

Synthesis and Characterization of CdSe/graphene Nanocomposites and their Catalytic Reusability Studies under Visible Light Radiation

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(Received September 5, 2015; Revised October 7, 2015; Accepted October 27, 2015)

ABSTRACT

We examined the photo catalytic activity and catalytic recyclability of CdSe/graphene nanocomposites fabricated via modified hydrothermal technique. The prepared composites were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) with energy dispersive X-ray (EDX), transmission electron microscopy (TEM), Raman spectroscopic analysis, and X-ray photoelectron spectroscopy (XPS). The photocatalytic behavior was investigated through decomposition of RBB as a standard dye under visible light radiation. Our results indicate that there is significant potential for graphene based semiconductor hybrids materials to be used as photocatalysts under visible light irradiation for the degradation of organic dyes from industry effluents.

Key words : XRD, TEM, XPS, Raman, Photo catalysis

1. Introduction

Recently, there has been a revelatory awareness and concern about the increasing pollution of water throughout the world. New ideas have been developed to achieve sustainable exploitation of water resources. A series of experiments and research studies have been attempted all over the world to find appropriate materials to degrade toxic pollutants. Synthetic dyes are vastly used by commercial industries. Thousands of different types of commercial dyes and pigments are produced in millions of tons annually. Approximately 10-15% of the dyes are released into the environment during manufacture or usage, which plays a key role in water pollution.^{1,2)} Low band gap semiconductor materials have gained attention as a photo catalytic material that can protect our environment. CdSe, as one of the II-VI group semiconductors, has attracted attention from many researchers due to its small band gap and good photocatalytic stability.³⁻⁶⁾ Tsai et al. have synthesized CdSe/Graphene composites through hydrothermal techniques and found that these materials have markedly high catalytic performance for hydrogen evolution.⁷⁾ CdSe/graphene composite has been used to degrade organic pollutants in dark ambience with drastic change of catalytic properties.⁸⁾ The degradation of MB as a standard dye through CdSe/TiO₂ was found to have minor degradation effect.⁹⁾ These results highlight the importance of graphene in the composites. Graphene is used as a key material in the energy, electronics, catalysis and biosensing industries due to its

excellent properties such as high surface area and good conductivity; also graphene composites can act as support materials due to the 2D structure, elevated conductivity, and optical as well as electrical properties.^{10,11)} Surface functionality plays an important role in the attachment of nanoparticles to graphene sheets. Graphene Oxide (GO), as an important derivative, has many oxygen functional groups such as epoxy groups, hydroxyl groups, and carboxyl groups; these functional groups increase the possibilities of GO applications in areas such as electrochemical sensors,¹²⁾ nanoelectronics,¹³⁾ lithium batteries,¹⁴⁾ supercapacitors,¹⁵⁾ and sensing biomolecules.^{16,17)} Reduced graphene oxide has been vigorously used to couple with various photocatalysts to increase photocatalytic activity. However, there are still some disadvantages of oxygen functional groups, i.e., a decrease of electrical conductivity and an agglomeration of graphene sheets due to Vander Waals interaction. To overcome some of these discrepancies, we used the chemical vapor deposition method to functionalize our graphene.^{18,19)} SEM and TEM images were obtained for a smooth surface rather than in plates broken off in different directions, as shown in our previous reports.²⁰⁻²¹⁾

In this study, we synthesized and characterized CdSe/graphene nanocomposites and attached them to the obtained functionalized graphene using the hydrothermal method. The photocatalytic properties were observed by degrading RBB as an industrial dye. Rh.B standard dye was also used as a degrading component. Cyclic tests were performed in detail to study the stability of our nanocomposites; results show that graphene based materials develop a highly efficient binary system for photocatalytic degradation of organic dyes. Photocatalytic experiments were performed under visible light irradiation. Results were analyzed using a UV/Vis spectrometer.

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2. Experimental Procedure

2.1. Materials

Graphene oxide was prepared in the laboratory following the Hummer's-Offeman method, as described in our previous studies.²²⁻²⁴ Cadmium acetate [$\text{Cd}(\text{CH}_3\text{COO})_2$, 98%), selenium powder (Se, 99%), ammonium hydroxide (NH_4OH , 25 - 28%), sodium sulfite ($\text{Na}_2\text{SO}_3 \cdot 7\text{H}_2\text{O}$, 95%), and ethyl alcohol (94%) were purchased from Duksan Pure Chemical Co. Ltd., Korea. RBB was purchased from Samchun Pure Chemicals Co. Ltd., Korea. All chemicals were used without further purification. All dilutions were carried out using distilled water.

