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ZnO decorated graphene nanosheets: an advanced material for the electrochemical performance and photocatalytic degradation of organic dyes

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The objective of the current research was mainly focused on synthesizing the Reduced Graphene Oxide (RGO) using modified Hummers method and ZnO functionalized reduced graphene oxide (RGO) composite was fabricated by a one-pot approach. The ZnO functionalized graphene nanosheets were characterized by X-ray diffractometer (XRD) and surface morphology was examined using Transmission Electron Microscopy (TEM). Electrochemical characteristics of the ZnO/RGO composite were investigated through cyclic voltammetry and electrochemical impedance spectroscopy (EIS). The composite was capable of delivering a high specific capacitance with excellent cycling stability. The ZnO decorated RGO catalyst was also applied to degrade different nonvolatile compounds such as Methyl Blue (MB) and Indigo carmine (IC). The performance of RGO/ZnO shows rapid degradation of dyes of high concentrations.

Keywords: Reduced graphene oxide, ZnO, Mn_2O_3, electrochemical, catalytic activity.

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1. Introduction

Graphene is one-atom thick two-dimensional sheet of carbon atoms fashioned in a honeycomb lattice and is considered as the future revolutionary material [1]. An exponential growth after 2004 in graphene-related research is reflected in the number of publications. Graphene is highly anticipated to be an excellent electrode material due to its notable characteristics such as high surface area to volume ratio, good electrical conductivity, good flexibility, fast electron mobility and good thermal and electrochemical properties [2–4].

Because of its outstanding mechanical properties compared to other carbon materials, has attracted enormous interest. Considering the excellent properties of graphene, ZnO and Mn_2O_3, a combination of graphene with ZnO and Mn_2O_3 nanoparticles (NPs) might provide enhanced performance. Several methods have been carried out to produce graphene/ZnO and graphene/Mn_2O_3 composites. Other researchers have also synthesized graphene/ZnO and graphene/Mn_2O_3, as they appear to be promising materials for pseudocapacitors due to their superior electrochemical performance, environmental friendliness, and lower production costs [5]. The present research is mainly focused on synthesizing Reduced Graphene Oxide (RGO) by using Hummer's method. RGO and metal oxides such as ZnO and Mn_2O_3 composite were fabricated by a one-pot approach. The obtained RGO with metal oxides were characterized using X-ray Diffractometry (XRD) and ZnO and Mn_2O_3 composites were concerning to electrochemical and photocatalytic activity [6–11].

In this report, a simple and facile synthetic route is developed to prepare graphene-ZnO composite as an electrode material and photocatalyst for the organic dyes. Initially, graphene oxide (GO) was synthesized using the well-known modified Hummer's method. ZnO nanorods are inserted between the graphene nanosheets layer-by-layer rather than simply appended to the surface of graphene during the GO hydrothermal reduction process. This strategy provides a novel method for preparing highly active materials (ZnO nanorods) directly grown on Gr surface that avoids the restacking of Gr sheets, which show high electrochemical activity at higher scan rates and superior long-term cycle stability applied in an all solid-state supercapacitor device. Such excellent electrochemical properties provide important prospects for graphene- ZnO hybrid to be widely used as electrode material in supercapacitor [12, 13].

2. Experimental

2.1. Materials

Graphite, zinc nitrate hexahydrate ($Zn(NO_3)_2{\cdot}6H_2O$), sodium nitrate ($NaNO_3$), sulfuric acid (H_2SO_4), hydrochloric acid (HCl), potassium permanganate ($KMnO_4$), hydrogen peroxide (H_2O_2), hydrazine hydrate ($N_2H_4{\cdot}H_2O$) and potassium chloride (KCl) were purchased from Sigma-Aldrich and used without additional purification.

2.2. Synthesis of Graphene Oxide

GO was prepared from natural graphite using a modified Hummers method. In a typical experiment, graphite (1.5 g), $NaNO_3$ (1.5 g) and H_2SO_4 (70 mL) were mixed and stirred in an ice bath. Subsequently, 9 g $KMnO_4$ was added slowly. In a particular reaction condition, water was added slowly, followed by the slow addition of 10 mL 30 % H_2O_2. The above mixture was centrifuged and purified, the sample was dispersed in deionized water to obtain highly exfoliated GO sheets. This as-prepared GO was reduced to obtain RGO.

