Synergistic Excited State Involved Catalytic Reduction of (NH₃-trz) [Fe(dipic)₂] Complex by SnO₂/TiO₂ Nanocomposite

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Abstract
In this study, cost-effective, environmentally friendly well-fabricated SnO₂/TiO₂ nanocomposite synthesized via hydrothermal route and the photocatalytic activity was validated using the (NH₃-trz)[Fe(dipic)₂] complex under ultra-violet illumination. The structural features of (NH₃-trz)[Fe(dipic)₂] complex and catalysts were systematically examined by various characteristics. The photoreactivity of the model compound (NH₃-trz)[Fe(dipic)₂] in water/binary solvent systems was investigated. The rate of photoreaction (k) of nanocomposite (0.1432 s⁻¹) is higher than the SnO₂ (0.0373 s⁻¹) and TiO₂ (0.1422 s⁻¹) in H₂O:PrOH (70:30%) than the rest of the solvents system. The pathways, mechanistic feature of accumulated reactive species on nanocomposite to induce adherent [Fe(dipic)₂]⁻ anion and photo-reductive products were studied.

Graphical Abstract

Keywords (NH₃-trz)[Fe(dipic)₂] · SnO₂/TiO₂ nanocomposites · Adsorption · Photoreduction · Hydroxyl radical

1 Introduction
Kinetically labile, high spin, hexacoordinated iron(III) complex shows enormous aspects in photophysics and photochemistry [1]. 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 [2–4]. The potential to form stable chelate complexes of 2,6-pyridinedicarboxylic acid (DPA) with Fe(III) pose to be an significant coordination compound the pyridine group in DPA augment electron-transfer activity [5, 6]. DPA is also available in various natural products, namely coenzymes, alkaloids and vitamins [7]. It is studied as a metallo-pharmaceutical model

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compound, owing to less toxicity with assorted biological activities [8]. DPA is used in spectrophotometric determination of Fe(II) and Fe(III) even at a very low concentration of 4 ppm. Fe(III)/DPA complex is evident in stabilizing unusual oxidation states, acts as a molecular tool in DNA cleavage, electron carrier in model systems and in corrosion obstruction [9]. Significantly, it is used in homogeneous catalysis in iron-induced initiation of hydrogen peroxide and dioxygen. It is reported that 4-chlorodipicolinic acid/Fe(III) complex reveals antiferromagnetic superexchange coupling [10]. The light induced electron transfer and followed by dissociation of coordination complex on TiO₂ assisted responsible for the photodegradation reactions [11]. Several reports found for photodegradation reactions of coordination complex and semiconductor, in-particularly Fe compounds containing pyridyl groups with –OH and –COOH groups. These –OH and –COOH groups can easily interact with surface hydroxyl groups of TiO₂ which are performed photodegradation experiments [12]. In the past years, nanoscale heterostructures have been rapidly developed through research objective due to their favorable performance in various fields [13–16]. Research investigations combined that the construction of semiconductor heterostructures proved to be an excellent method for improving the photosynthetic function of a material. [17]. 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 [18–20]. Tin dioxide (SnO₂) 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 [21, 22]. Tin oxide is a good electron acceptor comparing anatase TiO₂ (wide bandgap = 3.2 eV at 300 K) photocatalyst because SnO₂ has a more positive conduction band edge and makes it a suitable candidate for the preparation of heterostructure [23]. SnO₂ has large band gap, poor absorption of light, fast recombination e⁻/h⁺ pairs, poor separation of e⁻/h⁺ pairs and poor generation of reactive organic species. To circumvent these problems, ultra-violet sensitive TiO₂ based heterojunction photocatalyst introduced that can resolve the above issues to a great extent. SnO₂/TiO₂ composite shown improved the generation of photogenerated charges and charge dynamics separation from the surface region, bandgap, edge of the conduction band, matching the energy level and overlapping the wave function [24]. It is worthy enough to associate SnO₂ with TiO₂ 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 [25]. Nanocomposite SnO₂/TiO₂ engineering using SnO₂ with TiO₂ 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 [26]. It is reasonable to exploit the photocatalytic efficiency of SnO₂/TiO₂ nanocomposite, the effect would be higher than that of individual SnO₂ and TiO₂ nanoparticles. Second, synthesis of this nanocomposite with a tunable and uniform composition comprising a tight interface [27–29]. The hybrid formation of TiO₂ with SnO₂ modifies the electronic structure and can be used to control and enhance the surface chemical and physical properties of SnO₂/TiO₂ nanocomposites [30–32]. 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 [33, 34]. Levy et al. investigated the colloidal TiO₂ deposited on F-doped SnO₂ on the glass substrate to prepare double-layered TiO₂/SnO₂ heterostructured film and enhance the photo-generated carrier transfer process [35]. Feng et al. reported that diminished the recombination rate of electron–hole pairs to accomplish enhanced photocatalytic efficiency by coupled SnO₂/TiO₂ synthesized by solvo-thermal method. The combined SnO₂/TiO₂ framework has improved the physical and chemical properties of the surface and exhibits similar crystal properties (the tetragonal structure of the rutile type), electronic properties and ionic radii [36]. Wang et al. reported that SnO₂/TiO₂ nanocomposites fabricated by hydrothermal technique, which grown SnO₂ on TiO₂ nanofibers and significant photocatalytic degradation of Rhodamine B under ultra-violet light of composites rather than their individual constituent semiconductors [37]. Rajkumar et al. investigated that the composite of 5% SnO₂/TiO₂ nanotube showed improved degradation efficiency. Compared to TiO₂ nanotube, the PL spectra of the 5% SnO₂/TiO₂ nanotubes composite showed a decrease in intensity, indicating that the recombination rate is decreased and the acidic medium provides good degradation efficiency [38]. Gao et al. demonstrated that SnO₂-TiO₂ core–shell standardized DSSCs have a power conversion efficiency value that is more than five times higher than SnO₂ nanotubes [39]. Zhang et al. stated a novel hybrid TiO₂/SnO₂ nanofiber prepared by electrospinning technique with improved photocatalytic activity to encourage the separation of photogenerated (e⁻/h⁺) pairs [40]. Several chemicals have been used to quantify the photocatalytic efficiency as well as to identify the reactive organic species. Coumarin used as a model chemical probe to identify the photochemical formation of hydroxyl radicals. [41] Among the various photooxidative products, 7-hydroxycoumarin generates intensive emission which can be identified by using fluorescence spectra. Hence, it is very important to investigate hydroxyl (·OH)
radicals generated in nanocomposites and bare nanoparticles based photocatalytic systems.