2.2. Preparation of CdSe particles

For the syntheses of CdSe nanoparticles, 6 g of anhydrous sodium sulfite (Na_2SO_3) and 0.5 g of crude selenium powder (Se) were vigorously stirred with 50 mL of distilled water at a temperature of 80°C. In another reaction vessel, 2 mL of ammonium hydroxide solution (NH_4OH) was added to an aqueous solution of 0.675 g of cadmium acetate [$\text{Cd}(\text{CH}_3\text{COO})_2$]. The prepared solution was added to Na_2SeSO_3 solution and transferred to an autoclave for 2 h at 150°C. The CdSe precipitates were obtained using 47 mm Whatman filter paper. The residue was washed with distilled water at least five times. The collected CdSe powder was dried in a vacuum oven at a temperature of 350 K for 10 h.

2.3. Synthesis of CdSe-graphene composites

CdSe-graphene composite particles were prepared using hydrothermal techniques. In this process, CdSe particles were put into 200 mL distilled water to which 1 g of graphene oxide (previously obtained by Hummer's-Offeman method) had been added at a ratio of 1:1. After a hydrothermal reaction at 150°C at the end of 2 h, graphene oxide was reduced to graphene nanosheet. CdSe compounds were grown on the nanosheet surface to generate graphene-CdSe composites. The resultant solution was allowed to cool and settle at room temperature after filtering with the 47 mm Whatman filter paper, which had a pore size of 0.7 mm. The resultant powder was washed with distilled water 3 times, followed by drying in the vacuum oven. The powder was heated to 100°C for 8 h in the vacuum oven to form the CdSe-graphene composites. The preparation procedure is depicted in Fig. 1.

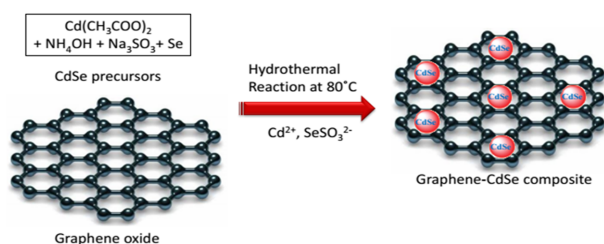


Fig. 1. Synthesis of CdSe-Graphene composite by simple hydrothermal method.

2.4. Characterization

The crystallinity of the prepared samples was investigated using monochromatic high intensity Cu K α radiation (λ D1.5406 Å) in XRD (Shimadzu XD-D1). The surface area and structures of the prepared simple were observed using SEM (JS M-5600 JEOL, Japan). EDX analysis (attached to SEM) was performed to determine the elemental analysis of the desired region of the prepared CdSe particles and CdSe-graphene composites attached to SEM. A more detailed study of the composite particles was determined by TEM (JE OL, JEM- 2010, Japan).

2.5. Catalytic activity

To investigate the synergistic effect of graphene on CdSe, RBB was used as sample dye solutions. First, 0.5 g samples of the CdSe-graphene catalyst composites were added to 50 ml of the organic dye (RBB) solution at 298 K temperature. The reactor was kept in a dark box over a magnetic churn dasher and magnetically stirred at a speed of 110 rpm to achieve continuous contact of the composite materials with the dye solution. After the dyes were exposed to visible light, the samples were withdrawn from the solution mixtures at regular intervals of 0 min, 30 min, 60 min, 90 min, 120 min, 150 min, and 180 min. The dispersed powders were removed using a centrifuge and analyzed by UV/Vis spectroscopy. The dye concentration in the solution was measured as a function of the irradiation time.

2.6. Recyclability test

The CdSe-graphene composites were cleaned by immersing them in ethanol for 6h and rinsed with deionized water, followed by drying at 353K in a hot air oven. The cleaned CdSe-graphene composites were reused to remove dyes by repetition of the experiments in dark conditions. This procedure was repeated several times.

