

*Electronic Supplementary Information for*

## **Homogeneous Interfacial Electron Transfer Promotes Photoinduced Hole Extraction for Phenol Mineralization**

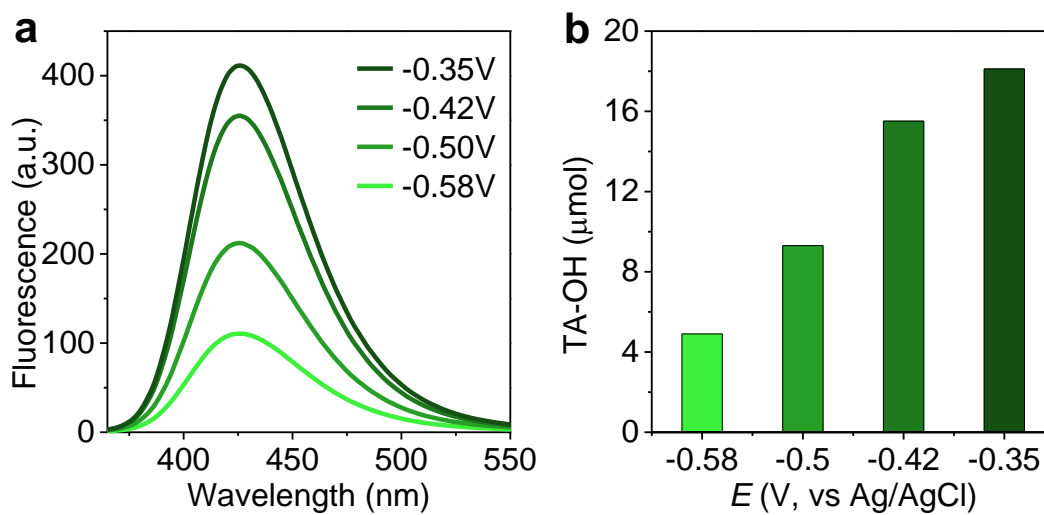
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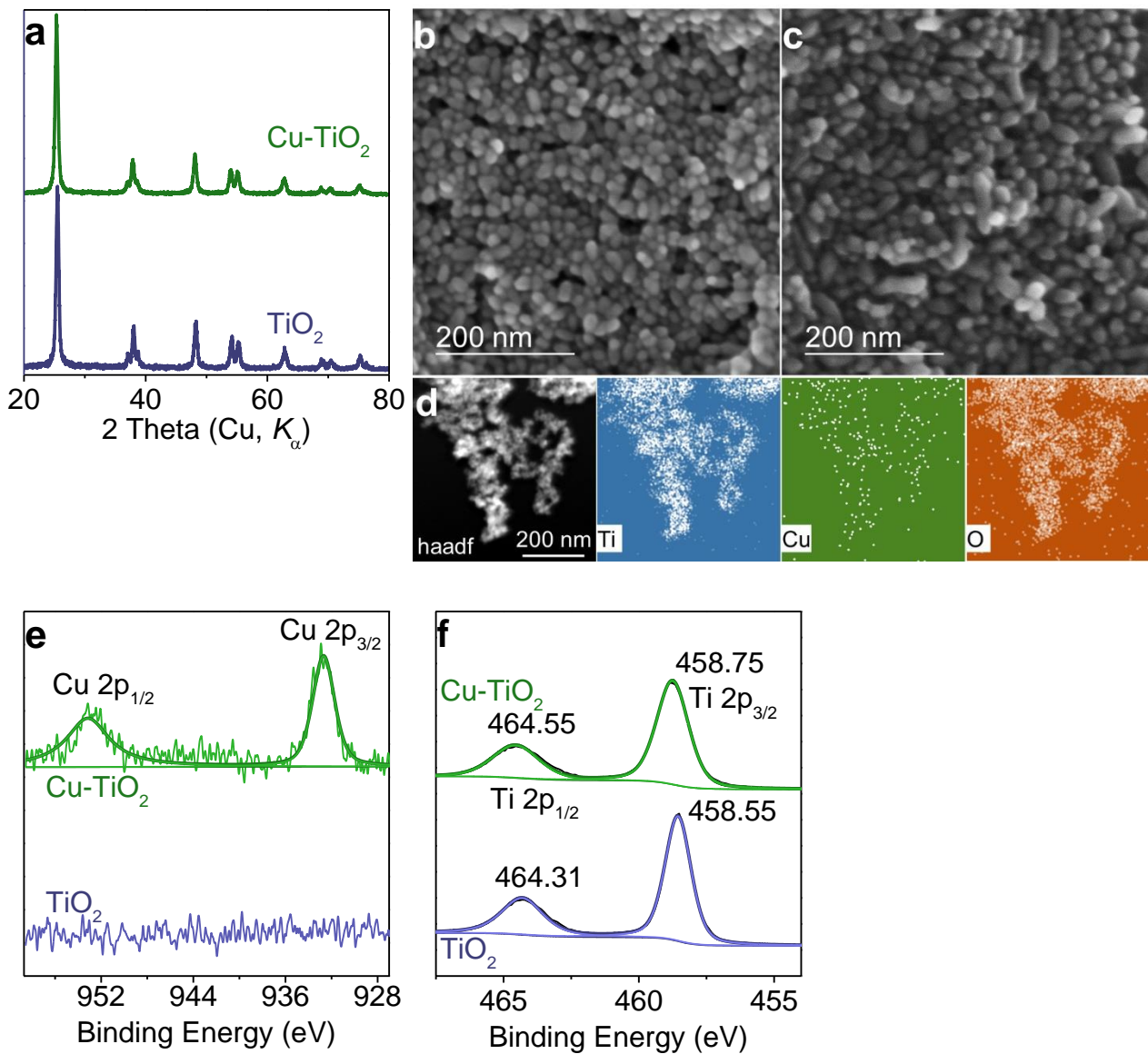
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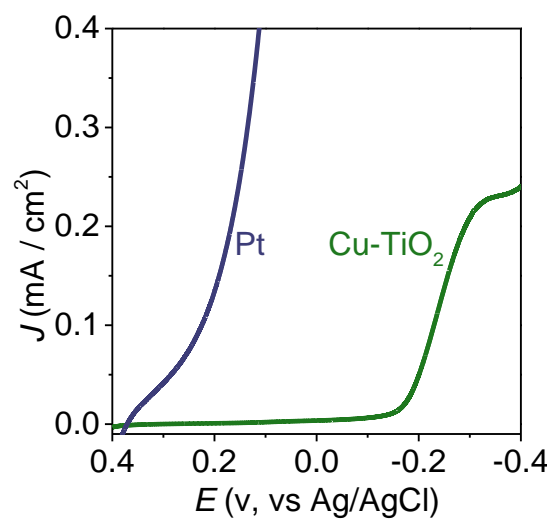
Email: chenjiazang@sxicc.ac.cn (J.C.); wangjunweilotus@163.com (J.W.)