Herein, we report for the first time to our knowledge the controlled synthesis of SnO$_2$/TiO$_2$ nanocomposite photocatalyst and characterized. We have adopted iron(III) complex as a precursor to absorb surface of nanocomposites to induce photo-reduction properties through interfacial electron transfer reactions probed under ultra-violet illumination. The reactions were performed controlled solvents ratio, scavengers and quantity of catalyst.

2 Experimental Section

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

(NH$_3$-trz)[Fe(dipic)$_2$] was prepared with some altered methodology from the published procedure [42]. Bis(pyridine-2,6-dicarboxylato)ferrate(III) anion for the present study was prepared using the starting material anhydrous FeCl$_3$ (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 C$_{16}$H$_{11}$Fe$_2$N$_6$O$_8$: 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) ($\nu_{asym}$ COO$^-$), 1578; 1459(s); 1414, 1380(s) ($\nu_{sym}$ 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 H$_2$O ($\lambda_{max}$, nm (ε, dm$^3$/mol cm)): 255 (31,434.22), 270 (30,800.17); 670 (0.84656); 477 (2.11640).

2.2 Synthesis of Tin Oxide Nanospheres

All the chemicals used in this experiment were Analytical Reagent grade. Tin oxide nanoparticles were synthesized with a modified route using dimethyl oxalate as the precipitator [43]. Stannous chloride (SnCl$_2$·2H$_2$O, 0.1 M) 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 3 h.

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 SnO$_2$/TiO$_2$ Nanocomposite

