Electronic Supplementary Information (ESI):

Enhancement of photochemical hydrogen evolution over Pt-loaded hierarchical titania photonic crystal

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Experimental section:

Synthesizing Procedure. In a typical synthesis, tetrabutyl titanate was dissolved in ethyl alcohol with stirring for 1 hour. Then certain amount of acetic acid, hydrochloric acid and ethyl alcohol were mixed homogenously and followed with adding dropwize into the above solution and stirred for another 3 hours. Thus, the molar ratio of ethyl alcohol, tetrabutyl titanate, hydrochloric acid, acetic acid in the precursor sol was 10:1:0.7:0.6. Before the P(St-MMA-AA) colloidal crystal films[s1] were infiltrated with TiO_2 precursor through dip-coating method, the films were annealed at 80 °C for half an hour. The as-infiltrated films were left to dry and subsequently programmed to 450 °C at a ramp rate of 1 °C /min and calcined for 4 hours to remove the colloidal crystal templates.

For photodeposition of platinum nanoparticles, 10 mg of i-TiO_2 PC segments scrapped from the substrate was suspended in a mixture of 20% (v/v) aqueous methanol containing certain amount of $H_2PtCl_6 \cdot 6H_2O$ aqueous solution. The suspension was thoroughly flushed with nitrogen to remove oxygen and CO_2. The reaction mixture was irradiated with a Xenon lamp. After reaction, the product was collected by filtration, washed twice with 10 ml aliquots of water, and stored in fresh 20% (v/v) methanol aqueous solutions for further uses.

Photocatalytic Water Splitting. The photosplitting of water was performed in LabSolarH2 system. Prior to use, the reaction setup was vacuumed and should be air-free. The stirred mixture containing PC segments and methanol aqueous solution in the quartz reaction cell was successively irradiated for 8 hours with periodic detection

of gaseous samples every 2 hours. Gaseous samples were analyzed with a Techcomp gas chromatograph employing a molecular 60/80 sieve 5A column with Ar gas the carrier gas and a thermal conductivity detector.

The quantum yield (QY) was measured under the same photocatalytic reaction condition with irradiation light by using 500 W Xe lamp, and the QY was calculated according to Eq. (1):

$$\text{QY [\%]} = \frac{\text{number of reacted electrons}}{\text{number of incident photos}} \times 100$$

$$= \frac{\text{number of evolved H2 molecules} \times 2}{\text{number of incident photos}} \times 100 \quad (1)$$

The number of incident photos was $6.9 \cdot 10^{17}$ photons/s.

Characterization. SEM images were taken by JEOL FE-SEM 6700F microscopy operating at 3.0 kV. TEM images were obtained on a JEOL JEM-2010 transmission electron microscope operating at 200 kV. Samples obtained by scratching the films from the substrate for TEM measurements were dispersed in ethanol. Carbon coated copper grids were used as the sample holder. XRD patterns were collected on a Rigaku D/MAX 2500 X-ray powder diffractometer using a high-power Cu Kα radiation. XPS data were obtained with an ESCALab220i-XL electron spectrometer from VG Scientific using 300W Al Kα radiation. Reflectance spectra were measured by Ocean optics fiber spectrophotometer. The diffuse reflectance UV/Vis spectra (DRS) were recorded in Hitachi U-4100 spectroscopy. The nitrogen adsorption and desorption isotherms at the temperature of liquid nitrogen (77 K) were measured on a Quantachrome Autosorb-1 sorption analyzer with prior degassing under vacuum at 300

°C overnight. Multipoint BET surface area was estimated from the relative pressure range from 0.05 to 0.2.

Reference

S1. Wang, J. X.; Wen, Y. Q.; Ge, H. L.; Sun, Z. W.; Zheng, Y. M.; Song, Y. L.; Jiang, L. Simple fabrication of full color colloidal crystal films with tough mechanical strength. *Macromol. Chem. Phys.***2006**, *207*, 596–604

Supplementary Figures:

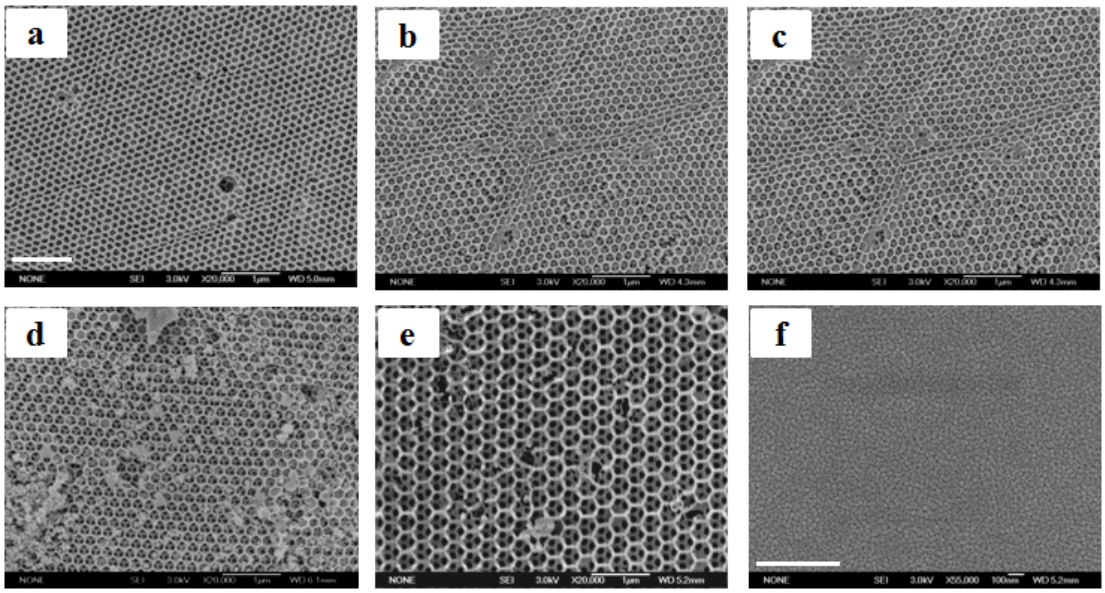

Figure S1. SEM image of a series of i-TiO_2 PC films and nc-TiO_2 films. (a) i-TiO_2-120; (b) i-TiO_2-133; (c) i-TiO_2-150; (d) i-TiO_2-170; (e) i-TiO_2-300. The scale bars of (a-e) and (f) were 1μm and 500 nm, respectively.

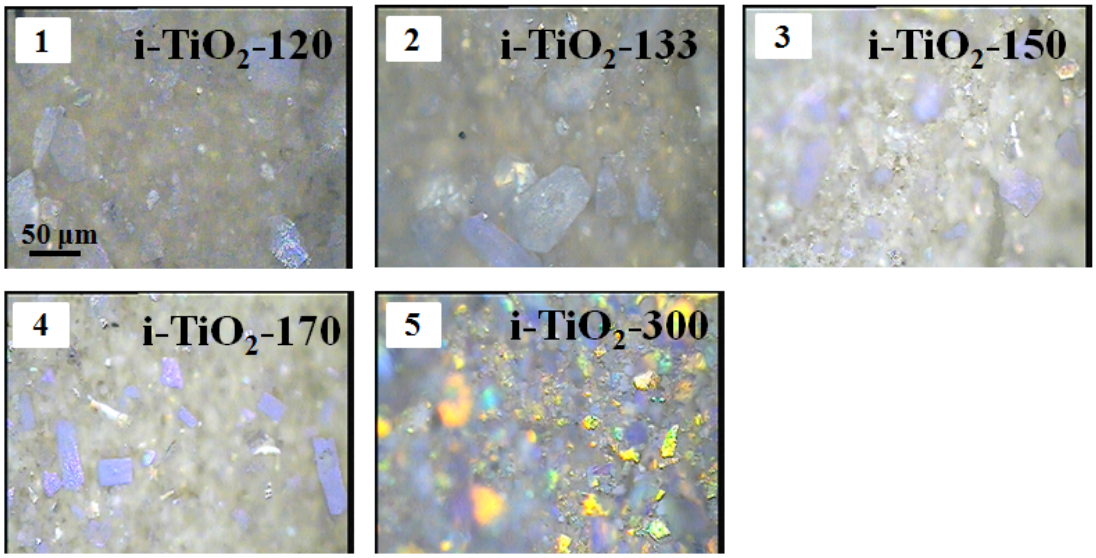

Figure S2. Optical microscopy images of different PC segments recollected from methanol aqueous solutions after photocatalytic water splitting experiment. The scale bar is 50 μm.