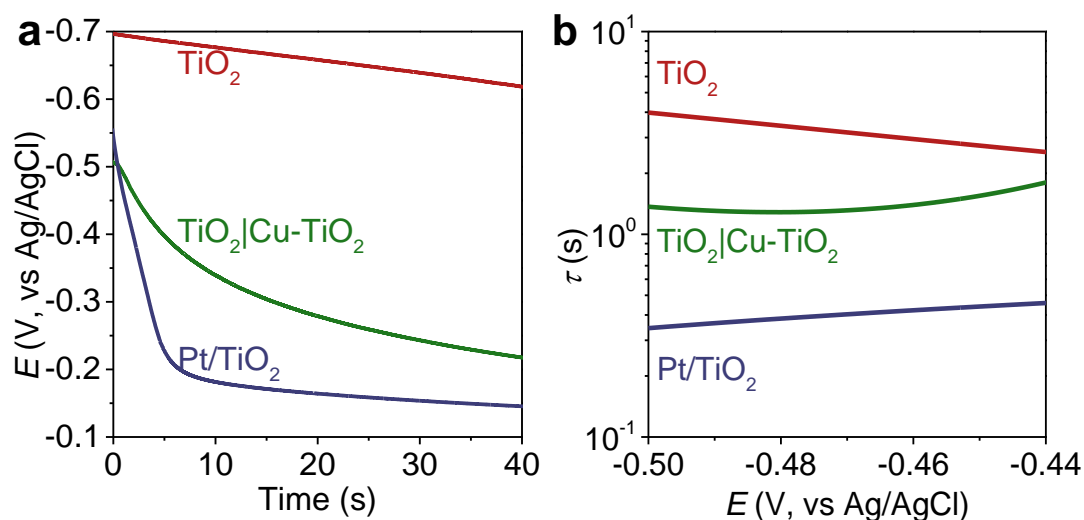
**Figure S1.** Dependence of hydroxyl radical generation on the bias of TiO<sub>2</sub> electrode. The generation of hydroxyl radicals can be reflected by detecting the fluorescence (a) of *o*-hydroxyterephthalic acids (TA-OH), which formed by reacting terephthalic acid with trapped •OH (b). The experiment was conducted by immersing the TiO<sub>2</sub> electrode in 2 mM NaOH that containing 0.5 mM terephthalic acid (TA). The reaction time is 20 min.



