Graphene-Coupled ZnO: A Robust NIR-Induced Catalyst for Rapid Photo-Oxidation of Cyanide

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ABSTRACT: Herein, we report the modulation of ZnO for enhancement of its ability toward plasmonic absorption of near-infrared (NIR) photons through coupling of graphene (GR). The reported modification led GR–ZnO to be a promising photocatalyst by the complete removal of poisonous and nonvolatile potassium cyanide from water. The photocatalytic degradation of cyanide was revealed by exposing it to NIR laser and comparing with the rate of UV, visible, and sunlight using their apparent reaction rate constants derived from the Langmuir–Hinshelwood model. The heteronanostructured GR–ZnO promoted rapid photo-oxidation of cyanide under illumination with NIR laser rather than UV, visible, and sunlight. It was assessed that the photothermal effect (PTE) is the main cause for higher catalytic efficiency of GR–ZnO in the presence of NIR radiations. Except for the NIR radiations, GR–ZnO does not show any indication of PTE by irradiating with UV, visible, or sunlight. On account of its significance, the PTE of GR–ZnO in KCN solution was evaluated and compared with its individual components viz., GR and ZnO upon exposure to a 980 nm laser system. Furthermore, it has been revealed that the PTE of GR–ZnO was proportional to its concentration. In addition to its effectiveness in the degradation of cyanide, GR–ZnO retained its special structure and exhibited an outstanding photostability after its repeated use in three successive cycles.

1. INTRODUCTION

It is identified that the distribution of energy in the solar spectrum over earth’s surface is about 54.3% of near-infrared (NIR, 760–3000 nm), 38.9% of visible (vis, 400–760 nm), and 6.8% of ultraviolet (UV, <400 nm) range. Apart from the abundant availability of NIR light in solar energy, majority of the present research is devoted to the design of heterogeneous catalysts which are exceptionally active in UV and visible energy. Therefore, fabrication of NIR-active heterogeneous photocatalysts is one of the current critical needs for the proficient use of solar energy. It is recognized that the semiconductor-based catalysts are promising candidates for conversion of solar energy, although the absorption aptitude of semiconductor to NIR radiations is absolutely low. Under this circumstance, it is identified that the semiconductor catalysts are not ideal and their performance is poor upon exposure to NIR radiations. Hence, it is a challenging task to improve the absorption ability of semiconductors to NIR radiations and creating them as robust NIR-operating catalysts.

Zinc oxide (ZnO), a direct band gap II–VI semiconductor is recognized as a current frontline photocatalyst because of its wide band gap, high exciton binding energy, and excellent electron mobility of 3.37 eV, 60 meV, and 200–300 cm² V⁻¹ s⁻¹, respectively. In addition, ZnO possesses tremendous photosensitivity and offer an elevated driving force for oxidation and reduction processes. The electron mobility in ZnO is nearly 2 orders of magnitude higher than that in TiO₂. However, ZnO is highly responsive to UV light; therefore, in the presence of sunlight, ZnO can absorb only about 7% of UV radiation available, which forbids the real employment of ZnO in photocatalysis. Therefore, extending the band gap of ZnO into the NIR region and elevating its photocatalytic performance by making it responsive to NIR photons is the current major interest. ZnO exhibits excellent tunable plasmonic absorption especially in the NIR region; hence, it is a good candidate for the construction of plasmon-enhanced photocatalysts. An additional cause for the current limited applications of ZnO is its photocorrosive nature. Therefore, to overcome these confines, the binding of ZnO with a secondary functional material such as graphene (GR) is an superlative premise as GR holds unique properties such as high specific surface area (~2600 m²/g) and excellent mobility of charge carriers (200 000 cm² V⁻¹ s⁻¹), desirable for an optimum photocatalyst. In GR, the electrons behave as massless Dirac fermions, and it facilitates the photoinduced charge separation and inhibits the electron–hole recombination during photocatalysis. In addition, the single-layered GR possesses zero band gap, and hybridizing GR with ZnO could modify its band gap and result in charge transfer between ZnO and GR, enhancing the lifetime of photogenerated charge.
Moreover, the heterojunction electric field created over the interface of GR and ZnO because of the variation in Fermi levels cause rapid transfer of photogenerated electrons from the surface of ZnO to GR, thus enhancing the catalytic activity of the catalyst. Moreover, the presence of GR with ZnO can significantly improve the absorption level of both contaminants and photons of light over the surface of a catalyst. Over all as fascinating individuals, the assembly of GR and ZnO could result in an exceptional hybrid structure with enhanced photocatalytic efficiency.

