

Facile Synthesis of Graphene Oxide-ZrO₂ Nanocomposite and their Photocatalytic Degradation of Cadmium(II) Under Solar Light Irradiation

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ABSTRACT

Hexagonal-shaped ZrO₂ nanoparticles doped with graphene oxide (GO) sheets using hydrothermal method. The photocatalytic activity of GO-ZrO₂ and the individual materials were studied through the photodegradation of Cd(II) ions from water under solar irradiation. A significant increase in the photodegradation activity using the nanocomposite was obtained after 70 min (~98% of cadmium degradation). The highest activity resulted from the synergy of this graphitic structure with ZrO₂, which could absorb a wider portion of the solar spectrum, adsorb higher quantities of Cd(II) ions on the surface, and improve the effective separation of the generated electron-hole pairs.

Key words: Graphene oxide ZrO₂ nanocomposite, Photo catalyst, Solar light irradiation, Cd(II) ions degradation.

1. INTRODUCTION

Heavy metal ions of more concern are arsenic, cadmium, chromium, lead, and mercury as they pose a serious threat to living organisms [1]. These heavy metals may enter the human body through food, air, and water and small concentration of these elements may cause acute or chronic toxic effects [2]. In addition, heavy metals affect growth, yield, and quality of the crops [3]. Cadmium usually is a trace ion in the ground water and surface water. It may be hydrated ions, complexes – such as inorganic carbonate, hydroxide, chloride, sulfate, or as organic complexes with humic acids in water [4]. Cadmium is a metal of most toxicological concern because of its bioaccumulation and non-biodegradability even at low concentrations. Materials in the nano-sized range are considered the best candidates in the removal of organic and inorganic pollutants from the environment because of their unique physicochemical properties and the availability of different forms of nanomaterials [5]. Conventional methods for heavy metal removal from wastewater include reduction, precipitation, ion exchange, filtration, electrochemical treatment, membrane technology, and evaporation, all of which may be ineffective or extremely expensive when metals are dissolved in large volumes of solution at relatively low concentrations [6,7]. The most current, efficient, and economical method to remove heavy metals by photocatalytic degradation using day-light driven in the presence of an appropriate photocatalyst that is able to promote the reduction of toxic metals to favorable byproducts.

Graphene has high-chemical stability and versatile platform for photocatalysis due to specific surface area (2630 m²/g), excellent electrical conductivity, and outstanding optical transmittance [8]. At present, major problems affecting the mankind are energy crisis and environmental problems. The potential solution of these problems is utilization of solar energy for photocatalytic degradation using suitable semiconducting photocatalysts. In the process of photo catalysis, graphene to enhancing the separation and exchange of photo-generated charge carriers from semiconductors [9].

Modification of graphene with metal oxides nanoparticles (NPs) can produce various nanocomposites and enhancing adsorption capacity [10]. Among various photocatalytic materials, ZrO₂ NPs have the suitable material for photocatalytic activities because of its semiconducting properties [8,11], low thermal conductivity, water insolubility, catalysis [12-14], and optical properties [15,16]. It is inorganic oxide, whose band gap estimates from 5 to 7 eV [17,18] depending on the phase (cubic, tetragonal, monoclinic, or amorphous) and preparation methods. Researchers have also demonstrated that ZrO₂ has a strong affinity to negatively charge moieties [19], which motivated us to use graphene oxide (GO)-ZrO₂ nanocomposite as selective photocatalyst for heavy metals. Moreover, various papers have been published recently on the graphene-ZrO₂ nanocomposites applications, which include the deoxyribonucleic acid sensing detection [20], organophosphorus agents [21], supercapacitor energy-storage application [22], and photocatalytic degradation of antimonia (Sb(III)) and antimonate (Sb(V)) from aqueous solution [23].