Nanocomposite formation is a complex process that consists of dissolution, precipitation, reorganization, and hydro-thermal process [44]. Tin oxide nanopowders and titanium isopropoxide were used as source materials for the hybrid material. First, SnO$_2$ 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 2θ = 10–80°, step scanning using 20 increments of 0.02° and a fixed counting time of 5 secs/step) with Cu-Kα radiation (wavelength of the X-ray source, λ = 1.541 Å). 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 ($\lambda_{ex} = 295$ 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 Niconel-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 $\omega$ and $\varphi$ scan modes to obtain single crystal analysis. All diffraction measurements were performed at 293(2) K using graphite monochromated Mo–Kα radiation ($\lambda = 0.71073$ Å). 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 Dolomanor 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: 3 nm @ 30 kV HV mode; 10 nm @ 3 kV HV mode Detectors: Secondary Electron; Semiconductor BSE (Quad type) Magnification: $\times 5 \times 300,000$; Vacuum System: TMP & Rotary to 1.5 $\times 10^{-3}$ Pa Specimen Stage: Motorised 5-axis, Eucentric Specimen height: 80 mm at 10 mm 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 LaB$_6$ filament electron source, and image processing by digital micrograph software. Microscopic feature (AFM) of prepared SnO$_2$/TiO$_2$ nanocomposites, bare SnO$_2$ and TiO$_2$ 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 1 mm $\times$ 1 mm. 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, ($\text{NH}_3$-trz)[Fe(dipic)$_2$], on SnO$_2$/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 $\times 10^{-6}$ M) in neat water and in binary solvents (H$_2$O:PrOH = 70:30; H$_2$O:CH$_3$CN = 70:30; H$_2$O:DMSO = 70:30; H$_2$O:Bu′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 NaClO$_4$·H$_2$O, purged with nitrogen gas in 125 ml stopped 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 nanoparticles 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 ($\text{NH}_3$-trz)[Fe(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, 6 W, Heber Scientific; model: LX-1108). Potassium ferroxalate, $\text{K}_3[\text{Fe(C}_2\text{O}_4)_3] \cdot \text{H}_2\text{O}$, actinometry ($\lambda = 254$ nm, 8.50 $\times 10^{17}$ photons/s) was employed to calculate the intensity of light source [45]. 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), (NH₃-trz)[Fe(dipic)₂] complex (9.4478 × 10⁻⁶ M) and 1 M NaClO₄·H₂O in neat water and in binary solvents (H₂O:Pr¹OH = 70:30; H₂O:CH₃CN = 70:30; H₂O:DMSO = 70:30; H₂O:Bu¹OH = 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, λ = 480 nm). Photoreduction efficiency was calculated using the equation \( X = \frac{C_t - C_0}{C_t} \times 100 \) [where \( X \) is the photo efficiency, \( C_0 \) is the initial concentration of the complex and \( C_t \) 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 (NH₃-trz)[Fe(dipic)₂] Complex

3.1.1 Description of Crystal Structure

As presented from X-ray analysis crystal data, the complex (NH₃-trz)[Fe(dipic)₂] crystallizes in orthorhombic space group \( P2_12_12_1 \). The asymmetric unit of complex reported here comprises of an \([Fe(dipic)₂]^−\) anion with inorganic counter cation of 4-amino-4H-1,2,4-trizol-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 roto-inversion axis [46, 47]. 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 2.055(2) up to 2.055(1) Å and 2.002(1) up to 2.060(1) Å, respectively [48]. These bonds are comparable with those reported for (NH₃-trz)[Fe(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 [49, 50]. 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(O...H) and angle < (N–H...O) vary from 2.736(3) to 3.020(3) Å and 141–169°, respectively] form into the 3D supramolecular networks. The N–H...O hydrogen bonds are obtained between uncoordinated 4-amino-4H-1,2,4-trizol molecule (N3) and between atrazine nitrogen atoms (N4) and carboxylate oxygen atoms (O7, O8) of [Fe(dipic)₂]^+ anions [51]. The existence of weaker π...π stacking relationships between the pyridine rings also leads to the crystal structure stability.

![ORTEP diagram of (NH₃-trz)[Fe(dipic)₂] illustrating molecular geometry and atom labeling scheme](image-url)
Empirical formula C₃₃H₂₀Fe₂N₁₂O₁₅

Largest diff. peak/hole Å⁻³ 0.56/−0.52

Final R indexes [all data] R₁ = 0.0647, wR₂ = 0.1288

CCDC. No 2,039,804

Flack parameter 0.564(17)

Final R indexes [I > 2σ (I)] R₁ = 0.0463, wR₂ = 0.1155

Index ranges −14 ≤ h ≤ 14, −21 ≤ k ≤ 21, −26 ≤ l ≤ 24

Radiation Mo Kα (λ = 0.7107)

Crystal size/mm³ ? × ? × ?

F(000) 1896.0

m/mm⁻¹ 0.895

ρcalcmg/mm³ 1.719

Z 4

Independent reflections 8912

Data/restraints/parameters 8912/0/562

Goodness-of-fit on F² 1.070

Final R indexes [I > 2σ (I)] R₁ = 0.0463, wR₂ = 0.1155

Final R indexes [all data] R₁ = 0.0647, wR₂ = 0.1288

Largest diff. peak/hole Å⁻³ 0.56/−0.52

Flack parameter 0.564(17)

