



Supplementary Materials

S.1.1. Raman Analysis

The structural properties of materials were investigated using Raman analysis. Structural defects, non-stoichiometry, bond modifications, and phase changes are related to the changes in Raman spectra [1]. Fig. S2(a) illustrates the Raman spectra of TS and TSFC1 catalyst. Both the samples showed six Raman active modes, i.e. 142 cm^{-1} (E_g), 200 cm^{-1} (E_g), 397 cm^{-1} (B_{1g}), 520 cm^{-1} ($A_{1g} + B_{1g}$), and 640 cm^{-1} (E_g), characteristic of the anatase phase of TiO_2 [3]. There was no Raman peak detected from iron or copper, which evinced that the materials analysed involve the anatase phase, reconfirming the results obtained from XRD analysis. However, at 142 cm^{-1} , the Raman peak position of E_g mode was little shifted towards a longer wave number, preceded by a sharp decrease in intensity (inset, Fig. S2(a)). Similar behaviour of the Raman mode signals after doping the TiO_2 NPs has been reported Mragui *et al.* [1], and it is considered to be a sign of the existence of a structural defect resulting from the present study of the incorporation of Ti^{4+} by Fe^{3+} and Cu^{3+} within the lattice host. The following results obtained are consistent with the existing literature and confirms the results obtained by FTIR and XRD.

S.1.2. PL Spectroscopy Analysis

The photoluminescence emission (PL) spectra are beneficial for analysing the efficiency of charge carrier trapping, transfer, and migration and understanding the fate of electron-hole pairs in semiconductor particle [4]. The PL emission spectra in nanomaterials are related to the photoinduced holes and electrons transfer behaviour, which can determine the charge carrier recombination rate. Fig. S2(b) shows the TS and TSFC1 samples' PL spectra calcined at 800°C . There is a wide photoluminescent band in the wavelength range of 420-600 nm. The main emission peak was observed for TS and TSFC1 at 430 and 432 nm. TSFC1's PL intensity was reduced, and the shape of the PL spectrum was split into many side peaks, demonstrating that resolved manifold lines were founded on well-defined lattice sites. Since PL emissions are caused by the recombination of photoinduced holes and electrons, a lower PL intensity value implying a lower electron and hole recombination rate, indicating a higher photocatalytic activity of the sample. Besides, Fe^{3+} and Cu^{2+} favour the photoinduced electrons transfer and restrict the recombination of holes and electrons by forming an energy barrier at the interface of TiO_2 -Cu or Fe [4]. Because the excited state in the former case was long-lived, the PL intensities of the Fe, Cu-codoped sample were significantly lower than those of the undoped TS sample. The more effective electron-hole separation of the TSFC1 sample is expected to improve photocatalytic activity as Fe^{3+} and Cu^{2+} can act as electron sinks, inhibit recombination, and prolong the electron-hole pair's lifetime

