



ZnO-rGO nanocomposite as high-performance photocatalyst in dye degradation

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The heterogeneous photocatalytic process has been considered as one of the most emerging methods for treatment of dye wastewater due to its cost-effectiveness, efficiency and stability. This study focuses on achieving excellent photocatalytic performance by dispersing Zinc oxide within the rGO sheets. In a two-step method, Zinc oxide-reduced graphene oxide (ZnO-rGO) composites were synthesized, initially KOH reacts with Zinc acetate in the aqueous dispersions of graphene oxide (GO) to form a Zn(OH)₂/graphene oxide precursor, followed by thermal treatment follows.

It is found that the dispersion of Zinc oxide within the rGO sheets is a key for achieving an excellent catalytic performance of the samples. ZnO-rGO composite with suitable mass ratio achieved more photocatalytic activity than pure ZnO. ZnO's ability to accept electrons is promoted by the rGO support. As a result, enhancement in photocatalytic activity is obtained. The samples are characterized by XRD, SEM, EDAX and UV-VIS diffuse reflectance spectroscopy methods. The photocatalytic activity of ZnO-rGO has been examined by degradation of the Direct blue 199 dye wastewater. 99.6% of dye degradation was obtained using ZnO-rGO composites.

Keywords: Direct blue 199, Dye Degradation, Photodegradation, ZnO-rGO composites, Photocatalyst

The photocatalytic degradation of Dye has received significant and persistent attention for the removal of contamination in wastewater treatment. Photocatalysis is a catalytic process occurring under the irradiation of light on the surface of semiconductor particles¹⁻⁴. The drawback for achieving efficient photocatalytic activity is the quick recombination of photogenerated electron-hole pairs, which is faster than the surface redox reactions due to which the quantum efficiency of photocatalysis is drastically reduced⁴.

Graphene oxide is obtained by oxidizing graphite crystals which are affordable and can be obtained in bulk. Reduced graphene oxide (rGO) is obtained by reducing the oxygen content in graphene oxide by thermal process¹. It has been reported that metal or metal oxide nanomaterials (Au, Pt, TiO₂, ZnO, SnO₂, etc.) on graphene sheets can exhibit enhanced efficiencies in photocatalytic reactions due to excellent electron accepting property of graphene⁴⁻⁶. Among them, ZnO shows high efficiency for photodegradation of some dyes in polluted water and has been a widely studied semiconductor because of its strong oxidation and reduction abilities under solar light. rGO when added to ZnO as a novel nanocomposite that increases the activity of the degradation process. ZnO spheres possess large surface area, increase the photocatalytic performance

and have the efficiency to transport organic pollutants as well. Superior photoelectrochemical and photocatalytic performance can be expected for the rGO structured ZnO composites^{7,8}.

The aim of the present work was to synthesize ZnO-rGO nanocomposites and to analyze its performance by photocatalytic process by using Direct blue 199. ZnO-rGO were successfully synthesized by modified Hummer's method and characterized by various techniques such as powder X-ray diffraction (PXRD), Scanning electron microscopy (SEM) and UV-VIS diffuse reflection spectroscopy. Remarkably the photo-degradation activity of ZnO-rGO for direct blue 199 was greatly enhanced under visible light irradiation as compared to either pure rGO or ZnO due to its improvement in its efficiency to separate photogenerated electron-hole pairs in the ZnO-rGO composites.

Experimental Section

Materials

Zinc sulphate, sodium hydroxide, zinc acetate, potassium hydroxide, graphite powder (30 mesh), sulphuric acid (99.9%), sodium nitrate, potassium permanganate, hydrogen peroxide, direct blue 199 dye, were purchased from SRL Private Ltd and used without further purification.

