Electrical Characterization of Thin Films (TiO$_2$: ZnO)$_{1-x}$ (GO)$_x$ / FTO Heterojunction Prepared by Spray Pyrolysis Technique.

M J Alsultani$^1$, H H Abed$^2$, R A Ghazi$^3$ and M A Mohammed$^4$

$^1$ Department of environmental health, Al Qasim Green University, Iraq.
$^2$ Physics Department, University of Babylon, Iraq.
$^3$ Department of Medical Physics, AL- Mustaqbal University College, Iraq.
$^4$ Department of Soil Science & Water Resources, University of Al-Qadisiyah, Iraq

Abstract. Thin films from (TiO$_2$: ZnO)$_{1-x}$ (GO)$_x$ (x=0.2, 0.4, 0.6, 0.8) ml have been prepared by spray pyrolysis technique through depositing on FTO coated glass substrates. Electrical characteristic was investigated by current-voltage (I–V), capacitance-voltage (C–V) measurements. The (I–V) measurement showed that heterojunction from symmetric type (isotope), Ideality factor ($\beta$) value increased from 1.63 to 2.48 where ($\beta$) > 1 the recombination current was dominates, rectification ratios increased from 30.62 to 77.43 because of reduction in the depletion layer from 127nm to 56.4nm which investigated by (C–V) measurements, as well as the built-in voltage ($V_{bi}$) and the barrier height ($\phi_b$) decreased from 1.42 V to 0.65 V and 1.62 to 0.79eV respectively. The increase in graphene oxide ratio lead to increase in the majority carriers in turn leads to reduction in Fermi levels. Such tests showed that the electrical properties of the prepared thin films improved and indicated that GO acts as a semiconductor and can be used for flexible and transparent optical-electronic devices.

1. Introduction

Semiconductor photocatalysis has much interest in last decade due to its potential uses to reduce conservational difficulties $^1$, $^2$. TiO$_2$ is a many-sided material, a very good photocatalyst for environmental pollutant inspection, non-toxicity, comparatively low cost, and brilliant chemical stability $^3$, $^4$. The wide bandgap and long life of holes and electrons gave the TiO$_2$ excellent photocatalytic characteristic, electrons – holes pairs generated by the TiO$_2$ photocatalyst causing series of reactions them ultimately mineralize the pollutants $^5$, $^6$. Zinc oxide (ZnO) is one of the metal oxide semiconductors that have drawn great attention due to its noticeable combination of physical properties. ZnO has wide bandgap 3.370 eV at 300K, high exciton binding energy 60 mV $^7$, n-type semiconductor has wurtzite structure and varied growth morphology, all of these properties makes ZnO as a majority material in the broad-band semiconductors and nanotechnology fields $^8$. Also, ZnO exhibited unique electrical properties which makes it useful for different applications such as in ultraviolet emitting diodes (LEDs) $^9$, photovoltaic devices $^{10}$, optical waveguides $^{11}$, gas sensors, etc. $^{12}$.

GO is another admirable entry in a field of photocatalysis, which support a duo in achieving effective of degradation as it scatters and transmits shuttles electron. Therefore it can greatly reduce the problem of recombination $^{13}$. Two-dimensional nanosheet carbonaceous has much caution lately due to its impressive properties like amazing electrical $^{14}$, mechanical and thermal properties $^{15}$, $^{16}$, superior mechanical strength, large specific surface area, and excellent charge mobility $^{17}$, $^{18}$. Graphene incorporation into TiO$_2$ has been extensively studied to improve the photocatalytic activity of TiO$_2$ $^{19}$, $^{20}$. TiO$_2$-graphene nanocomposite also demonstrated a good performance in solar cells because of the ability of graphene to enhance charge collection and reduced recombination $^{21}$. The chemical, physical, and photochemical properties of the formed TiO$_2$ / ZnO compounds depend on the prepared methods. To improve the photodegradation efficiency of the TiO$_2$ catalyst, TiO$_2$/ZnO coupled semiconductors
were prepared by various methods such as solid-state reaction method, thermal evaporation, and a hydrothermal reaction. The spray pyrolysis technique has a relatively low cost, applicable to large-scale areas, and easy to manipulate. Moreover, this technique can be used for deposition on tubing walls. The present work describes the effect of adding graphene oxide in different ratios on the optical, (I-V) and (C-V) electrical properties of (TiO$_2$:ZnO)$_{1-x}$(GO)$_x$ thin films deposited on FTO glass.

