. This causes a change in the emission to the low WL of blue spectra due to the high energy of bandgap. Energy has an inverse relationship with the light WL. In semiconductor material having bulk form, the electrons are in continuous levels of energy but in the form of nanomaterials, the electrons exist in discrete energy levels because of the quantum confinement [23, 24].



Fig. 1. Schematic illustration ligand-linked Quantum dots (QDs).



Fig. 2. The size-tunable optical characterization of QDs.

2.2. Composition tunable light emission

The core chemical composition has an effect on light emission. In other words, different emissions are formed based on the quantum dots associated elements. For example, wavelength emission of the cadmium sulfide (CdS), the cadmium tellurium (CdTe), and the cadmium selenium (CdSe) are near UV blue region, infrared region (NIR) and under visible region, respectively [25].

2.3. Spectra of absorption and emission

The spectra of absorption refer to the spectra that are generated by the photon energy absorption (hu) resulting in the atom transition from the lower to higher energy levels. On the other hand, the emission spectra refer to the spectra generated by a molecule or atom transition from higher to lower energy levels by a photon energy emission (hu). The multiple quantum dots can be excited from a single light source with WL lower than emission WL because of its wide absorption band. The mentioned feature causes simplified designing of high speed and inexpensive sets. The emission spectra width of QDs can be decreased to 20 nm in the range of visible spectra, which provides separate signals detection without cross talk [26, 27].

2.4. Coefficients of absorption extinction

The absorption extinction coefficient is defined as the amount of light being absorbed in a specific wavelength by a chemical material that makes materials brighter probes in in-vivo conditions. In this condition, light intensities are significantly decreased due to absorption and scattering [28].

2.5. High quantum fluorescent yields

Fluorophores are known by high fluorescent quantum yield as the intrinsic properties. This feature is the ratio of absorbed photons to emit-



Fig. 3. Application of GQDs in nanomedicine.

ted photons during fluorescence and it is determined by Lumina fluorescence spectrometry [29].

2.6. Photo chemically robust

The high photo and chemical degradation resistance of QDs are due to their inorganic nature. Due to these properties, QDs have become an effective and excellent imaging instrument in the long term [30].

2.7. Photobleaching resistance

The decrease in intensity of fluorescence occurs due to light responding reactions or optical excitation that is the result of irreversibly luminescent material decomposition and is known as photobleaching [29].

Generally, QDs show a blinking behavior that is an attractive phenomenon because it is observed during continuous excitation of the molecule. This occurs due to photo-excited carriers trapping and detraining that leads to the QDs fluctuation between non-emissive and emissive states. In a short time, the fluctuation intensities known as 'quantum jumps' usually remain for small periods in comparison with fluorophores. However, the quantum dots containing thick crystalline shells would not blink [7].

Table 1.

Various methods for the fabrication of GQDs used in biomedical applications

Method of synthesis & precursors	Application	Ref.
Top-down Approach		
GQD synthesized through the chemical treatment from ethanolamine	diagnosis	[1]
GQD-ssDNA: chemical oxidation of candle soot	diagnosis	[2]
CL-GQD:GQD fabricated by MWCNT conjugated with anti-desman and functionalized with-COCL	Cancer diagnosis	[3]
GQD-PEG-AG; Acidic oxidation of CNT and graphite	Radiotherapy	[6]
Bottom-up Approach		
GQD-PEI; hydrothermal and oxidation reaction of polyethyleneimine	Gene transfection	[8]
MSN-SS-CD-DOX: Hydrothermal polymerization route using poly-acrylic acid	Targeted and controlled drug delivery along with booming	[14]
Microwave synthesis route using ethylene diamine and acrylic acid as well as functionalization with glicidyl methacrylate.	Targeted cancer drug delivery	[16]
Thermal combustion of rice straw	Detection and counting of bacteria	[17]
GQD-RhB-silka	Diagnosis	[18]
Hydrothermal treatment of citric acid monohydrate	Glsoma targeting and bio	[20]

3. Graphene quantum dots

In the past, carbon quantum dots (CQDs) were found by accident during working on single-walled carbon nanotubes (SWCNT) [31]. Then, the CQDs fluorescence features were reported so CQDs have become a new group of the smallest viable fluorescent nanomaterials with high biocompatibility. Recently, graphene quantum dots (GQDs) have attracted significant attention because of their advantages such as environmental compatibility, biocompatibility, photo-stability, and low toxicity [32-36]. Thus, carbon quantum dots can be used as good substitutes and applied in biological fields instead of unstable organic fluorophores or semiconductor quantum dots that are toxic [37]. Various simple fabrication routes for GQDs have been reported viz. laser ablation, hydrothermal method, acid oxidation, pyrolysis, electrochemical method, acid oxidation, and microwave-assisted methods [38-43]. Also, green GQDs prepared by organic compounds without chemical exposure, which has good availability, self-passivation, and high quantum yield (QY) [44]. As GQDs showed tunable and stable optical fluorescence, compatibility, and photostability, they are able to function as electron acceptors and donors [42, 45-47]. The GQDs have been investigated in bio-imaging as fluorescent nanoprobes [41, 42, 48-53], drug/gene delivery agents [38, 54-56], and antibacterial agents [57]. Furthermore, GQDs have been used in various applications ranging from catalysts to light-emitting devices [58-60]. In addition, their usages in clinical applications are expected to be expanded in the future [59, 61].

There are various methods to produce nanomaterials such as sol-gel [62-66], electrospinning method [67-69], coprecipitation [70], metallurgy powders [71, 72], SHS methods [73], and mechanical alloys [74, 75]. Moreover, there are several nanomaterials as nanoparticles [76, 77], nanolayers [78], nanosheets [79], and quantum dots [80]. Among the mentioned materials, GQDs have attracted more attention due to their unique applications.

3.1. Graphene quantum dot synthesis

The synthesis method has a major role in the properties of GQDs as well as their applications. Thus, the GQDs production should be tuned during and after their production [81]. Since the emergence of GQDs, different methods have been used to produce GQDs such as chemical, physical, and electrochemical techniques [56]. These methods of GQDs

synthesis can be categorized into the "top-down" and "bottom-up" procedures. These routes are based on the source of carbon that is utilized for the GQDs fabrication. In the bottom-up approach, the basic building units are collected to produce the desired material. Hence, to produce fluorescent GQDs by the bottom-up method, the block is operated in carbonization, condensation, and polymerization processes at optimized conditions of synthesis [82]. In the top-down approach, a bulk source of carbon (e.g. fullerenes, candle shoots, and graphite rods) is broken down into a diameter of less than 10 nm with fluorescent properties [83-85]. General examples of the last method are the mechanical and chemical treatment of C60 fullerenes that produce carbon quantum dots with small sizes (2-3 nm) [86, 87]. The top-down method requires chemical routes such as electrochemical carbonization, chemical ablation, and laser ablation to break down the molecules with large size. In the case of the bottom-up method, greener methods are used such as hydrothermal/solvothermal treatment and microwave irradiation. Indeed, the top-down procedures require complex instrumentation and severe chemical treatments but the bottom-up processes are greener and need simple procedures for the synthesis of GQDs. Among bottom-up routes, the hydrothermal/solvothermal techniques are more common due to the high quantum production efficiency and environment-friendly nature. In addition, these routes are cost-effective, easily scalable, and fast. It has been reported that the GQDs size controllability is hard through this method, but some post-treatments can be used in this case like dialysis, filtration, sonication, column chromatography, centrifugation, gel-electrophoresis and column chromatography [56]. Table 1 lists the routes used for the fabrication of GQDs used in biomedical applications.

4. Applications

As common organic label dyes cannot have emission around 650 nm, which belongs to near-infrared emission, QDs have attracted attention because of their tunable optical characteristics. QDs exhibit some characteristics including size-tunable light emission, high quantum yield, and improved chemical and photo-stability. A specific light wavelength is able to excite different types of QDs, and the simultaneous detection of their narrow emission bands for multiple assays is possible. The simultaneous imaging, sensing, and therapy is widely studied by developing nano-theranostics platforms such as QDs (Fig. 3) [88, 89]. In this paper, the latest progress in QDs utilization and biomedical applications has been reviewed.

4.1. Sensors

Due to electronic and optical properties, luminescent graphene quantum dots (GQDs) have lately been of great interest. GQDs are composed of single, double, and multiple layers of graphene sheets having the di-

Table 2.

Summary of works performed on GQDs as sensors

•	-	-			
Electrode	Linear range (µM)	LOD (µM)	Conditions	Real sample	Ref.
MWCNT. COOH/SPCEs	14.5.100	4.6	Nacl(PH=7.0)	Blood serum	[93]
MT/HMDE	25-375	0.5	BR buffer (PH= 7.2)	Blood serum	[94]
GO.MWNTs/ GCE	1.3-26	0.192	KCL(PH= 7.4)	Blood serum	[95]
GQDs-thio/ npGCE	0.2-110	0.09	PBS,K- CL(PH= 7.0)	Blood serum, urine	[96]

ameters between 3 to 20 nanometers and lateral size less than 100 nanometers [90, 91]. Excellent photostability, robust chemical inertness, high fluorescent activity, high biocompatibility, and low toxicity are among the properties of GQD [92], which are the result of quantum confinement effect and edge effect (zigzag or armchair).

