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# A comparison of optical properties of ZnO nanorods and ZnO nanotips for improving light absorption in rGO/ZnO nanostrctures

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## ABSTRACT

In this study, two types of ZnO nanostructures (ZnO nanotips and ZnO nanorods) were synthesized through a chemical bath deposition (CBD) method. These two structures were then compared by optical and structural analyses. The result showed the significant effect of ammonia concentration and the preferential etchings along the c axis on the formation of ZnO nanotips (NTs). To improve the absorption, nanostructures were optimized by reflectance analysis. To enhance the optical properties of the optimized sample, reduced graphene oxide (rGO) layers were transferred on the ZnO NTs surface by the electrophoretic deposition (EPD) method. The deposition of rGO layers on ZnO NTs can increment the optical absorption over a wide range of frequencies. The reflectance results showed enhanced adsorption capacity in the case of rGO/ZnO NTs.

## ARTICLE INFORMATION

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## 1. Introduction

Zinc oxide (ZnO) nanomaterials have found extensive applications due to their low cost , high refractive index (≅2.0 at $\lambda = 632.8$ nm) and it has also wide direct band gap (3.37 eV) [1,3]. One of the significant approaches to obtain high-efficiency optical devices is to improve the optical absorption by light capturing [4]. The large surface-to-volume ratio of nanostructures can increase the absorption index. Moreover, nanostructures have been investigated in various fields because of their excellent physical and chemical features. ZnO nanostructures have shown great optoelectronic properties compared to their bulk and other materials [5,7]. Some methods have been employed for the synthesis of nanostructures such as nanobelts, nanorods, and nanotips; among which, physical evaporation [8], spray pyrolysis [9], laser ablation [10], and chemical bath deposition (CBD) can be mentioned [11]. Among these methods, CBD exhibited several advantages such as easy, affordable, and low-temperature procedures. The size and shape form of the nanomaterial are relatetd to several factors such as time, temperature, solution concentration, and pH of the solution [12-13]. This paper reports a highly controllable growth method for the synthesis of two types of ZnO nanostructures (nanotips and nanorods) in solutions with different pH levels. The optical characteristics of ZnO depend on its size and morphology. This research is thus aimed to compare the optical characteristics and morphological of the ZnO nanorods (NRs) and nanotips (NTs) in terms of their reflection spectrum. The outcomes showed an increment in the optical properties of the ZnO NTs arrays compared to ZnO NRs.

Additionally, graphene oxide has received high consideration due to its unique mechanical and high electron mobility. Therefore, ZnO nanostructure along with other materials, such as graphene, can capture electrons from ZnO due to its larger surface area.

In addition, a large number of papers reported in recent years studied the deposition of rGO on ZnO nanorods using the spin coating method [14,17]. One of the foremost drawbacks of spin coating is related to the size of the substrate. If the size of the substrate rises, the control of speed spinning is problematic.

A novelty is introduced in this investigation on deposition rGO to enhance light absorption by EPD (electrophoretic deposition) method on ZnO nanotips. The main and positive advantage of this process is its large-scale built-up of rGO layer which can be simply achieved. Morover, it is low cost for transfering graphene at room temperature. To the best of our knowledge, the effect of the deposition of reduced graphene oxide (rGO) layers on the optical characteristics of ZnO NTs has been rarely explored. We investigated the optical effects of EPD-deposited graphene on ZnO NTs.

The improved optical properties of ZnO NTs arrays by graphene layers can expand its potential applications in optical devices such as high-efficiency solar cells, and detector applications.

## 2. Experimental

The experiments were performed on a highly doped p-type silicon (100) wafer at a resistivity range of 1-30 Ωcm. The silicon substrate was cleaned using a conventional RCA (Radio Corporation of Ameri-

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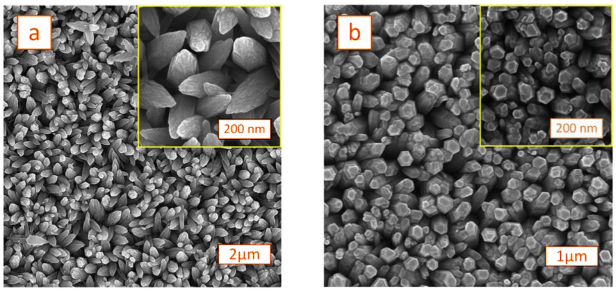

**Fig. 1.** FESEM images of (a) ZnO NTs array obtained using 4 ml ammonia and, (b) ZnO NRs array obtained using 6ml ammonia.