In this paper, a GO-ZrO₂ nanocomposite was synthesized by hydrothermal method using GO and zirconium nitrate (ZrNO₃) as raw materials. The hybrid composite utilization for photodegradation of cadmium ions from water under solar light irradiation. Moreover, also compared with those of GO, ZrO₂, and physically mechanical mixture and also studied by restability of the composite.

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2. EXPERIMENTAL

2.1. Materials

Natural graphite flakes were commercially obtained from Sigma-Aldrich. In addition, zirconium nitrate (ZrNO_3) $_2$ $2\text{H}_2\text{O}$, sulphuric acid (H_2SO_4), potassium manganese oxide (KMnO_4), sodium nitrate (NaNO_3), sodium hydroxide (NaOH), hydrogen peroxide (H_2O_2), hydrochloric acid (HCl), and all these chemicals procured from the Merck and used without further refinement and ethanol was supplied by China Medicine Co., Ltd. The double-distilled water was used for the total process.

2.2. Synthesis of Graphite Oxide

Graphite oxide was synthesized from graphite, using a modified Hummer's method [24]. In a typical procedure, about 5 g of graphite powder was added to 115 mL of concentrated (98%) H_2SO_4 in an ice bath with stirring for 30 min. A 15 g of KMnO_4 was added slowly to the above mixture with stirring and cooling for 30 min. Subsequently, 2.5 g of NaNO_3 was added with continuous stirring for 1 h. So that, the temperature of the mixture maintained below 15°C during that time. The temperature of mixture then raised to 40°C with water bath, and the mixture was continuously stirred for 30 min. After that, the mixture was diluted by 800~1000 mL of distilled water, the temperature of which then raised to 98°C . The mixture was then added by H_2O_2 (30%) until gas evolution ceased followed by filtering. The color of the dispersion turned from black-to-yellow. The product was washed repeatedly with 1 M HCl (5%) and distilled water until the pH value of the product arrived at near 7. Then, the product was dried in an air oven at 60°C to obtain graphite oxide.

2.3. Synthesis of GO-ZrO₂ Nanocomposite

To synthesis GO-ZrO₂ composite, synthesized graphite oxide (20 mg) dissolved in 20 ml distilled water and sonication for 1h to get suspension GO. Moreover then, mixed ZrNO_3 was dissolved in distilled water and zirconium hydroxide was precipitated by drop-wise addition of sodium hydroxide (maintaining constant pH about 11) with stirring. The mixture was transferred autoclave for hydrothermal treatment at 170°C for 24 h. The final resulting mixture was washed with distilled water then dried at 80°C for overnight in hot air oven. The synthesis procedure was shown in Figure 1.

2.4. Characterization of Photocatalysts

The structure and morphology of the samples were characterized by X-ray diffractometry (XRD) Bruker D8 using $\text{CuK}\alpha_1$ (1.5406 Å) and $\text{K}\alpha_2$ (1.54439 Å) radiations, scanning electron microscope (SEM) imaging with energy dispersive spectroscopy (EDS) using a Carl Zeiss model Ultra 55 microscope operating at 5 and 20 kV, and transmission electron microscope (TEM) measurements were performed on a Tecnai G²FEI F12 I at 200 kV. Raman spectra were recorded using a WiTec alpha 200 SNOM system. Nitrogen adsorption and desorption experiments were carried out on Micromeritics ASAP 2020 analyzer. The samples were out gassed at 150°C for 12 h in a dynamic vacuum before physisorption measurements. The specific surface area was calculated using Brunauer–Emmett–Teller (BET) method. A photoluminescence spectrum (PL) was recorded using JOBIN YVON Fluorolog-3 spectrofluorometer with a YSOW Xenon lamp as used broad band source. Shimadzu-1800 ultraviolet-visible (UV-vis) spectrometer to determine the concentration of heavy metal ions. pH of the solution was calculated by Elico pH meter.

