

Electronic Supplementary Information

Low-cost sensitizer based on phenolic resin for charge-transfer type photocatalyst working under visible light

Guan Zhang and Wonyong Choi*

School of Environmental Science and Engineering, Pohang University of Science and Technology (POSTECH), Hyoja-dong, Pohang, 790-784, Republic of Korea

I. Experimental procedure

Materials: TiO₂ powder (Degussa P25), a mixture of anatase and rutile (8:2) with a BET surface area of 50 m²g⁻¹ and primary particle size of 20-30 nm, was used as a base catalyst material. Phenol (Aldrich, 99.5% redistilled), formaldehyde solution (Aldrich, 37%), oxalic acid (Aldrich, >98%) sodium fluoride (Aldrich, >99%), sodium sulfide (Aldrich), Poly ethylene glycol (Aldrich, molecular weight 2,000)

Synthesis of novolac resin: The novolac type phenolic formaldehyde resin was synthesized by reacting phenol with formaldehyde in the presence of acid catalyst according to the literature method (Polymer 2002, 43, 2609). Briefly, phenol (2 g), 37% formaldehyde solution (1.3 ml), oxalic acid (49 mg) with the molar ratio of P: F: O = 1.25: 1: 0.025 were used as starting materials. First, phenol was melted in a 10 ml reactor in a hot water bath. The oxalic acid catalyst was charged into reactor and kept stirring for 30 min, and then the formaldehyde solution was added drop-wise to it. The reaction mixture was refluxed for 6 h under stirring at 90 °C. The sticky resin was first washed with small amounts of hot water several times, then dissolved in acetone and re-precipitated in water to remove the unreacted phenol and catalyst. Finally, the white-colored resin after separation from water was dried under vacuum at 50 °C for 10 h. The final PR product is transparent and yellowish.

Grafting of novolac PR resin onto TiO₂ surface (PR/TiO₂): Bare TiO₂, surface platinized TiO₂ (TiO₂@Pt) and surface fluorinated and platinized TiO₂ (F-TiO₂@Pt) for the H₂ production were used as base materials for PR grafting.

Surface fluorinated TiO₂ (F-TiO₂) was prepared by adding 10 mM NaF to an aqueous TiO₂ suspension. The TiO₂ suspension was refluxed at 90 °C for 20 h, and the water was removed by using vacuum evaporator. The collected powder was dried overnight and re-suspended in water for 30 min to remove unattached fluorine ions. Finally, the F-TiO₂ powder was collected by filtration and dried in the air.

Platinized TiO₂ (TiO₂ and F-TiO₂) with a typical Pt loading of 0.1 wt% was firstly prepared by photodeposition method. A 500 ml TiO₂ (0.5 gL⁻¹) suspension with 20 ml methanol as electron donor and 0.263 ml of 2 gL⁻¹ chloroplatinic acid (H₂PtCl₆) was irradiated with a 200 W mercury lamp for 30 min. After irradiation, Pt-deposited TiO₂ powder was filtered, washed with D.I. water, and dried under air.

In the surface complexation process, typically 0.3 g platinized TiO₂ powder was dispersed in 200 ml acetone and sonicated for 15 min, then a calculated amount of PR resin (PR/TiO₂ = 0.5 wt.%, 2 wt.%, 5 wt.%, 10 wt.%, 20 wt.%) was added, the suspension was immediately changed to yellow color within 5 s. The suspension was further refluxed at 50 °C for 20 h to get uniform dispersion of PR. The acetone solvent was removed under elevated temperature (80 °C), and the final powder was dried under vacuum at 50 °C. After drying, the brownish powder of PR/TiO₂ was obtained. The PR grafted TiO₂ samples were denoted according to the loading content of PR (e.g., 10 wt.% designed as 10%PR/TiO₂). The 10 wt.% PR grafted bare TiO₂ (10%PR/TiO₂) and F-TiO₂ (10%PR/F-TiO₂) samples were also prepared in the same way. For comparison, 10 wt.% phenol complexed platinized TiO₂ (10%Ph/TiO₂) was also prepared in the same way. The representative structures of surface complexed TiO₂

samples are shown in Scheme 1.

