Enhanced Photocatalytic Degradation of Phenol Using Urchin-Like ZnO Microrod-Reduced Graphene Oxide Composite under Visible-Light Irradiation

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In this study, visible-light-driven ZnO microrod-rGO heterojunction composites were successfully synthesized via a facile and scalable hydrothermal process. The prepared photocatalyst heterojunction was examined using different techniques including XRD, SEM, FTIR, UV-Vis spectroscopy, and TGA to reveal their crystal phase, morphology, and other optical properties. The photocatalytic performance of the obtained ZnO-rGO composites was measured by the photodegradation of phenol under visible light illumination. The addition of graphene over the catalyst exhibited an enhanced photocatalytic activity for phenol degradation due to its high surface area and decreasing rate of electron-hole separation. Kinetic studies proved that the degradation of phenol process happened by following the pseudo-first-order kinetic model. The effective conditions for degradation of phenol using ZnO-rGO composite were 0.2 g L⁻¹ catalyst dose, pH -4, and initial concentration 20 ppm of phenol solution. Comparing with ZnO microrods, the heterojunction composite degraded the organic pollutants of phenol solution up to 84.2% of efficiency displaying the highest photocatalytic activity, whereas urchin-like ZnO catalyst exhibited much less photocatalytic activity for phenol degradation under visible light irradiation. This result envisages immense properties, showing a great potential industrial application for the removal of phenolic wastewater.

1. Introduction

In today’s industrialization, environmental pollution has been booming day by day. Industries that use plenty of water include textile companies, refining petroleum, automotive manufacturing, and primary metals [1]. The discharge from these industries produces plenty of organic contamination which makes severe damages to the ecosystem especially to the aqueous system by decreasing the concentration of oxygen dissolved in the environment. Among the biorecalcitrant toxic compounds, phenol is the most harmful organic compound which is a ubiquitous water pollutant that plays a vital role in industries such as pharmaceuticals, coal conversion, paint, cresols, dyeing, and pulpmill [2]. The European Union regulation has declared the maximum permitted amount of phenolic compounds in freshwater as 0.5 mg L⁻¹ [3].

Therefore, there has been a growing interest to eliminate these contaminations from the industrial water and make it usable for the ecological systems like plant, animal, and human beings. Thus, researchers have done a lot of work to develop fascinating methods for the removal of water pollutants in this area including the approaches like ion flotation, sonocatalytic degradation, photocatalytic degradation, swirling jet-induced method, hydrodynamic cavitation, electrochemical oxidation, and advanced oxidation processes [4–11]. Among these, heterogeneous photodegradation is the most remarkable and effective method for converting toxic organic pollutants into carbonaceous products [12].

Nowadays, many researchers prefer heterogeneous photodegradation process owing to its good electron conduc-tivity, huge specific surface area, material consumption, high stability, high absorption, conduction empty band (CB), and
Among semiconducting nano/microstructure, ZnO is a promising candidate with suitable bandgap energy of approximately 3.4 eV and versatile material for photodegradation under the removal of various types of organic dyes in an aqueous or gaseous medium [22]. It has been confirmed that ZnO can exhibit high photocatalytic degradation than TiO$_2$ for some dyes owing to its economic viability and ecofriendly nature [23]. These are diverse experimental methods for the synthesis of ZnO-rGO heterojunction materials [24], including solvothermal, hydrothermal, microwave synthesis, electrochemical deposition, precipitation method, and solution combustion synthesis. In this paper, a hydrothermal approach was used for synthesizing urchin-like ZnO with the addition of graphene material with the idea to enhance the photocatalytic performance. Furthermore, the morphology plays a significant role for the better performance of photocatalytic activity. In the recent studies, hierarchically ordered ZnO microstructures are found to exhibit high photocatalytic performance due to their high stability against aggregation and large specific surface area [25, 26]. Literature reviews suggest that graphene sheet enhances various properties such as large values of Young modulus, extremely high surface area, high visible light optical transparency, superior mobility of charge carriers (200,000 cm$^2$ V$^{-1}$ s$^{-1}$), and thermal conductivity [27, 28]. Thus, reduced graphene oxide-(rGO-) based metal oxide photocatalytic materials have recently gained a lot of attention among the scientists to improve the charge transfer at the interface; it reduces the recombination of charge carriers on the surface of catalysts and offers high performance to absorb pollutants. These multifunctional heterojunctions have been demonstrated to be outstanding candidate fruits in fields like photocatalytic degradation of organic pollutants over visible light irradiation. Research has been conducted for several decades on ZnO-based nanocomposite due to its better photocatalytic performance and high surface area, but the complexity to recover from the reaction system and agglomeration are two major problems that restrict its practical application [29, 30]. Thus, microsized ZnO with a high surface area is an alternative pathway to overcome these problems.

