Supplementary Information

Studies on the substrate-dependent photocatalytic properties of Cu_2O heterojunctions

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1. Preparation method of TNA/Ti, Cu_2O/TNA/Ti, Cu_2O/Ti, and Cu_2O/FTO

TiO_2 nanotube arrays (TNA) /Ti and Cu_2O on different substrates, i.e. TNA/Ti, Ti, and fluorine-doped tin oxide (FTO), were prepared according to Chang et al. [1]. A source meter (Keithley 2400) was used to fabricate TNA through the electrochemical anodization of Ti plate.

Before the fabrication, the Ti plate was cleaned by acetone, ethanol, and deionized water in an ultrasonic cleaner. A mixed solution of ethylene glycol (99.8%, Sigma-Aldrich), 0.25 wt % NH_4F (98.0%, Sigma-Aldrich) and 2 vol% H_2O was used as an etching solution. The anodization was done using two electrodes (Ti plate served as a working electrode and Pt wire served as a counter electrode) under the voltage of 40 V DC for 1 h. Then, TNA was calcined in a tubular furnace for 3 h at 450°C with a temperature increase of 2°C/min.

Cu_2O was electrodeposited on the different substrates, which were TNA/Ti, Ti, and FTO, by the square wave voltammetry electrochemical (SWVE) deposition method. A potentiostat (ΩMetrohm-Autolab B.V. PGSTAT204) was used in the preparation of Cu_2O under three electrodes, where TNA/Ti, Ti, and FTO served as a working electrode, Pt plate served as a counter electrode, and Ag/AgCl served as a reference electrode. A mixed solution of $Cu(CH_3\text{-}COO)_2.H_2O$ 0.02 M (99.9%, Sigma-Aldrich) and $NaCH_3COO$ 0.1 M (99%, Sigma-Aldrich) whose pH value was adjusted to 5.7 via CH_3COOH 0.5 M (99.8%, Sigma-Aldrich) was used as an electrolyte. Before the deposition process, the substrate was immersed in the solution for 30 minutes. The SWVE deposition was started in the applied voltage of -1 V to 0 V, with an amplitude of 5 mV and a frequency of 5 Hz. The formation of Cu_2O follows the equation (1).

$$2Cu^{2+} + H_2O + 2e^- \rightarrow Cu_2O + 2H^+ \quad (1)$$

2. Morphology and XRD pattern of commercial Cu_2O

The morphology of commercial Cu_2O was captured in the form of powder, shown in Fig. S1 (a). The commercial Cu_2O exhibited non-uniform size with the average particle size of approximately 5.2 μm. The X-ray diffraction (XRD) pattern in Fig. S1 (b) indicates 2θ values of 29.54°, 32.26°, 42.26°, 52.42°, 61.30°, 73.46°, and 77.30°, indexed to (110), (111), (200), (211),

(220), (311), and (222), respectively, representing Cu_2O crystalline phase (ICSD file no. 98-006-0719).

