Synthesis of Superparamagnetic Cu_{0.4}Zn_{0.6}Fe_{2}O_{4}-Implanted Bi_{2}S_{3}-Capped TiO_{2} 2D and 3D Nanostructures for Visible Light Photocatalysis

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ABSTRACT: Sharp narrow nanopetal-like and wrinkled nanoball-like cubic Cu_{0.4}Zn_{0.6}Fe_{2}O_{4}-implanted orthorhombic Bi_{2}S_{3}-capped anatase TiO_{2} heterostructures have been synthesized by a two-step hydrothermal process in acidic and basic environments. They have been characterized by high-resolution scanning and transmission electron microscopies, energy-dispersive X-ray spectroscopy, selected area electron and powder X-ray diffractometries, vibrating sample magnetometry, UV–visible diffuse reflectance and photoluminescence spectroscopies, and nitrogen adsorption–desorption analysis. Both the nanostructured composites are superparamagnetic. While the nanocomposite synthesized in acidic environment absorbs in the entire visible and UV spectral regions, the absorption edge of nanocomposite obtained in basic environment narrowly misses the red end of the visible spectrum. The emission spectra of both the nanomaterials are strikingly similar, indicating similar crystal defects in anatase TiO_{2} lattice of both the nanocomposites. Although both the nanocomposites degrade dye under visible light, the photocatalytic activity of the sample obtained in acidic environment is superior to that prepared in basic condition. The enhanced photocatalytic activity of the nanocomposite synthesized in acidic environment is rationalized in terms of nanostructure, surface area, and optical properties.

INTRODUCTION

Population growth with enhanced per capita purchasing power in developing countries exerts pressure on the per capita availability of safe water. Water pollution due to industrial effluents and domestic sewage is a common occurrence in such territories. Semiconductor-photocatalytic mineralization of organic pollutants is an emerging technology to treat industrial effluents and domestic sewage; it requires no chemical but only air and a semiconductor photocatalyst, where the latter is recoverable for reuse. TiO_{2} is a cheap, nontoxic, stable, industrially manufactured n-type semiconductor with unique optoelectronic properties, and its use as a self-cleaning material has turned commercial. Its band gap is ca. 3.2 eV and requires UV light radiation of wavelength less than 390 nm for photoactivation. The UV light in the natural sun shines on the earth surface is only about 4% of the total solar energy incident on earth. The sunlight shining on the earth surface is 1000 W m^{-2}, and the UV light contribution is only 40 W m^{-2}. Hence, development of photocatalytic materials that absorb visible light of the solar radiation is of interest, the requirement of artificial light is bypassed cutting the cost and the technology could be used in remote rural areas where availability of electricity is restricted. Bi_{2}S_{3} is an n-type narrow-band-gap (ca. 1.3 eV) semiconductor. It is black and absorbs all UV and visible light. Furthermore, it has a high absorption coefficient (ca. 10^4–10^5 cm^{-1}) and reasonable incident photon to electron conversion efficiency. Visible light photocatalytic mineralization of organic pollutants by nanostructured Bi_{2}S_{3} is well established. TiO_{2} could be sensitized and enabled to absorb light of longer wavelength, by coupling with a narrow-band-gap semiconductor such as Bi_{2}S_{3}. Bi_{2}S_{3}/TiO_{2} heterojunction enhances charge separation, and nanocrystalline Bi_{2}S_{3}/TiO_{2} shows improved photocurrent (J) with visible light. Further, Bi_{2}S_{3} nanoparticle/TiO_{2} nanotube heterostructure, fabricated by hydrothermal treatment, shows superior photoelectrochemical property to that of Bi_{2}S_{3} and TiO_{2}, all under sunlight at AM 1.5 (100 mW cm^{-2}). Visible light photocatalytic degradation of pollutants by Bi_{2}S_{3}/TiO_{2} heterojunction obtained by precipitation method or through hydrothermal treatment have been reported. Defect-free interfaces in Bi_{2}S_{3}/TiO_{2} nanorod–nanoparticle heterostructures favor electron–hole separation and transfer, exhibiting improved photocatalytic activity under visible light. Bi_{2}S_{3}/TiO_{2} heterojunction could be tailored to generate hydrogen; Bi_{2}S_{3} nanowire @ TiO_{2} nanorod heterostructure photoelectrochemically generates hydrogen under visible light. Recovery of the photocatalytic nanomaterials after mineralization of pollutants is a challenge for adoption of this technology by industries or domestic sewage treatment plants. Magnetic nanocore inside photocatalytic nanomaterial enables magnetic separation feasible. The buried magnetic core enables recovery of the magnetic photocatalyst nanoparticles through application of a magnetic field. The implanted magnetic nanocore is...
completely wrapped by the photocatalytic semiconductor, and this isolation forbids any physical contact between the magnetic core and pollutant molecules. The absence of magnetic core at the photocatalyst–effluent interface renders photocorrosion of the core impossible. With this in mind, we synthesized, through a two-step process, \( \text{Cu}_{0.4}\text{Zn}_{0.6}\text{Fe}_2\text{O}_4 \)-implanted \( \text{Bi}_2\text{S}_3 \)-capped \( \text{TiO}_2 \) nanostructures in acidic and basic environments, for application as magnetically retrievable visible light photocatalyst for environmental remediation. We used carbon microsphere, prepared by solvothermal carbonization of glucose,\(^24\) as a templating agent for first-stage synthesis, prior to \( \text{Bi}_2\text{S}_3 \)-capping.