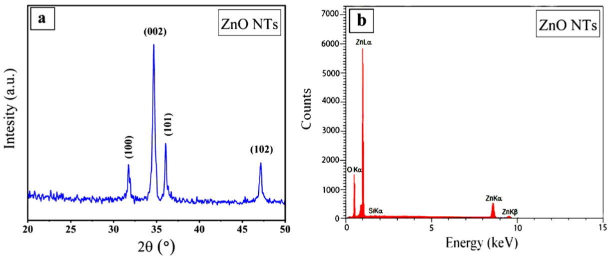

**Fig. 3.** (a) XRD pattern of ZnO NTs array and, (b) EDX spectrum of ZnO NTs grown on silicon substrate.

ca**)** method to eliminate the both organic and ionic contaminants from wafers [18]. ZnO thin film was deposited onto the cleaned silicon (Si) wafer by Radio Frequency (RF) magnetron Sputtering sputtering technique to serve as a seed layer. Then, two types of ZnO nanostructures were prepared by the CBD method. Typically, samples were dipped in a solution including zinc dehydrate ($Zn((O_2CCH_3)_2(H_2O)_2)$) and ammonia ($NH_4OH$) for 1 hour. The optimal bath temperature was set at 85 . The concentration of zinc acetate was fixed 0.1 M. Although, the shape of ZnO nanostructure depends on ammonia concentration which ZnO NTs changed to ZnO NRs by increasing the ammonia concentration from 4 ml to 6 ml. Graphene was synthesized by the modified Hummers technique [19].

Graphene oxide (GO) was synthesized using modified Hummers technique. A solution containing a mixture of $H_2SO_4/H_3PO_4$ (9:1) was added to a mixture of graphite flakes and $KMnO_4$, producing a slight exotherm to 30~40 °C. The solution was stirred for 24 h at the temperature of 50 °C. Then, the temperature of solution was gradually decreased to RT and it was poured onto ice with $H_2O_2$ (30%). Then, in order to eliminate the supernatant, the mixture was centrifuged at 5000 rpm. The residual solids were washed sequentially with water, HCl and ethanol and dried overnight at RT. The material remaining after washing process was vacuum-dried overnight at RT. Then, the colloidal GO suspension was prepared via dissolution of final product in water and sonicated for 10 min at RT.

Finally, rGO solutions with excellent dispersion were prepared. The rGO was then coated on the ZnO NTs as optimized sample for improving optical properties via the EPD method at a constant current density of 0.01 $mA.cm^{-2}$ and a steady voltage of 20 V at room temperature using platinum cathode and silicon substrate anode.

Scanning electron micrographs were recorded using VEGA\\TESCAN-LMU instrument. X-ray diffraction patterns were identified using a XRD Phillips APD 3520 powder with Cu K-alpha radiation (40 keV,30 mA). The reflectance spectra were measured via Avaspec-2048-TEC spectrometer. Zinc dehydrate and ammonia were purchased from Merck, Germany. distilled water was used in the current of this research.

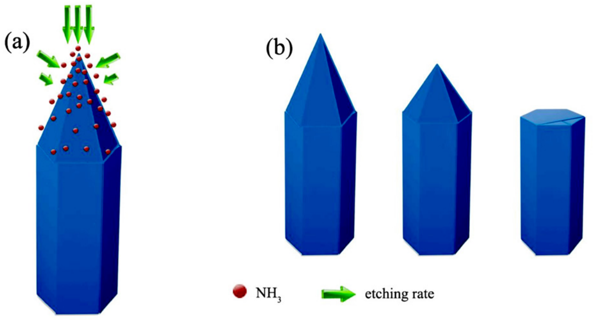

**Fig. 2.** F(a) Distribution of ammonia molecule on the tip of the ZnO nanostructure, (b) schematic representation of morphology of the ZnO NRs in the ammonia solution..

