Research Article

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

S. Mary Margaret, Albin John P. Paul Winston, S. Muthupandi, P. Shobha, and P. Sagayaraj

Loyola College (Autonomous), Nungambakkam, Chennai, Tamil Nadu, India

Correspondence should be addressed to P. Sagayaraj; sagayaraj1962@gmail.com

Received 2 February 2021; Revised 8 June 2021; Accepted 26 June 2021; Published 26 July 2021

Academic Editor: Baskaran Rangasamy

Copyright © 2021 S. Mary Margaret et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

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 floatation, 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 conductivity, huge specific surface area, material consumption, high stability, high absorption, conduction empty band (CB), and

electronic structure packed valance band (VB) [13–16]. The method of phenol degradation through semiconducting metal oxide has been under usage as photocatalyst materials involving TiO_2 [17], ZnO [18], V_2O_5 [19], Fe_3O_4 [20], and MgO [21] and is well known and ascribed to the arrangement of electron-hole pair at the valance and conduction band after absorption of less amount of energy from UV or visible light.

Among semiconducting nano/microstructure, ZnO is a promising candidate with suitable bandgap energy of $\sim 3.4\text{ eV}$ 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 ($200,000\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$), 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 char-

acterized 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 ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), polyethylene glycol (PEG 4000), ammonium hydroxide ($\text{NH}_3 \cdot \text{H}_2\text{O}$), potassium persulfate ($\text{K}_2\text{S}_2\text{O}_8$), sulfuric acid (H_2SO_4), phosphorus pentoxide (P_2O_5), hydrochloric acid (HCl), potassium permanganate (KMnO_4), ethylene glycol ($\text{C}_2\text{H}_6\text{O}_2$), hydrogen peroxide (H_2O_2), and ascorbic acid ($\text{C}_6\text{H}_8\text{O}_6$) 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_2O_5 , and 2 g of $\text{K}_2\text{S}_2\text{O}_8$ were added into 24 mL of concentrated H_2SO_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_2SO_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_2O_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 $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 2.5 wt. % of rGO, 30 mL of $\text{C}_2\text{H}_6\text{O}_2$, and 0.6 g PEG 4000 were dissolved in distilled water (120 mL). Then, $\text{NH}_3 \cdot \text{H}_2\text{O}$ 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:

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

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:

$$-\ln \left(\frac{C_t}{C_0} \right) = k_{app} t, \quad (2)$$

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 $K\alpha$ (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°

FIGURE 1: X-ray patterns of the rGO, ZnO, and ZnO-rGO composites.

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 diameter of about 10 μm is self-assembled by micro/nanorods. It has a length of approximately 3–5 μm and a diameter of 600–800 nm as shown in Figure 2(c). The network of

FIGURE 2: SEM images of (a) rGO, (b) c) urchin-like ZnO microrods, and (d) ZnO microrod-rGO composite.

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 $3200\text{--}3500\text{ cm}^{-1}$ 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-

FIGURE 3: FT-IR spectra of the rGO, ZnO, and ZnO-rGO composites.

ture and residual epoxy and hydroxyl functional groups of the rGO [40, 44, 45].

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

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.

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:

$$\alpha h\nu = A(h\nu - E_g)^{1/2}, \quad (3)$$

where α is the absorption coefficient of the catalyst, ν 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

FIGURE 5: TGA curves of (a) rGO, (b) urchin-like ZnO, and (c) ZnO-rGO composites.

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

FIGURE 6: (a, b) UV-Vis absorption spectrum changes of phenol at every 15 min time interval of (a) urchin-like ZnO and (b) ZnO-rGO composite, respectively.

FIGURE 7: (a) Study of linear apparent first-order kinetics for the photodegradation of phenol solution using urchin-like ZnO and ZnO microrod-rGO catalyst under visible light illumination. (b) Photodegraded efficiencies for the ZnO-rGO nano/microcomposites and urchin-like ZnO, variation in $-\ln(C_t/C_0)$ as function of irradiation time and linear fits of photocatalysts. The kinetic rate of phenol degradation by the photocatalysts was also investigated.