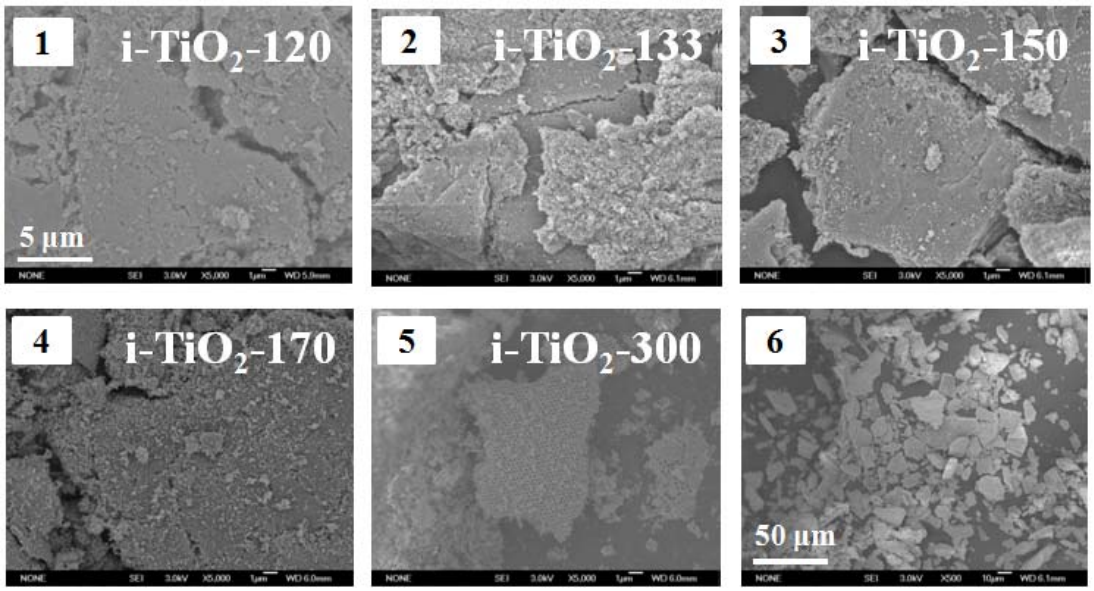

Figure S3. SEM images of different PC segments recollected from methanol aqueous solutions after photocatalytic water splitting experiment. The scale bars of 1-5 and 6 were 5 μm and 50 μm, respectively.

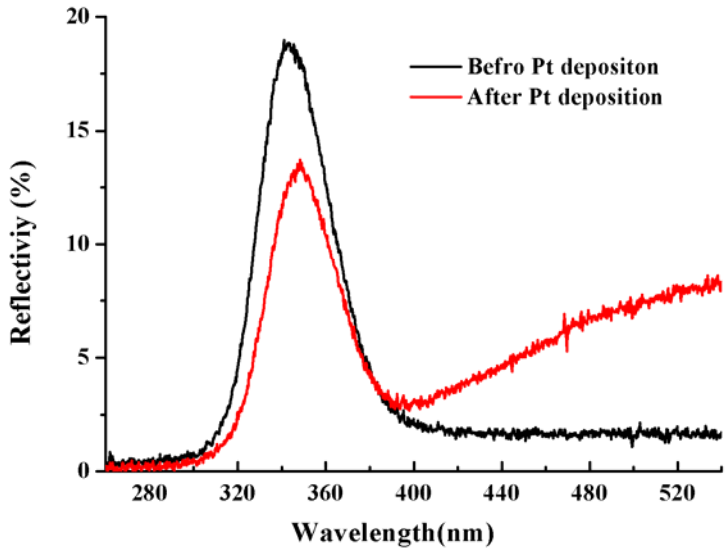

Figure S4. Reflectance spectra comparisons between before Pt deposition and after Pt depositon.

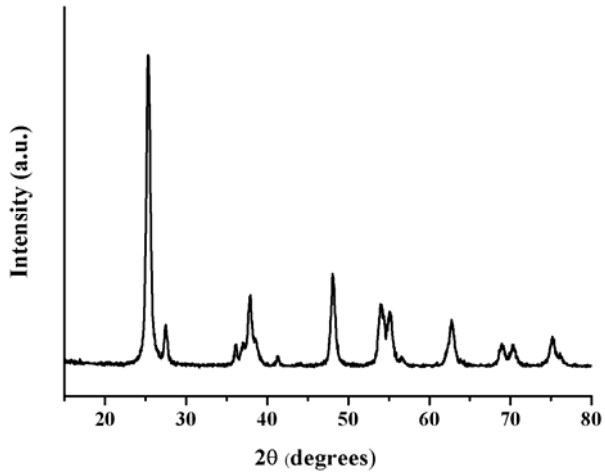

Figure S5. X-ray diffraction pattern of i-TiO_2 calcined at 450 °C for 4 hours indicating good anatase crystallinity.