CCDC. No 2,039,804

Table 1: Crystal data and the structure refinement for the (NH₃-trz)[Fe(dipic)₂] complex

| Name of the complex | (NH₃-trz)[Fe(dipic)₂] |
|---------------------|-----------------------|
| Empirical formula   | C₃₃H₂₀Fe₂N₁₂O₁₅       |
| Formula weight      | 936.31                |
| Temperature/K       | 293(2)                |
| Crystal system      | Orthorhombic          |
| Space group         | P₂₁2₁2₁               |
| a/Å                 | 10.7553(6)            |
| b/Å                 | 16.9963(11)           |
| c/Å                 | 19.7945(10)           |
| α/°                 | 90.00                 |
| β/°                 | 90.00                 |
| γ/°                 | 90.00                 |
| Volume/Å³           | 3618.4(4)             |
| Z                   | 4                     |
| ρcalc/mg/mm³        | 1.719                 |
| m/mm⁻¹              | 0.895                 |
| F(000)              | 1896.0                |
| Crystal size/mm³    | ? × ? × ?             |
| Radiation           | Mo Kα (λ = 0.7107)    |
| 2Θ range for data collection | 6.44 to 58.86° |
| Index ranges        | −14 ≤ h ≤ 14, −21 ≤ k ≤ 21, −26 ≤ l ≤ 24 |
| Reflections collected | 39,995              |
| Independent reflections | 8912 [Rint = 0.0418, Rsigma = 0.0371] |
| Data/restraints/parameters | 8912/0/562 |
| Goodness-of-fit on F² | 1.070                |
| Final R indexes [I > 2σ (I)] | R₁ = 0.0463, wR₂ = 0.1155 |
| Final R indexes [all data] | R₁ = 0.0647, wR₂ = 0.1288 |
| Largest diff. peak/hole Å⁻³ | 0.56/−0.52 |
| Flack parameter     | 0.564(17)             |
| CCDC. No            | 2,039,804             |

3.2.1 PXRD Analysis

The crystal structures and phase purity of hydrothermally prepared bare SnO₂, TiO₂ nanospheres, and SnO₂/TiO₂ nanocomposite were characterized by powder X-ray (XRD) Diffraction. Figure 3 exhibits all the diffractions peaks well indexed to the pure tetragonal phase (space group P4₂/mmm) of SnO₂ (JCPDS card No. 041-1445) [52]. The XRD pattern of SnO₂/TiO₂ nanocomposite can be easily distinguished with two separate phases from the mixture, the smaller particle size of the anatase phase of TiO₂ combined with the slightly larger particle size of the tetragonal phase of SnO₂ [53, 54]. After annealing at ~500 °C for 3 h, the absence of impurities or secondary phase was inducted as supported in the XRD analysis. All diffraction peaks of bare TiO₂ nanospheres are well indexed to anatase phase and matched with the standard pattern (JCPDS card No. 021-1272) [55]. The mean crystallite particle size of the samples of SnO₂/TiO₂ nanocomposite, nano SnO₂, and TiO₂ were calculated by using the Scherrer equation, \( D = \frac{0.9\lambda}{β(\cosθ)} \), 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 SnO₂ tetragonal phase and TiO₂ anatase phase coexisted in these nanocomposites, in good agreement with the SEM and TEM results.

3.2.2 Raman Analysis

Raman spectroscopy is one of the versatile characterization tool for hydrothermally prepared SnO₂/TiO₂ nanocomposite, bare SnO₂ and TiO₂ nanospheres at the excitation wavelength of 784 nm as shown in Fig. 4 and presented in Table 2. As can be seen, the rutile phase of SnO₂ has a \( D_{th} \) symmetry with two formula units per primitive cell and lattice constants \( a = b = 4.7373 \text{ Å} \) and \( c = 3.1864 \text{ Å} \) [56]. The Raman scattering spectra of SnO₂ has three vibrational active modes \( A_{1g}, E_g, B_{2g} \) at 144 \( \text{cm}^{-1} \), 399 \( \text{cm}^{-1} \), and 637 \( \text{cm}^{-1} \) respectively. The anatase modification has six Raman active modes \( A_{1g}, E_g, B_{1g}, B_{2g}, E_{2g}, B_{1u} \) at 514 \( \text{cm}^{-1} \), 637 \( \text{cm}^{-1} \), and 197 \( \text{cm}^{-1} \) respectively. The tetragonal phase of TiO₂ has 2717Journal of Inorganic and Organometallic Polymers and Materials (2022) 32:2712–2728
3.2.3 Microstructure Analysis

