The Enhancement Of UV Sensor Response By Zinc Oxide Nanorods /Reduced Graphene Oxide Bilayer Nanocomposites Film

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Abstract. Zinc oxide nanorods (ZnO NRs) /reduced graphene oxide (rGO) nanocomposites assisted by sodium dodecyl sulfate surfactant (ZnO NRs/rGO-SDS) showed a good response for UV sensor application that has sensitivity of around ~32.54. Whereas, the UV sensor response on pristine ZnO NRs showed almost 15 times lower response than the ZnO NRs/rGO-SDS nanocomposites. The pristine ZnO NRs were prepared by sol-gel immersion method before rGO solution was sprayed on the ZnO films using spraying method. The GO solution was produced via electrochemical exfoliation method at 0.1 M SDS electrolyte then the solution was reduced using hydrazine hydrate under 24 hours magnetic stirring at a temperature of around ~100 °C. The samples were characterized using energy dispersive X-ray, field emission scanning electron microscope, micro-Raman, ultraviolet visible, X-ray diffraction, UV lamp and four-point probe measurement. The aim of this study was to improve the UV sensor response based on ZnO/rGO-SDS nanocomposites. In conclusion, the fabricated ZnO NRs/rGO-SDS nanocomposites assisted with SDS is a good candidate for the use in UV sensor applications as compared to pristine ZnO NRs films.

1. Introduction

The Ultraviolet sensor (UV) becomes interesting research field due to it has many applications such as flame detection, space research, missile launching detection, optical communication, environmental monitoring and so on [1]. The UV sensor was fabricated based on due to its properties [2], ZnO has direct energy gap 3.37eV and it has also binding exciton energy ~60 meV [3]. In the recent years, a lot of effort has been devoted to improve different nanostructure of ZnO such as nanowire (NWs) [4], Nanorods (NRs) [5] nanotubes [6] nanoplate [7] and nanobelts [6]. There are a lot of literature reports on preparation of ZnO nanostructure by many methods such as; vapour liquid solid (VLS) [8], vapour–solid
(VS) [9], magnetron sputtering [10], pulse laser deposition (PLD) [11], metal organic chemical vapour deposition (MOCVD) [12], chemical vapour deposition (CVD) [13], hydrothermal [14] and arc discharge [15] used to obtained one dimensional semiconductor nanostructure technique. But all these methods were complex to controlled parameters [16]. There are another simple way to syntheses ZnO based on one dimensional nanostructure namely sol-gel immersion methods [17], this method has many advantages such as; low cost process, low temperature deposition process, environment friendly and, simple set up [18]. Pristine ZnO has been showed weak responsivity and small operating sensitivity UV detector. Jiang et al. [19] they reported the responsivity of pristine ZnO thin film is so poor to applied in practical applications. Coung et al.[20] they hybrid ZnO nanorods with nanostructure from GO/CNT, They found the ZnO NRs increase absorption ultraviolet after hybrid by spray coated on top of ZnO NRs. The ZnO also composite with rGO for many application and shows a big improvement such as hybrid ZnO/rGO for photocatalyst application [21], and also showed improvement in the supercapacitor applications where synthesis by sol-gel method [22]. The graphene shows good improving in tensile strength and electrical conductivity by compositing with aluminum based on pyrolysis method [23]. The rGO shows also enhancement in photovoltaic performance [24]. Thus, it seems the structure of rGO has an advantageous to improve the UV sensitivity and responsivity and it’s the main objective to this study.

