

Supporting Information

Masking Effect of Copper Oxides Photodeposited on Titanium Dioxide: Exploring UV, Visible, and Solar Light Activity

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Determination of quantum efficiency

The quantum efficiency was determined based on a previously reported method.¹ Quantum efficiency is defined as the percentage ratio between the number of converted 2,4-D ($N_{\text{converted}}$) and number of absorbed photon (N_{photon}) as shown in Eq. (1),

$$\text{Quantum efficiency (\%)} = \frac{N_{\text{converted}}}{N_{\text{photon}}} \times 100 \quad \text{--- (1)}$$

Where $N_{\text{converted}}$ was calculated from Eq. (2), while (N_{photon}) was determined from Eq. (3) and (4).

$$N_{\text{converted}} \text{ (mol/s)} = \frac{\text{No. of mol of converted 2,4-D}}{\text{time}} \quad \text{--- (2)}$$

$$N_{\text{photon}} \text{ (mol/s)} = \frac{I \times A}{U_{\lambda}} \quad \text{--- (3)}$$

where I is the light intensity absorbed by the photocatalyst in W/m², A is the area of the reactor with the photocatalyst exposed to the light and U_{λ} is the mole of photon energy for the representative wavelength.

$$U_{\lambda} (J/mol) = \frac{hc \times N_A}{\lambda} \quad \text{--- (4)}$$

where h is the Plank constant, c is the speed of light in vacuum, N_A is the Avogadro number, λ is the representative wavelength of the light source used.

Hence, the following data were collected and used for calculation of quantum efficiency under UV and visible light irradiation:

	UV reaction	Visible light reaction
Catalysts ^a	CuO(0.75)/TiO ₂	CuO(0.1)/TiO ₂
Wavelength, λ (nm) ^b	365	450
Photon energy, U_{λ} (J/mol) ^c	327744	265837
Absorbed light intensity, I (W/m ²) ^d	61.6	0.63
Surface area, A (m ²) ^e	0.00031416	0.0019635
No. of converted 2,4-D, $N_{\text{converted}}$ (mol/s) ^f	5.20×10^{-9}	3.08×10^{-11}
Quantum efficiency (%)	8.8	0.7

Notes:

^a The best catalysts under each irradiation conditions were selected for the quantum efficiency reaction.

^b The representative wavelengths of 365 and 450 nm were selected for the determination of quantum efficiency under UV and visible conditions, respectively. Bandpass filters (Edmund Industrial Optics) were used to limit the specific wavelengths to within ± 10 nm range.

^c The photo energy was calculated by using equation (4) shown above.

^d After the bandpass filter was inserted, the light intensity near the surface of the 2,4-D solution was measured. The UV light intensity was measured directly (in W/m²) with a digital radiometer equipped with a 365 nm detector. The visible light intensity (illuminance = 16.37 lux) was measured with a lux meter and converted to power with the following equation: Power, P (W) = ($E_v \times A$) / η , where E_v (lux) represents illuminance, A (m²) represents area and η represents luminous efficacy (lm/W). The luminous efficacy at 450 nm is 25.954 lm/W. This value is then converted to W/m² by dividing with the surface area.

^e The reactions were carried out in a 100 mL beaker irradiated from the top. The surface area, A is defined as the circular area at the surface of the solution exposed to irradiation. In the case of the UV reaction, the radius of the circular region is 1 cm. For the visible reaction, the radius was measured as 2.5 cm. The surface area was calculated as $A = \pi r^2$.

^f Calculated by equation (2), whereby the reaction times for the UV and visible reactions were 1 h and 6 h, respectively.

