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Cubic Cu₂O nanoparticles decorated on TiO₂ nanofiber heterostructure as an excellent synergistic photocatalyst for H₂ production and sulfamethoxazole degradation

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Abstract

We report a simple strategy for providing a homogenous TiO₂ nanofibre host environment to stabilize Cu₂O nanoparticles with an average size of ~60 nm and high dispersibility. We found that the small fraction of Cu₂O nanoparticles in direct contact/partially submerged with TiO₂ nanofibre arrays (diameter ~300 nm and length ~650 nm) showed excellent synergistic photocatalytic performance for an H₂ production rate of 48 μmol g⁻¹ h⁻¹ with an apparent quantum efficiency of 3.6 %. The H₂ production rate was much higher (factor of ~6.5 times) compared with unmodified TiO₂-NF. In addition, the synergistic Cu₂O/TiO₂-NF photocatalyst showed significant oxidative-degradation of sulfamethoxazole (7×10⁻² mmol g⁻¹ min⁻¹) and was highly stable during five cycles. The small fraction of Cu₂O nanoparticles are well dispersed and form heterojunction interfaces to promote charge transfer and provide active sites. This argument is verified by morphology characterisation, band alignment, energy-resolved distribution of electron traps, electrochemical transient photocurrent, and electrochemical impedance (EIS). In addition, a detailed discussion is provided regarding the surface and bulk elemental composition determined by X-ray photoelectron spectroscopy (XPS), X-ray fluorescence (XRF), and X-ray absorption near edge structure (XANES).

Keywords: *Cu₂O/TiO₂-nanofibre, photocatalysts, hydrogen production, sulfamethoxazole visible light.*

1. Introduction

For efficient solar energy usage, there has been interest in heterogeneous catalysts for various photocatalytic applications, such as water splitting to produce H₂, CO₂ reduction into solar fuels, fine chemical production and organics decomposition reactions [1]. In the last few decades, TiO₂ has been considered the most promising benchmark photocatalyst in various applications [2]. However, titanium dioxide activates only 5 % of the UV light region because of the wide bandgap (Eg 3.2 eV) and also easily recombines the photoinduced charge carrier, which limits the successful utilization of solar light in practical applications [3].

To achieve high-efficiency photocatalytic activity and charge separation of TiO₂, methods in the literature including integrating co-catalysts or modification with narrow band gap semiconductors [4, 5]. Among the semiconducting co-catalysts, copper oxide (Cu₂O) is an economical and earth rich p-type semiconductor (band gap of 2.0 to 2.4 eV) with favourable valence and conduction band positions for effective photocatalytic activity in numerous research areas, such as water splitting and organics decomposition [6, 7], CO₂ reduction, etc., towards the visible region [8, 9]. However, stability of Cu₂O is a major limitation under light illumination due to photocorrosion.

The combination of these two materials (p-Cu₂O and n-TiO₂) has great advantage and overcomes the Cu₂O photocorrosion for efficient photocatalytic performance [10, 11]. Additionally, the band energy gap of Cu₂O is lower than that of TiO₂, and both the valence band and conduction band positions are above those of TiO₂, which enables excellent charge transfer and separation processes in the photogenerated carriers to improve the photo response and lifetime of the charge carrier [12]. In addition, the heterojunction formation at the interface of p-Cu₂O/n-TiO₂ creates a built-in-inner electrostatic field and might improve the electron-hole pair separation. There are many reports on the Cu₂O/TiO₂ heterojunction, such as defect modulation [13], Quantum dot TiO₂ [14], controlled facets [15], and TiO₂ nanotube arrays [12] for various photocatalytic applications. Interfacial interaction of the co-catalyst, electronic band structures and the intrinsic light-absorption of the catalyst are important parameters for efficient and stable photocatalytic applications.

It is still a challenge to understand the interface formation and interfacial interaction when p-Cu₂O and n-TiO₂ combine. A particular mesoporous nanofibre TiO₂ we had developed previously can be an excellent host for incorporation of metal nanoparticles due to its pore arrangement, providing a homogenous surface for stabilizing nanoparticles with high dispersibility [16]. Meanwhile, our other recent work [17-19] reported that size and morphology controlled Cu₂O nanostructures can be design and synthesised without the needs of surfactants which commonly lead to severe hindrance of active sites and thus photocatalytic performance [20-23].

The combination of these two materials will provide a synergistic photocatalyst for enhanced performance and a perfect platform to reveal their interface formation and interfacial interaction. Here, we report a simple strategy for the partially submerged ultrafine Cu₂O (20-100 nm) nanoparticles decorated/modified on the TiO₂ nanofibre (diameter ~300 nm and length

~650 nm) architecture, which significantly improved the surface electronic and optical properties, yielding an excellent synergistic visible-light photocatalyst.

We have found that the small fraction of Cu₂O nanoparticle surface in direct contact with the TiO₂ nanofibre arrays showed excellent photocatalytic H₂ production and sulfamethoxazole (as a model antibiotic organic molecule) oxidative-degradation applications. Detailed discussion is provided regarding the Cu₂O nanoparticle growth on TiO₂ nanofibre structure, Cu₂O/TiO₂-NF interfacial interaction, and surface and bulk elemental composition determined by XPS, XRD, XRF, and XANES. Energy-resolved Distribution of Electron Traps (ERDT) near the conduction band bottom position (CBB) of TiO₂, TiO₂-NF and Cu₂O/TiO₂-NF composites using reversed double-beam photoacoustic spectroscopy (RDB-PAS) were investigated for the first time. The interfacial interaction was confirmed by band alignment, and the charge carrier mechanism was confirmed by electrochemical transient photocurrent and EIS. In addition, by-products of sulfamethoxazole decomposition were identified (LC/MS/MS) and, finally, stability of the catalysts are discussed in detail.

2. Experimental section

2.1. Anatase TiO₂ Nanofibre (TiO₂-NF) synthesis

K₂Ti₂O₅ powders with water were taken for a hydration reaction after that aqueous solution of HCl (0.5 mol/L) was added into the above reaction mixture for ion exchange for the formation of hydrated titanate (H₂Ti₂O₅). The solid-aqueous products were separated by filtration, washed several times with deionised water, and then dried at 60°C in an oven under vacuum. Inductively coupled plasma-mass spectrometry (ICP-MS) was used to measure the final residual K⁺ ions, which were found to be less than 0.2 wt%. Finally, the hydrated H₂Ti₂O₅ was calcined at 500°C in a muffle oven for 2 h to attain anatase TiO₂-NF.

2.2. Cu₂O decoration on the TiO₂ Nanofibre structure

Well-defined size-controlled Cu₂O nanoparticles on TiO₂ nanofibre were synthesised at different temperatures (50 to 100°C). For example, Cu₂O synthesized by 0.1 M copper acetate monohydrate (2 mL) was mixed with 90 mg of TiO₂ nanostructure with 5 mL of distilled water, which was stirred at 50°C-100°C for 10 min. In a separate vessel, 1 M NaOH (0.8 mL) and 0.2 M ascorbic acid (0.8 mL) were taken to initiate the redox reaction. The mixture of NaOH/ascorbic acid was then quickly added to the above copper acetate/TiO₂ reaction mixtures under continued stirring for 5 min. The reactions of solid-liquid mixtures were shifted to a centrifuge tube and then separated into whitish-yellow Cu₂O/TiO₂-NF precipitate.

2.3. Reversed Double-Beam Photoacoustic Spectroscopy (RDB-PAS)

The synthesized photocatalysts of Cu₂O/TiO₂-NF products were taken, approximately 200 mg, and added into a PAS cell equipped with an electret condenser microphone and a quartz window on the upper side under N₂ flow saturated with methanol vapour for at least 30 min. A light beam from an Xe lamp with a grating monochromator modulated at 80 Hz by a light

chopper was irradiated from 650 nm to 350 nm through the cell window to detect the PAS signal using a digital lock-in amplifier. The energy-resolved distribution of electron traps (ERDT) was obtained by determining the amount of photoabsorption change for the accumulated electrons [24, 25].

2.4. Photoelectrochemical Characterization

Three electrode photoelectrochemical cells were used in this experiment, the counter electrode was a Pt wire, and Hg/Hg₂SO₄ was used for the reference electrode. The working electrode of glassy carbon electrode (GC) was constructed by dropcasting 5 μ L of homogeneous colloid on a 3-mm dia in the GC electrode. The working electrode was prepared by synthesised catalysts made of colloid mixtures by 30-minute sonication of catalysts with Nafion dispersed in a water/ethanol mixture (0.5 mL, 1:1 v/v). A 200-W Hg-Xe arc lamp (plus a $\lambda > 420$ nm cut-off filter) was used as the light source. Autolab potentiostat with Nova software was used for electrochemical measurements. Nyquist plots were recorded using a 10-mV AC signal between 100 kHz and 0.1 Hz in frequency. Mott Schottky plots of the synthesised products were measured at a frequency of 1000 Hz under a DC signal over a potential range of -1 to 0 V with a potential step of 10 mV.

2.5. Photocatalytic H₂ evolution

Photocatalytic H₂ production was carried out using synthesised Cu₂O, TiO₂-P25, TiO₂-NF and their composites in a sealed quartz photoreactor. Photocatalytic H₂ evolution experiments was carried out in 20 mg of catalysts dispersed into 50 mL of deionised water with 2 mL of methanol as a sacrificial electron donor under sonication for 5 min for uniform distribution. The gas was purged for 1 h prior to light irradiation to remove the excess oxygen in the reactor. Gas samples before and after the reaction mixtures were withdrawn periodically in a 1-mL airtight syringe to determine the H₂ production by gas chromatography.

