

Revealing the Role of Elementary Doping in Photocatalytic Phenol Mineralization

Houkui Xiang^{1,2}, Zhijian Wang¹ and Jiazang Chen^{1,2*}

¹State Key Laboratory of Coal Conversion, Institute of Coal Chemistry, Chinese Academy of Sciences, Taiyuan 030001, China

²Center of Materials Science and Optoelectronics Engineering, University of Chinese Academy of Sciences, Beijing 100049, China

*Corresponding author. Email: chenjiazang@sxicc.ac.cn (J.C.)

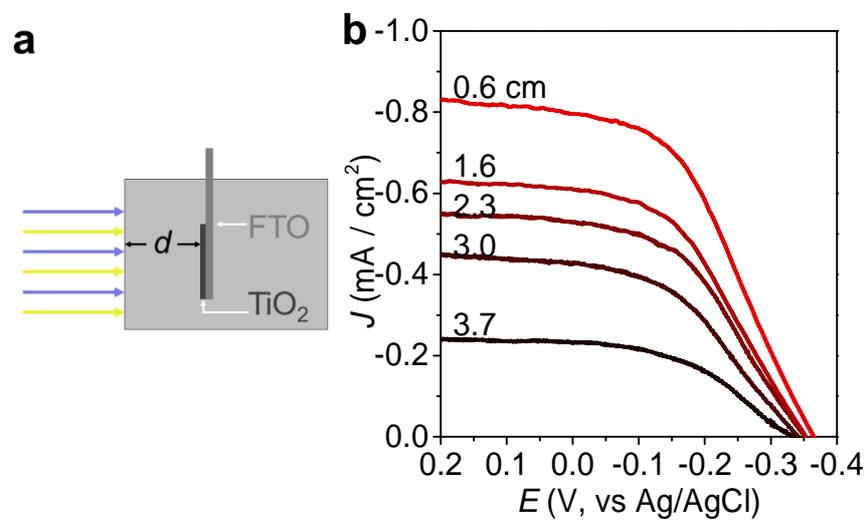


Figure S1. Schematic diagram (a) for measuring the distance-dependent photoelectrochemical behaviors (b) of TiO₂ electrode in the phenol-containing aqueous solution (0.1 M phenol + 0.5 M Na₂SO₄). Various voltammetry behaviors (b) can be obtained by adjusting the distance (d) from the wall of the quartz cell to the electrode (a). The irradiation was provided by performing a Hg-lamp (485 mW/cm² at the exterior wall of the quartz cell). The Ag/AgCl reference electrode was shaded to avoid the shift of the reference potential.