The surface morphology of SnO_2 and TiO_2 nanospheres and SnO_2/TiO_2 nanocomposite annealed at 500 °C were investigated by the SEM and TEM images. The low magnified SEM images of all the samples in Fig. 5a–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 SnO_2 nanoparticles well dispersed on the surface of TiO_2 nanoparticles uniformly by the hydrothermal method are shown in Fig. 6, S7 and S8. The particle size histogram of the samples SnO_2, SnO_2/TiO_2, TiO_2 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 SnO_2 and TiO_2 nanoparticles. In the SAED pattern, the SnO_2/TiO_2 nanocomposites four-fold symmetric diffraction spots correspond to the presence of SnO_2 and TiO_2 nanoparticles. While a series of concentric circles correspond to the electron diffraction of (101), (110), (210) planes of the crystal [59]. AFM imaging demonstrated useful information.
as a feature dispersion in aqueous medium regarding the various agglomeration tendencies. Figure 7a–f shows two and three-dimensional atomic force microscopic images of SnO$_2$, SnO$_2$/TiO$_2$ and TiO$_2$ nanoparticles on a glass substrate. The images were recorded at the scan rate of $10.17 \text{ Hz}$ of $1 \, \mu\text{m} \times 1 \, \mu\text{m}$ planar in contact mode. SnO$_2$ nanoparticle sample is not uniformly distributed with spherical grains of varying size of 500 nm magnifications. TiO$_2$ nanoparticles shown the uniform size with spherical shape was observed. The average particle size ranges between 15 and 59 nm, resulting in very good agreement with SEM and TEM Images. SnO$_2$/TiO$_2$ nanocomposites are irregular dispersion of two distinct interaction of bare nanoparticles with spherical shape appeared at 400 nm magnifications [60].

### 3.2.4 Optical Properties

Figure 8a displays the UV–Vis absorption spectra of TiO$_2$ and SnO$_2$, SnO$_2$/TiO$_2$ 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 SnO$_2$, SnO$_2$/TiO$_2$ nanocomposite and nano TiO$_2$ respectively are presented in Table 2. The optical band gap energy of the samples was estimated by Tauc approach according to the following equation

$$\alpha h\nu \approx \alpha (h\nu - E_g)^n$$

where $\alpha$, $h\nu$, and $E_g$ are the absorption coefficient, photon energy, and bang gap, respectively. In the relationship, $n$ is related to the characteristics of the transition of a semiconductor (indirect transition: $n = \frac{1}{2}$; direct transition: $n = 2$) [23, 61].

### Table 2: Spectral information of Raman, XRD pattern, UV–Vis absorption spectra, bandgap energy, photoluminescence spectra and decay data of SnO$_2$/TiO$_2$ nanocomposite, nano SnO$_2$ and nano TiO$_2$ at room temperature

| Raman mode (cm$^{-1}$)$^a$ | Average crystal-lite Size (nm)$^b$ | UV–Vis absorption spectra | photoluminescence spectra | Average lifetime (ns)$^c$ |
|---------------------------|----------------------------------|--------------------------|--------------------------|-------------------------|
|                           |                                  | Absorption edge          | Bandgap energy (eV)      | $\lambda_{emi}$ (nm)    | Intensity $\times 10^3$ |
| nano-SnO$_2$              | 476                              | 360                      | 3.69                     | 399                     | 27.5123                 | 32.59                   |
|                           | 633                              |                          |                          | 467                     | 27.6930                 |                         |
|                           | 778                              |                          |                          | 521                     | 20.7131                 |                         |
| SnO$_2$/TiO$_2$ nanocomposite | 639                              | 400                      | 3.30                     | 398                     | 7.6502                  | 37.77                   |
|                           | 449                              |                          |                          | 467                     | 2.9549                  |                         |
|                           | 515                              |                          |                          | 521                     | 2.8114                  |                         |
| nano-TiO$_2$              | 146                              | 395                      | 3.28                     | 397                     | 25.0259                 | 34.70                   |
|                           | 399                              |                          |                          | 468                     | 13.3975                 |                         |
|                           | 515                              |                          |                          | 521                     | 12.2596                 |                         |
|                           | 639                              |                          |                          |                         |                         |                         |

$^a$Recorded laser power at 784 nm

$^b$Calculated by the Scherrer equation from XRD measurements

$^c$Lifetime decay studies were performed at the excitation wavelength of 290 nm

![Fig. 4](image-url) Raman scattering spectra of SnO$_2$/TiO$_2$ nanocomposite, nano SnO$_2$ and nano TiO$_2$ using an excitation laser source of 784 nm with a range between 50 and 800 cm$^{-1}$ at room temperature
Fig. 5  SEM micrographs of the photocatalysts synthesized by hydrothermal technique with magnification range ×5 to ×300,000; Eucentric Specimen height: 80 mm at 10 mm W.D. a nano SnO$_2$ at 10 µm; b SnO$_2$/TiO$_2$ nanocomposite at 10 µm; c nano TiO$_2$ at 10 µm, d SnO$_2$/TiO$_2$ nanocomposite at 5 µm, at room temperature.