Preparation of graphene oxide (GO)

GO was synthesized by Modified Hummer's method^{9,10}. In this method graphite powder, sodium nitrate and potassium permanganate were taken in a weight ratio of (1:1:4) along with concentrated sulphuric acid. Graphite and sodium nitrate were mixed with sulphuric acid. The above mixture was then stirred in an ice bath for 4 h, then potassium permanganate was added pinch by pinch and stirred for 12 h at room temperature. The setup was then kept in the oil bath. Followed by addition of water and hydrogen peroxide, was added then the reaction mixture turns to golden yellow in colour. After 30 min the mixture turns brown. The obtained mixture was pH adjusted to 7 followed by drying the sample at 60°C for 12 h to get GO sheets¹¹⁻¹³

Preparation of zinc oxide

Zinc oxide nanoparticles were synthesized using a simple precipitation method¹⁴. In this method, an aqueous solution of zinc sulphate and sodium hydroxide solution in a molar ration of 1:2 was added dropwise and stirred vigorously for 12 h. The precipitate thus obtained was filtered and washed thoroughly with deionized water. A fine powder was then obtained by drying the precipitate in an oven at 100°C and ground using an agate mortar.

Preparation of zinc oxide and reduced graphene oxide nanocomposite

The ZnO - rGO with different mass ratios were synthesized through a two-step method. The typical route is as follows, Zinc acetate (0.01 mol) was dissolved in distilled water (50 mL) with vigorous stirring in an ice-bath¹⁵. Then, GO (0.0904 g) was exfoliated in distilled water (100 mL) with ultrasonic treatment for an hour. Subsequently, the above GO solution was dropped into an aqueous solution of Zinc with continuous stirring. Later, 1 M KOH solution was added dropwise to the above mixture till a pH 8.5 was obtained. After aging for 12 h, the product was then separated by suction filtration, followed by rinsing with distilled water several times, and then dried at 60°C for 12 h under vacuum. By this method, the Zn(OH)₂/GO precursors were obtained. In the second step, the precursors were heated at 200°C for 5 h in a muffle Furnace to obtain ZnO-rGO nanocomposite.

Characterization of samples

X-ray diffraction (XRD) patterns were recorded for phase analysis and crystallite size measurement on a diffractometer (Bruker AXS KAPPA APEX-II), operated at 45 mA and 45 kV by using X radiation, in

the 2-theta range from 10° to 70° in steps of 0.02°, with a sampling time of 2s per step. The crystallite size was estimated using Bragg's equation¹⁰. XRD patterns were recorded for GO, calcinated ZnO and ZnO-rGO nanocomposites. The structural changes of the ZnO-rGO nanocomposites were investigated by the Raman spectroscopy, using FT-Raman spectrometer (Bruker RFS27) in the range of 5000-50 cm⁻¹. The compounds were characterized by their structure and morphology by SEM¹⁴. SEM images and EDAX data of the samples were taken using an (FEI Quanta- 200 MK II scanning electron microscope). UV-VIS diffuse reflectance spectroscopy was used to find out the band gap of ZnO-rGO. The UV-VIS absorption spectra of the samples were recorded in the wavelength of range 200 to 2500 nm using a UV-VIS spectrometer (Hitachi U-3010) in diffuse reflectance mode.

Photocatalytic test

The photocatalytic test was carried out using a UV-photo reactor. Blue light fluorescent bulbs were positioned at the axis of the reactor to supply UV illumination. The reaction suspension was irradiated by UV light at a power of 18 W. The Direct blue 199 dye was degraded by photocatalysis using UV-Photoreactor. The different concentrations of direct blue 199 dye solutions (100, 200, 300, 400, 500 and 600 ppm) are placed in a cuvette. The blank dye absorbance value was noted and the calibration chart was plotted by using these values¹⁶. The following parameters play a vital role in the dye degradation process: Concentration, Catalyst dosage, Time and pH¹⁷. The percentage of degradation was measured by applying the following equation:

$$\% \text{ Degradation} = \frac{(C_0 - C)}{C_0} \times 100 \quad \dots (1)$$

Where C₀ is the initial concentration and C is the concentration of uncomplexed dye solution.