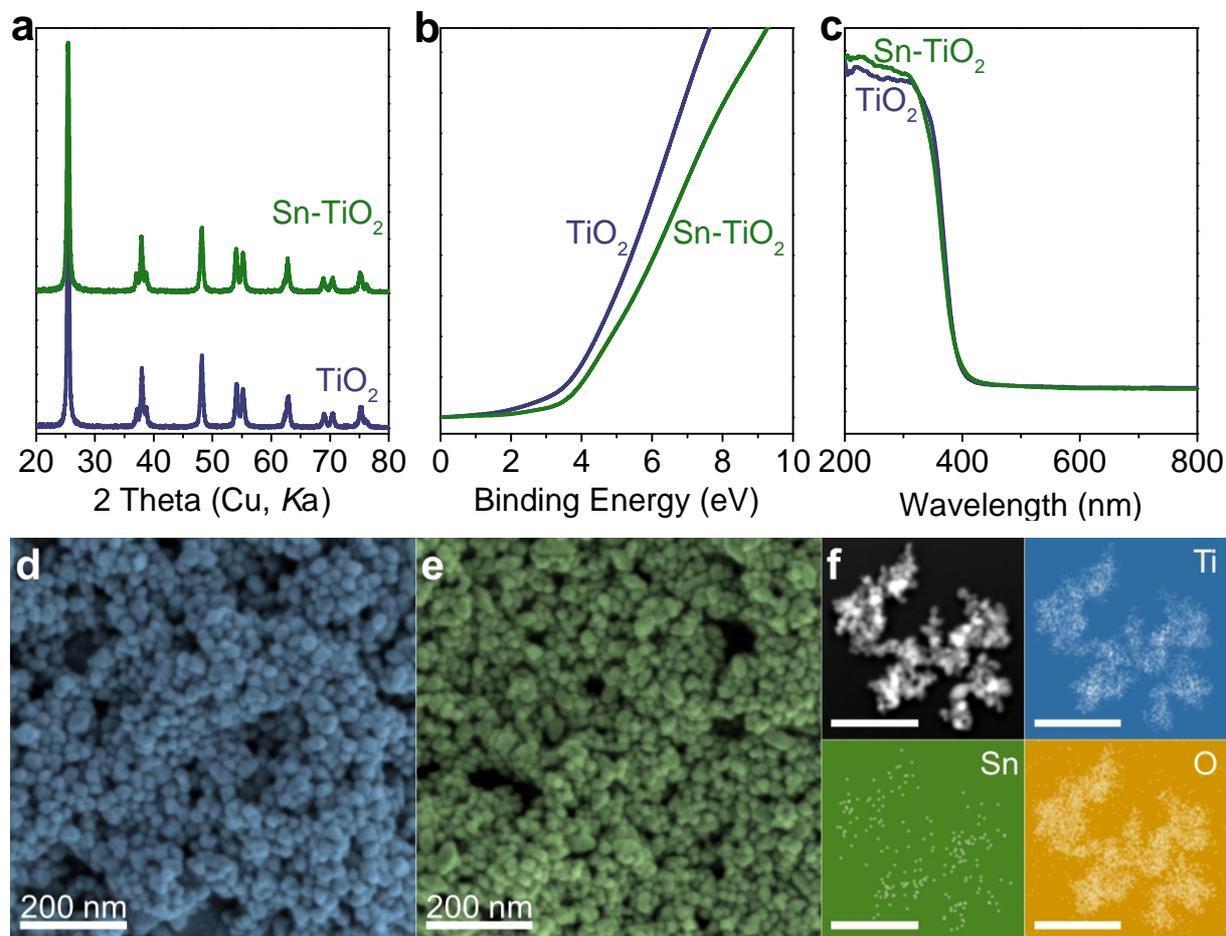


Figure S2. X-ray diffraction patterns (a), ultraviolet photoelectron spectra (b), UV-vis absorption spectra (c), and electron microscopy images (d, e) for the TiO₂ with (e) and without (d) tin dopant. The elemental mapping shows that the distribution of tin matches the profile of the Sn-TiO₂ (f). The scale bar shown in elemental mappings (f) is 200 nm.

