One-pot sonochemical synthesis of CdS-reduced graphene oxide composite and its application for photocatalytic degradation of methylene blue

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A one-pot synthesis of CdS-reduced graphene oxide (RGO) composite via sonochemical reduction of graphite oxide and simultaneous CdS formation is reported. The composite is characterized by scanning electron microscopy, transmission electron microscopy, X-ray diffraction spectroscopy and UV-vis absorption spectroscopy and its photocatalytic performance is evaluated for the degradation of methylene blue. Results show that in the composite the RGO nanosheets are densely decorated by CdS nanoparticles, displaying a good combination between RGO and CdS. The CdS-RGO composite exhibits enhanced photocatalytic performance for the dye degradation with a maximum removal rate of 96% under visible light irradiation due to increased light absorption intensity as well as the reduced electron-hole pair recombination in CdS.

Keywords: Sonochemical reduction, Photocatalysis, Graphene oxide, Reduced graphene oxide, Composites, CdS-RGO composite, Methylene blue, Cadmium sulphide

The development of various methods for producing graphene, a single layer of carbon atoms bonded together in a hexagonal lattice, has stimulated research in recent years owing to its excellent conductivity, superior chemical stability and high specific surface area\textsuperscript{1,3}. Many researchers have studied the application of graphene in many fields, such as photocatalysis,\textsuperscript{4-7} energy storage,\textsuperscript{8-10} solar cells,\textsuperscript{11,12} transparent electrodes,\textsuperscript{13,14} field emission,\textsuperscript{15} etc.

Recently, graphene/metal oxide and graphene/metal sulphide nanoparticle composites have aroused extensive interest\textsuperscript{6-15}. However, such an attachment of metal sulphide particles onto graphene may also prevent the restacking and agglomeration of graphene sheets during the reduction process due to van der Waals interactions between them. Nethravathi \textit{et al.}\textsuperscript{20} and Wang \textit{et al.}\textsuperscript{21,22} fabricated CdS-graphene composites by passing H\textsubscript{2}S gas through mixed solution of Cd(NO\textsubscript{3})\textsubscript{2} and graphite oxide (GO) and shows the effect on luminescent of CdS particles. Zhang \textit{et al.}\textsuperscript{23} and Liu \textit{et al.}\textsuperscript{24} synthesized CdS-graphene composites by one-step conventional pyrolysis of Cd(C\textsubscript{7}H\textsubscript{4}NS\textsubscript{2})\textsubscript{2} in an aqueous dispersion of GO, which showed obvious quantum confinement and fluorescence quenching effects. Chang \textit{et al.}\textsuperscript{25} showed the enhanced photocurrent generation capability of CdS-graphene composite obtained by \textit{in situ} growth of CdS on pyrenebutyrate functionalized graphene under visible-light irradiation as compared to pure CdS. Jia \textit{et al.}\textsuperscript{26} found that both graphene content and calcination atmosphere can affect the photocatalytic H\textsubscript{2} evolution activity of the composites prepared by a calcination method to synthesize CdS-graphene composites. In the photocatalysis process, graphene can act as an excellent electron-acceptor/transport material to effectively facilitate the migration of photo-induced electrons and hinder the charge recombination in electron-transfer processes due to electronic interaction between CdS and graphene, which enhances the photocatalytic performance of CdS. Recently Liu \textit{et al.}\textsuperscript{27} synthesized CdS-RGO composite by microwave method using GO, Cd(NO\textsubscript{3})\textsubscript{2} solution and CH\textsubscript{3}N\textsubscript{2}S solution in one step and used it for photocatalytic Cr(VI) reduction. Despite recent progress in studies on promising hybrid materials for photocatalysis, Investigations on CdS-graphene composites still have a long way to go. Recently, sonochemical processing has proved to be a useful technique for generating novel materials with unusual properties\textsuperscript{28,29}. Sonochemistry arises from acoustic cavitation phenomenon, that is, the formation, growth and implosive collapse of bubbles in a liquid medium\textsuperscript{30}. An inexpensive, quick and versatile technique, sonochemical-assisted reactions have seldom been employed to synthesize CdS-reduced graphene oxide (RGO) hybrid composite materials for photocatalysis although such a method has been used successfully to fabricate RGO\textsuperscript{30} and CdS\textsuperscript{30} separately. Therein, we report the successful synthesis of
CdS-RGO composites via a one-step sonochemical reduction of GO in CdS precursor suspensions using an ultrasonic system. In comparison to earlier reported methods, the present method provided CdS nanoparticles of uniform size distribution and with much larger surface area with particle size of ∼ 4–8 nm.

