

Electronic Supplementary Information

Concentration dependent effect of CuCl₂ on the photocatalytic degradation of phenol over anatase, rutile and brookite TiO₂

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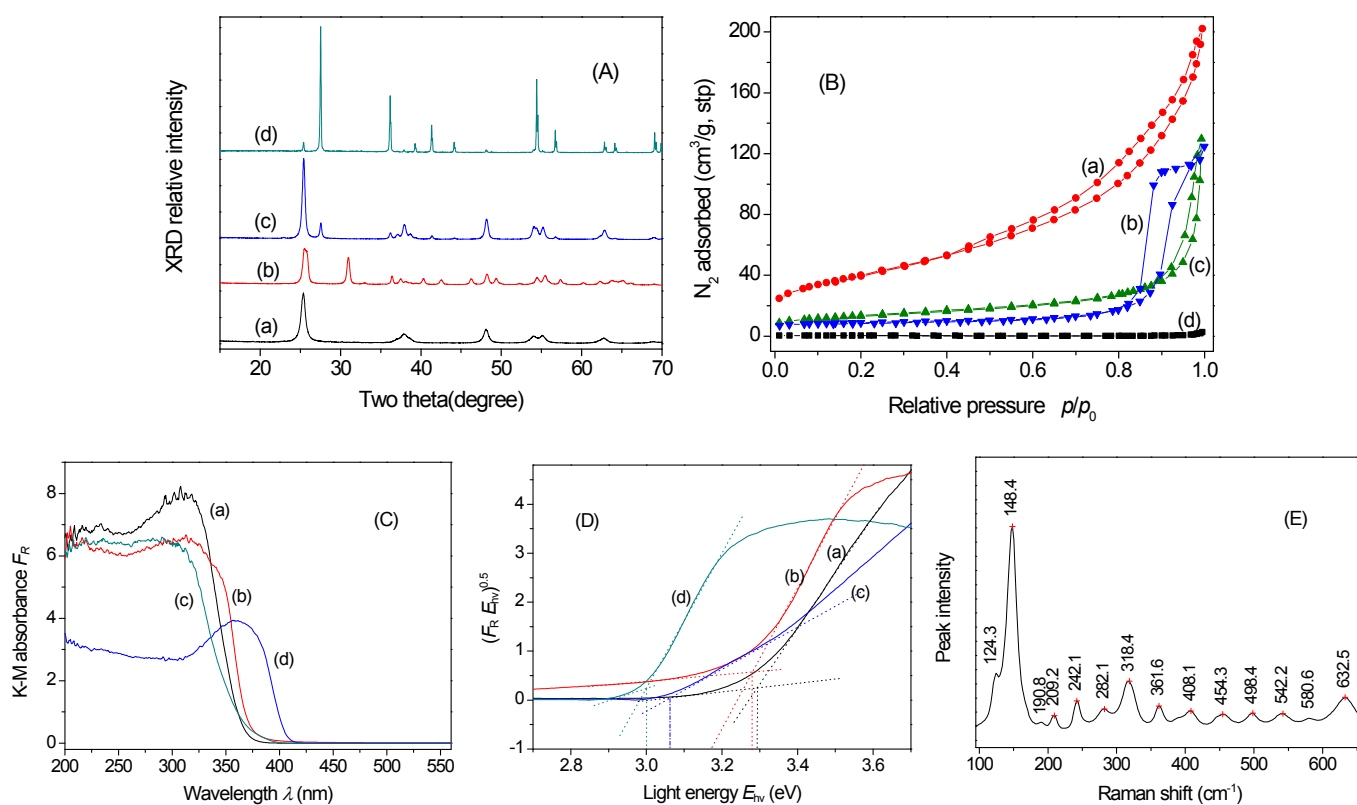