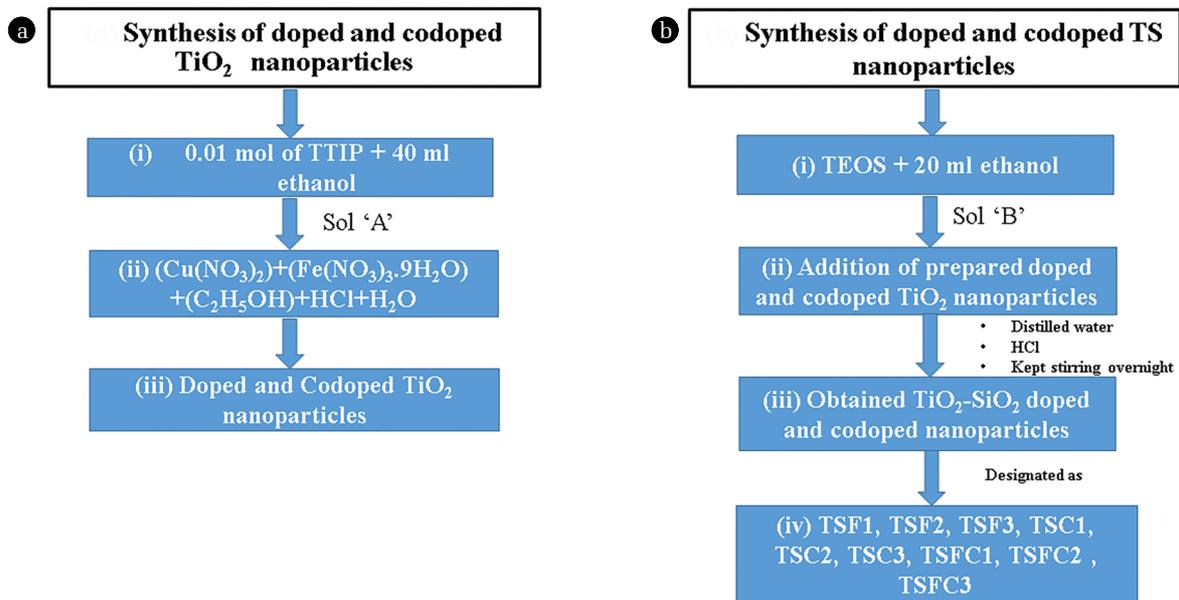


Fig. S1. Preparation schematic for doped and codoped TiO₂-SiO₂ nanoparticles.

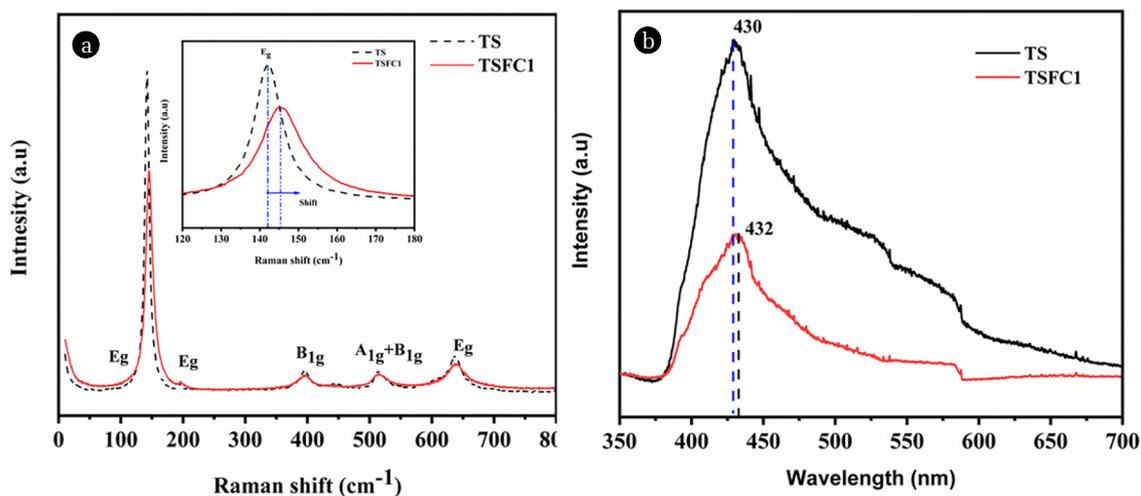


Fig. S2. (a) Raman spectra (b) PL spectra of TS and TSFC1 catalyst.

