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Synergistic Excited State involved Catalytic Reduction of $(\text{NH}_3\text{-trz})[\text{Fe}(\text{dipic})_2]$ Complex by $\text{SnO}_2/\text{TiO}_2$ Nanocomposite

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Graphical abstract

Abstract

The photocatalytic activity of well-fabricated, economical $\text{SnO}_2/\text{TiO}_2$ nanocomposite synthesized via hydrothermal route was validated using the $(\text{NH}_3\text{-trz})[\text{Fe}(\text{dipic})_2]$ complex under ultra-violet illumination. The structural features of $(\text{NH}_3\text{-trz})[\text{Fe}(\text{dipic})_2]$ complex was explored in detail. The catalysts were systematically examined with XRD, SEM, FT-IR UV-vis, PL, micro-Raman, VSM, AFM, HRTEM. The photoreactivity of the model compound $(\text{NH}_3\text{-trz})[\text{Fe}(\text{dipic})_2]$ in water/binary solvent systems was investigated. The rate of photoreaction (k) of nanocomposite (0.1432 sec^{-1}) is higher than the SnO_2 (0.0373 sec^{-1}) and TiO_2 (0.1422 sec^{-1}) in $\text{H}_2\text{O}:\text{Pr}^i\text{OH}$ (70:30%) than the rest of the solvents system. The pathways, mechanistic feature of accumulated reactive species on nanocomposite to induce adherent $[\text{Fe}(\text{dipic})_2]^-$ anion and photo-reductive products were studied. The generation of hydroxyl radical on the surface of each catalyst can be identified as 7-hydroxycoumarin and discussed

Keywords: $(\text{NH}_3\text{-trz})[\text{Fe}(\text{dipic})_2]$, $\text{SnO}_2/\text{TiO}_2$ nanocomposites, adsorption, photoreduction, Hydroxy radical.

1 Introduction

In the past years, *nanoscale* heterostructures have been rapidly developed through research objective due to their favorable performance in various fields. The impacts are more obvious and precise in high-technology applications and the dimension dependence of *nanoparticles* brings novel electronic, optical, magnetic, and mechanical properties [1-4]. Research

investigations combined that the construction of semiconductor heterostructures proved to be an excellent method for improving the photosynthetic function of a material. [5]. More formulations have been emphasized on hybrid heterostructure systems in recent years by coupling two/more metal oxides and the resulting new *nanocomposites* exhibit high photocatalytic reactivity compared with bare components [6-8]. Tin dioxide (SnO_2) is one of the acceptable n-type semiconductors with chemical and thermal stability (wide bandgap = 3.6 eV at 300 K) and it was used in transparent conductive electrodes, electronics, solar cells, energy storage, gas sensors, and photocatalysis [9,10]. Tin oxide is a good electron acceptor comparing anatase TiO_2 (wide bandgap = 3.2 eV at 300 K) photocatalyst because SnO_2 has a more positive conduction band edge and makes it a suitable candidate for the preparation of heterostructure [11,12]. It is worthy enough to associate SnO_2 with TiO_2 to obtain a unique heterostructure to achieve the synergistic effect between the two semiconductors. This modifies the electronic states of the composite, allows the transfer of photogenerated charge carriers to be switched between the two semiconductors, promotes electron/hole pair separation, and changes the lifetime of the carrier. *Nanocomposite* $\text{SnO}_2/\text{TiO}_2$ engineering using SnO_2 with TiO_2 becomes the anticipated best material from the point of matching bandgap, low in toxicity, good durability, high stability, promising in the separation of photogenerated electrons/holes, and results in highly efficient photocatalyst [13,14]. It is reasonable to exploit the photocatalytic efficiency of $\text{SnO}_2/\text{TiO}_2$ *nanocomposite*, the effect would be higher than that of individual SnO_2 and TiO_2 *nanoparticles*. Second, synthesis of this *nanocomposite* with a tunable and uniform composition comprising a tight interface [15-17]. The hybrid formation of TiO_2 with SnO_2 modifies the electronic structure and can be used to control and enhance the surface chemical and physical properties of $\text{SnO}_2/\text{TiO}_2$ *nanocomposites* [18-20]. The immobilizing of *nanocomposite* with the synthesized coordination compound can be considered as a good way for additional processes such as photocatalyst recovery and recycling [21, 22]. Kinetically labile, high spin, hexacoordinated iron(III) complex shows enormous aspects in photophysics and photochemistry [23]. Transition metal complexes with nitrogen donor can provide versatile properties such as limited steric hindrance, structural lability, and sensitivity to surface platforms as functional materials [24-26]. The spin cross over (SCO) is possible in d^5 system of the metal complex at the metal centre. Due to external stimuli such as irradiating light source, temperature and pressure changes, it affects the spin states to switch over between high spin state to low spin state or *vice versa*. This induces notable modifications in the structural, vibrational, magnetic, or optical properties of the complex [27]. In the present piece of investigation, we report for the first time to our knowledge the controlled synthesis of

SnO₂/TiO₂ *nanocomposite* photocatalyst coupled with an iron(III) complex to induce photo-reduction activities probed under UV illumination.

2 Experimental Section

2.1 Synthesis of 4-amino-4H-1,2,4-triazol-4-ium-bis(pyridine-2,6-dicarboxylato)ferrate(III) Complex

(NH₃-trz)[Fe(dipic)₂] was prepared with some altered methodology from the published procedure [28]. Bis(pyridine-2,6-dicarboxylato)ferrate(III) anion for the present study was prepared using the starting material anhydrous FeCl₃ (0.33 mmol) and 2,6-pyridine dicarboxylic acid (0.66 mmol) in dehydrated methanol to obtain brown colored solution after 90 min stirring. To this 4-amino,1,2,4-triazole (0.5 mmol) was added under slow addition and constant stirring, this produced dark green color. The resulting solution was further stirred for 180 min at room temperature, allowed to stand in dark, filtered, and left for evaporation in the air at ambient temperature. After one week, green crystals of the complex suitable for X-ray analysis were extracted (yield, 60%). The recrystallized sample was subjected to elemental analysis: Anal. Calc. for C₁₆H₁₁Fe₂N₆O₈: C, 40.79; H, 2.35; N, 17.84. Found: C, 40.45; H, 2.33; N, 17.82%. FT-IR (KBr disk, cm⁻¹): 3359 (br); 3234(v NH); 3083; 2430; 1650(s) (ν_{asym} COO⁻), 1578; 1459(s); 1414, 1380(s) (ν_{sym} COO⁻); 1264(w) 1081(s); 991(m); 914(s); 852(m),751(s); 699(s), 671, 619(s); 584(m); 511(s); 414(m). UV-Vis is in H₂O (λ_{max}, nm (ε, dm³/mol cm)): 255 (31434.22), 270 (30800.17); 670 (0.84656); 477 (2.11640).

2.2 Synthesis of Tin Oxide Nanospheres

All the chemicals used in this experiment were AR grade. Tin oxide *nanoparticles* were synthesized with a modified route using dimethyl oxalate as the precipitator [29]. Stannous chloride (SnCl₂.2H₂O, 0.1M) was dissolved in 1-propanol under magnetic stirring for 15 min, leading to a transparent solution. To this, dimethyl oxalate (0.1 M) dissolved in distilled water was added in drops and regulated over a period of 10 min. The obtained precipitate was transferred into 150 ml Teflon-lined autoclave and kept at 200°C for 12 h then cooled to room temperature, centrifuged, washed several times with 10% ethanol in water. Afterwards, the precipitate was dried in an oven at 110°C for 10 h and annealed at 500°C for 3h.

2.3 Synthesis of Titanium Dioxide Nanospheres

The starting solution was prepared by adding titanium isopropoxide (0.4 M, Aldrich) in 30 ml of 1-propanol and to this Triton X-100 surfactant (0.04 M) was added followed by slow addition of 0.5 M of urea with constant stirring. The mass was then allowed to stand 1 h at room temperature to complete the precipitation. The precipitate formed was transferred into 150 ml autoclave and maintained at 200°C for 12 h, cooled, filtered, washed with 10% ethanol in water thrice, dried annealed at 500°C for 3 h.