2.3. Synthesis of RGO/ZnO Composite

Pure ZnO Nano rods were synthesized by hydrothermal method. In a typical experiment, 100 mg of $Zn(NO_3)_2$ was first dispersed into 30 ml deionized water. Then, 15 μl of hydrazine hydrate was added dropwise under stirring, followed by ultrasonication for 30 min. Then, the solution was transferred to a 50 ml Teflon-lined autoclave and heated at 160 °C for 12 h. Finally, the RGO/ZnO nanostructures were collected after washing and centrifugation.

3. Result and Discussion

3.1. X-Ray Diffractometer

Crystalline structure of the materials were examined by an X-ray diffractometer (XRD). It can be seen (Fig. 1) that the ZnO XRD patterns of the nanocomposites with different mass ratios are similar to that of pure zinc oxide, indicating that no other impurity peaks were detected. It can be readily assigned to pure ZnO with hexagonal structure [2]. The XRD pattern confirms the crystalline nature of the as-prepared RGO/ZnO material and the Transmission electron microscopy (TEM) images indicate the presence of nanosheets around the centers.

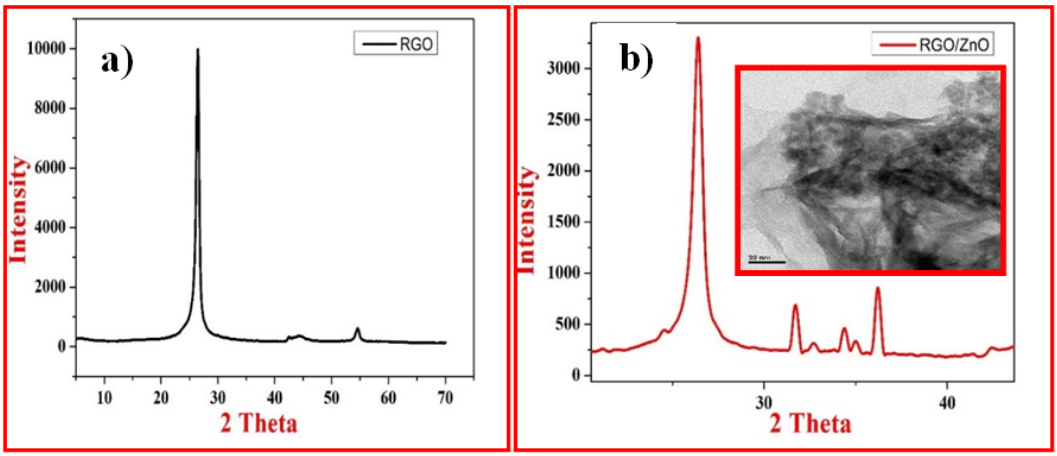

FIG. 1. XRD of a) RGO; b) XRD and TEM image of RGO/ZnO

3.2. Electrochemical Studies

The electrochemical activities of RGO and RGO/ZnO were assessed by cyclic voltammetry, which can provide additional information for material characterization from the shape, the number and the position of the different peak like the redox processes. The obtained black paste was immersed into a homemade disk electrode with glass walls and graphite bar as current collector. A CHI604E work station was used for all electrochemical measurements. Electrochemical measurement utilized three electrode system having working electrode, Ag/AgCl reference electrode and a platinum wire as counter electrode. Cyclic voltammetry (CV) studies were performed in potential between $+0$ to -1 V using electrolytes at constant scan rate. Cyclic voltammetry was used to determine the influence of RGO/ZnO on the overall charge capacity of the electrode. The value of $E_0 - E_R$ measures

the electrode reversibility (E_R), which is one of the predominant factors influencing the power capabilities of electrodes in 0.5 M Na_2SO_4 electrolyte. In Fig. 2(a) the smaller value of $E_0 - E_R$ indicates greater reversibility for the electrode reaction. In the current studies, several scan rates ranging from 10 to 50 mVs^{-1} were used. The effect of scan rate is presented in Fig. 2(b). As the scan rate increased, the CV profile deviated from the ideal capacitive behavior. A smaller the value of RGO/ZnO showed greater reversibility for the electrode reaction. Decreased solution resistance (Rs) values indicate greater conductivity values for the sample. In Fig. 3(a), one can clearly see that the sample RGO/ZnO in 0.5 M Na_2SO_4 shows lower charge transfer resistance (Rct) than the RGO electrode, indicating the enhanced conductivity and confirming that the capacitive behavior is faster, as is shown in Table 1. The simulation of RGO/ZnO is shown in Fig. 3(b).