Experimental
Graphene oxide (GO) was prepared according to the modified Hummer's method. GO (100 mg) was dispersed into 250 mL of cadmium nitrate solution (0.01 M) prepared in deionized (DI) water by sonication for ten minute to obtain a clear brown dispersion and then stirred for about 1 h. The above well stirred reaction mixture was kept again for sonication for about one hour with simultaneous addition of 0.01 M solution of sodium sulphide. A brown black colored product was obtained; color change indicates the composite formation. The product was centrifuged and washed with acetone several times and dried at 70 °C in a vacuum oven. For comparison, pure CdS was prepared by using the same sonochemical method without GO.

The surface morphology, structure and composition of the samples were characterized by high resolution scanning electron microscopy and energy dispersive X-ray spectroscopy (EDS) with (SEM, FEI Quanta FEG 200), high-resolution transmission electron microscopy (HRTEM, Philips-CM200), Fourier transform infrared spectroscopy with ATR (FTIR, Bruker model Alpha), and X-ray diffraction (XRD, XPERT-PRO) with Cu-Kα radiation (V = 40 kV, I = 30 mA). The UV-vis absorption spectra were recorded using a Shimadzu UV-1800 spectrophotometer. Photoluminescence (PL) spectra were recorded on a Shimadzu RF-5301 PC spectrofluorophotometer with a 450W Xe-lamp as the excitation source.

The photocatalytic performance of the as-prepared samples was evaluated by the photocatalytic degradation of MB under visible light irradiation. Photo-irradiation was carried out using a Philips lamp (40 W/230 V) placed 10 cm away from the reaction vessel, which was used to provide a full-spectrum emission without any filter to simulate the sunlight source. For the photo-degradation experiment, 0.05 g of photocatalyst was added to 100 mL of 2 ppm MB aqueous solution. Before starting the illumination, the reaction mixture was stirred for 30 min in the dark in order to reach the adsorption-desorption equilibrium between the dye and the catalyst. At certain time intervals, 3 mL aliquots were withdrawn, and then centrifuged to remove the photocatalyst. The concentration of the remnant dye was spectrophotometrically monitored by measuring the absorbance of solutions at 663 nm during the photodegradation process.

Results and discussion
Surface morphology of the prepared material was investigated by SEM and it was observed that the RGO nanosheets are curled and corrugated and CdS displays uniform spherical particles shown in the Fig. 1. It shows that the surface of RGO nanosheets is packed densely by CdS nanoparticles, exhibiting a good combination between RGO and CdS. The existence of CdS in the composite has been proved by the peaks of Cd and S in EDS data (Fig. 1(c)).

Figure 2 shows the HRTEM images of CdS-RGO composites, which confirmed that the CdS grains can nucleate and grow in the interlayer and outer layer of RGO. This agrees with the SEM analysis that CdS particles are uniformly distributed in both sides of RGO layers. It is clearly seen that some CdS nanoparticles are attached onto the surface of RGO sheets. The RGO sheets act as bridges for connecting the different CdS nanoparticles, which could significantly increase the separation of photo-
generated carriers, and enhance the photocatalytic performance. The average size measured for these crystallites was found to be 4-8 nm (Fig. 2d).

FT-IR spectra of GO and CdS-RGO composites show the bands at bands at 1028, 1143 and 1713 cm\(^{-1}\) the oxygen-containing functional groups of GO (Supplementary data, Fig. S1a), which correspond to C–O stretching vibrations, C–OH stretching peak, and C=O stretching of COOH groups, respectively. The peak at 1632 cm\(^{-1}\) can be assigned to the vibrations of adsorbed water molecules and also the skeletal vibrations of unoxidized graphitic domains. However, all these bands of the oxygen-containing groups almost vanished in the FT-IR spectra of CdS-RGO composites (Supplementary data, Fig. S1b), revealing that these oxygen containing functional groups were removed during reduction with sonochemical irradiation, and thus the GO was transformed into RGO during syntheses. The peaks at about 1623 cm\(^{-1}\) can be attributed to the skeletal vibration of graphene sheets. These results are consistent with data reported in the literature\(^{33,34}\), and further confirm that oxygen-containing functional groups were almost totally removed after the reduction. Raman analysis of CdS-RGO composite also supports the findings of the FTIR analysis. (Supplementary data, Fig. S2).