Photocatalytic activity test: For the hydrogen generation test, sample powder was dispersed in D.I. water ($[\text{TiO}_2] = 0.5 \text{ gL}^{-1}$) with various electron donors (Na_2S , CH_3OH , Na_2SO_3 , triethanolamine (TEOA)). A 300-W Xe arc lamp (Oriental) was used as a light source. Light pass through a 10 cm^{-1} IR water filter and a UV cutoff filter ($\geq 420 \text{ nm}$), and then the filtered light was focused onto a 55 ml Pyrex glass reactor (25 ml headspace) which was sealed with a rubber septum. The incident light intensity ($420 \text{ nm} \leq \lambda \leq 645 \text{ nm}$) was determined to be about 200 mW/cm^2 . The suspension was deaerated by Ar purging 30 min before irradiation. The amount of H_2 was monitored using a HP6890 A GC equipped with a TCD detector. For the degradation of 4-chlorophenol (4-CP) test, sample powder (bare TiO_2 and PR/ TiO_2) was dispersed in distilled water (1g/L). An aliquot of the 4-CP stock solution was subsequently added to the suspension to give a desired concentration of $20 \mu\text{M}$, and then the visible light ($\geq 420 \text{ nm}$) was irradiated to the Pyrex reactor after 30 min stirring in dark. Sample aliquots were withdrawn from the reactor intermittently during the illumination and filtered through a 0.45 μm PTFE syringe filter. The degradation of 4-CP was monitored using a high performance liquid chromatograph (Agilent 1100 series). For the multi-cycle tests, ca. $20 \mu\text{M}$ 4-CP was recharged into reactor in the beginning of each cycle.

Photocurrent measurement: The photocurrent was measured with the catalyst (PR/ TiO_2 and bare TiO_2) deposited electrodes. The electrodes were prepared over a transparent conducting substrate (F: SnO_2 (FTO) Pilkington, 15 Ω/square). P25 nanopowder of 0.4 g was mixed with 2 ml solution of polyethylene glycol (15g) and water (15 ml). The mixture was ground for 2-3 minutes until a homogeneous sticky dispersion was obtained. Then some drops of the milky slurry were spread by the doctor blade method over a transparent FTO, defining an approximate area of $1.5 \times 1.5 \text{ cm}^2$. Finally, the electrode was dried in open air and subsequently heated at $450 \text{ }^\circ\text{C}$ for 1 h for sintering and burning out the organic binder. For attaching the PR resin onto TiO_2 surface, the as-prepared TiO_2 electrode was immersed into 10 ml acetone solution containing 10 mg and 50 mg PR resin for 1 min, and then dried in air. After drying for several hours, the color of immersed electrodes changed to yellowish. The PR contents loaded onto TiO_2 electrodes were measured by a gravimetric method. According to the mass ratio of PR to TiO_2 , the as-prepared electrodes were designed as 15%PR/ TiO_2 and 30PR/ TiO_2 , respectively.

A coiled Pt wire, standard Ag/AgCl/ KCl(3.5 M) electrode, and a TiO_2 deposited FTO electrode were used as a counter, reference and working electrode, respectively. An aqueous solution of 50 mM Na_2S was used as electron donor and Ar gas was continuously purged into the aqueous solution. Photocurrents were collected by applying a potential (0 V vs Ag/AgCl) to the working electrode using a potentiostat (Gamry Reference 600) connected to a computer.

Cyclic voltammetry (CV) experiments for as-prepared PR were performed using a potentiostat (Gamry, Reference 600). FTO glass, coiled Pt wire and Ag/AgCl were used as the working, counter, and reference electrodes, respectively. The CV experiment was performed using these three electrodes immersed in a solution of 0.1 M tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) in anhydrous acetonitrile at room temperature under argon purging with scan rates of 20 mV/s and 50 mV/s.