2.4 Synthesis of SnO₂/TiO₂ Nanocomposite

Nanocomposite formation is a complex process that consists of dissolution, precipitation, reorganization, and hydrothermal process [30]. Tin oxide *nanopowders* and titanium isopropoxide were used as source materials for the hybrid material. First, SnO₂ *nanospheres* (300 mg) were dispersed in 30 mL of 1-propanol by sonication for 1 h to obtain clear ash dispersion. Second, the simultaneous realization of building up the desired architecture and incorporation of a second functional component in this step makes this method very appealing. Titanium isopropoxide (0.4 M, Aldrich) in 30 ml of 1-propanol was added instantaneously followed by Triton X-100 surfactant (0.04 M) to the dispersed medium. Urea solution (0.5 M) was slowly added to the medium, stirred well, the mass was allowed to stand for 1 h to obtain the completion of precipitation at room temperature. Third, is the thermal treatment given to the precipitate in 150 ml capacity autoclave raised to a temperature of 200°C for 12 h and cooled. The resultant solid was washed thoroughly with 10% ethanol and deionized water to remove the impurities, filtered, dried and annealed at 500°C for 3 h.

2.5 Materials and instrumentation

The structural and phase identification of *nanomaterials* were carried out employing X-ray diffractometry (PXRD patterns: the range of $2\theta = 10\text{--}80^\circ$, step scanning using 2θ increments of 0.02° and a fixed counting time of 5 secs/step) with Cu-K α radiation (wavelength of the X-ray source, $\lambda = 1.541 \text{ \AA}$). Raman spectra of phases expected in materials under study were collected on the inVia, RENISHAW micro-Raman spectrophotometer at room temperature. UV-Vis absorption measurements were carried out on a double beam spectrophotometer (Shimadzu model 2450, Japan) consists of integrating sphere attachment (ISR-2200). Steady-state fluorescence emission was made on the Spex FluoroLog-3 spectrofluorometer (Jobin-Yvon Inc.) using 450 W Xenon lamp and equipped with a Hamamatsu R928 photomultiplier tube. The instrument works on the principle of time-correlated single-photon counting (TCSPC) technique. Time-resolved fluorescence decay measurements were carried out using Nano-LED ($\lambda_{ex} = 295 \text{ nm}$) source for excitation (repetition rate 10 kHz). The photons were collected from the front face of the sample with TBX-4-X single-photon-counting detector. Lifetimes were determined by fitting the data to exponential decay models using software packages.

Cyclic voltammetry data were obtained using Autolab interface electrochemical analyzer consisting of three-electrode configuration; Pt working electrode (0.3 mm diameter), auxiliary electrode (Pt), and Ag/AgCl-KCl (sat.) reference electrode with Nova software, version: 2.9.3743-23, S. No. AUT84470. The Pt working electrode surface was polished with 0.05 μm gamma-alumina powder ensuring a clean and uniform electrode surface rinsed thoroughly with

distilled water and acetone. The FT-IR spectra of the compounds were recorded on a Thermo Nicolet-6700 FT-IR instrument in the range 4000-400 cm^{-1} (KBr pellet technique).

Single crystal of the complex was mounted on an Oxford Diffraction Xcalibur diffractometer with an Eos (Nova) detector consists of ω and ϕ scan modes to obtain single crystal analysis. All diffraction measurements were performed at 293(2) K using graphite monochromated Mo- $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). The structure was solved by direct methods and refinement by full-matrix least-squares on F2 using 32-bit Olex 2-1.1 version program. The other computer programs include data collection: CrysAlis PRO (Oxford Diffraction, 2009); cell refinement: CrysAlis PRO, data reduction: CrysAlis PRO, absorption correction: multi-scan (CrysAlis PRO), these programs were used to solve the structure. The structure refinement was undertaken using; 32-bit Olex 2-1.1 version (Oleg Dolomanov and Horst puschmann, Durham University, UK), molecular graphics: ORTEP-3 for windows-version 2.02 (University of Glasgow, 2008), Mercury 2.3 version copyright work belonging to CCDC software package, 32-bit Olex 2-1.1 version software was used to generate material for publications.

The morphology and microstructure of the synthesized sample were examined by scanning electron microscopy. Resolution: 3nm @ 30kV HV mode; 10nm @ 3 kV HV mode Detectors: Secondary Electron; Semiconductor BSE (Quad type) Magnification: 5 x to 300,000x; Vacuum System: TMP & Rotary to $1.5 \times 10^{-3} \text{ Pa}$ Specimen Stage: Motorised 5-axis, Eucentric Specimen height: 80mm at 10mm W.D. and TEM investigations, the samples were prepared by placing a drop of oxide powder and ultrasonically dispersing in aqueous medium. Microstructure analysis was undertaken on a high-resolution transmission electron microscope (HRTEM) JEM 3010 JEOL (Tokyo, Japan) equipped with a field emission gun operating at 200 kV, a high brightness LaB₆ filament electron source, and image processing by digital micrograph software. Microscopic feature (AFM) of prepared SnO₂/TiO₂ *nanocomposites*, bare SnO₂, and TiO₂ *nanoparticles* at 300 K were collected on a Universal Scanning Probe Microscope (Innova SPM) in tapping mode imaging using glass plate with the size range of 1mm x 1mm. The *nanoparticles* are dispersed in an aqueous medium, drop-casted on the glass plate, and keep it spin coating machine. After spin-coating, the sample has dried at 60-70°C, then analyzed for atomic force microscopy. The magnetic properties of the sample were observed on a vibrating sample magnetometer, quantum design magnetic property measurement system (Lake Shore, 7404) equipped with a reciprocating sample option (vibration frequency: 82.5 Hz; magnet: 400'' (200'' at Pole face); max field: 15 kGauss; moment range: 1 μemu to 56 emu; and 80-1400 K temperature).

2.6 Surface adsorption experiments

Surface adsorption property of iron(III) dipicolinato complex, $(\text{NH}_3\text{-trz})[\text{Fe}(\text{dipic})_2]$, on $\text{SnO}_2/\text{TiO}_2$ nanocomposite, *nano* SnO_2 and *nano* TiO_2 was examined by dispersing 300 mg of each adsorbent in 100 ml of water. Subsequently, the sorption process was initiated by adding iron(III) complex (9.4478×10^{-6} M) in neat water and in binary solvents ($\text{H}_2\text{O}:\text{Pr}^i\text{OH} = 70:30$; $\text{H}_2\text{O}:\text{CH}_3\text{CN} = 70:30$; $\text{H}_2\text{O}:\text{DMSO} = 70:30$; $\text{H}_2\text{O}:\text{Bu}^t\text{OH} = 70:30$ (v/v)). All equilibrium sorption experiments were conducted at 25 °C in dark at neutral pH, ionic strength was maintained by adding 1 M of $\text{NaClO}_4\cdot\text{H}_2\text{O}$, purged with nitrogen gas in 125 mL stoppered bottle. The flask was sealed, sonicated to adsorption-desorption equilibrium, and transferred to a rotatory shaker to perform an adsorption experiment at room temperature. The adsorption process of iron(III) complex on *nanosphere* particles was examined by following the change of the electronic absorption spectrum. Adsorption experiments were conducted by exposing iron(III) complex on *nanoparticles* with different time intervals (0, 5, 10, 15, 30, 45, and 60 min). The particles were separated from the suspension by centrifugation and the concentration of $(\text{NH}_3\text{-trz})[\text{Fe}(\text{dipic})_2]$ complex was estimated from UV-Vis spectral analysis ($\lambda = \sim 480$ nm) with a Shimadzu spectrophotometer.