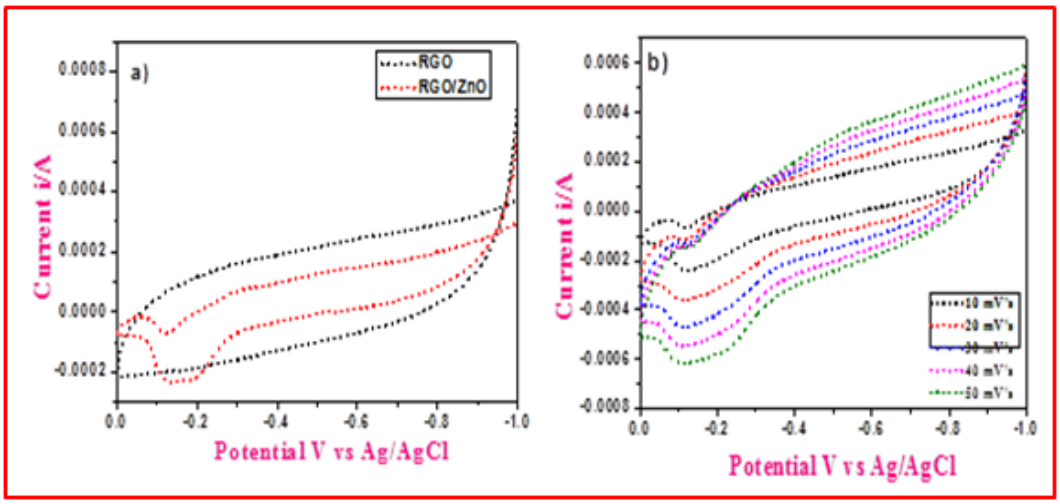

FIG. 2. a) Cyclovoltagramms of RGO and RGO/ZnO; b) different scan rate of RGO/ZnO

TABLE 1. Electrochemical reversibility and EIS of RGO, RGO/ZnO and RGO/Mn_2O_3 electrodes

Electrodes	$\mathbf{E_0(V)}$	$\mathbf{E_R(V)}$	$\mathbf{E_0 - E_R}$	$\mathbf{Rct(\Omega)}$	$\mathbf{C(F) \times 10^{-4}}$
RGO	0.8675	0.4480	0.4195	23.7	0.01
RGO/ZnO	0.3963	0.3077	0.0886	36.74	2.021

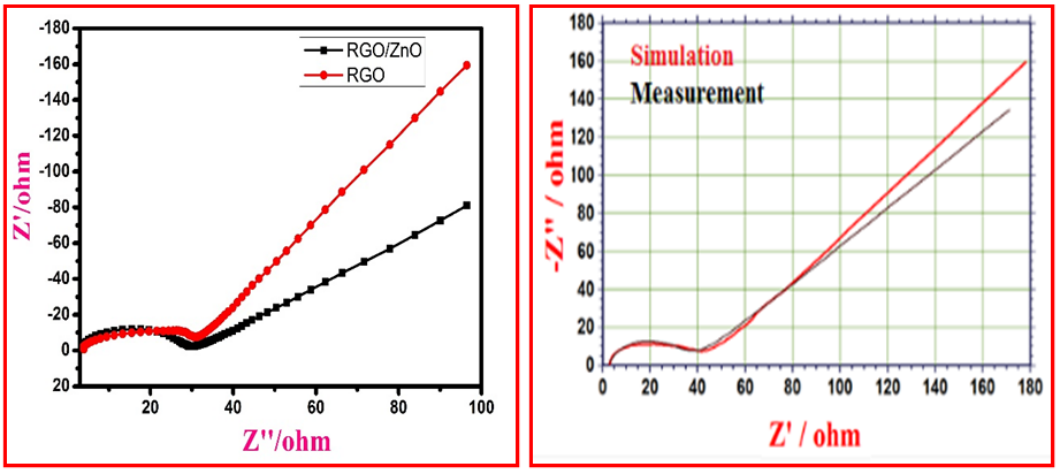

FIG. 3. a) Nyquist plots of RGO and RGO/ZnO; b) fitted simulation of RGO/ZnO

3.3. Photocatalytic Activity

In the existing work, Methylene blue (MB) and Indigo carmine (IC) dyes were used as ideal pollutants to estimate the photocatalytic activity of RGO/ZnO under UV light irradiation [12, 13]. In an experiment, 60 mg of RGO/ZnO was dispersed in 250 ml MB (20 ppm). The mixed suspensions were first magnetically stirred in the dark for 30 min to reach the adsorption–desorption equilibrium. Under ambient conditions and stirring, the mixed suspensions were exposed to visible light irradiation produced by a 400 W metal Philips lamp (wavelength: 254 nm). At certain time intervals, 5 ml aliquots of the mixed suspensions were extracted. The filtrates were analyzed by recording UV–vis spectra of MB and IC using a Spectratreats 3.11.01 Release 2A UV–vis spectrophotometer. In UV light, RGO/ZnO can absorb UV light (254 nm) and generate electron–hole pairs. These photo-generated electron and hole pairs can migrate into the catalyst surface and react with surface adsorbed O_2 to form active oxygen species. The photo degradation of MB and IC by RGO/ZnO nanoparticles and the effect of various parameters, like initial catalyst loading, initial dye concentration etc., were thoroughly investigated. RGO/ZnO nanomaterials exhibited the highest photocatalytic activity.