Fig. 6  TEM micrographs of SnO$_2$/TiO$_2$ nanocomposite a and b magnifications at 100 nm (Inset) showing particle size distribution histogram and 20 nm. c SAED pattern, d lattice fringes.
The direct transition of semiconductor samples is the plot of \((\alpha h \nu)^2\) against \(h \nu\) as shown in Fig. 8b, the bandgap values are found to be 3.69, 3.30, 3.28 eV for SnO\(_2\), SnO\(_2\)/TiO\(_2\) nanocomposite, and TiO\(_2\) respectively. SnO\(_2\)/TiO\(_2\) nanocomposite could absorb photon on the selective near region of ultraviolet range indicating promising photocatalyst.

### 3.2.5 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 SnO\(_2\), SnO\(_2\)/TiO\(_2\) nanocomposite, and nano TiO\(_2\) 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. 9a. 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 SnO\(_2\) (421 nm) > nano TiO\(_2\) (398 nm) > SnO\(_2\)/TiO\(_2\) nanocomposite (397 nm). Table 2 illustrates the high-intensity emission band at \(\sim 400\) nm (weak ultraviolet emission) is assigned to self-trapped excitons and \(\sim 467\) 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 $\tau_1$, $\tau_2$, and $\tau_3$ lifetime scales. These lifetime components can be fitted in the relation: $A + B_1 \exp\left\{-\tau_1\right\} B_2 \exp\left\{-\tau_2\right\} B_3 \exp\left\{-\tau_3\right\}$ 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 SnO$_2$, nano TiO$_2$ and SnO$_2$/TiO$_2$ nanocomposite (excitation wavelength at 292 nm, Fig. 9b–d fits well to a triexponential function $I(t) = \sum_n A_n \exp\left(-t/\tau_n\right)$, where $A_n$ and $\tau_n$ represent the amplitude and lifetime of the component, respectively. The fast component, $\tau_1$, represents the near band edge relaxation lifetime, and the second one, $\tau_2$, indicates photogenerated charge carriers relaxation lifetime of the shallow-trap states. The fast lifetime associated with, $\tau_3$, can be matched with deep state relaxation of the photogenerated charge carriers [65]. The average PL lifetime ($\tau_{avg}$) of each samples can be calculated using this equation:

![Fig. 9](image_url)
\[ \tau_{\text{avg}} = \left( B_1 \tau_1^2 + B_2 \tau_2^2 + B_3 \tau_3^2 \right) / \left( B_1 \tau_1 + B_2 \tau_2 + B_3 \tau_3 \right) \]
and are presented in Table 2. This is equated with the efficiency of the various nanoscale photocatalysts of SnO\(_2\) (32.59 ns) TiO\(_2\) (34.70 ns) nanospheres, and SnO\(_2\)/TiO\(_2\) 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].

### 3.2.6 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. Figure S9 shown that the FT-IR spectra for SnO\(_2\)/TiO\(_2\) composites and bare components in the region of 4000–400 \(\text{cm}^{-1}\). The characteristic vibrational peaks at 513 and 631 \(\text{cm}^{-1}\) are attributed to the Sn–O and Sn–O–Sn stretching vibrations of SnO\(_2\) respectively [67]. The vibrational modes between 730 to 470 \(\text{cm}^{-1}\) can be assigned to Ti–O–Ti stretching vibrations [68]. The broad region between 460 and 715 \(\text{cm}^{-1}\) obtained shows the co-existence of Sn–O–Ti vibrations in the composites [69].

### 3.2.7 Magnetic Property Analysis

The magnetic properties of the as-prepared nanocomposite were also explored for their inherent magnetic characteristics. The \(M–H\) curves of SnO\(_2\)/TiO\(_2\) nanocomposites, bare SnO\(_2\) and TiO\(_2\) nanospheres are depicted in Fig. S10a–c 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 SnO\(_2\)/TiO\(_2\) nanocomposites, bare SnO\(_2\) and TiO\(_2\) 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.