2.7 Photocatalytic Test

A homemade three-jacket quartz immersion well reactor was designed with an internal light source (low-pressure mercury-vapor lamp $\lambda = 254$ nm, 6W, Heber Scientific; model: LX-1108). Potassium ferrioxalate, $\text{K}_3[\text{Fe}(\text{C}_2\text{O}_4)_3]\cdot 3\text{H}_2\text{O}$, actinometry ($\lambda = 254$ nm, 8.50×10^{17} photons/sec) was employed to calculate the intensity of light source [31] The inner jacket was cooled by water circulation and the outer jacket with a capacity of volume = 100 mL was devoted to photolyte solution containing a magnetic pellet. Photolyte solution consists of *nanoparticles* (300 mg), $(\text{NH}_3\text{-trz})[\text{Fe}(\text{dipic})_2]$ complex (9.4478×10^{-6} M) and 1 M $\text{NaClO}_4\cdot\text{H}_2\text{O}$ in neat water and in binary solvents ($\text{H}_2\text{O}:\text{Pr}^i\text{OH} = 70:30$; $\text{H}_2\text{O}:\text{CH}_3\text{CN} = 70:30$; $\text{H}_2\text{O}:\text{DMSO} = 70:30$; $\text{H}_2\text{O}:\text{Bu}^t\text{OH} = 70:30$ (v/v)). The solution was sonicated in dark to obtain dispersion and to allow adsorption-desorption equilibrium between iron(III) complex and *nanoparticle* surface. The photocatalytic reaction was started by switching on the UV lamp and samples were discontinuously taken at various times during the irradiation (0, 3, 6, 9, 12, 18 min). Sampling analysis was performed using a syringe and the accuracy of the experiment was verified by repeated blank experiments (analytical absorbance, $\lambda = \sim 480$ nm). Photoreduction efficiency was calculated using the equation $X = [C_i - C_0/C_i] \times 100$ (where X is the photo efficiency, C_0 is the initial concentration of the complex and C_i is the concentration of the complex after reduction of Fe(III) ions). The generation of hydroxyl radical formation during heterogeneous catalysis was identified by systematic calibration of the emission of 7-

OH coumarin, which is a highly fluorescent product. A certain quantity of coumarin (1×10^{-3} M) was dissolved in 100 ml of water and 300 mg of catalyst dispersed, the mixture was placed under ultra-violet irradiation for 60 min. After irradiation, the mixture was filtered and measured by fluorescence spectra at excitation wavelength of 450 nm.

3 Results and Discussion

3.1 Characterization of $(\text{NH}_3\text{-trz})[\text{Fe}(\text{dipic})_2]$ Complex

3.2 Description of crystal structure

As presented from X-ray analysis crystal data, the complex $(\text{NH}_3\text{-trz})[\text{Fe}(\text{dipic})_2]$ crystallizes in orthorhombic space group $P2_12_12_1$. The asymmetric unit of complex reported here comprises of an $[\text{Fe}(\text{dipic})_2]^-$ anion with inorganic counter cation of 4-amino-4H-1,2,4-triazol-4-ium. As depicted in Fig. 1, the crystal structure of Fe(III) ion is coordinated with two equivalent of pyridine-2,6-dicarboxylic acids of four carboxylate oxygen atom in equatorial position and two pyridine nitrogen atoms coordinated in axial positions. Fe(III) complex has distorted *trans*- N_2O_4 octahedral of two tridentate pyridine-2,6-dicarboxylic acid ligands which are almost in a perpendicular position and Fe(III) ion is situated on a crystallographic fourfold rotoinversion axis [32, 33]. The crystal structure data, structural refinement, and geometric parameters are presented in Table 1, T1. The bond angles of O1-Fe1-O2 and O3-Fe1-O4 of two trans oxygen and nitrogen atoms (N1-Fe1-N2) of pyridine-2,6-dicarboxylic acid ligands are 150.39° and 174.27° , respectively. The Fe-N and Fe-O bond distances in the anionic complex are in the range 2.059(2) up to 2.055(1) Å and 2.002(1) up to 2.060(1) Å, respectively [34]. These bonds are comparable with those reported for $(\text{NH}_3\text{-trz})[\text{Fe}(\text{dipic})_2]$ complex, where Fe-N bond distances are in the range 2.058(1) up to 2.068(1) Å, and the Fe-O bond distances are in the range from 2.012(1) up to 2.035(1) Å [35, 36]. In the complex, the intermolecular hydrogen bonds comprising the N-H groups of the inorganic counter ion and the pyridine C-H groups as donors and the non-coordinating oxygen atoms of the carboxylate groups as acceptors [length $d(\text{O}\cdots\text{H})$ and angle $\angle(\text{N-H}\cdots\text{O})$ vary from 2.736(3) to 3.020(3) Å and $141\text{--}169^\circ$, respectively] form into the 3D supramolecular networks. The N-H...O hydrogen bonds are obtained between uncoordinated 4-amino-4H-1,2,4-triazole molecules (N3) and between atrazine nitrogen atoms (N4) and carboxylate oxygen atoms (O7, O8) of $[\text{Fe}(\text{dipic})_2]^-$ anions [37]. The existence of weaker $\pi\cdots\pi$ stacking relationships between the pyridine rings also leads to the crystal structure stability.

3.3 HR-MS analysis

High-resolution mass spectrometry (HRMS) analysis was performed to confirm the formation of $(\text{NH}_3\text{-trz})[\text{Fe}(\text{dipic})_2]$ complex. As presented in Fig. 2, the observed isotopic ionic peak obtained by dilution of acetonitrile in water. A set of ion peak signals obtained at m/z 472.0056

corresponds to the $[M+H]^+$, which is ascribed to the monoanionic complex of $(\text{NH}_3\text{-trz})[\text{Fe}(\text{dipic})_2]$; *Calc*: 470.9988 and this result gave remarkable evidence of the formation of the complex.

3.4 UV-Vis Spectrum

The electronic transitions of the anionic complex $(\text{NH}_3\text{-trz})[\text{Fe}(\text{dipic})_2]$ were characterized by UV-Visible spectroscopy in neat water in the region of 200-800 nm as depicted in Fig. S1. The complex exhibits four absorption bands at 670, 477, 270, 255 nm. The absorption bands can be assigned to the intra-ligand transitions including $n \rightarrow \pi$ at $\lambda = 255$ and 270 nm due to the dicarboxylate ligand. The UV-Visible spectrum of complex shows ligand to metal charge transfer transition at $\lambda = 477$ nm and can be assigned to ${}^6A_1 \rightarrow {}^4E$, ${}^4A_1({}^4G)$. The weak and broad absorption bands are observed at 670 nm can be ascribed to the ${}^4T_1({}^4G) \rightarrow {}^6A_1$ transition (d^5 iron(III)) with the high spin state, the transition is both spin forbidden and orbital forbidden [38]. The spectral redshift of the visible absorption bands relative to $[\text{Fe}(\text{dipic})_2]^-$ has been studied and assisted by the cathodic shift of the Fe(III)/Fe(II) redox potential of $(\text{NH}_3\text{-trz})[\text{Fe}(\text{dipic})_2]$ complex.

3.5 Photophysical analysis

The photophysical and photochemical properties of transition metal coordination complex have been studied to understand the excited states of complex rapidly developed through photochemistry. Photoluminescence (PL) behaviour of $(\text{NH}_3\text{-trz})[\text{Fe}(\text{dipic})_2]$ complex has been studied in water at the excitation wavelength of 270 nm as shown in Fig. S2 to understand the characteristics of the various excited states. The emission bands appear at $\lambda = 296, 331, 378, 390, 412, 437, 486$ and 511 nm with high and weak energy peaks. The absorption bands appeared at the range between 296-390 nm with a high-intensity energy shoulder of ligands [39]. Fe(III) ion is coordinated with ligands, the emission bands at 378 nm with slight redshift and weak intensity shoulder enhancement were observed for the emission band of $(\text{NH}_3\text{-trz})[\text{Fe}(\text{dipic})_2]$ complex [40]. The bands appeared in a blue region between 412 to 486 nm due to intra-ligand $\pi\text{-}\pi^*$ transition.