For instance, Qin et al. reported ZnO microsphere-rGO nanocomposites for photodegradation of methylene blue pigment under UV irradiation [31]. Pant et al. synthesized ZnO microflowers arranged on reduced graphene oxide of MB dye over UV irradiation [32]. To the best of our knowledge, there are limited works which used urchin-like ZnO microrod-rGO composites as a heterojunction for degradation of phenol in visible light irradiation. Herein, we report the synthesis of urchin-like ZnO microrod-rGO composites by a facile and environmentally friendly hydrothermal method. The synthesized composite was examined and characterized for photocatalytic degradation of phenol under visible light illumination. Moreover, the effect of special parameters including optical, magnetic, photoconductivity, phenol concentration, catalyst dosage, and photocatalytic properties of urchin-like ZnO microrod-rGO composite was also investigated.

2. Materials and Methods

2.1. Materials. Graphite, zinc nitrate hexahydrate (Zn(NO$_3$)$_2$·6H$_2$O), polyethylene glycol (PEG 4000), ammonium hydroxide (NH$_4$H$_2$O$_2$), potassium persulfate (K$_2$S$_2$O$_8$), sulfuric acid (H$_2$SO$_4$), phosphorus pentoxide (P$_2$O$_5$), hydrochloric acid (HCl), potassium permanganate (KMnO$_4$), ethylene glycol (C$_2$H$_6$O$_2$), hydrogen peroxide (H$_2$O$_2$), and ascorbic acid (C$_6$H$_8$O$_6$) were purchased from Aldrich and used as received.

2.2. Preparation of Graphene Oxide (GO). Graphene oxide was synthesized from graphite powder by using the modified Hummers method [33]. Typically, 3 g of graphite, 2 g of P$_2$O$_5$, and 2 g of K$_2$S$_2$O$_8$ were added into 24 mL of concentrated H$_2$SO$_4$ under stirring at 95°C for 6 h. The mixture was cooled down to normal room temperature and 1 L of deionized (DI) water was added into the mixture and kept under ageing for 48 h. The mixture was then washed, filtered, and dried out to obtain the black powder. Subsequently, 15 g of KMnO$_4$ and 125 mL of concentrated H$_2$SO$_4$ were added into the mixture and kept in an ice bath below 10°C and magnetically stirred at 40°C for 3 h. The obtained grey sample was diluted with the dropwise addition of 10 mL of H$_2$O$_2$ followed by the slow addition of 0.5 L of DI water to quench the solution, and the colour of the solution became yellowish. The obtained product was centrifuged, cleaned with HCl to remove impurities, and washed with DI water. The final product was dried at 40°C in a vacuum oven to attain the GO sample.

2.3. Preparation of Reduced Graphene Oxide (rGO). Reduced graphene oxide (rGO) was synthesized from graphite oxide (GO) by using ascorbic acid as a reductant [34]. 0.1 mg/mL of GO solution and 0.1 M ascorbic acid were mixed and kept at 70°C on a heating shield and stirred for 35 min; the colour of the solution turned from yellow to black. The product was centrifuged and dried at 120°C in a vacuum.

