Synthesis of superparamagnetic biocidal superior solar photocatalytic Fe_3O_4 -implanted Ag_2S -capped ZnO micro-clubells

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Abstract

Semiconductor-photocatalytic mineralization of organics is an emerging technology. However, recovery of the photocatalytic particles post pollutant-mineralization is a stumbling block for adoption of this technique. Implantation of magnetic core in the particulate photocatalyst ensures magnetic recovery. The magnetic core, deeply buried in the photocatalytic semiconductor lattice, is secluded from the photocatalyst/effluent interface and has insignificant influence on the photocatalytic processes. As the magnetic core is concealed its photocorrosion is overcome. With this, we report synthesis of Fe_3O_4 -implanted Ag_2S -capped ZnO microstructure by a two-step hydrothermal process. Scanning electron micrograph shows the synthesized particles as micro-clubbell-shaped. The energy dispersive X-ray spectrum confirms the presence of the constituent elements and the elemental mapping images display the even distribution of the constituent elements in the micro-clubbells. The X-ray diffractogram and the Raman spectrum show ZnO in zincite structure and Ag_2S in acanthite phase. The synthesized microstructure and precursor Fe_3O_4 nanocrystals are superparamagnetic and their magnetic properties are comparable. The charge-transfer resistance of the microstructure is more than 20-fold that of Fe_3O_4 nanocrystals (New J Chem 40:1845–1852, 2016). The micro-clubbells absorb in the entire visible region and displays strong absorption in the UV-A region. The microcomposite exhibits green and strong blue-green emissions and the lifetime of photogenerated charge carriers is 10 ps. The synthesized microclubbell is mesoporous and its specific surface area is comparable to those of nanostructured composites. The synthesized microcomposite (1) displays superior photocatalytic activity under natural sunlight and (2) is reusable and magnetically recoverable. In addition, the title microstructure exhibits bactericidal activity, even without direct illumination.

Graphic abstract

Keywords Sunlight · Photocatalysis · Dye-degradation · Magnetic separation · Bacteria-inactivation

Electronic supplementary material The online version of this article (<https://doi.org/10.1007/s42452-019-0758-z>) contains supplementary material, which is available to authorized users.

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SN Applied Sciences (2019) 1:740 | <https://doi.org/10.1007/s42452-019-0758-z>

Received: 12 May 2019 / Accepted: 11 June 2019 / Published online: 18 June 2019

1 Introduction

Global warming impacting the rain fall, high population growth-rate in densely populated large nations, globalization of economies improving the per capita purchasing power in underdeveloped countries, etc., exert pressure on availability of uncontaminated water in developing nations. Contamination of surface water by untreated or undertreated industrial effluents and domestic sewage along with bacterial contamination due to poor hygiene is prevalent in tropical countries. Semiconductor-photocatalysis is an emerging technology for water purification as it mineralizes organic pollutants indiscriminately at ambient conditions; it requires no chemicals but only air and moisture and the photocatalytic semiconductor nanocrystals are recoverable for reuse. TiO_2 is a preferred photocatalyst because of its chemical and thermal stability, nontoxicity, low cost and optoelectronic characteristics [1, 2]. ZnO displays unique optoelectronic properties and the band gap energy of ZnO (3.2 eV) is not different from that of TiO_2 [3, 4]. Further, the valence band (VB) potential of ZnO (2.89 V) is not significantly different from that of TiO_2 (2.91 V) and so is the conduction band (CB) edge of ZnO (−0.31 V) with CB edge of TiO_2 (−0.29 V). ZnO is stable in the environmental pH range and there are reports that the photocatalytic activity of ZnO is larger than that of TiO_2 ; the mobility of charge carriers in ZnO ($100\text{--}205\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$) is much higher than that in TiO_2 ($0.1\text{--}1.0\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$) [5]. In addition, ZnO is an environment friendly bactericide [6]. Medicinal use of ZnO ointment is in practice for decades and Zn^{2+} is a micronutrient for crops. Both TiO_2 and ZnO require UV A light for photocatalysis and the UV component in the natural sunlight that reaches earth's surface is only about 5%; visible light (45%) and near-infrared radiation (50%) are the major components of natural sunlight [7]. Hence photocatalysts which utilize natural sunlight for mineralization of pollutants are of interest, especially in tropical regions. Ag_2S is a highly stable (solubility product 6.3×10^{-50} [8]– 8×10^{-51} [9]) *n*-type narrow band gap (0.9–1.05 eV) [7, 10–12] semiconductor with a large absorption coefficient [7, 11]. It is black in color and displays negligible toxicity [7, 13]. It sensitizes TiO_2 or ZnO-photocatalysis. Ag_2S -deposited (1) TiO_2 [7, 12–20] or (2) ZnO [21–24] absorbs near infrared, visible and ultraviolet light, the whole solar spectrum, and mineralizes organic pollutants. Ag_2S acts as a photosensitizer, enables visible light absorption and enhances charge carrier separation between Ag_2S and TiO_2 [7, 13–18, 20] or ZnO [23, 24]. Further, Ag_2S itself is a visible light-near infrared-photocatalyst [10]. Although extensive research on semiconductor-photocatalytic mineralization of organic pollutants towards water purification have been made recovery of