2.5. Photocatalytic Activity Studies

The photodegradation tests of heavy metal Cd(II) ions were performed using the GO, ZrO₂, GO-ZrO₂, and mechanical mixture of

GO and ZrO₂ solids according to the following procedure: The initial concentration of Cd(II) (C_0) was 5.0×10^{-5} mol/L. The photocatalyst powder (0.03 g) was dispersed in a 100 mL sealed glass beaker containing 30 mL of Cd(II) solution. The mixture was sonicated for 5 min and stirred for 30 min in the dark to reach adsorption-desorption equilibrium. At the given time intervals a sample of 3 mL was taken from the mixture and immediately centrifuged to remove the dispersed photocatalysts. The concentration of the clean transparent solution was analyzed by checking the absorbance at 370 nm for Cd(II) with the UV-vis spectrophotometer, which denoted as C_t . The reproducibility was checked by repeating the measurements at least three times and was found to be within the acceptable limit ($\pm 5\%$).

3. RESULTS AND DISCUSSION

3.1. Characterization of Photocatalysts

3.1.1. X-ray diffraction studies

The synthesized graphite oxide and GO-ZrO₂ were first characterized with XRD. As displayed in (Figure 2a and b), the pattern of graphite oxide has a typical characteristic peak centered at $2\theta = 9.92^\circ$. The most intense peak for graphite at $2\theta = 26.37^\circ$ is absent in the GO sample, confirming the high quality of graphite oxide. In the pattern of graphite oxide, the reappearance of the diffraction line at 24.37° and disappearance of the diffraction peak at 9.92° give evidence that the graphite oxide was restored the ordered crystal structure. From Figure 2c gives the XRD patterns of as-synthesized GO-ZrO₂. The dominant peaks located at ca. 24.06° , 24.45° , 28.18° , 31.47° , and 51.20° are indexed to (011), (110), (111), (111), and (221) crystallographic planes of monoclinic ZrO₂ consistent with GO-ZrO₂ composite. Through search and contrast through the JADE 5.0 database, it was found that the XRD pattern matched the standard XRD pattern (JCPDS No. 83-0937), the corresponding diffraction is indexed in Figure 2c, and no characteristic peaks of impurities are observed, suggesting pure ZrO₂ was prepared [25]. Notably, no typical diffraction peaks of the GO are observed in the GO-ZrO₂. The reason can be attributed to the fact that the low amount and the relatively low diffraction intensity of GO.

3.1.2. Raman spectroscopy measurements

Raman spectroscopy is a powerful and widely used technique for characterizing the sp^2 and sp^3 hybridized carbon atoms contained in GO to identify disorder and defect structures. In general, in GO based samples, the disorder-induced D bands arise from the tangential stretch and sp^3 -hybridized carbon and the G band represents the crystalline graphite with E_{2g} zone center mode; moreover, the I_D/I_G ratio depends strongly on the amount of disorder in the graphitic material. The I_D/I_G ratio should increase when more defects are introduced into GO. According to Figure 3, the I_D/I_G ratio of GO-ZrO₂ composite is 0.992 which is higher than 0.970 calculated from GO. That is to say, ZrO₂ modification can be effective in bringing an amount of defects into the structure of GO [26].

3.1.3. FE-SEM micrographs

The SEM of nanocomposite was taken as powder synthesized, images were taken on carbon tape. From the Figure 4a shows the SEM images it is unambiguous that the morphology of intercalated nanocomposite particles are really in nanosize and it shows the clumsy morphology due to the aggregation of particles in the solution while synthesis. From Figure 4b shows the EDS results of the GO-ZrO₂ nanocomposite. Zr, O and C elements are observed.