2.4. Preparation of the Urchin-Like ZnO Microrod-rGO Composite Materials. In a typical experiment, 10.8 g Zn(NO$_3$)$_2$·6H$_2$O, 2.5 wt. % of rGO, 30 mL of C$_6$H$_4$O$_2$, and 0.6 g PEG 4000 were dissolved in distilled water (120 mL). Then, NH$_4$H$_2$O was added dropwise until the pH adjusted to 8. After being magnetically stirred for 35 min, the solution was transferred into a 250 mL Teflon-lined stainless steel autoclave. The autoclave was kept at 120°C for 24 h in an oven and then cooled down to the room temperature naturally. The product was washed with distilled water and absolute ethanol several times and dried at 60°C for 24 h.

Finally, the product of urchin-like ZnO microrod-rGO was obtained.
2.5. Evaluation of Photocatalytic Activity. The degradation reaction of urchin-like ZnO microrod-rGO of the prepared catalysts was conducted by measuring the photodegradation of the phenol in aqueous solution (10 mg/L) under visible light illumination at ambient temperature. The adsorption process was kept under a dark region as a batch process. Typically, 30 mg of photocatalyst was added to 50 mL of the aqueous solution and stirred for some time to evade residue of the catalyst. Prior to irradiation, the experimental set-up was placed in a complete dark portion and magnetically stirred for 60 min in the dark to achieve adsorption-desorption equilibrium. Subsequently, the photocatalytic reaction was in progress by the exposure of a 50 W tungsten lamp as a visible light source. The distance between source and photoreaction sample was 20 cm, and 5 mL of sample was taken out with the help of a syringe (~5 mL) at time interval of each 15 min. The mixture solutions were then centrifuged, and the supernatant of the dye was analysed by using a UV-Vis spectrophotometer (Shimadzu 2450 series, Japan). The degradation efficiency of the phenol can be defined as follows:

\[
D(\%) = \left(1 - \frac{C_t}{C_0}\right) \times 100\%,
\]

where \(C_0\) is the initial dye concentration (mg/L) at time \(t = 0\) and \(C_t\) is the residual concentration of phenol (mg/L) at different irradiation intervals \(t\), respectively. The photodegradation follows pseudo-first-order kinetics, which can be expressed as follows:

\[
-ln \left( \frac{C_t}{C_0} \right) = k_{app} t,
\]

where \(k\) (min\(^{-1}\)) is the rate constant of photodegradation [35].

2.6. Characterization. The X-ray diffractogram patterns of the prepared samples were recorded using an X-ray diffraction system (XRD 3003 TT) from 10 to 70° with Cu Ka (1.5406 Å) radiation. High-resolution scanning electron microscopy (HRSEM) was employed for morphological study by using GMS 5900, JEOL, Japan. Fourier transform infrared (FT-IR) spectrum studies were recorded using a PerkinElmer Spectrum 2 spectrometer in the wavenumber ranging from 4000 to 400 cm\(^{-1}\). Thermogravimetric (TGA) analysis was carried with the instrument (NETZSCH STA 449F3, Germany), to investigate the stability of samples at higher temperatures. A UV-Vis spectrometer (PerkinElmer Lambda 25) was used to collect the UV-visible absorption spectra of the dye samples.

3. Results and Discussion

3.1. X-Ray Diffraction Analysis. The recorded powder XRD patterns of the as-prepared rGO, ZnO, and the ZnO-rGO composite is shown in Figure 1. The diffraction pattern of rGO shows a broad peak at 2θ value 25.6° corresponding to the (002) planes of interlayer distance of 3.47 Å [36]. The XRD peak of ZnO shows sharp and intense diffraction peaks at 2θ of 31.5°, 34.1°, 36°, 47.2°, 56.3°, 62.6°, 66.1°, 67°, and 68.8° and its corresponding lattice planes (100), (002), (101), (102), (110), (103), (002), (112), and (201), respectively. The as-prepared urchin-like ZnO microstructure exhibited good crystalline nature with hexagonal wurtzite structure and is in agreement with the standard JCPDS card No: 36-1451 [37]. In addition, the ZnO-rGO composite reveals a similar XRD pattern of ZnO-related diffraction peaks with the rGO-related wide peak that confirms the heterojunction structure. However, the rGO peak is not seen in the ZnO-rGO composite due to the relatively less intensity [38]. No proof of any other impurities is detected conforming that the ZnO-rGO composite is successfully prepared.