Figure 4 shows the UV-vis absorption spectra of MB and IC as a function of the catalytic reaction time. Both MB and IC solutions turned colorless after 80 min, indicating complete degradation of the dye molecules by RGO/ZnO. After 80 min of reaction, the RGO/ZnO showed good catalytic degradation of IC. When using the as-prepared composite material, the MB solution with concentration 60 mg/L can be degraded up to 79.9 % and mineralized up to 21 % in 80 minutes, as is shown Fig. 5.

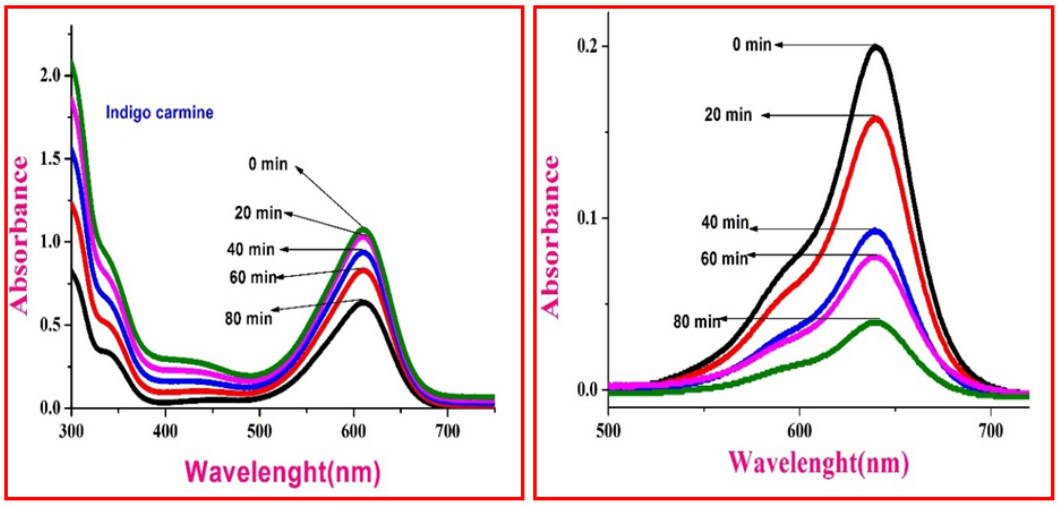

FIG. 4. Time-dependent UV-vis absorption spectra of RGO/ZnO in IC and MB

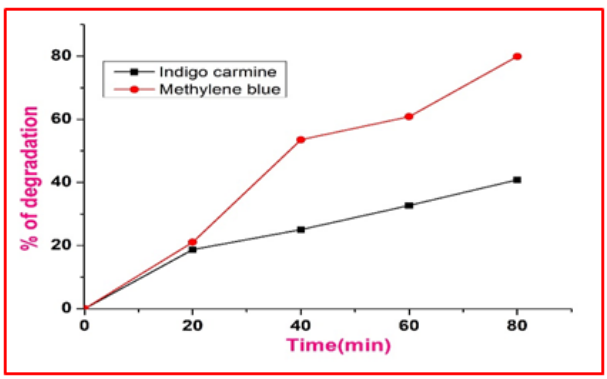

FIG. 5. UV-visible spectra of IC and MB degradation

4. Conclusion

RGO and RGO/ZnO composites were successfully prepared and their applications as electrode materials for electrochemical applications and photocatalytic activities were investigated. Cyclic voltammetry showed ideal capacitive behavior for RGO and RGO/ZnO hybrid nanosheets. Table 1 shows RGO/ZnO having less $E_0 - E_R$ and hence electrochemical reversible reactions will be more, and RGO/Mn_2O_3 having lesser Rct value and hence capacitance will be more. The photocatalytic activity was assessed through UV-Visible spectra, from which, we conclude that RGO/ZnO showed a good catalytic degradation of IC. This test showed that using the as-prepared composite material, the MB solution with concentration 60 mg/L can be degraded up to 79.9 % and mineralized up to 21 % and IC degraded up to 40.85 in 80 minutes.

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