3.1.4. TEM micrographs study

From Figure 5 illustrates the typical TEM images of GO-ZrO₂ nanocomposite. It can be clearly seen that the exfoliated GO sheet

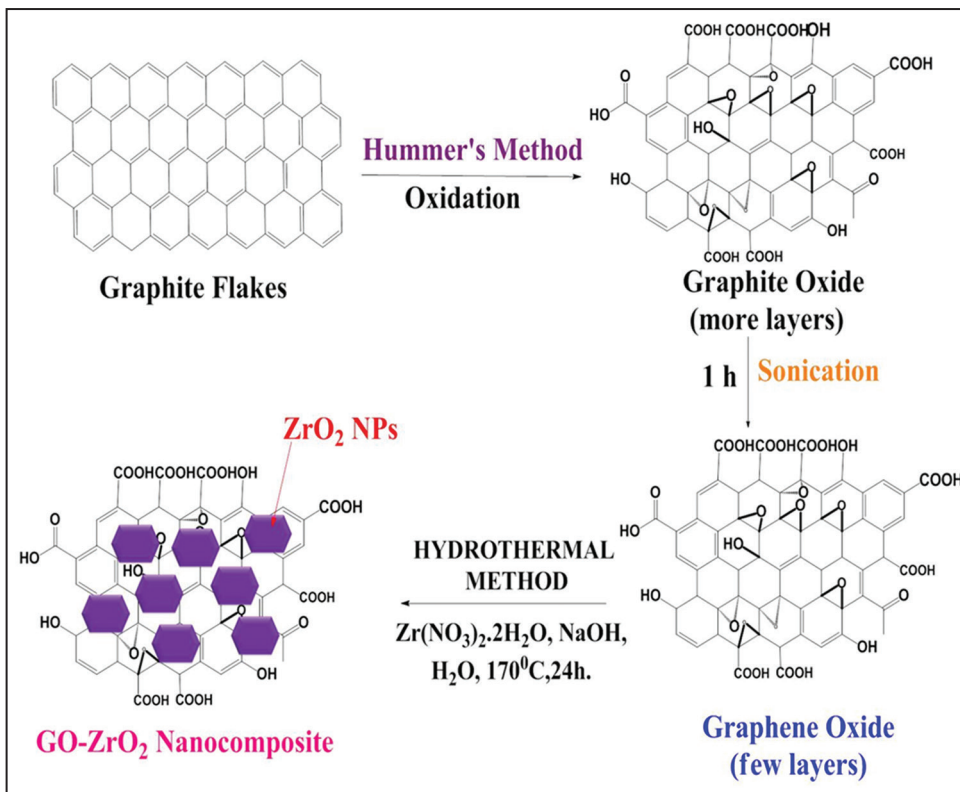


Figure 1: Illustration of chemical route synthesis of graphene oxide-ZrO₂ nanocomposite.

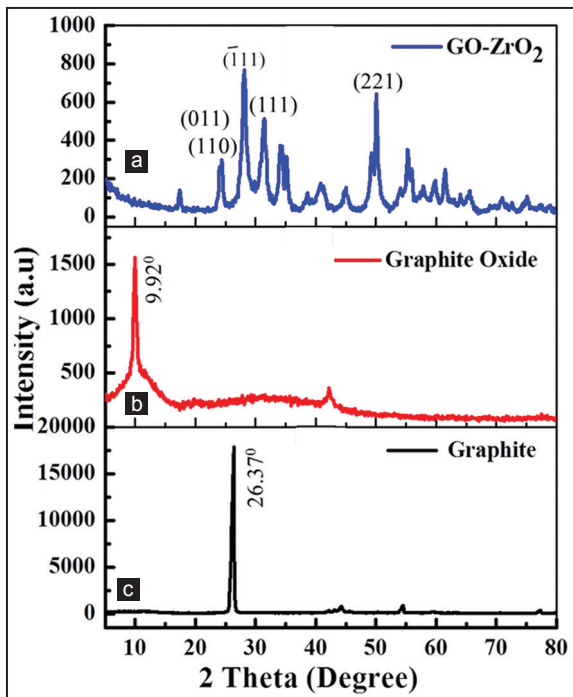


Figure 2: X-ray diffractometry pattern of the (a) graphene oxide (GO)-ZrO₂, (b) graphite oxide and (c) graphite.