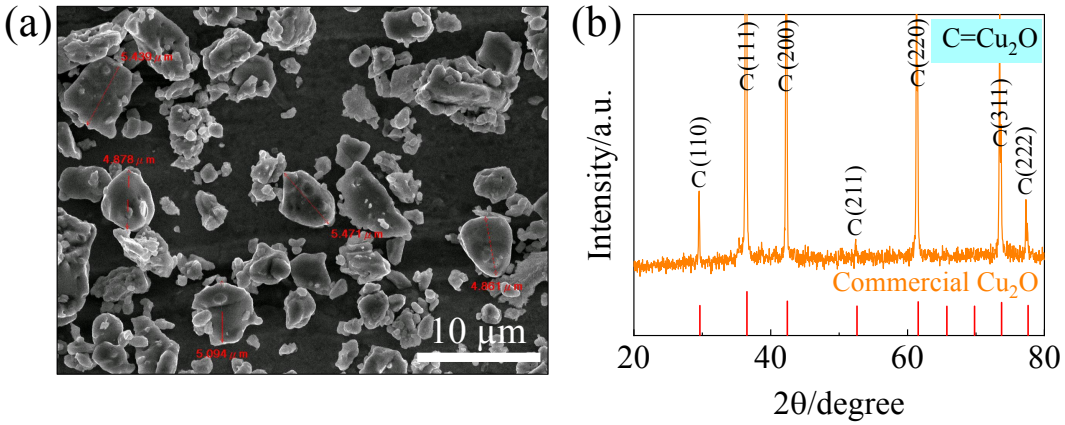

Fig. S1. (a) Morphology and (b) XRD pattern of commercial Cu_2O. The red sticks in (b) are the phases of Cu_2O taken from ICSD file no. 98-006-0719.

3. Optical absorption of Cu_2O/FTO

The optical absorption (A) spectra of Cu_2O/FTO was obtained from the optical reflection (R) and transmission (T) spectra according to the equation of $A(\%) = 100\% - R(\%) - T(\%)$, shown in Fig. S2. The bandgap of Cu_2O/FTO was approximately 2.47 eV (500 nm).

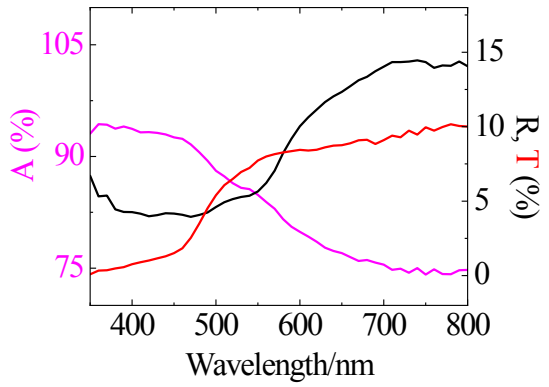

Fig. S2. Optical reflection, transmission, and absorption spectra of Cu_2O/FTO.

4. Optical absorption of Commercial Cu_2O

The optical transmission and reflection spectra of the commercial Cu_2O powder was measured on glass substrate, shown in Fig. S3. The optical absorption spectra shows that the commercial Cu_2O has a high absorption in the visible light with the bandgap of about 2.06 eV (600 nm).

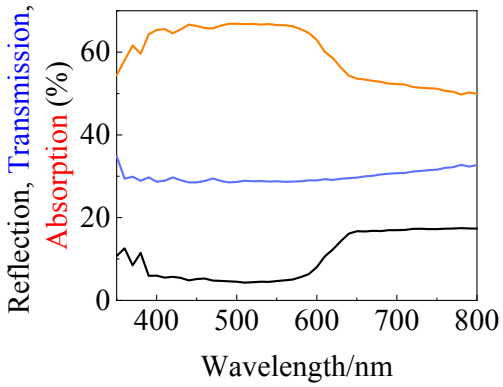

Fig. S3. Optical reflection, transmission, and absorption of commercial Cu_2O.

5. Photocurrent density under different monochromatic wavelength

The photocurrent density under different chopped monochromatic wavelengths with the identical light intensity of 5 mW/cm^2 without applied bias is shown in Fig. S4. TNA/Ti and Cu_2O/TNA/Ti performed the positive photocurrent density, representing the photoanodic behavior, whereas Cu_2O/Ti and Cu_2O/FTO performed the negative photocurrent density, representing the photocathodic behavior. TNA/Ti only demonstrated the high photoresponse in UV range. On the other hand, Cu_2O/TNA/Ti, Cu_2O/Ti, and Cu_2O/FTO responded to UV−visible light because of the narrow bandgap of Cu_2O (2.47 eV). This photocurrent density was then normalized against the light intensity and plotted to show spectral responses, as shown in Fig. 3.