2.6. Sulfamethoxazole (SMX) photodegradation experiment

Typically, 20 mg of Cu₂O and Cu₂O/TiO₂-NF products were dispersed in 50 mL of SMX (0.01184 mM) in a 250-mL quartz cell photoreactor and then sonicated for 10 min to complete dispersion. Before photoreaction, the above mixtures of the reaction were performed in a dark condition to ensure any adsorption and sample was collected for HPLC analysis. After 1 hr of adsorption, samples were periodically collected and filtered using a CPO20AN filter for HPLC analysis. The SMX removal efficiency was calculated according to **equation 1** as follows:

$$\text{SMX removal (\%)} = \frac{\text{SMX}_{\text{initial}} - \text{SMX}_{\text{final}}}{\text{SMX}_{\text{initial}}} \times 100 \quad \mathbf{1}$$

2.7. HPLC analysis of SMX

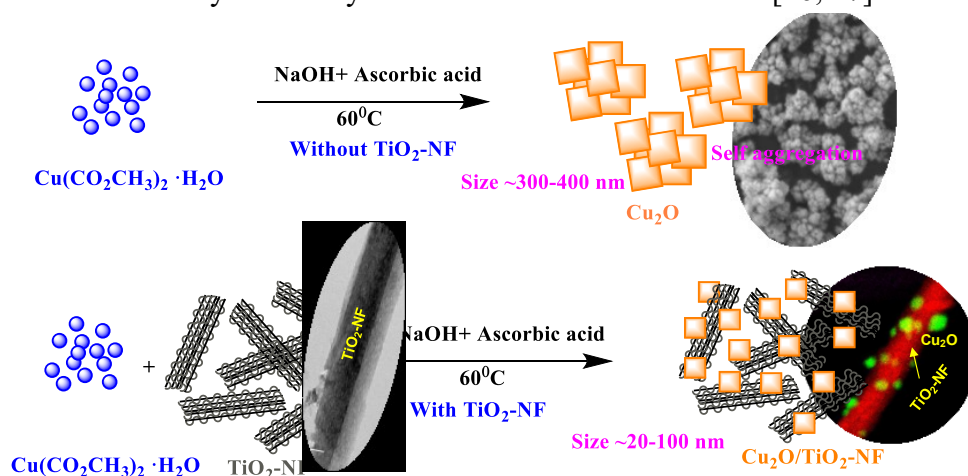
The SMX concentration was analysed using a high-performance liquid chromatography system (JASCO UV plus 2075 serious, Japan) coupled with an intelligent UV/Vis detector selected at $\lambda = 254$ nm and a Shodex C18M 4E analytical column (4.6 I.D \times 250 mm). Separation factor ($\alpha_1 = 2.42$ and $\alpha_2 = 1.47$) with a constant temperature of 25°C, pressure maximum of 20 MPa,

and pressure minimum of 0.2 MPa. The eluent consists of 60:10:30 (v/v) acetonitrile:water:formic acid (25 mM) (TCI, Japan) with a flow rate of 0.6 mL/min.

3. Results and discussion

3.1. Catalyst characterization

The formation of size-controlled cubic Cu_2O nanoparticles on $\text{TiO}_2\text{-NF}$ is displayed in **Scheme 1**. As shown in the scheme, 0.1 M copper acetate monohydrate (2 mL) was mixed with 90 mg of TiO_2 nanofibre nanostructure with 5 mL of distilled water, and the mixtures were thoroughly mixed using ultrasonication to obtain the $\text{Cu(II)-TiO}_2\text{-NF}$ complex; Cu^{2+} ions penetrated and diffused into the TiO_2 nanofibre structure under air atmosphere due to expulsion [10]. In the second step, the complexed/diffused Cu(II) ions were precipitated for copper hydroxide, followed by reduction to Cu(I) oxide by adding alkaline $\text{NaOH/ascorbic acid}$ mixture at 60°C under stirring. The cubic Cu_2O nanoparticles are in a size range of 20-100 nm (more SEM and TEM images are shown later in **Fig. 2 and 3** and also in supporting materials **Fig. S1**). However, in contrast, when $\text{TiO}_2\text{-NF}$ is absent, Cu_2O particles self-aggregated to form agglomerated Cu_2O nanoparticles (~ 400 nm), indicating that the Cu_2O size was better controlled using TiO_2 nanofibre. This is a great advantage comparing to the use of additional templates/surfactants, which will introduce impurities unavoidably block Cu_2O active surface sites and reduce the catalytic activity in the surface-related reactions [26, 27].



Scheme 1 Synthetic diagram for the construction of Cu_2O and $\text{Cu}_2\text{O/TiO}_2\text{-NF}$ (60°C) nanocomposite.

Fig. 1 shows the PXRD patterns of $\text{Cu}_2\text{O/TiO}_2\text{-NF}$ nanocomposites as well as Cu_2O and $\text{TiO}_2\text{-NF}$ references. The XRD pattern of Cu_2O showed the reflection at $2\theta = 29.58$ (3.01 \AA), 36.44 (2.46 \AA), 42.33 (2.13 \AA), 61.41 (1.50 \AA), and 73.56 (1.28 \AA) corresponding to the (1 1 0), (1 1 1), (2 0 0), (2 2 0), and (3 1 1) planes, which indicated the cubic cuprite (Cu_2O) phase (with space group $Pn\text{-}3m$, no. 224) and cell parameters of $a = 4.27$, $b = 4.27$, $c = 4.27$, and $\beta = 90.38$ (JCPDS number 01-071-3645). The XRD pattern of $\text{TiO}_2\text{-NF}$ showed the diffraction at $2\theta = 25.30$ (3.52 \AA), 38.50 (2.33 \AA), 48.04 (1.89 \AA), 53.88 (1.70 \AA), 55.06 (1.66 \AA), 62.75 (1.48 \AA), and 75.04 (1.26 \AA) corresponding to the (101), (112), (200), (105), (211), (204), and

(215) planes, which indicated a tetragonal crystal system of TiO₂-NF anatase with space group *I41/amd* (*I41* and cell parameters of $a = 3.78$, $b = 3.78$, $c = 9.51$, and $\beta = 90.0$ (JCPDS number 03-065-5714).

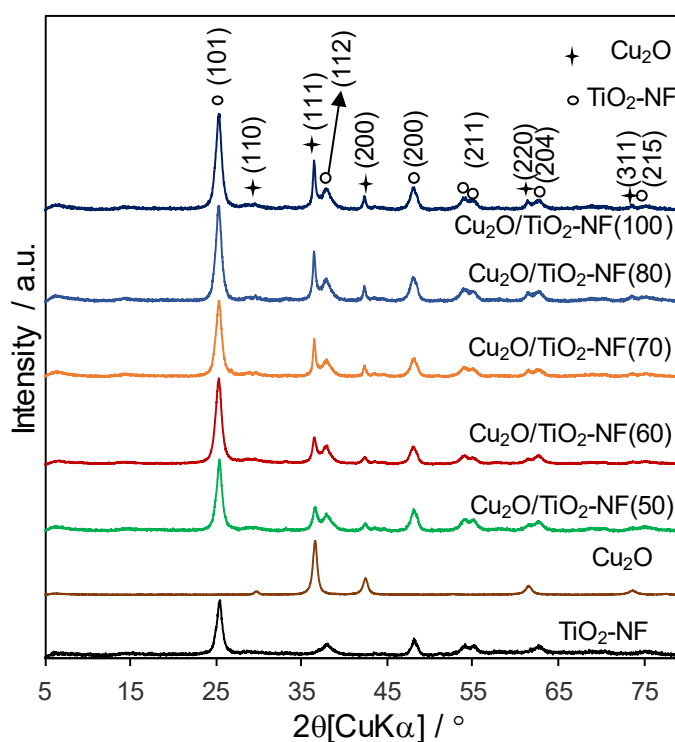


Fig. 1 Powder XRD patterns spectrum of Cu₂O, TiO₂-NF and their composites (50 to 100°C).

Patterns of Cu₂O/TiO₂-NF nanocomposites at diverse temperatures clearly demonstrate the characteristic planes of the TiO₂-NF anatase phase and low but observable Cu₂O peaks, indicating that the cuprite nanoparticles were evenly distributed on the TiO₂-NF structure [28]. From the XRD patterns, no other characteristic impurities such as Cu(OH)₂ and others were found, indicating that the composites contain only Cu₂O and TiO₂-NF. The crystalline sizes were calculated using the Scherrer equation, and the phase compositions of the Cu₂O/TiO₂-NF composites were analysed by the Rietveld method displayed in **Table 1**.

Fig. 2 displays high-resolution TEM images of well-dispersed/submerged Cu₂O nanoparticles (20-100 nm) on the TiO₂ nanofibre (diameter ~300 nm and length ~650 nm) structure in the Cu₂O/TiO₂-NF (60°C) sample. **Fig. 2a** clearly shows that the lattice d-spacing of 0.26 nm corresponds to the d₁₁₁ planes of Cu₂O and, the d-space of 0.23 nm and 0.35 nm corresponds to the d₁₁₂ and d₁₀₁ anatase phase of TiO₂-NF, which is in good agreement with XRD patterns. In addition, images in **Fig. 2c-e** and **Fig. S3a-e** clearly indicate that the Cu₂O nanoparticles interpenetrated as well as partially submerged into the TiO₂ nanofibre surface.

