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COPPER-CONCENTRATION-DEPENDENT OPTICAL ABSORPTION AND PHOTOLUMINESCENCE OF SOL–GEL-DERIVED Cu–TiO_2 NANOPARTICLES

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ABSTRACT

Copper-modified titanium dioxide (Cu–TiO_2) is investigated as a route to alter the ultraviolet–visible response and photoluminescence of anatase nanoparticles. Pure TiO_2 and Cu–TiO_2 containing nominal Cu loadings of 2, 4, 6 and 8 wt.% were prepared by a sol–gel route and examined using UV–visible diffuse reflectance spectroscopy (DRS) and room-temperature photoluminescence (PL) spectroscopy. Reflectance in the visible region decreased progressively from approximately 85% for undoped TiO_2 to 67%, 56%, 49% and 43% for the 2, 4, 6 and 8 wt.% Cu samples, respectively. The absorption edge shifted towards longer wavelengths with increasing Cu loading. Tauc analysis of Kubelka–Munk-transformed reflectance data gave optical band-gap energies of 3.25, 3.05, 3.00, 2.90 and 2.82 eV, corresponding to a total decrease of 0.43 eV between undoped TiO_2 and the 8 wt.% Cu composition. PL spectra collected at an excitation wavelength of 320 nm showed emission features near 418, 455 and 470 nm. Their positions remained approximately constant, whereas their intensities varied with Cu concentration; the 4 wt.% Cu sample exhibited the lowest intensity across the three features. The optical changes are consistent with Cu-induced modification of the electronic and defect-state landscape, while the higher-loading response may also include a contribution from the CuO phase detected by X-ray diffraction in the parent study. Because neither Cu oxidation states nor photocatalytic rates were measured, the data do not establish a unique microscopic mechanism or an optimum photocatalyst composition. The results identify a concentration-dependent optical response and provide a basis for targeted electronic-structure and photocatalytic measurements.

KEYWORDS: *Cu-doped TiO_2; diffuse reflectance; optical band gap; photoluminescence; defect states; sol–gel synthesis.*

1. INTRODUCTION

Titanium dioxide (TiO_2) remains a widely investigated semiconductor for photocatalytic and photoelectrochemical systems because of its chemical stability, availability and strong oxidative capability [1–3]. Its practical use under sunlight is constrained by the wide band gap of anatase, commonly reported near 3.2 eV, which restricts intrinsic excitation mainly to the ultraviolet portion of the spectrum. Photogenerated electrons and holes can also recombine before reaching reactive surface sites, reducing the fraction of absorbed photons that contributes to interfacial redox chemistry [2,3].

Transition-metal modification provides one route to alter this response. Dopant-derived electronic states, local charge compensation and lattice defects can change the energy required for optical excitation; depending on their concentration and spatial distribution, the same states may also act as carrier traps or recombination centres. The optical response therefore reflects more than a simple shift of the host band edges. It can include transitions involving localized states, defect-tail absorption and contributions from secondary phases.

Copper is a relevant modifier because Cu can occur in more than one oxidation state and can participate in electron-transfer processes. Cu-modified TiO_2 systems have consequently been investigated across several synthesis routes and applications, including pollutant degradation, antimicrobial surfaces, self-cleaning materials and photoelectrodes [4–9]. Reported optical and functional responses vary with Cu loading and synthesis conditions, making direct comparisons difficult. Studies of Cu-modified TiO_2 thin films and defect-mediated Cu-containing nanocrystals likewise report concentration-dependent changes in optical absorption and electronic structure [15,16]. At higher loadings, Cu-containing secondary phases may also contribute to the measured absorption rather than acting solely as dopants within the TiO_2 lattice.

Photoluminescence provides complementary information. Emission from anatase TiO_2 can involve near-band-edge excitonic processes and defect-associated transitions, including states related to oxygen vacancies and trapped carriers [10–12]. A reduction in steady-state PL intensity is often consistent with reduced radiative emission, but it does not independently prove improved charge separation: non-radiative pathways, absorption differences, scattering and changes in emitting-centre populations can also alter the measured signal. PL trends must therefore be interpreted alongside optical absorption and structural evidence.

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Here, the optical response of sol–gel-derived TiO_2 containing 2–8 wt.% Cu is examined through diffuse reflectance and PL spectroscopy. The concentration-dependent reflectance edge, indirect-transition Tauc estimates and emission features are compared to identify how Cu loading modifies the measured optical response. Structural observations from the same sample series are used only as supporting context when discussing possible origins of the optical trends.