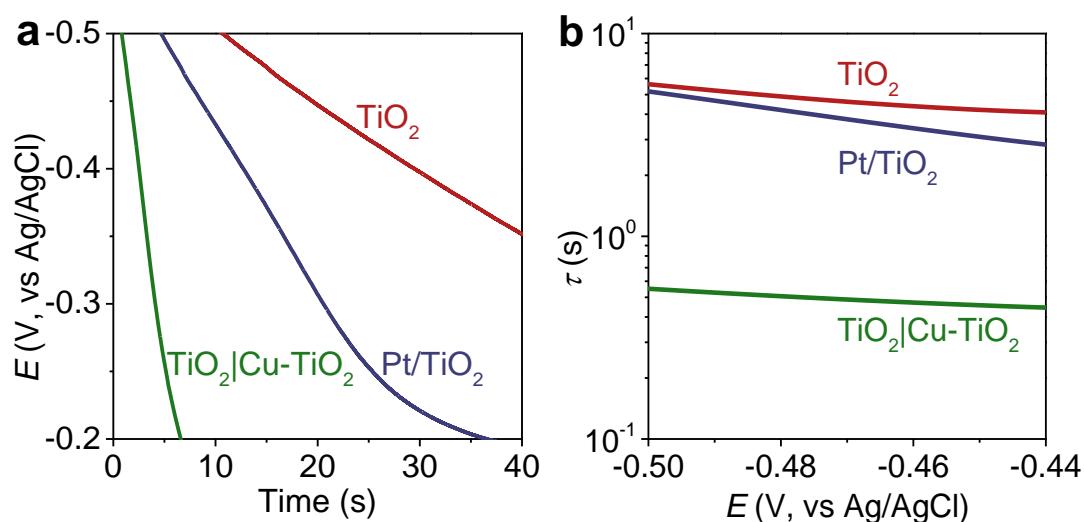
**Figure S2.** X-ray diffraction (a) and scanning electron microscopy (b, c) characterizations show that TiO<sub>2</sub> (b) and Cu-TiO<sub>2</sub> (c) are of phase-pure anatase with similar size. Together with elementary distribution that matches the profile of the high angle annular dark field image (d), the appearance of Cu<sub>2p</sub> signal (e) and blueshift of Ti<sub>2p</sub> peaks (f) in the X-ray photoelectron spectra suggest successful doping of copper into the TiO<sub>2</sub> lattice.



