Supplementary Material (ESI) for Energy & Environmental Science

Supplementary Information

Hydrogen producing water treatment through solar photocatalysis

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Experimental Details

Materials. Pt deposition on the surface of TiO_2 (Degussa P25) was done by the photocatalytic reduction of chloroplatinic acid (Pt content = 3.7 wt%) in the presence of methanol as an electron donor. For the fluorination of the TiO_2 surface, 10 mM NaF was added into the aqueous suspension of TiO_2 (or Pt/TiO_2) and then pH was adjusted to 3.0 to maximize the fluoride adsorption. The coexistence of Pt and F on the surface of TiO_2 powder that was prepared by the above procedure was confirmed by X-ray photoelectron spectroscopy (XPS, Kratos XSAM 800 pci) using Mg KR lines (1253.6 eV) as an excitation source.

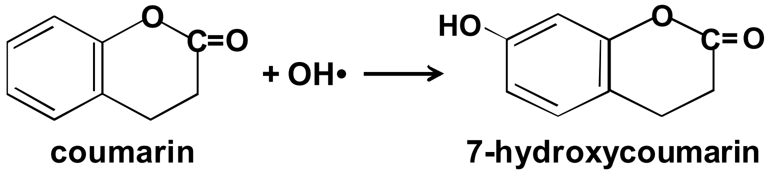
Photocatalytic Experiments. The catalyst powder was dispersed in distilled water (0.5 g L^{-1}) by sonication for 30 seconds in an ultrasonic cleaning bath. An aliquot of the substrate stock solution was subsequently added to the suspension to give the initial substrate concentration of 300 μM and then the pH of the suspension was adjusted to 3.0 with perchloric acid solution. The suspension was equilibrated for 30 min in the dark before the light irradiation. Photoirradiation employed a 300-W Xe arc lamp (Oriel) as a light source. Light passed through a 10-cm IR water filter and a UV cutoff filter ($\lambda > 300$ nm), and then the filtered light was focused onto a 30-mL glass reactor with a quartz window which is closed with a rubber septum. The incident light intensity ($300 \text{ nm} < \lambda < 500 \text{ nm}$) was measured by using ferrioxalate actinometry[1] and estimated to be about 2.3 × 10^{-3} einstein min^{-1} L^{-1} (3.0 × 10^{-3} einstein min^{-1} L^{-1} in Figure 2 experiment).

The outdoor tests were carried out on the roof of the Environmental Engineering building at POSTECH (Pohang, Korea: 36°N latitude) between 9 AM and 5 PM under clear or partly cloudy sky condition in August. The solar light intensity was recorded every 1 min by using pyranometer (apogee, PYR-P) and a daily average varied from 63 to 69 mW cm^{-2}. The ambient temperature ranged between 26.2 and 34.5 ^{o}C. A flat circular quartz reactor (diameter 5.5 cm, volume 40 mL) was used for the outdoor tests.

To remove dissolved oxygen, N_2 was purged for 30 min prior to irradiation. Sample aliquots were withdrawn intermittently from the irradiated reactor and filtered through a 0.45 μm filter for the analysis of substrates and intermediates. The degradation of 4-CP and BPA was monitored using a high performance liquid chromatograph (HPLC, Agilent 1100 series) equipped with a diode array detector and a ZORBAX 300SB C-18 column (4.6 mm × 150 mm). Quantification of Cl^- was performed by using an ion chromatograph (IC, Dionex DX-120) equipped with a conductivity detector and a Dionex IonPac AS-14 (4 mm × 250 mm) column. The amount of hydrogen in the headspace of the reactor was analyzed using a gas chromatograph (GC, HP6890A) equipped with a thermal conductivity detector and a molecular sieve 5A column. CO_2 and CO were measured using the GC equipped with a flame ionization detector and a porapak column N. The total organic carbon (TOC) of organic substrates was measured using a TOC analyzer (TOC-VCSH, Shimadzu).

An isotope experiment was carried out with using deuterated phenol (99atom% D, Aldrich) and BPA (98atom% D, ISOTEC^{TM}), and analyzed by using a quadrupole mass spectrometer (QMI 422, Pfeiffer Vacuum).

The OH radical generation in the irradiated suspensions of photocatalysts was monitored by measuring the fluorescence of 7-hydroxycoumarin resulted from the reaction between OH radical and coumarin (eq S1).[2] Fluorescence intensity was recorded at the emission wavelength of 460 nm using a Shimadzu RF-5301PC spectrofluorophotometer with the excitation wavelength of 332 nm.



(S1)

Photoelectrochemical Experiment. Open-circuit potentials (E_{oc}) were measured with a catalyst-coated FTO (fluorine-doped SnO_2, Pilkington) electrode immersed in an aqueous electrolyte solution (10 mM $LiClO_4$). For preparing the catalyst/FTO electrode, a FTO plate was coated with TiO_2 (or Pt/TiO_2) film using Carbowax as a binder.[3] The TiO_2 (or Pt/TiO_2) coated FTO plate was then dried for 30 min in air and calcined at 450 °C for 30 min to burn off the organic binder. For the fluorination, the catalyst/FTO electrode was immersed in 10 mM NaF (pH = 3.0) for 30 min and then dried. The catalyst/FTO electrode, a saturated calomel electrode (SCE), and a graphite rod were immersed in a reactor as a working (collector), a reference, and a counter electrode, respectively. E_{oc} was stabilized under irradiation and its decay was monitored as a function of time upon turning off the light in the absence and presence of 4-CP (300 μM) using a potentiostat (EG&G 263A2) connected to a computer. Other experimental conditions were identical to those of the above photocatalytic experiments except for reactor volume = 9 mL and continuously N_2 purged.