the particulate photocatalyst after treatment is the bottle neck for adoption of this technology by industries and sewage treatment plants. Magnetic recovery is a solution and for this magnetic core is to be implanted in the particulate photocatalyst [25, 26]. The deeply buried magnetic core (iron oxide) is completely and fully wrapped by the photocatalytic semiconductor lattice and is insulated from the semiconductor-effluent interface. This excludes the unwanted photocorrosion of the magnetic core; the core serves the purpose of magnetic separation of the photocatalyst. With this in view, we synthesize Fe_3O_4 -implanted Ag_2S capped ZnO micro-clubbeds for use as solar photocatalyst for water decontamination; microscale ZnO is reported to be more photostable than nano ZnO [5]. The synthesized composite micro-clubbeds disinfect bacteria even in the absence of light, thus serving as a multifunctional material—excellent photocatalytic decontamination of organic pollutant under natural sunlight, disinfection of bacteria and magnetic recovery of the catalytic microparticles.

2 Experimental

2.1 Synthesis

Stage I. Polyethylene glycol 20,000 (2 g) was dissolved in distilled deionized water (15 mL) and Fe_3O_4 nanocrystals (50 mg, Sigma Aldrich) were dispersed in it under sonication. A Toshcon SW2 ultrasonic bath of 100 W at $37 \pm 3\text{ kHz}$ was employed for sonication. To the dispersion, aqueous zinc nitrate solution (5 mmol in 10 mL) was added with stirring. To this was added drop wise aqueous ammonia (1:1) under stirring to reach a pH of 7.8. A white precipitate was obtained. However, the stirring was continued for an hour and the contents were transferred into a Teflon-lined autoclave vessel (100 mL). The vessel was placed for 12 h in a hot air oven at 150 °C. The autoclave with contents was allowed to cool to room temperature naturally, the solid was separated by filtration and washed several times with distilled water and ethanol and dried at 110 °C for 2 h. The dried solid was calcined at 500 °C for 2 h in a muffle furnace equipped with a PID temperature controller. The heating rate was set at $10\text{ }^\circ\text{C min}^{-1}$.

Stage II. The obtained solid (200 mg) was dispersed in 30 mL of 33% (v/v) aqueous ethylene glycol under sonication. To the dispersion was added in drops aqueous AgNO_3 (100 mg in 10 mL) with stirring and H_2S gas was bubbled to get a black precipitate. The contents were taken in a 100 mL-Teflon-coated autoclave vessel, sealed and placed in a hot air oven at 150 °C for 12 h. It was allowed to cool to room temperature naturally, the

solid separated through filtration, washed several times with distilled water and then with ethanol and dried at 200 °C for 2 h in an air oven.