Fig. S1. (A) XRD patterns, (B) N₂ adsorption–desorption isotherms, and (C) UV–vis diffuse reflectance spectra of TiO₂ samples, (a) cAT, (b) sBT, (c) P25 and (d) cRT. The Kubelka–Munk (K–M) absorbance (F_R) is calculated by using the equation, $F_R = (1 - R)^2 / 2R$, where R is the solid reflectance. The diffraction patterns of cAT and sBT were in good agreement with those of anatase (PDF #65-5714) and brookite (PDF #29-1360) TiO₂, respectively. Both cRT and P25 showed a mixed pattern of anatase and rutile (PDF #21-1276). According to the integrated intensities of the (101) anatase and (110) rutile, the relative content of anatase in cRT and P25 were about 1% and 80%, respectively. Figure D is a Tauc plot for the indirect transition of TiO₂, from which a band gap energy is extrapolated. Figure E is the Raman spectrum of sBT. In the range from 100 cm⁻¹ to 700 cm⁻¹, there were 14 Raman peaks, typical of brookite, whereas the characteristic vibrations of anatase at 512 cm⁻¹, and of rutile at 442 cm⁻¹ were absent. This Raman analysis confirms that sBT is in the pure form of brookite.

Experimental Details. XRD pattern was recorded on a D/max-2550/PC diffractometer (Rigaku) using Cu K α 1 radiation (0.154 nm), operated at 40 kV and 30 mA. By using the Scherrer equation, the average crystallite diameter of TiO₂ (d_{XRD}) was calculated, according to the full-widths at half-maximum of the (121) brookite at $2\theta = 30.8^\circ$, the (101) anatase at $2\theta = 25.3^\circ$, and the (110) rutile at $2\theta = 27.4^\circ$, respectively. Diffuse reflectance spectra were recorded on a Shimadzu UV-2550 using BaSO₄ as a reference. The band gap energy of TiO₂ for indirect transition was calculated from a Tauc plot (Fig. S1D). Adsorption isotherm of N₂ on solid was measured at 77 K on a Micromeritics ASAP2020 apparatus, from which the Brunauer–Emmett–Teller specific surface area (A_{sp}) was calculated. Raman spectra were obtained on a Jobin Yvon LabRam

1B with a He-Ne laser excitation at 632.8 nm. XPS data were obtained with an ESCALab220i-XL electron spectrometer from VG Scientific using 300 W Al $K\alpha$ radiation. The binding energies were calibrated with the C1s line at 284.6 eV. Scanning electron microscope (SEM) measurement were acquired on a Hitachi SU-70 electron microscope working at an accelerating voltage of 25.0 kV, and the specimens were sputtered with gold to increase the electrical conductivity.