## RESULTS AND DISCUSSION

**Morphology.** The high-resolution scanning electron microscopy (HRSEM) images of the samples synthesized in (i) acidic environment, \( \text{Cu}_{0.4}\text{Zn}_{0.6}\text{Fe}_2\text{O}_4/\text{TiO}_2\)-\( \text{Bi}_2\text{S}_3 \) (A) and (ii) basic environment, \( \text{Cu}_{0.4}\text{Zn}_{0.6}\text{Fe}_2\text{O}_4/\text{TiO}_2\)-\( \text{Bi}_2\text{S}_3 \) (B), are presented in Figure 1 under different magnifications. The nanocomposite obtained in acidic environment takes the form of narrow nanopetals while that prepared in basic environment

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**Figure 1.** HESEM images of the samples synthesized in acidic (a) and basic (b) environments.
appears to be wrinkled nanoballs. As the synthetic procedures adopted differ only by the addition of an acid (nitric acid) or a base (triethanol amine), it is concluded that the acidic or basic environment determines the morphology of the nano-composite. However, it is pertinent to state that the morphology of electrochemically synthesized fungus-like mesoporous Bi$_2$S$_3$ ball/TiO$_2$ nanotube arrays (balls with wrinkled surface)\textsuperscript{17} is similar to that of the sample synthesized

Figure 2. HRTEM images of the samples synthesized in acidic (a) and basic (b) environments.
in the present work in basic environment. The high-resolution electron microscopy (HRTEM) images of the samples prepared in acidic and basic environments are displayed in Figure 2. The nanocomposite obtained in acidic environment appears to be sharp, narrow, and petal-like in nanodimension. The sample prepared in basic environment looks like a nanolump with nanorods buried inside.

**Crystalline Structure.** The energy-dispersive X-ray spectroscopy (EDS) images of the samples synthesized in acidic and basic environments are presented in Figure 3. They show the presence of copper, zinc, iron, titanium, bismuth, sulfur, and oxygen, thus confirming the presence of the constituent elements of the obtained nanomaterials. The absence of any other element indicates the purity of the synthesized materials. The powder X-ray diffraction (XRD) patterns of precursor Cu_{0.4}Zn_{0.6}Fe_{2}O_{4} nanocrystals obtained in acidic environment show the interplanar distances of 1 1 0-, 2 0 0- and 0 2 0-planes of anatase TiO_{2}, respectively (JCPDS card no. 89-7409). The XRD pattern of the sample obtained in basic environment displays the 3 1 1- and 4 4 0-planes of orthorhombic Bi_{2}S_{3}. The observed interplanar distances (JCPDS no. 89-7409) are also observed in the HRTEM image. The corresponding images of the nanocomposite synthesized in basic environment display the interplanar distances of the 1 2 1-planes of orthorhombic Bi_{2}S_{3} (0.31 nm) and the 3 1 1-planes of cubic Cu_{0.4}Zn_{0.6}Fe_{2}O_{4} (0.30 nm, JCPDS no. 89-7409) is also observed in the HRTEM image.