Cyanide is known for its toxicity and can cause irreparable adverse effects on living organisms. The short-term exposure to cyanide leads to rapid breathing, tremors, and other neurological effects, whereas its long-term exposure results in rapid weight loss, thyroid effects, and nerve damage and might cause death in severe condition. Under this circumstance, cyanide is still employed in many industrial processes including electroplating, metal processing, petroleum refining, steel hardening, photographic applications, and hydrometallurgy. Moreover, cyanide is employed in the production of organic chemicals such as nitrile, nylon, acrylic plastics, and synthetic rubber. After its usage, cyanide is released through industrially generated wastewater as a hazardous material owing to its high solubility in water. Therefore, to prevent its harmful effects and protect the environment and water resources, cyanide containing effluents should be treated for its complete removal before releasing. Therefore, because of its importance, herein, we reported an alternate method for the complete removal of potassium cyanide using a novel nanostructured photocatalyst, GR–ZnO, generated by the immobilization of ZnO nanotrapezoids (NTs) over the surface of GR nanosheets. The GR–ZnO was able to remove the KCN entirely by the process of photo-oxidation after irradiating with NIR radiations. Furthermore, the rate of photo-oxidation of KCN upon exposure to NIR laser was compared with that of UV, visible, and sunlight. It has been exposed that the photothermal effect (PTE) is the main cause for rapid degradation of KCN, which occurred in the presence of NIR laser.

2. RESULTS AND DISCUSSION

The X-ray diffraction (XRD) of GO (Figure 1a) revealed a high intensity peak at 9.9° corresponding to its (002) crystallographic plane, and the additional low-intensity peak appeared at 42.7° was indexed to the (100) plane of GR. It was found that the interlayer d-spacing value in GO (0.89 nm) was efficiently higher than the value calculated for graphite (0.34 nm) (Figure 1b), which is accounted for the introduction of oxygen-containing functional groups such as carboxyl, hydroxyl, and epoxy groups and grafting of water molecules to the surface of GO. The significant difference perceived in the value of the interlayer d-spacing between graphite and GO indicates the successful conversion of graphite to GO. After subjecting the mixture of GO and zinc nitrate to the hydrothermal process, the resulting GR–ZnO (Figure 1c) provided the well-resolved peaks analogous to (100), (002), (101), (102), (110), (103), (200), (112), (201), (004), and (202) crystallographic planes of hexagonal ZnO at 31.8°, 34.5°, 36.2°, 47.5°, 56.6°, 62.8°, 66.4°, 67.9°, 69.1°, 72.6°, and 76.9°, respectively (JCPDS no. 36-1451). In addition, a weakly resolved peak at 23.7° was found, which depicted (002) reflection of GR. This peak of GR in GR–ZnO can be distinctly identifiable in Figure S1. The lower intensity of the GR peak in GR–ZnO could be ascribed to the successful exfoliation of GR nanosheets due to anchoring of ZnO NTs over their surface. Also, the absence of a characteristic peak related to GO in GR–ZnO facilitates the successful conversion of GO to GR. It is found that there is no considerable shift was recorded in the position of ZnO reflections in GR–ZnO compared to pristine ZnO (Figure 1d), which reveals the nondisruption of the crystalline structure of ZnO after its conjugation with GR nanosheets. Therefore, the GR did not dope in the crystal lattice of ZnO, instead the GR nanosheets provided an ideal platform to grow ZnO NTs. Moreover, the coupling of ZnO with GR has prevented the restacking of GR nanosheets in GR–ZnO.