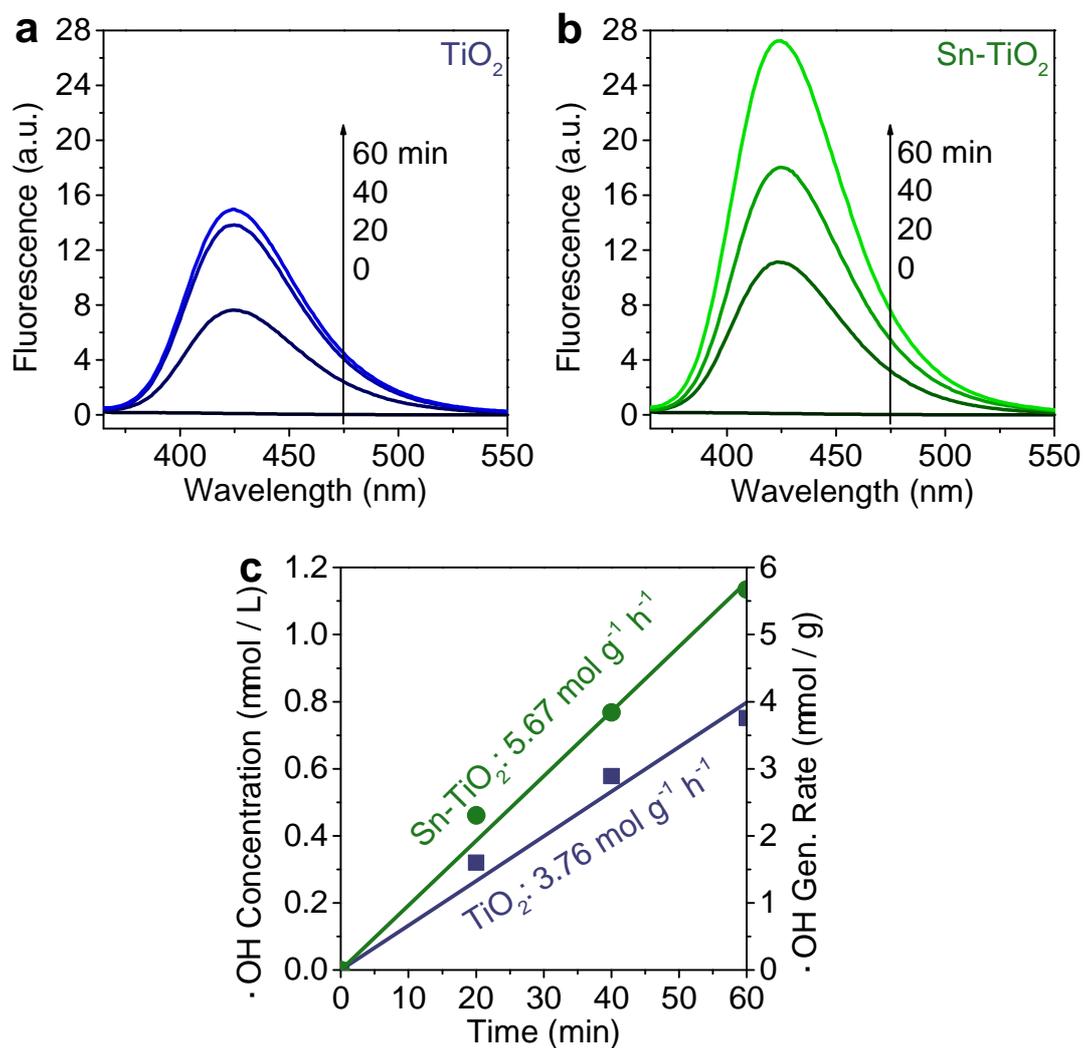


Figure S3. The photoinduced generation of hydroxyl radicals upon irradiation on TiO_2 (a) and Sn-TiO_2 (b). The integrated intensity of fluorescence for TA-OH increases with the irradiation time. The generation rate and concentration of hydroxyl radicals in the dispersion containing 10 mg (Sn-TiO_2), 2 mM NaOH, and 0.5 mM terephthalic acid can be evaluated from the fluorescence intensity (c).

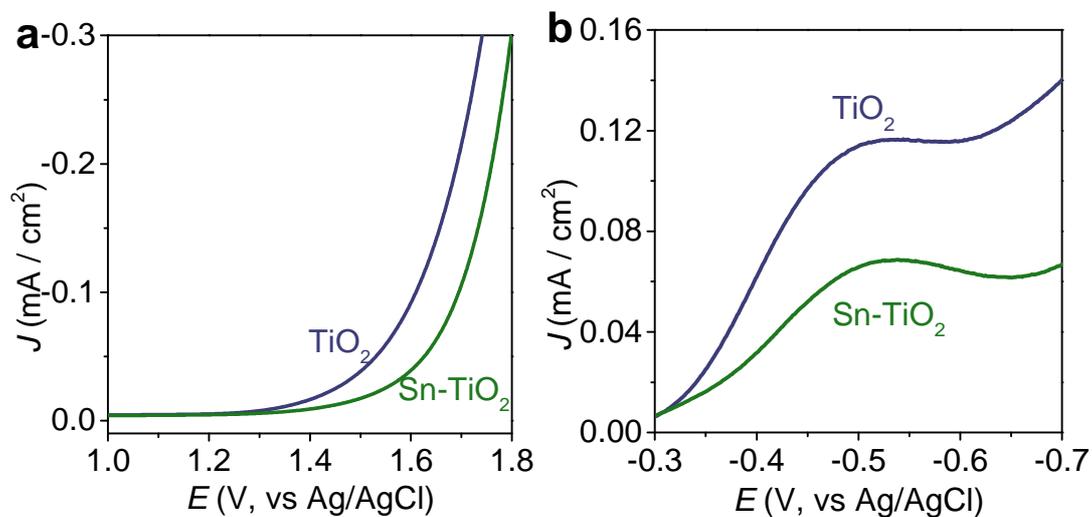


Figure S4. Water oxidation (a) and oxygen reduction (b) behaviors of TiO_2 and Sn-TiO_2 . The water oxidation behaviors (a) were measured by immersing the $\text{FTO}|\text{TiO}_2$ ($\text{FTO}|\text{Sn-TiO}_2$) electrodes in argon bubbled PBS solution (0.1 M, pH = 6.7). For measuring oxygen reduction (b), TiO_2 (or Sn-TiO_2) was deposited onto the glassy carbon substrate of a rotating disk electrode (RDE). During the measurement, the RDE was rotating at 1600 rpm in KOH solution (0.1 M).