2.2 Characterization

Scanning electron microscopic (SEM) images and the energy dispersive X-ray spectrum (EDS) of the synthesized sample were recorded using a JEOL JSM-5610 SEM with EDS attachment. A FEI-Quanta FEG 250 field emission scanning electron microscope (FE-SEM) was used to obtain the elemental mapping of the sample. A PANalytical X-ray diffractometer (XRD) employing Cu K α rays of wavelength 0.15406 nm was used to record the powder XRDs in the 2 θ range 10–80° at 40 kV. The tube current was 30 mA. The Raman spectrum of the sample was obtained with a Renishaw inVia Reflex confocal Raman microscope employing 0.6 mW argon laser as excitation source. The sample was excited at 488 nm. The magnetic measurements were made at room temperature with a LakeShore 7404 vibrating sample magnetometer (VSM). A CH Instrument Electrochemical Analyzer 604C was employed to obtain the solid state electrochemical impedance spectrum of the sample in the frequency range 0.1 MHz–1 Hz at room temperature. The disk area of the sample pellet was 0.5024 cm² and the thickness of the pellet was 1.11 mm. A Micromeritics ASAP 2020 sorption analyzer was employed to study the adsorption and desorption on the surface of the synthesized materials. The sample was degassed at 150 °C for 12 h. Nitrogen gas was the adsorbate used and the adsorption and desorption were performed at –195.56 °C. The Brunauer–Emmett–Teller (BET) multipoint method of analysis using a least-square fit provided the specific surface area. The pore volume and pore size were obtained by adopting the Barrett–Joyner–Halenda (BJH) method. The UV visible diffuse reflectance spectrum of the synthesized sample was recorded using a Shimadzu UV-2600 spectrometer with ISR-2600 integrating sphere attachment. The photoluminescence (PL) spectrum of the sample was obtained with a PerkinElmer LS 55 fluorescence spectrometer. The sample was dispersed in carbon tetrachloride under sonication and excited at 340 nm. A Horiba Jobin Yuon Fluorolog FL-3-11 spectrofluorimeter was used for the time-correlated single photon counting (TCSPC) measurement. A pulsed nano-LED was used to excite the sample at 295 nm.

2.3 Solar photocatalytic study

The solar photocatalytic dye-degradation was made under clear open sky at noon. A Daystar solarmeter (USA) was used to measure the solar irradiance. As the time of

sunlight irradiance was short (10 min) and the sky was clear there was no significant fluctuation in the sunlight intensity measured (460 W m⁻²) during the experiment. Rhodamine B was used as the test substrate. In a cylindrical vessel of area of cross-section 15.9 cm² 25 mL of the dye solution was taken along with 50 mg of the synthesized sample. Air was bubbled through the dye solution using a micro air-pump to have the microparticles under continuous motion, to stirrer the solution and to saturate the solution with oxygen. The airflow rate was 7.8 mL s⁻¹. It was determined by soap bubble method. The dissolved oxygen in the dye solution was measured using an Elico dissolved oxygen analyzer PE 135. It was 9.3 mg L⁻¹. The measured pH of the solution was 5.5. Prior to solar irradiance sufficient time was provided for the adsorption of the dye to attain a saturation. At different time of sunlight exposure, a finite volume of the dye solution was withdrawn and the dye was estimated spectrophotometrically. A calibration curve was constructed by measuring the visible light absorbance of rhodamine B of different concentrations (ppm) at 552 nm.

2.4 Visible light photocatalytic study

Photodegradation of the dye with visible light was done using a 150 W tungsten halogen lamp fixed into a double-walled borosilicate vessel provided with inlet and outlet nozzles for coolant circulation. Aqueous sodium nitrate was employed as a UV light cutoff filter. Use of 2 M NaNO₂ solution as coolant cuts off 99% of UV A light (320–400 nm) [27]. The dye-degradation experiment was carried out in a wide cylindrical borosilicate glass vessel of uniform diameter with area of cross-section as 15.9 cm². The vessel was placed 13 cm below the tungsten halogen lamp. The light intensity, measured with a Daystar solarmeter, was 415 W m⁻². Rhodamine B was used as the test dye for the photocatalytic degradation. One hundred mL of freshly prepared aqueous solution of rhodamine B of required concentration was taken in the reaction vessel along with accurately weighed 100 mg of the synthesized material. It was air-saturated by bubbling air using a micro air pump. The rate of air flow was 7.8 mL s⁻¹ and the dissolved oxygen was 9.3 mg L⁻¹. The solution was stirred continuously. After allowing sufficient time for the dye-adsorption on the sample to attain equilibrium, the setup was exposed to illumination. The dye degradation was analyzed spectrophotometrically (552 nm) at different time of illumination as stated already.

