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Photoluminescence and enhanced photocatalytic activity of mechanically activated graphite-zinc oxide composites

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Abstract

In this work, we show evidence of enhanced photocatalytic activity in mechanically activated graphite-zinc oxide (ZnO) composites using time-resolved photoluminescence (TRPL) and time-integrated photoluminescence (TIPL) spectroscopy. The graphite-ZnO composites were synthesized through facile mixing and grinding of graphite and ZnO precursors without any heat treatment. The precursors were ground at room temperature with varying graphite to ZnO mass ratios of 3:1, 2:2, and 1:3 for 0, 2, and 4 h. Raman spectroscopy and x-ray diffractometry confirm the presence of both graphite and ZnO and corroborate the graphite-to-ZnO ratio. XRD results also show a hexagonal wurtzite ZnO crystal structure. To determine the photocatalytic activity of the composites, the degradation of methylene blue (MB) under UV light was measured with a UV-vis spectrophotometer. Nearly full degradation was achieved within a half hour for all composite samples. The kinetic rates of 0.10 min^{-1} were also estimated for mixed and unground samples and samples ground for 2 h. Time-resolved photoluminescence (TRPL) and time-integrated photoluminescence (TIPL) spectroscopy reveal longer lifetimes and more intense UV emissions, respectively, for composite samples compared to pure ZnO. We propose that the even agglomeration of zinc oxide particles on graphite due to grinding enhances the photocatalytic degradation by the zinc oxide. TRPL and TIPL spectroscopy implies the excellent binding between ZnO and graphite, which greatly contributes to the decreased charge recombination resulting in the superior photocatalytic activity observed with our samples.

1. Introduction

In recent years, an increase in the number of studies utilizing semiconductor materials for environmental remediation has been reported. More specifically, concentrated efforts have been put into the treatment of dye-contaminated wastewater through photodegradation. Zinc oxide (ZnO) is one of the commonly used semiconductors for the photodegradation of dyes due to its wide band gap of 3.37 eV at room temperature [1], mechanical [2] and thermal stability [3], photosensitivity [4], and cost-effective production [5, 6].

Just like other semiconductors, the efficiency of ZnO as a photocatalyst is limited by the rapid recombination of photo-induced electron-hole pairs. This results in a significant reduction in photocatalytic activity [7]. To prevent or slow down the recombination rate in ZnO, the synthesis of carbon-based/ZnO composite materials has been studied for improved effective surface area, electron transport, and adsorptive capacity [8–10].

Previous methodologies employed in the synthesis of graphene/ZnO, graphene oxide/ZnO, and graphite/ZnO composite include but are not limited to solvothermal [11], combustion method [12], sol-gel [13], the one-pot chemical method [14] and hydrothermal synthesis [15]. Most of the mentioned techniques make use of high temperatures and pass through a chemical solution stage. A recent work [16] utilized ground graphite/ZnO

Table 1. Summary of parameters in the synthesis of G/Z composites through a solid-state reaction at room temperature.

Sample	Amount of pre-cursor (mg)		Sample label		
	Graphite	ZnO	0-hour grinding	2-hour grinding	4-hour grinding
Graphite	500	0	0HG	2HG	4HG
ZnO	0	500	0HZ	2HZ	4HZ
Graphene oxide	500		0HGO	2HGO	4HGO
G/Z Composite	375	125	0HGZ1	2HGZ1	4HGZ1
G/Z Composite	500	500	0HGZ2	2HGZ2	4HGZ2
G/Z Composite	125	375	0HGZ3	2HGZ3	4HGZ3

composites for energy storage applications. To the best of our knowledge, there is no other literature on ground graphite/ZnO composites for photocatalytic applications.

Typically, enhanced photocatalytic activity is demonstrated by examining the degradation of dyes, such as methylene blue, under UV exposure using UV-vis spectrometry. We demonstrate nearly 100% degradation efficiency and a kinetic rate of 0.10 min^{-1} for the composites. In this work, we show further evidence of photocatalytic superiority through time-resolved photoluminescence (TRPL) and time-integrated (TIPL) spectroscopy measurements. The composite samples exhibited UV emissions with longer average lifetimes compared to pure ZnO. This means that electrons on the composite remain in their excited state longer than when in pure ZnO. Since ZnO is a good electron donor, while graphite is a good electron acceptor, their synergistic effect effectively reduces electron/hole pair recombination. In turn, this leaves more charge carriers in graphite to form reactive species for the degradation of MB leading to the enhancement of the photocatalytic performance.