Owing to these characteristics, GQDs can be employed for a wide range of applications including sensors, biosensors, bioimaging, and photovoltaic devices [97]. Gholivand et al. [96], used the grapheme quantum dots-thionine and nanocarbon electrode (porous glassy structure) to detect an anticancer drug (cisplatin). Their results showed that the combination of dyes with nanomaterials would lead to tuned electroanalytical applications of the modified electrodes in chemistry. Also, it was shown that the glassy nanoporous QDs, which are produced with thionine, could interact with drugs (cisplatin) and increase the accumulated target at the electrode. Their as-prepared electrode had good sensitivity, selectivity, and reproducibility compared to other cisplatin sensors reported in other works. Table 2 summarizes the studies conducted on the application of QDs as sensors.

4.2. Biomedicine

Kaur et al. [98] doped nitrogen (heteroatom) to graphene and produced GQDs with promising properties based on carbon nanomaterials. Their doping approach resulted in an improvement in the properties of QDs in environmental and energy fields. This caused the residual reagents elimination such as acids. Their as-synthesized materials showed excellent properties for the use in different fields like fuel cells, sensors, photocatalytic processes, batteries, solar cells, and photocatalytic processes. Lah et al. [99] used quantum dots for fluorescence sensing application by a tapered optical fiber (TMMF). The quantum dots were introduced with the aim of increasing the sensing process. In their study, nano-sized GQDs particles were produced by organic biochar. Subsequently, they coated the GQDs with the purple solution of gold nanoparticles that were functionalized by cysteamine. The GQDs with the coating layer of Au nanoparticles were obtained by carbon-nitrogen bonding reaction from carboxyls and nitrogen-hydrogen from amine groups. In their investigation, various annealing treatments were analyzed to determine the optimum sensitivity for the sensor. Fastening between the sensing element and TMMF occurs through the annealing process that changes the GQDs coating layer thickness. They reported that TMMF, which was coated by GQDs and annealed at 70 °C had a higher peak of fluorescence emission at 652 nm. In addition, the best linearity and the detecting sensitivity were achieved by the samples annealed at 70 °C. They reported that the linearity was 81% and the sensitivity was equal to 0.047 au. %. Meanwhile, TMMF coated with Au-GQDs showed higher intensity of fluorescence emission in comparison with others.

In order to detect the full RH range, Qi et al. [100] produced a quartz crystal microbalance (QCM) humidity sensor which was coated by a film of GQDs-chitosan (CS). They used the oscillating circuit technique for the investigation of the dynamic response and used impedance analysis to determine the recovery behaviors and performance of static humidity sensing. The results showed that GQDs as fillers in nanometer size can lead to good dispensability in the CS matrix, which causes enhanced mechanical properties. Moreover, more adsorption sites are achieved due to the hydrophilicity nature of CS and GQDs. They reported that the highest humidity sensitivity, and also high recovery time and rapid response, long-term reversibility, tiny humidity hysteresis (approximately 1.6% RH), long-term stability, and ideal reproducibility were achieved for the optimized QCM sensor, which makes these sensors capable of sensing a wide range of water vapor content.

Safardoust et al. [101] doped nitrogen and sulfur in graphene quantum dots (S, N-GQDs) by the hydrothermal method. Their sources of carbon and nitrogen sulfur were citric acid and thiourea, respectively. Their results indicated that the fluorescence emission of S, N-GQDs was depended on the excitation. In order to detect ascorbic acid (AA), they applied the produced S, N-GQDs as photoluminescence probe. They used the "off-on" mode for detection. Addition of Cu^{2+} to S, N-GQDs solution, caused the fluorescence quenching and addition of ascorbic acid to Cu^{2+}/S , NGQDs solution resulted in the improvement in the solution fluorescence intensity. At AA concentration from 10 to 500 µm, a linear response was observed with a 1.2 µM-detecting limit.

Tang et al. [102] produced a modified carbon electrode with a glassy structure by electrodeposition of gold nanoparticles and graphene quantum dots (GQDs/GNPs/GCE). Their prepared electrode showed good electrocatalytic activity, stability, and large surface area that is electrochemically active. They reported that the GQDs/GNPs/GCE produced in optimized conditions had good performance related to, linear calibration range, reproducibility, detection limit, and stability for luteolin determination. In addition, they proposed that the prepared sensor was able to detect luteolin content in real samples such as *peanut hulls*.

Zhao et al. [103], synthesized a new carbon nanocomposite MoS2-carbon nanotube - @ graphene oxide nanoribbons (CNTs@ GONRs) for the production of an ultra-sensitive quercetin sensor, which showed good detection performance for a wide linear range of quercetin (Que) and an ultra-low limit of detection (LOD). Also, their sensor showed accurate, stable, and good detection for Que in real specimens. Thus, their sensor was promising for applying in electrochemical detection fields. The summary of the above-mentioned work is presented in Table 3.

4.3. Imaging

One of the major recent advances in QDs applications is their application in multicolor and sensitive cellular imaging, because of noticeable enhancement in their synthesis, surface conjugation, and chemistry [104].

Sheng et al. [105] doped quantum dots with nitrogen (N-GQDs) using a hydrothermal process. In this study, PVP K90, glutamate, and citric acid were used as raw materials and the prepared sensor showed a 64.2 % quantum yield. They reported that the new fluorescence probe of nitrogen-doped GQDs can be used both for marking MCF-7 cells and the detection of Cr(VI).

Fan et al. [2] prepared GQDs with specific properties for imaging of the mitochondria or cell nucleus by a facile method suitable for largescale production. Their aim was to solve the weak points of GQDs such as low-targeted specificity and selectivity, unachievable large-scale synthesis by green methods, and unreported imaging of mitochondria. The synthesized GQDs- tetraphenylporphyrin (TPP) and GQDs- polyethyleneimine (PEI) had low cytotoxicity, a high yield of about 60%,

Table 3.

Summary of the QDs used in biomedicine	
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Researcher	Composite	Application	Ref.
Gholivand	GQD-thno/ npGCE	Voltammetric sensor	[96]
Lah	Au-GQD		[99]
Qi	CS-GQD	Optical sensors	[100]
Safardoust	S,N- GQD	Humidity Sensor	[101]
Tang	GQD/GNP/GCE		[102]
Zhao	CD/GQD/GCE	Ascorbic acid con- centration sensitive sensors	[103]

and good optical properties. They reported that both GQDs have high target selectivity for the cell nucleus and can be used for mitochondria imaging. They claimed that the synthesized GQDs did not exhibit the photobleaching and cytotoxicity compared to common fluorescent dyes.

In addition, the synthesized GQDs can be used as new materials for monitoring and locating mitochondria and the cell nucleus in the field of biomedical. In other work, Gvozdev et al. [106] synthesized semiconductor nanocrystal composed of polycationic aluminum phthalocyanines (Pc) complex and the human transferrin in hollow form. Due to the hydrophobic and electrostatic interactions, Pc molecules diffuse into the shell of QD while protein formed covalent bonding onto the organic shell of QD. The results showed high Pc delivery efficiency to the A431 cells. Moreover, HC was stable in cells. They reported the successful transfer of energy from the QD to Pc and the HC photodynamic influence in the cells, which offers QDs as light-harvesting antennas to enhance the effective absorption photosensitizer molecules cross-section in the blue-green spectral region and the increase of the photodynamic action of Pc.

Hai et al. [107] prepared an imaging system and pH sensing by encapsulating graphene quantum dots in folic acid (FA-GQDs) as a probe. Their tests showed that encapsulated FA-GQDs are stable and homogenous and the FA was bound to the GQDs surface. The synthesized FA-GQDs showed pH-sensitive properties and multicolor emission characteristics. In addition, they proposed a pH sensor with ratio-metric fluorescence based on the response of pH at low excitations (280 nm). It has been used for the pH determination of cell suspensions and aqueous specimens. The pH-sensitive, broad emission properties of FA-GQDs offer a great potential for application related to particular living cells multicolor imaging and pH sensing.

Huang et al. [32] introduced a new and effective method for GQDs preparation from graphene oxide (GO) by the one-step thiolene click reaction which is efficient and cheap compared to conventional routes. In addition, the results showed good biocompatibility, strong green fluorescence, uniform nanoscale size, and stable photostability. They purposed the impartment of carboxyl groups with GQDs having great suitability and water solubility to be modified with different polymers for drug delivery applications. Overall, the suggested that the one-step thiolene click reaction is a high-efficiency method for designing the characteristics of GQDs for applications in various biomedical fields.