XRD measurements were employed to investigate the phase and structure of synthesized samples. Figure 3 (curve 1) shows XRD pattern of GO having a sharp peak centered at 20=10.20\(^{\circ}\), corresponding to (001) reflection of GO. The XRD pattern of CdS-RGO composites (Fig. 3, curve 2) is similar to that of pure CdS only (JCPDS No. 41-1049), which indicates that RGO does not alter the changes in preferred
orientation of CdS particles. Typical diffraction peak of the GO was not observed indicating that the GO has been exfoliated to a great extent and CdS groups in the solution are adsorbed on the surface of graphene oxide. Then the nucleation and growth of CdS particles takes place in the lamellar structure of GO and forms CdS-GO nanocomposite, which was finally reduced to CdS-RGO composite under sonochemical treatment.

The UV-vis absorption spectra of CdS-GO and CdS-RGO composites are shown in Fig. 4. The UV-visible spectra before addition of sodium sulphide shows many peaks corresponding to various functional groups present in the GO. The addition of sodium sulphide and ultrasound irradiation shows remarkable changes in the composite such as appearance of peak at 500 nm corresponding to CdS nanoparticle formation and disappearance of various peaks in to single peak below 300 nm, corresponding to \(\pi\rightarrow\pi\) transition of graphitic structure. The appearance of an absorption peak at 262 nm, which is generally attributed to the excitation of \(\pi\)-plasmon of the graphitic structure at final composite material, suggests the formation of RGO\(^{18}\). The absorbance of CdS-RGO composite increases with the incorporation of RGO, which is similar to that reported in the literature\(^{35,36}\). Such an increase in absorbance may be due to the contribution from RGO and the enhancement of the process of electron-hole pair formation during irradiation, which is beneficial to the photocatalytic performance.

Comparative PL spectral study demonstrates that the emission intensity in the case of CdS decreases sharply in CdS-RGO composite (Supplementary data, Fig. S3), which indicates that the recombination of photo-induced electrons and holes in CdS can be effectively inhibited in the composite. The result obtained in our study shows that the material prepared by this method is suitable for the photocatalytic applications while the material prepared by Nethravathi et al.\(^{20}\) would not be suitable for the same. The inhibition effect may be due the incorporation of RGO into CdS which plays an important role in the photocatalytic performance of CdS-RGO composite.

Photocatalytic degradation of MB by CdS and CdS-RGO composite was performed under visible light (Fig. 5). The normalized temporal concentration changes \((C/C_0)\) of MB during the photocatalytic process are proportional to the normalized maximum absorbance \((A/A_0)\), which can be derived from the change in the MB absorption profile at a given time interval. The reactions show first order kinetics. The removal rate of MB for pure CdS is 83%, with order rate constant as \(8.5\times10^{-2}\) min\(^{-1}\). When RGO was introduced into CdS, the removal rate increased to 96% with rate constant \(9.3\times10^{-2}\) min\(^{-1}\) for CdS-RGO composite. It is known that during photocatalysis, the light absorption and the charge transportation and separation are crucial factors. The enhancement of the photocatalytic performance may be ascribed to the increase of the light absorption intensity and range, and the reduction of electron-hole pair recombination in CdS in the presence of RGO in the composite, which have also been confirmed from absorption and PL measurements.

The present study shows that the sonochemical method can be effectively employed for the one-step synthesis of CdS-RGO composites via sonochemical
reduction of GO in the CdS suspension. Results show that CdS-RGO composites exhibit better photocatalytic performance than pure CdS. The photocatalytic performance of CdS-RGO is dependent on the proportion of RGO in the composite and achieves removal rate of 96% for methylene blue. The enhance photocatalytic performance is ascribed to the electronic interaction between CdS and RGO.

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Supplementary data

Supplementary data associated with this article, i.e., Figs S1-S3, are available in electronic form at http://www.niscair.res.in/jinfo/ijca/IJCA_52A(05)614-618_SupplData.pdf.

References