2. Methods

2.1. Synthesis of GZ composites

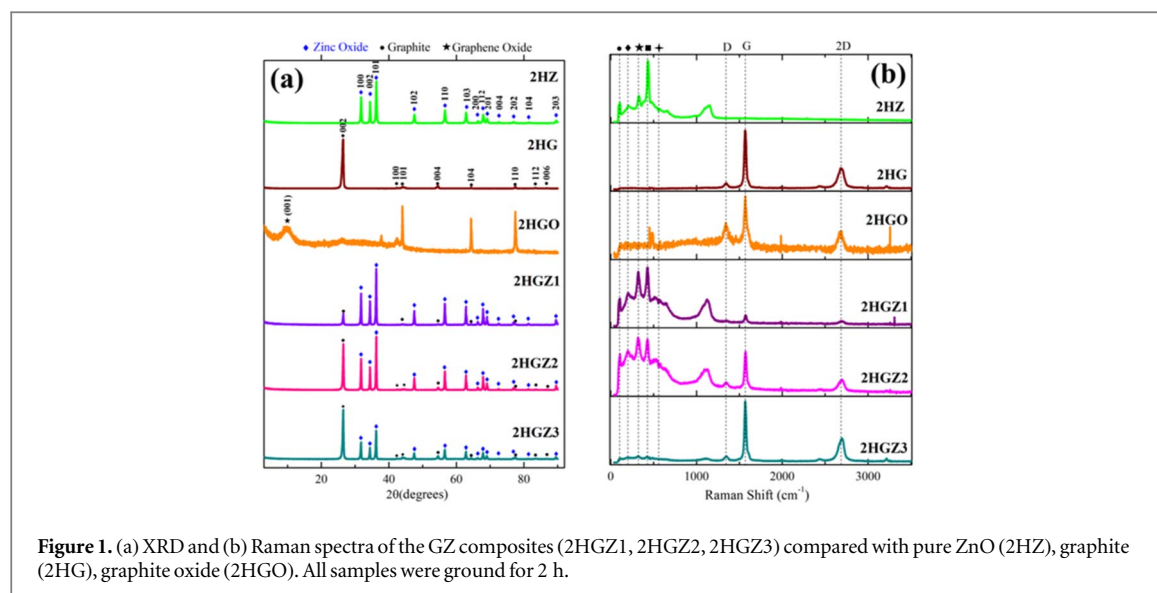
The methodology presented in this section is a low-cost, energy-efficient, and environment-friendly technique for producing graphite-ZnO composites. Graphite-ZnO (GZ) composites were synthesized through simple mixing and manual mechanical grinding of graphite and ZnO using an agate mortar and pestle. Graphite (Sigma Aldrich) and ZnO (Himedia) powders with varying mass ratios were continuously ground for 2 and 4 h. The control samples include graphite, ZnO, graphene oxide synthesized via modified Hummer's method, and the unground GZ mixture. Sample parameters are summarized in table 1.

Field emission scanning electron microscopy (FESEM) images were obtained using an FEI Helios Nanolab 600i to study morphology and the sizes of crystals present in the samples. To characterize the crystal phase and lattice parameters of the composites, x-ray diffractometry ($\text{CuK}\alpha$ radiation $\lambda = 1.54 \text{ \AA}$ at 40 kV and 30 mA at room temperature) was used. The x-ray diffraction (XRD) patterns of the samples were obtained in the 2θ range of $3^\circ - 90^\circ$ with 2 deg min^{-1} resolution. Raman spectra of the samples were also measured using an argon-ion laser source ($\lambda = 514.5 \text{ nm}$). TRPL spectroscopy and TIPL spectroscopy were conducted to give light on the origin of the photocatalytic activity of the composites. The ultraviolet (UV) excitation light used was generated from the third harmonics ($\lambda = 290 \text{ nm}$) of a Ti:sapphire laser with a 100 fs pulse duration and 1 kHz repetition rate.

2.2. Photocatalytic test

Photocatalytic properties of GZ composites were studied through the photodegradation of methylene blue (MB). 50 ml of $20 \text{ }\mu\text{M}$ MB aqueous solution was prepared to which 20 mg catalyst was added. The catalyst-MB suspension was magnetically stirred inside a dark chamber for 30 min to achieve absorption-desorption equilibrium. Then, the suspension was exposed to UV light from a 15 W light source for 60 min. Every 5 min, 3 ml of solution was collected and analyzed at the maximum absorption wavelength of MB (664 nm) using a UV-vis spectrophotometer (Jinan Hanon Instruments). All photocatalytic tests were accomplished in triplicates. Kinetic analysis was performed to quantify the degradation efficiencies of test catalysts.

We also compared with samples annealed at 200 and 600 $^\circ\text{C}$ and studied the recyclability and reusability of the composites. For this part of the study, 30 mg of the composite sample with equal graphite and ZnO ratios and ground for 2 h were used. For the recyclability and reusability test, the catalyst was recovered from MB dispersion through vacuum filtration after every photocatalytic test, washed with deionized water, oven dried for 4 h at 40 $^\circ\text{C}$, and reused for photodegradation of fresh MB solution.



3. Results

In sections 3.1 and 3.2, we show the structural and morphological properties of the GZ composite for samples ground for 2 h only and compare them with pure ZnO, graphite, and graphite oxide. In section 3.3, the results of the photocatalytic efficiency for all samples are presented, as well as the corresponding kinetic rates. We utilize TRPL spectroscopy and TIPL spectroscopy to shed light on the mechanism of photocatalysis for GZ composites. These results are shown in section 3.4. We compare these results with the photocatalytic activity of annealed GZ composites in section 3.5 and present the recyclability and reusability of the composite samples in section 3.6. We discuss our results in section 4 and present our conclusions in section 5.

3.1. XRD and raman spectroscopy

The XRD spectra of the GZ composites ground for 2 h (2HGZ1, 2HGZ2, 2HGZ3), compared with that of pure ZnO (2HZ), graphite (2HG) and graphite oxide (2HGO), are shown in figure 1. For 2HZ, 2HGZ1, 2HGZ2, and 2HGZ3, we have identified thirteen (13) peaks indexed to the hexagonal wurtzite phase of ZnO (ICDD Card No. 00-036-1451). The most prominent Bragg peaks of 2HZ located at $2\theta = 32^\circ, 44^\circ, 36^\circ, 48^\circ, 57^\circ$, and 63° correspond to (100), (002), (101), (102), (110), and (103) planes of crystalline ZnO. On the other hand, eight (8) diffractions peaks of 2HG around $2\theta = 26^\circ, 42^\circ, 44^\circ, 54^\circ, 64^\circ, 77^\circ, 84^\circ$, and 85° are attributed to the (002), (100), (101), (004), (104), (110), (112), and (006) reflection planes of hexagonal graphite (ICDD Card No. 56-0159). Similar peaks were observed for graphite in samples 2HGZ1, 2HGZ2, and 2HGZ3. For the GO sample, (001) peak at $2\theta = 10^\circ$ is found. There are no GO peaks in all the other samples, which indicates the absence of the formation of GO.