3. Results and Discussion

The X-ray diffraction (XRD) patterns of the CdSe graphene composites are shown in Fig. 2. For the CdSe compound, XRD diffraction peaks were found at around 2θ of 25.300, 42.013, and 49.63; it was possible to index these peaks to the characteristic peaks of the (1 1 1), (2 2 0), and (3 1 1) plane reflections of the cubic crystal structure CdSe according to the standard power diffraction data (JCPDS No. 19-0191 for CdSe, cubic).²⁵ For the graphene-CdSe composite, only the peaks from CdSe were detected. The (002) of graphene and the (100) reflection of CdSe occurred at $2\theta \sim 25.30$, 24.88. Therefore, it was very difficult to distinguish both peaks. No peak for graphene oxide or for the impurities was detected, indicating that the hydrothermal method used in this study led to the formation of a graphene-CdSe composite and that the graphene oxide was reduced completely during the synthesis processes. For further assessment of the content of the composites and the elemental weight% of the prepared CdSe compounds (CG1, CG2, and

CG3), composites particles were examined by EDX; the weight% of the main elements in the composites are shown in Table 1. The main elements in the composites (Cd, Se, O, and C) were detected. From the data it was observed that the amount of C decreases with the increase in Cd and Se in the CdSe-graphene composites. The surface characteristics of the CdSe-graphene composites were determined using SEM micrographs. The SEM micrographs of CdSe-graphene are shown in Fig. 3. The spherical shaped agglomerated CdSe particles were attached to the surface of the graphene nanosheets. The distribution of the CdSe particles with the graphene nanosheets was observed. It was found that the CdSe particles were unevenly distributed. Further enhancement showed a detailed structure of the nanoscale CdSe-graphene composites, as can be seen in the TEM image (Fig. 4). CdSe dark imaged compounds were almost spherical materials, whereas the graphene components were found to be relatively lighter than CdSe, with irregular edges and a flat, sheet-like structure that had an occasional distribution of CdSe on the surface. The CdSe particles decorated on the surface of the graphene nanosheets were approximately 50 nm in diameter. The Raman spectra of the CdSe/graphene nanocomposites showed a D value of $\sim 1351 \text{ cm}^{-1}$ and a sharp G band at 1588 cm^{-1} (Fig. 5); it can be seen then that the micro Raman spectra of our nanocomposites indicate a G band and a D band corresponding to the vibration of carbon atoms in disorder or defect sites and in the plane vibration of the sp^2 bonded carbon atoms, respectively.²⁶⁾ The GO

Table 1. EDX Elemental Microanalysis (W%) of CdSe-Graphene Composites

| Sample | C | O | Se | Cd |
|--------|-------|-------|-------|-------|
| CG1 | 54.02 | 12.35 | 13.78 | 19.84 |
| CG2 | 51.18 | 10.17 | 12.75 | 22.9 |
| CG3 | 32.35 | 8.85 | 23.83 | 34.96 |

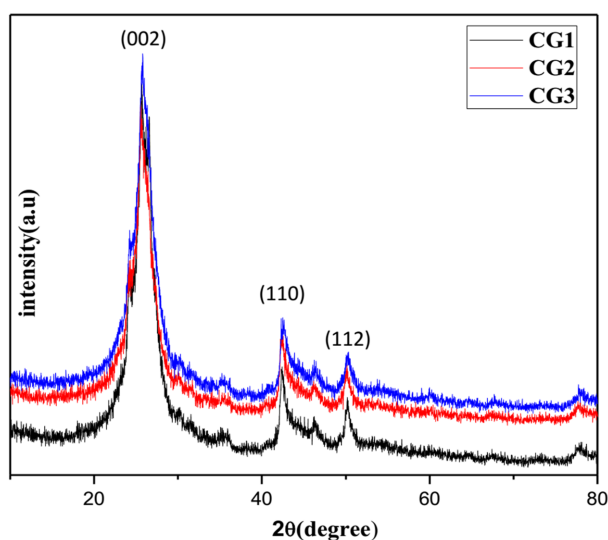


Fig. 2. X-ray diffraction (XRD) patterns of CdSe graphene Composites.

