

Supporting information

Experimental Detail

Model TiO₂ support was synthesized by hydrothermal method. 60 ml TiCl₄ solutions (0.6 M, in the case of rutile TiO₂,) or TiSO₄(0.6 M, in the case of anatase TiO₂) was charged into a 100 mL Teflon-lined stainless steel autoclave in a heated furnace maintained at 220 °C for 12 hours. After the autoclave apparatus was cooled to room temperature in 2 hours, the product (suspension) was allowed to stand for 24 hours and was filtered after removing the supernatant, washed with water and alcohol several times till PH to 7 and no Cl⁻ or SO₄²⁻ could be detected. The white powder was then dried at 80 °C and calcined at 400 °C for 2 hours. The rutile and anatase TiO₂ is denoted as TiO₂(A) and TiO₂(R) respectively. 2 wt% Pt was deposited on the TiO₂ by wet impregnation method. In a typical process, 1g of TiO₂ powder was mixed with calculated amounts of chloroplatinic acid (H₂PtCl₆, Sinoreagent) in 120 ml water solution, followed by 30 mins ultrasonic dispersion, stirring to dry at 80 °C water bath. Then all catalysts were dried at 120 °C overnight, followed by calcined at 400 °C in air, which is denoted as PtO_x/ (type of TiO₂) for the samples after calcinations and before reduction. The PtO_x/TiO₂ was then reduced in the flow of hydrogen(H₂)/Argon(Ar) (10%) at 400 °C for 4 hours, denoted as Pt/ (type of TiO₂), such as Pt/ TiO₂(R).

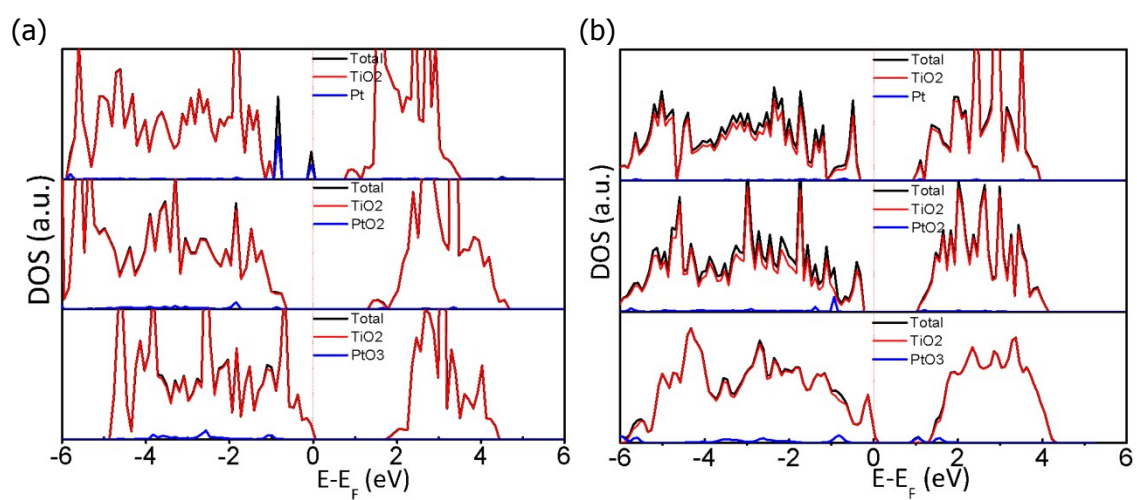


Figure S1 The partial density of state (pdos) of Pt, PtO_2 and PtO_3 cluster adsorption (from top to bottom) on the anatase (a) and rutile (b) TiO_2 surface .