Characterization of Catalyst: UV-visible absorption spectra were recorded on a UV-vis spectrometer (Shimadzu UV-2401PC). Fourier transform infrared spectroscopy (FT-IR) was recorded with pelletized samples on FT-IR spectrophotometer (Bome, MB104). Each sample was mixed with KBr powder and compressed to a thin disk with a high-pressure pelletizer (Carver). High resolution transmission electron micrographs (HR-TEM) were recorded using a JEOL JEM-2200F microscope with Cs-corrected. The gel permeation chromatography (GPC) measurement determined the molecular weight (M_n and M_w) of the PR. The GPC column system was calibrated with polystyrene standards. The tetrahydrofuran (THF) was used as the solvent to dissolve PR powder. ^{13}C -NMR (125 MHz) spectrum was obtained on a JEOL ECA 500 spectrometer. Chemical shifts for ^{13}C NMR were reported

as δ , parts per million, relative to the center line signal of the CDCl_3 triplet at 77.0 ppm. X-ray photoelectron spectra (XPS, Kratos XSAM 800pci) of TiO_2 and PR/ TiO_2 powders were obtained using the Mg $K\alpha$ line (1253.6 eV) as the excitation source.

II. Experimental results

Scheme S1. Synthetic process of novolac type phenolic resin from phenol and formaldehyde

Fig. S1 GPC trace profile of as-prepared PR

Fig. S2 FT-IR spectrum of as-prepared PR and assignment of absorption peaks

Fig. S3 C^{13} -NMR spectrum of as-prepared PR and assignment of chemical shifts

Fig. S4 FT-IR spectra of bare TiO_2 , PR and as-prepared PR/ TiO_2 samples

Fig. S5 TEM and EELS mapping images of bare TiO_2 sample

Fig. S6 XPS spectra of bare TiO_2 and as-prepared PR/ TiO_2 samples

Fig. S7 Electron donor effect on H_2 production under visible light ($\lambda \geq 420$ nm) with 0.5%PR/ TiO_2 catalyst

Fig. S8 PR loading effect on H_2 production with 50 mM Na_2S ($\lambda \geq 420$ nm)

Fig. S9 (a) j_{ph} generated under visible light illumination ($\lambda \geq 420$ nm) on bare TiO_2 and PR/ TiO_2 electrodes. (b) j_{ph} as a function of the irradiation wavelength. All photocurrents were collected by applying a potential (0 V vs Ag/AgCl) to the working electrode. An aqueous solution of 50 mM Na_2S was used as electron donor and Ar gas was continuously purged into the aqueous solution.

Fig. S10 CV measurement of HOMO and LUMO levels of as-prepared PR and phenol : (a) as-prepared PR in a scan rate of 20 mV/s; (b) as-prepared PR in a scan rate of 50 mV/s; (c) phenol in a scan rate of 20 mV/s; (d) phenol in a scan rate of 50 mV/s.

Scheme S1. Synthetic process of novolac type phenolic formaldehyde resin from phenol and formaldehyde