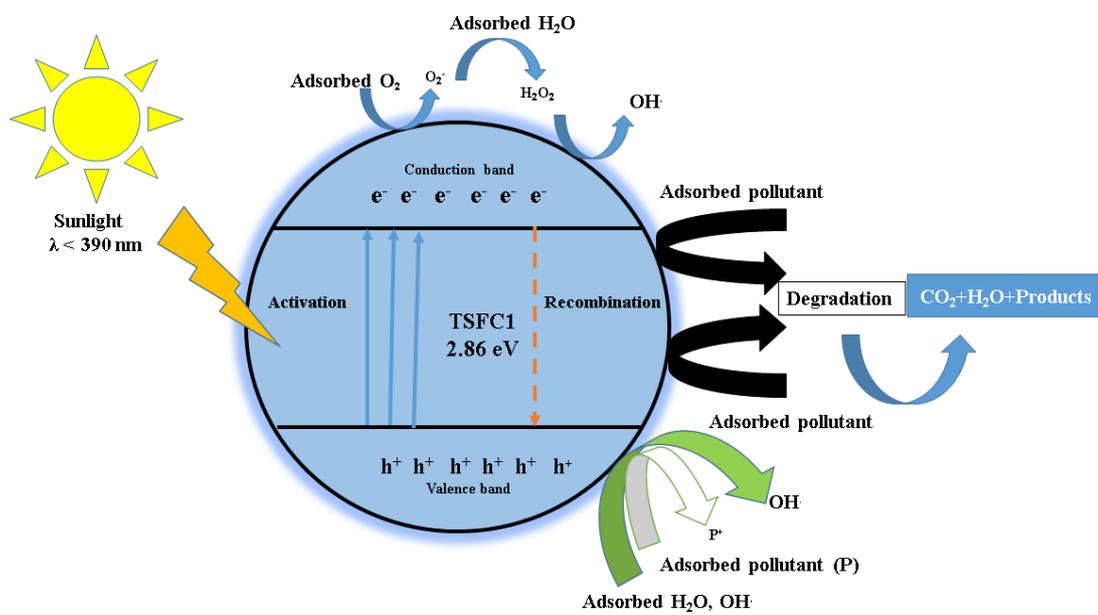


Fig. S3. Photocatalytic degradation mechanism of TSFC1 photocatalyst.

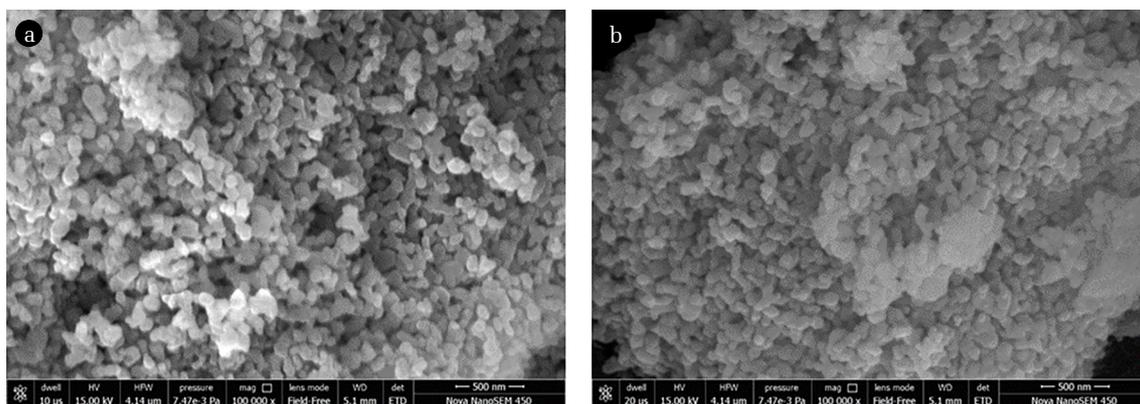


Fig. S4. FESEM images of the TSFC1 photocatalyst before and after the recycle experiment.

S.1.3. pH Effect

When it comes to the degradation of various organic pollutants on oxide surfaces, the pH values plays an important role. The pH values of sample solutions were adjusted to a range of 3 to 9 in order to determine the effect of pH. The results shown in Fig. S5(a) and (b) show that increasing pH values from 3 to 9 increased degradation of DOX and OFLX on TS composite, respectively. The result of the effect of pH on the degradation of DOX and OFLX revealed that the quantitative degradation (> 95%) was found for DOX and OFLX in the pH range 5–6 and therefore the initial pH (without adjustments which was 6.6 for DOX) and (with adjustments which was 5 for OFLX) was taken as the compromise condition. The catalyst surface is positively charged in acidic mediums (pH < 7.4) and negatively charged in basic mediums (pH > 7.4). Doxycycline is an amphoteric molecule with pKa values of 3.5, 7.7, and 9.5 that cause the predominance of certain species as a function of pH. At pH < 4, doxycycline is mostly in its protonated form (DOX⁺), at pH values between 4 to 8, the neutral form (zwitterion) is predominant, and at pH > 8 doxycycline is an anionic molecule (DOX⁻) (Mohammadi and Pourmoslemi 2018). Degradation experiments were performed on 100 mL of 20 mgL⁻¹ doxycycline aqueous solutions adjusted to pH values 3, 5, 6.6 (natural pH) and 9 using 1N HCL or NaOH, by adding 0.1 gL⁻¹ of TS photocatalyst. Doxycycline degradation was favoured at neutral pH or its natural pH value. This result demonstrated the significance of zwitterion formation in enhancing electrostatic interactions between photocatalyst and doxycycline molecules. Because the pH of doxycycline aqueous solution is close to neutral, degradation experiments in this study were carried out on doxycycline aqueous solution with no further pH adjustment. At pH 5, OFLX is positively charged. As a result, neither an acidic nor an alkaline pH is advantageous for OFX degradation on the catalyst surface.