On the Cu₂O/TiO₂-NF (60°C) sample, scanning transmission electron microscopy (STEM) combined with energy-dispersive X-ray spectroscopy (EDS) images clearly evidenced the even distribution of Cu₂O nanoparticles (20 to 100 nm) on the TiO₂ nanofibre surface (**Fig. 3a-g**). Elemental analysis shows ~10% Cu atom and ~53% Ti atom, as presented in **Fig. 3g and 3h**.

FE-SEM images of $\text{Cu}_2\text{O}/\text{TiO}_2\text{-NF}$ prepared at different temperatures (50 to 100°C) are shown in **Fig. S2a-e**. It can be noted that, with the increase of temperature, the density of the Cu_2O nanoparticles increased, and they agglomerated on the $\text{TiO}_2\text{-NF}$ surface. The increase in the amount of Cu_2O nanoparticles with increasing temperature is in good agreement with the XRF results (**Table 1**).

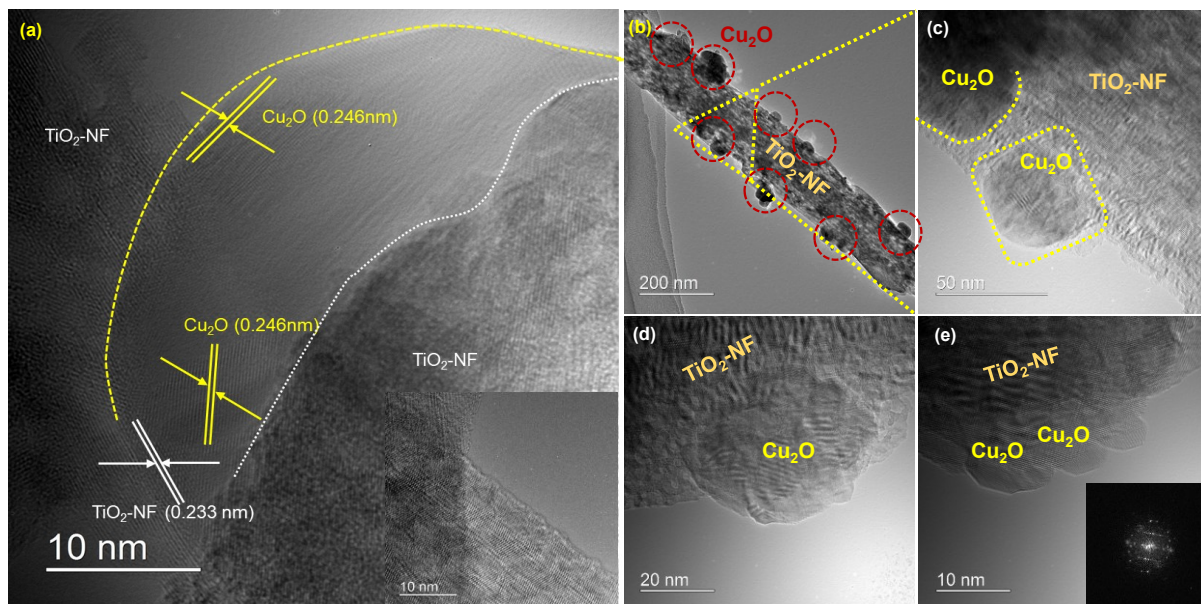


Fig. 2 a-e) HR-TEM images of $\text{Cu}_2\text{O}/\text{TiO}_2\text{-NF}$ (60°C) captured an Ultra-scan camera.

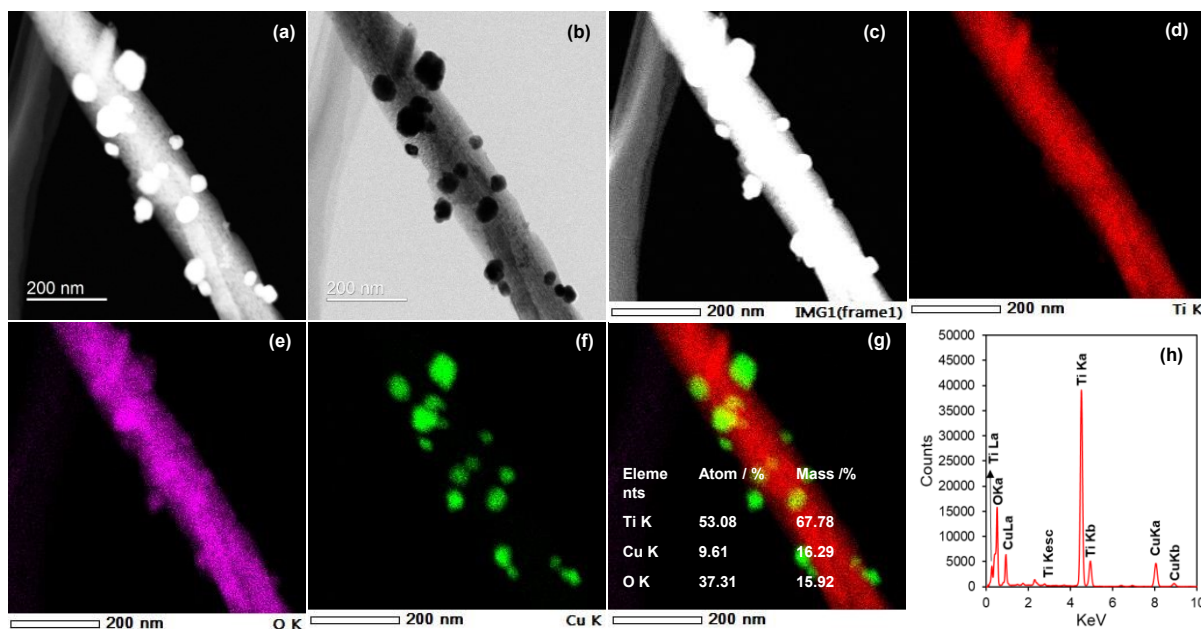


Fig. 3 a-g) STEM and elemental mapping of synthesised $\text{Cu}_2\text{O}/\text{TiO}_2\text{-NF}$ (60°C).

The optical absorption and electronic characteristic of synthesised Cu_2O , TiO_2 and their composites were observed by DR UV-vis spectra, as shown in **Fig. 4**. The DR UV-vis spectra of Cu_2O showed a broad light absorbance due to interband absorption consistent with reports

[29, 30], while the TiO₂-NF showed only in the UV region ~380 nm. The composites show a combination of the two individuals. The corresponding band gap energies were calculated using Tauc plots, as shown in **Fig. S4** and the following **Eq. (2)**:

$$\alpha h\nu = A(h\nu - E_g)^n \quad 2$$

where α is the linear absorption coefficient, A is the absorption coefficient, h is Planck's constant, $h\nu$ is the photon energy, and E_g is the band gap. The energy gap of synthesised Cu₂O, TiO₂-NF and their composites were also obtained from the Kubelka-Munk function presented as **Eq. (3)**:

$$a = \frac{(1-R)^2}{2R} \quad 3$$

From the KM function, the calculated direct band gap (E_g) values of 2.46 eV for Cu₂O, indirect band gap of 3.17 eV for TiO₂-NF, and their composites are presented in **Table 1**. Results from Tauc plots agreed very well with those from KM function.

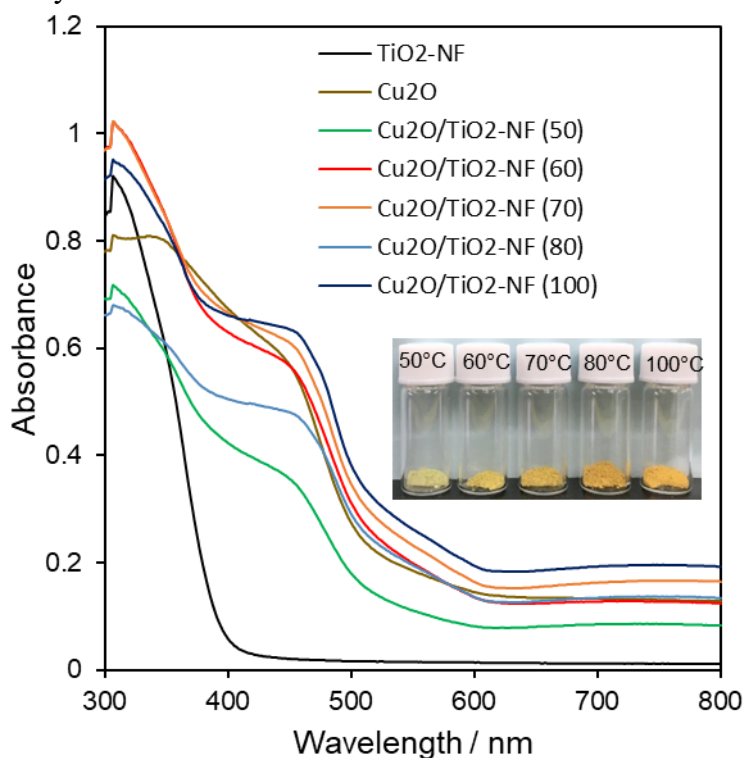


Fig. 4 DR UV-vis spectra of Cu₂O, TiO₂-NF and their composites (50 to 100°C).