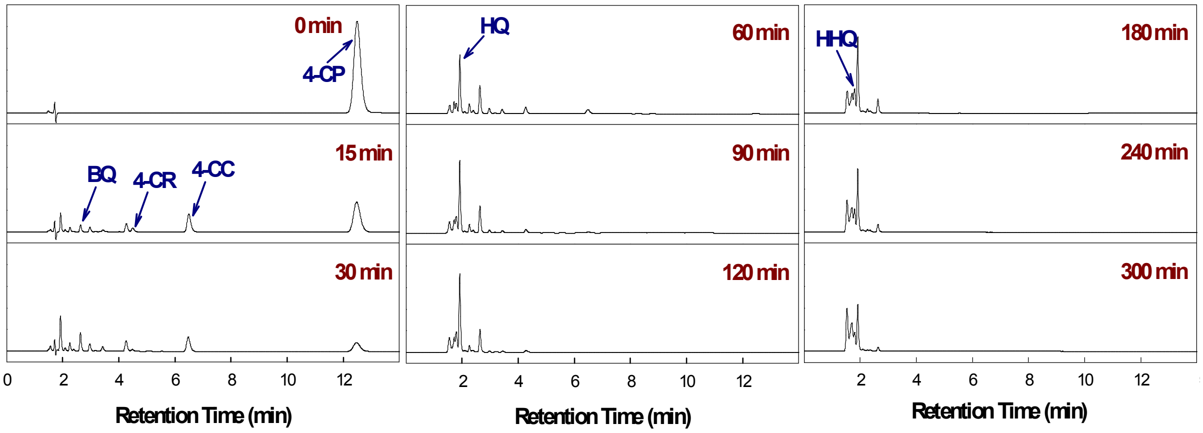


Fig. S1. Intermediates generated from the anoxic photocatalytic degradation of 4-CP on F-TiO_2/Pt. (4-CP: 4-chlorophenol, 4-CC: 4-chlorocatechol, 4-CR: 4-chlororesorcinol, BQ: benzoquinone, HQ: hydroquinone, HHQ: hydroxyl-hydroquinone)

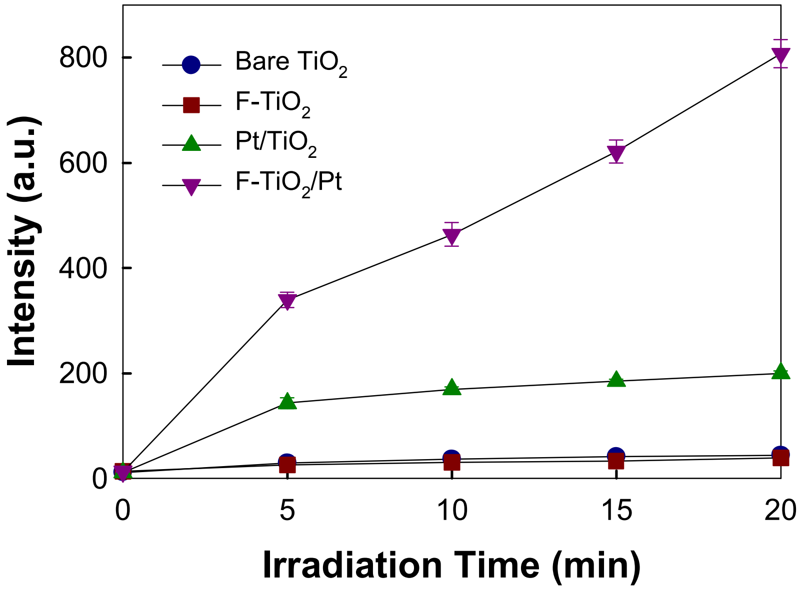


Fig. S2. Photocatalytic production of OH radical in aqueous suspensions of bare TiO_2, F-TiO_2, Pt/TiO_2 and F-TiO_2/Pt under irradiation. The ordinate axis represents the fluorescence intensity of 7-hydroxycoumarin that resulted from the reaction between OH radical and coumarin. Experimental conditions were: [catalyst] = 0.5 g L^{-1}, [NaF] = 10 mM (for F-TiO_2 and F-TiO_2/Pt), [coumarin] = 1 mM, reactor volume 30 mL, pH_i = 3.0, $\lambda > 300$ nm, continuously N_2 purged during irradiation.

References

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3. A. Mills, N. Elliott, G. Hill, D. Fallis, J. R. Durrant and R. L. Willis, *Photochem. Photobiol. Sci.*, 2003, **2**, 591.