3.6 Raman Spectrum

Raman spectral features of $(\text{NH}_3\text{-trz})[\text{Fe}(\text{dipic})_2]$ complex were measured 50-2000 cm^{-1} using an excitation laser power of 784 nm and are depicted in Fig. S3. Raman spectral bands of $(\text{NH}_3\text{-trz})[\text{Fe}(\text{dipic})_2]$ were observed at 198, 397, 648, 682, 766, 891, 1002, 1094, 1152, 1208, 1383, 1274, 1349, 1453, 1580, 1676, 1728 cm^{-1} . The bands observed at 198 and 397 cm^{-1} can be ascertained to the symmetric and asymmetric stretching vibrations of Fe-O bond in $(\text{NH}_3\text{-trz})[\text{Fe}(\text{dipic})_2]$ complex, respectively. The band appeared at 1349 cm^{-1} can be ascribed to the disappearance of vibrations of the hydroxyl group $\nu(\text{OH})$, $\beta(\text{OH})$ and $\gamma(\text{OH})$ as well. The most

intensive region is observed in 1580, 891, 1453 cm^{-1} corresponds to the stretching vibrations of aromatic rings ($\nu_{\text{C-H}}$, $\nu_{\text{C=N}}$, $\nu_{\text{C-C}}$) and bending β (C-O) vibrations, respectively. The band appeared at 1676-1580 cm^{-1} can be assigned to the $\nu_{\text{sym}} \text{COO}^-$ and $\nu_{\text{asym}} \text{COO}^-$ vibrations respectively [41]. The metal ion is substituted on the two carboxylic acid results in the disappearance of the characteristic symmetric and asymmetric vibrations of carboxyl groups. The band appears at 648 and 682 cm^{-1} can be attributed to vibrations of Fe-N and O-Fe-N groups respectively [42].

3.7 Electrochemical measurements

The redox behavior of $(\text{NH}_3\text{-trz})[\text{Fe}(\text{dipic})_2]$ complex was investigated by cyclic voltammetry in acetonitrile at room temperature. The experiments were carried out using a three-electrode system (working electrode as platinum foil, counter electrode as platinum rod, and Ag/AgCl in KCl (sat.) as reference electrode) and tetrabutylammonium perchlorate as the supporting electrolyte. A cyclic voltammogram of $(\text{NH}_3\text{-trz})[\text{Fe}(\text{dipic})_2]$ complex is displayed in Fig. 3 and exhibits one quasi-reversible reduction region and one irreversible region and the potential values are presented in the Table T2 at various scan rates: 50-350 mV/s. First quasi-reversible reduction region corresponds to the ligands; can be associated with an anodic region at -1.1920 V coupled with a cathodic region at -1.2096 V [43]. The first reduction potential observed is more negative represents ligand-based reduction behaviour showing superior electron donor effect influences the electrochemical properties of $(\text{NH}_3\text{-trz})[\text{Fe}(\text{dipic})_2]$ complex. Second irreversible cathodic region appears at 0.6896 V. The second reduction potential peak can be ascribed to Fe(III)/Fe(II) generation in the anionic complex ion [44, 45].

3.8 FT-IR Analysis

Fourier transform infra-red spectroscopy reveals vibrations of functional groups such as the N-H group coordinated to 4-amino-4H-1,2,4-triazol-4-ium cation, nitrogen atom and aromatic CHs of pyridine dicarboxylate groups and binding interaction of metal to the ligand in the complex. As depicted in Fig. S4, the strong bands at 1650 and 1380 cm^{-1} can be attributed to asymmetric ($\nu_{\text{asym}}(\text{COO}^-)$) and symmetric ($\nu_{\text{sym}}(\text{COO}^-)$) stretching vibrations of the carboxyl acid groups, respectively. The separation between asymmetric and symmetric vibrations of COO^- groups are in the range 306-372 cm^{-1} , which indicates that the carboxylic group is coordinated to the central metal Fe(III) ion. The band at 735- 752 cm^{-1} and 619-699 cm^{-1} can be ascribed to the vibrations of $\nu_{\text{O-C-O}}$ in dipicolinate ring and wagging vibrations of pyridine ring [46, 47]. The strong and broad absorption bands at 1595-1602 cm^{-1} can be assigned to $\nu_{\text{C=N}}$. The broad absorption bands at 3234-3479 cm^{-1} can be attributed to the O-H groups in the crystal lattice

and $\nu_{\text{N-H}}$ of the inorganic cation of counter-ion of 4-amino-1,2,4-triazole moiety as disclosed by the X-ray crystal structure [48, 49].

3.9 Magnetic property

The magnetic property of Fe^{3+} ion in $(\text{NH}_3\text{-trz})[\text{Fe}(\text{dipic})_2]$ complex was measured at room temperature by vibrating sample magnetometer as presented in Fig. 4a. The saturation magnetization was measured in the range between ± 3000 Oe. A low saturation magnetic moment $M_s = 0.1285$ to -0.1294×10^{-3} emu/g and coercive field $H_c = 59.08$ to 65.58 emu/g were observed. The linear curve of iron (III) complex shows paramagnetic nature to the applied magnetic field versus magnetization, which identifies that the mononuclear arrangement of iron (III) complex with 2,6-pyridine dicarboxylic acids and 4-amino-1,2,4-triazole complex. In complex, $[\text{Fe}(\text{dipic})_2]^-$ anion binding properties of the more electron-donating group and average bond lengths of Fe–N ($2.0551(3)$ Å) are closely related to high-spin molecules at room temperature [50].

4 Characterization of nanocomposite photocatalyst

4.1 PXRD analysis

The crystal structures and phase purity of hydrothermally prepared bare SnO_2 , TiO_2 nanospheres, and $\text{SnO}_2/\text{TiO}_2$ nanocomposite were characterized by powder X-ray (XRD) spectroscopy. Fig. 5 exhibits all the diffractions peaks well indexed to the pure tetragonal phase (space group $P4_2/mnm$) of SnO_2 (JCPDS card No. 041-1445) [51]. The XRD pattern of $\text{SnO}_2/\text{TiO}_2$ nanocomposite can be easily distinguished with two separate phases from the mixture, the smaller particle size of the anatase phase of TiO_2 combined with the slightly larger particle size of the tetragonal phase of SnO_2 [52, 53]. After annealing at $\sim 500^\circ\text{C}$ for 3 h, the absence of impurities or secondary phase was inducted as supported in the XRD analysis. All diffraction peaks of bare TiO_2 nanospheres are well indexed to anatase phase and matched with the standard pattern (JCPDS card No. 021-1272) [54]. The mean crystallite particle size of the samples of $\text{SnO}_2/\text{TiO}_2$ nanocomposite, nano SnO_2 , and TiO_2 were calculated by using the Scherrer equation, $D = 0.9\lambda/\beta(\cos \theta)$, where, λ is the wavelength of the X-ray (1.54 Å), β is the full-width at half maximum (FWHM) in radians, and θ is the Bragg angle in the diffraction pattern. From this equation, the mean crystalline particle size was estimated to be 35.36 nm, 32.09 nm, and 66.42 nm and different parameters are presented in Table 2. Consequently, it could be deduced that the SnO_2 tetragonal phase and TiO_2 anatase phase coexisted in these nanocomposites, in good agreement with the SEM and TEM results.

4.2 Raman Analysis

Raman spectroscopy is one of the versatile characterization tool for hydrothermally prepared $\text{SnO}_2/\text{TiO}_2$ nanocomposite, bare SnO_2 and TiO_2 nanospheres at the excitation wavelength of

784 nm as shown in Fig. 6 and presented in Table 2. As can be seen, the rutile phase of SnO₂ has a D_{4h} symmetry with two formula units per primitive cell and lattice constants $a = b = 4.7373 \text{ \AA}$ and $c = 3.1864 \text{ \AA}$ [55]. The Raman scattering spectra of SnO₂ has three vibrational active modes A_{1g} , E_g , and B_{2g} were identified and corresponding to 445, 624, and 775 cm⁻¹ modes respectively. The anatase phase of TiO₂ has a tetragonal symmetry with point group $4/mmm$, four active modes are observed 141 cm⁻¹ (E_g), 394 cm⁻¹ (B_{1g}), 514 cm⁻¹ (A_{1g}), 637 cm⁻¹ (E_g) [56]. The anatase modification has six Raman active modes ($A_{1g} + 2B_{1g} + 3E_g$). In single crystals, these modes are located at 144 (E_g), 197 (E_g), 399 (B_{1g}), 513 (A_{1g}), 519 (B_{1g}), and 639 cm⁻¹ (E_g). All these lines are present in the observed spectra. The E_g band can be assigned to the symmetric stretching vibration of O-Ti-O, the B_{1g} peak is corresponding to the symmetric bending vibration of O-Ti-O, and the A_{1g} can be ascribed to the anti-symmetric bending vibration of O-Ti-O in TiO₂ [57]. Raman spectra confirmed that no additional peaks existed in the composites and bare components belong to impurity.