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/Ag ₂ CO ₃ /A g ₂ O	50-200	0.1	1	420	Visible	—	50-200	[51]
rGO/ZnO/TiO ₂	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]
Fe ₃ O ₄ -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]
TiO ₂ /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

degradation rate of phenol solution has shown a maximum absorption wavelength at $\lambda_{\text{max}} = 270 \text{ nm}$ [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 decolourization of photocatalyst, and ascribed to the oxidation of phenol in the existence of $\cdot\text{OH}$ radicals. The degradation result shows that the ZnO nano/micro-rGO heterojunction degrades the organic pollutants of phenol solution up to $\sim 84.2\%$ and urchin-like ZnO catalyst degrades $\sim 71.5\%$ in just 150 min under similar operating conditions. Therefore, 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 $\pi - \pi$ 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 photodegradation 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 $-\ln(C_t/C_0)$ 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_{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 photoelectrons 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). It is concluded that ZnO microrod-rGO composites are an efficient catalyst for decontamination of phenol over visible light irradiation. It may be beneficial for the use of industrial applications due to its cost-effective and great performance.

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 photodegradation 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*)

References

- [1] N. Yusoff, S.-A. Ong, L.-N. Ho, Y.-S. Wong, and W. Khalik, "Degradation of phenol through solar-photocatalytic treatment by zinc oxide in aqueous solution," *Desalination and Water Treatment*, vol. 54, pp. 1621–1628, 2014.
- [2] N. C. Saha, F. Bhunia, and A. Kaviraj, "Toxicity of phenol to fish and aquatic ecosystems," *Bulletin of Environmental Contamination and Toxicology*, vol. 63, no. 2, pp. 195–202, 1999.
- [3] F. Hayati, A. A. Isari, M. Fattahi, B. Anvaripour, and S. Jorfi, "Photocatalytic decontamination of phenol and petrochemical wastewater through ZnO/TiO₂ decorated on reduced graphene oxide nanocomposite: influential operating factors, mechanism, and electrical energy consumption," *RSC Advances*, vol. 8, no. 70, pp. 40035–40053, 2018.
- [4] A. Lakshmanan, P. Surendran, S. SakthiPriya et al., "Effect of fuel content on nonlinear optical and antibacterial activities of Zn/Cu/Al₂O₄ nanoparticles prepared by microwave-assisted combustion method," *Journal of King Saud University - Science*, vol. 32, no. 2, pp. 1382–1389, 2020.
- [5] M. Ahmad, E. Ahmed, Z. L. Hong, W. Ahmed, A. Elhissi, and N. R. Khalid, "Photocatalytic, sonocatalytic and sonophotocatalytic degradation of rhodamine B using ZnO/CNTs composites photocatalysts," *Ultrasonics Sonochemistry*, vol. 21, no. 2, pp. 761–773, 2014.
- [6] S. Fang, K. Lv, Q. Li, H. Ye, D. Du, and M. Li, "Effect of acid on the photocatalytic degradation of rhodamine B over g-C₃N₄," *Applied Surface Science*, vol. 358, pp. 336–342, 2015.