| Reaction conditions | Catalyst/adsorbent | Surface removal\(^a\) | Photodegradation \(*\) |
|---------------------|-------------------|------------------------|------------------------|
|                     | \(k (\text{s}^{-1})\) | \(R^2\)               | \(k (\text{s}^{-1})\) | \(R^2\)               |
| Water\(^x\)         | SnO\(_2\)         | 0.0086                 | 0.6992                 | 0.0310                 | 0.8713                 |
|                     | SnO\(_2\)/TiO\(_2\)| 0.0156                 | 0.8168                 | 0.0779                 | 0.8429                 |
|                     | TiO\(_2\)         | 0.0106                 | 0.9557                 | 0.0573                 | 0.9788                 |
| H\(_2\)O:Pr\(^y\)OH\(^z\) | SnO\(_2\)         | 0.0109                 | 0.5348                 | 0.0373                 | 0.8748                 |
|                     | SnO\(_2\)/TiO\(_2\)| 0.0159                 | 0.5654                 | 0.1432                 | 0.9736                 |
|                     | TiO\(_2\)         | 0.0090                 | 0.8530                 | 0.1422                 | 0.9427                 |
| H\(_2\)O:CH\(_3\)CN\(^w\) | SnO\(_2\)         | 0.0169                 | 0.7254                 | 0.0618                 | 0.9843                 |
|                     | SnO\(_2\)/TiO\(_2\)| 0.0274                 | 0.7639                 | 0.1099                 | 0.9938                 |
|                     | TiO\(_2\)         | 0.0216                 | 0.4599                 | 0.0741                 | 0.9799                 |
| H\(_2\)O:DMSO\(^v\) | SnO\(_2\)         | 0.0104                 | 0.4023                 | 0.0372                 | 0.8748                 |
|                     | SnO\(_2\)/TiO\(_2\)| 0.0466                 | 0.7846                 | 0.0703                 | 0.9956                 |
|                     | TiO\(_2\)         | 0.0260                 | 0.7782                 | 0.0572                 | 0.9308                 |
| H\(_2\)O:Bu\(^w\)OH\(^x\) | SnO\(_2\)         | 0.0116                 | 0.6089                 | 0.0486                 | 0.9690                 |
|                     | SnO\(_2\)/TiO\(_2\)| 0.0270                 | 0.8214                 | 0.0858                 | 0.7287                 |
|                     | TiO\(_2\)         | 0.1010                 | 0.8610                 | 0.0656                 | 0.9152                 |

Ionic strength: 1 M NaClO\(_4\)/H\(_2\)O; Dosage of adsorbent: 300 mg/100 ml. Concentration of iron(III) Complex: 9.4478×10\(^{-6}\) M

\(^x\)Triply distilled water

\(^y\)Ratio of the solvent medium maintained 70:30 (v/v)

\(^z\)Surface adsorption was performed duration of 60 min

\(*\)Photocatalytic experiments was carried out with the wavelength of 254 nm and 18 min duration
4 Surface Adsorption Experiments

The removal of \((\text{NH}_3\text{-trz})[\text{Fe(dipic)}_2]\) complex was carried out by batch experimentation in neat water and in binary solvents \((\text{H}_2\text{O}:	ext{PrOH}=70:30; \text{H}_2\text{O}:	ext{CH}_3\text{CN}=70:30; \text{H}_2\text{O}:	ext{DMSO}=70:30; \text{H}_2\text{O}:	ext{Bu}^\prime\text{OH}=70:30 (v/v))\) at room temperature. 300 mg of nanoparticle absorbent and 1 M NaClO4·H2O as a function of ionic strength of the solution have been used to remove \((\text{NH}_3\text{-trz})[\text{Fe(dipic)}_2]\) (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. S11a–f, 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 s⁻¹, which is higher than the SnO2 (0.0104 s⁻¹) and TiO2 (0.0260 s⁻¹) bare components in \(\text{H}_2\text{O}:	ext{DMSO}=70:30\) than the other solvents medium. 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.

5 Photocatalytic Reduction

It was explored to deduce the apparent kinetic model to estimate the photocatalytic reduction of \((\text{NH}_3\text{-trz})[\text{Fe(dipic)}_2]\) complex by SnO2, TiO2 nanospheres, and SnO2/TiO2 nanocomposite in water and binary solvent media under ultraviolet irradiation. Figure 10a–f display the degradation efficiency and rate of photoreduction of \((\text{NH}_3\text{-trz})[\text{Fe(dipic)}_2]\) complex on the SnO2/TiO2 heterostructures in water and in binary solvents \((\text{H}_2\text{O}:	ext{PrOH}=70:30; \text{H}_2\text{O}:	ext{CH}_3\text{CN}=70:30; \text{H}_2\text{O}:	ext{DMSO}=70:30; \text{H}_2\text{O}:	ext{Bu}^\prime\text{OH}=70:30 (v/v))\) medium at 18 min time intervals. The reactions were performed without catalyst and observed, no appreciable degradation efficiency was observed. The electronic absorption spectra of photodegradation of \((\text{NH}_3\text{-trz})[\text{Fe(dipic)}_2]\) by catalysts under UV
light irradiation ($\lambda = 254$ nm) in various solvents medium at room temperature are presented in Figs. S12–S16(a–c). (NH$_3$-trz)[Fe(dipic)$_2$] precursor adsorbed on surface of the SnO$_2$/TiO$_2$ nanocomposites and enhance the reduction of Fe(III) to Fe(II) via interfacial electron transfer reactions under ultra-violet illumination. 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 [74]. SnO$_2$/TiO$_2$ heterostructures showed superior photocatalytic activity rather than bare SnO$_2$ and TiO$_2$ 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 SnO$_2$, TiO$_2$, SnO$_2$/TiO$_2$ nanocomposite are 49%, 88%, and 91% in H$_2$O/PrOH (70:30% (v/v)) at 18 min time duration is higher than the other medium are presented in Table 3. The role of organic reactive species involved in photocatalytic reaction quenching experiments by adding various scavengers such as acetoni-trile, isopropanol, tert-butanol for hydroxyl radicals (·OH) and dimethyl sulfoxide for electrons (e$^-$) respectively [76–79]. The photocatalytic experiments were carried out in the presence and absence of scavengers with these two active species (e$^-$ and ·OH) on (NH$_3$-trz)[Fe(dipic)$_2$] complex in presence of photocatalyst. During the photolysis experiment, H$_2$O/PrOH (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 than the rest of the scavenging agents. 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.