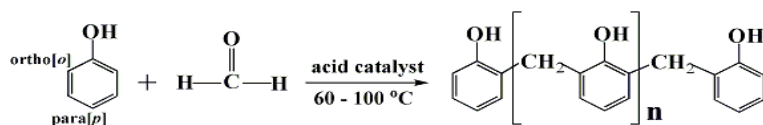


Fig. S1 GPC profile of as-prepared PR

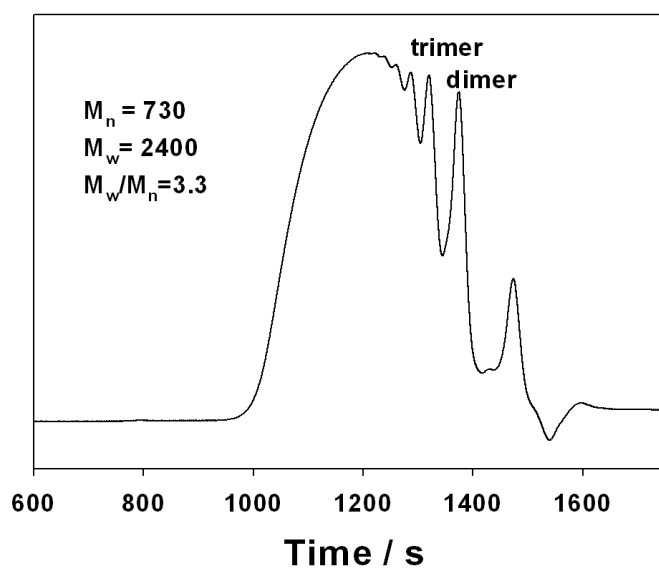
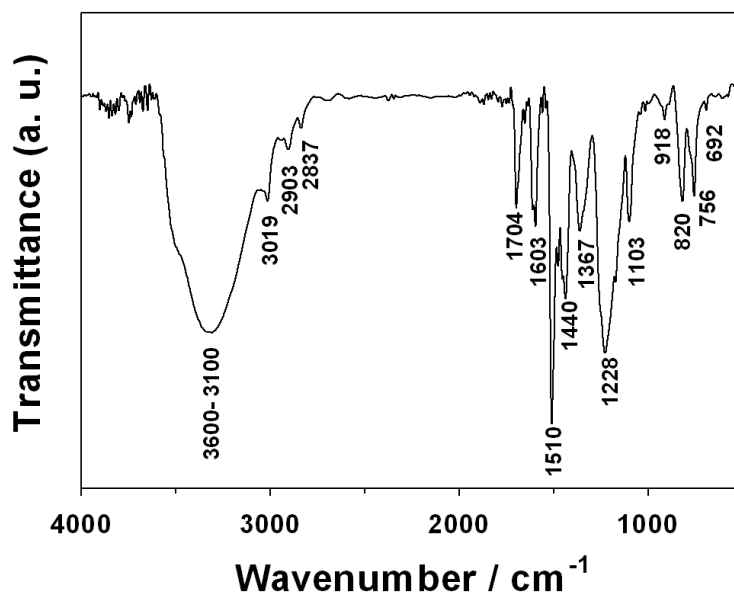


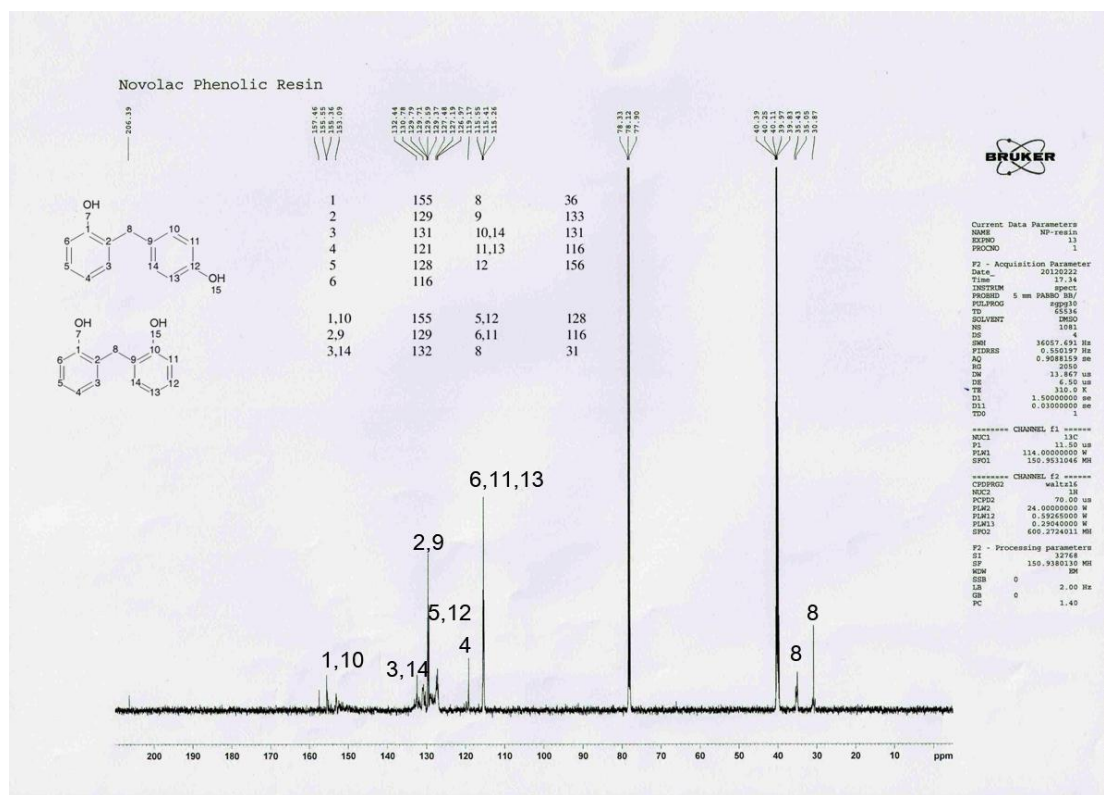
Fig. S2 FT-IR spectra of as-prepared PR and the assignment of IR absorption peaks