2.5 Antibacterial study

Nutrient broth (13.0 g) was dissolved in distilled deionized water (1 L) and sterilized in an autoclave at 121 °C to

get a nutrient broth culture of pH 7.4. MacConkey agar (55 g) was dissolved in boiling water (1 L), sterilized in an autoclave at 121 °C and poured into Petri dish to get MacConkey agar plates. *Escherichia coli* (*E. coli*) bacteria were incubated in nutrient broth culture at 37 °C for 24 h under shaking. The cultured bacteria were centrifuged at 3500 rpm, washed with water and resuspended in and diluted with 1.5% nutrient broth solution. To the bacteria culture (25 mL) in 60 mL bottle accurately weighed sample (20 mg) was added and shaken continuously without any illumination. At desired time intervals, the sample was removed and the bacteria solution was diluted step wise to required level. Ten μL of the diluted *E. coli* solution was streaked on the nutrient agar plate, incubated at 37 °C for 24 h and the CFU (colony forming unit) was counted by a viable count method.

3 Results and discussion

3.1 Micro-clubbell

The morphology of the synthesized sample was assessed using electron microscopy. Figure 1 is the SEM image of the title material. The image shows the prepared composite in microdimensions. The micromaterial appears to be of clubbell shape. The measured thickness is 950 nm and the length exceeds 8 μm .

3.2 Fe_3O_4 -implanted Ag_2S -capped ZnO

EDS of the synthesized sample, displayed as Fig. 2a, shows the presence of zinc, iron, silver, sulfur and oxygen, the constituent elements of the title material. The absence of any other element indicates the purity of the synthesized composite. The elemental mapping of the sample, presented as Fig. 2b–f, reveals even distribution of all the constituent elements (zinc, iron, silver, sulfur and oxygen) in the obtained micro-clubbells. The powder XRD

pattern of the precursor Fe_3O_4 nanocrystals, used in the stage I-synthesis of the title material, is presented in Fig. 3a (bottom). It fully agrees with JCPDS card no. 85-1436 and shows the crystal structure of Fe_3O_4 as cubic. Adopting the Scherrer formula $D = k\lambda/\beta \cos \theta$, where D is the mean crystallite size, λ is the wavelength of X-rays employed, θ is the angle of diffraction, β is the full width at half-maximum of the most intense peak and k is the shape factor (dimensionless), the D of Fe_3O_4 nanocrystals was determined. The actual shape of the nanocrystallite influences the k value and for spherically shaped nanocrystals its value is about 0.94. The deduced mean crystallite size of Fe_3O_4 is 32 nm. The recorded powder XRD pattern of the title material is displayed as Fig. 3a (top). It shows the diffraction peaks of zincite (JCPDS card no. 89-7102) confirming the hexagonal ZnO crystal lattice in the synthesized micro-clubbells. The obtained XRD of the sample further displays the $-1\ 0\ 1$, $1\ 1\ 0$ and $-1\ 2\ 1$ -reflections of monoclinic Ag_2S , confirming Ag_2S capping of the micro-clubbells. JCPDS card no. 14-072 was the reference used to index deposited Ag_2S . Careful examination of the SEM image (Fig. 1) of the title material shows deposits on clubbell-structure. These deposits are attributed to Ag_2S -capping of the clubbell. Interestingly, the XRD of the title composite does not show any reflection of Fe_3O_4 although the EDS and elemental mapping confirm the presence of iron. It is known that the intensity of X-rays reflected decreases sharply with increase of the order of diffraction (n), which is determined by the depth of the reflecting crystal plane; more is the depth (from the crystal surface) higher is the ' n ' value. The diffraction by deeply buried Fe_3O_4 core is so weak to be detected [25, 26]. Further, it has been shown that the intensity of XRD peaks of Fe_3O_4 core decreases with increase of the thickness of ZnO shell and the X-ray reflections of Fe_3O_4 core is completely suppressed by thick ZnO shell [28]. Raman spectroscopy affords information on the local crystalline structure. Figure 3b provides the Raman spectrum of the synthesized sample. The recorded Raman spectrum is characteristic of hexagonal ZnO lattice. The observed Raman frequency at 427 cm^{-1} corresponds to the $E_2(\text{high})$ mode representing the vibration of oxygen atom of wurtzite lattice [25, 26]. The intensity of $E_2(\text{high})$ mode reflects the crystallinity of the ZnO lattice and also intrinsic defects stemming from oxygen vacancies (V_o). The Raman frequency at 427 cm^{-1} is also attributed to second order longitudinal optical phonon mode (2LO) of monoclinic Ag_2S [29]. The strong peak at 543 cm^{-1} is assigned to $A_1(\text{LO})$ mode [25, 30] and that at 323 cm^{-1} to second order $E_2(\text{high}) - E_2(\text{low})$ [25, 30, 31]. The strong broad peak at 1126 cm^{-1} corresponds to the second-order $2A_1(\text{LO})$ Raman mode [32]. Thus the Raman spectrum identifies the zincite lattice of ZnO and acanthite Ag_2S phase in the synthesized microstructure. The EDS analysis of the sample