The relative intensities of the peaks reveal that for samples 2HGZ31 and 2HGZ2 with graphite:ZnO mass ratios of 1:3 and 2:2, the preferred crystal orientation is at the ZnO (101) plane, while for sample 2HGZ1 with graphite:ZnO mass ratio of 3:1, the preferred lattice plane is (002) of graphite.

Using Bragg's law, we also computed the d -spacing values for 2HZ, 2HG, 2HGZ1, 2HGZ2, and 2HGZ3. In GZ composites, the peak locations of ZnO are shifted to lower 2θ values, while the graphite peaks shifted to higher 2θ values. This shifting is an indication of the widening and narrowing of d -spacing for ZnO and G respectively.

The lattice parameters were then computed and the values of a and c for ZnO and G found were in good agreement for the hexagonal wurtzite phase of ZnO and hexagonal graphite, respectively. The lattice constants in the composites are larger than those of 2HZ, indicating that the presence of graphite can make the lattice constants of 2HZ larger.

The average crystallite sizes D for 2HZ, 2HG, and the composites were calculated using the Debye-Scherrer equation as follows [17]:

$$D = \frac{0.9\lambda}{\beta \cos \theta_B} \quad (1)$$

where λ is the wavelength of the CuK_α emission line, β is the full width at half-maximum (FWHM) of the peak, and θ_B the Bragg angle. The crystallite sizes were determined from the FWHM of the (101) and (002) peaks of

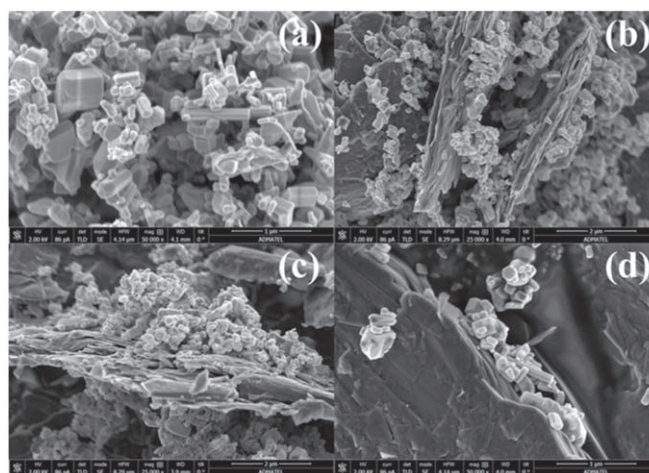


Figure 2. FESEM images of (a) pure ZnO (2HZ) compared with the GZ composites: (b) 2HGZ1, (c) 2HGZ2, and (d) 2HGZ3 ground for 2 h.

2HZ and 2HG, respectively. The crystallite sizes of ZnO and graphite both decrease as the graphite component increases.

The Raman spectra in figure 1(b) show three prominent features of graphene at 1346 cm^{-1} , 1568 cm^{-1} , and 2678 cm^{-1} known as the D, G, and 2D bands, respectively. The G band is related to the presence of sp^2 hybridization in the graphite structure and gives information on the in-plane vibration of sp^2 bonded carbon atoms [18, 19]. The D band arising from sp^3 hybridized C atoms is associated with the presence of disorder in the graphitic lattice [20]. The 2D band is attributed to the first overtone of the D band and is observed in 2HG and in all the composites with varying intensity, becoming higher for increased graphite loading. The parameter, I_D/I_G , is used to determine the ratio between the quantities of sp^3 and sp^2 hybridized carbon, as well as the quality of the graphitic material [19]. For the composites, the I_D/I_G increases with increasing ZnO content and moves away from the I_D/I_G value of graphite.

The main Raman peaks for pure ZnO (2HZ) are observed at 435 cm^{-1} , 107 cm^{-1} , 572 cm^{-1} , and 587 cm^{-1} assigned as E_2^{High} (■), E_2^{Low} (•), $A_1(\text{LO})$, and $E_1(\text{LO})$ (✦), respectively. The relatively higher intensity peak of the E_2^{High} mode compared to other observed peaks demonstrate that the structure of 2HZ is that of a wurtzite hexagonal phase. Multi-phonon features $2E_2^{\text{Low}}$ (◆) at 202 cm^{-1} (overtone of the E_2^{Low}) and $E_2^{\text{High}} - E_2^{\text{Low}}$ (★) at 330 cm^{-1} (due to the combination of $E_2^{\text{High}} - E_2^{\text{Low}}$) are also identified. A broad second order band due to optical combinations was also detected at $1016 - 1220\text{ cm}^{-1}$. The presence of $E_1(\text{LO})$ mode is the confirmatory existence of oxygen vacancies and zinc interstitials in the samples [21].

3.2. Scanning electron microscopy

Figure 2 shows the FESEM image of the (a) pure ZnO sample 2HZ compared with the GZ composites: (b) 2HGZ1, (c) 2HGZ2, and (d) 2HGZ3 ground for 2 h. The images clearly depict the typical hexagonal shape of the microcrystals in all samples. On the other hand, the average sizes of the ZnO microcrystals decreased upon the introduction of the graphite. The reduction of the sizes is not due to the grinding alone, since the 2HZ was also ground for 2 h and has a larger average size compared with the ZnO microcrystals interspersed with graphite. Increasing the graphite content corresponds to a decrease in the average size of the ZnO microcrystals present in the material. It is also evident that the grinding process aided in the adherence and the agglomeration of the ZnO particles on the surface of graphite.

3.3. Photocatalytic activity

To determine the photocatalytic activity, the degradation of MB by UV light was observed by monitoring the relative intensity of the UV-vis absorption peak at 664 nm . This was done for all composites ground for 0, 2, and 4 h, and was compared with pure ZnO and graphite, which were also ground for the same amounts of time. For control, MB without any composite was simultaneously measured under UV exposure. The relative intensity was then calibrated against the relative concentration.