IR Band (cm ⁻¹)	Chemical functional group
692	Phenol with 5 adjacent free H atoms
756	Phenol with 4 adjacent free H atoms(o-substituted)
820	Phenol with 2 adjacent free H atoms (p-substituted)
918	o,p-substituted phenol
1103	Aromatic C-H in plane deformation
1228	Phenolic C-O stretch
1367	Phenolic OH in plane deformation
1440	CH ₂ banding
1510	C=C stretch for Phenolic ring
1603	C=C stretch for Phenolic ring
2980-2820	Aliphatic C-H stretch
3019	Aromatic C-H stretch
3600-3100	OH stretch from phenol

The middle region of 1100 cm⁻¹ ~ 1700 cm⁻¹ are related with the aromatic C-H plane deformation, phenolic C-O stretch, phenolic OH plane deformation, C=C stretch for phenolic ring. While the bands at 3000 cm⁻¹ ~ 3600 cm⁻¹ are corresponding to the aliphatic and aromatic C-H stretch, and OH stretch from phenol.

Fig. S3 C^{13} -NMR spectrum of as-prepared PR and the assignment of chemical shifts



The average resonance positions in ^{13}C -NMR spectrum of as-prepared PR sample are well matched with those of standard phenolic model compounds.

Fig. S4 FT-IR spectra of bare TiO_2 , PR and as-prepared PR/ TiO_2 samples

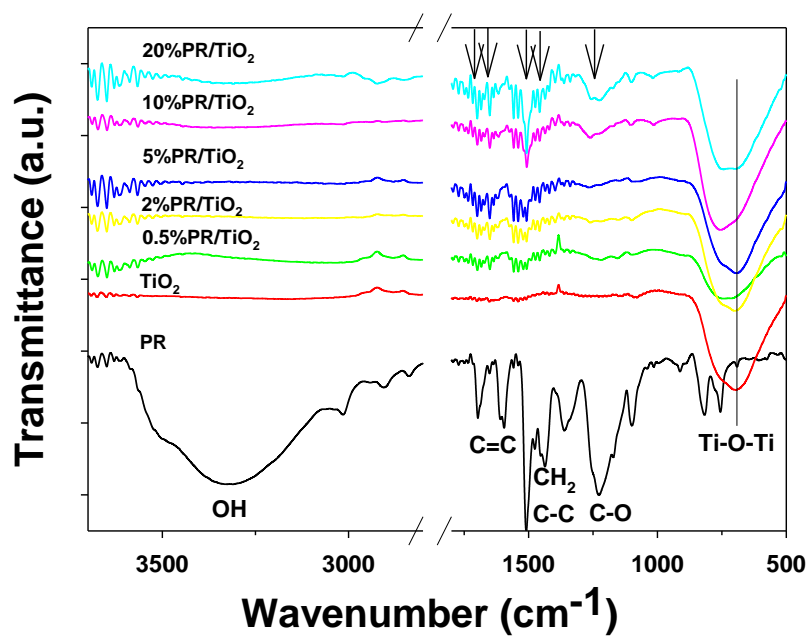


Fig. S5 TEM and EELS mapping images of bare TiO_2 sample

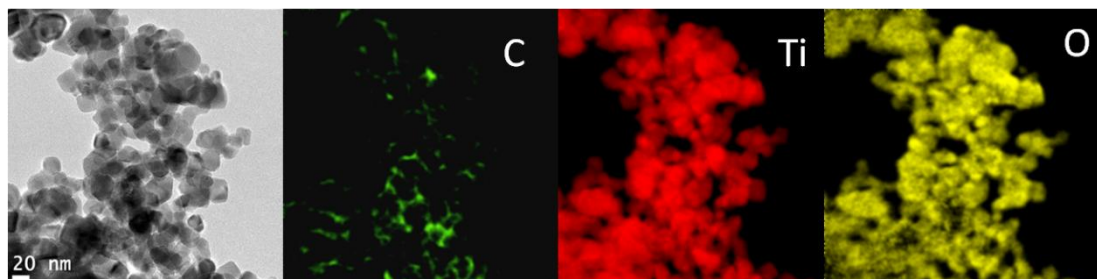


Fig. S6 XPS spectra of bare TiO_2 and PR/ TiO_2 sample

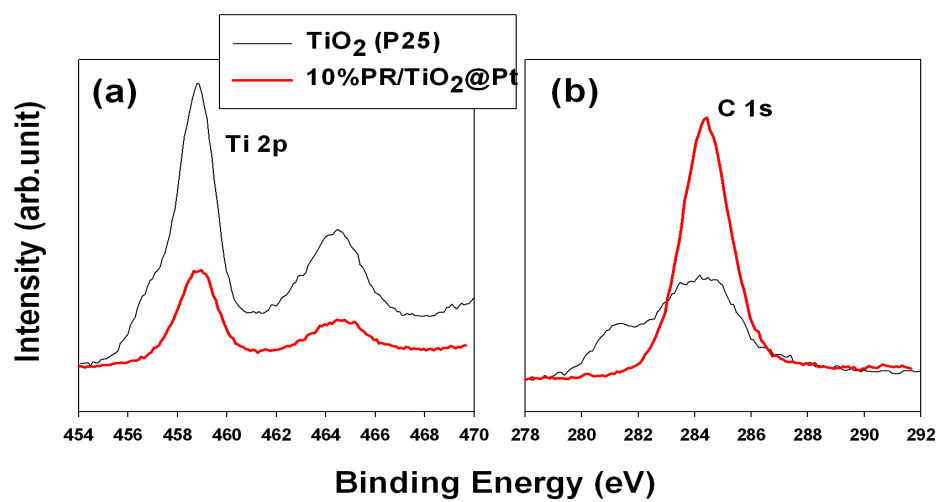


Fig. S7 Electron donor effect on H₂ production under visible light ($\lambda \geq 420$ nm) with 0.5%PR/TiO₂ catalyst

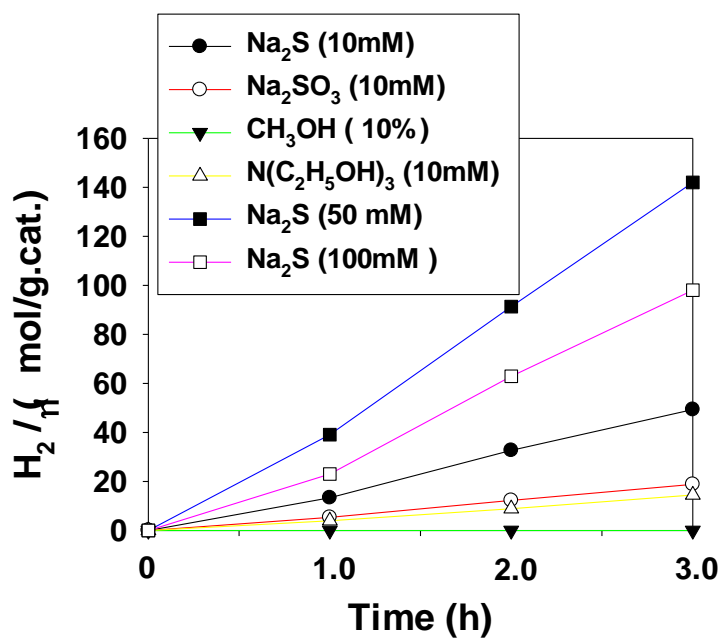


Fig. S8 PR loading effect on H₂ production with 50 mM Na₂S ($\lambda \geq 420$ nm)