Jin et al. [108] selected a nontoxic and cost-effective source of sulfur to prepare S-GQDs with high luminescence by a simple hydrothermal approach in one-step. Their objective of doping sulfur was the improvement of the fluorescent intensity of QDs. The synthesized S-GQDs showed low cytotoxicity that would simply diffuse into the membranes of the HeLa cell. Also, they reported that incubated S-GQDs with the common bacteria medium had low antiseptic qualities. They suggested that sulfur doping enhances the optical properties and indicates the potential of these GQDs for bioimaging applications.

In the Mahmood Kashan et al. [109] study, a simple, low-cost, green, bottom-up synthesis approach was suggested for the production of a biocompatible probe of His-GQDs using histidine and citric acid. The luminescent probe had excellent solubility in water, low cytotoxicity, and optimal fluorescence efficiency. The size distribution was near to 2 nm. They reported that the synthesized His-GQD were able to enter the cytoplasm of human ACHN cells and showed low cytotoxicity and high viability, hence, they are promising candidates for in-vitro cellular imaging.

Mondla et al. [110] prepared smart graphene quantum dot (NSGQD) with S and N donor having good fluorescence properties. The radiative recombination of trapped holes and electron on the surface of NS-GQD was the reason for the smart fluorescence properties. They reported that the unique fluorescence characterization of NS-GQD is due to heteroatoms (N and S) existence. The term "smartness" is due to its performance



as a promising fluorescent probe in the field of intracellular imaging, which is comparable to the available commercial dye. In addition, DCQ was formed due to interaction between the functional group in NS-GQD and drug streptomycin, in which Stm and NS-QGD are mixed with each other in a simple approach to form a carbogenic structure. On the other hand, the antibacterial efficacy was improved by DCQ due to the free radicals generation in bacteria and it is safe in terms of synthesis processes.

Rajender et al. [111] synthesized edge controlled GQDs with few layers and high fluorescence yield through a solvent dependent process. To investigate the cancer cells' bioimaging, the high photoluminescence (PL) production of GQDs was used. Their study proposed that the functional groups and edge sites of graphene quantum dots can be controlled by the addition of various solvents in the GQDs top-down processing. Different analyses demonstrated the oxygenated functional groups on the edge of GQDs. A high 32% PL quantum yields (QY) (32%) was obtained by the GQDs synthesis using dimethylformamide (DMF) solvent. This high amount is resulted from defects of oxygen functional groups and the enriched edge sites. They reported that the PL emission efficiency in the solvent medium is related to GQDs dielectric constant. The cancer cell lines bio-imaging results showed blue PL emission inside the cells, which demonstrated their good ability for bio-imaging applications. Also, good biocompatibility of synthesized graphene quantum dots with A-375 cells was observed in comparison with that of HeLa cells.

Wang et al. [112] prepared theranostic nanoparticles by doping boron and nitrogen in GQDs. The nanoparticles had a PL emission spectrum from 950 nm to 1100 nm. They presented the first results of near-Infrared-II (NIR-II) imaging (>1000 nm) in-vivo for blood vessels and internal organs in a mouse model using a metal-free QD. They reported that the NIR light was absorbed and transferred into heat by the nanoparticle, so the nanoparticles can be used as photothermal therapy (PTT) agents in cancer treatment applications. Their study results revealed that the irradiation of NIR for 5 minutes, while the nanoparticle was injected systemically, led to complete suppression of the growth of tumor cells [113]. Furthermore, they reported its potential for imaging-guided therapy for cancers due to its desirable therapeutic and fluorescent characterizations. Table 4 summarizes the above-mentioned research.

4.4. Drug delivery

The use of GQDs for in-vivo drug delivery is broadly investigated. QDs have high delivery efficiency because of their intermediate size that decreases the uptake by the reticuloendothelial system and the renal clearance leading to the increase in the blood circulation time [80].

Senel et al. [114] synthesized N-doped GQD and reported its properties such as cost-effective production, DNA interaction, potential cell growth, and antioxidant and antimicrobial activities. They observed that GQDs doped with nitrogen could be linked to DNA through electrostatic and intercalation route. According to their report, the formulations

Application of GQDs in tumor treatmen	t field	1
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Researcher	Composite	Application	Ref.
Fan	GQD	Mitochondria vector illustration	[2]
Hai	PH sensitive FA-GQD	Cellular Imaging	[107]
Huang	GQD	Cellular Imaging	[32]
Ragender	GQD	Biological imaging of cancer cells	[111]
Wang	-	Biological imaging of cancer cells	[112]

Table 5.

GQDs applied in the field of drug delivery

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	Researcher	Composite	Application	Ref.
	Senel	SiRNA/GQD/ DOX	Therapy of A549 cancer cells	[114]
	Akbarzadeh	Hybrid silica / GQD/PEGylated	Therapy cancer	[115]
	Innazzoa			[116]
	Javanbakht	CMC/GQDDOX	Therapy of K562Leu- kemia cells	[117]
_	Nasrollahi	GQD/CDDP	Breast Cancer Cells	[118]

containing short interfering RNA (siRNA) synthesized by GQDs can decrease and minimize the side effects and anticancer drug toxicities resulting from common chemotherapy methods. They reported that due to the QDs luminescence characteristics, the GQD-containing formulations led to the penetration into cells and the reduction in cancer cell numbers based on ephrin-A (EpHA2) reduction, which showed high efficiency in A549 cells. They reported that this is the result of the GQDs shearing effect on DNA and siRNA. Based on their research, the QDs effect can be maximized in higher doses and cause lower cell viability by breaking the cancer cells DNA. Also, they showed the bioimaging capability of QDs in low doses. In addition, a complex of siRNA-GQDs is effective at low dose for A549 cells.

Akbarzadeha et al. [115] studied the silica-coated dipole quantum dots. They reported the synthesis of smart nano aptamer-targeted by mesoporous silica-coated QDs having bimodal imaging capacity. In addition, their in-vivo experiment results indicated that the prepared targeted hybrid system showed the capability of MR and fluorescent imaging.

Iannazzoa et al. [116], studied the graphene QDs for drug delivery as well as a cancer treatment. They indicated that the prepared GQDs have a great ability of drug delivery into cancer cells and biocompatibility. Also, the multimodal conjugation provides the possibility of incorporating both targeting ligands and drugs in nanomaterials. This led to minimizing the toxicity and side effects of conventional chemotherapy.

Javanbakhta et al. [117] reported that a hydrogel film of nano-carboxymethyl cellulose/graphene quantum dots (CMC/GQDs) could be applied for drug delivery applications. They synthesized the film using the casting route to introduce GQDs as in the CMC hydrogel as a polymeric matrix. The hydrogel film of CMC/GQDs exhibited an excellent degradation, mechanical properties, swelling, and permeability. The presence of GQD in CMC film led to the prolonged doxorubicin (DOX) release and pH-sensitivity. According to cytotoxicity results, the DOX/ CMC/GQD nanocomposite had a great capability to act as an anticancer agent with high efficiency. They also reported that the prepared nanocomposite did not have noticeable toxicity against K562 blood cancer cells.

Nasrollahi et al. [118] studied GQD nanoparticles, which were bond-

ed to an antibody (scFvB10) for targeted cellular imaging and Cisplatin (CDDP) delivery.

Using strong GQDs fluorescence as bioimaging agents, the mechanism of targeting and efficient uptake of antibody-linked GQDs through the EGFR-mediated endocytosis were conformed. Using 50% loading of CDDP, targeted delivery of the drug was achieved by the antibody-linked GQDs.

In a study conducted by Li Ruiyia et al. [119], core-shell drug delivery agents consisting of, MGC-803 cell membrane shell and gold nanoparticle as the core, were synthesized. In comparison with free DOX, the prepared sample showed both light and pH-stimulated DOX release, homotypic cancer cells targeting, and chemo/photothermal therapy having a higher activity against cancerous cells. Their excellent biocompatibility and high anticancer activity were confirmed by in-vivo and in-vitro investigations. A new approach to design and synthesize nanocarriers for the diagnosis of cancer in the early stages and in-situ treatment has been suggested in this research.

In a study carried out by Xiaoqian Su et al. [120], nanoparticle uptake in cells and secretion of drug molecules into cells by altering FRTE signal in cancer cells were checked out. They also observed an increase in the therapeutic effect of doxorubicin in combination with Fe_3O_4 SiO₂@GQD-FA nanoparticles. In general, the reported nanoparticles can be considered as a suitable basis for the effective diagnosis and treatment of cancer. Table 5 lists the above-mentioned research

4.5. Diagnosis

One of the applications of GQDs in the field of biomedicine is in diagnosis. The advantages of having low toxicity of GQDs over traditional semi-conductive QDs has made them suitable for in-vivo labeling [6, 121].