Fig. 1 SEM image of the title material

Fig. 2 **a** EDS and **b–f** elemental mapping images of the synthesized sample

provides the molar abundance of Ag_2S deposited on the sample surface as 1.3%. The elemental mapping of Ag as well as that of S shows fairly uniform deposition of Ag_2S on the sample surface, turning the surface largely homogeneous. The abundant presence of zinc (46 at% with almost equal amount of oxygen) with the iron in trace (2 at%) supports that precursor Fe_3O_4 nanocrystals are deeply buried in the ZnO lattice; the mean crystallite size of precursor Fe_3O_4 is 32 nm whereas the clubbells are of 0.95 μm thick and about 8 μm long.

3.3 Superparamagnetic clubbells

Magnetization (M) of the synthesized micro-clubbells along with that of precursor Fe_3O_4 nanocrystals used for the clubbell-synthesis is presented as a function of applied field (H) at room temperature (Fig. 4a). The M – H loops show the magnetic response of the materials and

enable to deduce the magnetic properties such as saturation magnetization (M_s), coercivity (H_c) and remanence magnetization (M_r). The size and shape of the hysteresis loops form the core of information; the obtained M – H loops are of normal S -shape and the “thickness” of the middle of the loop affords the extent of hysteresis – hysteresis is related to the H_c of the magnetic crystals. The synthesized micro-clubbells and precursor Fe_3O_4 nanocrystals are superparamagnetic. The hysteresis curves of both the materials show that the H_c of synthesized micro- $\text{Fe}_3\text{O}_4/\text{ZnO}/\text{Ag}_2\text{S}$ and nano- Fe_3O_4 are too small; the H_c of micro-clubbells and Fe_3O_4 nanocrystals are 58 and 35 Oe, respectively. The observed insignificant coercivities reveal the superparamagnetic nature of micro-clubbells and nanocrystalline Fe_3O_4 . The H_c of precursor Fe_3O_4 nanocrystals used for the title synthesis is comparable to that of Fe_3O_4 microspheres (37 Oe) [33] and is less than those of hydrothermally obtained Fe_3O_4 octahedra (74 Oe)

Fig. 3 **a** XRDs of precursor Fe_3O_4 (bottom) and the sample (top) and **b** Raman spectrum of the sample

[34] and Fe_3O_4 microoctahedra (102.8 Oe) [35]. The M_R of the synthesized micro-clubbeds and pristine nanocrystalline Fe_3O_4 are 0.15 and 0.10 emu g^{-1} , respectively. The near zero M_R values show the superparamagnetic character of both the materials. The M_R of precursor Fe_3O_4 nanocrystals is much less than those of hydrothermally prepared Fe_3O_4 octahedra (4.2 emu g^{-1}) [34] and Fe_3O_4 microoctahedra (13.5 emu g^{-1}) [35]. Further, the M_S of the synthesized micro-material and its precursor nanocrystalline Fe_3O_4 are comparable; the former is of 1.9 emu g^{-1} while the latter is of 1.6 emu g^{-1} . The VSM results show that the precursor Fe_3O_4 nanocrystals are deeply buried in the obtained micro-clubbeds.