2. OBJECTIVES

The study aimed to: (i) determine how nominal Cu loading changes the UV–visible diffuse reflectance of TiO_2 nanoparticles; (ii) estimate the optical band gap of each composition using Kubelka–Munk and Tauc analysis; and (iii) evaluate the variation in PL emission position and intensity across the Cu concentration series.

3. METHODOLOGY

3.1. Synthesis of Cu–TiO_2 nanoparticles

Pure and Cu-modified TiO_2 nanoparticles were prepared by a sol–gel method. Titanium(IV) isopropoxide (TTIP, 97%) was used as the titanium precursor, while copper(II) nitrate trihydrate supplied Cu. Ethanol, nitric acid and deionized water were used as received. Solution A was prepared by adding 0.017 M TTIP to 52 mL of absolute ethanol under stirring for 30 min. Solution B contained the required mass of $Cu(NO_3)_2 \cdot 3H_2O$ dissolved in 1 M HNO_3 (5 mL distilled water) to obtain nominal Cu loadings of 2, 4, 6 and 8 wt.% relative to TiO_2. No Cu precursor was added to the undoped control.

Solution B was added to Solution A under continuous stirring at 500 rpm for 3 h. The resulting sol was aged for 24 h, oven-dried at 80 °C for 6 h and calcined at 500 °C for 3 h. The samples are referred to as undoped TiO_2, 2 wt.% Cu–TiO_2, 4 wt.% Cu–TiO_2, 6 wt.% Cu–TiO_2 and 8 wt.% Cu–TiO_2.

3.2. Diffuse reflectance and optical band-gap analysis

UV–visible diffuse reflectance spectra were recorded using an Ocean Optics USB400 miniature spectrometer equipped with combined deuterium and tungsten-halogen light sources. The reflectance data were transformed using the Kubelka–Munk function:

$$F(R) = \frac{(1-R)^2}{2R} = \frac{K}{S} \quad (1)$$

where R is the diffuse reflectance of an optically thick sample (R_∞) expressed as a fraction (percentage values divided by 100), K is the absorption coefficient and S is the scattering coefficient. Optical band-gap energies were estimated from Tauc plots of $[F(R)h\nu]^{1/2}$ against photon energy (hν), corresponding to the indirect-allowed transition representation adopted in the original analysis (Eq. (3), Section 3.4). The band gap was obtained by extrapolating the linear absorption-edge region to the photon-energy axis.

3.3. Photoluminescence spectroscopy

Room-temperature PL spectra were recorded using a PerkinElmer LS 50B spectrophotometer fitted with a pulsed xenon flash lamp. The excitation wavelength was 320 nm and the emission range was 300–600 nm. Emission positions and relative intensity trends were compared across the undoped and Cu-modified samples.

3.4. Optical transitions and interpretation of diffuse-reflectance data

Diffuse reflectance is appropriate for strongly scattering powders for which conventional transmission measurements are not readily obtained. In the Kubelka–Munk treatment, the measured reflectance is transformed to F(R), which is proportional to the absorption coefficient only under the model assumptions of an optically thick, diffusely scattering sample with an approximately wavelength-independent scattering coefficient. Consequently, F(R) is an absorption-related function rather than a direct measurement of the absolute absorption coefficient. Differences in particle packing, agglomeration and refractive-index contrast can influence the measured reflectance and should be considered when comparing powders with different compositions [14].

The optical transition analysis follows the indirect-allowed Tauc representation used in the original data treatment. The general Tauc relation is written as

$$(\alpha h\nu)^{1/\gamma} = B\left(h\nu - E_g\right) \quad (2)$$

where α is the absorption coefficient, hν is the photon energy, B is a proportionality constant, E_g is the optical band-gap energy and the exponent $1/\gamma$ depends on the assumed transition type: $\gamma = 1/2$ for direct allowed, $\gamma = 2$ for indirect allowed, $\gamma = 3/2$ for direct forbidden and $\gamma = 3$ for indirect forbidden transitions [18]. Replacing α by F(R), which is justified only under the Kubelka–Munk assumptions stated above, gives for the indirect-allowed case adopted here [19]