2. Experimental procedures:

2.1 Preparation of MgZnO seed layer
In this study MgZnO used as a seed layer for both pristine and hybrid samples; the MgZnO was deposit on the glass substrate (2×2) cm². The quartz substrate was cleaned with DI water one time and with acetone two times in ultra–sonicated by water bath (Hwashin Technology Power sonic 410, 50 Hz) at room temperature for 5 minute for each time. The MgZnO solution was produced from [0.88 g zinc acetate dehydrate (Zn (CH₃COO)₂·2H₂O), 0.44 g magnesium nitrate hexahydrate (Mg (NO₃)₂·6H₂O), 0.25 ml of stabilizer mono-ethanolamine (C₂H₇NO), and 10 ml of 2-methoxyethanol (C₃H₈O₂) as a solvent]. The solution was sonicated at 50 °C for 30 minutes, the finally step was stirred the solution for 2 hours at room temperature to get a clean and homogeneous solution. The solution prepared was deposit on the glass substrate by spin-coating method at 3000 rpm for 60 second, 10 drops for each layer than preheated in the oven model (memmert 30-1060, type UF 55) for 10 minutes at 150°C by using spin-coater model (WS-400 BZ-6NPP/A1/AR1), this process were repeated for 5 times. The final annealing for the samples at 500 °C for 1 hour in the furnace two-zone tube, model (2ZTF-1100-20-35).

2.2 Preparation of pristine ZnO nanorods and ZnO nanorods hybrid with rGO-SDS
The ZnO NRs were grown on the MgZnO seed layer that was deposit on the glass substrate. The solution was prepared by mixing (1.409 g) hexamethylenetetramine (C₆H₁₂N₄), HMT with (2.79 g) from zinc nitrate hexahydrate Zn (NO₃)₂·6H₂O in (200ml) deionised (DI) water. The solvent sonicated at room temperature for 30 minutes and then stirred at room temperature for 2 hours to get a clean and homogeneous solution. The samples placed down facing top position in the bottle, where the bottle immersion in the water bath at 95 °C for 4 hours. After immersion process the samples were taken out of the bottle and cleaned by rinsing in DI water, and then the samples dried in oven at 130 °C for 10 minutes. The samples were post annealed in two-zone furnace at 500 °C for 1 hour. To hybrid the pristine ZnO NRs with rGO-SDS, where spray 0.1M concentration of rGO-SDS on the top of the ZnO samples by spray coating method, and annealed the samples at 400 °C for 1hour in furnace tow-zone tube. The prepared samples were coated with Aurum (Au), where (Au) as an electrode by using sputters coater model (EMITECH K550X) for current–voltage (I–V) measurements.

The morphology surface of images and cross-section of the samples examined by field emission scanning electron microscopy (FESEM) model (HITACHI SU8020). The Energy Dispersive X-ray (EDX)
model (E-MAX) where used to know the chemical compounds of the pristine ZnO NRs and hybrid ZnO NRs/rGO-SDS. Raman spectroscopy was used to investigate the crystal phase by using wavelength 633 nm, model (Renishaw inVia Reflex). The properties of ZnO NRs crystallinity were studied via X-ray diffraction model (Bruker D8 Advance). The optical properties of ZnO were investigated by using ultraviolet-visible spectrophotometer model (Cary 60 UV-Vis). The UV lamp model (UVGL-55 Handheld) was used to investigate sensor performance supported by measurement sensor system model (Keithley 2400). The four-point probes were used to investigate the electrical properties of ZnO and ZnO/rGO-SDS by using device model (SR-4-6) supported by system model (Keithley 2400).

3. Result and discussion

FESEM image shown in 'Figure (1)' for pristine ZnO NRs and hybrid with rGO-SDS where grown by sol-gel method as shown below.

![Figure 1](image-url)

**Figure 1.** (a) Top surface morphology of ZnO. (b) Top surface of ZnO/rGO-SDS nanorods. (d) Top surface of ZnO with diameter of ZnO/GO-SDS nanorods. (c) Top surface of ZnO nanorods and nanoflower. (e) Cross-section of ZnO nanorods.
'Figure (1)' shows the morphologies surface for ZnO NRs pristine where the magnification was very low, the low magnification shows the ZnO NRs grown on top of MgZnO as seed layer have very high dense and uniform sample. However, Fig 2 (b) shows that rGO-SDS deposit on top of NRs by spray coating method. According to Fig 1 (c) the image shown that the grown a small amount of nanoflowers on top of ZnO NRs. Fig 1 (d) shows that the diameter of ZnO NRs around 47.6 nm up to 99.2 nm according to FESEM image and shows also very clearly that the ZnO NRs have hexagonal shape. However, the cross-section image of ZnO NRs Fig 1(e) shows that the ZnO NRs aligned shape with length around 1.7 μm and thickness of MgZnO was around 0.7 μm.