3.4 Charge-transfer resistance

Electron-hole migration across the photocatalytic semiconductors plays a significant role in semiconductor-photocatalysis. The photogenerated charge carriers diffuse to the semiconductor crystal surface and initiate photocatalysis. The holes and electrons, migrate to the crystal surface,

react with water molecules or hydroxide ions and oxygen molecules, all adsorbed on the photocatalyst surface, to produce reactive oxygen species (ROS) which mineralize the organics. Solid state impedance spectroscopy is useful to study the electrical properties of semiconductor photocatalyst. It throws light on the dynamics of the bound and mobile charges in the bulk or interface of semiconductors. The measured impedance of micro-clubbeds pellet decreased with increase of frequency. The observed decrease of impedance with increase of frequency shows the capacitance of the studied material. The obtained impedance data were analyzed through the Nyquist plot. Figure 4b presents the solid state impedance spectrum of the synthesized micro-clubbeds. The observed semi-circular Nyquist plot is the expected response of the simple circuit [36]. The overall crystal resistance arises out of intergranular (or grain boundary) resistance and intragranular (or bulk) resistance. The charge-transfer resistance (R_{CT}), also called as polarization resistance, stems from intragranular resistance. The R_{CT} is related to the resistance to mass transfer, the latter is known as Warburg resistance and the former is controlled by specific conductance (σ). The ohmic resistance (R_Ω), also known as uncompensated resistance, arises out of intergranular resistance. The constant phase element is equivalent to double layer capacitance (C) and is related to non-uniform distribution of current because of material heterogeneity. The determined (1) R_Ω , (2) R_{CT} , (3) σ and (4) C of the synthesized micro-clubbeds are (1) 0.36 k Ω , (2) 116 k Ω , (3) 19 $\mu\text{S m}^{-1}$ and (4) 0.54 nF. The R_Ω , R_{CT} , σ and C of precursor Fe_3O_4 nanocrystals, used for the synthesis of the title micro-clubbeds, are 1.7 k Ω , 5 k Ω , 6.7 mS m^{-1} and 0.57 nF, respectively [32]. Although the ohmic resistance of the micro-composite is less than that of precursor Fe_3O_4 nanocrystals the charge-transfer resistance is more than 20-fold. A possible reason is the synthesized microstructure is a composite with heterojunctions. This is also a cause for the observed very low of specific conductance of the microstructure. However, the capacitance of the precursor Fe_3O_4 and the synthesized microstructure are comparable.

3.5 Surface specifics

The characteristics of photocatalytic semiconductor-surface decisively influence the catalytic activity. The surface characteristics such as specific surface area, pore volume and pore radius have been determined using nitrogen adsorption and desorption processes. Both the adsorption and desorption processes are reversible and the adsorption-desorption isotherms are presented in Fig. 4c. The adsorption is of type III isotherm which is characteristic of unrestricted multilayer adsorption. The lateral interactions among adsorbate molecules are strong compared to

Fig. 4 The **a** M – H hysteresis loops, **b** Nyquist plot, **c** adsorption–desorption isotherms, **d** UV–visible DRS, **e** PL spectrum and **f** time-resolved PL trace of $\text{Fe}_3\text{O}_4/\text{ZnO}/\text{Ag}_2\text{S}$

that between the semiconductor surface and the adsorbate molecules. The specific surface area of the synthesized micro-clubells, determined by the BET method, is $20.8 \text{ m}^2 \text{ g}^{-1}$. The pore volume in the prepared micro-clubells is $0.13 \text{ cm}^3 \text{ g}^{-1}$. The synthesized title micro-material is mesoporous. Its pore radius, determined by BJH desorption, is 12 nm . The specific surface area of the micro-clubells is comparable to those of photocatalytic nanocomposites [37] and the likely reason is the micro-clubells are mesoporous.