It is clear that the combination of Cu₂O and TiO₂-NF has greatly influenced the band gap energies of the synthesised composites, which should be due to the interfacial interaction between Cu₂O and TiO₂-NF, as well as the intrinsic exciton band and d-d transition of Cu species. For example, the absorption range of 385 to 515 nm might due to the interfacial charge transfer (IFCT) of the TiO₂ valence band to Cu_xO- aggregates [28]. As a result, the Cu₂O/TiO₂-NF composites show strong visible light absorption properties to be ready to perform enhanced photocatalytic efficiency.

Table 1 Physicochemical properties of synthesised Cu₂O, TiO₂-NF and their composites

Catalyst	Cu ₂ O Crystalline size (nm) ^a	Composition of Cu ₂ O (%) ^b	Composition of Cu ₂ O at surface (%) ^c	Composition of Cu ₂ O in the bulk (%) ^d	Band gap (eV) ^e	BET surface area (m ² g ⁻¹) ^f	Total pore volume (cm ³ g ⁻¹) ^f	VB edge potential (eV) ^g	CB edge potential (eV) ^g
TiO ₂ -NF	11.59	-	-	-	3.17	79.49	0.275	1.69	-1.48
Cu ₂ O	14.87	-	-	-	2.46	15.2	0.190	0.23	-2.23
Cu ₂ O/TiO ₂ -NF (50)	13.34	11.23	31.7	14.85	2.52	67.25	0.266	1.13	-1.39
Cu ₂ O/TiO ₂ -NF (60)	15.28	11.85	22.9	15.59	2.48	67.82	0.251	0.78	-1.70
Cu ₂ O/TiO ₂ -NF (70)	16.31	12.04	23.2	16.92	2.48	61.1	0.264	0.54	-1.94
Cu ₂ O/TiO ₂ -NF (80)	24.1	14.79	23.8	17.04	2.42	58.7	0.262	0.32	-2.10
Cu ₂ O/TiO ₂ -NF (100)	24.7	14.81	25.3	19.89	2.40	55.26	0.261	0.28	-2.12

^aScherrer equation, ^bRietveld method, ^cXPS, ^dX-ray fluorescence, ^eTauc plots, ^fN₂ porosimetry, ^gVB XPS and DR UV-vis.

To elucidate the surface structure properties of the Cu₂O/TiO₂-NF composites, all of the samples were characterized using RDB-PAS. **Fig. 5** shows the ERDT/CBB patterns from EDB-PAS of each sample plotted as a function of energy from the VBT vs. electron-trap density. The ERDT/CBB patterns of TiO₂-NF and TiO₂-P25 (anatase phase of TiO₂) show the high electron accumulation density approximately centred at 3.1 eV. Interestingly, the ERDT/CBB patterns of the composites all shifted to higher energy around 3.3 eV. The extent of shifting

increased when the synthetic temperature increased. The shifting of ERDT/CBB patterns indicates the distortion of the surface of TiO₂-NF by impaction of Cu₂O to form heterojunction with TiO₂-NF. The ERDT/CBB patterns of the composite are in good agreement with the TEM observation which shows that the surface of TiO₂ was modified by Cu₂O.

The surface oxidation states of synthesised Cu₂O and their Cu₂O/TiO₂-NF products were observed using core-level Cu 2p, Ti 2p X-ray photoelectron spectroscopy (XPS) shown in **Fig. S5**. The XPS binding energy peak of 458.5 eV and 464.1 eV, consisted with characteristic peak of Ti 2p_{3/2} and Ti 2p_{1/2} in TiO₂-nanofibre and binding energy peaks at 931.4 eV and 951.2 eV, consisted to Cu 2p_{3/2} and Cu 2p_{1/2} spin-orbit split of Cu/Cu₂O; the weak binding energy at 934.3eV and 954.1 eV with satellite shakeup at 941 eV, in all the synthesised products corresponds to CuO [31]. The characteristic of strong shakeup features was due to the unoccupied 3d⁹ shell arrangement of Cu²⁺ species, while the presence of CuO prevented the surface stability of Cu₂O to further oxidation [32]. The surface Cu(I): Cu(II) composition form XPS results also consistent with the XRD Rietveld method and XRF results.

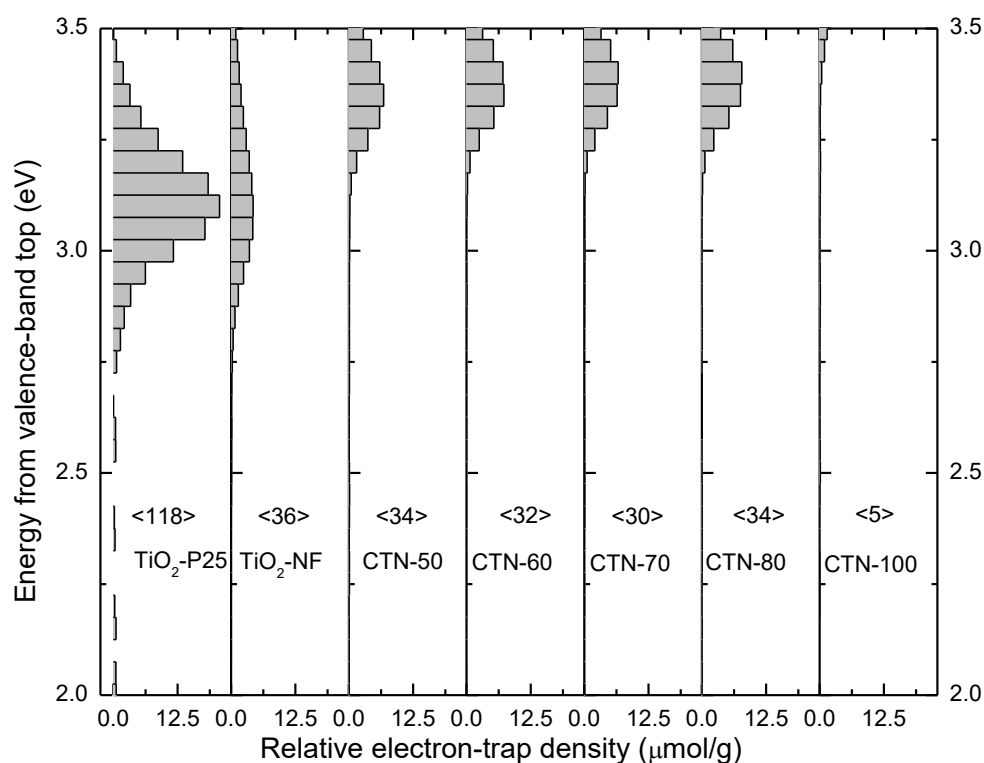


Fig. 5 ERDT pattern of TiO₂, TiO₂-NF and Cu₂O/TiO₂-NF products, named CTN, from 50 to 100°C.

The “fingerprint” of X-ray absorption near edge structure (XANES) spectroscopy was measured to further investigate the Cu₂O or CuO compositions in the synthesised products. The Cu K-edge XANES were analysed for Cu₂O samples, as well as synthesised Cu₂O/TiO₂-NF composites, which are compared with standards in **Fig. 6A** (Cu-metal, Cu₂O and CuO). Quantitative compositions obtained from linear combination fitting (LCF) are presented in **Table S1**. The formation of both Cu⁺ (> 70%) and Cu²⁺ (< 30%) species on the TiO₂ surface was further consistent with reported literature [4].

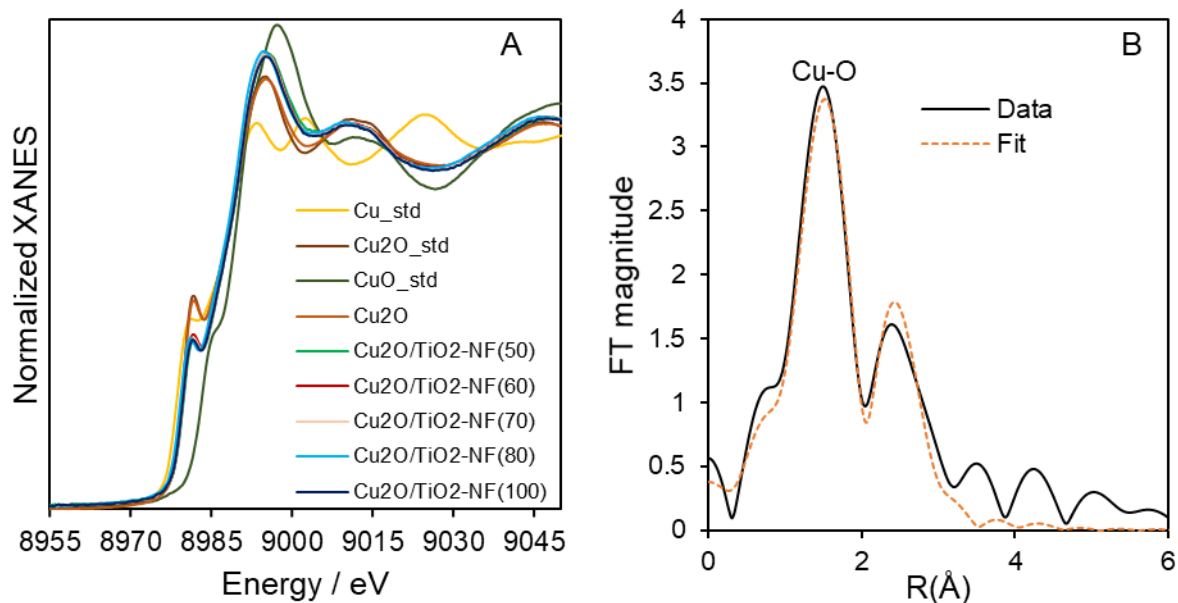


Fig. 6 A Cu K-edge XANES spectra of Cu_2O , $\text{Cu}_2\text{O}/\text{TiO}_2\text{-NF}$ (50 to 100°C) and reference materials, B) Cu K-edge EXAFS spectra of $\text{Cu}_2\text{O}/\text{TiO}_2\text{-NF}$ (60°C) in k space.