Result and Discussion

XRD Analysis

Figure 1 a represents the X-ray diffraction pattern (XRD) of GO synthesized by modified Hummer's method, the sharp diffraction peak observed at 2θ = 10.35° indicates the GO¹⁸. Fig 1 c showed characteristic peaks centered at 2θ = 31.84, 34.52, 36.32, 47.6, 56.64, 62.92, 67.96 and 69.16 for ZnO. The higher crystallinity of ZnO peak was formed at 2θ = 36.32. The two reflection peaks of rGO appearing at 2θ values of 24.9 and 46.94 are theoretically expected to be observed in the XRD pattern of ZnO-rGO composites. This phenomenon stands to reason because the amount

of pure phase ZnO in this composite is very low, and the rGO sheets coated by ZnO (similar to thin-film) were in a state of increasingly disordered stacking. Therefore, it can be considered that the diffraction peaks of wurtzite ZnO result mainly from the pure phase ZnO in the composites.

Raman spectrum

The structural changes of the prepared ZnO-GO nanocomposites were investigated by the Raman

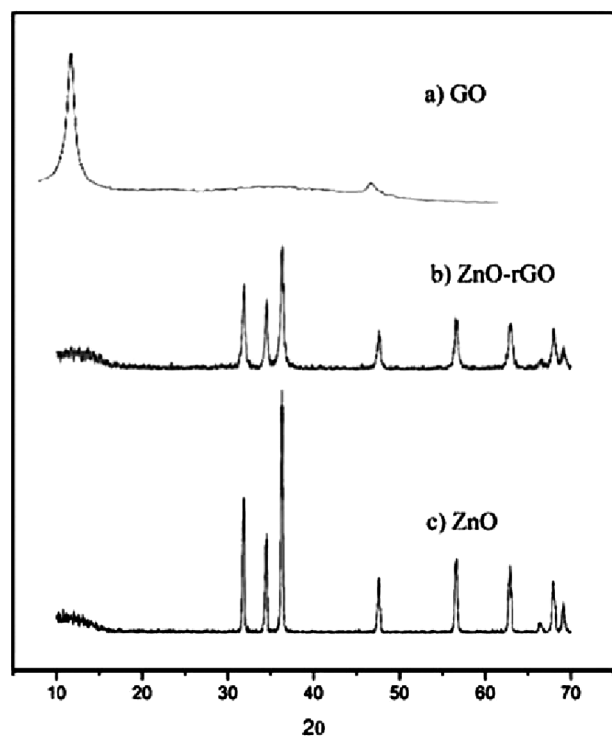


Fig. 1a—XRD for GO, Fig 1 b) XRD for ZnO-rGO and Fig 1 c) XRD for ZnO.

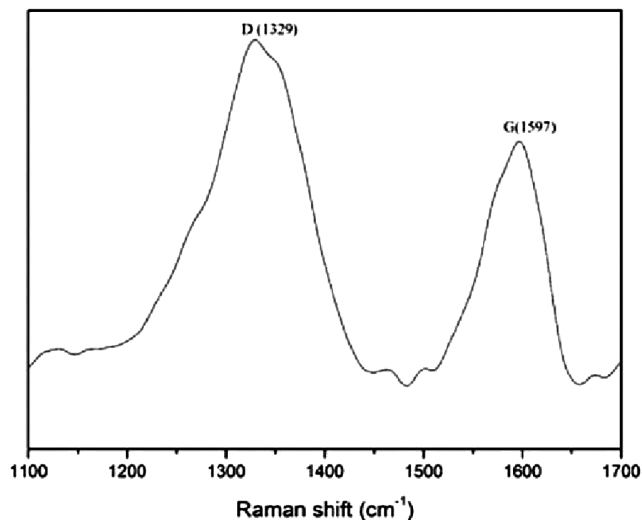


Fig. 2—Raman spectra of ZnO-rGO.

spectroscopy (Fig 2), which was a suitable technique to study the ordered/disordered crystal structures of graphitic materials. The spectrum of GO exhibited the characteristic G-band (1597 cm^{-1}) and D-band (1329 cm^{-1}). The Raman spectra of ZnO-rGO showed similar G and D bands structure of carbon, suggesting that the structure of graphene was maintained in the nanocomposites¹⁹.