**Surface Characteristics.** Catalytic activity of nanostructured semiconductor is largely influenced by its surface characteristics, which are evaluated through nitrogen adsorption process. The adsorption of nitrogen on both the nanocomposites are reversible, and Figure 7a presents the adsorption–desorption loops. Both the adsorptions are of type II isotherms, which indicate that the nanocomposites are nonporeous. The isotherms represent unrestricted monolayer-multilayer adsorption on Cu_{0.4}Zn_{0.6}Fe_{2}O_{4}/TiO_{2}-Bi_{2}S_{3}. Article

**Figure 3.** EDS of the materials obtained in acidic (a) and basic (b) environments.

**Figure 4.** XRD patterns of precursor Cu_{0.4}Zn_{0.6}Fe_{2}O_{4} nanocrystals and the samples synthesized in acidic [Cu_{0.4}Zn_{0.6}Fe_{2}O_{4}/TiO_{2}-Bi_{2}S_{3} (A)] and basic [Cu_{0.4}Zn_{0.6}Fe_{2}O_{4}/TiO_{2}-Bi_{2}S_{3} (B)] environments.
The specific surface areas of Cu_{0.4}Zn_{0.6}Fe_{2}O_{4}/TiO_{2}-Bi_{2}S_{3} (A) and Cu_{0.4}Zn_{0.6}Fe_{2}O_{4}/TiO_{2}-Bi_{2}S_{3} (B), determined by the Brunauer–Emmett–Teller (BET) method, are 26.76 and 18.26 m^{2} g^{-1}, respectively. The pore volumes of the samples synthesized in acidic and basic environments are 0.071 and 0.057 cm^{3} g^{-1}, respectively. The pore sizes of Cu_{0.4}Zn_{0.6}Fe_{2}O_{4}/TiO_{2}-Bi_{2}S_{3} (A) and Cu_{0.4}Zn_{0.6}Fe_{2}O_{4}/TiO_{2}-Bi_{2}S_{3} (B), obtained by the Barrett–Joyner–Halenda (BJH) method, are 3.93 and 5.12 nm, respectively.

Superparamagnetism. Figure 7b presents the magnetization (M) of Cu_{0.4}Zn_{0.6}Fe_{2}O_{4}/TiO_{2}-Bi_{2}S_{3} (A) and Cu_{0.4}Zn_{0.6}Fe_{2}O_{4}/TiO_{2}-Bi_{2}S_{3} (B) nanostructures as a function of applied field (H). The shape and size of the M–H curve are characteristic of the nanomaterials investigated, and the displayed hysteresis loops are of normal S-shape. The hysteresis curves afford the saturation magnetization (M_{s}), coercivity (H_{c}), and remanence magnetization (M_{r}). The “thickness” of the S-shaped loop at its middle shows the extent of hysteresis, which reflects the coercivity. Both the M–H loops are normal S-shaped and indicate the superparamagnetism of Cu_{0.4}Zn_{0.6}Fe_{2}O_{4}/TiO_{2}-Bi_{2}S_{3} (A) and Cu_{0.4}Zn_{0.6}Fe_{2}O_{4}/TiO_{2}-Bi_{2}S_{3} (B) nanostructures. The H_{c} values of Cu_{0.4}Zn_{0.6}Fe_{2}O_{4}/TiO_{2}-Bi_{2}S_{3} (A) and Cu_{0.4}Zn_{0.6}Fe_{2}O_{4}/TiO_{2}-Bi_{2}S_{3} (B), as obtained from the hysteresis loops, are 0.093 and 0.017 kOe, respectively. The very small coercivities confirm the superparamagnetism of both the nanocomposites synthesized.
The $M_S$ values of Cu$_{0.4}$Zn$_{0.6}$Fe$_2$O$_4$/TiO$_2$-Bi$_2$S$_3$ (A) and Cu$_{0.4}$Zn$_{0.6}$Fe$_2$O$_4$/TiO$_2$-Bi$_2$S$_3$ (B), as provided by the $M$–$H$ curves, are 0.27 and 0.66 emu g$^{-1}$, respectively. The hysteresis loops afford the $M_R$ values of Cu$_{0.4}$Zn$_{0.6}$Fe$_2$O$_4$/TiO$_2$-Bi$_2$S$_3$ (A) and Cu$_{0.4}$Zn$_{0.6}$Fe$_2$O$_4$/TiO$_2$-Bi$_2$S$_3$ (B) as 0.014 and 0.005 emu g$^{-1}$, respectively. The insignificant $M_R$ values further confirm both the synthesized composite nanostructures as superparamagnetic.