Figure 3 shows the relative concentration against the degradation time for a grinding time of (a) 0, (b) 2, and (c) 4 h. As expected, no degradation of MB under UV light exposure over time was observed. In addition, unground ZnO (0HZ) was degraded by as much as 81% within 30 min of UV exposure. Surprisingly, there was practically no degradation of MB by ground ZnO (2HZ and 4HZ) as seen in figures 3(b) and (c). Graphite alone

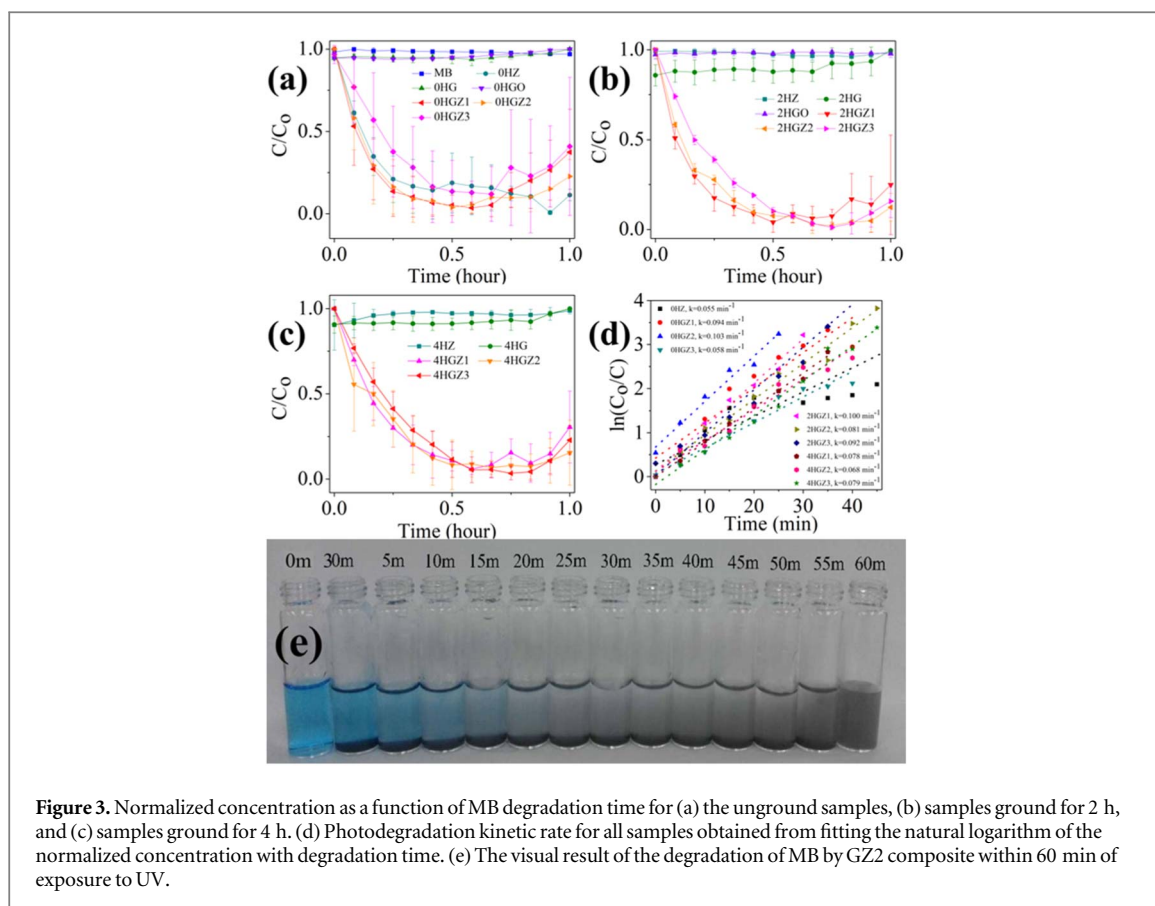


Figure 3. Normalized concentration as a function of MB degradation time for (a) the unground samples, (b) samples ground for 2 h, and (c) samples ground for 4 h. (d) Photodegradation kinetic rate for all samples obtained from fitting the natural logarithm of the normalized concentration with degradation time. (e) The visual result of the degradation of MB by GZ2 composite within 60 min of exposure to UV.

also does not influence the degradation of MB, regardless of the grinding time. Thus, we can conclude that the synergy between ZnO and graphite contributes to photocatalysis. On average, the composite samples 0HGZ1, 0HGZ2, 0HGZ3, 2HGZ1, 2HGZ2, 2HGZ3, 4HGZ1, 4HGZ2, and 4HGZ3 degraded MB by as much as 95%, 96%, 86%, 100%, 92%, 90%, 89%, 92%, and 89%, respectively, in 30 min of UV irradiation. Figure 3(e) shows a representative result of the degradation of MB by sample 0HGZ2. Within 30 min of exposure to UV, MB was completely degraded.

The increase in the concentration of MB at 664 nm at times greater than 40 min is attributed to a phenomenon called photobleaching. Generally, in UV-vis spectroscopy, this can result in a decrease in absorbance at the wavelength of interest. However, in some cases [22–25], photobleaching can also cause an increase in absorbance, because of the formation of a new product from the photobleaching of MB or a shift in the absorbance spectrum, resulting in a higher absorbance at 664 nm. It would be interesting to investigate this further in a subsequent investigation.

To determine the photodegradation rate, plots of $\ln(C_0/C)$ versus irradiation time for all samples were made as a function of time. The linear relationship of $\ln(C_0/C)$ versus t evidenced by least-square regression values $R^2 > 0.9485$ of pseudo-first-order rate constants indicates that the photodegradation of MB over the catalyst followed the pseudo-first-order kinetic model [26]

$$\ln\left(\frac{C_0}{C}\right) = kt \quad (2)$$

Performing a linear regression of $\ln(C_0/C)$ versus t for all curves provided for the estimation of the slope of a line, which corresponds to the rate constant k . These rate constants are then shown in figure 3(d).

