Electronic Supplementary Information

Quantitative analysis of the PtO structure during photocatalytic water splitting by operando XAFS

Yu Hang Li, Chunzhong Li*, Hua Gui Yang*

Experimental methods

Fabrication of photocatalyst.

The PtO/TiO₂ photocatalyst was synthesized according to our previous work (*J. Catal.*, 2015, **330**, 120). In a typical experiment, 50 mg of anatase TiO₂ and 24.6 mg of polymer ligands (polymethyl methacrylate) were added into a screw-neck glass bottle containing chloroplatinic acid solution (5 mL, 0.2 mg/mL). After the suspension becoming uniform by sonication, 0.5 mL of freshly prepared sodium borohydride (NaBH₄) aqueous solution (2 mg/mL) was injected for reducing chloroplatinic acid under vigorously stirring, and another 0.5 mL of freshly prepared NaBH₄ solution was injected after 2~3 hours. The solution was kept stirring for 12 h. The precipitate was separated by centrifuge and washed by deionized water and ethanol for three times. After dried at room temperature, PtO/TiO₂ photocatalyst with clean surface was harvested. The Pt loading amount of the as-prepared photocatalyst can be tested to be 0.5 wt% by inductively coupled plasma atomic emission spectroscopy.

Analytical methods and photocatalyst characterizations.

The crystal structure was determined using X-ray diffraction (XRD; D/MAX 2550 VB/PC). For XRD investigation, 100 mg of powdered sample was studied using a D/MAX 2550 X-Ray Diffractometer with Cu-K α radiation ($\lambda \approx 0.154$ nm) in a 2 θ range from 10 to 80°.

The structure of the catalyst was examined by scanning electron microscopy (S-3400N, 20 kV) and transmission electron microscopy (TECNAI F-30, 300 kV) (*Chem. Eng. J.*, 2017, **307**, 230).

The loading amount of the cocatalysts was tested by inductively coupled plasma atomic emission spectroscopy (ICP-AES, Varian 710ES). 5 mg of sample was firstly dissolved in 2 mL of hot H₂SO₄ solution (98%), and the transparent solution was then dilute to a total volume of 20 mL by adding distilled water.

Pt L₃-edge X-ray absorption fine structure (XAFS) spectra and in-situ analysis were performed at the 1W1B beamline of the Beijing Synchrotron Radiation Facility (BSRF), China, operated at ~200 mA and ~2.5 GeV. Standard Pt foil and PtO₂ powder were used as reference samples. A UV torch (365 nm, average intensity of irradiation is ca. 3.5 mW cm⁻²) was used in operando XAFS analysis to illuminate the equipment during the operando XAFS spectra collection. In preparation for XAFS spectroscopy, 100 mg of photocatalyst sample was affixed to a polyester film attached to a Teflon cell, which can be further filled with distilled water and subjected to light irradiation from UV torch.

After collecting the XAFS spectrum of initial dry photocatalyst (curve 1), the Teflon cell was filled with 1 mL of distilled water by needle tubing, and aged for 10 min for further XAFS spectrum collection (curve 2). After collecting the XAFS spectrum of the photocatalyst in water, the Teflon cell with distilled water was irradiated by the UV torch for 10 min for stabilizing the structure of PtO cocatalyst, and then the XAFS spectrum was collect during UV torch irradiation (curve 3). After that, the UV torch was turn off for 10 min, and the next XAFS spectrum was collect in darkness (curve 4). Then, the photocatalyst was carefully re-dried for the last XAFS spectrum collection (curve 5). The photocatalyst was measured in the fluorescence mode and the reference samples were measured in the transmission mode. We used IFEFFIT software to calibrate the energy scale, to correct the background signal and to normalize the intensity.

Photocatalytic tests.

The photocatalytic water splitting test was carried out in a glass closed-gas-circulation system with a top-irradiation-type reaction vessel (LabSolar H2). The temperature of the reactant solution was maintained at 20 °C by a flow of cooling water during the test. A quantity of 100 mg of photocatalyst that dissolved and precipitated in 10 mL of pure water was added into the reaction vessel for the water splitting test under the illumination of a UV torch. The reactants were sonicated for 10 min for better dispersion and then purged with argon for 5 min to expel the dissolved oxygen. The amounts of evolved hydrogen and oxygen were monitored by an online gas chromatograph (GC2060) equipped with a thermal conductivity detector (TCD) with argon as carrier gas. No air should have remained in the system after evacuation by a vacuum pump.



Fig. S1 Schematic illustration of operando XAFS measurements during photocatalytic water splitting. The sample is fixed on a polyester film over a Teflon cell filled with distilled water under light irradiation from a UV torch.



Fig. S2 The normalized XANES spectra at the Pt L₃ edge (a) and the k^3 -weighted Fourier transform spectra from EXAFS (b) of the Pt foil and PtO₂ as reference samples.



Fig. S3 Experimental EXAFS data of PtO/TiO₂ photocatalyst during the operando XAFS measurements and the corresponding calculated data.



Fig. S4 Experimental k^3 -space EXAFS oscillations as well as their curve-fitting waves (dotted line) of PtO/TiO₂ photocatalyst during the operando XAFS measurements. The notation 1-5 present the initial sample (dry), only addition of solvent, under light irradiation (operating), in darkness (stop light) and used sample (re-dry), respectively.



Fig. S5 Photocatalytic activities for water splitting reaction of PtO/TiO₂ photocatalyst suspended in distilled water. The reactions were performed using 100 mg of samples under light irradiation from a UV torch. Purple and green arrows present that the UV torch was turn off and on, respectively.