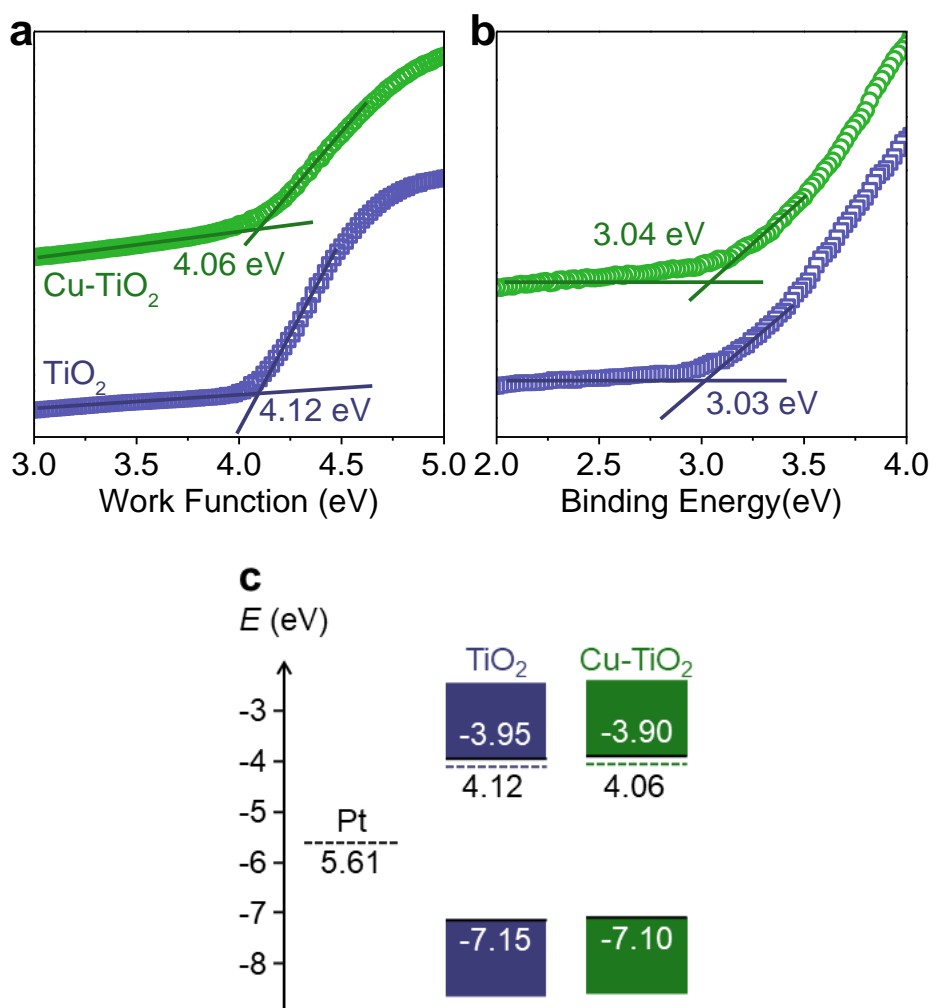
**Figure S3.** Voltammetry behaviors of platinum and Cu-TiO<sub>2</sub> in oxygen-saturated aqueous solution of Na<sub>2</sub>SO<sub>4</sub> (0.5 M). The voltammetry curves were recorded when the rotating disk electrodes were rotating at a speed of 1600 rpm. The electrodes can be formed by depositing Pt and Cu-TiO<sub>2</sub> onto the glassy carbon disk.



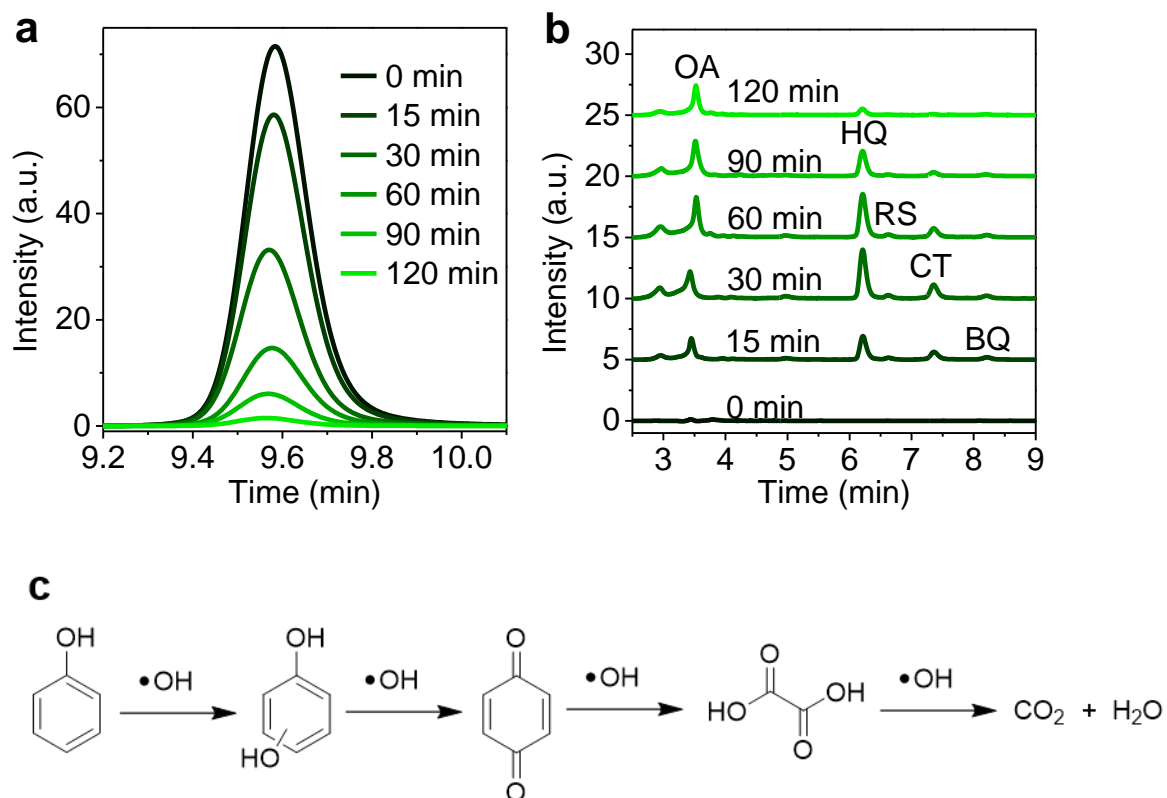
**Figure S4.** The open-circuited potential (OCP) decay behaviors of  $\text{TiO}_2$ ,  $\text{TiO}_2|\text{Cu-TiO}_2$ , and  $\text{Pt/TiO}_2$  electrodes in 0.2 M PBS solution bubbled with argon (a). The time constants (b) evaluated from the OCP decay behaviors represents the transfer of electrons from  $\text{TiO}_2$  to water (protons) with ( $\text{TiO}_2|\text{Cu-TiO}_2$  and  $\text{Pt/TiO}_2$ ) and without ( $\text{TiO}_2$ ) the aid of the catalytic sites. The inclusion of catalytic sites ( $\text{Cu-TiO}_2$  and  $\text{Pt}$ ) makes transfer of electron from  $\text{TiO}_2$  to water fast. Although the potential barrier for SC interfacial electron transfer is high, the sufficient supply of water to the platinum catalyst can makes electrocatalytic step and SCS interfacial electron transfer efficient, as compared with the case of  $\text{TiO}_2|\text{Cu-TiO}_2$ . This situation is rather different from the case of oxygen reduction (e.g.: Figure S5), in which the dissolved oxygen in water is of very concentration. The very low solubility of oxygen in water limits the collision of oxygen to the catalytic sites especially the loading weight is low (e.g.: the loading weight of  $\text{Pt}$  on  $\text{TiO}_2$ ). This makes the SCS interfacial electron transfer for oxygen reduction inefficient (refer Figures 3, S5).