A higher photocatalytic reaction rate constant implies higher photocatalytic activity [27–29]. From figure 3, the photocatalytic activity trend follows the order 0HGZ2 > 2HGZ1 > 2HGZ3 > 0HGZ1 > 2HGZ2 > 4HGZ3 > 4HGZ1 > 4HGZ2 > 0HGZ3 > 0HZ. The rate constant of all GZ composites is higher than pure ZnO. The highest rate constant obtained were from 0HGZ2 (0.103 min^{-1}) and 2HGZ1 (0.100 min^{-1}), which showed an 88% and 82% increase in the reaction rate, respectively, compared to pure ZnO (0HZ) (0.055 min^{-1}).

For samples that were not ground, the optimum loading was 0HGZ2 (4:4) followed by 0HGZ1 and 0HGZ3. The kinetic rate of 0HGZ3 is lowest among all composites probably because too much graphite without adherence to ZnO adds to the turbidity of the solution, screening UV light, preventing UV activation of the ZnO surface, and thus decreasing photocatalytic activity. For 2 h of solid-state reaction, there was an increase in the

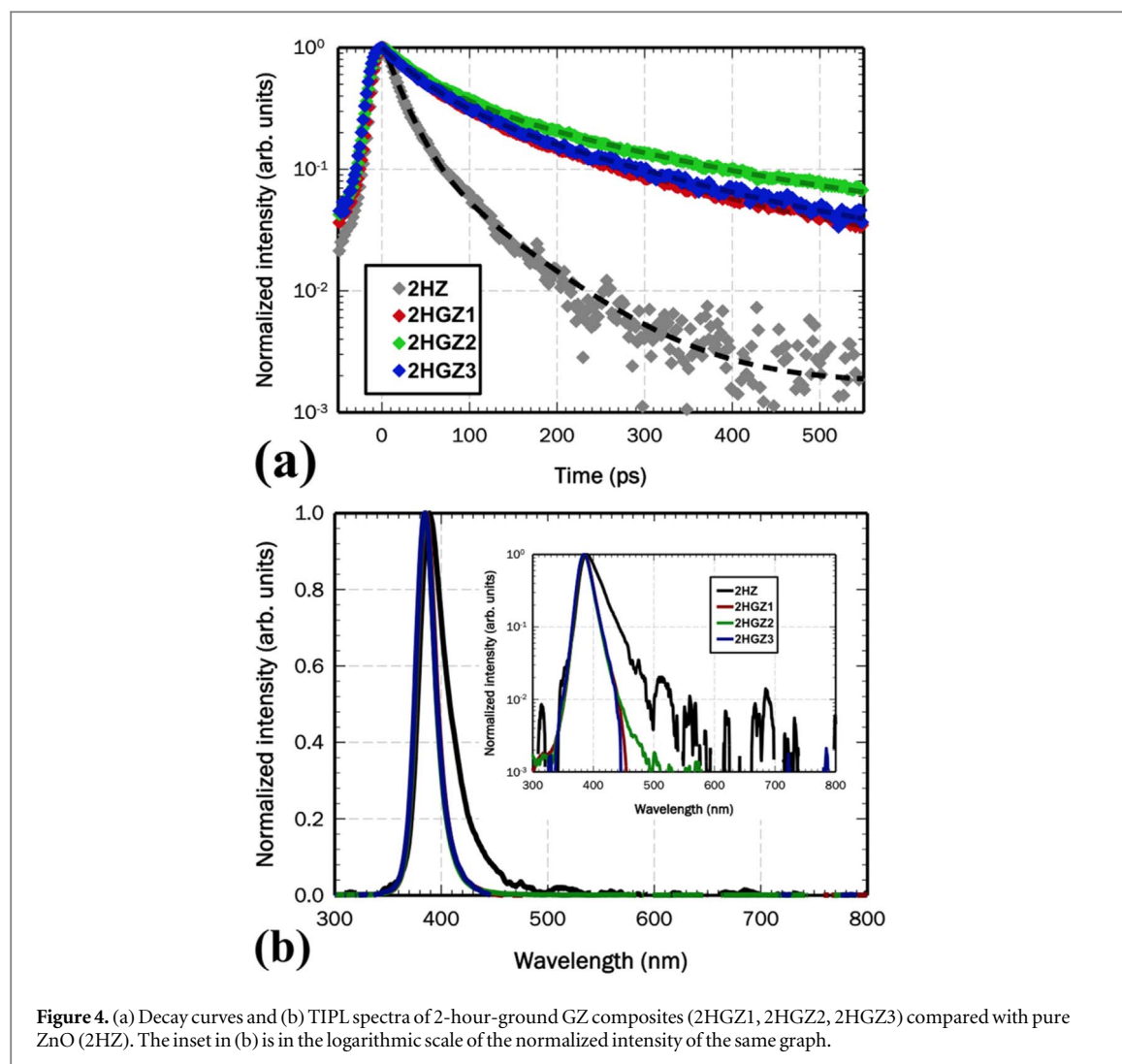


Figure 4. (a) Decay curves and (b) TIPL spectra of 2-hour-ground GZ composites (2HGZ1, 2HGZ2, 2HGZ3) compared with pure ZnO (2HZ). The inset in (b) is in the logarithmic scale of the normalized intensity of the same graph.

kinetic rate for 2HGZ1 and 2HGZ3 compared to 0HGZ1 and 0HGZ3. This might be due to the intimate contact between ZnO and graphite upon grinding. The intimate contact is crucial for the formation of electronic interaction and interelectronic transfer at the interface of ZnO and graphite [29].