**Absorption.** Band gap excitation of semiconductor with light of appropriate wavelength is the basis of semiconductor photocatalysis. Diffuse reflectance spectroscopy (DRS) enables to probe the band gaps of semiconducting nanomaterials. Figure 7c shows the DRS of precursor Cu$_{0.4}$Zn$_{0.6}$Fe$_2$O$_4$ nanocrystals and nanostructured Cu$_{0.4}$Zn$_{0.6}$Fe$_2$O$_4$/TiO$_2$-Bi$_2$S$_3$ (A) and Cu$_{0.4}$Zn$_{0.6}$Fe$_2$O$_4$/TiO$_2$-Bi$_2$S$_3$ (B). The DRS displayed are in terms of $F(R)$, obtained from the measured reflectance ($R$) applying the Kubelka–Munk algorithm: $F(R) = (1 - R)^2/2R$. Although all of the stated nanomaterials show visible light absorption, their absorption edges are different. While the absorption edge of precursor Cu$_{0.4}$Zn$_{0.6}$Fe$_2$O$_4$ nanocrystals is not longer than 600 nm, the composite nanostructure synthesized in acidic condition absorbs visible and UV lights in the entire spectral range (200–800 nm). The absorption edge is blue-shifted on switching from acidic to basic environment while capping Cu$_{0.4}$Zn$_{0.6}$Fe$_2$O$_4$/TiO$_2$ with Bi$_2$S$_3$.

**Emission.** Photogenerated electron–hole pairs recombine predominantly, radiatively, nonradiatively, or by both processes, thereby suppressing the photocatalytic efficiency of the semiconductor nanocrystals. Photoluminescence study enables to probe radiative recombination of photoproduced charge carriers. The emission spectra of both the nanocomposites are presented in Figure 7d. Both the nanocomposites exhibit strong blue-green emission at 483 nm and prominent green emission centered around 522 nm. These two emissions stem from the TiO$_2$ anatase lattice. They are assigned to the transition of doubly trapped and singly trapped electrons in the oxygen vacancies to the valence band (VB) of TiO$_2$, respectively. The energy levels of the two types of oxygen vacancies are, respectively, 0.51 and 0.82 eV lower than those of the conduction band (CB) minimum. Because of the said energy levels, the photoformed electrons in the CB readily slip over to the two kinds of oxygen vacancies through nonradiative processes, and this is followed by radiative combination of VB holes with the trapped electrons in the two types of oxygen vacancies. Emission of fluorescence at two wavelengths is the consequence of the radiative combinations of electrons trapped at two energy levels with VB holes. The observed bands in the visible region (at about 2.35 and 2.35 eV) are ascribed to the radiative recombination of excitons of the shallow traps identified with oxygen vacancies and Ti$^{4+}$ adjacent to oxygen vacancies. Band edge-free excitons and -bound excitons also give rise to blue-green emission. The energy of green emission corresponds to transition of electron from deep-level donor of the ionized oxygen vacancies to the VB hole. The blue-green band is also attributed to charge-transfer transition from Ti$^{3+}$ to oxygen anion of TiO$_6$ octahedra associated with oxygen vacancies at the surface. The blue-green bound excitation emission is said to arise from trapping of free excitations near defects.