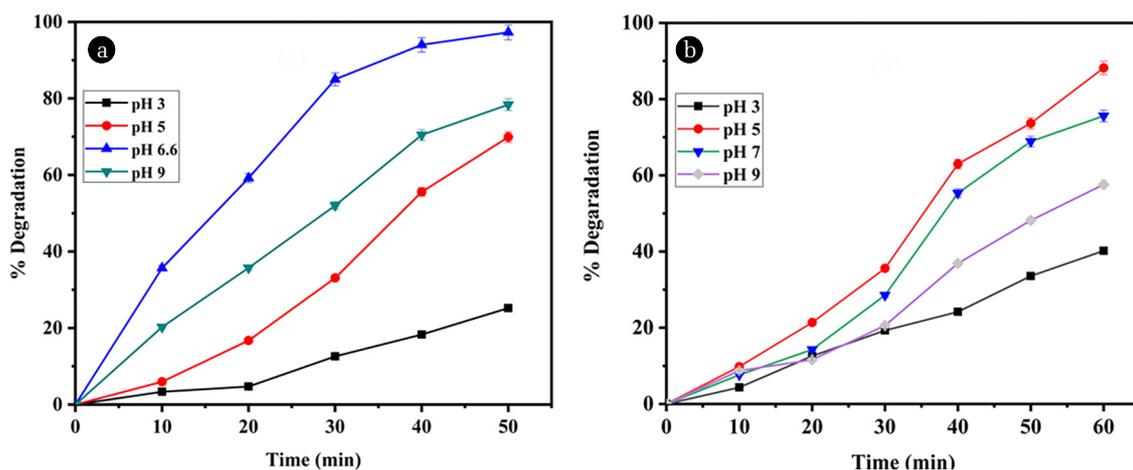


Fig. S5. pH effect study (a) DOX (b) OFLX.

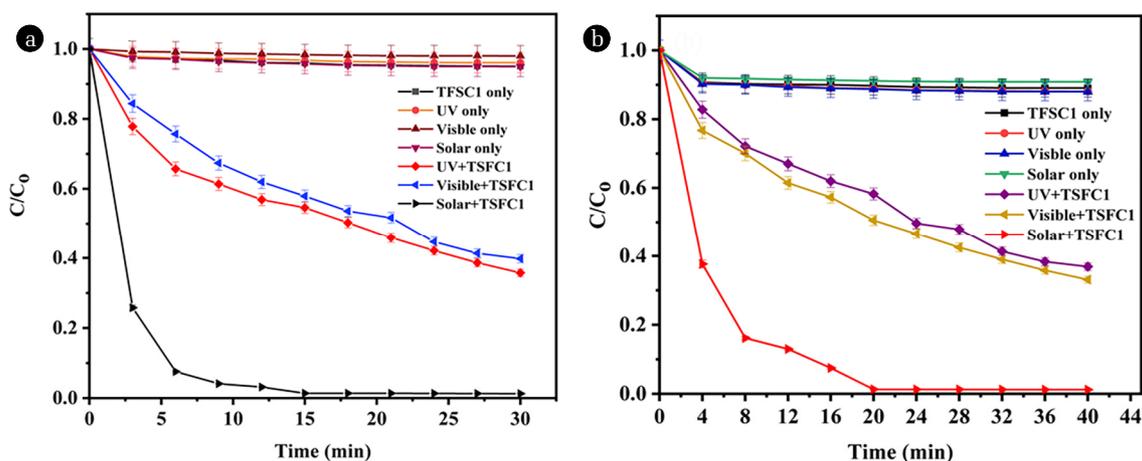


Fig. S6. Photolysis, photocatalytic degradation of (a) DOX (b) OFLX in the presence and absence of TSFC1 along with adsorption.