In the fields of diagnosis and cancer therapy, quantum dots show great potential to be applied as fluorescence labels. The quantum dotes are suitable for distinguishing and specific applications due to their physicochemical properties. The mode of QDs implementation has a specific effect on their applications. The GQDs are ideal candidates due to the size-dependent and symmetric photoluminescence band combined with very wide absorption bands. On the other hand, GQDs are good reactive oxygen species (ROS) producers and have excellent potential for applications in photodynamic therapy fields. Despite the QDs potentials, various unsolved problems have remained. One of the major issues is that QDs can be used for real-life applications if all interdependencies between their chemical and physical properties have been determined. This becomes the main concern for GQDs application due to the insufficient information about different aspects of their key optical properties such as extinction coefficients, lifetimes, PLQYs, photo brightening mechanisms, and photobleaching. It is promising that GQDs are relatively new-materials and the publications rate in cancer therapy applications and diagnosis is increasing rapidly (Fig. 4). Furthermore, there is a big gap in knowledge about the toxicity of both types of quantum dots and semiconductor QDs. This is the main factor that needs to be studied immediately because the main application of QDs is in biomedical fields specially and the important factors are their biocompatibility and cytotoxicity. Unfortunately, there is no standardized methodology for such assessment and it is, therefore, impossible to compare results obtained from different biomedical applications found in the literature [122].

Suleiman et al. [123] evaluated cancer cells using nitrogen-doped graphene quantum dots. To detect colon, breast, and stomach cancer cells, a novel silo sensor based on Rayleigh scattering was used. There are also groups of NH or NH_2 in the GQDs that provide more active sites for bonding between cells and matter. The biocompatibility of quantum dot nanomaterials was evaluated by the MTT method. Cellular uptake evaluation revealed that FA-N-GQD uptake increased in HT29, MKN45,

and MCT7 target cells, and the uptake of FA-N-GQD in non-target cells also decreased. The prominent features of the introduced cytosensor include its functional system based on the interaction between antigens, sensitivity to cancer cells, and low toxicity. He et al. [124] worked on quantum dots to detect cancer. In their studies, quantum dot performance in targeted drug delivery and imaging were checked out. Actually, these QDs are improved to reduce toxicity and increase the shelf life of blood with other nanoparticle dots.

Fan et al. [125] showed that pH-responsive fluorescent (pRF-GQDs) could detect cancer in the early stages of tumor formation. The reasons for the application of PRF-GQDs as a prospector are their high sensitivity against cancerous cells, high safety, and fluorescence switching between healthy weaves and tumors. Considering these properties, pRF-GQDs are good options to diagnose or treat cancer. In addition, electrochemical reaction, as an effective approach to dope carbon materials with heteroatoms make it possible to finely alter their intrinsic properties and introduce new characteristics. Tuning the properties through the atoms doping approach allows the synthesis of GQDs responding to pH deviates from 7.4.

5. Conclusions and future insights

QDs are nanoparticles with high photo-luminescence having the potential to be used for targeted drug delivery and imaging. Although GODs perform well in areas such as sensors, drug delivery, and bio-imaging, they have limitations such as overall toxicity and body clearance in biomedical applications. This has led to the synthesis of quantum dot-based composites. Indeed, by combining GQDs with biologically active molecules and/or nanoparticles, theranostic platforms are constantly being developed. This review on GQDs reported their potential properties and their applications as carriers for sensor and drug delivery applications. Additionally, research on synthesizing routes according to their application was investigated. There may be a need for future investigations focusing on other heteroatoms doping. Controlled doping of GQDs and graphene would be possible by performing more studies with theoretical analysis, which may lead to an increase in their efficiency for environmental and energy source applications. There might be an increasing interest in the utilization of N-doped carbon materials for the applications related to photocatalysis for the remediation of water pollutants. Moreover, there are few reports addressing nitrogen-doped graphene and nitrogen-doped GQDs to inactivate the microorganisms in water and air. The disinfecting effect of these materials on water and air may be environmental studies. In order to produce GQDs with various functional groups and characteristics, other components may be also investigated. Hence, certainly, all these promising properties of NS-GQD would introduce them as good candidates for biomedical applications in the recent future. According to recent studies, further research on doping nitrogen into GQDs for drug development is appealing. It is thus expected that many of the knowledge gaps mentioned above will be addressed.

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Recent developments and applications of nanocomposites in solar cells: a review

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ABSTRACT	ARTICLEINFORMATION
These days, solar cells have attracted considerable attentions because they are environment-friendly sources of	Article history:
electric power. The present review is focused on composites and materials that are used in the solar cells field, including Si-based solar cells, dye-Sensitized solar cells (DSSC), thin film solar cells, Quantum dot solar cells	Received 15 December 2019 Received in revised form 28 December 2019
(QDSC) and Perovskite solar cells (PSC). TiO_2 based nanocomposites, which are widely applicable in the solar cells are also reviewed.	Accepted 30 December 2019
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	Solar-cell
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1. Introduction

These days, fossil fuels can be considered as a major energy source globally. The main fossil fuel sources from the industrial revolution (19th century) are gas, coal, and oil. Human communities use the fossil fuels to produce electrical and thermal energies that are necessary for different domestic and industrial applications. Electricity supply increases the productivity and access to principal services. This finally improves the

quality of human lives [1]. Nevertheless, the energy produced through these kinds of sources is not sustainable. The main issue about these kinds of fossil fuel sources (oil, gas, and coal) is that they have limited natural resources that will be depleted in near future. On the other hand, these abovementioned non-renewable sources emit CO_2 during the power production that is a type of greenhouse gases [2, 3]. The formation of thermal insulating layers would be accelerated by greenhouse gases in the higher atmosphere of earth. This will avoid common heat

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dissipation that is the result of global warming. Furthermore, the influences of global warming on agronomic productions and the ecosystems cannot be denied. It is known that rise in sea level is another result of global warming. Statistics show that the world population increases to 10 billion in 2050. If this happens, carbon emissions should be limited by 75% in 2050 to decline the rise of 2 °C in the earth temperature [4]. Clean energy sources should be used to limit the environmental hazard considerably. The key step to achieve this aim is the use of environmentally friendly sources such as solar energy, biomass, geothermal energy, hydropower, biofuel, and wind power. Although the majority of these mentioned clean energy sources are rather non-polluting, solar energy can surely be considered the most attractive energy source due to its abundance, cleanness, and safety. Reports exhibit that if solar cells with the efficiency of 10% cover merely 0.1% of earth's crust, the immediate need of energy may be met worldwide [5]. Consequently, to meet the increasing need of energy around the world, solar energy can be taken into account to play a crucial role in this regard. To date, solar energy has been applied chiefly to produce electrical and thermal energies. Solar light can be collected by technologies, which can work based on solar energy. The collected solar light can produce heat immediately. Photovoltaic is the technology that can transfer the solar energy to electricity. Hence, solar cells can be called photovoltaic devices. This technology is classified into three generations (a) crystalline silicon based SCs, (b) hybrid and amorphous silicon based, GaAs-based or CuGa thin films selenide (CIS/CIGS), cadmium telluride (CdTe) based, and (c) materials such as metal oxide semiconductors with wide band-gap TiO2, Nb2O2, SnO₂, ZnO, and etc. [6-9]. The main instances of the newest generation of solar cells are quantum dots that are sensitized to dye, and organic solar cells, which makes them more effective for using the sunlight. The virtue of this novel generation is based on different kinds of novel materials are used to make them instead of conventional silicon. The favorite third generation solar cells can be perovskite based solar cells, a solar cell design that uses quantum dots as the absorbing photovoltaic material, and dye-sensitized solar cells (DSSCs). All of these different types of solar cells have both advantages and disadvantages. Efficient photovoltaic performance is one of the benefits of the first generation solar cells, whereas they are not adaptable enough. In addition, their considerable processing cost is their main limitation. The complex processing and toxic effect of second generation solar cells make them difficult to be used as photovoltaic devices, however, the photo-electric conversion efficiency of them is high. Now, dye-sensitized solar cells (DSSCs) are attracting attention scientifically and technologically, since they are easy to fabricate, extremely effective and inexpensive substitute for common photo-voltaic devices. The energy crisis resulting from the constant consumption of common energy resources, such as oil, natural gas and coal can be resolved by sustainable sources of energy like solar cell modules. Solar cells have been emerged to harvest and convert solar energy to electrical energy to provide an invaluable source.

2. Photovoltaic effect and principle of solar cell operation

The photovoltaic effect was observed for the first time by Becquerel through conversion of solar radiation. Photovoltaic effect is commonly known as the emergence of an electric voltage between two electrodes that are attached to either a liquid or solid system which is radiating light onto the system [10]. The modern age for photovoltaic devices commenced when Chapin developed the initial single-crystal silicon solar cell in 1954. The first Si solar cells with the efficiency of 6 % were fabricated at Bell Laboratories. In 1960, their efficiency was increased to 14% with a better technology [11]. A solar cell is able to convert light directly into electricity (Fig. 1).



Fig. 1. (a) The equivalent circuit and (b) schematic structure of a solar cell device.