**Visible Light Photocatalysis.** Photocatalytic activities of both the nanostructured composites are tested with visible light employing methylene blue as the test substrate. Figure 8 displays the dye-degradation profiles in the presence of Cu$_{0.4}$Zn$_{0.6}$Fe$_2$O$_4$/TiO$_2$-Bi$_2$S$_3$ (A) or Cu$_{0.4}$Zn$_{0.6}$Fe$_2$O$_4$/TiO$_2$-Bi$_2$S$_3$ (B) under visible light illumination. The dye-decay profiles demonstrate the visible light photocatalytic activity of the title nanomaterials. In the absence of nanocomposites, the dye remains undegraded. Reuse of the nanocomposites as photocatalysts for dye degradation shows sustainable photocatalysis (tested up to four cycles; data not presented). Copper zinc ferrite is buried in TiO$_2$ lattice, and the low-solubility product of Bi$_2$S$_3$ (Ks $\sim 10^{-97}$) confers chemical stability down
Phase, and Bi$_2$S$_3$ in orthorhombic crystalline state are the crystal lattices present in both the synthesized nanocomposites. Nanocrystalline Cu$_{0.4}$Zn$_{0.6}$Fe$_2$O$_4$ absorbs in the wavelength region 600–200 nm. However, it is unlikely to be responsible for the observed photocatalytic activity of the synthesized nanocomposites. This is because it is implanted in anatase TiO$_2$ lattice; Cu$_{0.4}$Zn$_{0.6}$Fe$_2$O$_4$ is completely wrapped by TiO$_2$ lattice. TiO$_2$ capped with Bi$_2$S$_3$ fully shields the implanted Cu$_{0.4}$Zn$_{0.6}$Fe$_2$O$_4$ from the illuminated light. The band gap of TiO$_2$, which through a series of reactions affords ROS. The ROS are responsible for visible light photocatalysis. Orthorhombic Bi$_2$S$_3$ (black in color) absorbs in the entire visible spectrum (besides the UV light); its band gap is about 1.3 eV only. The visible light photoexcites Bi$_2$S$_3$ in the nanocomposites; electrons are promoted from VB to CB of Bi$_2$S$_3$. The CB potential of Bi$_2$S$_3$ is more negative than that of TiO$_2$. The VB potential of Bi$_2$S$_3$ is less than that of TiO$_2$. This favors thermodynamically the movement of electron from CB of Bi$_2$S$_3$ to CB of TiO$_2$. However, the VB potential of Bi$_2$S$_3$ is less positive than that of TiO$_2$. Hence, migration of hole from the VB of Bi$_2$S$_3$ to that of TiO$_2$ is energetically forbidden. Thus, the photogenerated electron–hole pairs are separated across the Bi$_2$S$_3$/TiO$_2$ heterojunction (Figure 9). The hole in the VB of Bi$_2$S$_3$ picks up an electron from the surface-adsorbed hydroxyl ion or water molecule generating the reactive oxidizing species (ROS), HO$. The CB electron migrated to TiO$_2$ jumps to the oxygen molecule adsorbed on TiO$_2$ lattice affording superoxide radical ion (O$_2^-$), which through a series of reactions affords ROS. The ROS are responsible for the photocatalytic degradation processes. Thus, in the synthesized 2D and 3D nanostructures, the implanted Cu$_{0.4}$Zn$_{0.6}$Fe$_2$O$_4$ serves as magnetic core, TiO$_2$ functions as photocatalyst, and the capped Bi$_2$S$_3$ acts as photosensitizer. Further, the high optical absorption coefficient of Bi$_2$S$_3$ ($\sim 10^5$ cm$^{-1}$) enables effective absorption of light by the synthesized nanostructures. Photodegradation of methylene blue in the presence of Cu$_{0.4}$Zn$_{0.6}$Fe$_2$O$_4$/TiO$_2$-Bi$_2$S$_3$ nanomaterials is unlikely a dye-sensitized reaction. This proposition stems from the facts that methylene blue degradation on Bi$_2$S$_3$ is a photocatalyzed one and methyl orange and rhodamine B dyes are also photocatalytically degraded by Bi$_2$S$_3$. Furthermore, Bi$_2$S$_3$-deposited TiO$_2$ photocatalyzes degradation of methyl orange, orange G, orange II, 4-hydroxybenzoic acid, and 2,4-dichlorophenoxyacetic acid under visible light.