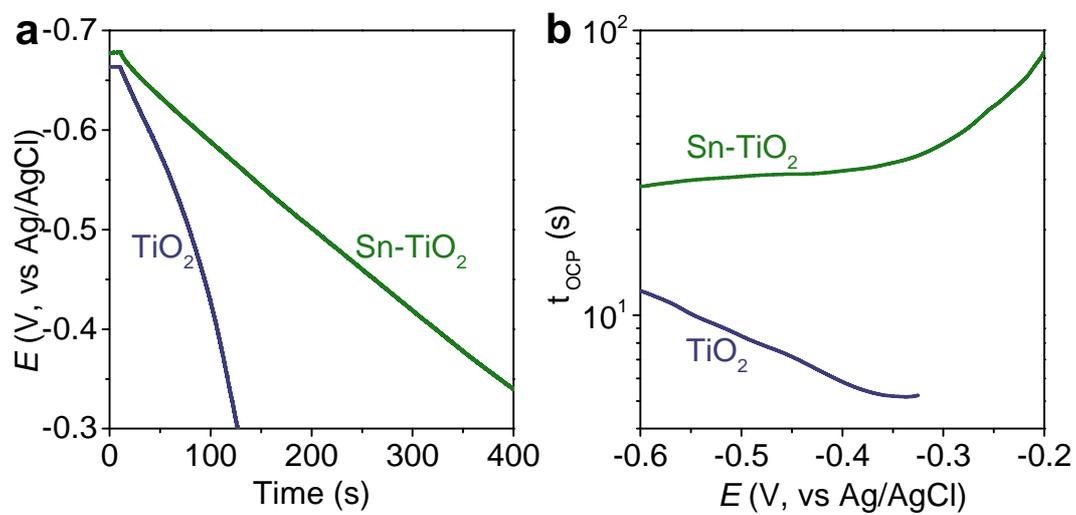


Figure S5. The OCP behaviors (a) and related time constant (b) of FTO|TiO₂ and FTO|Sn-TiO₂ electrodes in argon bubbled 0.5 M Na₂SO₄ solution.

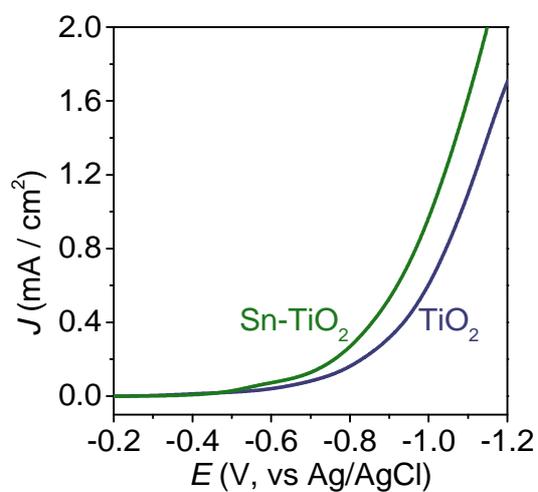


Figure S6. Voltammetry behaviors of FTO|TiO₂ and FTO|Sn-TiO₂ electrodes in argon bubbled PBS solution (0.1 M, pH = 6.7). As demonstrated by the OCP behaviors (e.g.: Figure S5), the tin dopant can passivate the surface activity of TiO₂. This means that the activation energy for electrochemical electron transfer to the solution increases and the onset potential for the electrochemical process alone becomes more negative. The fact is that, however, the onset potential for the whole semiconductor shifts towards less negative value after tin doping. This contradiction indicates that the downshift of the conduction band position occurs and is evident after tin doping.