4.3. Microstructure analysis

The surface morphology of SnO₂ and TiO₂ nanospheres and SnO₂/TiO₂ nanocomposite annealed at 500°C were investigated by the SEM and TEM images. The low magnified SEM images of all the samples in Fig. 7a-d depicts a large quantity of slightly aggregated, well-defined spherical shape in morphology and good uniform in size. The TEM images further confirm that existence of spherical morphology in composites with SnO₂ nanoparticles well dispersed on the surface of TiO₂ nanoparticles uniformly by the hydrothermal method are shown in Fig. 8, S5 and S6. The particle size histogram of the samples SnO₂, SnO₂/TiO₂, TiO₂ was found to be 30-60 nm, 20-50 nm, and 15-45 nm respectively. The lattice d spacing observed at 0.33 nm and 0.35 nm can be assigned to the SnO₂ and TiO₂ nanoparticles. In the SAED pattern, the SnO₂/TiO₂ nanocomposites four-fold symmetric diffraction spots correspond to the presence of SnO₂ and TiO₂ nanoparticles. While a series of concentric circles correspond to the electron diffraction of (101), (110), (210) planes of the crystal [58]. AFM imaging demonstrated useful information as a feature dispersion in aqueous medium regarding the various agglomeration tendencies. Fig. 9a-f shows two and three-dimensional atomic force microscopic images of SnO₂, SnO₂/TiO₂ and TiO₂ nanoparticles on a glass substrate. The images were recorded at the scan rate of 10.17 Hz of 1 μm x 1 μm planar in contact mode. SnO₂ nanoparticle sample is not uniformly distributed with spherical grains of varying size of 500 nm magnifications. TiO₂ nanoparticles shown the uniform size with spherical shape was observed. The average particle size ranges between 15-59 nm, resulting in very good agreement with SEM and TEM Images. SnO₂/TiO₂ nanocomposites are irregular dispersion of two

distinct interaction of bare *nanoparticles* with spherical shape appeared at 400 nm magnifications [59].

4.4 Optical Properties

Fig. 10a displays the UV-Vis absorption spectra of TiO₂ and SnO₂ *nanospheres* and the *nanocomposite*, indicating the light-harvesting capacity in the region 205-335 nm. The absorption curves illustrate adsorption edge at ~ 360 nm, ~400 nm and ~395 nm can be observed to *nano* SnO₂, SnO₂/TiO₂ *nanocomposite* and *nano* TiO₂ respectively are presented in Table 2. The optical band gap energy of the samples was estimated by Tauc approach according to the following equation $(\alpha h\nu)^n \propto (h\nu - E_g)$, where α , $h\nu$, and E_g are the absorption coefficient, photon energy, and band gap, respectively. In the relationship, n is related to the characteristics of the transition of a semiconductor (indirect transition: $n = 1/2$; direct transition: $n = 2$) [60, 61]. The direct transition of semiconductor samples is the plot of $(\alpha h\nu)^2$ against $h\nu$ as shown in Fig. 10b, the bandgap values are found to be 3.69, 3.30, 3.28 eV for SnO₂, SnO₂/TiO₂ *nanocomposite*, and TiO₂ respectively. SnO₂/TiO₂ *nanocomposite* could absorb photon on the selective region of UV and visible range indicating promising UV-Visible light photocatalyst.

4.5 Photoluminescence Spectra and Life time studies

Photoluminescence (PL) spectra of *nanostructured* materials convey the charge separation and photogenerated electron/hole recombination characteristics of the photocatalyst. The steady-state photoluminescence (PL) spectra of *nano* SnO₂, SnO₂/TiO₂ *nanocomposite*, and *nano* TiO₂ exhibit predominant emission peak at $\lambda \sim 400$ nm, two sub-peaks at $\lambda \sim 467$ and 521 nm, and additionally very weak peaks as depicted in Fig. 11a. It is imperative to understand that the emission is caused by the recombination, and free excitons as well as bound excitons (self-trapped excitons). It becomes also clear that the sub-peaks observed are induced surface defect states if compared with energetic positions. It is well known that lowering peak intensity refers to delay in electron/hole recombination, higher charge separation efficiency, and resulted in better photocatalytic activity [62]. The intensity of emission decreased in the order: *nano* SnO₂ (421 nm) > *nano* TiO₂ (398 nm) >> SnO₂/TiO₂ *nanocomposite* (397 nm). Table 2 illustrates the high-intensity emission band at ~ 400 nm (weak ultraviolet emission) is assigned to self-trapped excitons and ~ 467 nm free excitons [63]. The ~520 nm (green emission) is due to band-band transition along with a set of weak intensity emission bands mentioning the formation of a significant number of trapped states, which are responsible for various PL signals in the visible region [64]. Currently, an important experimental technique, time-resolved photoluminescence (TRPL) is frequently carried out to probe the recombination dynamics of the photogenerated charge carriers. Kinetic analysis data on the intensity decay

profile of the emission caused by the recombination of electron/hole and excitons and the lifetime distributions are illustrated. The curve implies the multi-exponential decay, in coincidence with three decay durations τ_1 , τ_2 , and τ_3 lifetime scales. These lifetime components can be fitted in the relation: $A + B_1 \exp\{-t/\tau_1\} + B_2 \exp\{-t/\tau_2\} + B_3 \exp\{-t/\tau_3\}$ to produce time-resolved dynamics of carriers, a more direct and important technique behind the high activity of prepared photocatalyst. The room temperature time-decay curve of the *nano* SnO₂, *nano* TiO₂ and SnO₂/TiO₂ *nanocomposite* (excitation wavelength at 292 nm, Fig. 11b-d fits well to a triexponential function ($I = \sum A_n \exp(-t/\tau_n)$), where A_n and τ_n represent the amplitude and lifetime of the component, respectively. The fast component, τ_1 , represents the near band edge relaxation lifetime, and the second one, τ_2 , indicates photogenerated charge carriers relaxation lifetime of the shallow-trap states. The fast lifetime associated with, τ_3 , can be matched with deep state relaxation of the photogenerated charge carriers [65]. The average PL lifetime (τ_{avg}) of each samples can be calculated using this equation: $\tau_{avg} = (B_1 \tau_1^2 + B_2 \tau_2^2 + B_3 \tau_3^2) / (B_1 \tau_1 + B_2 \tau_2 + B_3 \tau_3)$ and are presented in Table 2. This is equated with the efficiency of the various *nanoscale* photocatalysts of SnO₂ (32.59 ns) TiO₂ (34.70 ns) *nanospheres*, and SnO₂/TiO₂ *nanocomposite* (37.77 ns) at an excitation wavelength of 292 nm. The lifetime of excitons is increased for the *nanocomposites* since additional intermediate states introduced to reduce the recombination of charge carriers to act as best photocatalyst [66].

4.6 FT-IR analysis

Fourier transform infrared spectroscopy (FTIR) is an important and informative technique, which confirms the existence of the nature of the chemical bonding of metal oxide composites. Fig. S7 shown that the FT-IR spectra for SnO₂/TiO₂ composites and bare components in the region of 4000-400 cm⁻¹. The characteristic vibrational peaks at 513 and 631 cm⁻¹ are attributed to the Sn-O and Sn-O-Sn stretching vibrations of SnO₂ respectively [67]. The vibrational modes between 730 to 470 cm⁻¹ can be assigned to Ti-O-Ti stretching vibrations [68]. The broad region between 460-715 cm⁻¹ obtained shows the co-existence of Sn-O-Ti vibrations in the composites [69].

4.7 Magnetic property analysis

The magnetic properties of the as-prepared *nanocomposite* were also explored for their inherent magnetic characteristics. The *M-H* curves of SnO₂/TiO₂ *nanocomposites*, bare SnO₂ and TiO₂ *nanospheres* are depicted in Fig. 4b-d at room temperature. All the samples show a hysteresis loop with ferromagnetic behaviour. It could be the existence of either oxygen vacancies or cation vacancies present in the samples. The saturation magnetization, coercivity and magnetic remanence values of SnO₂/TiO₂ *nanocomposites*, bare SnO₂ and TiO₂ *nanospheres* are presented in Table T3. The saturation magnetization of *nanocomposites* is

much more prominent than the bare TiO_2 and SnO_2 nanospheres because of the spin reorientation emerging from the spin-spin interface between Sn-O and Ti-O dipoles [70]. The spins on the interface layer could have two distinct forms of SnO_2 and TiO_2 interaction to improve the nanocomposites coercivity and magnetic remanence. In nanocomposites with a strong probability of the existence of uncompensated bonds of Sn, Ti and O, there may be a significant amount of lattice mismatch at the synergetic effect of individual nanocomponents. This indicates that the synergetic effect influences magnetism to separate catalyst by the external magnetization.