The electric power produced by both bias voltage and electric current is the result of the produced shining light on a solar cell. During the process, firstly, electron and hole carriers are generated through the incident photons absorption. Secondly, the assembly of these carriers by the p-n junction inhibits the recombination made by a p-n junction to separate the electrons and holes spatially. With the short-circuited solar cell, (such as the solar cell and an emitter are connected), carriers generated from light would flow through the external circuit. It would be worthwhile to make an electrically equivalent model (Fig. 1a) to find out the electronic behavior of a solar cell. The behavior of an ideal solar cell is similar to diode, which can be modeled, with a diode in parallel mode via a current source. A p-n junction would be the basis of the diode formation and can make a less considerable electric current under reverse bias (V<O) in the dark condition than that under forwarding bias (V>O). PV devices show such rectifying behavior.

Upon illumination, photocurrent is produced, which is divided into two paths that go through the diode and load, respectively. It is interesting to say that the density of photocurrent is related to the illumination intensity. The current density related to each pathway is based on the level of illumination, the resistance of the diode and the load. For loads with higher resistance in contrast to the diode, higher proportion of the photocurrent flows over the diode. This results in a smaller current through the load and a potential difference between the cell terminals which leads to photo voltage provision by diode.

Solar cell generates the photocurrent which is dependent on the incident light, the active area of solar cell, semiconductors absorption coefficient, band gap, and the efficiency of charge collection [12].

3. Si-based solar cells

Silicon and silica are widely studied by researchers [13-18]. Generally, although Si is not an ideal material for photovoltaic conversion, it has been used in the production of solar cells in a large-scale. The low absorption coefficient of photons results in thicker cells in an indirect band gap semiconductor. Nowadays, crystalline Si has a 90% market share in almost equal shares for cast silicon and single crystal. In addition, amorphous Si has a 9% higher market share. Prior to the appearance of photovoltaics, high quality Si was produced in large scale for semiconductors. Thus, it is expected that silicon plays a dominant role in the market of world [19]. Estimates show that photovoltaic material production will be increased for next years along with the growing significance of multi-crystalline silicon. At present, Mono-crystalline Si can be used to develop the high efficiency solar cells. With the development of absorption in the junction area, wafers that are thinner than 200 µm are also used. The cost of viable Si is going to increase significantly in close future. Thus, it is expected that the use of thinner wafers would be increased in the future.

3.1. Amorphous Si solar cells

Varied affordable polymers as well as other elastic substances that consume a smaller quantity of energy are able to be applied in the manufacturing process of the amorphous silicon solar cells. This is due to the fact that their processing can be performed at a low temperature [20]. Consequently, not only the price of the a-Si solar cell is relatively reasonable, but also it is widely accessible. The fabricated silicon material of a cell without a fixed structure of atoms in the non-crystalline structure and lattice configuration can be defined as the "amorphous" in the field of solar cells. These are formed via coating the doped Si to the backside of the substrate/glass plate. They appear silverfish on the conducting side and dark brown on the opposite side (reflecting side) [21]. The key problem of a-Si solar cell is the weak and virtually unstable efficiency. It is acceptable that the cell efficiency at PV module level falls automatically and the range of variation for efficiencies of commercial PV modules is in the range of 4-8%. Moreover, a-Si solar cell can act at high temperatures and they are the right option for the variable climate situations [22].

3.2. Crystalline silicone solar cells

Crystalline silicon SCs contain monocrystalline and polycrystalline technologies. They enjoy a photovoltaic market share of nearly 90% globally, thus they can be considered the most substantial photovoltaic technology. Currently, monocrystalline and polycrystalline silicon solar cells with common surface field process of Al-back have shown the efficiency value of 18.5% and 19.8%, respectively [23-26], which is very similar to the limit of the common production line of crystalline silicon. The solar cells are made of crystalline silicon produce PV power that includes the following physical processes: (i) absorption photon resulting in the excitation of the pairs of electron hole and (ii) dissociation and transportation process to the external electrodes for electron-hole pairs [27-32] . Thus, generally the technology of high efficiency crystalline silicon solar cell include: 1) the design of a modern cell structure, 2) the optimized-light absorption, 3) the efficient assembly of photo-generated carriers and 4) the elimination of the recombination loss of photo-generated carriers as well as the area reduction and the electrode resistance . A categorization of crystalline silicon solar cells with high efficiency include intrinsic heterojunction thin-layer cell (HIT), interdigitated back contact cell (IBC), heterojunction interdigitated back contacts solar cells (HBC) and passivated emitter rear cell (PERC).

3.3. Monocrystalline silicone solar cells

Czochralski process, is a process in which single crystals of silicon would become mono crystalline solar cell [33-35]. Si crystals are sliced from the large ingot. Their production needs exact processing since the recrystallizing process of cell is not cheap and includes several processes. The efficiency of silicon solar cells with mono-crystalline single-crystalline structure is between 17 - 18% [36]. Amorphous Si (a-Si) PV modules are the elementary solar cells that are first to be manufactured industrially.

4. Thin film solar cells

It is possible to reduce the cost of photovoltaics production. More affordable thin-film technology, which involves different semiconductors such as CuInGaSe2 (CIGS), CuInSe2 (CIS), CdTe and CdS, can replace the wafer-based solar cells. Many appropriate options can be applied to produce the thin film second-generation solar cells. Recently, thin-film Si and amorphous silicon (a-Si) have also been suggested to be suitable candidates [37]. It is possible to remove the silicon wafer by using thin-films. This will reduce the material costs significantly. An increment in the unit of manufacturing from a silicon wafer (the order of 100 cm² compared to a glass sheet of 1 m²) is another advantage of this technology. The matured second-generation "thin-film" technology will surely provide domination by the costs of the component materials in the future. In this regard, they are encapsulants including top cover sheet. Nevertheless, there is a limit for the cost of constituent materials. It cannot be below a minimum limit. Cu_S and CdTe are promising materials as absorbers in heterojunction solar cells, which have the direct band-gaps of 1.2 eV and 1.45 eV, respectively. Under sunlight radiation, the energy gap of the Cu_sS and CdTe absorbers is about optimal value for maximum efficiency. Thin films are suitable for preparing photovoltaic cells with great efficiency due to the 8 direct transition types of their band structure, which can present excellent absorption coefficients. In association with other p-type semiconductors, CdS that have the energy gap value of 2.54 eV and as a native n-type semiconductor) can be used as window layer. If the thickness of device is optimised, the conversion efficiency will be improved by CdS.

4.1. Thin-film crystalline Si cells

Since last years, companies such as Kaneka and Astropower took promising steps towards the thin-film monocrystalline silicon (mc-Si) solar cell with 10% efficiency as well as thin-film large-grained poly-Si solar cell with an efficiency of 16%. These corporations made significant developments regarding crystalline Si thin-film solar cells [38]. At present, the efficiencies of poly-Si cells with large grains can be enhanced from 15%-17% to nearly 18%. Furthermore, the efficiency is expected to increase to 20% in the future, since there is no limit for monocrystalline Si thin-films by material constraints. Considering the cost of crystalline Si thin-film solar cells, the association of glass as a substrate and crystalline Si offer the most economical method for large-area monolithically integrated modules. With this in mind, the efficiency of this technique is not as high enough as those produced from other processes, which is the most significant drawback for this method. To produce thin film solar cells with reasonable price and high efficiency, transferring thin films of monocrystalline-Si to glass is an alternative method.

5. Tandem cells

If the energy absorbed by photon is slightly higher compared with the cell bandgap, energy losses in solar cells can be mainly ignored. The tandem or multijunction cell (multiple cells with various bandgaps) is a direct application of this effect. Each cell converts a narrow range for photon energies near its bandgap.

Most recently, the tandem cell is produced commercially. Double and triple junction cells based on Ge/GaAs/GaInP have been used for use on spacecraft. They exhibit about 30% terrestrial conversion efficiencies [39]. Good resistance to radiation damage and low temperature coefficient are their main advantages. Besides, they are ideal for high concentration optical systems applications. Tandem cells can be used to enhance the reliability and performance of thin-film amorphous silicon cells so that they get fixed efficiencies up to 12% confirmed for Ge:Si:H triple junction cells [37].

6. Dye-Sensitized Semiconductor

The modern era of work on organic solar cells has commenced in 1960s. The progress was due to the clarification of the mechanism related to spectral sensitization of semiconductors through absorbed monolayers of dye molecules. It is well-known that Coulomb interactions between adsorbed molecules and charged defects play an essential role



Fig. 2. Illustration of the OSC working mechanism.

to create light harvesting that is the result of a distribution of ionization energies of the adsorbed molecules [40]. Depending on the surrounding environment of the molecule, which absorbs the light, polarization effects and other corrections can reduce the ionization energy to an acceptable value for transformation of electrons [41]. It is necessary to find out the primary processes, depending on relations of the energy levels. Charge carrier injection, transport, trapping, and photogeneration, are based on these energy levels. The research on dye sensitized devices using porous TiO₂ has shown promising results. The monolayer dye molecules are excited after the photons absorption on porous TiO2. If the energy of excited state is higher than the lower edge of the conduction band of TiO,, electron transferring can occur (form the dye to the semiconductor). A redox species dissolved in an electrolyte is needed for completing the cell, which is able to fill the distance in the porous matrix. Moreover, it gives an electron to the oxidized dye. Then, the mediator redox species is oxidized. Next, it can be reduced at the metallic cathode of the cell. To replace the p/n junction, organic materials can be applied in soft junction cells (organic cells). Polymer/fullerene blends, interpenetrating polymer networks, devices based on small molecules can be used. There are no limits for the choices and large area cheap cells are very attractive.