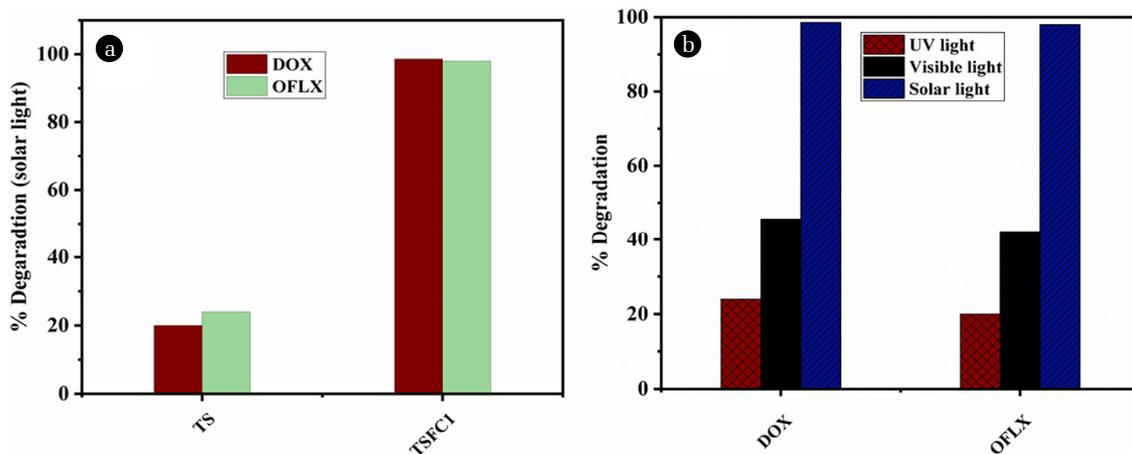


Fig. S7. Comparative degradation study of DOX & OFLX (a) under natural sunlight using TS and TSFC1 catalyst (b) under different irradiations using TSFC1.

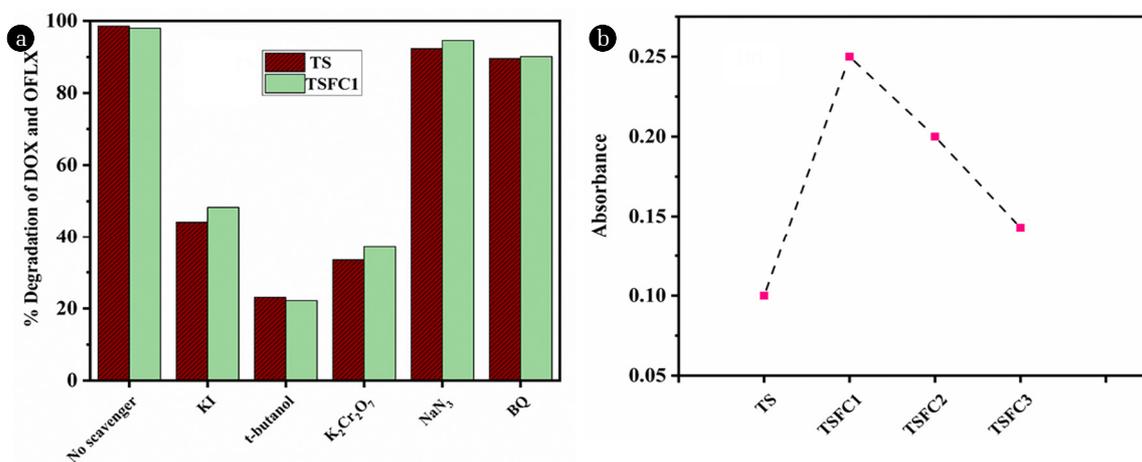


Fig. S8. (a) Scavenger Study of TSFC1 (b) Hydroxyl radical amount on prepared catalysts.