5 Surface Adsorption experiments

The removal of $(\text{NH}_3\text{-trz})[\text{Fe}(\text{dipic})_2]$ complex was carried out by batch experimentation in neat water and in binary solvents ($\text{H}_2\text{O}:\text{Pr}^i\text{OH} = 70:30$; $\text{H}_2\text{O}:\text{CH}_3\text{CN} = 70:30$; $\text{H}_2\text{O}:\text{DMSO} = 70:30$; $\text{H}_2\text{O}:\text{Bu}^t\text{OH} = 70:30$ (v/v)) at room temperature. 300 mg of *nanoparticle* adsorbent and 1 M $\text{NaClO}_4\text{-H}_2\text{O}$ as a function of ionic strength of the solution have been used to remove $(\text{NH}_3\text{-trz})[\text{Fe}(\text{dipic})_2]$ (9.4478×10^{-6} M) complex at various time intervals. During all experiments, *nanoparticles* are well dispersed and the concentration of the complex gradually decreased and finally attained the equilibrium at 60 min. After surface adsorption, the ability of iron(III) complex and *nanoparticle* interactions are agglomerated and disappearance of the colour of the solution. As can be seen in Fig. 12a, b, the results have shown that the removal efficiency and rate constant of *nanocomposites* are much higher in the specified solvent medium at 60 min time duration. The apparent photoreaction rate (k) of *nanocomposite* is 0.0466 sec^{-1} , which is higher than the SnO_2 (0.0104 sec^{-1}) and TiO_2 (0.0260 sec^{-1}) bare components in $\text{H}_2\text{O}:\text{DMSO}$ (70:30%) than the other solvents medium as displayed in Fig. S8. Among the various solvent proportions, the impact of dimethyl sulfoxide (DMSO) gave much higher than the other medium, due to more interaction of complex and *nanocomposites*. In addition, the effects of solvent on the less formation of hydrogen-bond interaction between template molecules to interact with the surface of the *nanoparticles* [71-73], could also be the reason that led to the different adsorption capacity and selectivity as presented in Table 3, T4.

6 Photocatalytic Reduction

It was explored to deduce the apparent kinetic model to estimate the photocatalytic reduction of $(\text{NH}_3\text{-trz})[\text{Fe}(\text{dipic})_2]$ complex by SnO_2 , TiO_2 *nanospheres*, and $\text{SnO}_2/\text{TiO}_2$ *nanocomposite* in water and binary solvent media under ultra-violet irradiation. Fig.13a, b display the degradation efficiency and rate of photoreduction of $(\text{NH}_3\text{-trz})[\text{Fe}(\text{dipic})_2]$ complex on the $\text{SnO}_2/\text{TiO}_2$ heterostructures in water and in binary solvents ($\text{H}_2\text{O}:\text{Pr}^i\text{OH} = 70:30$; $\text{H}_2\text{O}:\text{CH}_3\text{CN} = 70:30$; $\text{H}_2\text{O}:\text{DMSO} = 70:30$; $\text{H}_2\text{O}:\text{Bu}^t\text{OH} = 70:30$ (v/v)) medium at 18 min time intervals. $\text{SnO}_2/\text{TiO}_2$ heterostructures showed superior photocatalytic activity rather than bare SnO_2 and

TiO₂ *nanospheres*. In a coupled system, efficient separation of photogenerated electron-hole pairs and less recombination played a significant role in the reduction of the coordination complex. It can be observed that the photo efficiency of SnO₂, TiO₂, SnO₂/TiO₂ *nanocomposite* are 49%, 88%, and 91% in H₂O/PrⁱOH (70/30% (v/v)) at 18 min time duration is higher than the other medium are presented in Table T5. The apparent photoreaction rate (*k*) of nanocomposite is 0.1432 sec⁻¹, which is higher than the SnO₂ (0.0373 sec⁻¹) and TiO₂ (0.1422 sec⁻¹) bare components in H₂O:PrⁱOH (70:30%) than the other solvents medium as shown in Fig. S9. The order of the photocatalytic reduction as follows SnO₂/TiO₂ > TiO₂ >> SnO₂. The peak intensity of (NH₃-trz)[Fe(dipic)₂] complex increased significantly, confirming the reduction of Fe(III) ions. The formation of Fe(II) ion has confirmed by Kitson's technique with the presence of phenanthroline as a complexing agent [74]. The photo efficiency of formation of Fe(II) ion presented in Table T6. The photocatalytic degradation kinetics of the samples were systematically analyzed by fitting the data to the Langmuir-Hinshelwood model. The model is expressed in its simple form as a pseudo-first-order kinetic reaction when the initial dye concentration (*C*₀) is low, and it is expressed as $\ln C_0/C_t = kt$ where *C*_{*t*} and *C*₀ are the initial concentration of complex at time *t* = *t* and *t* = 0 and *k* is the reaction rate constant. The values of rate constant for the samples were determined in neat water and binary solvent medium are presented in Table 3. The role of organic reactive species involved in photocatalytic reaction quenching experiments by adding various experiments such as isopropanol, tert-butanol, dimethyl sulfoxide for electrons (e⁻), and hydroxyl radicals (•OH), respectively. The photocatalytic experiments were carried out in the absence and presence of scavengers with these two active species (e⁻ and •OH) on (NH₃-trz)[Fe(dipic)₂] complex in presence of photocatalyst. During the photolysis experiment, H₂O/PrⁱOH (70:30 (v/v)) medium were able to trap more number of hydroxyl radical, thus enhancing the availability of electrons to reduce coordination complex more effectively. After photocatalytic reduction of complex, the efficiency of catalyst decreased in the presence of scavengers. It is confirmed that, the reactive species involved in the photocatalytic reduction reactions and the importance of hydroxyl radicals and electrons in the environmental remediation.

6.1 Mechanism of photodegradation

The photoconversion of Fe(III) centre into Fe(II) due to effective separation of electron-hole separation in SnO₂/TiO₂ *nanocomposite* is illustrated in Fig. 14. The mechanism of electron flow in the heterojunction of the photocatalyst was calculated by using the EQs (1) and (2) with the band positions of the conduction band (*E*_{CB}) and valence band (*E*_{VB}) of SnO₂ and TiO₂ semiconductors.

$$E_{CB} = \chi - E^e - 1/2 E_g \quad (1)$$

$$E_{VB} = E_{CB} + E_g \quad (2)$$

where E_{CB} and E_{VB} are the CB and VB band edge potential, respectively; χ is the electronegativity of the semiconducting material, which is the geometric mean of the electronegativity of the constituent atoms; E^e is the energy of free electrons on the hydrogen scale (4.5 eV), and E_g is the bandgap energy of the semiconductor. The SnO₂ and TiO₂ conduction band (CB) edges are located at -0.13 eV and -0.33 eV relative to the standard electrode of hydrogen (NHE) at pH 7. The observed difference between SnO₂ and TiO₂ on the conduction band edges makes it much easier for the photogenerated electrons on the TiO₂ surface to migrate to the SnO₂ conduction band. This increases the rate of charge separation of the photogenerated charge carriers, while because of their higher VB level, the photogenerated holes accumulate on TiO₂. The intensity of the PL signal in the composite has decreased and ascribed to the enhanced charge separation of the photogenerated electron-hole pairs. The electrons in the TiO₂ once excited to the CB get easily transferred to the CB of SnO₂ of the SnO₂/TiO₂ nanocomposite. These electrons induce adhered iron(III) dipicolinato, [Fe(dipic)₂]⁻, anion and generate photo-reductive products. The holes in the VB of SnO₂ get transferred to TiO₂ and reacts with OH⁻ to form hydroxyl radicals. In addition, the lifetime of photogenerated species of composite is higher than bare SnO₂ and TiO₂ nanospheres. The plausible mechanism is as follows;

Reactions (3) - (11) imply that the possible pathway of the photocatalytic process.