- [7] X. Wang, J. Wang, P. Guo, W. Guo, and C. Wang, "Degradation of rhodamine B in aqueous solution by using swirling jet-induced cavitation combined with H_2O_2 ," *Journal of Hazardous Materials*, vol. 30, pp. 486–491, 2009.
- [8] S. Ravichandran and G. Ramalingam, "Synthesis, optical and morphological studies of sol-gel derived ZnO/PVP one dimensional nano-composite," *Journal of Nanoscience and Nanotechnology*, vol. 1, pp. 39–43, 2013.
- [9] K. Mishra and P. Gogate, "Intensification of degradation of rhodamine B using hydrodynamic cavitation in the presence of additives," *Separation and Purification Technology*, vol. 75, no. 3, pp. 385–391, 2010.
- [10] I. Oller, S. Malato, and J. A. Sánchez-Pérez, "Combination of advanced oxidation processes and biological treatments for wastewater decontamination—a review," *Science of The Total Environment*, vol. 409, no. 20, pp. 4141–4166, 2011.
- [11] G. Theophil Anand, D. Renuka, R. Ramesh et al., "Green synthesis of ZnO nanoparticle using *Prunus dulcis* (almond gum) for antimicrobial and supercapacitor applications," *Surfaces and Interfaces*, vol. 17, p. 100376, 2019.
- [12] M. Antonopoulou, E. Evgenidou, D. Lambropoulou, and I. Konstantinou, "A review on advanced oxidation processes for the removal of taste and odor compounds from aqueous media," *Water Research*, vol. 53, pp. 215–234, 2014.
- [13] M. R. S. Joice, T. M. David, and P. Wilson, "WO₃ nanorods supported on mesoporous TiO₂ nanotubes as one-dimensional nanocomposites for rapid degradation of methylene blue under visible light irradiation," *Journal of Physical Chemistry C*, vol. 123, no. 45, pp. 27448–27464, 2019.
- [14] H. Huang, H. Ouyang, T. Han, H. Wang, and X. Zheng, "Construction of carbon quantum dots/single crystal TiO₂ nanosheets with exposed {001} and {101} facets and their visible light driven catalytic activity," *RSC Advances*, vol. 9, no. 7, pp. 3532–3541, 2019.
- [15] S. G. Kumar and L. G. Devi, "Review on modified TiO₂ photocatalysis under UV/visible light: selected results and related mechanisms on interfacial charge carrier transfer dynamics," *The Journal of Physical Chemistry. A*, vol. 115, no. 46, pp. 13211–13241, 2011.
- [16] G. Ramalingam, C. Ragupathi, K. Kaviyarasu et al., "Up-scalable synthesis of size-controlled white-green emitting behavior of core/shell (CdSe/ZnS) quantum dots for LED applications," *Journal of Nanoscience and Nanotechnology*, vol. 19, no. 7, pp. 4026–4032, 2019.
- [17] A. L. Linsebigler, G. Lu, and J. T. Yates, "Photocatalysis on TiO₂ surfaces: principles, mechanisms, and selected results," *Chemical Reviews*, vol. 95, no. 3, pp. 735–758, 1995.
- [18] S. Anas, S. Rahul, K. B. Babitha, R. V. Mangalaraja, and S. Ananthakumar, "Microwave accelerated synthesis of zinc oxide nanoplates and their enhanced photocatalytic activity under UV and solar illuminations," *Applied Surface Science*, vol. 355, pp. 98–103, 2015.
- [19] H. Yin, K. Yu, C. Song, R. Huang, and Z. Zhu, "Synthesis of Au-decorated V₂O₅/ZnO heteronanostructures and enhanced plasmonic photocatalytic activity," *ACS Applied Materials & Interfaces*, vol. 6, no. 17, pp. 14851–14860, 2014.
- [20] X. Feng, H. Guo, K. Patel, H. Zhou, and X. Lou, "High performance, recoverable Fe₃O₄/ZnO nanoparticles for enhanced photocatalytic degradation of phenol," *Chemical Engineering Journal*, vol. 244, pp. 327–334, 2014.