The Raman spectrum recorded for GO (Figure 2a) demonstrated two characteristic peaks situated at 1328 and 1598 cm⁻¹, and these peaks are assigned as D and G band, respectively. The D band is related to the breathing mode of k-point phonons of A1g symmetry that arise owing to local defects and disorder, particularly at the edges of GR, whereas the G band is ascribed to the E2g phonon mode of sp²-hybridized carbon atoms. The spectrum of GR–ZnO (Figure 2b) has displayed both D and G bands located at 1304 and 1588 cm⁻¹, respectively. The blue shift observed with D and G bands for
GR–ZnO compared to GO details the successful conversion of GO to its reduced form, GR by a hydrothermal process. The characteristic peak in GR–ZnO was slightly shifted compared to the spectrum of GR (Figure 2c), which is ascribed to the structure of GR in GR–ZnO that was not ruined by its conjugation with ZnO. There are no obvious characteristic peaks observed for ZnO (Figure 2d) in the measured region; therefore, the minute shift in the peaks observed for GR–ZnO compared to GR is accounted for the strong interaction that persists between GR nanosheets and ZnO NTs. However, the intensity ratio of D and G bands ($I_D/I_G$) calculated for GO was 1.14, which was lower than the ratio found for GR–ZnO (1.31). This indicates the increase in the number of smaller sp² domains in GR–ZnO. However, this ratio for GR was found to be 1.61, which is higher than the value calculated for GR–ZnO. This indicates that the defective sites persisting over GR nanosheets were reduced by the deposition of ZnO NTs over their surfaces. Furthermore, the FWHM of the D band for GO and GR was found to be 124 and 94 cm⁻¹, respectively, whereas it was 130 cm⁻¹ for GR–ZnO. This attenuation reveals that the anchoring of ZnO NTs with GR nanosheets improves the degree of crystallinity in GR. The FT-IR spectrum of GO (Figure 3a) has exhibited the characteristic absorption bands consistent with oxygen-containing functional groups, viz., $\text{O–H}$ stretching of water and $\text{C–O}$ stretching of COOH groups at 3395 and 1719 cm⁻¹, respectively. The epoxy symmetrical ring $\text{C–O}$ deformation vibrations or phenolic $\text{C–O–H}$ stretching was observed at 1161 cm⁻¹ and the alkoxy $\text{C–O}$ stretching was observed at 1039 cm⁻¹. In addition, the representative band owing to aromatic $\text{C=\pi\pi}$ vibrations mixed with $\text{–OH}$ of water was found at 1620 cm⁻¹. Compared to GO, the spectrum of GR–ZnO (Figure 3b) did not exhibit any absorption band related to oxygen-containing functional groups; instead, it displayed a new band at 1505 cm⁻¹ generated by the skeletal vibration of GR. The additional absorption band displayed at 551 cm⁻¹ in Figure 3b is accounted for vibrations of $\text{Zn–O}$.

The efficient exfoliation of GO prepared by oxidation of graphite is accessible with its FESEM image shown in Figure 4a. The GO nanosheets possess a two-dimensional structure having layered sheet morphology with a wrinkled surface. In addition, the porous structure of GO nanosheets generated by the opening of planar carbon networks wedged at the edge of the crystallite due to oxidation is distinctly observable. ZnO (Figure 4b) exhibits the formation of uniform nanocrystals, which have a tetragonal trapezoid shape with a smooth surface. The well-faceted tetragonal end planes of ZnO NTs designate their single crystalline nature. The GR–ZnO nanocomposite (Figure 4c,d) demonstrates the deposition of homogeneous ZnO NTs and their dense packing over GR nanosheets. Furthermore, the GR nanosheets are clearly definable, and they have typical crumpled sheet-like morphology. The morphology of ZnO NTs found in pristine ZnO (Figure 4b) and GR–ZnO nanocomposite (Figure 4c,d) is identical, such that the inherent structural morphology of ZnO NTs is retained after their coupling with GR nanosheets also. During in situ formation of ZnO NTs, the GR nanosheets behave as a supportive template by providing the active sites for nucleation to ZnO, which induces uniform distribution of ZnO NTs over GR nanosheets.