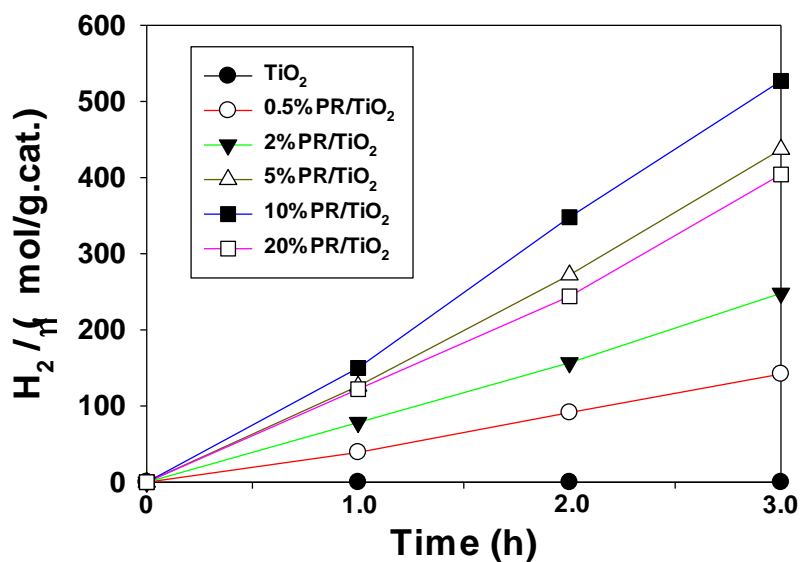


Fig. S9 (a) j_{ph} generated under visible light illumination ($\lambda \geq 420$ nm) on bare TiO_2 and PR/ TiO_2 electrodes. (b) j_{ph} as a function of the irradiation wavelength. All photocurrents were collected by applying a potential (0 V vs Ag/AgCl) to the working electrode. An aqueous solution of 50 mM Na_2S was used as electron donor and Ar gas was continuously purged into the aqueous solution.