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$$[F(R)h\nu]^{1/2} = B'(h\nu - E_g) \quad (3)$$

where B′ is a constant. The band-gap estimate is obtained by extrapolating the approximately linear edge region to the energy axis [13,14]. This procedure yields an apparent optical gap for the measured powder; it does not independently establish the fundamental electronic band gap or prove that the same transition dominates every composition.
Photon energy and wavelength are related by

$$E = \frac{hc}{\lambda} \approx \frac{1239.84}{\lambda} \quad (4)$$

where E is the photon energy in eV, λ is the wavelength in nm and hc ≈ 1239.84 eV nm. This conversion is used below to compare the measured PL emission positions with the optical gap of undoped TiO_2. Such comparisons are descriptive: the energy separation between the Tauc edge and an emission maximum does not uniquely identify a defect level because exciton relaxation, lattice relaxation and distributions of localized states can all contribute to broad emission bands.

4. RESULTS AND DISCUSSION

4.1. Cu-dependent diffuse reflectance response

The diffuse reflectance spectra show a clear concentration-dependent change in the optical response (Figure 1). Undoped TiO_2 exhibits a steep reflectance edge in the approximate 350–380 nm region and a visible-region reflectance of about 85%. Cu addition lowers the reflectance across the visible range. The reported reflectance values decrease to approximately 67% for 2 wt.% Cu, 56% for 4 wt.%, 49% for 6 wt.% and 43% for 8 wt.% Cu. The absorption edge also shifts towards longer wavelengths as the Cu loading increases.

The progressive reduction in reflectance indicates that the Cu-containing samples absorb or attenuate a larger fraction of incident visible light than the undoped material. In a diffuse powder measurement, however, reflectance is influenced by both absorption and scattering. The spectra therefore establish a systematic change in optical response but do not, by themselves, identify the microscopic transition responsible for the additional visible-region absorption. Cu-related localized states, defect-associated transitions and contributions from CuO at higher loadings are plausible contributors.

Figure 1. UV–visible diffuse reflectance spectra of undoped and Cu-doped TiO_2 nanoparticles.

The concentration series produces a systematic ordering in the visible reflectance. The values reported for the visible region decrease by 42 percentage points between the undoped and 8 wt.% samples. The trend is monotonic over the full nominal loading range, unlike the PL intensity, which reaches a minimum at an intermediate composition. The reflectance maxima of the doped samples occur in the green-visible region, and their lower magnitude relative to the undoped spectrum is consistent with stronger attenuation of visible light. Since diffuse reflectance includes both absorption and scattering contributions, the trend is best described as an enhanced visible-region optical response rather than as a direct quantitative measure of absorbed photon flux.

Table 1. Approximate visible-region reflectance values extracted from the reported DRS results.

Nominal Cu loading	Visible-region reflectance (%)	Change relative to undoped (percentage points)
0 wt.%	≈85	—
2 wt.%	≈67	−18
4 wt.%	≈56	−29
6 wt.%	≈49	−36
8 wt.%	≈43	−42

4.2. Optical band-gap variation with Cu loading

The Kubelka–Munk-transformed data were analysed using Tauc plots (Figure 2). The extracted optical band-gap energies are listed in Table 2. The estimated gap decreases from 3.25 eV for undoped TiO_2 to 3.05 eV at 2 wt.% Cu and 3.00 eV at 4 wt.% Cu. Further increases in Cu loading reduce the estimated values to 2.90 eV at 6 wt.% and 2.82 eV at 8 wt.%. The overall decrease is 0.43 eV.

Figure 2. Tauc plots, $[F(R)h\nu]^{1/2}$ versus photon energy, for undoped and Cu-doped TiO_2 nanoparticles.

The monotonic decrease in the Tauc-derived gap is consistent with the red-shifted reflectance edge. The 8 wt.% sample shows the largest change relative to undoped TiO_2, indicating that the optical response continues to evolve even after the structural study detects a secondary CuO phase at higher Cu loadings. The measured gap should be interpreted as an apparent optical transition energy derived from the chosen Tauc representation. In a doped, potentially multiphase powder, it need not equal the fundamental band gap of a single, chemically homogeneous TiO_2 phase.