Raman spectrum was different among the composites, as shown in Fig. 4. The intensity of the D peak was high compared to CdSe/graphene composite, further confirming the functional density on the GO surface. The CdSe/graphene composite spectrum showed a relatively lower intensity D band to G band as compared to GO. It is known from the literature that the D band is from imperfections created by the functional groups on the basal planes of carbon.²⁷⁾ Our results suggest that the attachment of CdSe nanoparticles onto the surface of graphene might have reduced the functional densities. No characteristic peak of CdSe was observed. This might be due to the higher intensity of GO, which could have suppressed the lower intensity peaks in the semiconductor CdSe.

For a qualitative analysis of the composite containing CdSe-graphene nanocomposites, XPS was used. The survey spectrum had peaks corresponding to Cd, O, C, and Se (Fig. 6), which was consistent with the formation of the CdSe-graphene composite. Two main peaks of the Cd 3d core level corresponding to 3d_{3/2} at 404 eV and 3d_{5/2} at 412 eV were observed. The peak corresponding to 0 1s was at 532.75 eV. The C 1s peak was located at 284.01 eV (Fig. 6). The

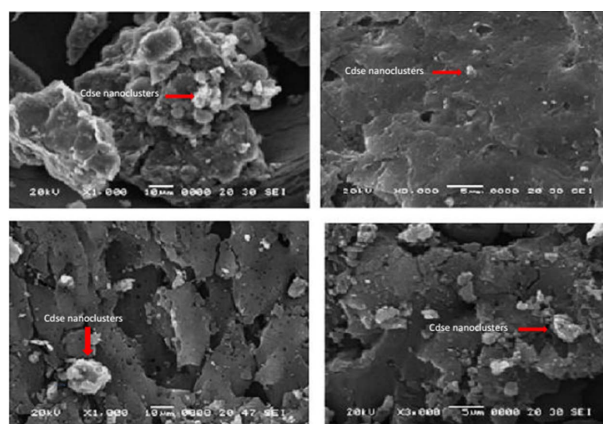


Fig. 3. SEM image of CdSe-graphene composites.

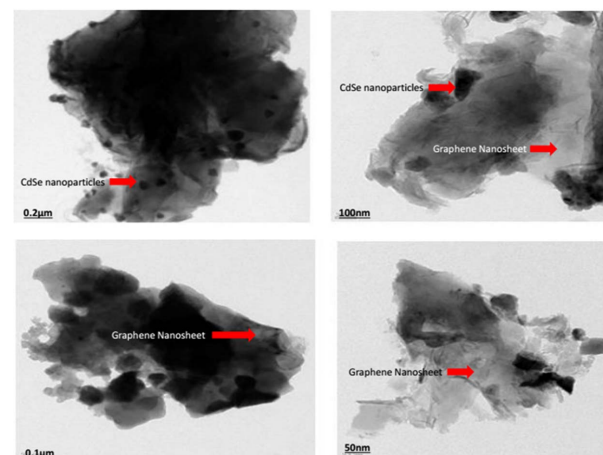


Fig. 4. TEM image of CdSe-graphene composites.

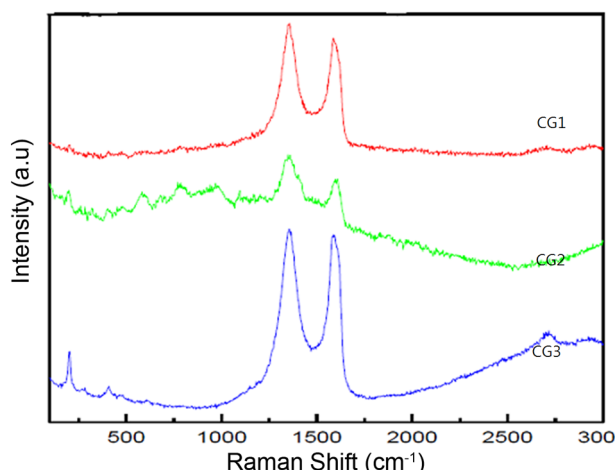


Fig. 5. Raman spectra of CdSe/graphene nanocomposites.

observed C 1s region spectra exhibited weak peaks at 287.1 eV and 289.01 eV, corresponding to C-O and C=O groups. These results demonstrate that our composite consisted of a reduced graphene oxide sheet. The selenium 3d core level peak was confirmed at 54.60 eV (Fig. 6(e)).