**Figure S5.** The OCP decay behaviors (a) of TiO<sub>2</sub>, TiO<sub>2</sub>|Cu-TiO<sub>2</sub>, and Pt/TiO<sub>2</sub> electrodes in 0.2 M PBS solution bubbled with oxygen and the evaluated time constants (b). Despite of intrinsically low catalytic activity (Figures S3-S4), the large loading weight of Cu-TiO<sub>2</sub> increases the probability for collision with oxygen that is of very low solubility in water. This can promote the oxygen reduction and facilitate the transfer of electrons from TiO<sub>2</sub> to the dissolved oxygen (TiO<sub>2</sub>|Cu-TiO<sub>2</sub>|O<sub>2</sub> interfacial electron transfer). The ratio of TiO<sub>2</sub> to Cu-TiO<sub>2</sub> in a fixed bed reactor is ~1. For the case of Pt/TiO<sub>2</sub>, the ratio of cocatalyst to the semiconductor is 1: 100 in mass (~1: 500 in vol.). The volume ratio of the cocatalysts of Cu-TiO<sub>2</sub> to Pt can be ~500. The large loading volume of Cu-TiO<sub>2</sub> can evidently increase the probability for collision with dissolved oxygen, as compared with that of platinum.

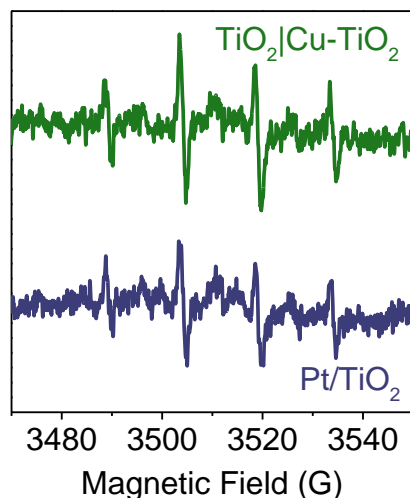


**Figure S6.** Although copper doping shifts the work function from 4.12 to 4.06 eV (a), it only slightly changes the position of valence band with respect to the Fermi level (b), as determined by ultraviolet photoelectron spectroscopy. The very close position of electronic Fermi level for TiO<sub>2</sub> and Cu-TiO<sub>2</sub> indicate the activation energy for homogeneous interfacial electron transfer can be negligibly low (c). In contrast, the barrier height for heterogeneous TiO<sub>2</sub>-Pt contact reaches as high as ~1.5 eV. The formed very high potential barrier would severely slow the TiO<sub>2</sub>-Pt interfacial electron transfer.<sup>1-4</sup>