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The magnitude of the change is substantial relative to the undoped reference. The decrease from 3.25 to 2.82 eV corresponds to approximately 13.2% of the undoped gap. Using Eq. (4) with E = E_g, these values correspond to nominal absorption-edge wavelengths of about 381 nm and 440 nm, respectively. These wavelengths are calculated from the extracted Tauc energies; they are not independent edge measurements. The estimate illustrates the shift towards the visible region but should not be interpreted as proof that all incident visible photons are absorbed efficiently or that the resulting carriers possess sufficient redox potential for a particular photocatalytic reaction.

The first concentration increment produces the largest individual reduction: 0.20 eV between 0 and 2 wt.% Cu. Subsequent changes are smaller, amounting to 0.05 eV between 2 and 4 wt.%, 0.10 eV between 4 and 6 wt.% and 0.08 eV between 6 and 8 wt.%. This pattern suggests a relatively strong initial perturbation of the host optical response followed by continued, more gradual evolution. The near-constant anatase (101) peak position above 4 wt.% and the appearance of CuO reflections at 6 wt.% and above indicate that the origin of the continued optical-gap decrease may change at higher loading. The DRS/Tauc analysis alone cannot separate a modified anatase absorption edge from overlapping absorption by CuO-containing regions.

Table 2. Optical band-gap values and corresponding wavelength estimates. Wavelengths were calculated from E_g using Eq. (4).

Cu loading (wt.%)	E_g (eV)	Calculated λ_g (nm)	Decrease from previous composition (eV)
0	3.25	381	—
2	3.05	407	0.20
4	3.00	413	0.05
6	2.90	428	0.10
8	2.82	440	0.08

Several mechanisms could contribute. Cu incorporation or Cu-associated defects may introduce electronic states within the TiO_2 gap, enabling lower-energy optical transitions. Local lattice distortion and charge-compensating defects may also modify the absorption tail. For the 6 and 8 wt.% samples, XRD detected CuO reflections in the parent characterization study; absorption associated with this secondary phase may therefore contribute to the composite diffuse-reflectance response. The available measurements do not separate these contributions, and the observed narrowing should not be assigned exclusively to substitutional Cu or to a specific Cu oxidation state.

4.3. Photoluminescence response

The PL spectra collected under 320 nm excitation contain three principal emission features centred near 418, 455 and 470 nm (Figure 3). Their positions remain approximately unchanged across the composition series, whereas their intensities vary with Cu loading. The corresponding photon energies are approximately 2.97, 2.72 and 2.64 eV, respectively. Relative to the 3.25 eV optical gap of undoped TiO_2, these emission energies lie below the estimated band edge and are consistent with emission involving localized or defect-associated states.

The 418 nm feature has an energy difference of approximately 0.28 eV from the undoped optical gap, close to values associated with self-trapped exciton emission in anatase [10]. The 455 and 470 nm features are separated from the same gap by approximately 0.53 and 0.61 eV, respectively; these energies fall within ranges previously discussed for oxygen-vacancy-related emission in TiO_2 [11,12]. These assignments remain tentative. PL peak positions alone cannot uniquely identify defect chemistry, and confirmation would require complementary measurements such as X-ray photoelectron spectroscopy, electron paramagnetic resonance or time-resolved spectroscopy.

The emission intensity follows the reported order: undoped TiO_2 > 8 wt.% Cu–TiO_2 > 6 wt.% Cu–TiO_2 > 2 wt.% Cu–TiO_2 > 4 wt.% Cu–TiO_2. The 4 wt.% sample exhibits the weakest emission across all three features. This suppression is consistent with a lower radiative emission yield, potentially arising from Cu-associated trapping or enhanced non-radiative carrier relaxation. It does not, on its own, demonstrate a longer carrier lifetime or more efficient charge separation. At higher Cu loading, the partial recovery of PL intensity may reflect changes in defect populations, additional radiative centres or the contribution of CuO-containing regions.

Figure 3. Room-temperature photoluminescence spectra of undoped and Cu-doped TiO_2 nanoparticles (λex = 320 nm).

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Table 3. Photon energies of the principal PL features and their separation from the undoped optical gap.