The presence and property of Cu_2O in the $\text{Cu}_2\text{O}/\text{TiO}_2\text{-NF}$ (60°C) was further studied by extended X-ray-absorption fine-structure (EXAFS) analysis in Cu k-edge. The fitting is in good agreement with real parts of Fourier transform spectra, as shown in **Fig. 6B** and **Fig. S6**. The fitting clearly indicates that there are two separated shells in the radial structure function (RSF). The first peak of the EXAFS spectra could be fitted to the first coordination shell of the Cu-O bond. While the second shell of the EXAFS spectra probably comes from Cu species interacting with TiO_2 , indicating Cu_2O formation on $\text{TiO}_2\text{-NF}$ surface confirmed STEM, and elemental mapping (**Fig. 3 a-g**).

Finally, surface area is an important factor for surface-related photoreaction, and the specific surface areas of the synthesized $\text{TiO}_2\text{-NF}$, Cu_2O , $\text{Cu}_2\text{O}/\text{TiO}_2\text{-NF}$ samples were measured by nitrogen adsorption-desorption BET analysis as shown in **Fig. S7 a-g**). The specific surface areas of pristine $\text{TiO}_2\text{-NF}$ and Cu_2O were shown at $79.49 \text{ m}^2 \text{ g}^{-1}$ and $15.2 \text{ m}^2 \text{ g}^{-1}$, respectively. In particular, $\text{Cu}_2\text{O}/\text{TiO}_2\text{-NF}$ composites were prepared under different temperatures from 50 to 100 °C. The surface areas were increased from 50 to 60 °C and then decreased gradually from 70 to 100 °C, which is due to the formation of particle size and aggregation of Cu_2O on the surface of $\text{TiO}_2\text{-NF}$. These results are well supported in the SEM and HRTEM images. The surface area and pore volume of synthesis products were calculated by the BET method, as summarised in **Table 1**. The high surface area and pore volume of the composites is beneficial for their photocatalytic activity.

3.2. Photocatalytic H_2 production

Fig. 7a-b shows the rates of photocatalytic H_2 generation of P25, Cu_2O , $\text{TiO}_2\text{-NF}$ and $\text{Cu}_2\text{O}/\text{TiO}_2\text{-NF}$. Under UV-Vis light illumination for 8 h, the rates were $4.7 \mu\text{mol g}^{-1} \text{ h}^{-1}$ for P25, $7.2 \mu\text{mol g}^{-1} \text{ h}^{-1}$ for $\text{TiO}_2\text{-NF}$ and $6.7 \mu\text{mol g}^{-1} \text{ h}^{-1}$ for Cu_2O . Meanwhile, the hydrogen production rates of $\text{Cu}_2\text{O}/\text{TiO}_2\text{-NF}$ products were $34 \mu\text{mol g}^{-1} \text{ h}^{-1}$ for $\text{Cu}_2\text{O}/\text{TiO}_2\text{-NF}$ (50°C), 48

$\mu\text{mol g}^{-1} \text{h}^{-1}$ for both $\text{Cu}_2\text{O}/\text{TiO}_2\text{-NF}$ (60 and 70°C), $36 \mu\text{mol g}^{-1} \text{h}^{-1}$ $\text{Cu}_2\text{O}/\text{TiO}_2\text{-NF}$ (80 and 100°C). H_2 production rates of synthesised composites (~ 6.5 times higher compared with $\text{TiO}_2\text{-NF}$) were significantly enhanced. The reason could be the formation of the heterojunction at the interface between p- $\text{Cu}_2\text{O}/\text{n-TiO}_2\text{-NF}$, which will be discussed in details in later sections and also illustrated in **Scheme 2**. The apparent quantum efficiency (AQE) was calculated according to the previous methods[6, 18], and AQE of $\text{Cu}_2\text{O}/\text{TiO}_2\text{-NF}$ (60°C) composites ($\sim 3.6\%$) significantly increased by a factor of ~ 6 -fold compared with $\text{TiO}_2\text{-P25}$ and $\text{TiO}_2\text{-NF}$ presented in Supporting information, **Fig. S8**. H_2 production and AQE of $\text{Cu}_2\text{O}/\text{TiO}_2\text{-NF}$ synthesised at higher temperature (80 and 100°C) dropped slightly, probably due to the Cu_2O nanoparticles agglomerated on the $\text{TiO}_2\text{-NF}$ surface.

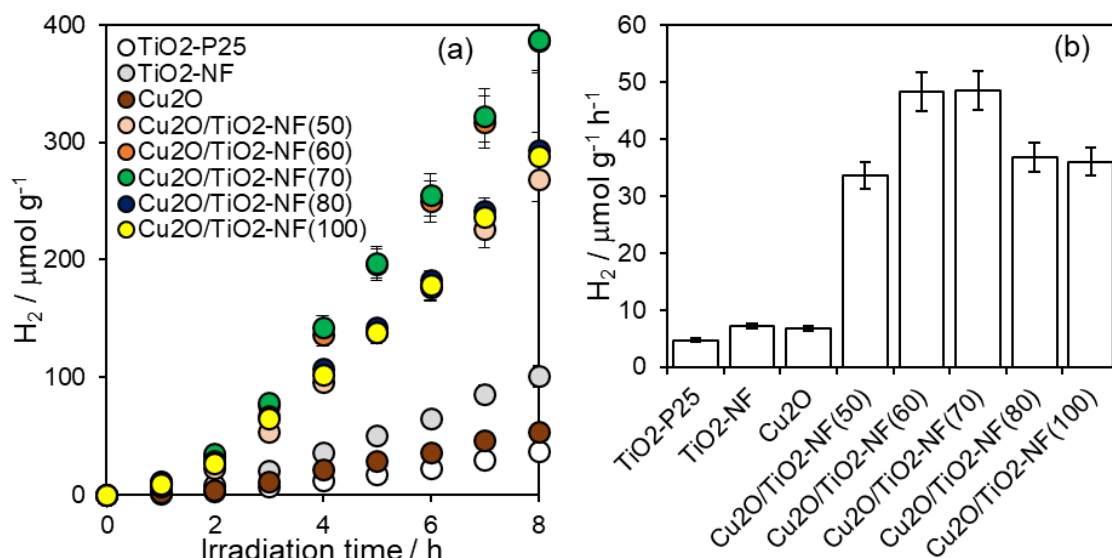


Fig. 7 a) Photocatalytic H_2 production amount and b) corresponding H_2 production rates over Cu_2O , $\text{TiO}_2\text{-P25}$, $\text{TiO}_2\text{-NF}$ and their composites with methanol as a sacrificial electron donor.

In addition, we compared the H_2 generation rates of $\text{Cu}_2\text{O}/\text{TiO}_2\text{-NF}$ (60 and 70°C) with other $\text{Cu}_2\text{O}/\text{TiO}_2$ composites and also noble metal modified TiO_2 composites. For various $\text{Cu}_2\text{O}/\text{TiO}_2$ composites, our $\text{Cu}_2\text{O}/\text{TiO}_2\text{-NF}$ was more efficient (at least a factor of ~ 1.47) compared with previously reported core-shell nanowire arrays tested under UV irradiation with no AQE reported [33]. For a range of noble metal modified TiO_2 composites, comparison was summarised in **Table S2**. It is impossible to compare H_2 generation rates directly when the reaction set-ups are significantly different. However, it is very promising that $\text{Cu}_2\text{O}/\text{TiO}_2\text{-NF}$ (using only cheap and earth abundant materials) shows comparable activity to many of the noble metal modified TiO_2 composites.

3.3. Photocatalytic sulfamethoxazole (SMX) oxidative degradation

The photocatalytic activity of $\text{Cu}_2\text{O}/\text{TiO}_2\text{-NF}$ composites was also evaluated using SMX as an emerging antibiotic complex organic compound commonly used for both humans and animals worldwide for bacterial infections. The recent survey indicated that 59 t/year of SMX is used for animals and 24 t/year for humans in Japan [34]. Additionally, the discharges of SMX concentrations were unacceptable in the municipal and livestock wastewaters. In Europe, the discharged SMX concentration ranges from 0.01 to $2 \mu\text{g L}^{-1}$ in the municipal wastewater, and

the concentration varies in the surface waters from 0.03 to 0.48 $\mu\text{g L}^{-1}$ [35]. The survey indicated that unacceptable SMX concentrations range from ng/L to $\mu\text{g/L}$ in the United States [36]. The existence of antibiotic organics in the aqueous environment has a negative effect due to resistance to bacteria, resulting in the possibility of bacteria developing new resistant genes in the water bodies [37]. The present report was focused on the removal of persistent SMX pharmaceutical organic compounds (especially those low in concentration) under visible light.