The sequential washings performed during purification of GR–ZnO could not lead to the detachment of ZnO NTs from GR nanosheets, which reveals the strong adherence of ZnO NTs over GR nanosheets and the intimate contact existing between them. The elemental composition of GR–ZnO was analyzed by energy-dispersive spectrometry (EDS) (Figure S2), and this indicates the presence of $\text{C}$, $\text{Zn}$, and $\text{O}$ elements; of these, $\text{Zn}$ and $\text{O}$ signals are generated by ZnO NPs, and the strong C signal is originated from GR nanosheets. The EDS of GR–ZnO depicts the presence of only $\text{C}$, $\text{Zn}$, and $\text{O}$ elements, which reveals the purity of GR–ZnO.

The UV–vis–NIR spectrum of GO shown in Figure 5a demonstrated the characteristic $\pi\rightarrow\pi^*$ transitions of aromatic $\text{C–C}$ bonds and $\pi\rightarrow\pi^*$ transitions of $\text{C=\pi\pi}$ in terms of an absorption band at 229 nm and a shoulder around 300 nm, respectively. The spectrum of ZnO (Figure 5b) possesses the typical absorption at 365 nm, which is comparable with the value reported for ZnO. The spectrum of GR–ZnO (Figure 5c) displayed a shoulder around 215 nm and a weak absorption at 280 nm. Both of these are barely recognizable in Figure 5c, whereas distinctly visible in Figure S3. These absorptions are corresponding to $\pi\rightarrow\pi^*$ transition of GR, and it is consistent with the absorption found in aqueous stable GR. Apart from this, an obvious band was revealed at 369 nm in Figure 5c, which corresponds to ZnO. Therefore, the existence of both GR and ZnO in GR–ZnO has been experimentally observed by its UV–vis–NIR spectrum. Moreover, GO, ZnO, and GR–ZnO have exhibited strong absorption in the NIR region, which signifies the high absorption ability of these samples to NIR radiations.

The photocatalytic activity of GR–ZnO was assessed by photodegradation of potassium cyanide under illumination using a NIR laser system in consideration of its nonvolatility and common availability of cyanide in industrial waste water. Figure 6 shows the kinetic profile of degradation of KCN over the surface of GR–ZnO and its comparison with discrete components viz., GR and ZnO. Interestingly, complete or 100% degradation of KCN occurred in 60 min of exposure in the presence of GR–ZnO, whereas it was 46 and 59% for GR and ZnO, respectively. It reveals that the absorption of NIR radiations over the surface of GR–ZnO has been significantly improved because of the complex structure generated by the strong binding of ZnO NTs to the surface of GR nanosheets. However, the degradation rate of KCN measured without any catalyst in the presence of NIR laser and with catalyst in the absence of NIR laser was minute or negligible, which implies...
that both the catalyst and light source are absolutely necessary for the process of photodegradation.