3.2. Morphological Analysis. The morphologies and microstructures of rGO, urchin-like ZnO, and ZnO microrod-rGO composites were investigated via HR-SEM and shown in Figures 2(a)–2(d), respectively. The compact wrinkled-like rGO sheet confirms the formation of the 2D structure which clearly indicates that the graphene oxide has been well reduced during the hydrothermal process (Figure 2(a)) [35]. The pure urchin-like ZnO (Figures 2(b) and 2(c)) with a length of approximately 3-5 μm and a diameter of 600-800 nm as shown in Figure 2(c). The network of
urchin-like ZnO also shows a compact distribution of nanorods, and hence, it caused the well-ordered shape of nanorods. In the SEM image of ZnO-rGO (Figure 2(d)), it can be identified that urchin-like ZnO micro/nanorods are anchored and well dispersed on the rGO sheet. After the growth of ZnO micro/nanostructures on the rGO, the graphene has changed its morphology due to larger size of ZnO particles. Hence, the larger size of composites will enhance a conductive to recycling and the more channels in the nanorods will provide better transportation of electrons during the process of photodegradation [39].

3.3. Fourier Transform Infrared (FT-IR) Analysis. Figure 3 shows the FT-IR spectra of rGO, urchin-like ZnO, and ZnO-rGO composite. All samples exhibit a strong and wide absorption peak around 3200-3500 cm\(^{-1}\) which is attributed to the stretching of O-H vibration of the amide group [40]. In the case of rGO, we observed that the absorption bands decreased distinctly to less intensity and oxygen functionalities disappeared, which conforms the surface of GO has been reduced to rGO [41]. Besides, the strong peaks at 459 cm\(^{-1}\) are assigned to the stretching vibration of the Zn-O hexagonal phase [42]. The absorption peaks at 1627 cm\(^{-1}\), 1385 cm\(^{-1}\), and 893 cm\(^{-1}\) correspond to the aromatic C=C bond and skeletal ring vibrations from the graphitic domain, C-OH stretching vibrations, and bending vibration of C-OH, respectively [40, 43]. But after hydrothermal reaction, the intensity of the peak significantly decreased. However, this peak was red shifted to 534 cm\(^{-1}\) in the ZnO-rGO composite due to interactions between the urchin-like ZnO microstruc-

3.4. UV-Visible Absorbance Analysis. To examine the optical properties of the as-synthesized materials, UV-Vis optical absorption spectra were recorded (Figure 4(a)). It is an effective way to study about surface defects and is strongly associated with the photocatalytic activity of ZnO-rGO composites [46]. The strong characteristic absorbance peak at about 377 nm indicated highly crystalline and inherent bandgap
absorption of ZnO particles [28]. rGO shows the absorption peak seen at 264 nm and is attributed to $\pi - \pi^*$ orbital transition [47], while the characteristic spectra of ZnO-rGO composites show a peak at 264 nm which belongs to the rGO, and another absorption peak at 382 nm is attributed to ZnO microstructure. Therefore, the ZnO in the composite material got red shifted from 377 to 382 nm mainly due to the addition of rGO through ZnO. The overall peak shows that the composite material of urchin-like ZnO-rGO microstructure has higher absorption capacity than pure ZnO which is confirmed from the UV-spectrum. Thus, the higher absorption capacity plays an important role in the photocatalytic performance of visible light irradiation for dyes.

To estimate the bandgap energy of synthesized catalysts, the UV-visible absorbance spectra of samples were analysed by performing by the Kubelka-Munk theory. The material was calculated by plotting $(\alpha h\nu)^2$ versus $(h\nu)$ photon energy by using the following equation:

$$a h\nu = A(h\nu - E_g)^{1/2},$$

where $\alpha$ is the absorption coefficient of the catalyst, $\nu$ is the frequency of light, $h\nu$ is the photon energy, $A$ is the constant energy, and $E_g$ is the bandgap energy, respectively. From Figures 4(b) and 4(c), the estimated bandgap energy values

![Graph showing UV-visible absorbance spectra and bandgap energy calculations.](image)

**Figure 4:** (a) UV-visible absorbance spectra for the as-synthesized rGO, ZnO, and ZnO-rGO; (b, c) Tauc plot to examine the bandgap of ZnO and ZnO-rGO.
for ZnO and ZnO-rGO composites are 3.20 eV and 2.97 eV, respectively. It can be seen that the $E_g$ value of the composite material is red shifted from the $E_g$ value of ZnO microstructure, suggesting the bandgap reduction of ZnO-rGO catalyst, which can enhance high visible light absorption for the photocatalytic performance of phenol.