Emission feature (nm)	Photon energy (eV)	Energy below 3.25 eV gap (eV)	Tentative interpretation
418	2.97	0.28	Near-band-edge/self-trapped exciton-related emission
455	2.72	0.53	Defect-associated emission; oxygen-vacancy-related assignment proposed
470	2.64	0.61	Defect-associated emission; oxygen-vacancy-related assignment proposed

The three PL features are common to all five compositions and remain at approximately the same wavelengths after Cu addition. This persistence indicates that the emitting-state energies are not strongly displaced within the resolution of the reported spectra, even though the emission yield changes. The result is compatible with Cu modifying the probability of carrier capture and radiative decay without producing a resolvable shift in the dominant emission maxima. It does not rule out changes in the density, spatial distribution or occupation of defect states.

The 418 nm feature is assigned cautiously to near-band-edge or self-trapped-exciton-related emission, consistent with the anatase PL literature [10]. The 455 and 470 nm features are discussed as defect-associated emissions, with oxygen-vacancy-related states among the possible origins [11, 12]. Oxygen vacancies are not directly quantified in this work. In addition, Cu incorporation can require local charge compensation and may alter the balance among oxygen vacancies, Ti^{3+} centres and Cu-related electronic states. Without XPS, EPR or another defect-sensitive method, a unique assignment to a specific vacancy charge state would exceed the evidence.

Steady-state PL intensity is governed by the competition among radiative and non-radiative pathways and by the number of carriers generated under excitation. A weaker signal can arise when non-radiative relaxation becomes more probable, when carriers are trapped in optically inactive states, or when the concentration of a particular radiative centre decreases. It may therefore be consistent with suppressed radiative recombination, but it cannot be translated directly into a longer carrier lifetime or improved charge separation. Time-resolved PL, transient absorption and photocurrent measurements would be required to distinguish these possibilities.

4.4. Relationship between absorption and emission

The absorption and emission measurements reveal distinct concentration dependencies. The apparent optical gap decreases continuously with Cu loading, whereas PL intensity reaches a minimum at 4 wt.% and then increases at 6–8 wt.%. This divergence indicates that the optical-gap estimate and steady-state emission intensity probe different aspects of the material. The former reflects the onset of allowed optical transitions in the diffuse-reflectance analysis; the latter depends on the population and radiative decay of emissive states under the selected excitation conditions.

The lowest PL intensity at 4 wt.% occurs in the concentration range where the parent XRD analysis did not resolve CuO reflections. At 6 and 8 wt.% Cu, CuO reflections become detectable, while the PL intensity partially recovers. This correlation is compatible with a change in the distribution of Cu-related states or the emergence of a secondary phase, but it does not establish causation. The XRD data also show that the anatase (101) reflection shifts slightly at low Cu loading and then remains nearly stationary at higher concentrations, suggesting that the structural response does not continue linearly with nominal Cu content.

Taken together, the results identify 2–4 wt.% Cu as a composition range in which the optical response is modified without XRD-resolvable CuO formation, and 4 wt.% as the composition with the weakest steady-state PL signal. These observations justify further investigation of the lower-loading compositions; they do not establish 4 wt.% Cu as the optimum photocatalyst. No hydrogen evolution or pollutant-degradation measurements were performed, and PL intensity alone is insufficient to rank photocatalytic activity.

4.5. Optical response in relation to structural evolution

The structural data provide a useful boundary for interpreting the optical trends. The anatase (101) reflection shifts from 25.32° in undoped TiO_2 to 25.29° and 25.26° at 2 and 4 wt.% Cu, respectively, while the refined position remains close to 25.26° at 6 and 8 wt.%. The corresponding d-spacing increases from 3.514 Å to 3.522 Å. This small expansion is consistent with a change in the local TiO_2 structure, although it does not prove substitutional Cu occupation. The proposed explanation based on the larger effective ionic radii of Cu^{2+}/Cu^{+} relative to Ti^{4+} remains plausible rather than definitive [17].

At the same time, the structural study detects monoclinic CuO (tenorite) at 6 and 8 wt.% Cu, while no XRD-resolvable CuO reflections are observed at 2 and 4 wt.%. The measured Cu concentrations from EDS are 1.9, 4.2, 6.5 and 8.7 wt.% for the nominal 2, 4, 6 and 8 wt.% samples, respectively. These results support the intended concentration sequence and indicate that the higher-loading materials contain a Cu-rich phase detectable by XRD. The optical gap continues to decrease across this phase boundary, whereas the PL intensity partially recovers after its minimum at 4 wt.%. A reasonable interpretation is that the optical response at high loading reflects a combination of Cu-modified TiO_2 and CuO contributions, alongside changes in defects and microstructure. The available data do not quantify the fraction of each contribution.