3.1. Photocatalytic studies

The photocatalytic performance of the CdSe/graphene nanocomposites in term of photo degradation of the RBB molecules under visible light irradiation was investigated. Fig. 7 (a) - (d) shows the UV-visible absorption spectra of the RBB solution after visible light irradiation of different exposure time in the presence of CdSe/graphene. When the irradiation time was increased, the intensity of the characteristic absorption band of RBB (595 nm) was significantly

decreased. The results of RBB decolorization under visible light irradiation in the presence of the CG1, CG2, and CG3 composites are shown in Fig. 7. In order to further demonstrate the photo-stability, cyclic experiments were carried out to degrade RBB as organic dyes. As shown in Fig. 7(a) - (d), the photo-catalysts did not exhibit any significant loss of photo-catalytic activity after the 4th run of RBB degradation, indicating that the CdSe/graphene photo-catalyst has high stability and is not photo-corroded during the photo-catalytic oxidation of the RBB molecules. Thus, the CdSe/graphene composite photo-catalyst is promising for practical applications in the area of environmental purification. The reused catalyst did not show any noticeable change in the degradation efficiency, which indicates the excellent chemical stability of our photocatalyst materials.²⁸⁻³¹ These results confirm that we improved the catalytic behavior of our nanocomposites as compared to the behavior demonstrated in our previous report.³² The catalytic behavior of the sample was studied carefully by performing stability tests. After the 7th cycle of the stability test we did not find any measurable differences between the first and last cycles. The reason for the successful obtaining of a stable CdSe/graphene nanocomposite may be the one pot synthesis technique, which allowed the CdSe nanoparticles to attach to the graphene sheet. This means that the improved interfacial contact may have arisen due to the reduction of GO at a higher temperature than was used in previous reports. The reduction reduces the density of the functionalities on the surface of the graphene sheet, allowing nanoparticle attachment. Furthermore, the band gap energy of the prepared CdSe compound composite particles is roughly estimated to be 1.59 eV, which is slightly smaller than that of pure CdSe compound (1.75 eV), which can be attributed to the

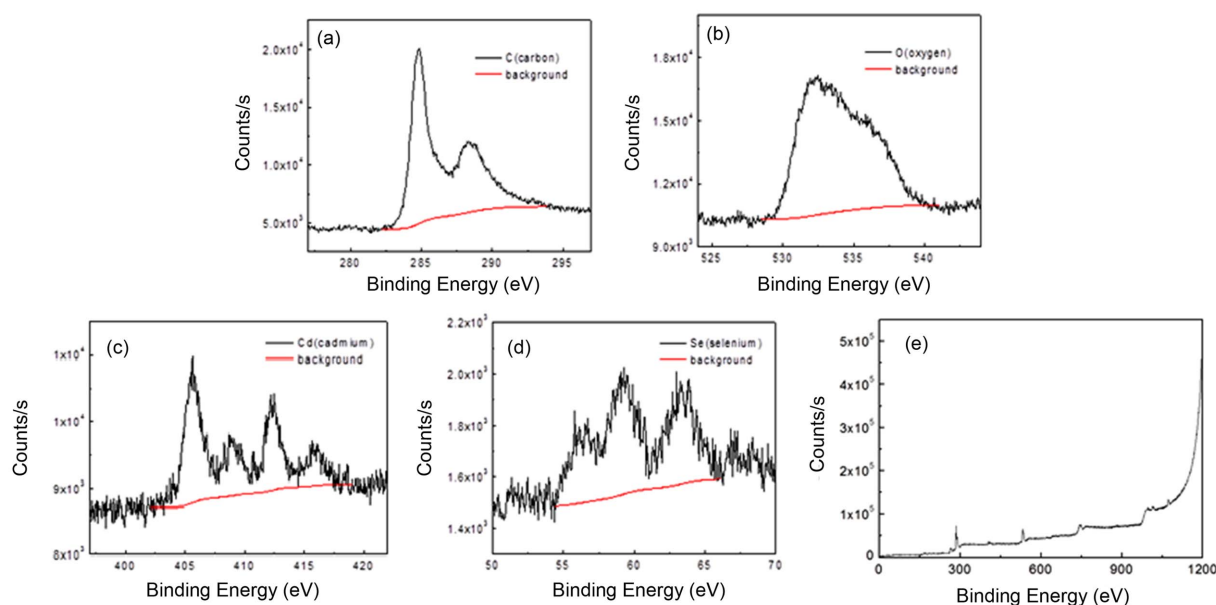


Fig. 6. XPS analysis of the CdSe/graphene nanocomposites ; (a) C peaks, (b) O peak, (c) Cd peaks, (d) Se peaks and (e) Se 3d core level.