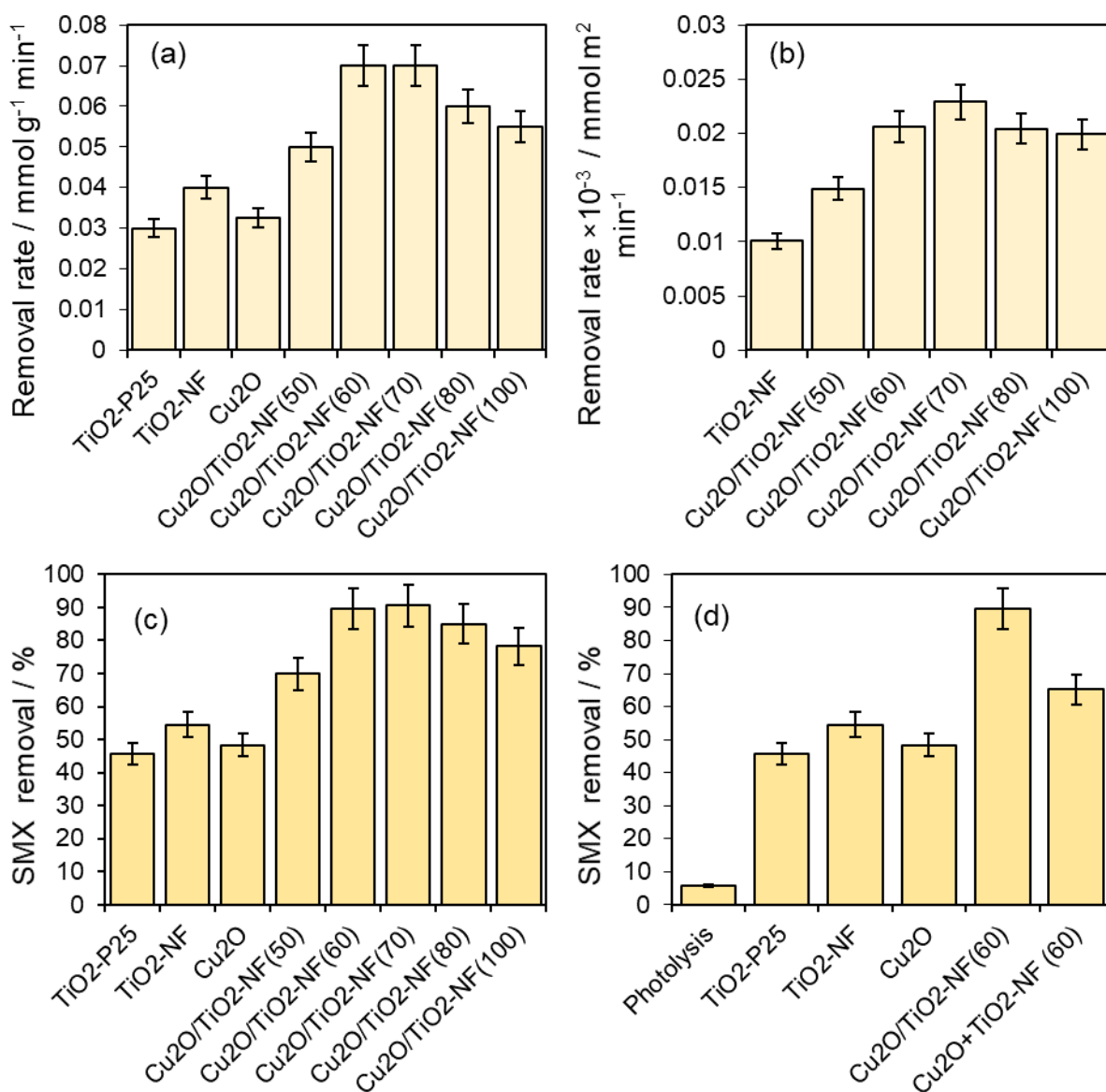


Fig. 8 a) photocatalytic initial removal rates of Sulfamethoxazole (SMX), b) corresponding area normalized rates (at 10 min), c) SMX photocatalytic degradation over synthesized Cu₂O, TiO₂ and Cu₂O/TiO₂-NF (60°C) catalyst, d) comparative SMX degradation efficiency over photolysis, TiO₂, Cu₂O, Cu₂O/TiO₂-NF (60°C) and Cu₂O+TiO₂-NF (60°C) physical mixture. Reaction conditions: 0.01184 mmol SMX; 50 mL of water; 20 mg of catalyst; reaction time of 10 min, corresponding degradation efficiency at 30 min.

The photocatalytic activity of as-synthesised Cu₂O, TiO₂-NF, Cu₂O/TiO₂-NF composites, as well as the physical mixture of Cu₂O+TiO₂-NF (60°C), was systematically applied for SMX

photodegradation under visible light as presented in **Fig. 9a-d**. The SMX organic molecule was intentionally selected in this study because it is not a dye molecule and it does not have visible light absorption ability. While if dye molecule was applied, it would be difficult to distinguish the catalytic mechanism initiated by either dyes or photocatalysts [38]. Initially, the 0.01184 mmol of SMX antibiotic organic molecule with synthesised photocatalysts (20 mg) were conducted for adsorption study for 1 h in a dark condition. Meanwhile, oxidation of SMX with light-only without any photocatalysts was checked, the removal rate was only 5.8 % of SMX, probably due to photolysis.

When TiO₂-P25, TiO₂-NF and Cu₂O were applied as photocatalysts, initial removal rates of SMX were 0.03, 0.04 and 0.03 mmol g⁻¹ min⁻¹ after 10 min, and the corresponding removal efficiencies were 45.7 %, 54.5 %, and 48.4 % after 30 min of reaction, respectively. SMX initial oxidation rates after 10 min and removal percentages after 30 min were much higher. Cu₂O/TiO₂-NF (60 and 70 °C) showed the highest rates of 0.07 mmol g⁻¹ min⁻¹ and highest removal percentage 91%. In addition, the AQE was 35, 46, and 38% for TiO₂-P25, TiO₂-NF and Cu₂O, while Cu₂O/TiO₂-NF (60 and 70 °C) showed the highest of 81%, as presented in **Fig. S9**. The photocatalytic activity was reduced beyond the optimal synthesis temperature (60 and 70 °C) of Cu₂O, agreed with H₂ generation results.

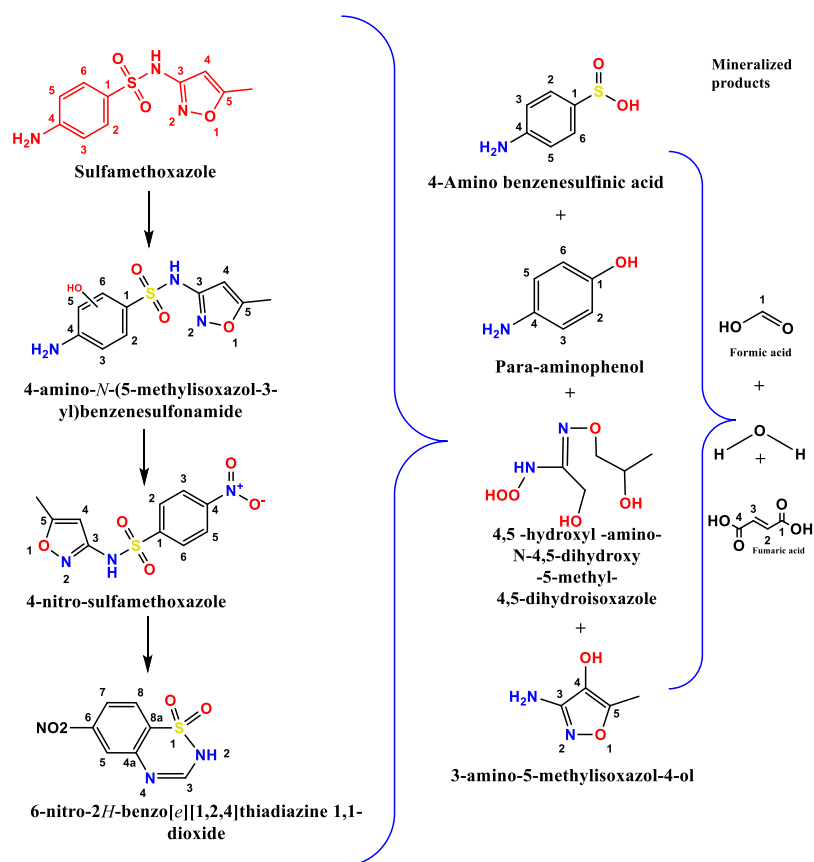
Physical mixture of Cu₂O+TiO₂-NF was also tested for SMX degradation and showed 65% removal percentage after 30 min which is much lower than 91% of Cu₂O/TiO₂-NF (60 °C). This indicates that the excellent photocatalytic activity in the composites might be an effective synergistic heterojunction followed by carrier charge transfer at Cu₂O to TiO₂-NF interfaces.