2. **Experimental**

Procedures consist of mixing two compounds TiO$_2$ and ZnO in the same ratios with graphene according to relation (TiO$_2$: ZnO)$_{1-x}$(GO)$_x$, TiO$_2$: ZnO. Solution has been prepared by dissolving 0.40 mg of TiO$_2$ and ZnO nanopowders separately in 10 ml of distilled water on room temperature; a magnetic stirrer was integrated for 30 minutes to facilitate the complete dissolution. The modified Hummer method was used. Temperature was adjusted to constant at 95 °C for 60 min although water was added constantly. Further addition from deionized water was added so that the volume of the suspension was 200 mL, after 5 min the 7.50 mL of H$_2$O$_2$ was added. The resultant was centrifuged and washed with deionized water and a 5% HCl solution repeatedly. Lastly, the product was dried at 60 °C. After the preparation of the solutions is mixed according to the following ratios (x=0.2, 0.4, 0.6 and 0.8) ml where x represents the ratio of Graphene Oxide. The resulting solution was stirred for about (10-20) minutes to be homogenized. Thin films were prepared by using this mixture. FTO glass slides (15 mm ×15 mm) were washed by using detergents and then dried ultrasonically. Spray pyrolysis technique has been used to deposit a thin film on the heated substrate at (70 °C) with spray time 4s for each minute and deposition time 12 minutes is schematically presented in scheme1. Shimadzu 6000 XR diffraction was used for XRD analysis. The absorbance of thin films were distinguished by using Shimadzu 1800 UV spectrometer. A Keithley model 2400 source meter and HIOKI 3532-50 LCR meter were used for measurement I-V and C-V characterization respectively.

![Schematic1](image)

**Schematic1.** Illustration for the synthesis of (TiO$_2$:ZnO)$_{1-x}$(GO)$_x$/ FTO thin films.

3. **Results and Discussion**

The TiO$_2$, ZnO, and Graphene Oxide (GO) XRD findings are shown in Fig.1. TiO$_2$ which exhibits a moral crystallinity and a 2θ peak values at 25.06°, 37.98°, 48.35°, 54.33°, and 55.57° can index to (101), (004), (200), (015), and (211) planes in that order. It is good settlement with (JCPDS No. # 52-6932). It is also found ZnO peak values at 31.85°, 34.51°, 36.35°, 47.57° and 56.6° with planes (100), (002), (101), (012) and (110) according to (JCPDS No. # 900-8887). Graphene Oxide (GO) shows a peak at 11.32° indexed to (001) plane.
Current-Voltage (I-V) characteristics of prepared films are tested electrically by using a two-point probe, the first probe is contact $(\text{TiO}_2: \text{ZnO})_{1-x}(\text{GO})_x$ thin films and the other probe on FTO, with sweeping voltages at (-2 V to 2 V). It indicates that well-ohmic contact formed between the electrodes and the prepared films. The current varies exponentially with voltage for all the prepared films we notes form the forward bias the increase of applied voltage leads to increase current value, but in the reverse bias the current value increases and gives a gradual breakdown voltage, this behaviour is one of general traits in symmetric heterojunction type (isotope) that I-V characteristics shown in Figure 2. The values of the rectification ratio (it is the ratio between the forward bias current and the reverse bias current at a particular voltage(1V) ) of the prepared thin films are increases because of reduction in the depletion layer as in Table (1). The Ideality factor ($\beta$) determined by taking slope of the linear region of the forward bias $(\ln I-V)$ curve through the relation:\n
$$\beta = \frac{q}{kT} \left[ \frac{dV}{d(\ln I)} \right]$$

(2)

Where $q$ is the charge of the electron, $k$ is the constant of the Boltzmann and $T$ is the temperature in Kelvin. We found increasing in ideality factor value that's mean the recombination current dominates when the ideality factor ($\beta > 1$) as in Table1, and this factor correlates between the processes of recombination that happen at the interlayer surface and the mismatch the materials lattice constants.