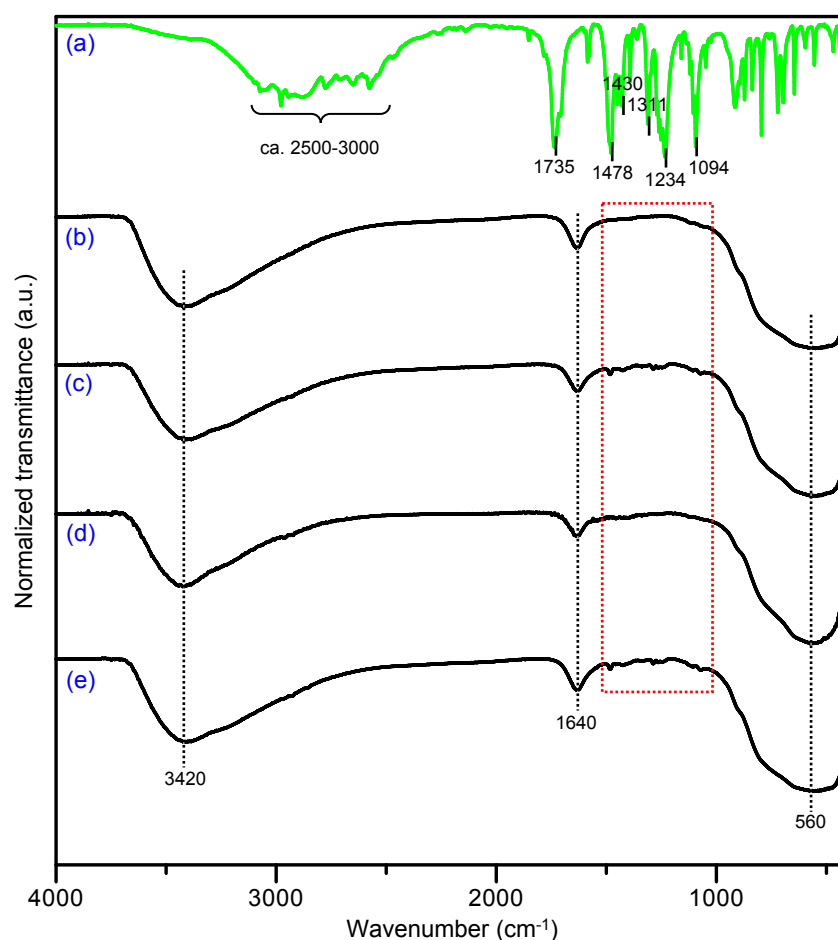


Figure S1: The FTIR spectra of (a) 2,4-D, (b) unmodified TiO₂ (c) unmodified TiO₂ adsorbed with 2,4-D (d) CuO(0.75)/TiO₂ and (e) CuO(0.75)/TiO₂ adsorbed with 2,4-D. The FTIR spectra were measured with a Nicolet iS50 FTIR spectrometer over the range of 4000-400 cm⁻¹ (average over 32 scans at a resolution of 4 cm⁻¹) using KBr discs technique.

The interaction between 2,4-D and TiO₂ was further investigated by FTIR spectroscopy. The FTIR spectra of the 2,4-D and the respective 2,4-D adsorbed TiO₂ samples were measured and shown in Fig. S1. The FTIR spectrum of 2,4-D (Fig. S1(a)) showed bands corresponding to water stretching $\nu(\text{O-H})$ vibrations (ca. 2500-3000 cm⁻¹), C=C vibrations of the aromatic ring (1478 and 1430 cm⁻¹), band assigned to the antisymmetric and symmetric C-O-C vibration (1311 and 1094 cm⁻¹, respectively), and bands corresponding to the carboxylic group ($\nu(\text{C=O})$ at 1735 cm⁻¹ and O-H deformation coupled with C-O stretching vibrations and 1234 cm⁻¹).² The FTIR spectra of the TiO₂ samples (Fig. S1(b)-(e)) displayed a wide band at 3420 cm⁻¹ attributed to the $\nu(\text{O-H})$ vibrations of free and H-bonded hydroxide groups. The low intensity band at 1640 cm⁻¹ is due to the water bending mode $\delta(\text{O-H})$. The broad band at ~560 cm⁻¹ could be attributed to the vibration of Ti-O-Ti bonds in TiO₂. The FTIR spectrum of the adsorption products (Fig S1 (c) and (e)) showed bands related to 2,4-D at the 1000-1500 cm⁻¹ range, indicating the presence of 2,4-D on the surface of TiO₂ after the dark adsorption process.