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The morphology data also caution against assigning every optical change solely to electronic doping. SEM shows agglomerate dimensions decreasing from approximately 166–181 nm for undoped TiO_2 to 133–144 nm at 2–4 wt.% Cu, followed by an increase to 149–151 nm and 159–170 nm at 6 and 8 wt.% Cu. Changes in agglomeration and powder packing can modify diffuse scattering and therefore influence reflectance spectra. The DRS trends are chemically plausible, but a stronger mechanistic claim would require measurements using controlled powder packing, integrating-sphere reflectance with a suitable reference standard, and preferably independent absorption measurements.

An important distinction emerges between the concentration associated with the lowest PL intensity and the concentration associated with the smallest apparent optical gap. The minimum PL intensity occurs at 4 wt.% Cu, whereas the minimum Tauc-derived gap occurs at 8 wt.% Cu. These are not contradictory results: optical absorption onset and radiative recombination probe different processes. The 4 wt.% composition is therefore a candidate for follow-up carrier-dynamics studies, while the 8 wt.% composition exhibits the strongest red-shifted optical response in this series. Neither can be designated the best photocatalyst without direct reaction-rate and stability measurements.

5. CONCLUSION

Cu addition systematically modifies the optical response of sol–gel-derived TiO_2 nanoparticles. Visible-region reflectance decreases from approximately 85% in undoped TiO_2 to 43% at 8 wt.% Cu, while the absorption edge shifts towards longer wavelengths. Tauc analysis gives a progressive decrease in apparent optical band gap from 3.25 to 2.82 eV across the 0–8 wt.% Cu series. PL spectra retain emission features near 418, 455 and 470 nm, but their intensities depend strongly on Cu loading; the 4 wt.% sample exhibits the lowest intensity. The combined trends indicate concentration-dependent changes in optical transitions and emissive defect populations. Cu-related states, defect modification and CuO contributions at higher loadings are possible explanations, but the present data cannot isolate their individual roles. XPS/XANES, time-resolved PL and direct photocatalytic measurements are required to establish Cu valence, carrier dynamics and functional performance.

6. SUGGESTIONS AND AREA FOR FURTHER RESEARCH

Future work should determine Cu oxidation states and local coordination using XPS and, where available, XANES/EXAFS. Time-resolved PL or transient absorption measurements would distinguish changes in radiative intensity from changes in carrier lifetime. Photocatalytic hydrogen evolution and pollutant-degradation tests should be conducted under controlled illumination, with appropriate dark, photolysis and undoped-TiO_2 controls. Integrating these measurements with quantitative phase analysis would help separate the optical contribution of Cu-modified anatase from that of secondary CuO.

7. LIMITATIONS OF THE STUDY

The optical interpretation is subject to several limitations. First, the optical band gaps were estimated from Tauc extrapolation of Kubelka–Munk-transformed diffuse reflectance, and no uncertainty intervals or fitting-range sensitivity analysis were reported. The numerical values should therefore be treated as estimates rather than exact band-edge positions. Second, the PL spectra were measured under one excitation wavelength and at room temperature; no absolute quantum yields, normalized emission efficiencies or time-resolved lifetimes were obtained. Third, the oxidation state and local coordination of Cu were not measured directly, and oxygen-vacancy concentrations were not quantified. Fourth, the 6 and 8 wt.% samples contain XRD-resolvable CuO, so their optical response cannot be attributed exclusively to Cu incorporated in anatase. Finally, photocatalytic hydrogen evolution and pollutant-degradation rates were not measured. The results establish optical-property trends and support hypotheses for subsequent testing, not photocatalytic performance.

8. NOMENCLATURE

DRS – diffuse reflectance spectroscopy; EDS – energy-dispersive X-ray spectroscopy; E_g – optical band-gap energy; F(R) – Kubelka–Munk function; hν – photon energy; PL – photoluminescence; SEM – scanning electron microscopy; TiO_2 – titanium dioxide; Cu–TiO_2 – copper-modified titanium dioxide; XRD – X-ray diffraction.

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DATA AVAILABILITY

The data supporting the findings are contained within the article and the associated underlying research records. Processed numerical spectral data and raw instrument files should be made available by the corresponding author upon reasonable request, subject to institutional data-sharing requirements.

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DECLARATION OF COMPETING INTEREST

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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