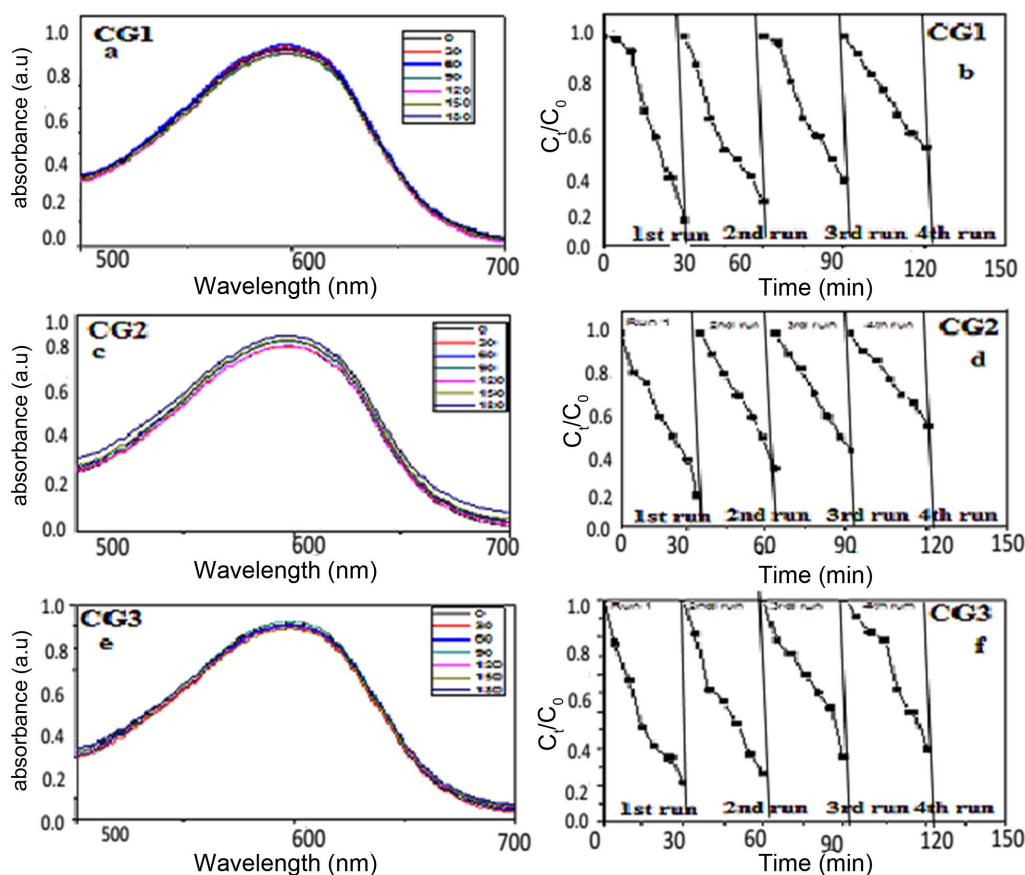


Fig. 7. Photocatalytic performance of the CdSe/graphene nanocomposites: (a), (c), and (e): the 1st set of data, (b), (d), and (f): recycling test.

induction of GO, which gave to rise to synergistic interaction between the semiconductor and the GO support.^{33,34}

4. Conclusions

In summary, CdSe/graphene was synthesized through a facile hydrothermal technique. TEM images clearly indicate that CdSe was distributed onto the surface of the graphene sheets. The promotion of the excited charge carriers at the interface of CdSe and graphene was found to be the highest due to the synergistic effect of graphene and attached nanoparticles. The graphene in the system was able to act as a solid state electron mediator to support the binary system, which can provide stable photocatalyst materials. Detailed cyclic studies revealed a stable photocatalytic effect. The stability suggests strong interfacial contact between the graphene and the CdSe nanoparticles. The present study has cemented a new way of using graphene based materials to develop highly efficient binary systems for photocatalytic degradation of organic dyes.

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