The interaction between 2,4-D and TiO₂ was further examined by enlarging the 2,4-D signals at the 1000 -1800 cm⁻¹ region (Fig. S2). When adsorbed to TiO₂, it was observed that some of the 2,4-D bands appear slightly shifted compared to those of the pure compound, but the most important feature is the disappearance of the $\nu(\text{C=O})$ band at 1735 cm⁻¹, indicating the formation of the anionic form of 2,4-D and its complexation to TiO₂ via the C=O oxygen atom of the carboxylate group.^{2,3} While the FTIR results

indicated the formation of 2,4-D surface complexes on the surface of TiO_2 , the DR UV-Vis results (Fig. S3) showed that the formed complexes do not absorb in the visible region. Hence, it could be inferred that these complexes do not contribute to the visible light activity of TiO_2 . Rather, the occurrence of visible light activity of the Cu/TiO_2 composites could be attributed to the presence of the copper species.

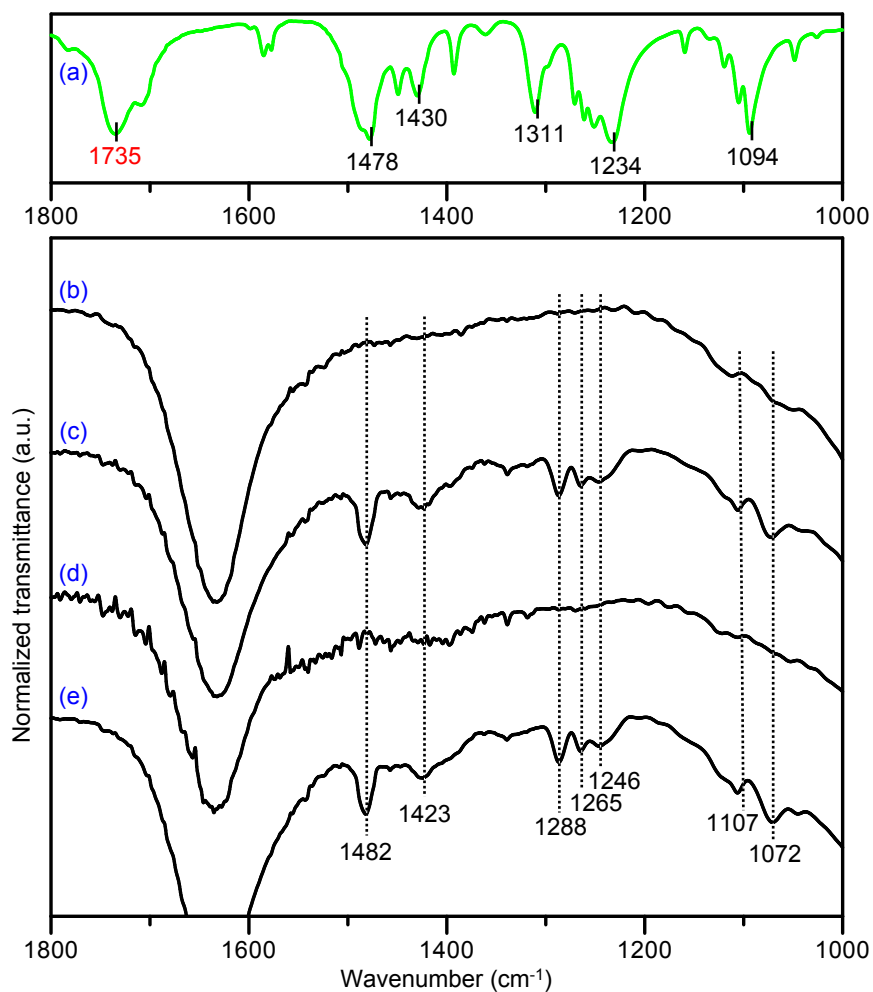


Figure S2: The enlargement of the FT-IR spectra at the 1000-1800 cm^{-1} region. The samples are labelled as (a) 2,4-D, (b) unmodified TiO_2 (c) unmodified TiO_2 adsorbed with 2,4-D (d) $\text{CuO}(0.75)/\text{TiO}_2$ and (e) $\text{CuO}(0.75)/\text{TiO}_2$ adsorbed with 2,4-D.