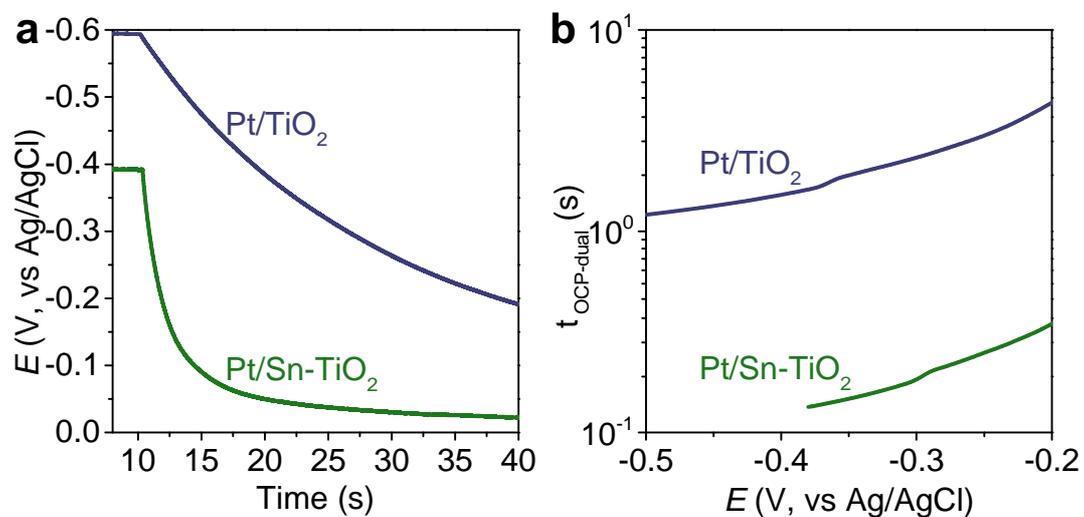


Figure S7. The OCP behaviors of TiO₂ and Sn-TiO₂ electrodes loaded with platinum catalyst (a) in argon bubbled 0.5 M Na₂SO₄ solution. The decay of OCP for Sn-TiO₂ electrode after loading with platinum becomes evidently fast, as compared with the case of TiO₂ (a). This is because the SM interfacial electron transfer for Pt/Sn-TiO₂ electrode is efficient. By these virtues, the time constant evaluated from OCP behaviors for Pt/Sn-TiO₂ is ~10 times smaller than that of Pt/TiO₂.

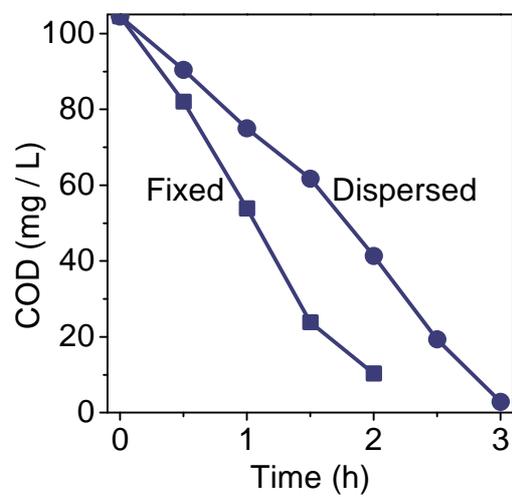


Figure S8. Comparison for the photocatalytic mineralization of phenol in a conventional system (dispersing photocatalyst into the solution) and in a fixed bed reactor (Figure 7a).

n EXPERIMENTAL PROCEDURES

Preparation and Characterizations of (Sn-)TiO₂. TiO₂ materials can be prepared by solvothermal treatment of tetrabutyl titanate in acetic acid. Firstly, 0.4104 g SnCl₄·5H₂O was dissolved in 13.4 mL acetic acid in a 100-mL PTFE autoclave. Then, 40 mL tetrabutyl titanate was added under vigorously stirring at room temperature for 30 minutes. After that, the autoclave was sealed and heated at 220 °C for 12 h. After reaction, the precipitate was collected and washed with pure water and ethanol for several times. Finally, the product was dried under vacuum at 60 °C for 12 h.