There was an observed decrease in photocatalytic activities of all samples 4HGZ1, 4HGZ2, and 4HGZ3 after 4 h of solid-state reaction compared to samples ground for 2 h. A study performed by Melcher *et al* [30] found that ball milling of TiO_2 for more than 2 h destroys the mesopores of the material. Porous structures of this type are extremely useful in the photocatalytic process [31], and their destruction leads to poor photocatalytic performance [30]. In that regard, it can be speculated that grinding the GZ composites for 4 h, as well as grinding ZnO for more than 2 h, does have similar effects.

3.4. Photoluminescence spectra

To ascertain the mechanism of photocatalytic degradation, we performed photoluminescence experiments on ZnO and all the composite samples ground for 2 h. Based on the results of figure 3, the samples ground for 2 h exhibited the best set of reaction rates based on grinding time.

Figure 4(a) shows the normalized intensity versus decay time in picoseconds of GZ composites and pure ZnO all ground for 2 h. The emission lifetimes were determined by fitting a double exponential function to the decaying parts of the profile given as:

$$I(t) = A_1 \exp\left(\frac{-t}{\tau_1}\right) + A_2 \exp\left(\frac{-t}{\tau_2}\right) \quad (3)$$

where I is the emission intensity, t is time, A_1 and A_2 are the amplitudes, and τ_1 and τ_2 are the decay constants (lifetimes).

Table 2. Summary of amplitudes and lifetimes (decay constants and average lifetimes) from the exponential fitting of the UV emission temporal profiles of 2HZ, 2HGZ1, 2HGZ2, and 2HGZ3 composites.

Sample	Amplitude (a.u.)		Lifetime (± 10 ps)		Ave. Lifetime (ps)
	A_1	A_2	τ_1	τ_2	$\bar{\tau}$
2HZ	0.93 ± 0.02	0.16 ± 0.02	20	78	44
2HGZ1	0.61 ± 0.01	0.41 ± 0.01	42	170	136
2HGZ2	0.59 ± 0.01	0.40 ± 0.01	50	224	180
2HGZ3	0.59 ± 0.01	0.39 ± 0.01	45	187	150

The average lifetime is computed by:

$$\bar{\tau} = \frac{A_1 \tau_1^2 + A_2 \tau_2^2}{A_1 \tau_1 + A_2 \tau_2} \quad (4)$$

Table 2 shows the results of the least square fit using multi-exponential curves. The decay curve was decomposed into double exponential functions. The samples 2HGZ1, 2HGZ2, and 2HGZ3 exhibited UV emissions with longer average lifetimes of 136, 180, and 150 ps, respectively compared to 2HZ which had an average lifetime of 44 ps. This means that electrons on the composite remain in their excited state longer than when in pure ZnO. Since ZnO is a good electron donor, while graphite is a good electron acceptor, their synergistic effect effectively reduces electron/hole pair recombination.

Figure 4(b) shows the TIPL measurements of the composites and pure ZnO sample normalized against the UV emission peak around 390 nm. The spectral linewidth of the UV emissions of the GZ samples is narrower by 9 nm compared to that of the pure ZnO sample. This is because of the higher UV emission intensities of the composites which are more intense by at least 3 to 14 times, which further supports the synergistic effect between ZnO and graphite. To resolve the peaks, the normalized intensity of the TIPL spectra was rescaled to a logarithmic scale as shown by the inset. The fluctuations in the pure ZnO spectrum within 500 and 750 nm are attributed to noise. Pure ZnO has the lowest emission intensity among all the samples, and thus has the lowest signal-to-noise ratio. Moreover, the UV center wavelength of the composites is blue-shifted by 5 nm compared to that of the pure ZnO sample. The higher UV intensities in the composites could be a possible reason why their UV emission peaks are blue-shifted relative to the pure ZnO, i.e., the center of the UV peak could have shifted as an effect of the increase in the intensity of the shorter wavelength components of the UV band.

3.5. Photocatalytic degradation at higher temperatures

To establish whether annealing influences photocatalytic activity, we further investigated the photocatalytic degradation of MB by samples annealed at higher temperatures. Using TG-DTA (Figure SF1), we observed minimal weight loss percentage and no visible endothermic or exothermic peaks from 30 to 995 °C. This indicates that the ground GZ composite did not undergo any phase change, supporting our XRD and Raman results, and that the photocatalytic activity is purely due to the electronic interaction between ZnO and graphite.

Figures 5(a) and (b) shows FESEM images of the annealed samples annealed at 200 and 600 °C, respectively. We observed no significant difference between that of the GZ composite ground for 2 h without annealing [figure 2(c)]. Similarly, the XRD and Raman spectroscopy measurements of the annealed samples, shown in figures 5(c) and (d), respectively, are consistent with the unannealed samples and with the TG-DTA measurement, and do not imply any change in crystal structure or phase. We observed an increasing I_D/I_G ratio in the Raman measurement with increasing annealing temperature implying an increase in the number of defects in graphite.

We then measured the photocatalytic degradation efficiency for the sample with equal amounts of ZnO and graphite and ground for 2 h with annealing temperatures of 200 and 600 °C and an annealing time of 1 h. The annealing time was determined from previous related works [32, 33]. The degradation efficiencies [figure 5(e)] for annealed samples decrease with increasing annealing temperature and are lower compared to the room temperature samples. On the other hand, the annealed samples have lower and decreasing first-order rate constants [figure 5(f)]. These results suggest that annealing the samples does not further contribute to the degradation of MB, because no physical or chemical change happens to the samples with annealing temperature as indicated by the TG-DTA measurements. The photocatalytic activity decreases because of the increasing number of defects on graphite with increasing annealing temperature.