3.6 Absorption

Photocreation of charge carriers in semiconductors forms the basis of semiconductor-photocatalysis. Electron–hole pairs are produced when the energy of impinging light is not less than the semiconductor-band gap. Figure 4d is the UV–visible DRS of the micro-clubells, presented

in terms of $F(R)$; the recorded reflectance (R) subjected to the Kubelka–Munk algorithm, $F(R) = (1 - R)^2 / 2R$, affords $F(R)$. The DRS shows strong visible light absorption by the synthesized sample. This is because of Ag_2S capping of the micro-clubells; the widely reported band gap of pristine Ag_2S is 0.9 – 1.05 eV [7, 10–12]. The displayed DRS, in addition to visible light absorption, exhibits a sharp UV absorption edge at 389 nm . This is characteristics of hexagonal ZnO crystalline lattice. Thus the recorded DRS is in accordance with the synthesized microstructure— Fe_3O_4 -buried Ag_2S -deposited ZnO . The (1) direct and (2) indirect UV band gap energies of the synthesized micro-structured composite have been obtained through the Tauc plots of (1) $[F(R)h\nu]^2$ and (2) $[F(R)h\nu]^{1/2}$ versus photon energy, $h\nu$ (not shown). The plots afford the direct and indirect band gap energies as 3.25 and 3.09 eV , respectively. These energies correspond to ZnO .

Fig. 5 **a** Time scan of dye-photodegradation with magnetic separation (inset) and **b** dye-degradation profiles

3.7 Emission

The photoproducted charge carriers predominantly recombine either radiatively or nonradiatively or by both means. The charge carrier-recombination suppresses the photocatalytic efficiency. The radiative recombination of electron-hole pair is probed using photoluminescence (PL) spectroscopy. The emission spectrum of the synthesized microstructure is presented in Fig. 4e. The title microstructure shows blue-green emission at 480 nm and green emission at 529 nm and the former is stronger than the latter. The blue-green emission stems from band-edge free excitons and bound excitons [38, 39]. The green emission arises out of oxygen vacancies and other vacancy-related defects [40]. The energy of green emission corresponds to the energy of electron-transition from deep-level donor of the ionized oxygen vacancies to the valence bond [25].

3.8 Charge-carrier lifetime

Time-resolved photoluminescence (TRPL) spectroscopy is a potential tool to probe excited states and it is useful to determine the lifetime of excitons. The lifetime of photoexcited states of the synthesized micro-clubbeds have been obtained using time-correlated single photon counting (TCSPC) lifetime spectroscopy. The UV band gap absorption edge of the obtained semiconductor-composite microstructure is 389 nm and the TRPL trace was recorded at 395 nm. This wavelength reflects the free excitonic band. Figure 4f displays the fluorescence decay profile. The microstructured semiconductor-composite was excited at 295 nm. This excitation wavelength corresponds to excitation energy 4.2 eV. This energy is very much larger than the UV band gap energy of the microstructure. Hence the excitation is subjected to thermalization to provide exciton and the excitation relaxes prior to emit radiation. The relaxation process, at room temperature, is very fast [41]. The TRPL decay profile

affords the lifetime of the title micro-clubbeds as 10 ps. This lifetime is in agreement with those of charge-carriers photogenerated in CdS-deposited Fe_3O_4 -implanted ZnO microrods (8 ps) [42], Fe_3O_4 -implanted Ag-loaded ZnO nanoflakes (6 ps) [32], CuFe_2O_4 -embedded Ag-deposited ZnO nanosheets (7 ps) [43] and Ag-decorated ZnFe_2O_4 -dispersed ZnO nanoflakes (7 ps) [44]. The determined lifetime corresponds to charge carriers generated in ZnO due to band gap excitation. Literature review reveals that the mechanism of radiative decay is not yet clear.

3.9 Solar-photocatalytic activity

The action spectra of degradation of the test dye rhodamine B, catalyzed by the title micro-clubbeds under natural sunlight at noon is given in Fig. 5a. The dye degrades almost completely in 8 min. This demonstrates the superior solar photocatalytic activity of the title micro-clubbeds. The concentration - illumination-time profile of the dye-degradation is presented in Fig. 5b. The synthesized composite photocatalyst is magnetically recoverable. The inset of Fig. 5a shows the separation the title micro-clubbeds with a weak magnet. Reuse of the synthesized photocatalyst to degrade the test dye under identical experimental conditions shows the reusability of the title material without any pre-treatment.