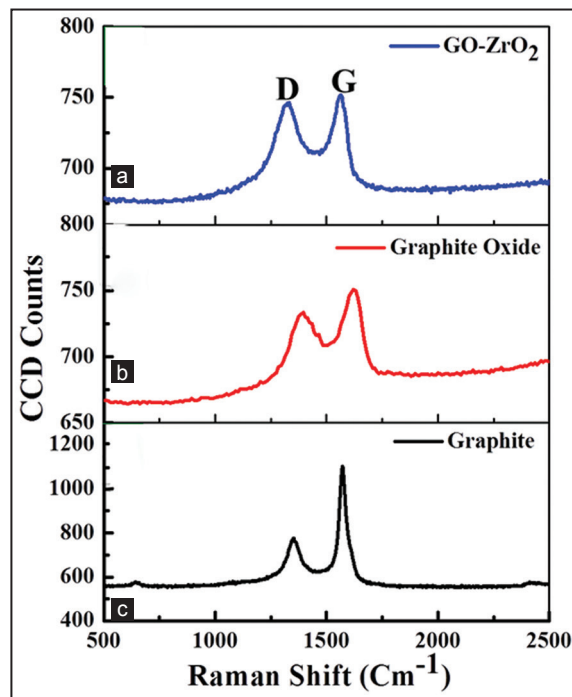


Figure 3: Raman spectra of (a) graphite, (b) graphite oxide (GO), (c) GO-ZrO₂.

was decorated by hexagonal shape of ZrO₂, with size range between 10 and 75 nm. From Figure 5d displays selective area electron diffraction pattern of hybrid material shows the fusion of super lattices which are characteristic nature of the layer structure of any kind of materials.

3.1.5. High-resolution (HR)-TEM micrographs measurements
HR-TEM images of the GO-ZrO₂ fusion material show springs in 5 nm range we observed this kind of springs only in the case of material is crystalline nature. From the powder XRD we observed the crystalline nature of the hybrid material as well as GO this is confirmed

by HR-TEM. In HR-TEM we observed springs on ZrO_2 shows hexagonal form (Figure 6).

We have carried out the BET analysis to understand the specific surface area of the as prepared GO and GO- ZrO_2 composites and the corresponding nitrogen adsorption-desorption isotherm curves are shown in Figure 7a. Surface area of GO- ZrO_2 ($207.1 \text{ m}^2 \text{ g}^{-1}$) was higher than that of GO ($186 \text{ m}^2 \text{ g}^{-1}$) due to the high density of ZrO_2 hexagonal-shaped nanocrystals. The high surface area of GO- ZrO_2 suggests enhanced photocatalytic activity of inorganic pollutants degradation. From Figure 7b shows the emission spectra of ZrO_2 and GO- ZrO_2 samples, respectively. The samples show a strong broad-band emission ranging from 350 to 600 nm centered at 388 nm. The emission peak and strength depends upon the species and densities of PL. High-crystal quality and quantum confinement in the nanostructures are two factors favoring the increase of the intensity of light emission at room temperature. Furthermore, the observed PL

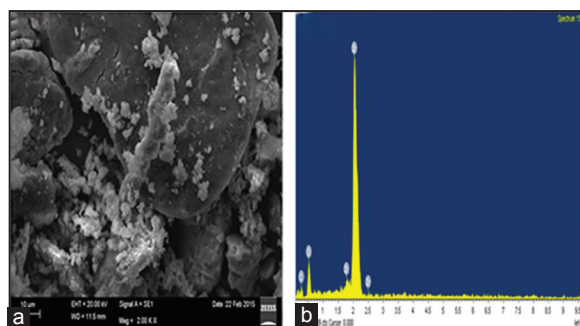


Figure 4: (a) Scanning electron microscope image and (b) energy dispersive spectroscopy spectrum of graphene oxide- ZrO_2 nanocomposite.