3.6. Recyclability and reusability

For practical applications, it is essential to determine how many times the photocatalytic material can be used and reused and is most favorable for large-scale application of photocatalysis water treatment. This result is

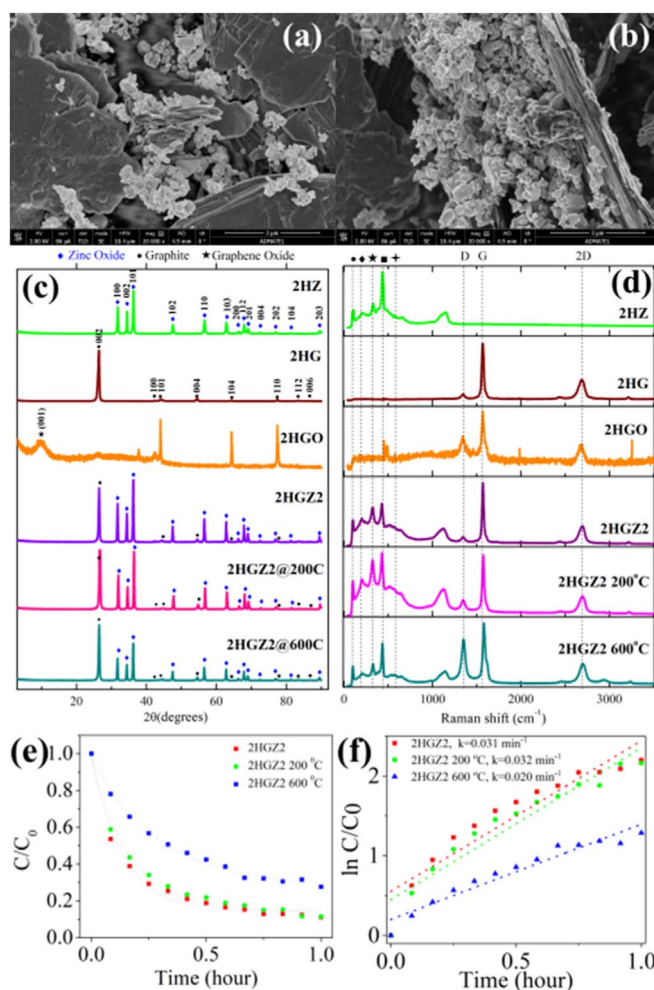


Figure 5. FESEM images of sample 2HGZ2 annealed at (a) 200 and (b) 600 °C. (c) XRD and (d) Raman spectra of the annealed samples in comparison to pure ZnO, graphite, graphene oxide, and GZ composite, all ground for 2 h. (e) Normalized concentration as a function of MB degradation time by the ground samples with and without annealing, and the (f) corresponding photodegradation kinetic rate for all samples obtained from fitting the natural logarithm of the normalized concentration with degradation time.

shown in figure 6. The photodegradation is efficient even after four cycles. This suggests that the composite has good stability and reusability. There is an increase in radiation time before total degradation, which is due to the mass loss of the photocatalyst during each recovery step.

4. Discussions

The photocatalysis of graphene-ZnO composites is generally well-known. The valence and conduction band of ZnO have a work function of -7.25 eV and -4.05 eV (versus vacuum) [34], respectively, while the work function of graphite is -4.6 eV [35]. The incident UV radiation causes electrons in ZnO to migrate from the VB to the conduction band. The lower work function of the CB of ZnO compared to graphite allows these excited electrons to transfer to graphite. This reduces electron/hole pair recombination and leads to more efficient charge separation in ZnO leaving more charge carriers in graphite to form reactive species for the degradation of MB molecules [36, 37]. This is the same mechanism that we have with our samples. Existing literature [38–46] on the successful photodegradation by zinc oxide-graphene/graphene oxide/graphite oxide composites reported various methods of synthesizing these composites. To the best of our knowledge, this is the first work reporting on the zinc oxide-graphite synthesis by a simple grinding method. It is, therefore, imperative to look at how this fundamental mechanism relates to our results.

The general result is that regardless of the relative amounts of graphite and ZnO or the annealing temperature of the composites, ZnO and graphite retain their crystalline structure. XRD and Raman spectroscopy measurements confirm this, FESEM supports this, and TG-DTA complements this confirmation for the annealed samples. Raman spectroscopy also provides a measure of the relative number of defects present particularly in graphite. Thus, we can eliminate the idea that photocatalytic activity depends on the crystal

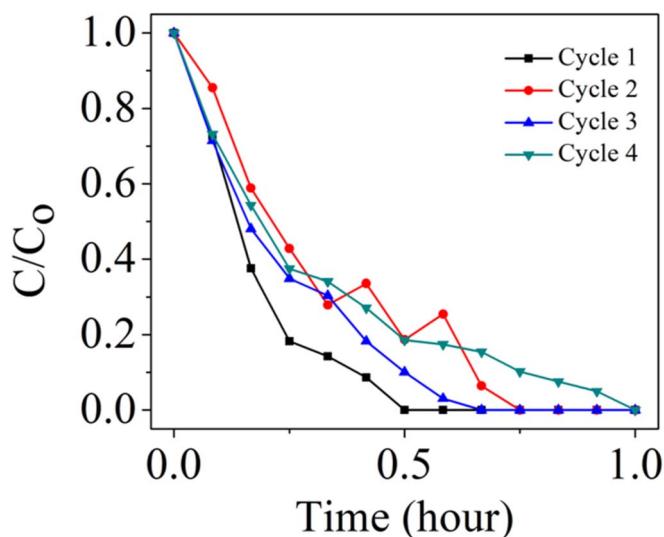


Figure 6. Relative concentration of MB after reusing three times.

structure of the composite material. We also observe from Raman measurements that as the ratio of the amount of graphite to ZnO is increased, I_D/I_G ratio also increases.