![Energy dispersive X-ray spectroscopy (EDX) of (a) ZnO nanorods and (b) ZnO/rGO-SDS nanocomposites.](image)

Figure 2. Energy dispersive X-ray spectroscopy (EDX) of (a) ZnO nanorods and (b) ZnO/rGO-SDS nanocomposites.

The ZnO NRs and ZnO NRs/rGO-SDS samples where syntheses by sol-gel immersion method for 4 hours at 95°C tested by Energy dispersive X-ray spectroscopy (EDX) model (E-MAX). to know the chemical composition for hours we examined the sample by EDX. Fig. 2 (a) shows (EDX) spectrum for ZnO NRs, where can observe very clearly have four peaks contain three of these peaks are zinc and one peak is oxygen. Fig 2 (b) shows there are five peaks three peaks are ZnO, one peak is carbon and one peak is oxygen, Fig 2 (b) shows carbon according to rGO where deposit on top of the ZnO NRs by spray coating.
method. However, the samples prepared have very small amount of impurities according to theoretical stoichiometric proved by (Bari et al. 2009 & Tarwal et al. 2011) the O =19.7% and Zn=80.3%.

![Figure 3. Raman shift for ZnO/rGO-SDS nanocomposites](image)

The suitable technique to test and shown the crystal structure for GO synthesis via electrochemical exfoliation method is Raman spectroscopy Fig 3 show the sharp peak of ZnO NRs was around 434 cm\(^{-1}\) \(E_2\) (high) mode corresponds to non-polar optical phonon. However, the peak 434 cm\(^{-1}\) related to the oxygen atoms motion and the active branch of a typical Raman for wurtzite hexagonal ZnO NRs and higher wavenumber is a red-shifted. The presence of \(E_2(h)\) vibrational mode in Fig 3 indicates clearly ZnO NRs structure is a hexagonal wurtzite [25]. Fig 3 shows appear D band at 1339.94 cm\(^{-1}\) due to surface modification process for graphite rod. However, the G band appears at 1580.04 cm\(^{-1}\) corresponding to carbon orbital sp\(^2\)-hybridized. The intensity of D band in Fig 3 is not very high comparing to G band that prove the sample has a good structure and the diffraction not so big. Fig 3 also shows 2D band at 2662.22 cm\(^{-1}\) which it’s appear due to there are multilayer of GO also it shows high intensity which is indicate the sample has a few layer of GO only. The \(I_D/I_G\) ratio calculated corresponding to 'Figure (2)' and shows smallest ratio 0.35, the smallest ratio indicate that the rGO has defects and least sp\(^3\) bond due to decrease the oxygen contain groups [26].
'Figure (4)' shows the ZnO NRs XRD pattern synthesis by sol-gel method where grown top on MgZnO. Fig 4 shows a highest peak it was at 33.4º (0,0,2) and (1,0,1) at 36.6º and shows that the ZnO NRs sample has a very high purity and degree of crystallinity. The pattern of XRD in Fig 4 shows the diffraction of peaks placed between 20º and 80º that prove the sample has hexagonal wurtzite phase. However these peaks all shows that the sample has no diffraction and it has also very clear hexagonal wurtzite phase according to reported file number (JCPDS#36-1451). That means this sample doesn’t have impurity structure effect or shows another peaks.

'Figure (5)' shows optical transmittance spectrum of ZnO NRs/rGO-SDS nanocomposites, and pristine ZnO NRs with wavelength rated between (200 up to 800) nm. The transmittance of pristine ZnO NRs
was 65% as shown in Fig 5 and the transmittance of ZnO NRs / rGO-SDS nanocomposites was 52% as shown in Fig 5 at wavelength 672 nm. According to 'Figure(5)' it’s very clearly that pristine ZnO NRs has higher transmittance comparing to pristine ZnO NRs/rGO-SDS. The ZnO NRs/rGO-SDS show lower transmittance because of extra layer of rGO assisted by SDS spray on top of ZnO NRs as shown in 'Figure(1)' (b). However, the pristine ZnO NRs and ZnO NRs/rGO-SDS nanocomposites have a good transparent in visible in the range of electromagnetic spectrum but show very low and at approximately been around zero at 380 nm in the range of ultraviolet spectrum.