3.5. Thermogravimetric Analysis. As presented in Figure 5(a), the thermogram of rGO, the weight loss at about 73.38 wt. % mainly occurs at the range of 400°C and drops drastically due to the increasing temperature range from 410°C and 735°C, indicating that rGO has a homogeneous composition distribution to the oxidation of carbon in air simultaneously. The residual weight of rGO which is about 12.66 wt. % denotes that rGO is totally combusted [47]. From Figure 5(b), the TGA traces of ZnO one could observe the three weight loss in the range of 50-150°C, 150-350°C, and 350-600°C. Weight loss of about 3.2 wt. % from 50 to 150°C is related to the dehydration of surface-adsorbed water molecules and removal of chemically absorbed alcohol. The weight loss of about 6.97 wt. % from 150 to 350°C is due to the degradation of the organic molecules and the hydroxide groups. Therefore, annealing at above 350°C assured the formation of ZnO particles [48]. The TGA trace of ZnO-rGO composites is illustrated in Figure 5(c). The weight loss of about 9.61 wt. % above 250°C is ascribed to be oxidation of graphene under atmosphere. A significant mass loss of about 19.49 wt. % is observed at the temperature range above 400°C-510°C which is supposedly due to decomposition of rGO in the composite [49]. Based on the above result, we can conclude...
that the residual weight ratio of ZnO-rGO composites is about 63 wt. % at 520°C, respectively.

3.6. Photocatalytic Activity. The photocatalytic performance of urchin-like ZnO and ZnO microrod-rGO composites was examined for their photodegradation of phenol solution as a model pollutant under visible light irradiation. Figure 6 represents the time-dependent UV-Vis absorption spectrum of the aqueous solution of phenol which leads to the decrease in its absorbance reduction with various duration. Prior to the irradiation, the sample was stirred magnetically in the completely dark area for 60 min to attain the adsorption equilibrium of phenol solution over the photocatalyst. The photodegradation was carried out for 150 min, and the
Table 1: Comparison of photocatalytic performance with previously reported literature.

| Photocatalyst                          | Concentration (mg L⁻¹) and volume of phenol (mL) | Catalyst dosage (g L⁻¹) | Percentage of degradation (%) | Irradiation time (min) | Irradiation source       | Rate constant (min⁻¹) | Concentration (mg L⁻¹) and volume of phenol (mL) | Reference |
|----------------------------------------|--------------------------------------------------|--------------------------|-------------------------------|------------------------|--------------------------|-----------------------|--------------------------------------------------|----------|
| Zn/Ag₂CO₃/A g₂O                       | 50-200                                           | 0.1                      | 1                             | 420                    | Visible                  | —                     | 50-200                                           | [51]     |
| rGO/ZnO/TiO₂                          | 60-250                                           | 0.6                      | 100                           | 160                    | Visible                  | 0.0124                | 60-250                                           | [37]     |
| Cerium doped-ZnO                      | 20-100                                           | 1                        | 80.7                          | 300                    | Visible                  | 0.0061                | 20-100                                           | [52]     |
| Nano ZnO500                           | 10-100                                           | 2.5                      | 72                            | 60                     | UV-laser                 | 0.0391                | -100                                             | [53]     |
| Fe₃O₄-ZnO                             | 10-200                                           | 0.32                     | 82.3                          | 150                    | UV                       | 0.0108                | -200                                             | [20]     |
| Aqueous ZnO                           | 70-100                                           | 2.5                      | 100                           | 480                    | Sunlight                 | 0.325                 | 70-100                                           | [30]     |
| ZnO                                    | 50-500                                           | 0.6                      | 100                           | 360                    | Solar                    | 0.3954 ± 0.008 h⁻¹    | 50-500                                           | [1]      |
| TiO₂/rGO-8%                            | 20-100                                           | —                        | 58.8                          | 720                    | Visible                  | 0.0014 h⁻¹            | 20-100                                           | [54]     |
| ZnO nanorods                           | 10                                               | —                        | 50                            | 300                    | Visible                  | —                     | 10                                               | [55]     |
| Urchin-like ZnO microrod-rGO          | 20-50                                            | 0.2                      | 84.2                          | 150                    | Visible                  | 0.02423               | 20-50                                             | This work |