The photocatalytic activity was best seen for samples ground for 2 h. Recent work [16] has shown that decreasing the size of zinc oxide particles enhances the photodegradation of rhodamine-B because of the increased surface area of the zinc oxide particles. With grinding, more zinc oxide particles adhere to the graphite surface and form agglomerates. We suspect that further grinding results in the uneven agglomeration and less homogeneous morphology of the zinc oxide particles [47], which leads to decreased photocatalytic activity. Furthermore, graphite is necessary for good agglomeration, which potentially explains why no photocatalytic activity by zinc oxide was observed when the samples were ground.

If we compare the TRPL and TIPL measurements of these composites to pure ZnO, we see that UV emissions of GZ composites are more intense and have longer average lifetimes compared to pure ZnO. Adding graphite enhances the UV emission of ZnO and increases the emission lifetime due to the reduced recombination rate. This implies that the photocatalytic activity is considerably enhanced due to the synergistic effect between graphite and ZnO. There is reason to believe that a chemical binding may occur between graphite and zinc oxide based on a similar study [48, 49]. Whether the nature of the synergy between graphite and ZnO is chemical or otherwise is for further investigation in future work.

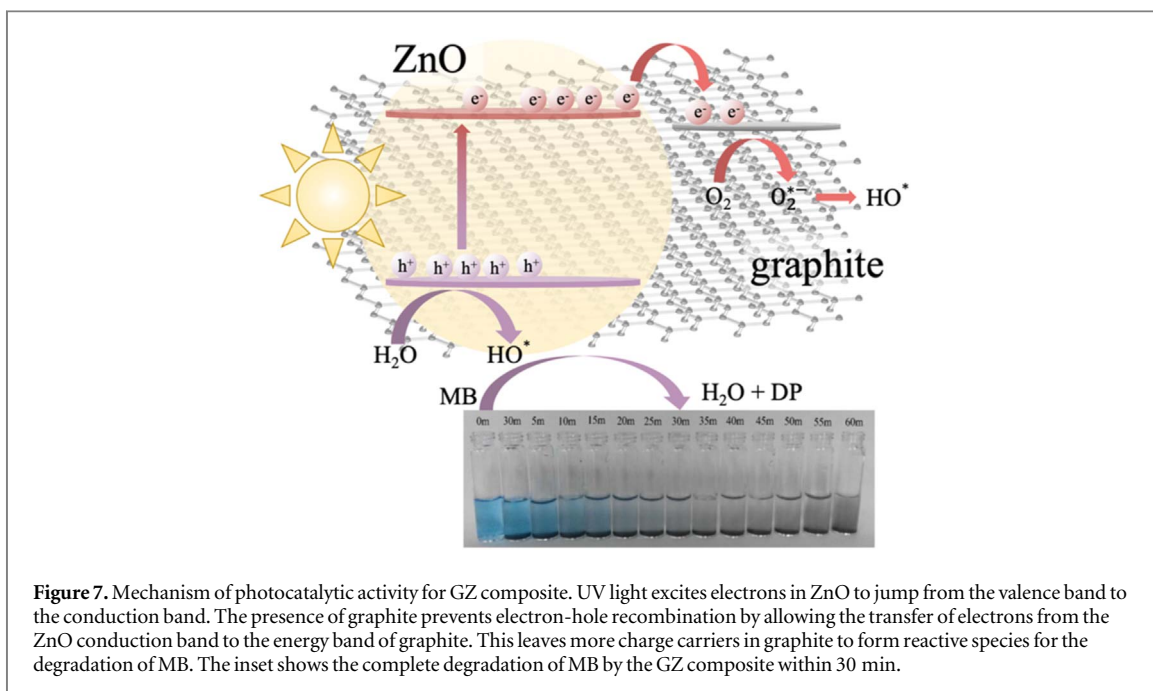
The mechanism of photocatalytic activity (figure 7) begins with the excitation of electrons in ZnO with UV light, jumping from the valence band to the conduction band. The presence of graphite prevents electron-hole recombination by allowing the transfer of electrons from the ZnO conduction band to the energy band of graphite. This leaves more charge carriers in graphite to form reactive species for the degradation of MB. The inset depicts how this degradation occurs over a period of 30 minutes.

In general, the GZ composite is highly effective in the degradation of MB. Without grinding, the best result was obtained from an equal mass ratio of graphite to ZnO. We speculate that the increased surface area due to an even agglomeration of the zinc oxide particles on the graphite surfaces is responsible for the photocatalytic degradation by the composite. Further, grinding results in the more uneven agglomeration and less effective photocatalytic degradation. On the other hand, with a relatively large amount of ZnO compared to graphite, absorption takes place. As supported by the TIPL and TRPL measurements, the lack of graphite reduces the photocatalytic activity due to the enhanced electron/hole recombination in ZnO and reduced charge separation by the graphite.

Finally, this work presents photocatalytic degradation by GZ composites, in contrast to the more extensively studied graphene- or graphene oxide- or graphite oxide composites. The methodology we presented is straightforward, simple, and very effective, without the need for any chemical processing, or, in fact, any other processing step.

5. Conclusions

GZ composites were synthesized via mechanical grinding and utilized for the photocatalysis of methylene blue under UV irradiation. The novelty in this work is that we utilized a facile process to synthesize GZ composites, which requires a very simple step of mechanical grinding without any thermal or chemical treatment, having



superior photocatalytic performance compared to most techniques which require numerous steps and complicated chemical reactions. The photocatalytic degradation of MB by the GZ composites under UV irradiation was enhanced with grinding compared to the control samples, pure ZnO, pure graphite, graphene oxide, and unground GZ composites. We suggest that the enhancement is due to the even agglomeration of the zinc oxide particles on the graphite surface due to the grinding process. TRPL and TIPL spectroscopy implies the excellent binding between ZnO and graphite, which greatly contributes to the decreased charge recombination resulting in the superior photocatalytic activity observed with our samples. The origin of the synergistic effect between the ZnO and graphite needs further investigation.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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