6.2 Hydroxyl radical study

In order to investigate the progress of hydroxyl radicals ($\bullet\text{OH}$) on the surface of photocatalyst during the photocatalytic reaction. The generation of reactive organic species of each catalyst has been investigated to the photochemical reduction of the $(\text{NH}_3\text{-trz})[\text{Fe}(\text{dipic})_2]$ complex [75]. In a typical process, coumarin used as the $\bullet\text{OH}$ -trapping agent, allowing the measurement

of photoluminescence intensity with an excitation wavelength at 332 nm are depicted in Fig. 15. The characteristic photoluminescence (PL) emission peak at about 450 nm of 7-hydroxycoumarin (7-OH coumarin) for all catalyst is measured for 60 min are presented in Table T7. Nanostructured TiO₂ offered much higher PL intensity than SnO₂/TiO₂ nanocomposites and bare SnO₂ nanoparticles. The results revealed that the TiO₂ nanoparticles generate more number of hydroxyl radicals on the surface of the catalyst rather than nanocomposites and SnO₂ nanoparticles.

7 Conclusion

By integrating nano TiO₂ and nano SnO₂ into a single-step hydrothermal process, a progressive hybrid design was successfully evolved. In comparison to pure SnO₂ and TiO₂ nanostructures, the SnO₂/TiO₂ nanocomposites had significantly improved self-sensitized degradation efficiency under UV radiation. Exceptionally high efficacy could be credited to acceptable contact and suitable energy band alignment cum arrangement of SnO₂ and TiO₂ phases, which empowered the solid coupling connection. The adsorption capacity of (NH₃-trz)[Fe(dipic)₂] by SnO₂/TiO₂ nanocomposites in H₂O/DMSO (70/30% (v/v)) is higher than that of other solvents mixtures. The photocatalytic reduction of the (NH₃-trz)[Fe(dipic)₂] complex in H₂O/PrⁱOH (70/30 % (v/v)) gives the best results compared to other solvent mixtures. Interestingly, the photogenerated electron's lifetime was enhanced when it was distributed across the progressive network. The SnO₂/TiO₂ nanocomposites acted as electron sinks, causing electrons to separate spatially, and as effective electron mediators, promoting the development of diminished products. The SnO₂/TiO₂ nanocomposites can explain light-harvesting ability, prompting improved photon retention in the metal complex. The synergistic effects of these components, together with their incredible light absorption ability, have resulted in a phenomenal improvement in photoreduction density. Coumarin has been used to probe the photocatalytic efficiency of the catalyst by observing 7-OH-coumarin at fluorescence excitation 332 nm (inner-filtering effect). These findings support efforts to expand this technique to manufacture metal-nanocomposite hybrid nanostructures, permitting mixtures for various metal nanostructures of divalent and trivalent cations, potentially opening up a wide range of applications due to the exceptionally tailored characteristics.

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Supplementary Material

Full crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC No. 2039804. This data can be obtained free of charge

via www.ccdc.cam.ac.uk or from Cambridge Crystallographic Data Center, 12 Union Road, Cambridge, CB2, 1EZ, UK (fax: +44 (0)1223336033 or email: deposit@ccdc.cam.ac.uk).

Supplementary data of UV-Visible absorption spectrum, photoluminescence, Raman and FT-IR spectra of iron(III) complex. Electronic absorption curves with various conditions, together with geometric and Cyclic voltammograms parameters. UV-vis DRS spectra, Photoluminescence spectra and FT-IR spectra of nanocomposites and its bare components. *M-H* loop curve parameters, intensity values of hydroxyl trapping experiments and efficiency data of Fe(II) formation.

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Author Contributions

D.Venkatesh designed the project, lab work, and write up. S. Pavalmalar contributed characterization and revised manuscript. R.Silambarasan assisted photodegradation experiments. K.Anbalagan supervised the work.

Conflict of interest The authors declare that they have no conflict of interest.

References

1. Q. Xiang, J. Yu and M. Jaroniec., Chem. Soc. Rev., **41**, 782-796 (2012).
2. M. S. Chavali and M. P. Nikolova, SN Applied Science, **1**, 607 (2019).
3. Y. Zhang, Z. R. Tang, X. Fu, and Y. J. Xu, ACS Nano, **4**, 7303-7314 (2010).
4. L Ge and J Liu. Appl. Catal. B., **105**, 289-297 (2011).
5. T. Zhou, M. Lu, Z. Zhang, H. Gong, W. S. Chin, and B. Liu, Adv. Mater., **22**, 403-406 (2010).
6. G. Liu, L. Z. Wang, H. G. Yang, H. M. Cheng and G. Q. Lu, J. Mater. Chem., **20**, 831-843 (2010).
7. L. Jinlong, J. Shuaiqiang, S. Guozhe, D. Lijuan and L. Boxin, RSC Adv., **7**, 34857, (2017).
8. Y. Cao, X. T. Zhang, W. S. Yang, H. Du, Y. B. Bai, T. J. Li and J. N. Yao, Chem.Mater., **12**, 3445-3448 (2000).
9. L. Cojocaru, C. Olivier, T. Toupance, E. Sellierb and L. Hirsch, J. Mater. Chem. A, **1**, 13789-13799 (2013).
10. M. S. Park, G. X. Wang, Y. M. Kang, D. Wexler, S. X. Dou, and H. K. Liu, Angew. Chem. Int. Ed. Engl., **46**, 750 (2007).
11. L.Xu, E.M. P. Steinmiller, and S.E. Skrabalak., J. Phys. Chem. C, **116**, 871-877 (2012).
12. Z. Liu, D. D.Sun, F.Guo and J.O. Leckie, Nano Lett. **7**, 1081-1085 (2007).

13. F. Gyger, M. Hubner, C. Feldmann, N. Barsan and U. Weimar, *Chem. Mater.*, **22**, 4821-4827(2010).
14. J. Shang, W. Yao, Y. Zhu, N. Wu. *Appl. Catal. A*, **257**, 25-32 (2004).
15. J. Q. Hu, X. L. Ma, N. G. Shang, Z. Y. Xie, N. B. Wong, C. S. Lee and S. T. Lee, *J. Phys. Chem. B*, **106**, 3823-3826 (2002).
16. Y. Tang, D. Wu, S. Chen, F. Zhang, J. Jia and X. Feng, *Energy Environ. Sci.*, **6**, 2447 (2013).
17. Z. R. Dai, Z. W. Pan and Z. L. Wang. *Solid State Commun.*, **118**, 351 (2001).
18. J. Xu, W. Dong, C. Song, Y. Tang, W. Zhao, Z. Hong and F. Huang, *J. Mater. Chem. A*, **4**, 15698-15704 (2016).
19. M. Li, Y. Hu, S. Xie, Y. Huang, Y. Tong and X. Lu, *Chem. Commun.*, **5**, 4341-4343 (2014).
20. X. Chen, B. H. Zhou, S. L. Yang, H.S. Wu, Y. Wu, L. Wu, J. Pan and X. Xiong, *RSC Adv.*, **5**, 68953, (2015).
21. C. Shifu, C. Lei, G. Shen and C. Gengyu, *Mater. Chem. Phys.*, **98**, 116-120 (2006).
22. X. Xu, X. Li, P. Lin, T. Chen, R. Yuan, Z. Ding, L. Wu, X. Wang, and Z. Li, *Chem. Commun.*, **47**, 2538-2540 (2011).
23. C. Enachescu, A. Hauser, J. J. Girerd and M. L. Boillot, *ChemPhysChem*, **7**, 1127-1135 (2006).
24. F. Ghasemi, K. Ghasemi, A. R. Rezvani, M. M. Rosli and I. A. Razak, *J. Mol. Struct.*, **1144**, 186-190 (2017).
25. I. P. Pozdnyakov, V. F. Plyusnin, V. P. Grivin and E. Oliveros, *J. Photochem. Photobiol. A: Chem.*, **307**, 9-15 (2015).
26. D. Dey, G. Kaur, M. Patra, A. R. Choudhury, N. Kole and B. Biswas, *Inorg. Chim. Acta*, **421**, 335-341 (2014).
27. K. Dankhoffa and B. Weber, *Dalton Trans.*, **48**, 15376-15380 (2019).
28. G. G. Bombi, R. Aikebaier, A. Dean, V. B. Di Marco, D. Marton and A. Tapparo, *Polyhedron.*, **28**, 327-335 (2009).
29. D. Venkatesh, S. Pavalamalar and K. Anbalagan, *J. Mater Sci: Mater Electron.*, **30**, 9245-9258 (2019).
30. C. K. Lim, Y. Wang and L. Zhang, *RSC Adv.*, **6**, 25114-25122 (2016).
31. M. T. Maurette, A. M. Braun and E. Oliveros, *Photochemical Technology*, Wiley, Chichester-New York-Brisbane-Toronto-Singapore, (1991).
32. M. P. Singh and J. B. Baruah, *Polyhedron.*, **138**, 103-108 (2017).
33. D. Moon and J. H. Choi, *Acta Crystallogr. Sect. E*, **71**, 210-212 (2015).
34. Rafizadeh, B. Mehrabi and V. Amani, *Acta Cryst.* **E62**, m1332-m1334 (2006).