SEM and EDAX analysis

The surface morphologies of the ZnO-rGO nanocomposites were provided by SEM images with different magnifications (Fig 3a, 3b and 3c). Through the SEM images of ZnO-rGO composites, we could

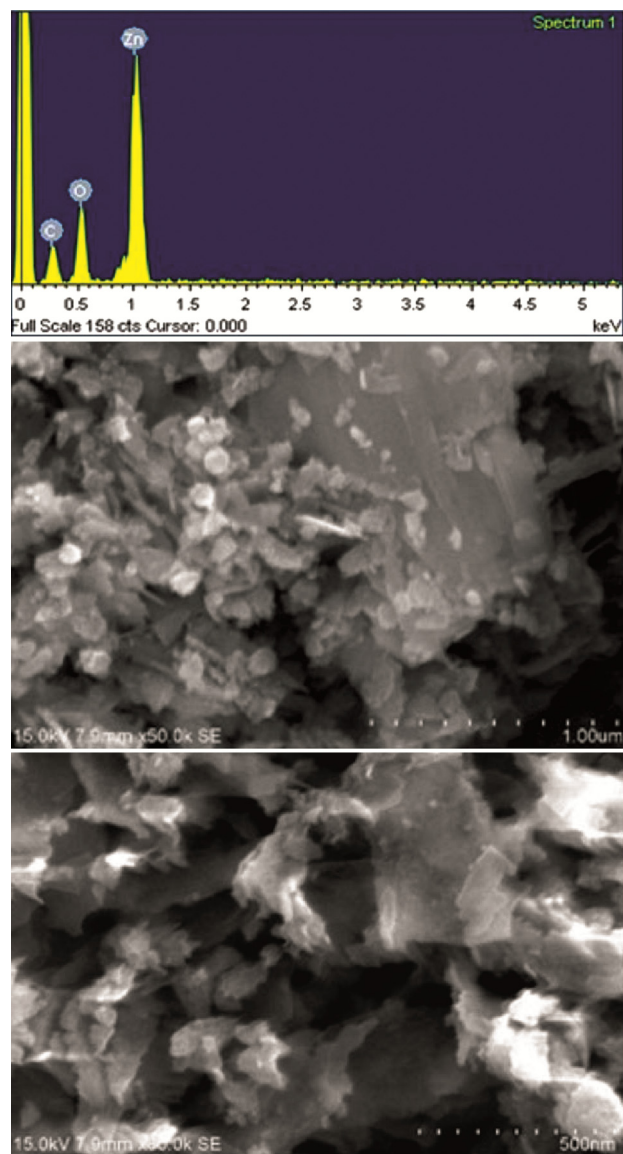


Fig. 3a-c—EDAX for ZnO-rGO; 3b—SEM image of ZnO homogeneously incorporated in graphene sheets; 3c—SEM image of graphene oxide.

see that the composites were significantly influenced by the mass ratio of ZnO to rGO. In Fig 3a it was observed that graphene sheets on which ZnO has grown uniformly. Graphene sheets are homogeneously incorporated with ZnO. It is shown in fig 3b that the composite appears in the SEM images to be almost filled with the rGO sheets coated by ZnO. A few particles of pure phase ZnO were also observed in the composite¹⁴. As for the ZnO-rGO nanocomposite (Fig 3a, 3b and 3c), it can be clearly observed that the ZnO nanospheres were well dispersed in the graphene framework. The EDAX for ZnO-rGO composite showed in Fig 3c. From this analysis, the elements- Zn, O, and C are presented in this composite.

DRS test

Diffuse Reflectance Spectroscopy (DRS) results show that the maximum wavelength was 401 nm for the ZnO-rGO composite. The band gap was found to be 3.1 eV., from the results the composite was found to be a semiconductor as well as it will serve as a good photocatalyst under UV region.

Photocatalytic activity

Direct blue 199 dye was degraded by photocatalysis using UV Reactor. The different

concentrations of direct blue 199 dye solutions were placed in 50 ml glass tube. The blank dye absorbance value was noted and the calibration graph was plotted by these values. The direct blue dye wastewater was added to the test tube and this solution was treated with the catalyst by the UV reactor, then the absorbance value was noted. The removal percentage was calculated for the different concentrations of direct blue 199 dye wastewater and plotted the graph. The parameters play the vital role in dye degradation process. The optimized parameters are concentration, catalyst dosage, time and pH. These parameters are optimized with the help of UV-Photo reactor.