In addition, the degradation of KCN was evaluated by replacing the NIR laser with UV, visible, and sunlight under identical experimental conditions used in NIR to reveal the effect of different light sources (Figure 7). Prior to their comparison, the influence of power of light by selecting visible light-producing lamps with different power viz., 40 and 90 W was estimated. It was observed that the degradation of KCN was not significantly influenced by varying the power of lamps (Figure S4), which elucidates that the degradation of KCN does not specifically depend on the power of the light source. Furthermore, upon exposure to UV light, the complete degradation of KCN was attained in 90 min in the presence of GR−ZnO, whereas it occurred at 140 min upon irradiation with visible light (90 W). However, the sunlight was unable to degrade the KCN completely; instead, it was degraded about 53% upon its exposure for 140 min. In detail, the photocatalytic degradation of KCN was quantitatively estimated by comparing the apparent reaction rate constants ($k_{app}$) calculated from a simple first-order rate equation derived from the Langmuir−Hinshelwood (L−H) model.\textsuperscript{20,22} In each experiment, the initial

Figure 4. FESEM images of (a) graphene oxide, (b) ZnO, and (c,d) GR−ZnO.

Figure 5. UV−vis−NIR spectra of (a) graphene oxide, (b) ZnO, and (c) GR−ZnO.

Figure 6. Degradation profile of KCN over the surface of GR−ZnO, ZnO, and graphene by irradiating with NIR laser.

Figure 7. Degradation profile of KCN in the presence of GR−ZnO upon exposure to different light sources.
concentration of KCN was low; thus, under this condition, the L–H equation becomes
\[
\ln\left[\frac{C_0}{C}\right] = k_{\text{app}} t
\]
where \(C_0\) is the initial concentration of KCN and \(C\) is its concentration at particular time of photocatalytic reaction. \(k_{\text{app}}\) is the apparent rate constant of the reaction and \(t\) is the time of irradiation. The L–H plots obtained for the degradation of KCN were linear, which suggests that the photodegradation of KCN follows the pseudo-first-order reaction kinetics (Figure 8). Accordingly, the values of \(k_{\text{app}}\) calculated for illumination of

**Figure 8.** Langmuir–Hinshelwood plot for photodegradation of KCN over the surface of GR–ZnO by illuminating with different light sources.

NIR, UV, visible, and sunlight were found to be 0.0722, 0.0363, 0.0242, and 0.0065 min\(^{-1}\), respectively. The rapid photodegradation of KCN was observed by irradiating the NIR laser compared to other light sources. The promoted degradation of KCN upon illumination of NIR laser could be related to the generation of PTE. As it has been already revealed that NIR radiations are primarily accountable for PTE, it plays a leading role in the enhancement of the photocatalytic process. Therefore, in order to evaluate the PTE of GR–ZnO, its dispersion in KCN solution was exposed to NIR radiations and the rise in temperature was recorded. The GR–ZnO dispersion at its concentration levels of 0.5, 1, and 2 mg/mL in KCN solution were illuminated with a 980 nm NIR laser, and the elevation in temperature was monitored. Figure 9 compares the PTE of GR–ZnO with GR and ZnO in KCN solution. By illumination with NIR laser for 7 min, the total temperature rise for GR–ZnO was 49.7 °C. Under similar conditions, temperature elevation recorded for GR was 47.6 °C, and it was 44.2 °C for ZnO NTs (Table 1). Conversely, the PTE shown by KCN solution and water was 17.1 and 8.3 °C, respectively. Therefore, the PTE of KCN and water were significantly lower than the PTE of GR, ZnO, and GR–ZnO. In particular, the PTE of GR–ZnO was found to be considerably higher than both, GR and ZnO, and this improvement is accounted for a special structure created in GR–ZnO by anchoring of ZnO NTs over the surface of GR nanosheets. The presence of GR with ZnO has substantially improved the aptitude of GR–ZnO in terms of their ability to absorb NIR radiations and their conversion to thermal energy. Moreover, it was found that the PTE of GR–ZnO in KCN solution was directly proportional to its concentration (Figure S5).

Specifically, the PTE of GR–ZnO was systematically enhanced with respect to its concentration of 0.5, 1, and 2 mg/mL. The PTE of GR–ZnO was measured for five cycles to evaluate its photostability (Figure 10). However, the absence of attenuation in thermal efficiency of GR–ZnO was noticed by its employment in five cycles, which demonstrates the excellent photostability of GR–ZnO.