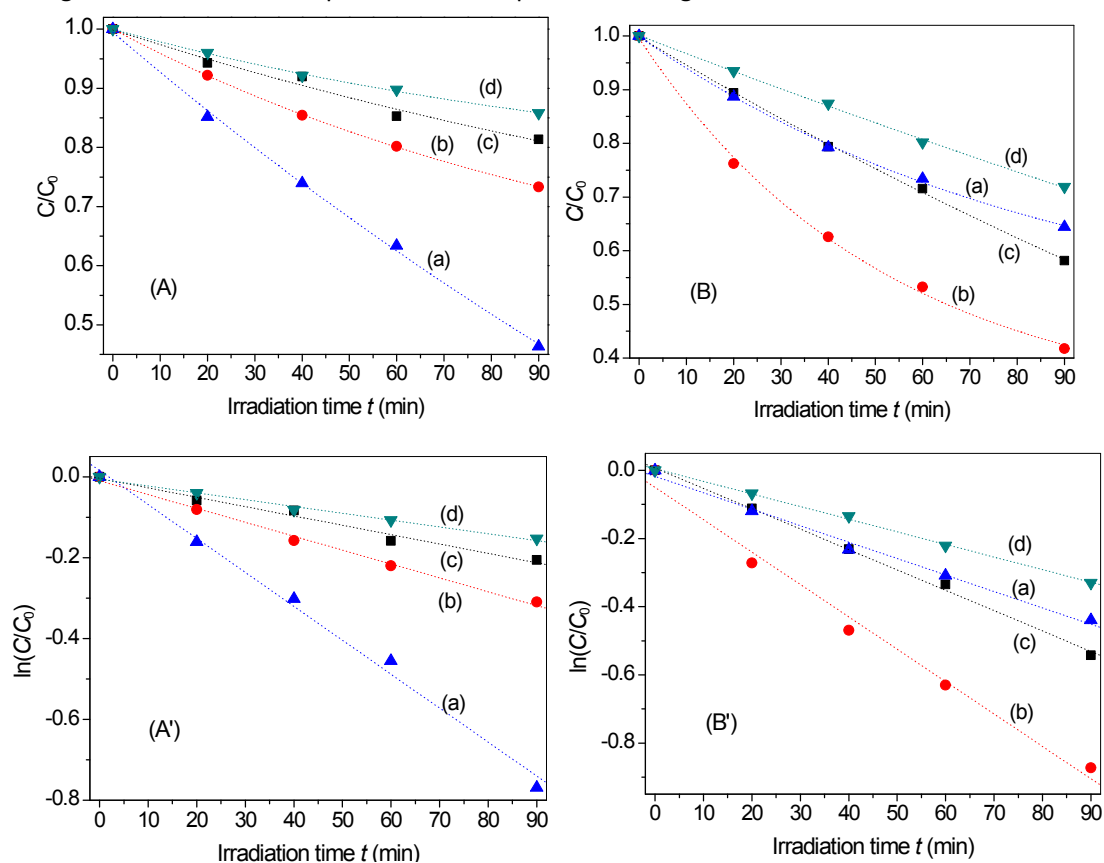


Fig. S2. Time profiles of phenol degradation over (a) P25, (b) CRT, (c) cAT and (d) sBT, (A) in the absence, and (B) presence of 0.5 mM CuCl_2 . Experiments were performed in an aerated aqueous suspension at pH 3.0. Fig. A' and B' are the corresponding plots of $\ln(C/C_0)$ versus t for Fig. A and B, respectively.