The morphologies of samples were characterized by field emission scanning electron microscope (JSM-7900F) equipped with energy-dispersed X-ray detector (Bruker Flat Quad 5060F). X-ray diffraction (XRD) patterns were recorded by a Bruker D8 Advanced diffractometer. X-ray photoelectron spectroscopy (XPS) and ultraviolet photoelectron spectroscopy (UPS) measurements were carried out on a ThermoFisher EscaLab 250Xi emission using a monochromatic Al K α source ($E_{\text{photon}} = 1486.6$ eV). UV-vis absorption spectra were recorded by performing a Shimadzu UV-3600 spectrometer.

Semiconductor (Photo)Electrochemistry and Photochemistry. The (photo)electrochemical measurements were generally carried out in a standard three-electrode system, in which a carbon cloth was used as counter electrode and the Ag/AgCl electrode was used as the reference.

The photoinduced anodic current increment and the related cathodic behaviors can be monitored by measuring the disk and ring currents of a rotating ring-disk electrode (RRDE) connected to a CHI 760D electrochemical workstation. To avoid the occurrence of oxygen reduction, the electrolyte (1 M Na₂SO₄) was bubbled with argon. The irradiation for the photoelectrochemical measurements was provided by a Hg-lamp (500 W). To prepare a working electrode, 10 μ L catalyst dispersion was drop-casted onto the precleaned glassy carbon disk electrode and dried naturally. The catalyst dispersion was prepared by dispersing 10 mg TiO₂ (or Sn-TiO₂) into 0.5 mL ethanol containing 200 μ L Nafion (5 %) under sonication. During measurement, the RRDE was rotating at 3600 rpm. To extract the photogenerated electrons, the disk electrode was biased at 0.8 V (vs. Ag/AgCl). The ring electrode was biased at 0.2 V (vs. Ag/AgCl) to monitor the reduction of the photogenerated products from the disk.

The FTO|TiO₂ (FTO|Sn-TiO₂) electrode for voltammetry and OCP measurements can be prepared by depositing the TiO₂ paste onto FTO glass. The TiO₂ paste can be prepared by mixing TiO₂ and PEG (MW: 20000) in aqueous dispersion (20 wt% TiO₂ + 20 wt% PEG + water). FTO|TiO₂ (FTO|Sn-TiO₂) can be obtained by heating the film at 500 °C for 60 min in air.

For the electrode deposited with platinum loaded semiconductor (Pt/TiO₂ or Pt/Sn-TiO₂), 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 μ L 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 cm². The coated FTO glass was then heated at 500 °C for 60 min in air. After that, 20 μ L catalyst dispersion (5 mg Pt/TiO₂ (or Pt/Sn-TiO₂) + 0.5 mL ethanol + 200 μ L Nafion solution (5%)) was deposited onto the compact layer to form the Pt/TiO₂ (or Pt/Sn-TiO₂) electrode.

The photoinduced generation of hydroxyl radicals in a dispersed photocatalytic system was characterized by dispersing 10 mg TiO₂ (or Sn-TiO₂) into 50 mL aqueous solution that contains 0.5 mM terephthalic acid (TA) and 2 mM NaOH. Prior to irradiation, the system was bubbled with argon to remove dissolved oxygen. The irradiation was provided by a Hg-lamp (ultraviolet intensity: 350 mW/cm²; wavelength: 200-400 nm). The generation rate of hydrogen radicals was determined by measuring the photoluminescence intensity of the formed TA-OH on a Hitachi F-7000 FL spectrophotometer.

Photocatalytic Mineralization. The photocatalytic mineralization of phenol was carried out in a fixed bed reactor with a Hg-lamp (PHILIPS, TUV, 30 W/G 30) inside (Figure 7a). Firstly, 2 mL catalyst slurry formed by dispersing 1 g (Sn-)TiO₂ 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. The lamp coated with (Sn-)TiO₂ was placed into the reactor, and the interspace of the reactor and the lamp was filled with 200 mL methanol aqueous solution (20 vol% methanol) containing 2 mg Pt (in H₂PtCl₆ precursor). Platinum can be deposited onto (Sn-)TiO₂ by in situ photoinduced reduction. After 4 h irradiation, the methanol aqueous solution was discharged. Then the reactor was dried by purging with cleaned air for 1 h.

Photocatalytic mineralization was performed by fluxing the phenol aqueous solution (42 mg/L \times 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).