35. G.W. Zhou, A. Q. Wu, M. S Wang, G. C. Guo and J. S. Huang, *Acta Cryst.*, **E63**, m2463-m2464 (2007).
36. K. Nakamoto, fifth ed., Wiley Interscience, New York, (1997).
37. K. R Krishnapriya and M. Kandaswamy, *Carbohydr. Res.*, **345**, 2013-2022 (2010).
38. P. Laid, A. Gourdon and J.P. Launay, *Inorg. Chem.*, **34**, 5129-5137 (1995).
39. X. Zhang, J. X. Yang, J.Zhang, J. K.Cheng, M. L. Sun, and Y. G. Yao, *Inorg. Chem. Commun.*, **14**, 986-989 (2011).
40. Y. Zhang, T. G. Zhan, T. Y. Zhou, Q. Y. Qi, X. N. Xu and X. Zhao, *Chem. Commun.*, **52**, 7588-7591 (2016).
41. S. Chakraborty, M. G. Walawalkar, and G. K. Lahiri, *J. Chem. Soc., Dalton Trans.*, 2875-2883 (2000).
42. J. Cho, S. Jeon, S. A. Wilson, L. V. Liu, E. A. Kang, J. J. Braymer, M. H. Lim, B. Hedman, K. O. Hodgson, J. S. Valentine, E. I. Solomon and W. Nam, *Nature*, **478**, 502-505 (2011).
43. J. Hohenberger, K. Ray and K. Meyer, *Nat Commun.*, **3**, 720 (2012).
44. P. M. Bush, J. P.Whitehead, C. C. Pink, E. C. Gramm, J. L. Eglin, S. P.Watton and L. E. Pence, *Inorg. Chem.*, **40**, 1871-1877 (2001).
45. I. Ucar, B. Karabulut, A. Bulut and O. Buyukgungor., *J. Mol. Struct.*, **834-836**, 336-344 (2007).
46. R. Uhrecký, Z. P. Iková, J. Moncol, M. Koman L. Dlhán, J. Titiš and R. Boca, *Polyhedron*, **56**, 9-17 (2013).
47. I. Uçar, Ö. Tamer, B. Saribog̃a and O. Büyükgüngör, *Solid State Sci.*, **15**, 7-16 (2013).
48. M. Tabatabaee, F. Abbasi, B. M. Kukovec and N. Nasirizadeh, *J. Coord. Chem.*, **64**, 1718-1728 (2011).
49. C.A. Akinremi, V. B. Oyelude, S. Adewuyi, S. A. Amolegbe and T. Arowolo, *J. Macromol. Sci., Part A: Pure Appl. Chem.*, **50**, 435-440 (2013).
50. I. Nemec, R. Herchel, R. Boca, Z. Travnicek, I. Svoboda, H. Fuess and W. Linert., *Dalton Trans.*, **40**, 10090-10099 (2011).
51. A. S. Ganeshraja, A. Clara, K. Rajkumar, Y. Wang, Y.Wang, J. Wang and K. Anbalagan., *Appl. Surf. Sci.*, **353**, 553-563 (2015).
52. A. Iwaszuk and M. Nolan, *J. Mater. Chem. A*, **1**, 6670-6677 (2013).
53. N. G. Park, M. G. Kang, K. S. Ryu, K. M. Kim, and S. H. Chang, *J. Photochem. Photobiol., A*, **161**, 105-110 (2004).
54. H. C. Yu and P. Shen, *J. Eur. Ceram. Soc.*, **28**, 91-99 (2008).
55. M.F. Abdel-Messih, M.A. Ahmed and A.S. E. Sayed, *J. Photochem. Photobiol. A Chem.*, **260**, 1-8 (2013).

56. I. Zardo, S. Conesa-Boj, F. Peiro, J. R. Morante, J. Arbiol, E. Uccelli, G. Abstreiter, *Phys. Rev. B*, **80**, 245324 (2009).
57. C. Pérez León, L. Kador, B. Peng and M. Thelakkat., *J. Phys. Chem. B*, **17**, 8723-8730 (2006).
58. G. Yang, Z. Jiang, H. Shi, T. Xiao, and Z. Yan. *J. Mater. Chem.*, **20**, 5301-5309 (2010).
59. Z. Yi, Q. Han, P. Zan, Y. Cheng, Y. Wu and L. Wang, *J. Mater. Chem. A*, **4**, 12850-12857 (2016).
60. J. Tauc, R. Grigorovici and A. Vancu, *Phys. Status Solidi*, **15**, 627-637 (1966).
61. L.Xu, E.M.P. Steinmiller and S.E. Skrabalak., *J. Phys. Chem. C*, **116**, 871-877 (2012).
62. S. Markovic, A. Stankovic, J. Dostanic, L. Veselinovic, L. Mancic, S. D. Skapin, G. Dražić, I. J.-Castvan, and D. Uskokovic. *RSC Adv.*, **7**, 42725-42737 (2017).
63. P.P. Sahay, R.K. Mishra, S.N. Pandey, S. Jha and M. Shamsuddin., *Curr. Appl. Phys.*, **13**, 479-486 (2013).
64. M. Borlaf, M.T. Colomer, R. Moreno, and A. D. Andres, *J. Am. Ceram. Soc.*, **98**, 338-345 (2015).
65. Z.C. Su and S.J. Xu., *Sol. Energy Mater. Sol. Cells*, **193**, 292-297 (2019).
66. R. S. Varma, N. Thorat, R. Fernandes, D. C. Kothari, N. Patela and A. Miotello., *Catal. Sci. Technol.*, **6**, 8428-8440 (2016).
67. L. C. Chen, C. M. Huang, M. C. Hsiao and F. R. Tsai, *Chem. Eng. J.*, **165**, 482-489 (2010).
68. S. Liu, J. H. Yang and J. H. Choy, *J. Photochem. Photobiol. A: Chem.*, **179**, 75-80 (2006).
69. M. C. León, E. Coronado, M. L.Jordà, C. Desplanches, S. Asthana, H. Wang and J.-F. Létard, *Chem. Sci.*, **2**, 1121-1127 (2011).
70. Y. Ren, G. Zhao and Y. Chen, *Appl. Surf. Sci.*, **258**, 914-918 (2011).
71. J. B. Asbury, E. Hao, Y. Wang, H. N. Ghosh and T. Lian, *J. Phys. Chem. B*, **105**, 4545-4557 (2001).
72. N. S. Langeroodi, Z. Farhadraresh and A. D. Khalaji, *Green Chem. Lett. Rev.*, **11**, 404-413 (2018).
73. W. Dong, M. Yan, Z. Liu, G. Wu and Y. Li, *Sep. Purif. Technol.*, **53**, 183-188 (2007).
74. R. E. Kitson, *Anal. Chem.*, **22**, 664-667 (1950).
75. V. Leandri, J.M. Gardner, and M. Jonsson, *J. Phys. Chem. C*, **123**, 6667-6674 (2019).

Figures

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