7. Organic solar cells

Organic solar cells (OSCs) have attracted the attention of researchers significantly, as they are not heavy, flexible and easy to fabricate (Fig. 2). Organic solar cells need to attain their potential Shockley-Queisser (SQ) power conversion efficiency (PCE) limit (approximately 33%). However, the enhancement of PCE (from <1% to 14%) in the recent decade has presented them as favourite solar-cell technologies among other solar-cells [42]. Organic semiconductors (as donor and acceptor materials) having optical and electrical characterizations are responsible to determine the performance of device and are able to be used in organic photovoltaic (OPV) devices. Large amounts of raw materials have been developed through adapting the structures in side chains and backbones by researchers, for optimization of the crystallinity and band gap. This was done with the goal of obtaining a well-matched donor/acceptor blend system, great charge transportation properties and the excitons dissociation. The power conversion efficiency of an organic solar cell can be controlled by photovoltaic properties of a bulk Hetero Junction OSCs. It is acceptable that the conjugated organic molecules selection in the nanostructure of a photoactive layer can induce morphology changes and this, can affect photovoltaic properties of a BHJ organic solar cell. With the improvement in extremely sensitive microscopy techniques and light sources, quantification of microscopic information has greatly improved. Methods such as transmission electron microscopy (TEM)



Fig. 3. Demonstration of device structures in OSCs: (a) single-layer, (b) bilayer, (c) BHJ, and (d) ordered-heterojunction.

and atomic force microscopy (AFM) have enhanced the evolution characterization of design and development of materials structurally. Recently, with the characterization improvement of an active layer via X-ray scattering, scientists are able to plan devices through ideal conditions of processing with the use of new conjugated organic materials molecular structures for the OSCs with optimal configuration (Fig. 3). Since the materials should be selected with respect to their function, the hole or electron transportation interlayers, a flexible Polyethylene terephthalate/ graphene-substrate or an ITO-glass, a photoactive layer, and metal electrodes, can constitute the structure of a traditional OSC device . The excitation of electrons can occur from the highest to lowest energy level of their HOMO when photons of solar energy can be absorbed by organic materials in the photoactive layer, which can lead to formation of an exciting state (electron-hole pair) bounded through attractive forces of Coulomb. Maximum photons from the solar spectrum of energy need to be absorbed by active-layer materials in order to fill a good population of excitons of the LUMO level. In fact, a right blend of organic species, is required to absorb the majority of the photons from the spectrum of solar energy including the NIR region Dielectric constant from 2 to 4 for organic materials can increase bonding energies in excitons. They should be diffused to a nearby interface of D/A for separation into free charges. The charge transfer (CT) excitons can be generated from photogenerated excitons owing to high binding energy at the D/A interfaces. Subsequently, dissociation occurs into courtesy of free charges of an inbuilt electric field made via an organic combination function offset of the acceptor/donor. Thus, free holes as well as electrons can be transferred through particular domains to create a photocurrent [43].

8. Quantum dot solar cells (QDSCs)

During the past few years, QDSCs have achieved popularity due to an increase in ECE of PV devices (about 42%) above common Silicon -based SCs and even S-Q limits. Three different methods, including (1) schottky SCs [30], (2) semiconductor nanostructure-polymer SCs [44], and (3) solar cells based on QDs [45] can be used to incorporate Semiconductor nanocrystals in PV cells. QDs have attractive properties such as excellent optic absorption coefficients (α , about 1,00,000 cm⁻¹), MEG, large dipole moments, solution process ability, high molar extinction coefficient, bandgap dependent on size, extinction coefficient, and photo-stability. QDs can be widely regarded in PV applications due to mentioned properties [46]. QDSSCs and their different components have been shown in Fig. 4(a). Furthermore, Fig. 4(b) shows charge carriers disorder between varied constituents. QDs which can be considered as light absorbents [47], lead to the production of charge carriers with transmit across elective local phases in QDSSCs. Incident photons generate electrons. The generated electrons transfer to a semiconducting



Fig. 4. (a) Schematic illustration of QDSSCs with their different components; (b) charge carriers shuffle between various components.

oxide layer (zinc oxide, titania, tin oxide [48], etc.) with QDs attached. Next, the transmission of transported electrons to the conducting ITO/ FTO glass will take place. This supports the oxide layers with nano structure. Next, QDs achieved their initial state again via a solid/liquid electrolyte, which contain a reversible redox couple. The counter electrode (CE) can be made from metal and it can be semiconducting. It should not have slow kinetics for the electrolyte redox couple. Effective QDSSCs need an excellent fill factor, high incident of photon-to-current efficiency (IPCE) and great open circuit voltages.

Recombination processes and the carrier mobilities can be considered to have a considerable impact on the effectiveness of Quantum dot sensitized SCs. Thus, it is accepted that the efficiency of electron collection in these cells can be dependent on morphology and the nature of the transporting phases of the charge carriers. The MEG phenomenon (as one of the most important benefits of QDSSCs), occurs in semiconducting nanocrystals, which provides the advantage of the use of hot carriers for the system. Pairs of electron holes can be generated by the MEG phenomenon and it can result in a single photon absorption in at least two times of band gap energy of the sensitized material. For PV applications, dyes are being substituted by QDs, since MEG provides much higher ECE (about 44%) than common DSSCs (in theoretical point of view) [49]. Moreover, the sensitivity of QDs to light, simple synthetic method and tunability of light absorption, make them great light absorbers. Besides, semiconducting nanocrystals enhance the robustness of the cell. The photovoltaic characteristics proved that the use of metal oxide (e.g. Cobalt Oxide), as counter electrode materials, and the CE can reach a PCE of 6.02% for QDSSCs, which was illustrated by Li et al. [50] in 2019. This technique increases the efficiency in contrast with common Cu₂S CE (32.7%). Badawi et al. [51] synthesized Ternary alloyed Cd_{1,x}Co_xS (in which x can be 0, 0.1, 0.2, 0.3 and 0.4) QDs onto TiO, nanoparticles electrodes to use in photovoltaic applications directly. Among them, the alloyed Cd_{0.9}Co_{0.1}S QDs sensitized solar cell, exhibited the best photovoltaic capability, which is because of the harmony that exists between the energetic levels of the QDs sensitized solar cell components and the improvement in the absorption of solar spectrum. The photovoltaic valuation of the collected QDs sensitized solar cell, show high reproducibility, and sensitiveness that undercut onoff solar illumination. Mahanandia et al. [52] synthesized monodisperse Cu₂ZnSnS₄ (CZTS) QDs through solvothermal method in 2018. They found that CZTS QDs are extremely pure with the optical band gap of larger than bulk CZTS ~1.5-1.6 eV (1.89 eV). This is because of the quantum confinement, which makes them suitable for solar cell applications. Moreover, the optical absorption spectra of CZTS QDs show a blue shift to a higher energy.

9. Perovskite solar cells

In contrast with the common silicon and thin film SCs, perovskite solar cells have many advantages, which have the formula of ABX₃, in which A and B are cations of different size and X denotes a halogen e.g. Cl-, Br-, I-. Among the solar cell research community, perovskite solar cells are recent finding, which have many benefits compared to thin film based and conventional Si solar cells. Conventional silicon based solar cells must be processed under high temperatures (>1000 °C) and they require many processing steps, high-priced and vacuums facilities [53, 54]. They usually have efficiency up to 31% [55]. However, we have to consider current problems with perovskite solar cells i.e. their durability and stability. The material degradation takes place over time. Thus, a decrease in overall efficiency is expected. Consequently, to bring these cells into the market place, more research is required. Table 1 illustrates the Perovskite solar cell efficiency at various temperatures.