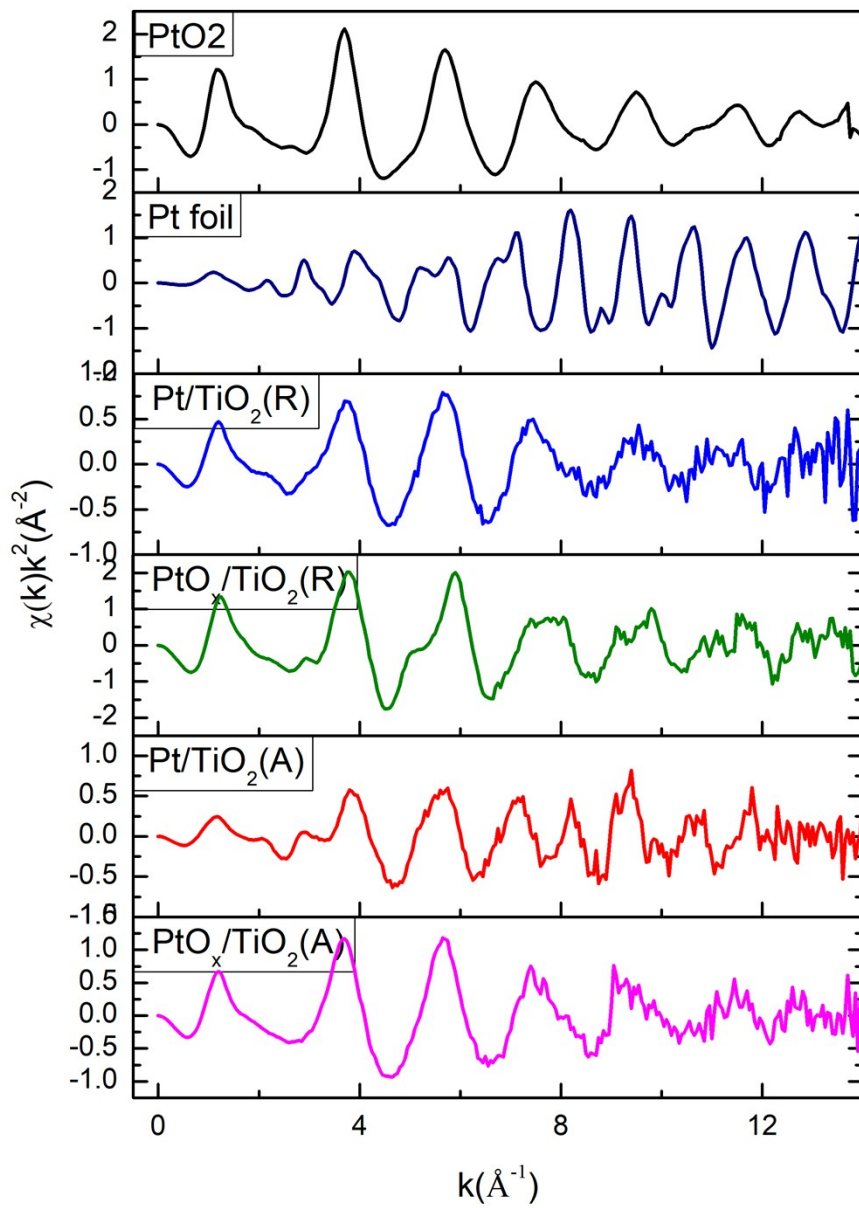


Figure S2 The $\chi(k)$ oscillation of the EXAFS spectrum for Pt/TiO₂

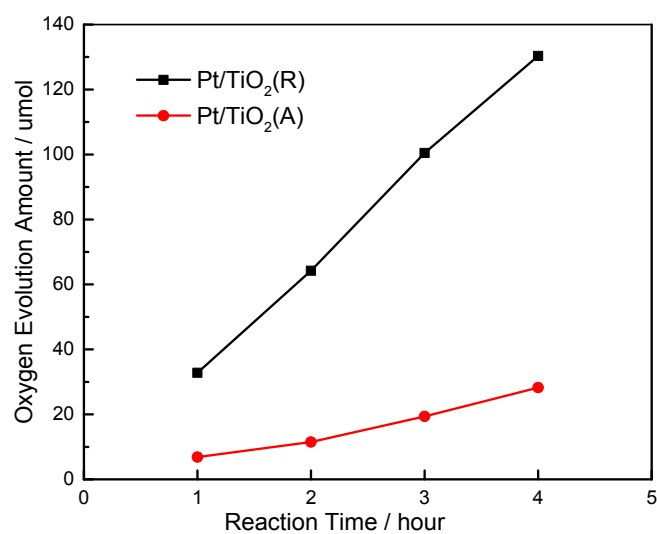


Figure S3 Photocatalytic oxygen evolution activity from water for 2wt% PtO_x/TiO₂(R) and Pt/TiO₂(R). Photocatalytic oxygen evolution reactions were conducted in a Pyrex top-irradiation reactor cell of employing 50 mg of Pt/TiO₂ catalyst dispersed in the mixture of 100 ml 0.02 mol/L AgNO₃ solution at 25 °C for 30 min to equilibrate any adsorption processes in the dark. The reaction cell was then evacuated and irradiated under a 300 W Xe lamp. Evolved gases were analyzed by gas chromatography (GC-9200 equipped with TCD, and 6m x 2 mm x 250 μm MS-5A column).

Table S1. Pt 4f XPS fitted parameters

Catalyst	Pt 4f _{7/2} binding energy / eV ^a	Pt-O-Ti 4f _{7/2} binding energy / eV	PtO 4f _{7/2} binding energy / eV	PtO ₂ 4f _{7/2} binding energy / eV	FWHM ^b / eV	Surface Pt / atom%	Surface Pt-O-Ti / atom%	Surface PtO / atom%	Surface PtO ₂ / atom%
PtO _x /TiO ₂ (A)	70.90	72.10	73.30	74.72	1.38	30.04	52.07	17.89	0
Pt/TiO ₂ (A)	70.90	72.10	73.30	74.72	1.38	73.2	24.54	2.26	0
PtO _x /TiO ₂ (R)	70.90	72.10	73.30	74.72	1.38	0	18.29	0	81.71
Pt/TiO ₂ (R)	70.90	72.10	73.30	74.72	1.38	8.98	20.71	70.31	0

^a Peak position followed :4f 5/2=4f 7/2+3.35; Peak area followed :4f 5/2=0.75*4f 7/2;

^b Common FWHM adopted for all Pt components.