Figure 6. Photocurrent of pristine ZnO and ZnO/rGO-SDS, illumination by UV light (365 nm).

This research focus on UV sensing for pristine ZnO NRs and ZnO NRs/rGO-SDS, where the samples tested by UV lamp model (UVGL-55 Handheld) with illuminations 365 nm supported by system model (Keithley 2400). According to Fig 6 shows the effective of UV sensor for pristine ZnO NRs and ZnO NRs/rGO-SDS where deposit by spray coating method on top of ZnO NRs. The ZnO NRs/rGO-SDS nanocomposite shows a very high sensitivity comparing to ZnO NRs (32.54 and 2.4) respectively according to equation no.1 as shown below. However, ZnO NRs/rGO-SDS and ZnO NRs responsivity were around (180 and 30) mA/W respectively according to equation no.2 [27] as shown below. The good result of ZnO NRs/rGO-SDS due to high surface area of rGO-SDS because of it has one tail to open the GO sheet. The one tail of SDS its help the photon movements easily because of that the sensitivity and responsivity improved. The Aurum (Au) was as an electrode where deposit by using sputters coater model (EMITECH K550X) for current–voltage (I–V) measurements on top of the pristine ZnO NRs and ZnO NRs/rGO-SDS nanocomposites. The response of photocurrent for the samples prepared under UV illuminations with 5V bias can explained according to ZnO NRs and ZnO NRs/rGO-SDS band gap is smaller than photon energy of UV light. However, the illuminated ZnO NRs and ZnO NRs/rGO-SDS by UV light leading to generated mobile carrier in form of electron jumped from valance band to conduction band.

\[ S = \frac{I_{ph}}{I_d} \quad (1) \]

\[ R = \frac{[I_{ph} - I_d]}{P_{op}} \quad (2) \]

Where: \( I_{ph} \) is the photocurrent.

\( I_d \) is dark current.
$P_{op}$ is the optical power of UV lamp

![Graph showing I-V measurement of ZnO and ZnO/rGO-SDS.](image)

Figure 7. I-V measurement of ZnO and ZnO/rGO-SDS.

'Figure (7)' shows the I-V curve characterization of pristine ZnO NRs and ZnO NRs/rGO-SDS better where done by using four-point probes model (SR-4-6) supported with system model (Keithley 2400) in room temperature. The ZnO NRs when coated by rGO-SDS shows a good result and it was best than pristine ZnO NRs. The ZnO NRs/rGO-SDS nanocomposites show a better result than the ZnO NRs due to the higher surface area because of rGO assisted by SDS has one tail to open the GO sheet. However, high surface area leads to increasing in the opportunity of photon movement. 'Figure (7)' shows the resistivity decreases when ZnO NRs spray by rGO-SDS due to high surface area.

4. Conclusion:

ZnO NRs grown on top of MgZnO as seed layer have very high dense and uniform sample, rGO-SDS deposit on top of NRs by spray coating method grown a small amount of nanoflowers on top of ZnO NRs, ZnO NRs have hexagonal shape, crystal structure for GO synthesis via electrochemical exfoliation method is Raman spectroscopy show the sharp peak of ZnO NRs was $E_2$ (high) mode corresponds to non-polar optical phonon. The presence of $E_2$(h) vibrational mode indicates clearly ZnO NRs structure is a hexagonal wurtzite. The pristine ZnO NRs and ZnO/rGO-SDS nanocomposites have good transparent in visible in the range of electromagnetic spectrum but show very low and at range of ultraviolet spectrum. The ZnO NRs/rGO-SDS nanocomposite shows a very high sensitivity to UV comparing to ZnO NRs. The illuminated ZnO NRs and ZnO NRs/rGO-SDS by UV light leading to generated mobile carrier in form of electron jumped from valance band to conduction band. ZnO NRs when coated by rGO-SDS shows a good result and it was best than pristine ZnO NRs. The ZnO NRs/rGO-SDS nanocomposites show a better result than the ZnO NRs due to the higher surface area because of rGO assisted by SDS has one tail to open the GO sheet. However, high surface area leads to increasing in the opportunity of photon movement.

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