- [21] S. Jorfi, G. Barzegar, M. Ahmadi et al., "Enhanced coagulation-photocatalytic treatment of acid red 73 dye and real textile wastewater using UVA/synthesized MgO nanoparticles," *Journal of Environmental Management*, vol. 15, pp. 111–118, 2016.
- [22] P. S. Chauhan, R. Kant, A. Rai, A. Gupta, and S. Bhattacharya, "Facile synthesis of ZnO/GO nanoflowers over Si substrate for improved photocatalytic decolorization of MB dye and industrial wastewater under solar irradiation," *Materials Science in Semiconductor Processing*, vol. 89, pp. 6–17, 2019.
- [23] A. Meng, J. Shao, X. Fan, J. Wang, and Z. Li, "Rapid synthesis of a flower-like ZnO/rGO/Ag micro/nano-composite with enhanced photocatalytic performance by a one-step microwave method," *RSC Advances*, vol. 4, no. 104, pp. 60300–60305, 2014.
- [24] P. Van Tuan, T. T. Phuong, V. T. Tan, S. X. Nguyen, and T. N. Khiem, "In-situ hydrothermal fabrication and photocatalytic behavior of ZnO/reduced graphene oxide nanocomposites with varying graphene oxide concentrations," *Materials Science in Semiconductor Processing*, vol. 115, p. 105114, 2020.
- [25] V. A. Tu and V. A. Tuan, "A facile and fast solution chemistry synthesis of porous ZnO nanoparticles for high efficiency photodegradation of tartrazine," *Vietnam Journal of Chemistry*, vol. 56, no. 2, pp. 214–219, 2018.
- [26] T. H. Le, Q. D. Truong, T. Kimura et al., "Synthesis of hierarchical porous ZnO microspheres and its photocatalytic deNO_x activity," *Ceramics International*, vol. 38, no. 6, pp. 5053–5059, 2012.
- [27] M. Darvishi, F. Jamali-Paghaleh, M. Jamali-Paghaleh, and J. Seyed-Yazdi, "Facile synthesis of ZnO/rGO hybrid by microwave irradiation method with improved photoactivity," *Surfaces and Interfaces*, vol. 9, pp. 167–172, 2017.
- [28] K. Huang, Y. H. Li, S. Lin et al., "A facile route to reduced graphene oxide-zinc oxide nanorod composites with enhanced photocatalytic activity," *Powder Technology*, vol. 257, pp. 113–119, 2014.
- [29] S. Xu, L. Fu, T. S. H. Pham, A. Yu, F. Han, and L. Chen, "Preparation of ZnO flower/reduced graphene oxide composite with enhanced photocatalytic performance under sunlight," *Ceramics International*, vol. 41, no. 3, pp. 4007–4013, 2015.
- [30] S. K. Pardeshi and A. B. Patil, "A simple route for photocatalytic degradation of phenol in aqueous zinc oxide suspension using solar energy," *Solar Energy*, vol. 82, no. 8, pp. 700–705, 2008.
- [31] J. Qin, X. Zhang, C. Yang, M. Cao, M. Ma, and R. Liu, "ZnO microspheres-reduced graphene oxide nanocomposite for photocatalytic degradation of methylene blue dye," *Applied Surface Science*, vol. 392, pp. 196–203, 2017.
- [32] H. R. Pant, C. H. Park, P. Pokharel, L. D. Tijing, D. S. Lee, and C. S. Kim, "ZnO micro-flowers assembled on reduced graphene sheets with high photocatalytic activity for removal of pollutants," *Powder Technology*, vol. 235, pp. 853–858, 2013.
- [33] N. Cao and Y. Zhang, "Study of reduced graphene oxide preparation by hummers' method and related characterization," *Journal of Nanomaterials*, vol. 2015, Article ID 168125, 5 pages, 2015.
- [34] E. Andrijanto, S. Shoelarta, G. Subiyanto, and S. Rifki, "Facile synthesis of graphene from graphite using ascorbic acid as reducing agent," *AIP Conference Proceedings*, vol. 1725, p. 20003, 2016.
- [35] Y. Feng, N. Feng, Y. Wei, and G. Zhang, "An in situ gelatin-assisted hydrothermal synthesis of ZnO-reduced graphene