SMX removal over other reported TiO₂ based photocatalysts are summarised in **Table S3**. Again, it is not possible to compare reaction rates directly when the reaction set-ups are significantly different. However, it is very promising that Cu₂O/TiO₂-NF shows comparable activity under visible light only to many other photocatalysts with some of them were tested under UV light.

The photocatalytic removal of SMX and their oxidation by-products were investigated using HPLC (**Fig. S10-12**) and LC-MS/MS analysis (**Fig. S13 a-e**). By-products and proposed pathway are presented in **Scheme 2**. The pathway might follow these subsequent steps: (I) •OH radicals attack on the benzene ring with formation of hydroxylated SMX and aminophenol; which leads to the cleavage of the S-N bond; (II) deamination to form a nitro-substituted benzene ring, which further cleavage into C-N bonds in SMX; (III) The hydroxylated and deaminated SMX further cleavage of several C-S, C-N, S-N bonds in SMX (especially, isoxazole and benzene rings) [39-42]. The photocatalytic oxidation of SMX over Cu₂O/TiO₂-NF (60°C) eliminating C-S bond, cleavage of carbon-nitrogen (C-N) bond, various carbon-carbon (C-C) cleaved followed by •OH radical attack for the aromatic ring opening in the sulfamethoxazole[43].

The total organic carbon (TOC) analysis of aqueous samples after SMX removal using Cu₂O/TiO₂-NF (60 °C) was carried out. The photocatalytically degraded solutions at different time intervals were collected and analysed. In the dark conditions, the TOC elimination was only 3.4% and this was increased to 73.5% upon light irradiation of 30 min, indicating majority

of SMX was mineralised and the final reaction mixture might contain small amount of shorter carbonaceous molecules, e.g. the carboxylic acids as suggested in **Scheme 2**.



Scheme 2 Proposed by-product formation over Cu₂O/TiO₂-NF (60°C) catalysts.

The influence of [•]OH radical in this photocatalytic reaction was further verified by radical quenching experiments. The SMX removal rates were considerably low after the addition of isopropyl alcohol (IPA) and ethylenediaminetetraacetic acid (EDTA) which quenched [•]OH radical-mediated reaction as presented in **Fig. S14a**. The [•]OH radical-mediated SMX elimination over Cu₂O/TiO₂-NF (60°C) photocatalyst was also verified through the generation of [•]OH radicals, whose generation was confirmed using fluorescence spectroscopy with terephthalic acid (TA) used as the probe molecule. The 2-hydroxy terephthalic acid (2-HTA) formation via [•]OH radical attack is well established. Higher intensity of 2-HTA in the fluorescence spectrum confirmed the generation of [•]OH radical in this specific reaction (**Fig. S14b**).

3.4. Photoelectrochemical performance

The effect of interfacial Cu₂O/TiO₂-NF heterojunction on transfer of photogenerated charge carriers was investigated using transient photocurrent measurements under chopped light illumination. **Fig. 9a** shows that Cu₂O/TiO₂-NF (60°C) > TiO₂-NF > Cu₂O in terms of photocurrent response. The significantly increased photocurrent of Cu₂O/TiO₂-NF (60°C) heterojunction showed improved separation of electrons from holes and efficient charge transport across the interface compared to individual components.[44]. There are noticeable current overshoot when the light is switched off due to the continuing flux of electrons into the

surface as holes remaining in the surface states recombine. It is a widely observed phenomenon in photocurrent measurements, known as cathodic current overshoot or anomalous transient photocurrent [45, 46]. We believe the significant overshoot for Cu₂O/TiO₂-NF links to its unique structure and superior photocatalytic performance. We are still exploring some clearer insights because the overshoot current links to quite a few factors, e.g. surface defects/trap states, surface recombination, hole transfer, band alignment and bending, etc.

Electrochemical impedance spectroscopy illustrates the characteristics of the charge transfer process, and the semicircle diameter indicates the charge transfer resistance [47]. From **Fig. 9b**, the charge transfer resistance of Cu₂O/TiO₂-NF (60°C) catalysts was smaller than those of TiO₂-NF and Cu₂O, which implies that the p-n heterojunction formation between Cu₂O and TiO₂-NF improves electron migration and increases the conductivity for enhanced electron transfer to active sites on the catalyst surface.

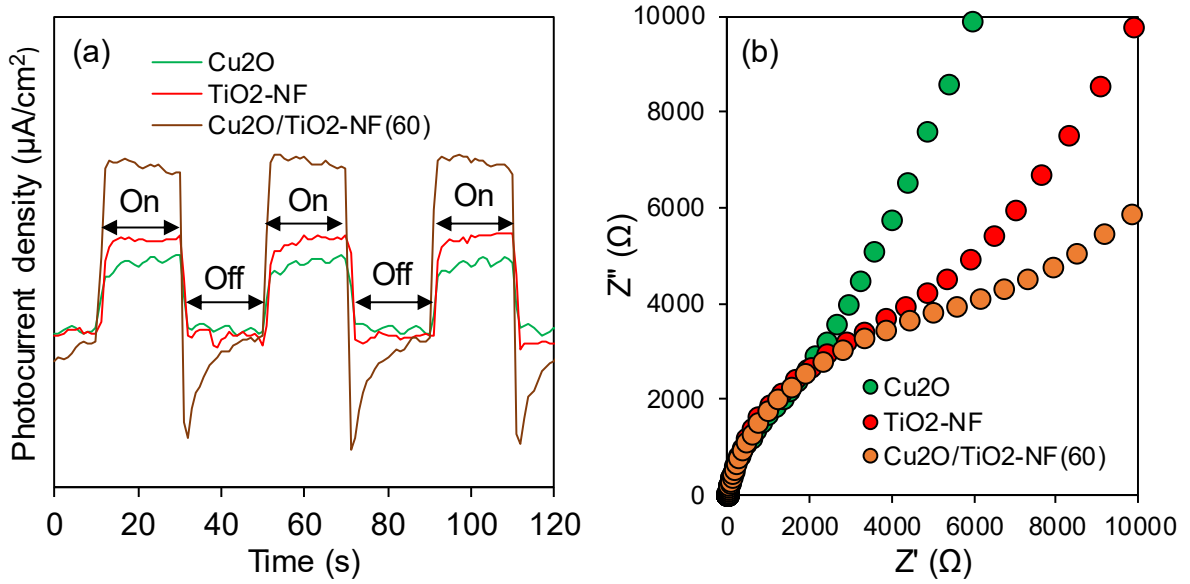


Fig. 9 a) Transient photocurrent, b) Electrochemical Impedance Spectroscopy (EIS).

3.5. Band energy alignment at the interface of Cu₂O/TiO₂-NF heterojunction

The band alignment between the p-Cu₂O/n-TiO₂-NF heterojunction interface can be calculated based on a well-established method described in the below eqs (5) and (6) [15, 48, 49]:

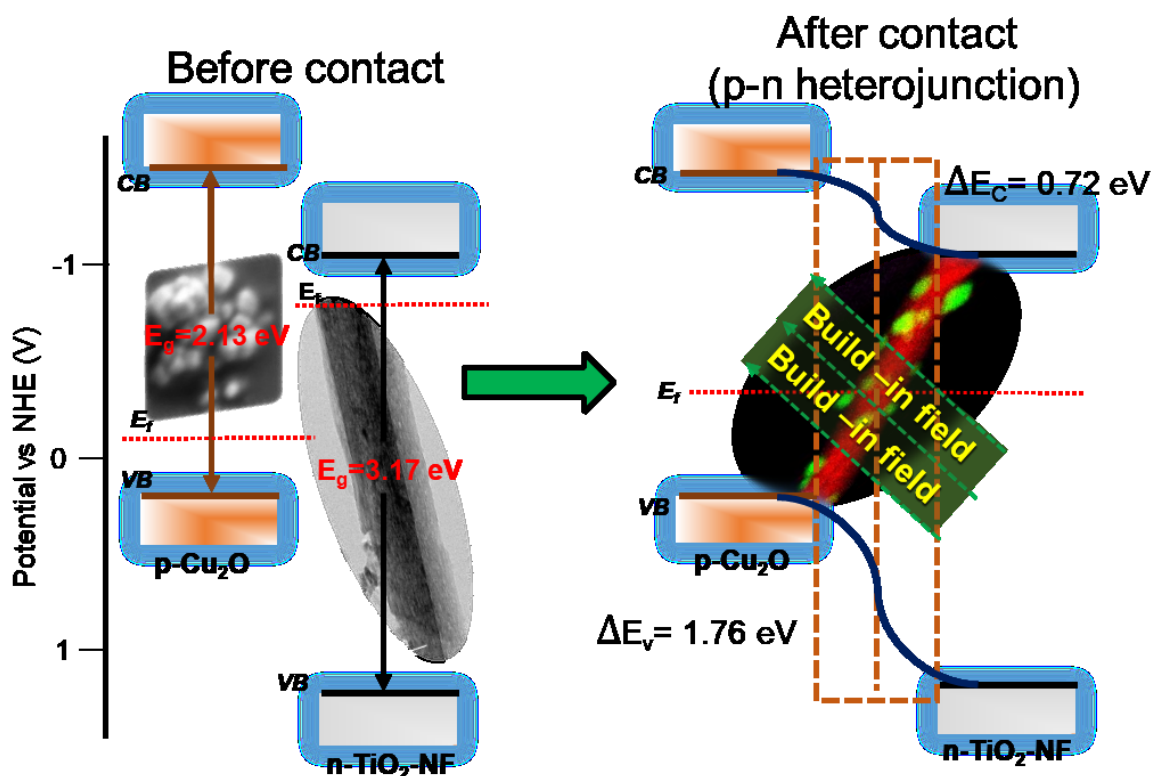
$$\Delta E_V = (E_{Ti2p}^{Cu_2O/TiO_2-NF} - E_{Cu2p}^{Cu_2O/TiO_2-NF}) + (E_{Cu2p}^{Cu_2O} - E_{VBM}^{Cu_2O}) - (E_{Ti2p}^{TiO_2-NF} - E_{VBM}^{TiO_2-NF}) \quad 5$$