**Figure S7.** The process of photocatalytic mineralization of phenol. By reaction with photogenerated hydroxyl radicals, the concentration of phenol decreases (a). During the photocatalytic reaction, catechol (CT), resorcinol (RS), hydroquinone (HQ), and benzoquinone (BQ) can be the intermediates (b, c). As the reaction continues, oxalic acid (OA) is the product of ring-opening (b, c). These intermediates can be eventually mineralized (c).





**Figure S8.** Electron spin resonance spectra of hydroxyl radicals trapped by DMPO (10 mM) in the dispersion containing  $\text{Pt/TiO}_2$  and  $\text{TiO}_2|\text{Cu-TiO}_2$  under irradiation for 15 min.

Table S1. Representative progress in photocatalytic mineralization/degradation of phenol.

Item	Specification of Phenol	Catalyst	Light Source	Time	Results <sup>b</sup>	Ref.
1	40 mg/L × 200 mL = 8 mg	Sn-modified calcites	Hg lamp ( $\lambda$ : 254 nm)	6 h	95% mineralization	5
2 <sup>a</sup>	80 mg/L × 150 mL = 12 mg	single-crystal WO <sub>3</sub> nanosheets	300 W Xe lamp ( $\lambda$ : 420-780 nm)	4 h	98 % mineralization	6
3	10 mg/L × 50 mL = 0.6 mg	Triazine-PDI Polymer	500 W Xe lamp ( $\lambda$ : >420 nm)	24 h	79 % TOC removal	7
4	20 mg/L × 100 mL = 2 mg	LaVO <sub>4</sub> /MCM	500 W xenon lamp	3 h	99 % degradation	8
5	10 mg/L × 50 mL = 0.5 mg	g-C <sub>3</sub> N <sub>4</sub>	300 W Xe lamp ( $\lambda$ : >420 nm)	1.5 h	~100 % degradation	9
6	50 mg/L × 150 mL = 7.5 mg	TiO <sub>2</sub> /biochar	125 W Hg lamp	4 h	64.1 % degradation	10
7	50 mg/L × 20 mL = 1 mg	TiO <sub>2</sub> /biochar	150 W Xe lamp ( $\lambda$ : 400-680 nm)	4 h	33.6 % degradation	10
8	~12mg/L × 200 mL = 2.4 mg	BiPO <sub>4</sub>	18 W Hg lamp ( $\lambda$ : 254 nm)	~20 min	~100 % degradation	11
9	42 mg/L × 1000 mL = 42 mg	Pt/TiO <sub>2</sub>	30 W Hg lamp ( $\lambda$ : 254 nm)	1.5 h	>88 % mineralization	This work
10	42 mg/L × 1000 mL = 42 mg	TiO <sub>2</sub>  Cu-TiO <sub>2</sub>	30 W Hg lamp ( $\lambda$ : 254 nm)	1.5 h	>96 % mineralization	This work

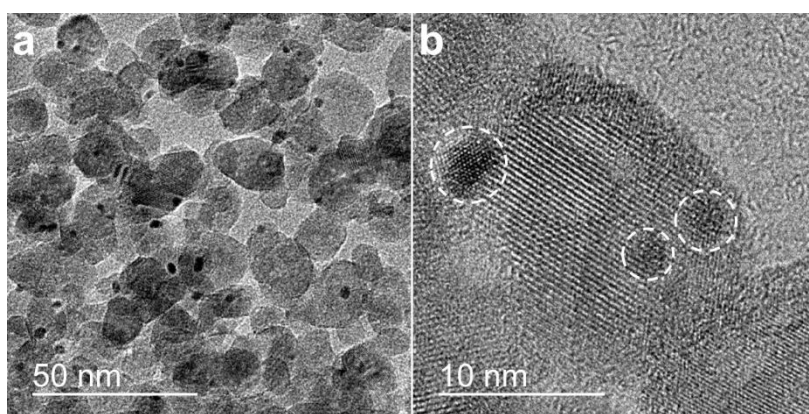
<sup>a</sup>Bubbled with ozone at a rate of 40 mL/min.