- oxide composites with enhanced photocatalytic performance under ultraviolet and visible light,” *RSC Advances*, vol. 4, no. 16, pp. 7933–7943, 2014.
- [36] M. Pusty, A. K. Rana, Y. Kumar, V. Sathe, S. Sen, and P. Shirage, “Synthesis of partially reduced graphene oxide/silver nanocomposite and its inhibitive action on pathogenic fungi grown under ambient conditions,” *ChemistrySelect*, vol. 1, no. 14, pp. 4235–4245, 2016.
- [37] H. Moussa, E. Giro, K. Mozet, H. Alem, G. Medjahdi, and R. Schneider, “ZnO rods/reduced graphene oxide composites prepared via a solvothermal reaction for efficient sunlight-driven photocatalysis,” *Applied Catalysis B: Environmental*, vol. 185, pp. 11–21, 2016.
- [38] H.-W. Wang, Z.-A. Hu, Y.-Q. Chang et al., “Design and synthesis of NiCo_2O_4 -reduced graphene oxide composites for high performance supercapacitors,” *Journal of Materials Chemistry*, vol. 21, no. 28, pp. 10504–10511, 2011.
- [39] Y. Zhou, D. Li, L. Yang et al., “Preparation of 3D urchin-like RGO/ZnO and its photocatalytic activity,” *Journal of Materials Science: Materials in Electronics*, vol. 28, no. 11, pp. 7935–7942, 2017.
- [40] H. N. Tien, V. H. Luan, L. T. Hoa et al., “One-pot synthesis of a reduced graphene oxide-zinc oxide sphere composite and its use as a visible light photocatalyst,” *Chemical Engineering Journal*, vol. 229, pp. 126–133, 2013.
- [41] L. Zhang, L. Du, X. Cai et al., “Role of graphene in great enhancement of photocatalytic activity of ZnO nanoparticle-graphene hybrids,” *Physica E: Low-dimensional Systems and Nanostructures*, vol. 47, pp. 279–284, 2013.
- [42] D. Gnanasangeetha and D. Saralathambavani, “One pot synthesis of zinc oxide nanoparticles via chemical and green method,” *Research Journal of Material Sciences*, vol. 1, pp. 1–8, 2013.
- [43] K. Rakesh, A. Nithya, K. Jeganathan, and K. Jothivenkatachalam, “A facile solid state synthesis of cone-like ZnO microstructure an efficient solar-light driven photocatalyst for rhodamine B degradation,” *Materials Today: Proceedings*, vol. 3, no. 10, pp. 4163–4172, 2016.
- [44] Q.-P. Luo, X.-Y. Yu, B.-X. Lei, H.-Y. Chen, D.-B. Kuang, and C.-Y. Su, “Reduced graphene oxide-hierarchical ZnO hollow sphere composites with enhanced photocurrent and photocatalytic activity,” *Journal of Physical Chemistry C*, vol. 116, no. 14, pp. 8111–8117, 2012.
- [45] Q. Zhang, C. Tian, A. Wu et al., “A facile one-pot route for the controllable growth of small sized and well-dispersed ZnO particles on GO-derived graphene,” *Journal of Materials Chemistry*, vol. 22, no. 23, pp. 11778–11784, 2012.
- [46] H.-B. Kim, D.-W. Jeong, and D.-J. Jang, “Morphology-tunable synthesis of ZnO microstructures under microwave irradiation: formation mechanisms and photocatalytic activity,” *CrystEngComm*, vol. 18, no. 6, pp. 898–906, 2016.
- [47] P. Liu, Y. Huang, and X. Zhang, “Cubic NiFe_2O_4 particles on graphene-polyaniline and their enhanced microwave absorption properties,” *Composites Science and Technology*, vol. 107, pp. 54–60, 2015.
- [48] J. Wang, G. Wang, S. Miao, J. Li, and X. Bao, “Graphene-supported iron-based nanoparticles encapsulated in nitrogen-doped carbon as a synergistic catalyst for hydrogen evolution and oxygen reduction reactions,” *Faraday Discussions*, vol. 176, pp. 135–151, 2014.
- [49] F. B. Dejene, A. G. Ali, H. C. Swart et al., “Optical properties of ZnO nanoparticles synthesized by varying the sodium hydroxide to zinc acetate molar ratios using a sol-gel process,” *Central European Journal of Physics*, vol. 9, no. 5, pp. 1321–1326, 2011.
- [50] X. Zhou, T. Shi, and H. Zhou, “Hydrothermal preparation of ZnO-reduced graphene oxide hybrid with high performance in photocatalytic degradation,” *Applied Surface Science*, vol. 258, no. 17, pp. 6204–6211, 2012.
- [51] N. Rosman, W. N. W. Salleh, A. F. Ismail et al., “Photocatalytic degradation of phenol over visible light active $\text{ZnO}/\text{Ag}_2\text{CO}_3/\text{Ag}_2\text{O}$ nanocomposites heterojunction,” *Journal of Photochemistry and Photobiology A: Chemistry*, vol. 364, pp. 602–612, 2018.
- [52] J.-C. Sin, S.-M. Lam, K.-T. Lee, and A. R. Mohamed, “Preparation of cerium-doped ZnO hierarchical micro/nanospheres with enhanced photocatalytic performance for phenol degradation under visible light,” *Journal of Molecular Catalysis A: Chemical*, vol. 409, pp. 1–10, 2015.
- [53] K. Hayat, M. A. Gondal, M. M. Khaled, S. Ahmed, and A. M. Shamsi, “Nano ZnO synthesis by modified sol gel method and its application in heterogeneous photocatalytic removal of phenol from water,” *Applied Catalysis A: General*, vol. 393, no. 1–2, pp. 122–129, 2011.
- [54] G. Wang, W. Guo, D. Xu, D. Liu, and M. Qin, “Graphene oxide hybridised TiO_2 for visible light photocatalytic degradation of phenol,” *Symmetry (Basel)*, vol. 12, no. 9, article ???, 2020.
- [55] J. Al-Sabahi, T. Bora, M. Al-Abri, and J. Dutta, “Controlled defects of zinc oxide nanorods for efficient visible light photocatalytic degradation of phenol,” *Materials (Basel)*, vol. 9, no. 4, p. 238, 2016.