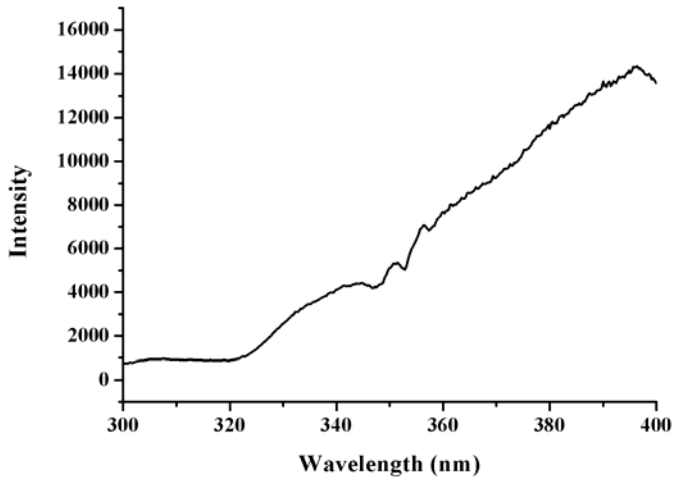

Figure S6. The spectrum of Xenon lamp in the UV region (300-400 nm), indicating that the light intensity in the region nearly linearly increased.

Table S1. Photocatalytic H_2 evolution over Pt loaded TiO_2 photonic crystals.

Catalysts	H_2 evolution rate (μmol/h)	QY (%)
i-Pt-TiO_2-120	238	11.5
i-Pt-TiO_2-133	247	11.9
i-Pt-TiO_2-150	179	8.6
i-Pt-TiO_2-170	197	9.5
i-Pt-TiO_2-300	128	6.2
nc-TiO_2	99	4.8

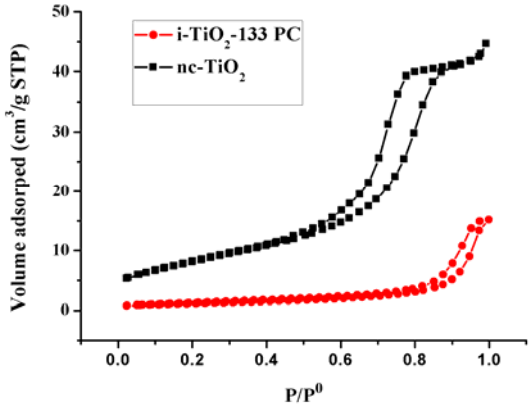

Figure S7. Nitrogen adsorption-desoprtion isotherms of i-TiO_2-133 PC and nc-TiO_2.

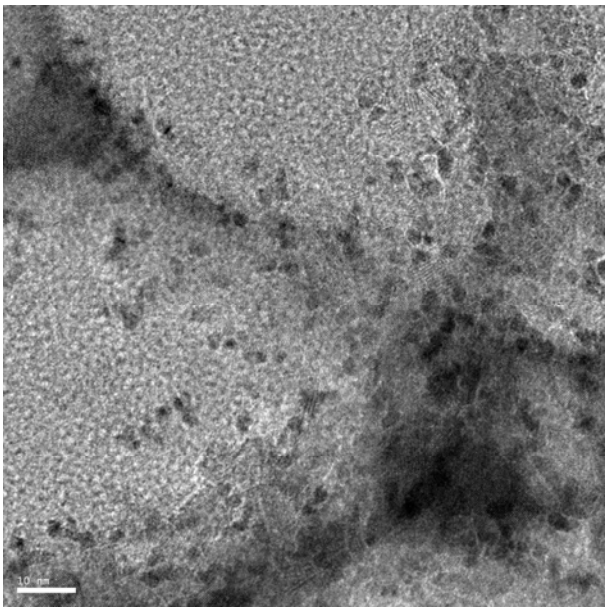

Figure S8. TEM image of Pt-loaded i-TiO_2 PC.

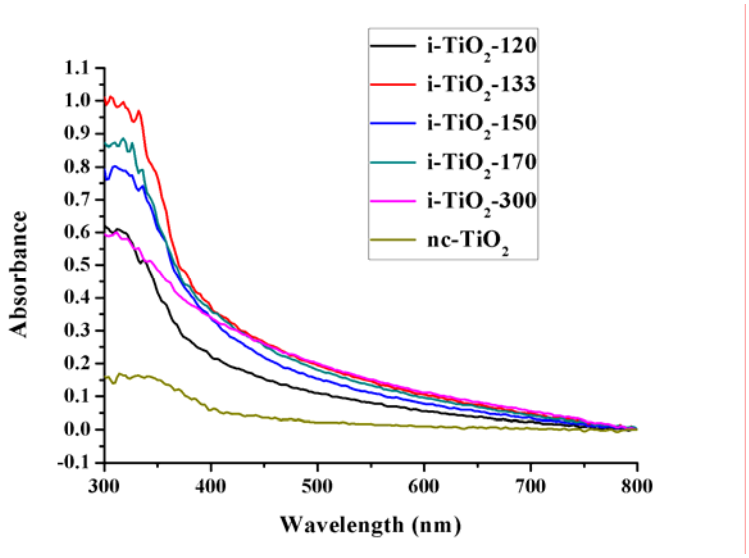

Figure S9. Diffuse reflectance UV-vis spectroscopy of i-TiO_2 PCs and nc-TiO_2.