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degradation rate of phenol solution has shown a maximum absorption wavelength at $\lambda_{\text{max}} = 270$ nm [3].

In general, the concentration of phenol or absorbance gradually decreases with the increasing illumination time in the presence of urchin-like ZnO and ZnO-rGO photocatalyst, respectively. After irradiation, the concentration of phenol is reduced, implying the decolorization of photocatalyst, and ascribed to the oxidation of phenol in the existence of reaction kinetics. The degradation result shows that the ZnO nano/microrod-rGO composites exhibit better photocatalytic activity than those of urchin-like ZnO microrods. As shown in Figures 6(a) and 6(b), the typical absorption peak at 270 nm does not change its wavelength even after 150 min, which indicated that the prepared photocatalyst of phenol is active under visible light irradiation.

According to literature, the addition of rGO in the catalysts favours a larger surface area to bind a phenol molecule through the π−π conjugation with face-to-face direction [50]. The dispersion of ZnO-rGO composites enhances the surface of oxygen species, improves the electron-hole pairs, and lowers the bandgap. Moreover, the absorption edge of ZnO-rGO composites shifted to the broad wavelength after 135 min and provides a favourable absorption of phenol under visible light irradiation. The observed normalized temporal concentration changes ($C_t/C_0$) of phenol during photocatalytic degradation activity of prepared photocatalysts (urchin-like ZnO and ZnO microrod-rGO composites) vs. time graph are shown in Figure 7(a). It is clear that ZnO-rGO with 84.2% demonstrates an outstanding enhancement in the photodegradation of phenol compared with urchin-like ZnO microrods.

Pseudo-first-order reaction. The reaction was calculated from the slope of $-\ln \left(\frac{C_t}{C_0}\right)$ and reaction time, $t$ (Figure 7(b)). From this graph, we can understand that urchin-like ZnO and ZnO microrod-rGO composites exhibit linear fit lines and confirm that the photocatalytic degradation reaction follows pseudo-first-order reaction kinetics. As shown in Figure 7(b), the rate constant of urchin-like ZnO exhibits a $K_{\text{app}}$ of 0.015 min$^{-1}$, whereas the ZnO microrod-rGO composites reach into 0.024 min$^{-1}$, which is about 1.5 times faster rate than that of pure ZnO microrods. The higher rate constant of ZnO microrod-rGO composites yields a large number of photogenerated carriers which enhance the photocatalysis. Herein, to better assess, the performance of the synthesized catalyst was compared with the detoxification of phenol reported in literature studies (Table 1).

4. Conclusion

In this investigation, we successfully synthesized a cost-effective and highly active ZnO microrod-rGO composite of heterojunction via a facile hydrothermal process. The ZnO-rGO (2.97 eV) displayed a narrow bandgap when compared to urchin-like ZnO (3.20 eV) and also showed strong visible light absorption and an enhanced photoresponse to visible light regions. The photocatalytic efficiency of the composite reached 84.2%, and the catalyst performance was evaluated by phenol degradation under the irradiation of visible light. The ZnO-rGO composite incorporated with additional electronic channels with the presence of urchin-like structure can absorb a large quantity of phenol because of its large surface area and transfer of electrons faster due to the presence of rGO in the composite. Therefore, the obtained results suggest that the prepared ZnO-rGO composite is a promising candidate for photodegradation process under visible-light-driven photocatalyst for decontamination of toxic compounds and effluents.

Data Availability

The data supporting this work is available from the corresponding author upon request.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Supplementary Materials

The pictorial representation of this work has been described in the form of graphical abstract available in the supplementary information. (Supplementary Materials)

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