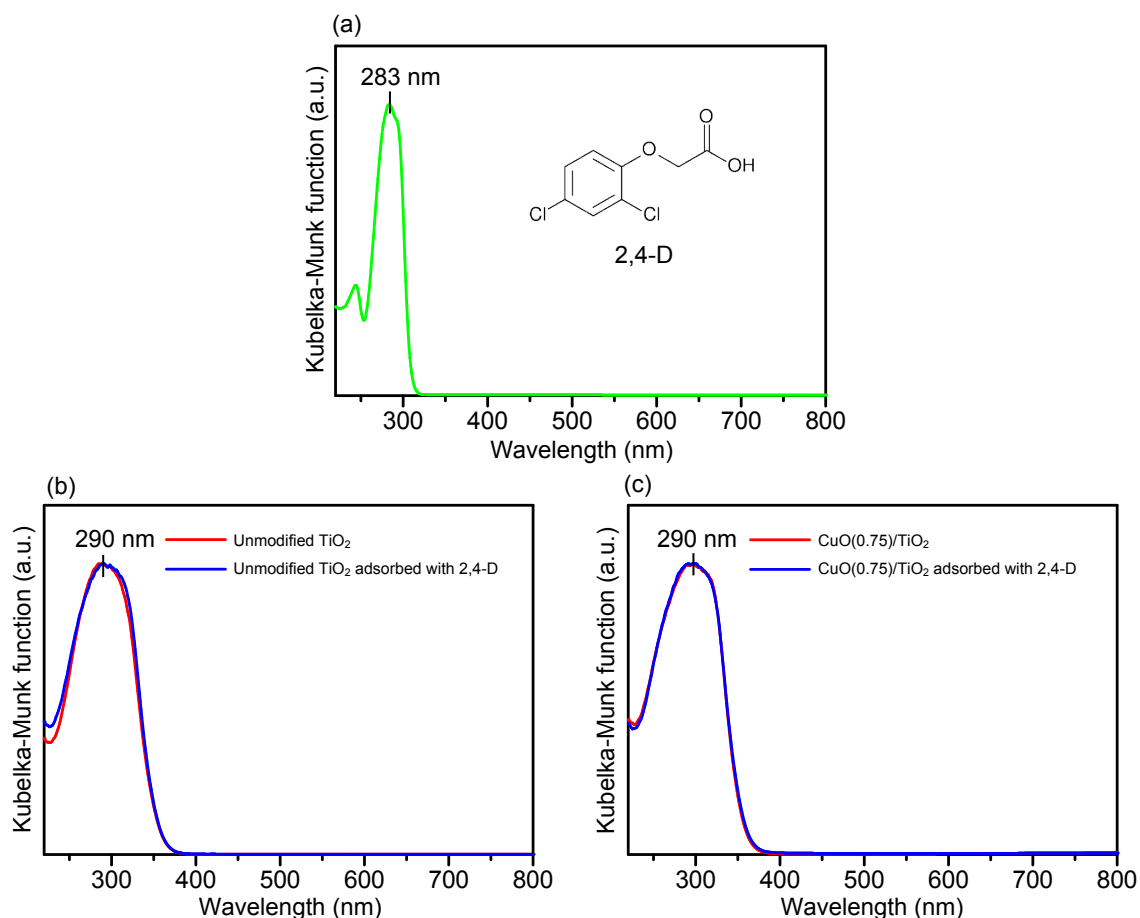


Figure S3: The absorption spectra of (a) 2,4-D (solid powder), (b) Unmodified TiO₂ and unmodified TiO₂ adsorbed with 2,4-D and (c) CuO(0.75)/TiO₂ and CuO(0.75)/TiO₂ adsorbed with 2,4-D. The TiO₂ and Cu/TiO₂ adsorbed with 2,4-D samples were prepared by dispersing 0.2 g of the samples in 200 mL 2,4-D solution (0.5 mM) and stirring the resultant suspension in the dark for 1 h. Then, the suspensions were centrifuged (3500 rpm for 10 min) to collect the 2,4-D adsorbed catalysts. The resultant pellet was dried in oven at 80 °C overnight. Finally, the dried samples were ground to a fine powder and the DR UV-Vis absorption spectra measured with a Shimadzu UV-2600 spectrophotometer.

References

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