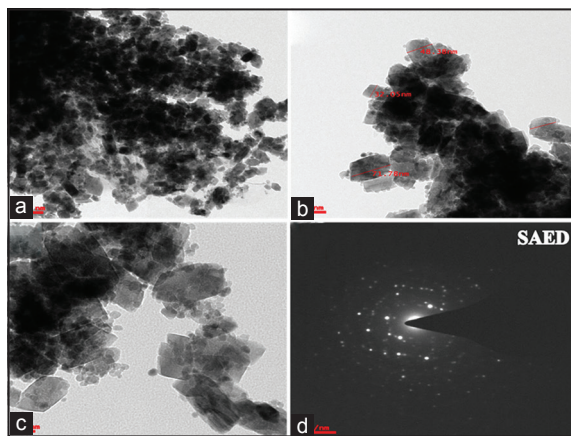


Figure 5: (a-c) Transmission electron microscope images and (d) selective area electron diffraction pattern of graphene oxide- ZrO_2 hybrid material.

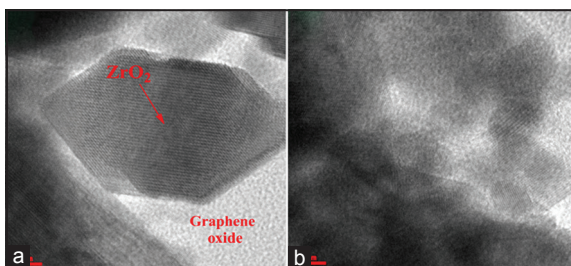


Figure 6: (a and b) High resolution transmission electron microscope images of graphene oxide- ZrO_2 .

emission peak of ZrO_2 at 388 nm is in good agreement with that of ZrO_2 NPs at 387 nm [27].

3.1.6. Photocatalytic activity of GO- ZrO_2

From Figure 8a and b shows the change in the UV-vis absorbance spectra of Cd(II) solution with different irradiation intervals over the GO- ZrO_2 samples. As mentioned in the experimental section, the catalyst was equilibrated with the Cd(II) ions to check for adsorption of the heavy metal on the solid photocatalyst. The UV-vis absorption spectra of Cd(II) have a characteristic peak at 370 nm. The UV-vis results indicate that Cd(II) was degraded during the reaction. The decrease in the absorbance of the solution was due to the destruction of the homo- and hetero-polyaromatic rings present in the Cd(II) ions.

The photocatalytic activity of the GO- ZrO_2 samples was determined by monitoring the degradation of the Cd(II) ions. A blank experiment was carried out to confirm that the photodegradation reaction did not proceed without the presence of catalyst or the solar light radiation. The photocatalytic degradation of Cd(II) in aqueous solution under the solar light irradiation was carried out at regular time intervals was shown in Figure 8c. The absorption of these solutions decreased gradually with irradiation time. The characteristic absorption of Cd(II) almost disappeared after about 70 min, and the color of Cd(II) solution changed gradually from yellow blue to colorless after irradiation for 70 min. At concentration $5 \times 10^{-5} \text{ M}$ of heavy metal Cd(II) ions degradation is 98%, which shows the GO- ZrO_2 is a worthy catalyst. The ZrO_2 shows the degradation of heavy metal Cd(II) removal is 45%, graphite oxide removal is 22%, and mechanical mixing of GO+ ZrO_2 is 62%. The GO- ZrO_2 composite material possesses much higher photocatalytic activity than pure ZrO_2 , GO and mechanical mixture of GO+ ZrO_2 . The catalyst was found to be active for three cycles without any major deactivation, and more than 95% degradation was achieved in all experiments within 70 min using the GO- ZrO_2 catalyst. The reusability of the GO- ZrO_2 nanocomposite was ascribed to the low photocorrosive effect and high catalytic stability of the synthesized GO- ZrO_2 sample. The reaction take places at the time of photocatalysis on the surface of GO- ZrO_2 are described in the following equations:

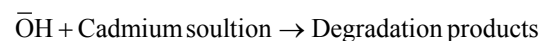
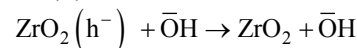
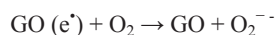
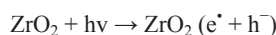


Figure 9 has explained the mechanism of high photocatalytic activity for GO- ZrO_2 . Under solar light, the photoelectron and hole are emitted. Then, the photoelectron is transferred to GO to resist the recombination photoelectron and hole because it is energetically favorable. The transferred photoelectrons react with the absorbed O_2 on the surface of GO to form $\cdot OH$, which is used to degrade heavy metal Cd(II) ion. In addition, the remaining hole in ZrO_2 takes part in the redox reaction to generate OH, which is further used to remove cadmium ions. Owing to the high specific surface area and superior electron mobility of GO, an appropriate integration of GO and ZrO_2 would give rise to a hybrid nanocomposite to achieve high photodegradation activity [22]. In this case, the recombination of photo-generated electrons and holes is suppressed, and their lifetime is prolonged. GO hybridized ZrO_2 exhibited enhanced photocatalytic efficiency for the degradation of inorganic pollutants.

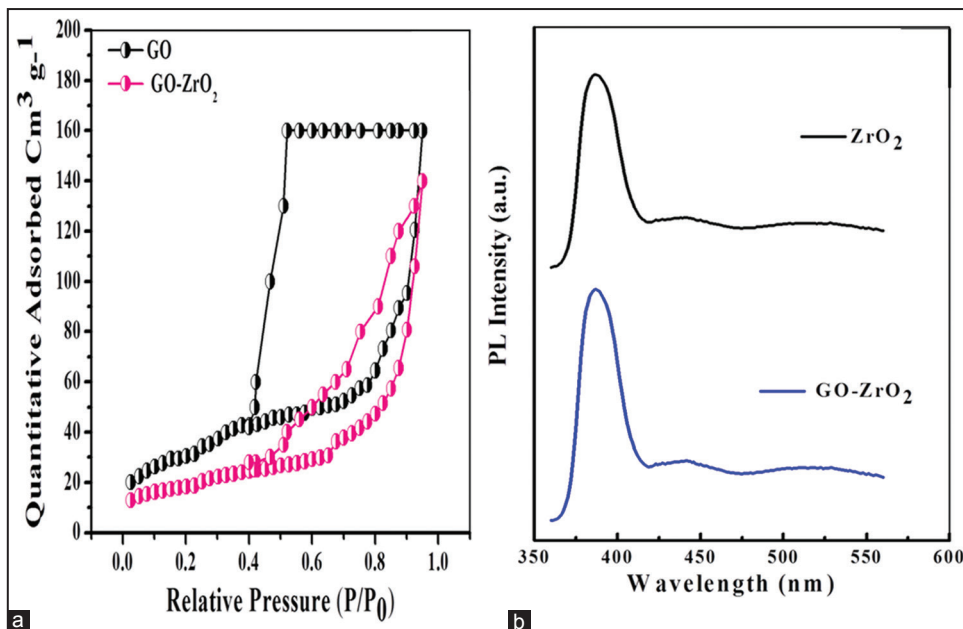


Figure 7: (a) Nitrogen adsorption-desorption isotherms and (b) photoluminescence spectra of ZrO₂ and graphene oxide-ZrO₂ composite.