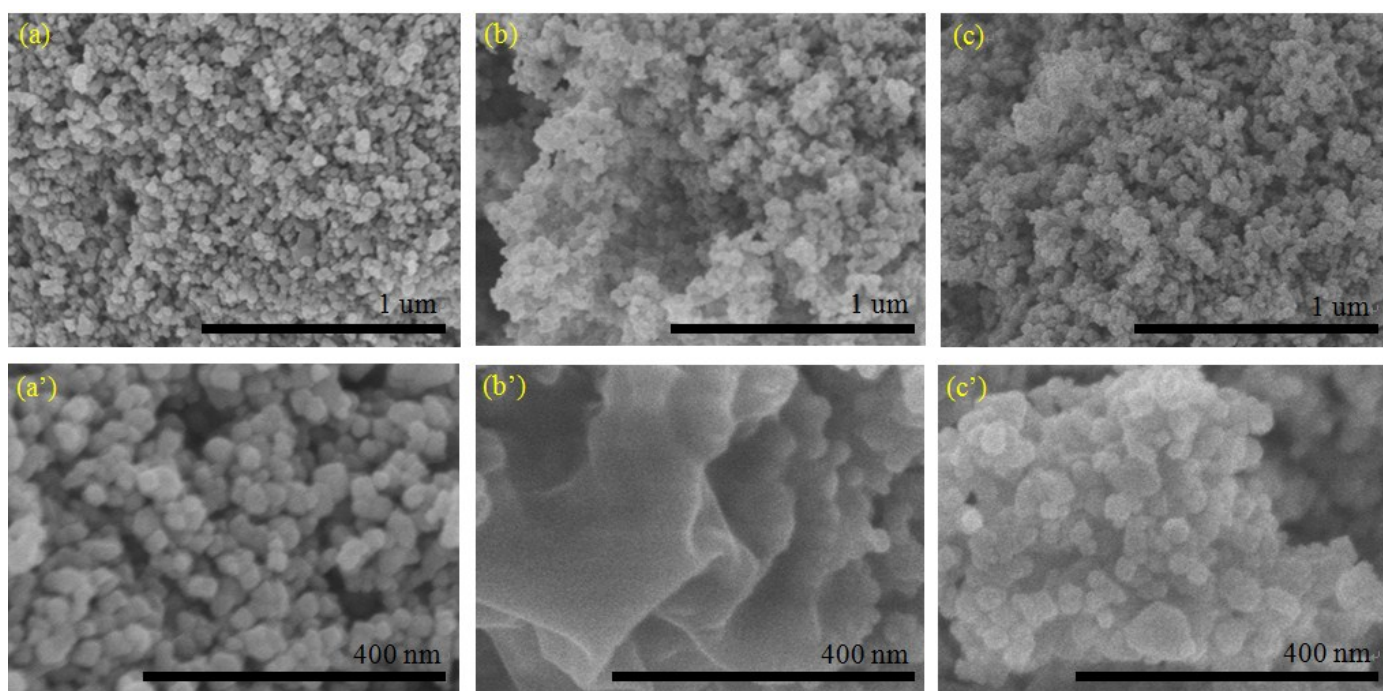


Fig. S3. SEM images for (a, a') P25, (b, b') CuCl_2 -treated P25, and (c, c') NaCl-treated P25. The suspension (4.00 g/L TiO_2 , 0.43 mM phenol, pH 3.0, 50 mM CuCl_2 or NaCl) was irradiated for 2 h under air, followed by collection, washing and drying.

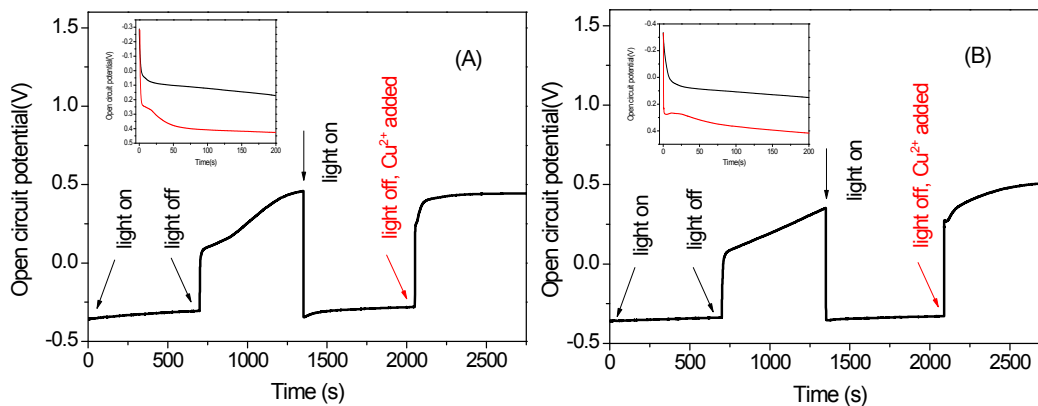


Fig. S4. Time profiles of open circuit potentials (OCP), measured under air in 0.5 M NaClO₄ at pH 3.0, with (A) the cAT film electrode, and (B) the P25 film electrode. The insert is the plot of OCP decay with time after the light was switched off, obtained in absence (black line) and presence of 80 μl 0.5 M Cu²⁺ (red line).

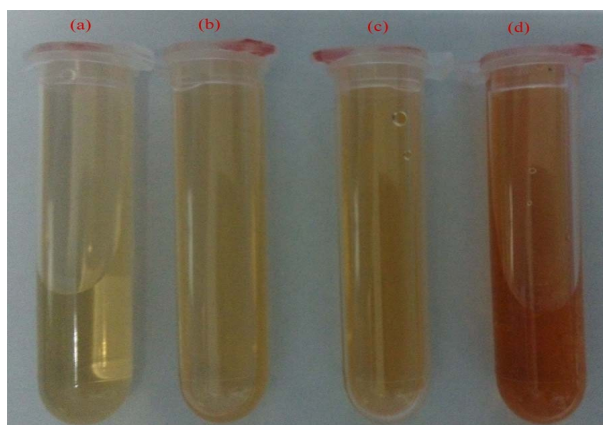


Fig. S5. The color reaction of Cu(I) with bathocuproine disulfonic acid collected after photoreaction under N₂ for (a) sBT, (b) cAT, (c) P25 and (d) cRT in the presence of 4 mM Cu²⁺.