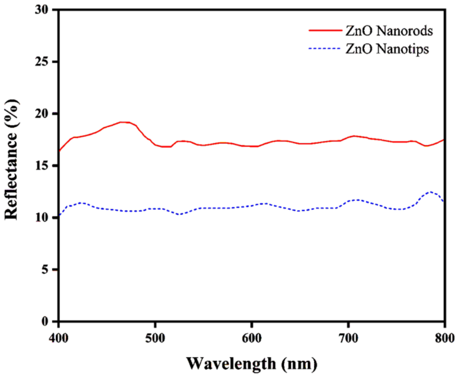

**Fig. 4.** Reflectance curves of ZnO NTs and ZnO NRs array.

## 3. Results and discussion

Figs. 1(a) and 1(b) show the FESEM micrographs of ZnO NTs and ZnO NRs at different pH values before graphene deposition. The ZnO NTs and ZnO NRs were uniformly grown on silicon substrates. The chemical reactions involved in the synthesis of ZnO NR were reported in previous papers [20]. In this study, the morphology of the ZnO nanostructure can be adjusted by the concentration of ammonia solution in the deposition bath. The ZnO nanostructures changed from ZnO NTs to ZnO NRs by increasing the ammonia concentration from 4 ml to 6 ml. The morphological differences between the two types of ZnO nanostructures can be assigned to the concentration of ammonia. Ammonia concentration directly influenced the relative growth rates of crystal planes, resulting in an optional growth of ZnO nanostructure with sharp pyramid or flat tips. The surface of the ZnO nanostructure will absorb the polar molecules of $NH_3$, as shown in Fig. 2(a). However, the quantity of the absorbed $NH_3$ molecules changed on the sharp ZnO NRs as the distribution of surface charge density is associated with the shape; i.e. the sharper the curve shape, the larger the amount of surface charges. Consequently, the peak area has the highest surface charge density and hence can drag more $NH_3$ molecules compared with other regions. The dissolution rate of ZnO increased by raising the concentration of ammonia; therefore the area of the pyramid tip will be declined slowly. Eventually, the entire tip peak was etched out, as shown in Fig. 2(b) [21].

Fig. 3(a) depicts X-ray diffraction patterns of ZnO NTs sample. ZnO NTs sample exhibited (100), (002), and (101) peaks corresponding to hexagonal wurtzite ZnO structure based on the reference card No. 01-089-0510, with no other peaks related to other phases. The emergence of a sharp peak at 2θ=34° indicates the hexagonal structure of the ZnO nanostructures as the formation energy of this plane is lower than other planes [22]. Fig. 3(b) shows EDX spectrum carried from ZnO NTs which illustrate zinc, oxygen, and silicon signals without the existence of any contamination in the sample. The Si peak is corresponding to the

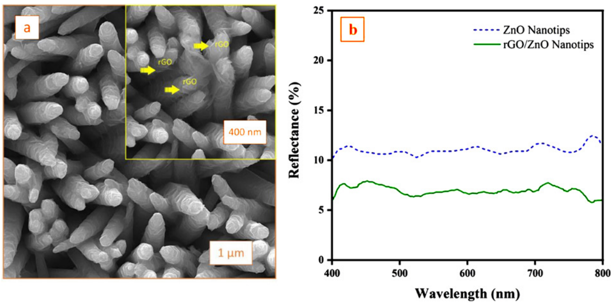

**Fig. 5.** FESEM images of (a) rGO/ZnO NTs array, (b) Reflectance spectra of ZnO NTs and rGO/ZnO NTs recorded in the range 400-800nm.

substrate. This analysis exhibits the good synthesized ZnO NTs.

ZnO NTs and NRs structures were experimentally compared via reflectance analysis. Fig. 4 compares the reflectance of the two types of ZnO nanostructure to select the best sample with lower reflectance. The average reflectance of ZnO NTs was ~%12 which incremented to ~%18 in the case of ZnO NRs. The ZnO NTs sample managed to reduce the optical reflectance due to its high specific surface area. Therefore, the ZnO NTs can be employed in diverse optoelectronic devices.

Fig. 5(a) illustrations the FESEM micrograph of the rGO layer on the ZnO NTs. The ZnO NTs were selected as an optimized morphology due to their high surface area and enhanced optical characteristics compared to the ZnO NRs. As seen, rGO layers were uniformly deposited on the ZnO NTs. The ZnO NTs of the sample were visible due to the transparency of rGO layers. In addition, the rGO layers did not demolish the shape of ZnO NTs on the substrate. Fig. 5(b) indications that the average reflectance of the rGO /ZnO NTs is less than 8 % while the reflectance of the ZnO NTs is over 10 % without rGO layers. The graphene layers enhanced their roughness and highly impacted their optical properties [23]. Hence, the obtained outcomes may lead to more satisfactory performance suitable for a wide variety of applications.

## 4. Conclusions

The significance of this work lies in two points. The first aspect is related to the effect of morphology on the reflectance of ZnO NTs and NRs, while the second aspect involves the effect of rGO deposition on ZnO NT samples. ZnO NTs arrays showed promising potential for improving the efficiency of optical devices. Moreover, the graphene was deposited on the ZnO NTs as best sample using the EPD method to improve the optical properties of the samples. Based on FESEM results, the ZnO nanostructures with a hexagonal wurtzite structure were densely grown and on the silicon substrate. Different concentrations of ammonia also altered the shape of nanostructures. The XRD pattern showed a main peak at 2θ=34° that is related to the (002) plane of hexagonal wurtzite ZnO nanostructure. The reflectance of the ZnO NTs array was lower than the ZnO NRs array due to the light-trapping features of ZnO NTs. Therefore, The ZnO NTs array can offer excellent antireflection performance compared to the ZnO NRs array.

## Conflicts of Interest

The authors declare that they have no conflict of interest.

## Acknowledgement

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