Figure 1.XRD patterns of the TiO$_2$, ZnO and GO nanosheets.

Figure 2. The I–V characteristics of $(\text{TiO}_2: \text{ZnO})_{1-x}(\text{GO})_x$ thin films.
Figure 3 shows the capacitance of the heterojunction changed with the reverse bias voltage in frequency range 100 KHz at room temperature. It is clear from the results the capacitance decreased with the bias voltage. Also the value of capacitance has become almost constant at high reverse bias voltage.

Figure 4. Shows the plot between $1/C^2$ and reverse voltage $V_r$. It can be seen that these curves are an abrupt type. From the slope of the fitted line of this plot and the equation

$$\frac{1}{C^2} = \frac{2}{q \varepsilon_0 \varepsilon_s S^2} \times (V_{bi} V - \frac{kT}{q})$$

Where $V_{bi}$ is the built-in voltage, $\varepsilon_i$ is the dielectric constant of the semiconductor, $\varepsilon_0$ is the dielectric constant of vacuum ($8.85 \times 10^{-12}$ F/m), $N_D$ is the concentration of ionized donors and $S$ is the thin film area, $V_{bi}$ can be calculated from intercept fitted line on the voltage axis at ($1/C^2=0$). The slope value gives the net doping concentration ($N_D$). The depletion-layer capacitance per unit area ($\omega$) calculated by

$$\omega = \frac{\varepsilon_0 \varepsilon_s S}{C_0}$$

Where $C_0$ is the capacitance value at $V_r=0$. From the obtained value we can calculate $E_F$ value for the structures by using following relation:

$$E_F = \frac{kT}{q} \ln \left( \frac{N_C}{N_D} \right)$$

Table 1 shows decreased built-in voltage and the height of the barrier resulting from decreases in the depletion layer depth due to the graphene oxide ratio leading to the injection of majority carriers, which in effect reduces the Fermi stage. These results improve the electrical properties of the prepared thin films.
Figure 4. Shows the plot between $1/C^2$ and reverse voltage $V_r$.

Table 1: I-V and C-V parameters for $(\text{TiO}_2: \text{ZnO})_{1-x}(\text{GO})_x$ thin films.

| X ml | R.R | $\beta$ | $V_{bi}$ (volt) | $N_D \times 10^{17}$ (cm$^{-3}$) | $C_0$ (nf) | $\omega$ (nm) | $E_F$ (eV) | $\Theta_B$ (eV) |
|------|-----|---------|----------------|-------------------------------|-----------|-------------|-----------|-------------|
| 0.2  | 3.66| 1.63    | 1.42           | 0.30                         | 3.2       | 127         | 0.20      | 1.62        |
| 0.4  | 5.42| 1.93    | 0.92           | 0.38                         | 4.5       | 90.3        | 0.20      | 1.12        |
| 0.6  | 10  | 2.18    | 0.79           | 1.37                         | 6.4       | 63.5        | 0.17      | 0.96        |
| 0.8  | 14.88| 2.48 | 0.65          | 3.34                         | 7.2       | 56.4        | 0.14      | 0.79        |

4. Conclusion

$(\text{TiO}_2: \text{ZnO})_{1-x}(\text{GO})_x$ / FTO thin films prepared using the technique of spray pyrolysis form heterostructured junctions with specific electrical properties depending on the GO ratio. The (I–V) and (C–V) characteristics showed that the heterojunction from symmetric type (isotope), The GO ratio leads to injecting majority carriers this in turn leads to decrease each of the barrier height, Fermi level, built-in voltage, and depletion layer. These results improved the electrical properties of the prepared thin films and indicated that graphene oxide acts as a semiconductor and can be used for flexible and transparent optical-electronic and detection devices.

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