Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supporting Information

Cl^- making the overall water splitting possible on TiO_2-based photocatalysts

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1. Experimental

1.1 Sample preparation.

Commercialized P25 was purchased from Degussa. A hydrothermal method was applied to make the chloride ion closely be adsorbed on the surface of TiO_2. In a typical process, desired volumes of HCl (38 %) were added dropwise to 15 mL of $Ti(OBu)_4$ (98%, Alfa) in a 100mL Teflon-lined stainless steel autoclave. The solution was then heated to180℃ and kept at the temperature for 36 h. When the solution was naturally cooled to room temperature, the obtained white products were connected by centrifugation at 10,000 rpm and washed several times with a mixture of ethanol and deionized water. The obtained products were dried in air at 105 ℃ for 12h and kept for further use. The obtained TiO_2 was in the form of rutilephase and denoted as Cl-TiO_2.

1.2 Characterization

X-ray photoelectron spectra (XPS) were obtained on an X-ray photoelectron spectroscopy (ESCALAB 250Xi, Thermo) equipped with a monochromatized Al Kα X-ray (hν = 1486.6 eV) and an electron flood gun. The samples were washed for three times by acetone and dried in vacuum before test. X-ray diffraction (XRD) analysis was carried out on an X-ray diffractometer (Rigaku; Mini-Flex diffractometer) using Cu Kα as radiation source, the applied current and voltage were 30 mA and 40 kV, respectively. UV-vis spectrum was detected on V-650 UV/VIS spectrometer (JASCO), scanning range, 200-800 nm, scanning rate, 200 nm/min.

1.3 Photocatalytic reaction

The photocatalytic reactions were carried out in a Pyrex reaction cell connected to a closed gas circulation and evacuation system. Typically, 0.050 g of TiO_2 sample was dispersed in 100 ml deionized water by sonication treatment. Desired amount of H_2PtCl_6 (or $RhCl_3$) solution was added dropwise in the solution for Pt (Rh) loading. The solution was then degassed for 30 min, followed by irradiation with a 300 W Xe lamp (ILC technology; CERAMAX LX-300). The reactant solution was stirred and maintained at room temperature by a flow of cooling water during the photocatalytic reaction. The amount of evolved H_2 and O_2 were determined with on-line gas chromatography (Tianmei; GC 7890, MS-5 A column, TCD, Ar Carrier).

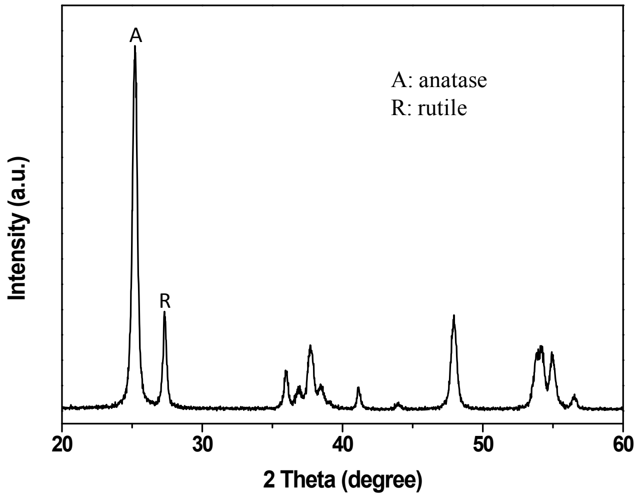

Figure S1. XRD patterns of the used P25 sample. It shows the mixed phases of anatase and rutile, which indicates the typical characteristics of standard sample of commercial P25.

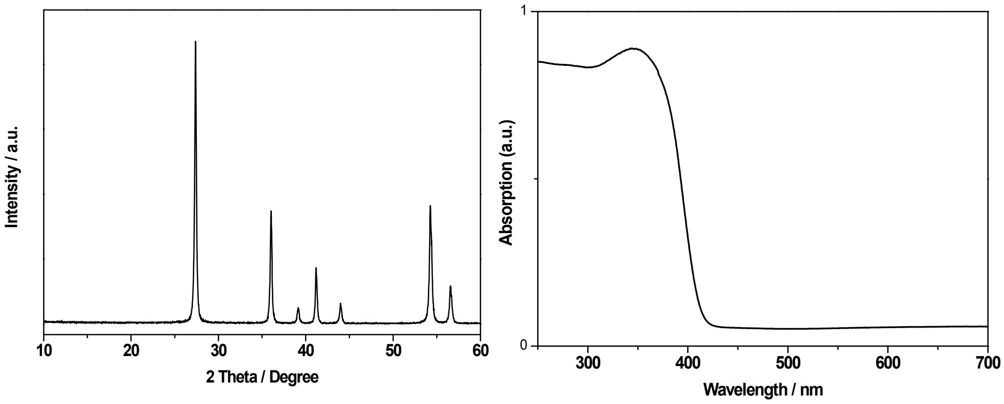

Figure S2. The XRD patterns (a) and UV-Vis reflection spectra (b) of prepared Cl-TiO_2.

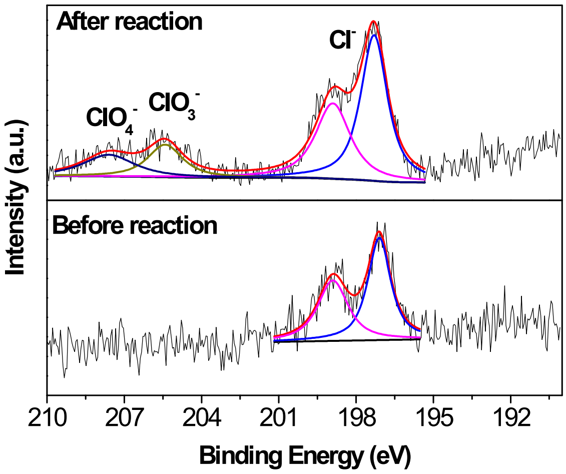

Figure S3. The XPS spectra of Cl 2p on Cl-TiO_2 (washed for 2 times) before and after photocatalytic water splitting reactions.

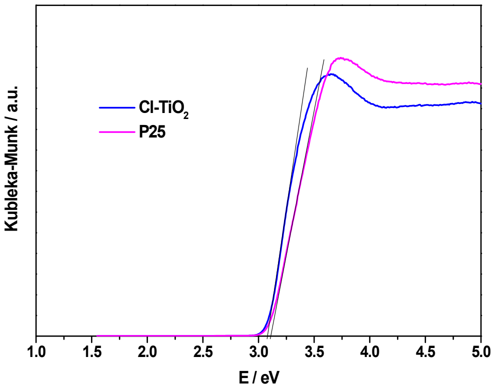

Figure S4. The kubelka-Munk function for P25 and Cl-TiO$_2$ samples.

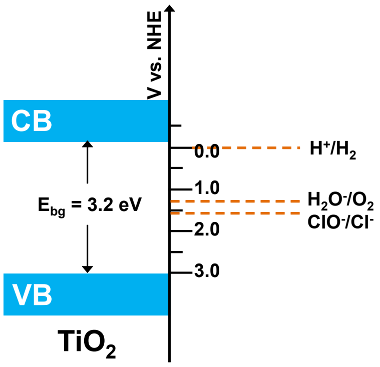

Figure S5. The corresponding energy level diagram for ClO^-/Cl^-.