$$\Delta E_c = \Delta E_V + E_g^{Cu_2O} - E_g^{TiO_2-NF} \quad 6$$

Where $(E_{Ti2p}^{Cu_2O/TiO_2-NF} - E_{Cu2p}^{Cu_2O/TiO_2-NF})$ indicates the core-level (CL) difference in energy between Ti2p and Cu2p obtained from the Cu₂O/TiO₂-NF heterojunction; meanwhile, $(E_{Cu2p}^{Cu_2O} - E_{VBM}^{Cu_2O})$ and $(E_{Ti2p}^{TiO_2-NF} - E_{VBM}^{TiO_2-NF})$ indicates the core-level as well as valency-band maximum energies in the Ti2p and Cu2p counterpart. $E_g^{Cu_2O} - E_g^{TiO_2-NF}$ indicates the

band gap difference of Cu_2O and TiO_2 materials. ΔE_V and ΔE_C are the valence band and conduction band offset in the $\text{Cu}_2\text{O}/\text{TiO}_2\text{-NF}$ (60°C) heterojunction.

All the values needed for eqs (5) and (6) come from XPS and UV-Vis measurements, the calculated ΔE_V is 1.76 eV and ΔE_C is 0.72 eV, which are consistent with similar previous reports [15, 48, 49], and presented in Scheme 3. From the band alignment, we can learn that the formation of p- $\text{Cu}_2\text{O}/\text{n-TiO}_2\text{-NF}$ heterojunction leads to build in electric field and space-charge regions followed by band bending, which is a great advantage to enhance electron transfer across the p- $\text{Cu}_2\text{O}/\text{n-TiO}_2\text{-NF}$ interface for higher catalytic activity [50].



Scheme 3. Band alignment energy diagram of Cu_2O , $\text{TiO}_2\text{-NF}$ before and after contact. (CB: conduction band, VB: valence band, E_f : Fermi level, ΔE_C : conduction bands offset, ΔE_V : valence bands offset.)

3.6. Catalyst durability

Catalyst durability is an important parameter for photocatalytic application, and in the present report, we have conducted the SMX degradation over $\text{Cu}_2\text{O}/\text{TiO}_2\text{-NF}$ (60°C) catalysts for five cycles. The multi-cycle test indicated that the SMX degradation percentage was not changed even after five cycles, and the synthesised $\text{Cu}_2\text{O}/\text{TiO}_2\text{-NF}$ (60°C) nanocomposite exhibiting high activity and excellent stability for photocatalytic applications.

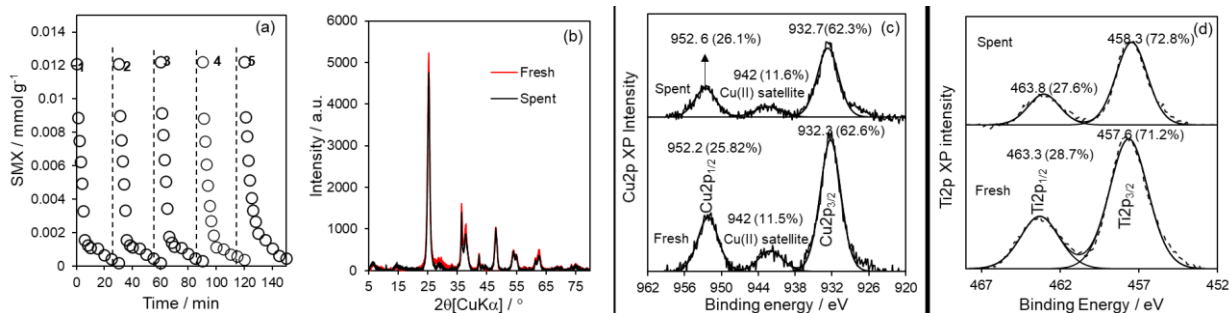


Fig. 10 a) Catalyst stability by recycle experiments, b) XRD patterns, c) and d) XPS spectrum, of fresh and spent Cu₂O/TiO₂-NF (60°C).

In addition, Cu₂O is normally unstable under light irradiation, and surprisingly, the TiO₂-NF structure enhances the photo stability and slows down the oxidation and aggregation of Cu₂O nanoparticles, evidenced by spent catalyst XRD, XPS and electron microscopy studies as presented in **Fig. 10** and **Fig. S15a-f**. Negligible changes in crystal phase, oxidation states and morphologies were observed over five consecutive cycles of SMX degradation under visible light illumination.

Last but not least, recovery and collection of fine catalyst particles in colloidal suspension is highly challenging for the photocatalytic application. However, because of the large overall size of Cu₂O/TiO₂-NF composite, the Cu₂O/TiO₂-NF can be easily separated from the post-reaction mixture of the SMX using simple precipitation after 1 h.

4. Conclusion

We demonstrated a simple synthetic approach for the construction of p-Cu₂O/n-TiO₂-NF synergistic photocatalyst for both H₂ production and organic decomposition applications with high durability. The simple strategy (low hydrothermal 60°C) constructed ultrafine Cu₂O (20-100 nm) nanoparticles partially submerged on the TiO₂ nanofibre (diameter ~300 nm and length ~650 nm) architecture, which significantly improved the surface electronic and optical properties, as well as displayed excellent synergistic visible light photocatalysis. Deeper insights of interfacial heterojunction formation and charge carrier transfer are their relationship with enhanced photocatalytic performance were evidenced and discussed in detail. Overall, the results not only offer a better photocatalyst for environmental remediation but also provide physical insights for further development of noble-metal-free concept for photocatalytic H₂ evolution and other solar energy conversion applications.

Supporting information

Material characterization, **Fig. S1** FE-SEM images of synthesised Cu₂O, TiO₂-NF and Cu₂O/TiO₂-NF (60°C). **Fig. S2** a-e) FE-SEM images of Cu₂O/TiO₂-NF at different temperature (50 to 100°C), **Fig. S3** a-e) HR-TEM images of synthesised Cu₂O/TiO₂-NF (60°C) captured an Orius camera, **Fig. S4** Solid state DR UV-vis spectra (Tauc plot) of Cu₂O, TiO₂ and their

composites (50 to 100°C), **Fig. S5** a-f) XPS spectra of Cu 2p, and Ti 2p of Cu₂O, TiO₂ and Cu₂O/TiO₂-NF composites (50 to 100°C), **Fig. S6** Cu K-edge EXAFS spectra of Cu₂O/TiO₂-NF (50 to 100°C) in k space, **Table S1** XANES linear combination fitting of Cu₂O, Cu₂O/TiO₂-NF composites, **Fig. S7** a-g) N₂ adsorption-desorption isotherm of Cu₂O, TiO₂ and their composites (50 to 100°C), **Fig. S8** Apparent quantum efficiency of H₂ production over Cu₂O, TiO₂-P25, TiO₂-NF and their composites, **Fig. S9** Apparent quantum efficiency of SMX removal over Cu₂O, TiO₂-P25, TiO₂-NF and their composites, **Fig. S10** a-b) HPLC reaction mixture of before and after photocatalytic SMX degradation over Cu₂O/TiO₂-NF (50 and 60°C), **Fig. S11** a-b) HPLC reaction mixture of before and after photocatalytic SMX degradation over Cu₂O/TiO₂-NF (70 and 80°C), **Fig. S12** HPLC reaction mixture of before and after photocatalytic SMX degradation over Cu₂O/TiO₂-NF (100°C), **Fig. S13**. a) LC-MS/MS spectra of SMX, **Fig. S13**. b) LC-MS/MS spectra of SMX products (5 min) over Cu₂O/TiO₂-NF (60°C) catalyst, **Fig. S13**. c) LC-MS/MS spectra of SMX products (10 min) over Cu₂O/TiO₂-NF (60°C) catalyst, **Fig. S13**. d) LC-MS/MS spectra of SMX products (20 min) over Cu₂O/TiO₂-NF (60°C) catalyst, **Fig. S13**. e) LC-MS/MS spectra of SMX products (30 min) over Cu₂O/TiO₂-NF (60°C) catalyst, **Fig. S14** a) Influence of SMX removal rates by trapping agent addition over Cu₂O/TiO₂-NF (60°C), b) PL emission spectra of HTA as a function of time over Cu₂O/TiO₂-NF (60 °C), **Fig S15** a-b) Fresh and spent SEM of Cu₂O/TiO₂-NF (60 °C), c-d) fresh HRTEM and e-f) Spent HR-TEM of Cu₂O/TiO₂-NF (60 °C), **Fig. S16** Wavelength distribution of the Xenon lamp light source.

Conflicts of interest

The authors declare no conflict of interest.

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