Table S1. Summaries of Crystallite Sizes, Phase Content, Band Gap and Surface Area of the Catalyst

Photocatalyst	Average Crystallite size (nm)	Phase %		Band Gap (eV)	BET surface area (m ² g ⁻¹)
		anatase	rutile		
TS	25	65	35	3.01	275
TSFC1	21	73	27	2.86	288

Table S2. Wavenumbers of TS, TSF2, TSC2, and TSFC1 for FTIR Characterization

Bond Type	TS	TSF2	TSC2	TSFC1
O-H stretching	3,365.4 cm ⁻¹	3,432.4 cm ⁻¹	3,431.3 cm ⁻¹	3,423.8 cm ⁻¹
O-H bending	1,626.7 cm ⁻¹	1,635.3 cm ⁻¹	1,635.9 cm ⁻¹	1,634.4 cm ⁻¹
Si-O-Si	1,082.9 cm ⁻¹	1,087.8 cm ⁻¹	1,087.6 cm ⁻¹	1,094.9 cm ⁻¹
Ti-O-Ti	624.2 cm ⁻¹	608.5 cm ⁻¹	584 cm ⁻¹	553.4 cm ⁻¹
Ti-O-Si	962.5 cm ⁻¹	968.5 cm ⁻¹	968.7 cm ⁻¹	970.1 cm ⁻¹

Table S3. Cost Analysis for Degradation of DOX and OFLX Using TSFC1

<i>Cost of raw material used</i>	
Cost of Titanium Tetraisopropoxide (TTIP) = 78 USD L ⁻¹	
Cost of Tetraethylorthosilicate (TEOS) = 125 USDL ⁻¹	
Cost of Hydrochloric acid (HCL) cost = 3.27 USDL ⁻¹	
Cost of Ferric nitrate (Fe (NO) ₃) = 10.34 USDKg ⁻¹	
Cost of copper nitrate (Cu (NO) ₃) = 3.31 USDKg ⁻¹	
Cost of Ethanol = 0.95 USDL ⁻¹	
Cost of Distilled water = 0.41 USDL ⁻¹	
Cost of electricity = 0.015 USD kWh	
Energy used for the calcination of catalyst = 3 kWh	
Cost of electricity = 3 × 0.015 = 0.045 USD	
<i>Amount of raw materials used to synthesise TSFC1</i>	
Amount of TTIP used = 2.6 L	
Amount of TEOS used = 0.71 L	
Amount of Ferric nitrate (Fe (NO) ₃) = 0.0047 L	
Amount of copper nitrate (Cu (NO) ₃) = 0.0118 L	
Amount of Ethanol used = 6 L	
Amount of HCL used = 0.01 L	
Amount of distilled water used = 0.4 L	
Energy used by Muffle furnace for calcination of TSFC1 at high temperature = 3 kWh	
Cost of electricity = 3 × 0.015 = 0.045 USD	
<i>Cost for manufacturing 1 Kg of TSFC1</i>	
Cost of TTIP used = 202.8 USD	
Cost of TEOS used = 88.75 USD	
Cost of Ferric nitrate (Fe (NO) ₃) used = 0.000049 USD	
Cost of copper nitrate (Cu (NO) ₃) used = 0.00004 USD	
Cost of Ethanol used = 5.7 USD	
Cost of HCL used = 0.032 USD	
Cost of distilled water used = 0.164 USD	
The total cost of manufacturing TSFC1 per Kg = 297.45 USD	
The total cost of TSFC1catalyst used for experimental analysis per Litre was found to be 0.297 USDL ⁻¹ .	

References

1. El Mragui A, Logvina Y, Pinto da Silva L, Zegaoui O, Esteves da Silva JC. Synthesis of Fe-and Co-doped TiO₂ with improved photocatalytic activity under visible irradiation toward carbamazepine degradation. *Materials* 2019;12(23):3874.
2. Mohammadi A, Pourmoslemi S. Enhanced photocatalytic degradation of doxycycline using a magnetic polymer-ZnO composite. *Water Sci. Technol.* 2017;2017:791-801.
3. Yu X, Liu J, Yu X, Zhu F, Li Y, Si J. Preparation of graphdiyne-doped TiO₂/SiO₂ composite for enhanced photocatalytic activity. *J. Nanoparticle Res.* 2020;22(12):1-10.
4. Zhang D. Enhanced photocatalytic activity for titanium dioxide by co-modification with copper and iron. *Transition Metal Chem.* 2010;35(8):933-938.