The photocatalytic activity of Cu$_{0.4}$Zn$_{0.6}$Fe$_2$O$_4$/TiO$_2$-Bi$_2$S$_3$ (A) is higher than that of Cu$_{0.4}$Zn$_{0.6}$Fe$_2$O$_4$/TiO$_2$-Bi$_2$S$_3$ (B) (Figure 8). One of the possible reasons is Cu$_{0.4}$Zn$_{0.6}$Fe$_2$O$_4$/TiO$_2$-Bi$_2$S$_3$ (A) is a 2D nanomaterial, whereas Cu$_{0.4}$Zn$_{0.6}$Fe$_2$O$_4$/TiO$_2$-Bi$_2$S$_3$ (B) is a 3D material and electron flow is directional and faster in 2D than in 3D nanostructures. Besides the nanostructures, the specific surface areas of the composites also determine the photocatalytic activity. The specific surface area of Cu$_{0.4}$Zn$_{0.6}$Fe$_2$O$_4$/TiO$_2$-Bi$_2$S$_3$ (A) is larger (26.8 m$^2$ g$^{-1}$) than that of Cu$_{0.4}$Zn$_{0.6}$Fe$_2$O$_4$/TiO$_2$-Bi$_2$S$_3$ (B) (18.7 m$^2$ g$^{-1}$) and hence the photocatalytic activity. The determined pore volume is also in accordance with the measured photocatalytic activity. More importantly, while Cu$_{0.4}$Zn$_{0.6}$Fe$_2$O$_4$/TiO$_2$-Bi$_2$S$_3$ (A) absorbs in the entire visible region and also UV radiation, Cu$_{0.4}$Zn$_{0.6}$Fe$_2$O$_4$/TiO$_2$-Bi$_2$S$_3$ (B) fails to exhibit such optical property. More is the light absorbed, higher is the photocatalytic activity. Hence, the observed photocatalytic activities are on the expected line.

**CONCLUSIONS**

Cubic copper zinc ferrite-implanted orthorhombic Bi$_2$S$_3$-capped anatase TiO$_2$ synthesized by hydrothermal method in acidic and basic environments differ in their morphology; while the former is a 2D nanocomposite, the latter is a 3D nanomaterial. Although the emission spectra of both the materials are identical, their XRD, micro- and nanostructures, magnetic properties, and absorption spectra are different. The 2D nanomaterial obtained in acidic environment shows higher visible light photocatalytic activity compared to the 3D nanomaterial prepared in basic condition. The differences in the photocatalytic activities are rationalized in terms of the nanostructures, light absorption, and surface area.

**EXPERIMENTAL SECTION**

**Synthesis.** Stage 1. Cu$_{0.4}$Zn$_{0.6}$Fe$_2$O$_4$ nanocrystals (50 mg, Sigma-Aldrich) were dispersed in 10 mL of 2-propanol under sonication (20 min). To the resultant dispersion, carbon microspheres (300 mg) were added and dispersed by sonication (20 min); carbon microspheres were synthesized following the procedure reported already. To the resultant dispersion, carbon microspheres (300 mg) were added and dispersed by sonication (20 min); carbon microspheres were synthesized following the procedure reported already. To the resultant dispersion, carbon microspheres (300 mg) were added and dispersed by sonication (20 min); carbon microspheres were synthesized following the procedure reported already.
were allowed to cool naturally. The solid was separated by filtration, washed with water and ethanol several times, dried at 60 °C for 6 h, and calcined at 400 °C for 2 h in a muffle furnace equipped with a PID temperature controller. The heating rate was 10 °C min⁻¹.