Furthermore, in consideration of the practical application of a catalyst, its recycling, stability, and employment in further cycles are crucial. Therefore, the GR–ZnO was recovered after its application in the degradation of KCN by illuminating with NIR laser through centrifugation and used in successive four cycles. It was observed that after its employment in five cycles, the photocatalytic activity of GR–ZnO was not considerably reduced (Figure S6). Apart from this, to verify the photostability, phase composition, and structure of GR–ZnO after its irradiation in five consecutive degradation cycles, the XRD pattern was recorded and compared with that of unused GR–ZnO (Figure S7), and no significant modification was found among those. This suggests that GR–ZnO possesses sufficient photostability for its reuse, and the photodegradation process could not rupture the structure of GR–ZnO and detach the ZnO NTs from the surface of GR nanosheets.

Overall, the mechanism for the degradation of cyanide in terms of its photooxidation over the surface of GR–ZnO can be illustrated as

\[
\begin{align*}
gR–ZnO + 2h^+ & \rightarrow gR–ZnO (2h^+2e^-) \\
o_2 + 2e^- + H_2O & \rightarrow 2OH^- \\
2OH^- + 2h^+ & \rightarrow 2OH^* \\
CN^- + 2OH^* & \rightarrow OCN^- + H_2O \\
OCN^- + O_2 & \rightarrow 2CO_2 + N_2
\end{align*}
\]

The process of catalytic degradation of cyanide is initiated by photoexcitation of ZnO that exists over GR nanosheets, followed by the generation of electron–hole pairs over the surface of GR–ZnO. Then, the electrons react with oxygen and water molecules to produce hydroxide ions (OH\(^-\)), and these hydroxide ions interact with holes to form hydroxyl radicals.
Thus, the created hydroxyl radicals oxidize the CN$^-$ into an intermediate species, cyanate (OCN$^-$), and it further oxidizes to CO$_2$ and N$_2$. The overall mechanism is schematically depicted in Figure 11.

3. CONCLUSIONS

In conclusion, the coupling of GR with ZnO significantly enhances the efficiency of ZnO toward absorption of NIR radiations. Unlike the traditional ZnO-based photocatalysts, which can assist the absorption of exclusive UV and visible radiations, herein, ZnO extends its absorption ability toward NIR photons. The heterostructured GR–ZnO is an excellent NIR-induced photocatalyst and is able to remove the cyanide completely from water by the process of photo-oxidation. For the enhancement of the photocatalytic activity of GR–ZnO by irradiating with NIR radiations, the PTE plays the key role. The GR–ZnO is a robust photocatalyst with excellent photo-stability, and it can be repeatedly used several times without reduction in its catalytic activity. Owing to its potential in the removal of cyanide, GR–ZnO can provide an alternate path to address the environmental issues. Overall, this study opens up wide possibilities in utilizing NIR radiations to improve the process of photocatalysis and designing of outstanding NIR-active photocatalysts.

4. EXPERIMENTAL SECTION

4.1. Materials. The chemicals used in the experiments were from Aldrich and were used as received without any additional purification. The aqueous solutions were prepared using ultrapure water produced by the Millipore’s Milli-Q Plus system.

4.2. Synthesis of GO and GR–ZnO. Graphene oxide (GO) was synthesized by graphite powder by the Hummers and Offeman method.20,24 The GO was implemented in the synthesis of GR–ZnO using the method reported priorly.25 To mention briefly, GO (10 mg) was dispersed in ethanol (15 mL) by sonication, followed by the addition of aqueous solution of zinc acetate (10 mL, 1 mmol). The resulting suspension was