Park et al. [56] reported the principles for the design of a high-power PSCs for inside light applications having low-intensity, with a special emphasis on the electron transport layers (ETLs). Their results showed that the procedure of power generation of Perovskite solar cells when it is under halogen lights and a low intensity LED is not similar with the 1 Sun standard test condition (STC). In comparison with the c-TiO₂ (the compact-titania) PSC, c-TiO₂ PSCs was able to generate much more power than mesoporous-Titania (m-Titania) PSCs under low-intensity condition (200-1600 Lux) situations, although a PCE was gained from the PSC based on m-Titania under STC. Methyl ammonium (MAI) and Pb(NO₃)₂ was used in perovskite film by SupaChoopun (as starting material). Spin coating technique was used for deposition of precursor of **Table 1.**

Efficiency of Perovskite sola	r cells (DSCC)) at various	temperatures
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Temperature (°C)	Efficiency (%)
30	9-10
35	9-10
40	8-9
45	8-9
50	8-9
55	7-8
60	8-9
65	7-8
70	6-7
80	5-6

perovskite in p-i-n perovskite solar cell construction. It was found that its power conversion efficiency, compared to perovskite film (made by traditional Lead (II) iodide), is weak. Nevertheless, toxic solvent operation with an easy evaporation (dimethylformamide) for green production of perovskite solar cells was removed by this process. The influence of non-uniform and pin-hole of perovskite films, weak coverage, incomplete formation and weak coverage result in their low performance. To replace Lead (II) iodide material for PSCs, they found Pb(NO₃)₂ as an substitute material [57]. Mufti et al. [58] studied the influence of temperature on the morphology of nanorod (NR) and optical properties for CH₃NH₃PbI₃perovskite solar cell device application. Zinc oxide NRs were prepared via a hydrothermal approach on the ITO substrate. The structure of solar cell was composed of ITO/ZnO oxide seed layer/zinc oxide NRs/ CH₃NH₃PbI₃, and zinc oxide NRs, (as nano shaped stem layer) where perovskite crystals form.

10. Nanocomposites in perovskites solar cells

In order to improve the perovskite films morphology with regard to device performance, crystallization kinetics, and crystal growth, the addition of nanoparticles in perovskite based solar cells was applied. Different nanoparticles because of their different physical and chemical properties, can play an essential role in the generation of perovskite thin film. A method, which is accepted extensively, involves mixing poly (3,4ethylenedioxylen -thiophene): poly (styrenesulfonic acid) (PEDOT: PSS) and metal NPs, active layer or as cathode interfacial materials. It is well-known that new metallic structure of NPs are able to show a high efficient absorption band in the UV-Vis area. It lies within the optical absorption band of the conjugated polymers which are applied in the active layer of organic photovoltaics. To promote absorption, plasmonic metallic nanoparticles (NPs) can be used either inside the active layers of OPV devices or buffer. This can enhance the optical thickness of Organic Photovoltaics materials in order to harvest light [59-61]. Considerable reduction of both the quantity of lead, which is present in the device structure and the thickness of the perovskite film can be seen by Plasmonic nanoparticles. They can ensure a broad-spectrum light absorption simultaneously.

11. Application of nanomaterials in solar cells

The nanoscale materials have high surface area to volume ratio. This property offers other wonderful optical, physical, and chemical properties. Several instances of physical extended capabilities of nanomaterials are as follows: (i) considerable reduction in the possibility of recombination of charge carriers which is because of the fact that light-generated carriers travel shorter path (ii), energy bandgap can be inter-changeable and flexible by changing the dimensions of nanoparticles, and (iii) increased optical path because of several reflections [62]. Due to these properties, nanomaterials are very interesting for PV applications. In fact, nanomaterials present flexible materials in PV assemblies which have the capability to convey solar heat by new approaches [63]. Therefore, the potential of PV devices for light trapping and the collection of photo-carriers can be improved greatly [64]. Furthermore, the manufacture of novel materials can be enhanced by synthesis approach. Take passivated nano-scale crystals and monodisperse as an example: they show optoelectronic properties, which results in more control over shape, composition and structure [65]. In other words, nanoparticles are able to reach the fundamental principle of PV devices for the optimization level so that the optic absorption of the active/ sensitizer layer can be increased and the loss of charge carrier is prohibited throughout transportation. To find out the best association of the nanomaterials to

increase both the performance and the properties of DSSCs, researchers have had many experiences. This can be achieved by using nanocomposite materials. As such, they are performing expansive studies using various composite nanomaterials for DSSCs. TiO, is attractive, because of its high chemical stability and dye adsorption ability. Moreover, TiO, enjoys longer electron lifetime and high surface area [66, 67]. Its considerable electrical and optical properties and low-priced production also cannot be denied. It is worthwhile to mention that it can be harmonized for several physical properties [68]. An electrolyte and injected electrons can be recombined, which is the essential loss path in the DSSCs. This recombination increases the dark current which can decrease the device performance finally [69]. Mesoporous structure TiO, experiences low electrical conductivity, which is the result of more interfaces between particles in spite of the fact that it has great dye adsorption ability. It should be said that electrolyte penetration into pores can elevate the recombination reaction, and these issues promote the development of novel morphologies or nanostructures of TiO2, which have great dye adsorption capability as well as electrical conductivity [70]. Nanostructures such as nanotubes, nanorods, nanowires, and hollow spheres have been made for efficient DSSCs. Scattering of light in a layer of TiO, nanofibers can extendoptical path length from the wavelength of incident light. This will be able to extend optical path length. Therefore, we can see intense light absorption for nanofibers in the visible region [71, 72]. To improve the light absorption of TiO, films and decrease the recombination for holes and electrons, the adjustment of novel metals can play a significant role in this regard (for dye-sensitized solar cell).

Zhao and Dong et al. [73], compared the power conversion efficiency (PCE) of composite photoanode of TiO_2 nanofibers/ nanoparticles (NF/NP) soaking in AgNO3 solution in comparison with the photoanode without Ag adjustment. Their results showed that soaking in AgNO3 solution increased the PCE of composite by 18.0%.

Hong et al. [74], developed the device which was fabricated from the perovskite solar cells. As an electron transporting material, they applied the electrospun reduced GO-TiO, composite nanofibers. This device showed an 3.27 % and 1.84% increase in power conversion efficiency in comparison to mesoporous- titanium oxide and pristine- titanium oxide naofibers, respectively. ZnO nanofibers web was used by Biji et al. [75], as photoelectrode. Using these nanofibes, they designed and developed a stainless flexible mesh-based quasi-solid DSSC. According to the photovoltaic performance examination, they exhibited overall solar conversion performance of 0.13% for the created DSSC with following characterizations: fill factor: 32.77%, short-circuit photocurrent density: 28-µA and open-circuit voltage: 0.321 V. In order to develop the TiO₂ efficiency in the dye-sensitized solar cells as a photoanode, Motlak et al. [76] came up with nanofibrous morphology and Cd-doping and empirical results revealed that Cd ions that interfere with crystalline TiO, nanofibers can make an enhancement in reduced re-bonding between the charge carriers between the working electrode and electrolyte in the barrier area, the transportation of the charges and the absorption in the visible spectra. In other reports, Chou et al. [77], prepared the TiO, nanofibers including silver (Ag) nanoparticles (NPs) and graphene oxide (GO), via combination of sol-gel technique and electrospinning method. Their results showed that TiO₂/GO/Ag NF or TiO₂/GO NF (as an extra layer) can increase η (40% or 16%, respectively) with respect to standard DSSC. Moreover, the additional composited TiO2 NFs layer can prevent recombination of electrons between the interface of electrolyte and TiO2 electrolyte. This can result in the increase of carrier transmit prohibition. The energy barrier can be improved by the insertion of nanowires at the interface of electrolyte and semiconductor. Besides, the transportation of the electron to the electrolyte can be decreased. This, consequently, can reduce the density of surface traps. Increase in the properties of electron transmission of TiO2 remarkably would be possible by one-dimensional nanotubes. Liu et al. [78], (2018) prepared nanowires directly on the