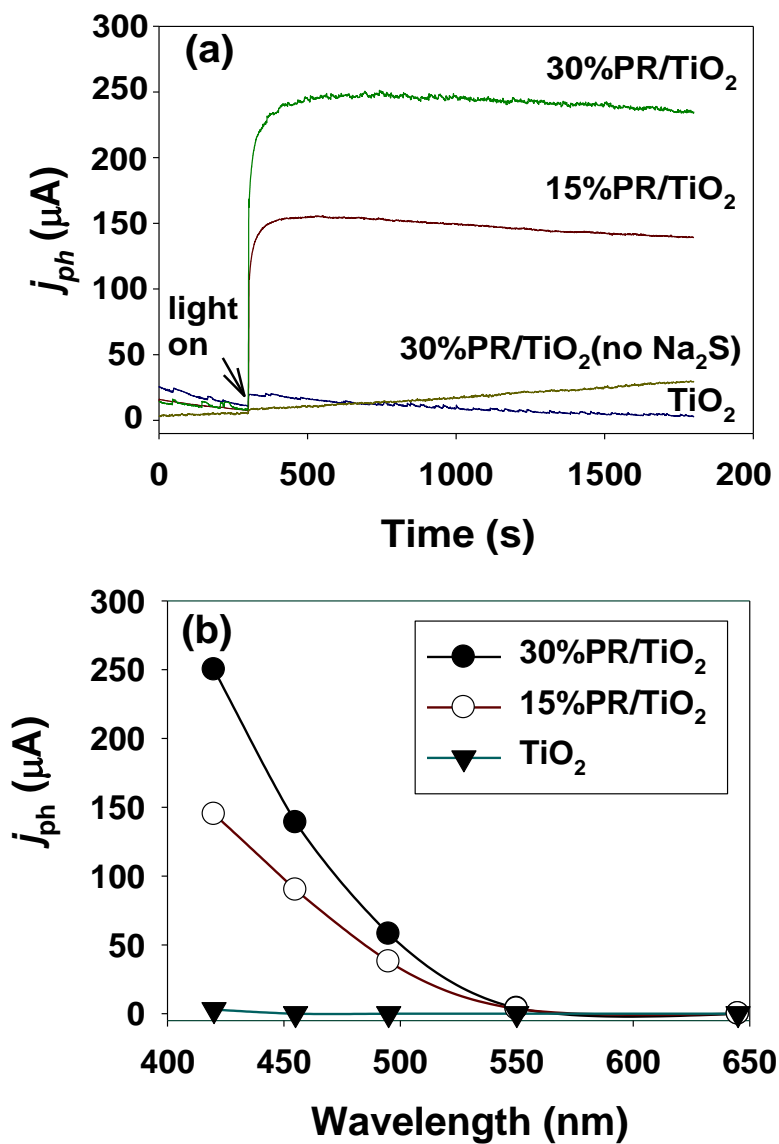
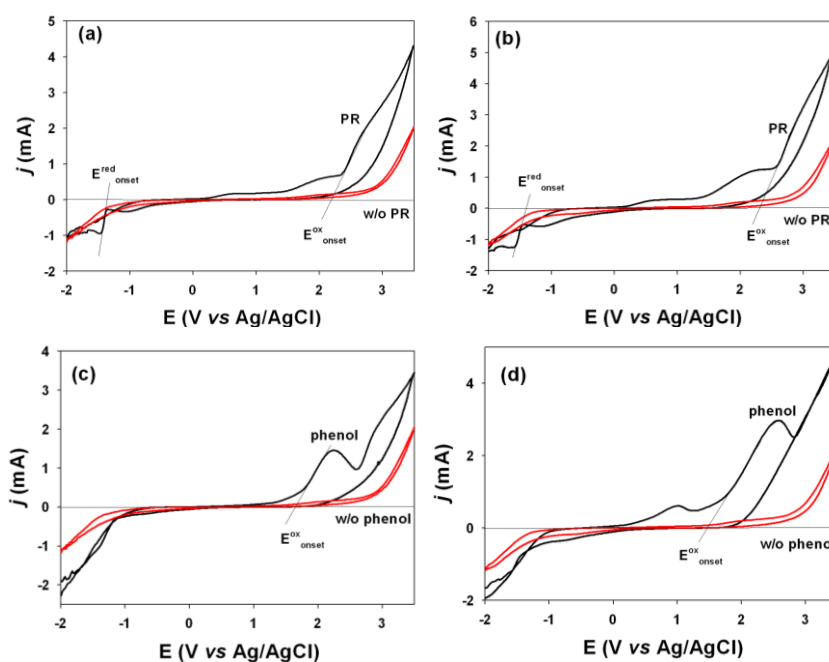


Fig. S10 CV measurement of HOMO and LUMO levels of as-prepared PR and phenol: (a) as-prepared PR in a scan rate of 20 mV/s; (b) as-prepared PR in a scan rate of 50 mV/s; (c) phenol in a scan rate of 20 mV/s; (d) phenol in a scan rate of 50 mV/s



Scan rate	E^{red} (eV)	E^{ox} (eV)	HOMO (eV)	LUMO (eV)	E_{BG} (V)
20 mV/s	-1.3	2.1	-6.5	-3.1	3.4
50 mV/s	-1.3	2.3	-6.7	-3.1	3.6
average	-1.3	2.2	-6.6	-3.1	3.5

The cyclic voltammetry (CV) measurement was conducted to determine the HOMO and LUMO levels of as-prepared PR. The HOMO and LUMO levels can be estimated according to onset values by taking the intersection point between the baseline and the tangent line drawn to the rising portion of the current and according to the following equation:^{R1}

$$E_{\text{LUMO}} = -(E'_{\text{red}} + 4.4) \text{ eV};$$

$$E_{\text{HOMO}} = -(E'_{\text{ox}} + 4.4) \text{ eV}$$

Where E'_{red} and E'_{ox} are onset reduction and oxidation potentials versus the Ag/AgCl reference electrode.

The oxidation peaks prior to PR oxidation in (a) and (b) are ascribed to the phenol oxidation as evidenced by the CV measurement of phenol in (c) and (d).

Reference:

[R1]: Admassie, S.; Ingnas, O.; Mammo, W.; Perzon, E.; Andersson, M. R. *Synth. Met.* **2006**, *156*, 614.