**Stage 2A.** The solid (200 mg) obtained in the first stage of synthesis was dispersed in 20 mL of deionized distilled water under sonication (20 min). To this was added 20 mL of aqueous solution of Bi(NO₃)₃ (500 mg) and nitric acid (2 mL), and the mixture was stirred for an hour. This was followed by the addition of aqueous thiourea (1 g in 10 mL) under stirring. The resultant mixture was transferred to a 100 mL Teflon-lined autoclave and heated at 150 °C for 12 h. The contents were cooled naturally. The solid was collected by filtration, washed repeatedly with (i) water and (ii) ethanol, and dried at 70 °C for 12 h.

**Stage 2B.** The solid (200 mg) obtained in the first stage of synthesis was dispersed in deionized distilled water (20 mL) through sonication (20 mL). Bi(NO₃)₃ (500 mg) and triethanol amine (4 mL) were dissolved in 20 mL of deionized distilled water (20 mL), and the mixture was stirred for an hour. This was added to the aqueous dispersion of the solid particles obtained in the first stage of synthesis and stirred for an hour. To the resultant was added aqueous thiourea (1 g in 10 mL) with stirring. The entire content was taken in a 100 mL Teflon-coated autoclave and heated at 150 °C for 12 h. The autoclave with content was allowed to cool naturally. The solid was separated by filtration, washed many times with water and ethanol, and dried at 70 °C for 12 h.

**Characterization.** High-resolution SEM images of the synthesized samples were obtained using an FEI Quanta FEG 200 SEM. A JEOL JEM 2100 HRTEM equipped with Gatan Orius CCD camera was used to record the HRTEM images, SAED patterns, and EDS images of the samples. The samples were dispersed on carbon-coated copper grids, and the acceleration voltage applied was 200 kV. A PANalytical X’Pert PRO diffractometer was used to record the powder XRD patterns. The XRD patterns were obtained using Cu Kα rays of wavelength 0.15406 nm at 40 kV with a tube current of 30 mA in a 2θ range of 10–80°. The magnetic properties of the materials were determined using a Lakeshore 7404 vibrating sample magnetometer (VSM) at room temperature (25 °C). A Shimadzu UV-2600 spectrometer with an ISR-2600 integrating sphere attachment was used to record the UV–visible DRS images. The photoluminescence (PL) spectra of the samples were recorded with a PerkinElmer LS 55 fluorescence spectrometer at room temperature. The nanoparticles were dispersed in carbon tetrachloride under sonication and excited at 340 nm. A Micromeritics ASAP 2020 sorption analyzer was employed to determine the specific surface areas (SSAs) of the nanostructured composites. The nanomaterials were degassed at 150 °C for 12 h, and adsorption and desorption were carried out at −195.56 °C with N₂ as the adsorbate gas. The SSAs were obtained by the BET multipoint method through a least-squares calculation.

**Photocatalytic Test.** The visible light photocatalytic activity was tested employing a 150 W tungsten halogen lamp fixed into a double-walled borosilicate vessel with an inlet and outlet for coolant circulation. Circulation of 2 M NaNO₂ solution cuts off 99% of UV light of wavelength 320–400 nm. Methylen blue was the test substrate used, and its photodegradation was carried out in a wide cylindrical borosilicate glass vessel of uniform diameter with an area of cross section 15.9 cm². The distance between the light source and the dye solution was 13 cm. The light intensity was measured with a Daystar solar meter (415 W m⁻²). A freshly prepared dye solution (100 mL) with 50 mg of photocatalyst was taken in the reaction vessel and saturated with air using a micro-air pump. The airflow rate was 7.8 mL s⁻¹. The dissolved oxygen was measured with an Elico-dissolved oxygen analyzer PE 135 (9.3 mg L⁻¹). The pH measured was 5.5. Purging of air keeps the photocatalyst particles afloat. After providing sufficient time for the completion of adsorption of the dye on the catalyst surface, the vessel was illuminated. At different times of illumination, a finite volume of the dye solution was withdrawn and the undegraded dye was analyzed spectroscopically. Absorption at 662 nm permits dye estimation.

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