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conductive substrate of glass by two-step solvothermal reaction. They used them as photoanode and found PCE of 5.30%. An increase in the PCE up to 8.28% was exhibited when associated nanowire arrays (NWAs) collected by monocrystalline rough-surface rutile-TiO, nanowires have been fabricated via straightforward solvothermal methods [79]. The effect of combining Ag nanowires TiO, nanofibers (NFs) and Ag nanowires (Ag NWs) nanofibers into a tri-layer photoanode DSSCs was examined by Kumari et al. [80] . They found that tri-layer TiO, P25/ P25/P25 photoanode is 45.6% more efficient than the reference DSSC (6.69%). It is known that nanotubes with one-dimension greatly advance the electron transportation performance of TiO2. As expected, there are lower contacts between crystals in TiO, nanotubes compared to NPs, resulting in an increase in the speed of electron transportation, and the electrical conductivity can be improved by Nanotubes, as they prepare the smooth electronic path for injected electrons. The recombination reaction can be reduced by the fast electron transmit considerably. To avoid complex synthesis, carbonaceous nanocomposites with TiO, have been suggested to get DSSCs with high efficiency. Liang et al [81] synthesized TiO, nanotube arrays with 2 appropriate diameters and heights directly on the fluorine-doped SnO, surface through applying the aqueous TiO, sol-gel methods and tubular photoresist templates. A considerable PCE ~14 % was indicated by the fabricated PVSCs. Liu et al [82], used TiO, gel to prepare the TiO, nanotubes (TNTs) via hydrothermal method. Ag nanoparticles (Ag-TNTs), then, were used to modify the synthesized TiO, nanotubes via in-situ photo deposition reaction. The filling factor (FF) for prepared photoanode was reported to become 53.63% and the efficiency (η) of 7.2% was obtained. Rho et al. [83], studied the performance of DSSCs with the investigation of the influence of Titania nanoparticles/Titania nanotubes-silver nanoparticles (TiO, NPs/NTs-Ag@TiO, NPs) composites. Because of the enhancement of electron transport via nanotubes, the power conversion efficiency (PCE) has increased as much as 0.74% with TiO, NPs/NTs in comparison with TiO, NPs film merely. Hydrothermal methods and facile sol-gel were used to prepare TiO, nanotubes (TNTs) and TiO, nanoparticles (TNPs), respectively. For the TNPs layer coated with TNTs (combined photoanode), the power conversion efficiency, was reported at 5.43%. This quantity was in contrast with the individual ones [84]. Carbon allotropes have remarkable properties such as excellent stability against electrolytes, great electron mobility and high electrical conductivity [85]. Especially, graphene and carbon nanotubes have considered being effective fillers for PE of DSSCs, which is due to their good ability to harvest light and good electron mobility [85, 86]. A better output voltage can be achieved by applying CB /TiO, as a PE. This is because of the conduction band energy level of CB /TiO, film which can be increased by the higher conduction band energy of CB C [87]. As a substitute for traditional platinum counter electrodes applied in DSSC applications, Jaafar et al. [88], proposed counter electrodes based on CB-TiO, composite. Their empirical results indicated the impact of the CB-TiO, composite on the photovoltaic performance, which can be through increasing the electro catalytic activity. It is expected that as the quantity of CB increase, the increase in the surface area would be unavoidable. This will enhance the catalytic activity that can lead to low charge-transfer resistance (R_{CT}) at CB electrode/ the electrolyte interface. Viable substitute counter electrode (the reformed photoanode along with natural dye sensitizers) can produce the highest energy conversion efficiency (2.5%). Rahman et al. [89], prepared the counter electrode by a facile method. This counter electrode (an electrode of nitrogen doped acetylene carbon black decorated palladium nanoparticles) shows a PCE of 7.95%, (higher than the cell fabricated of Pt counter electrode). At interfaces of electrolyte/TiO, and dye /TiO, in dye-sensitized solar cell, recombination can appear [90]. Thus, to reduce this reaction, 1-D nanostructure photoanode, has been employed. Carbon nanotubes (e.g. SWCNTs and MWCNTs) have good electron mobility. This favorable

member presents an efficient transportation path for injected electrons [91]. High conductivity of CNTs as well as high performance plays an essential role in the DSSCs present an efficient transmit path [92]. The use of CNTs instead of carbon black can cause a better upper limit conductivity and less percolation threshold in TiO₂/CNTs composites. It is understood that particles with large aspect ratio possess low threshold than spherical structures because of a higher excluded volume with the similar weight. Thus, reducing the percolation threshold can be a crucial concern in order to gain cost-effective conductive composite material [93]. Graphene can be regarded as a great additive material for the PE of dye-sensitize solar cells, because of its excellent electron mobility and surface area and tunable bandgap. Furthermore, to present an efficient charge transportation path for the injected electrons, 2D-graphene sheet is an ideal option [94]. Many empirical results exhibit that graphenebased PEs have better PCE in contrast with the carbon particles and CNTs [95-98]. This is because of the limited overall efficiency of DSSCs, which is the result of the better charge recombination with electrolyte versus graphene. This limitation of the total efficiency of dye-sensitize solar cells can be because of the feeble interaction of the spherical TiO, nanoparticles with CNTs. In contrast, single-sheeted graphene have higher contact with TiO2 nanocrystallites. The fabrication of hybrid TiO₂/reduced graphene oxide composites with many dimensional and self-collected structure for dye-sensitize solar cells, have been investigated by Manikandan et al. [99] .To quicken the electron transportation channel within the TiO2 matrix, GO in the TiO2 matrix can be loaded. This then can result in higher photo conversion efficiency in comparison with neat TiO2. 8.62% versus 6.3%. Graphene Oxide nanosheet suspensions which are coated on a glass plate and Titanium Tetra Isopropoxide (TIP) was used to prepare TiO2-GO nanocomposite thin films of several grades via a spin coating method by Timoumi et al. [100]. After the evaluation, optical absorption data exhibited the reduced band gap energy along with enhancing dopant quantity (3.62 to 1.40 eV), which is due to the hole or/and electron trapping at the acceptor /donor levels in the TiO2 band structure. Spin coating technique and liquid phase deposition were used to prepare TiO2 films, which are Graphene-coated. Next, they were employed as photoanode of dye-sensitized solar cell. The highest value of power conversion efficiency of DSSC ($\eta = 1.47$ % and Voc = 0.66 V), is the outcome of Coating TiO₂ films with graphene layer [101]. The perfect decoration of rGO (1.0 wt. %) in photoanodes develops electron lifetime, charge transport, and the biosensitizer loading. Besides, it can reduce the recombination of the Bio sensitized solar cells (BSSCs) significantly. Reduced graphene oxide (rGO) and mixed phase TiO, nanorods (NRs) can be used to make Nanohybrid photoanodes, which is fabricated via one step hydrothermal method [102]. TiO, photoanode sensitized with dye molecules was loaded by different amount of graphene nanoribbons (GNRs) by Akilimali et al. [103] . The report showed that the PCE of DSSCs could be enhanced by the incorporation of GNRs with the focus on the fact that the increase for 0.005 % loading was up to 20% better than the control devices efficiency. This enhancement is largely the result of improved electron lifetime, the enhancement of dye loading, and the reduction of carrier recombination.

 TiO_2/ZnO is an excellent composite for DSSCs for the application in heterogeneous photocatalysis owing to the superior properties of ZnO compared to TiO_2 . Moreover, the non-toxic ZnO nanoparticles with superior properties such as fast carrier mobility could be prepared with facile methods for better absorption of dye [104, 105]. Similar to TiO_2 , ZnO is a semiconductor oxide with good optical, mechanical and electrical properties [106]. Additionally, it has promising photo catalytic activity as well as antibacterial and antifouling effects [107]. It is worthwhile to note that the manufacturing cost of ZnO, is 75% less than that of Al_2O_3 and TiO_2 nanoparticles [108, 109].

ZnO/TiO2 multipod nanostructures as the anodes of DSSC with

photoelectric conversion efficiency of 3.1% has been used by Cui et al. [110]. They were synthesized by hydrothermal technique using hetero-seed medium. The increase in the conversion efficiency can be the consequence of promising one-dimensional nanostructures that can accelerate electron transportation leading to the decrease in charge recombination. It has been shown by Zhong et al. [111], that the photoelectric conversion efficiency (PCE) for the electron transport layer of ZnO@ TiO, nanorods in the form of core-shell structure is about 50 % higher than that of ZnO nanorod devices. This is because of following reasons; 1) the improved contact at the interface between perovskite layer and nanorods, 2) the inhibition of charge recombination. To enhance the power conversion efficiency of DSSCs based on TiO,/ZnO Core/shell nanostructure, a scattering layer has been applied. The efficiency of TiO2, ZnO, and TiO₂/ZnO nanostructures prepared via chemical methods is 1.76%, 1.65%, 2.41%, respectively whereas these quantities for ZnO / TiO2 and TiO2 /ZnO cells core/shell nanostructures coated without and with scattering layer are 4.1% and 5.89%, respectively [112] . Zhang et al. [113], prepared a heterostructured photoanode of titanium oxide nanorod arrays/zinc oxide nanosheets (TNRAs/ZNSs) by a manageable chemical bath deposition technique for the use in quantum-dot-sensitized solar cells (QDSSCs) taking the advantages of nanosheets and nanorods. The report indicated that the prepared photoanode with slower electronic recombination rate and better specific surface area, has power conversion efficiency of 260% in comparison with the TNRAs-based quantum dot solar cells

12. Conclusions and future insights

From the environmental point of view, solar cells have been the center of attention to be studied as a suitable electric power sources. Therefore, focal point of this review is based on different types of solar cells such as Si-based solar cells (amorphous Si solar cells, crystalline silicone solar cells and Monocrystalline silicone solar cells), Dye-Sensitized semiconductor, organic solar cells, tandem cells, DSSC, thin film solar cells, QDSC and PSC as well as TiO2-based nanocomposites, with various functions in the solar cells. Significant improvement of PCE is required to provide the more competitive DSSCs technology. Furthermore, the production price and preparation of sustainable DSSCs should be mostly regarded. Targeted specific changes of every element (including counter electrode, organic dye and the photoanode) as a key factor cannot be forgotten. In this field, the paramount aim would be the exploration of the light harvesting, electron losses, electron-hole pairs recombination and the light harvesting, and hence improving the efficiency of solar cells.

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