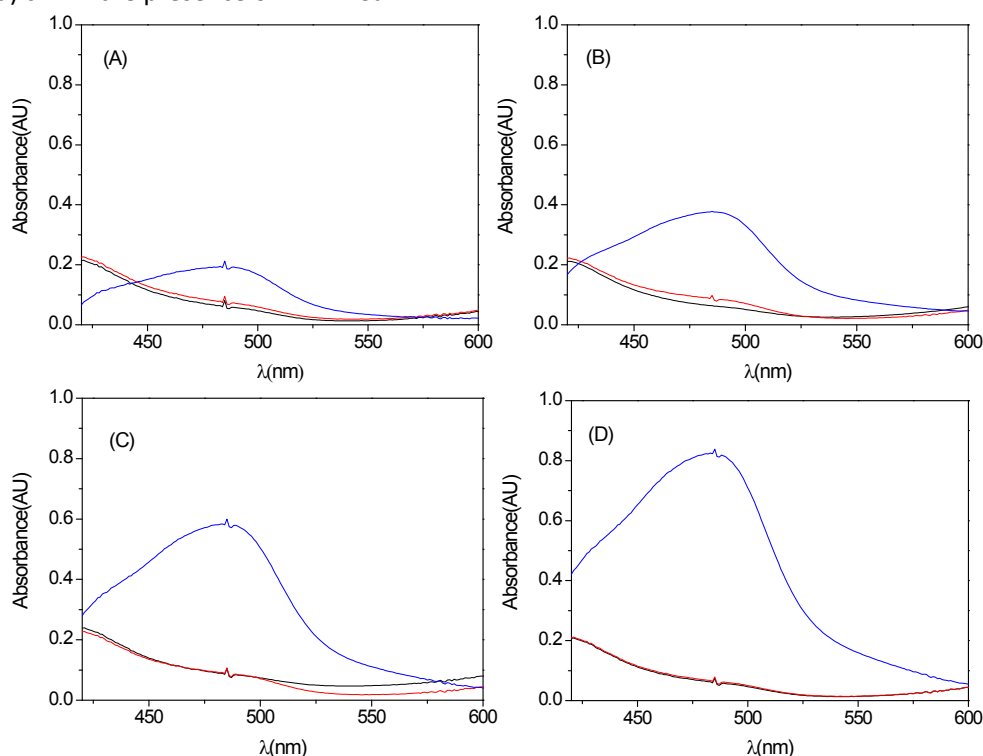


Fig. S6. UV - vis absorption spectra (blue lines) of the Cu(I) complexes with bathocuproine disulfonic acid, recorded with (A) sBT, (B) cAT, (C) P25 and (D) cRT. The suspension containing TiO₂ (1.00 g/L), CuCl₂ (4.0 mM), and phenol (0.43 mM) was degassed by N₂, and then irradiated with UV light for 1.5 h. The black lines correspond to those recorded before light irradiation. The red lines represent the spectra for the air-exposed samples. That is, after the suspension was irradiated

under N_2 for 1.5 h, it was exposed to air for 10 min. Then, copper reagent was added, and the filtrate spectra were recorded.