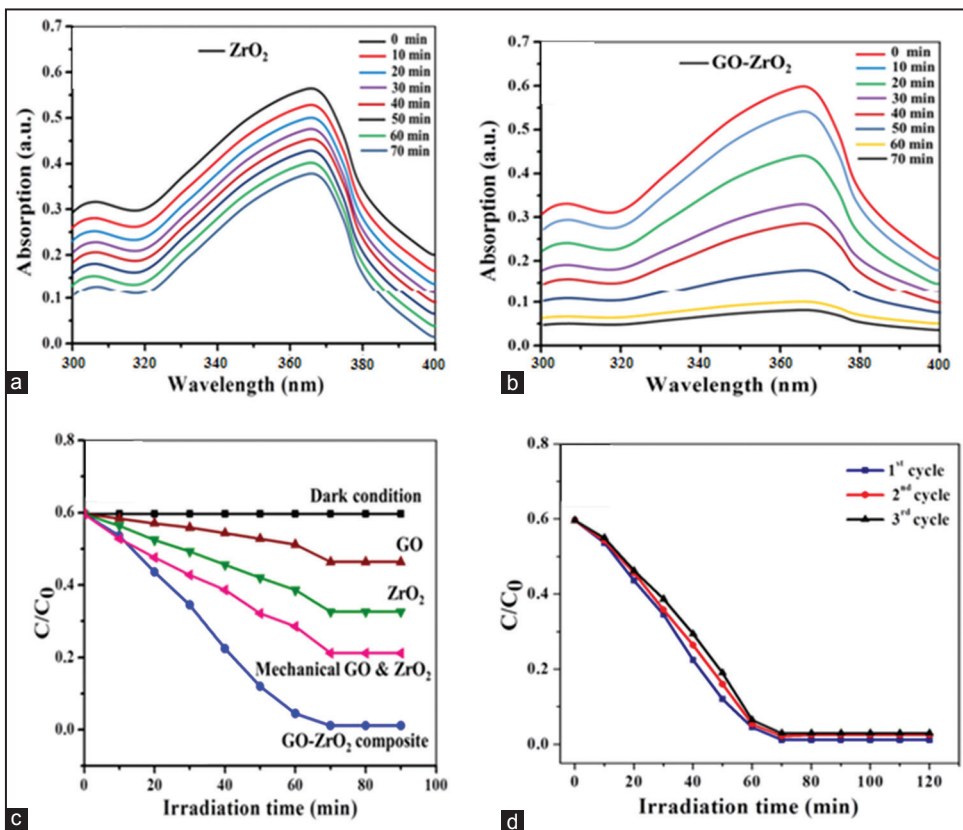


Figure 8: The progress of ultraviolet-visible spectra for Cd(II) solution with (a) ZrO₂, (b) graphene oxide (GO)-ZrO₂, (c) comparison study of photocatalytic activity, (d) three cycles of GO-ZrO₂ in photodegradation of Cd(II).

4. CONCLUSION

In summary, we propose a simple and effective method for the facile preparation of crystalline GO-ZrO₂ nanocomposite by a simple hydrothermal process. The GO-ZrO₂ nanocomposite displays good performance in the inorganic pollutant degradation which is a

result of its large specific surface area, hexagonal structures, and the crystallization degree of zirconia in the nanomaterials. Furthermore, from the regenerative tests of our synthesized GO-ZrO₂ nanostructures, it was proven that they demonstrate good reusability and stability properties. Therefore prepared composite is useful in environmental and energy-related applications.

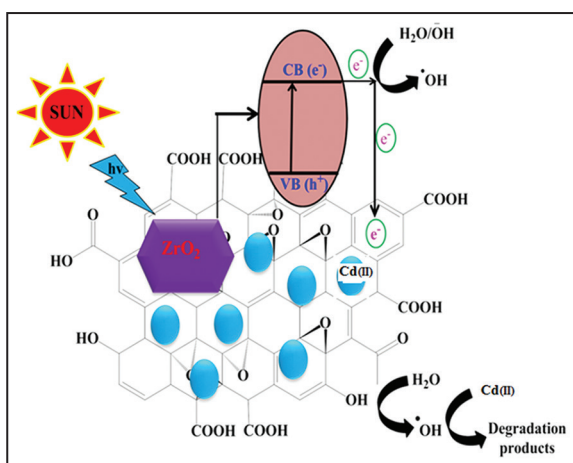


Figure 9: The mechanical illustration of high photocatalytic activity for graphene oxide-ZrO₂.

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