In Fig 4a, Different concentrations of dye solution treated with same concentration of catalyst using UV-Photoreactor. 1hr Absorbance value for dye sample of 100 ppm, 200 ppm, 300 ppm, 400 ppm, 500 ppm and 600 ppm concentrations were noted. Percentage of degradation was calculated and the graph was plotted. From the Fig 4a, the optimum degradation was obtained for 300 ppm concentration because the concentration above that exhibit the lower percentage removal as the time and amount of catalyst are not sufficient for the process^{20,21}.

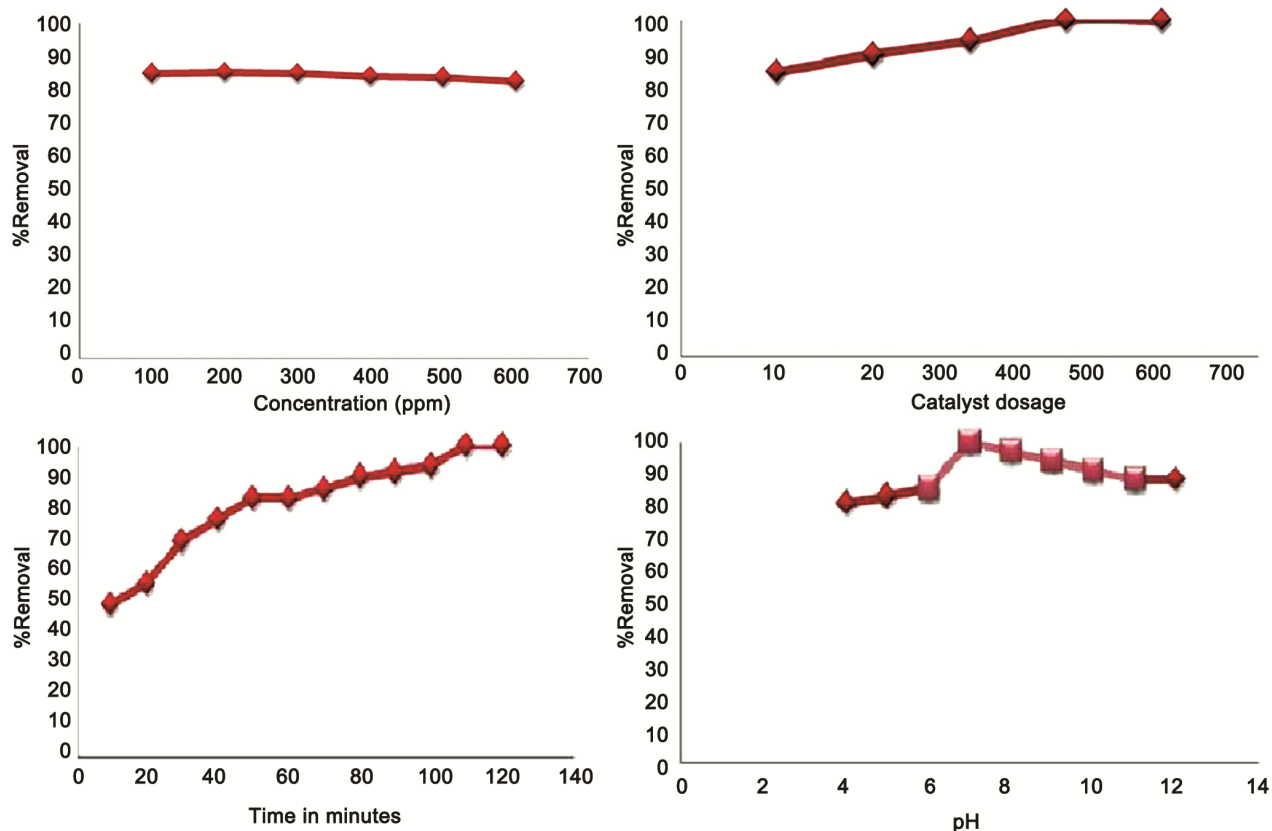


Fig. 4-a-d—Effect of concentration; b—Effect of catalyst dosage; c—Effect of time and d—Effect of pH.