3.10 Sustainable photocatalytic activity under visible light

Photocatalytic degradation rate highly depends on the quantity of band gap-excitation radiation impinged on the photocatalytic surface. The natural solar radiance through clear sky, even at noon, over a period of time, however short the duration is, is likely to fluctuate. Hence it is experimentally difficult to test the photocatalytic activity of a material under natural sunlight over many

Fig. 6 *E. coli*-inactivation by Fe₃O₄/ZnO/Ag₂S **a** bar graph and **b** CFU photographs

repeated reuse. However, it is possible to test the photocatalytic activity on repeated reuse employing a visible light-photoreactor. Figure 1S shows the sustainable photocatalytic activity of the title micro-clubbeds. The concentration–time profile of the degradation of the test dye by freshly synthesized micro-clubbeds overlaps with those of the reused title material; the photocatalyst was just washed and dried after use for subsequent usage. Figure 1S displays reuse of the title photocatalyst up to 6-times. This demonstrates the sustainable photocatalytic activity of the synthesized micro-clubbeds. The present results in turn indirectly reflect the stability of the synthesized microstructure. The dye-degradation profiles under natural sunlight and artificial visible light are not to be compared as the photoreactor-design, experimental setup, irradiance, the probability of photon-incidence on photocatalyst particle, etc., are different. The mechanism of Ag₂S-sensitized visible light photocatalysis by ZnO has been reported recently [23, 24] and the same mechanism is likely to operate in the photocatalysis by Fe₃O₄-implanted Ag₂S-capped ZnO micro-clubbeds as the magnetic core is deeply buried in the ZnO lattice of the microstructured composite.

3.11 Bacteria-inactivation

Figure 6a presents the *E. coli*-population, counted as colony forming units per millilitre (CFU/mL) in the presence of the title micro-clubbeds at different time intervals without any direct illumination. In the absence of the title microstructure the *E. coli* population remained unchanged. In 20 min the entire *E. coli* population was inactivated. Figure 6b displays a couple of photographs showing *E. coli* population before the addition of the microstructure and after the addition and at 20 min. This experiment demonstrates the biocidal activity of the title microstructured semiconductor-composite. Iron oxide is deeply buried in

the ZnO lattice and is not exposed to the solid-solution interface. Hence Fe₃O₄ has no role in the bactericidal activity as well as the photocatalytic activity of the synthesized microstructured semiconductor-composite. On the other hand, ZnO and Ag₂S are at the solid-solution interface and hence are responsible for the bactericidal as well as the photocatalytic activities. The bactericidal activities of ZnO [6] and Ag₂S [45] are well documented. Hence, here too the mechanism of bacteria-inactivation is less likely to be different.

4 Conclusions

Two-stage hydrothermal treatment is a convenient method to synthesis Fe₃O₄-implanted Ag₂S-capped ZnO micro-clubbeds. Scanning electron micrograph, energy dispersive X-ray spectrum, elemental mapping images, X-ray diffractograms, Raman spectrum, vibrating sample magnetometry and UV–visible diffuse reflectance and photoluminescence spectra confirm the morphology and the crystalline structure of the synthesized sample. The obtained microstructure is mesoporous and displays large charge-transfer resistance. The lifetime of photo-produced charge carriers is 10 ps. The title material shows superior photocatalytic activity under natural sunlight. The photocatalytic particles are magnetically recoverable and reusable many times without loss of photocatalytic activity. Furthermore, the microcomposite is an efficient bactericide.

Acknowledgements Prof. C. Karunakaran acknowledges the Council of Scientific and Industrial Research (CSIR), New Delhi [21(0887)/12/EMR-II], for the Emeritus Scientist grants. I. JebsSingh and P. Vinayagamorthy thank the CSIR for JRF and RA, respectively.

Compliance with ethical standards

Conflict of interest On behalf of all authors, the corresponding author states that there is no conflict of interest.

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