### 5.1 Mechanism of Photodegradation

The photoconversion of Fe(III) centre into Fe(II) due to effective separation of electron–hole separation in SnO$_2$/TiO$_2$ nanocomposite is illustrated in Fig. 11. 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 SnO$_2$ and TiO$_2$ semiconductors.

\[
E_{CB} = c - E^* - \frac{1}{2}E_g
\]  

(1)  

\[
E_{VB} = E_{CB} + E_g
\]  

(2)

where $E_{CB}$ and $E_{VB}$ are the CB and VB band edge potential, respectively; $\chi$ is the electronegativity of the semiconducting material, which is the geometric mean of the electronegativity of the constituent atoms; $E^*$ is the energy of free electrons on the hydrogen scale (4.5 eV), and $E_g$ is the bandgap energy of the semiconductor. The SnO$_2$ and TiO$_2$ 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 SnO$_2$ and TiO$_2$ on the conduction band edges makes it much easier for the photogenerated electrons on the TiO$_2$ surface to migrate to the SnO$_2$.
TiO$_2$(h$^+$) + OH$^-$ + O$_2$ + → TiO$_2$ + CO$_2$ + H$_2$O  \hspace{1cm} (8)

e$^-$ \hspace{1cm} _CB + O$_2$ + H$_2$O → H$_2$O$^+$ + OH$^-$  \hspace{1cm} (9)

e$^-$ \hspace{1cm} _CB + H$_2$O$^+$ + H$^+$ → H$_2$O$_2$  \hspace{1cm} (10)

e$^-$ \hspace{1cm} _CB + H$_2$O$_2$ → OH$^-$ + OH$^-$  \hspace{1cm} (11)

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

### 5.2 Hydroxyl Radical Study

In order to investigate the progress of hydroxyl radicals (·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 (NH$_3$-trz)[Fe(dipic)$_2$] complex [80]. In a typical process, coumarin used as the ·OH-trapping agent, allowing the measurement of photoluminescence intensity with an excitation wavelength at 332 nm are depicted in Fig. 12. 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 TiO$_2$ offered much higher PL intensity than SnO$_2$/TiO$_2$ nanocomposites and bare SnO$_2$ nanoparticles. The results revealed that the TiO$_2$ nanoparticles generate more number of hydroxyl radicals on the surface of the catalyst rather than nanocomposites and SnO$_2$ nanoparticles.

### 6 Conclusion

By integrating nano TiO$_2$ and nano SnO$_2$ into a single-step hydrothermal process, a progressive hybrid design was successfully evolved. In comparison to pure SnO$_2$ and TiO$_2$ nanostructures, the SnO$_2$/TiO$_2$ 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 SnO$_2$ and TiO$_2$ phases, which empowered the solid coupling connection. The adsorption capacity of (NH$_3$-trz)[Fe(dipic)$_2$] by SnO$_2$/TiO$_2$ nanocomposites in H$_2$O/DMSO (70/30% (v/v)) is higher than that of other solvents mixtures. The photocatalytic reduction of the (NH$_3$-trz)[Fe(dipic)$_2$] complex in H$_2$O/Pr/OH (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 SnO$_2$/TiO$_2$ nanocomposites acted as electron sinks, causing electrons to separate spatially, and as effective electron mediators, promoting the development of...
diminished products. The SnO$_2$/TiO$_2$ 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. The fluorescence spectra revealed that, TiO$_2$ is generating more number of hydroxyl radicals than the nanocomposites and SnO$_2$ nanoparticles. 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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**Declarations**

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

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