<sup>b</sup>Most of the published papers report the degradation of phenol, rather than mineralization. Here, we also list some of the papers that report the degradation of phenol.

## Experimental Procedure

**Preparation of Materials.** Cu-doped TiO<sub>2</sub> can be prepared by solvothermal treatment of titanium-containing precursor in the presence of copper ions. Firstly, 0.1786 g Cu (NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O were dispersed into 20 mL tetrabutyl titanate by vigorously stirring at room temperature for 30 minutes. Then, 15 mL acetic acid were added into the dispersion. After stirring for 1 hour, the dispersion was transferred into a sealed 100-mL PTFE autoclave that was heated at 200 °C for 10 h. After reaction, the precipitate was washed with water and ethanol for several times. After that, the product was dried in vacuum at 60 °C for 12 h.

Formation of Pt/TiO<sub>2</sub> photocatalyst can be realized by loading platinum cocatalyst onto TiO<sub>2</sub> semiconductor nanoparticles (Figure S9). Briefly, 0.2 g TiO<sub>2</sub> powders were dispersed into 200 mL 20 % methanol aqueous solution that contains 2 mg Pt (in H<sub>2</sub>PtCl<sub>6</sub> precursor). Then, the dispersion was irradiated under a 300-W Hg lamp for 90 min. During this process, the dispersion was bubbled with nitrogen. After irradiation, the precipitate was collected and washed with water and ethanol, and dried at 60 °C overnight.



**Figure S9.** Electron microscopy characterization of Pt/TiO<sub>2</sub> (a). The size of platinum nanoparticles deposited on the TiO<sub>2</sub> is ~4 nm in diameter (b).

**Material Characterization.** The morphologies of samples were characterized by Field Emission Scanning Electron Microscope (JSM-7900F). Powder X-ray diffraction (XRD) patterns were recorded by a Bruker D8 Advanced diffractometer using Cu  $K_{\alpha}$  irradiation. X-ray photoelectron spectroscopy (XPS) and ultraviolet photoelectron spectroscopy (UPS) measurements were carried out on an ThermoFisher EscaLab 250Xi emission using a monochromatic Al  $K_{\alpha}$  source.

**Semiconductor (Photo)Electrochemistry and Photochemistry.** The (photo)electrochemical measurements were conducted in tri-electrode systems, in which a piece of carbon cloth was used as counter electrodes, a liquid bridge containing an inert electrolyte (KCl) was used to connect the reference electrode (Ag/AgCl/Sat. KCl) and the cell.

The procedure for fabrication of semiconductor electrodes for linear sweep voltammetry measurements can refer to our previous publications with minor modification.<sup>2, 12-14</sup> Briefly, 10 mg TiO<sub>2</sub> (Pt/TiO<sub>2</sub>, Cu-TiO<sub>2</sub>, or TiO<sub>2</sub>) and 200  $\mu$ L Nafion solution (5wt.%) were dispersed into 1.5 mL ethanol under sonication for 20 min, then 10  $\mu$ L of the resulting solution was dropped onto the glassy carbon rotating disc electrode and dried at room temperature. To avoid the direct contact of platinum to the conducting substrate (glass carbon), TiO<sub>2</sub> film was firstly formed on the conducting substrate prior to deposition of Pt/TiO<sub>2</sub> (or Cu-TiO<sub>2</sub>). Formation of blocking TiO<sub>2</sub> film on glassy carbon can be realized by depositing 6  $\mu$ L of the paste (formed by dispersing 10 mg TiO<sub>2</sub> and 200  $\mu$ L Nafion solution into 1.5 mL ethanol) onto the rotating disc electrode and dried at room temperature. After that, the Pt/TiO<sub>2</sub> (or Cu-TiO<sub>2</sub>) nanostructures were deposited onto the TiO<sub>2</sub> film to form Pt/TiO<sub>2</sub> (or TiO<sub>2</sub>|Cu-TiO<sub>2</sub>) electrodes. The deposition of Pt/TiO<sub>2</sub> (or Cu-TiO<sub>2</sub>) onto the TiO<sub>2</sub> films can be realized by depositing 10  $\mu$ L of the above-mentioned dispersion [formed by dissolving 10 mg photocatalysts (Pt/TiO<sub>2</sub> or Cu-TiO<sub>2</sub>) and 200  $\mu$ L Nafion solution (5 wt %) into 1.5 mL ethanol under sonication] onto

the TiO<sub>2</sub> film coated glassy carbon rotating disc electrode and dried at room temperature. The electrochemical behaviors are characterized using linear sweep voltammetry with a scanning rate of 10 mV/s when the working electrode is rotated at 1600 rpm in an aqueous solution of Na<sub>2</sub>SO<sub>4</sub> (0.5 M). The linear sweep voltammetry measurements of Pt were carried out using a platinum rotating disc electrode.