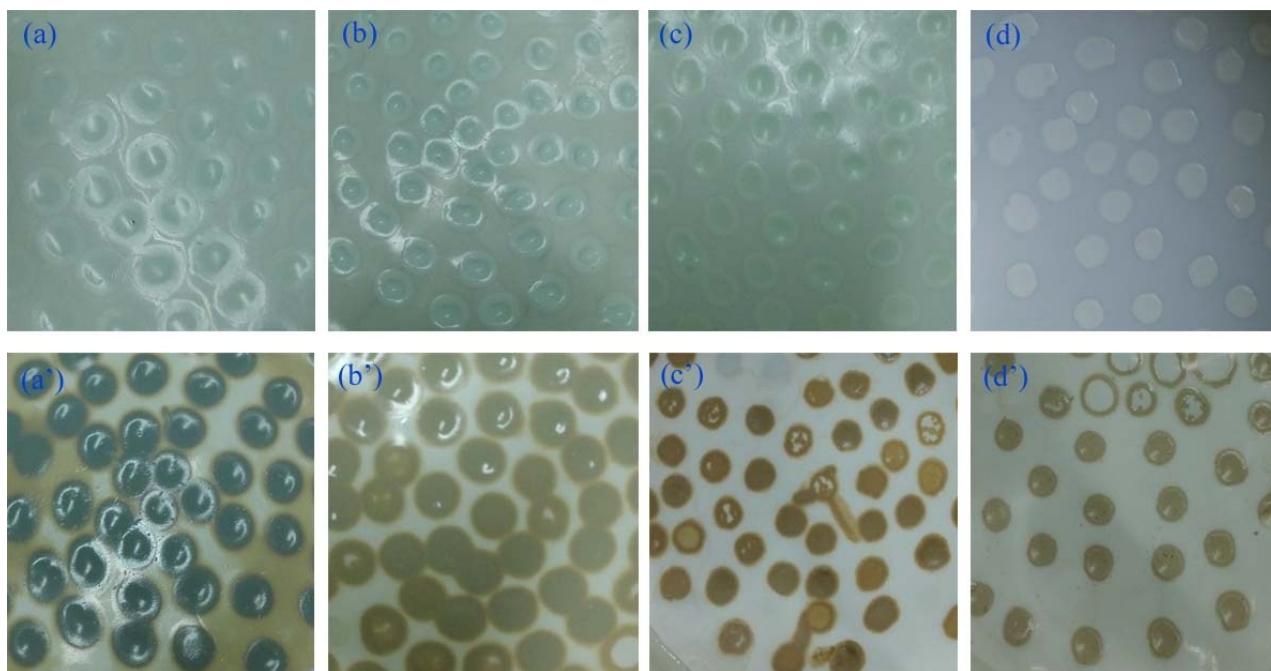


Fig. S7. Photographs for the filters of (a, a') P25, (b, b') cAT, (c, c') sBT, and (d, d') cRT, collected before (the first row) and after light irradiation (the second row). The samples were made as described in Figure S7. The filter used was 0.22 μm membrane, and the solid was washed thoroughly with distill water.

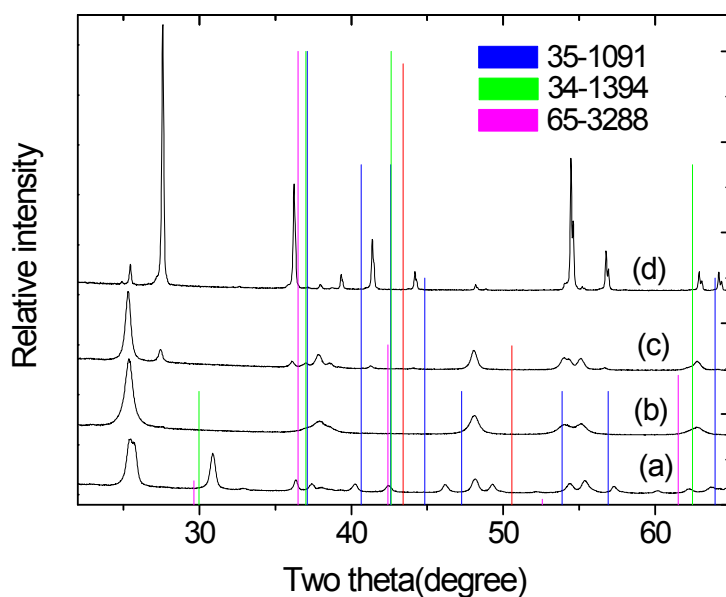


Fig. S8. XRD patterns of (a) sBT, (b) cAT, (c) P25, and (d) cRT. The aerated aqueous suspension containing TiO_2 (2.00 g/L), phenol (3.20 mM) and CuCl_2 (50 mM) at initial pH 3.0 was irradiated with UV light for 22 h. Then, the solid was collected by filtration, washed thoroughly with distilled water, and dried in a vacuum for XRD analysis. The red lines represent the standard pattern of metallic Cu (PDF No 65-9743), whereas other color lines represent the standard patterns for various Cu_2O , as indicated by the legends.