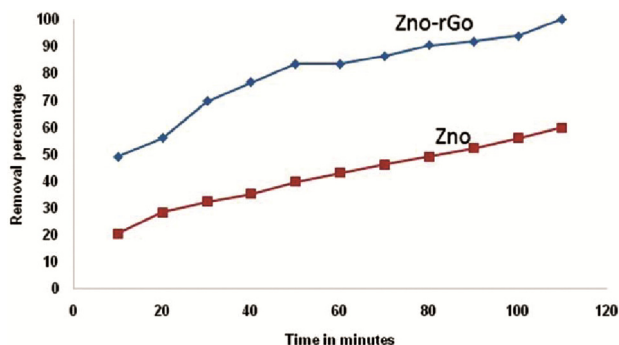


Fig. 5—Comparison of ZnO-rGO and ZnO.

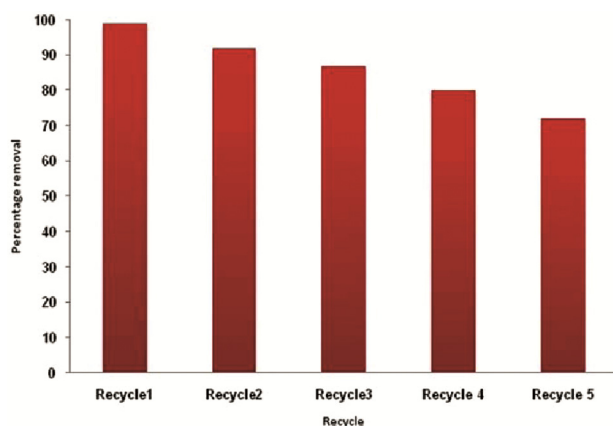


Fig. 6—Comparison of recycle efficiencies.

The 300 ppm dye wastewater was treated with different catalyst dosages of 10mg, 20mg, 30mg, 40mg, 50mg, and Under UV irradiation for one hour. The absorbance values are noted. Percentage of degradation was calculated and the graph was plotted. From the Fig 4b, it was observe that the percentage removal is increasing along with the catalyst dosage and saturated at 40 mg.

Effect of time

Figure 4c shows the effect of time, as the time taken for the process was increased the percentage removal is increased, the maximum percentage removal (99.6%) was achieved in 110 min as it reached saturation at that point, further the increment in the time for the process did not show any change.

Effect of pH

The pH of the dye was initially set at 12 when the catalyst was added and treated by the UV reactor. The absorbance value was noted and the removal percentage of dye was calculated. The experiment was repeated for various pH values (11, 10, 9, 8, 7, 6, 5 and 4) and respective removal percentages were calculated and studied. From Fig. 4d the maximum removal (99.6 percentage) was obtained for a solution of pH value 7.

Comparison of ZnO-rGO and ZnO performance

It is observed from Fig. 5 that the removal percentage of Direct blue dye 199 at 110 min was 59.7% when ZnO was used and 99.6% when ZnO-rGO was used as rGO on ZnO can enhanced the photocatalytic reaction.

Comparison of recycle efficiencies

ZnO - rGO has been recycled and tested for the process under same conditions to check the percentage removal at each recycle level, the calculated values are plotted as in Fig. 6. From the graph, the maximum removal in Recycle 1 was 99%, Recycle 2 was 92.9%, Recycle 3 was 86.8%, Recycle 4 was 80%, and Recycle 5 was 72% achieved at the time duration of 110 minutes.

Conclusion

ZnO-rGO composites have been successfully prepared using the two-step method starting with GO synthesis. The samples are confirmed as GO and zinc oxide by XRD analysis. The composite with the optimal mass ratio has homogeneous incorporation of ZnO in the rGO sheets. The morphology of ZnO-rGO composites is clearly seen by SEM analyses. ZnO-rGO were prepared by the thermal method exhibit good photocatalytic activity toward degradation of direct blue 199, using the UV irradiation. The obtained experimental results prove that the photocatalytic efficiency of ZnO-rGO is better than ZnO. The maximum removal percentage (99.6%) was observed when 40 mg ZnO-rGO was used for a 300 ppm solution of pH 7 for 110 min. The reusability of the catalyst also shows a good activity up to 5 recycles.

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