To determine the time constants for transfer of electrons from semiconductor (TiO<sub>2</sub>, Pt/TiO<sub>2</sub>, Cu-TiO<sub>2</sub>) to the solution, we monitor the open-circuit potential decay (OCP) behaviors in the tri-electrode systems, in which 0.2 M PBS solution bubbled with argon or oxygen were used as the electrolyte. The irradiation for the photoelectrochemical measurements was provided by a Hg-lamp (500 W). The FTO|TiO<sub>2</sub> electrode for voltammetry and OCP measurements can be prepared by depositing the TiO<sub>2</sub> paste onto fluorine-doped tin dioxide (FTO) conducting glass with an active area of 0.50 cm<sup>2</sup> and heated at 400°C for 0.5h. The TiO<sub>2</sub> (Cu-TiO<sub>2</sub>) paste can be prepared by mixing TiO<sub>2</sub> and ethanol in aqueous dispersion (20 wt% TiO<sub>2</sub> + 20 wt% ethanol + water). The FTO|TiO<sub>2</sub>|Cu-TiO<sub>2</sub> electrode can be prepared by depositing the Cu-TiO<sub>2</sub> paste onto the FTO that has been coated with TiO<sub>2</sub> paste.

For the electrode deposited with platinum loaded semiconductor (Pt/TiO<sub>2</sub>), we introduce a compact layer to avoid the direct contact of the metal to FTO substrate. The compact layer can be formed by the deposition of 10 μL titanium-containing alcoholic solution (10 mL ethanol + 1.485 mL Triton X-100 + 2 mL acetic acid + 0.102 mL tetrabutyl titanate) onto FTO glass by preparing an active area of 0.5 cm<sup>2</sup>. The coated FTO glass was then heated at 500 °C for 60 min in air. After that, 20 μL catalyst dispersion (5 mg Pt/TiO<sub>2</sub> + 0.5 ml ethanol + 200 μL Nafion solution (5%)) was deposited onto the compact layer to form the Pt/TiO<sub>2</sub> electrode.

**Photocatalytic Mineralization.** The photocatalytic mineralization of phenol was carried out in

a fixed bed reactor equipped with a Hg-lamp (PHILIPS, TUV, 30 W/G 30). Firstly, 1.6 mL catalyst slurry formed by dispersing 1 g TiO<sub>2</sub> into 10 mL ethanol and shaking in a 3D powder mixer for 12 h were coated on the surface of the Hg-lamp and dried naturally. After that, the TiO<sub>2</sub> film was heated at 400 °C for 1 h. The TiO<sub>2</sub> coated lamp was then placed into the reactor, which connected with a tank. The interspace of the reactor and the lamp was filled with 20 vol % methanol aqueous solution (200 mL containing 2 mg Pt in H<sub>2</sub>PtCl<sub>6</sub> precursor) that was pumped from the tank. Platinum therefore can be deposited onto TiO<sub>2</sub> by *in situ* photoinduced reduction. After 2 h irradiation, the methanol aqueous solution was discharged. The reactor was then dried by air stream for 1 h.

Photocatalyst with TiO<sub>2</sub>|Cu-TiO<sub>2</sub> configuration can be prepared by coating 1.6 ml Cu-TiO<sub>2</sub> slurry (formed by dispersing 1 g Cu-TiO<sub>2</sub> into 10 mL ethanol and shaking in a 3D powder mixer for 12 h) onto TiO<sub>2</sub> coated lamp. Then, the double-layered TiO<sub>2</sub> film was heated at 400 °C for 1 h.

Photocatalytic mineralization was performed by fluxing the phenol aqueous solution (42 mg/L × 1 L) in the fixed bed reactor connected with a tank. During reaction, the solution of phenol was bubbled with oxygen. COD values were monitored by sampling the phenol solution during the reaction with an interval of 0.5 h. The COD values were measured by a Water Quality analyzer (LH-T 725).

### Supplementary Information References

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