| sample            | concentration of dispersion in KCN solution (mg/mL) | initial temperature before irradiation (°C) | final temperature after irradiation (°C) | ΔT (T$_{final}$ − T$_{initial}$) (°C) |
|-------------------|----------------------------------------------------|-------------------------------------------|------------------------------------------|--------------------------------------|
| GR–ZnO            | 2                                                  | 24.5                                      | 74.2                                     | 49.7                                 |
| GR                 | 2                                                  | 24.4                                      | 72.0                                     | 47.6                                 |
| ZnO                | 2                                                  | 24.2                                      | 68.4                                     | 44.2                                 |
| GR–ZnO            | 1                                                  | 24.5                                      | 65.9                                     | 41.4                                 |
| GR–ZnO            | 0.5                                                | 24.2                                      | 45.4                                     | 21.2                                 |
| KCN                | 24.5                                               |                                           | 41.6                                     | 17.1                                 |
| water              | 24.4                                               |                                           | 32.7                                     | 8.3                                  |

Table 1. Temperature Variation Observed for the Samples by Illuminating with a 980 nm Laser for 7 min

Figure 10. Temperature variation measured for dispersion of GR–ZnO (2 mg/mL) in KCN solution for five cycles upon illumination with NIR laser.

Figure 11. The mechanism proposed for photo-oxidation of cyanide over the surface of GR–ZnO.
allowed to stir for 15 min, and an aqueous solution of NaOH (8 mmol) was added. Then, the mixture was transferred to a Teflon-lined stainless steel autoclave after stirring for 15 min. The autoclave was permitted to heat at 140 °C for 8 h, and the product, GR−ZnO, was purified by successive processes of centrifugation and washing with ethanol and DI water.

4.3. Photo-Oxidation of KCN. The photo-oxidation of KCN in the presence of GR−ZnO was assessed by illuminating the NIR (980 nm, 2 W/cm²), UV (450 W), visible (40 and 90 W), and sunlight. The process of photo-oxidation was studied in the natural atmosphere, without any external source of aeration. For all experiments, GR−ZnO (10 mg) was added to 100 mL aqueous solution of KCN (10 mg L⁻¹) and the suspension was stirred in the dark for 30 min to complete adsorption/desorption of KCN over the surface of GR−ZnO. Prior to the photocatalytic process, pH of the reaction mixture was adjusted in between 8 and 10 to prevent the evolution of toxic hydrogen cyanide gas. The reaction mixture was transferred to a double-walled quartz photocatalytic reactor having the facility of water circulation in order to maintain the catalytic mixture at room temperature. Subsequently, the reaction mixture was exposed to different light sources with constant magnetic stirring and at a given interval of time, and 5 mL of KCN suspension was taken out. Because KCN could not absorb in the visible region, its concentration was estimated with picric acid Fisher and Brown’s method. In detail, 5 mL of KCN suspension after photocatalysis was added to 5 mL aqueous solutions of 0.5% (w/v) picric acid and 0.25 M Na₂CO₃. The resulting solution was placed in a boiling water bath for 5 min, diluted to 15% with distilled water, and cooled. Then, the absorbance of the solution was evaluated using a UV−vis−NIR spectrophotometer at 520 nm using picric acid solution as reference. Using the absorbance value, the photodegradation rate of KCN was determined.

4.4. Photothermal Effect. The PTE of samples was assessed by irradiating their suspension in KCN solution with 980 nm laser having an output power of 2 W/cm² (ArmaLaser Inc., United States). In each, a cuvette containing 1 mL of sample, dispersed in KCN solution was irradiated by laser. The resulting variation in the temperature of suspension was recorded by a digital thermometer (Hanna, model: HI93510).

4.5. Characterization. Scintag X-ray diffractometer (PAD X), equipped with a Cu Kα photon source (45 kV, 40 mA) at a scanning rate of 3°/min was used to record XRD. Smiths ChemID diamond attenuated total reflection (DART) spectrometer was utilized to record the ATR−IR spectra of samples. A JEOL JXA-8900 microscope was employed to obtain the SEM images and EDS, and Renishaw R-3000QE was used to acquire Raman spectra. The Jasco V-770 spectrophotometer was used for UV−vis−NIR spectra of samples.

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