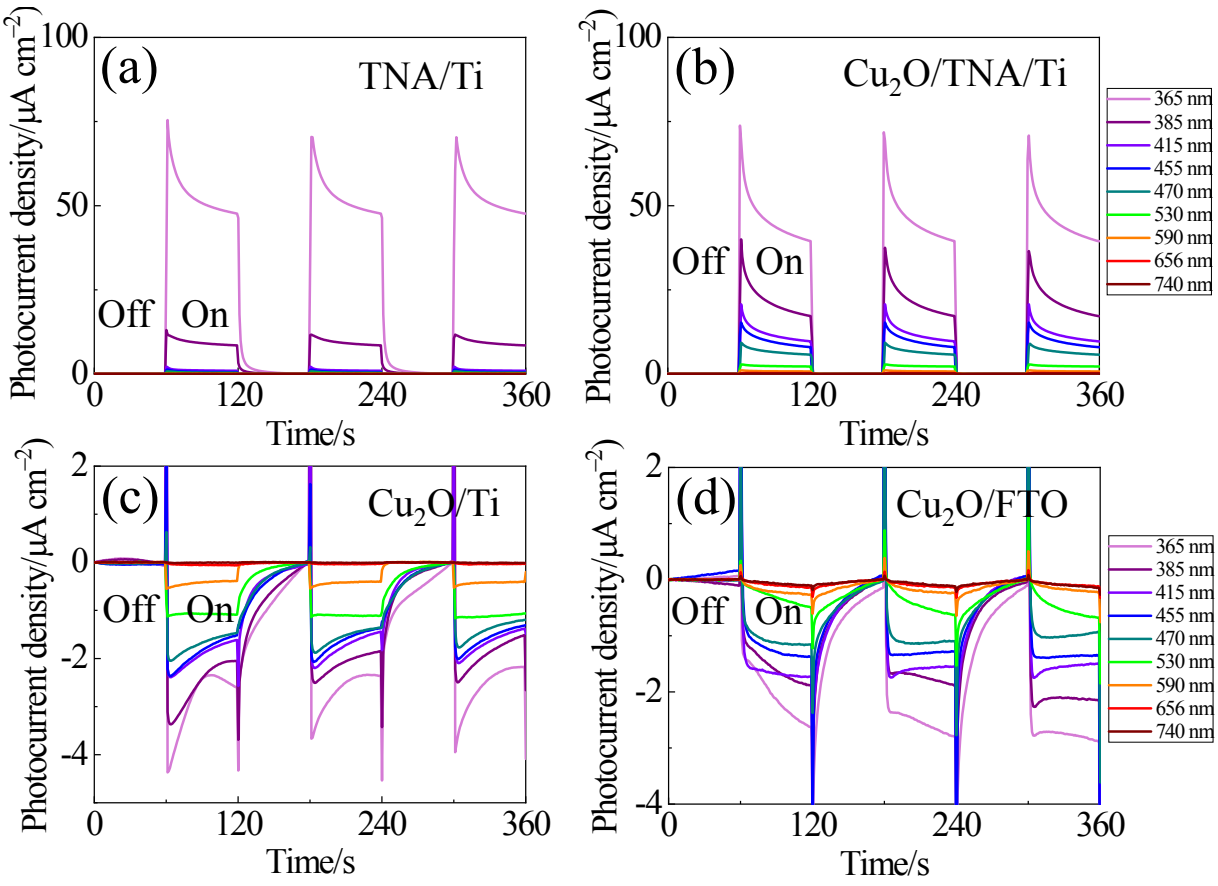

Figure S4. Photocurrent density of (a) TNA/Ti, (b) Cu_2O/TNA/Ti, (c) Cu_2O/Ti, and (d) Cu_2O/FTO under different chopped monochromatic wavelengths (5 mW/cm^2), measured in Na_2SO_4 0.05 M without applied bias.

References

1. K-L. Chang, Q. Sun, Y.-P. Peng, S.-W. Lai, M. Sung, C.-Y. Huang, H.-W. Kuo, J. Sun and Y.-C. Lin, *Chemosphere*, 2016, **150**, 605−614.