

Supporting Information

Optimization for Visible Light Photocatalytic Water Splitting: Gold-Coated and Surface-Textured TiO₂ Inverse Opal Nano-Networks

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Experimental Procedure

Chemicals used

Titanium(IV) Chloride ($\geq 98\%$), the triblock copolymer, poly(ethylene glycol)-*block*-poly(-propylene glycol)-*block*-poly(ethylene glycol) (EO₂₀PO₇₀EO₂₀, M = 5800), titanium(IV) isopropoxide, 2,4-pentanedione, chloroauric acid ($>99.9\%$), sodium citrate ($>98\%$), sodium Hydroxide (NaOH from Duksan) and Ethanol. All chemicals except NaOH were purchased from Sigma-Aldrich, and all chemicals were used without further purification.

Characterization

The morphology of the structures was examined by SEM (NOVA NANOSEM 230 FESEM, 15kV), TEM (JEM-2100, 200kV). The powder diffraction data were obtained using a Rigaku Co. High Power X-Ray Diffractometer D/MAZX 2500V/PC from 20° to 80°. Optical properties of structures were investigated by UV-Vis spectroscopy (VARIAN, Cary 100).

Raman Spectroscopy Measurements

The variation of the chemical structure was confirmed by Raman spectroscopy (WITec, alpha300R, excited by a 532nm laser). Plots of TiO and st-TiO are very similar each other confirming the surface-texturing does not affect on the chemical composition of TiO.

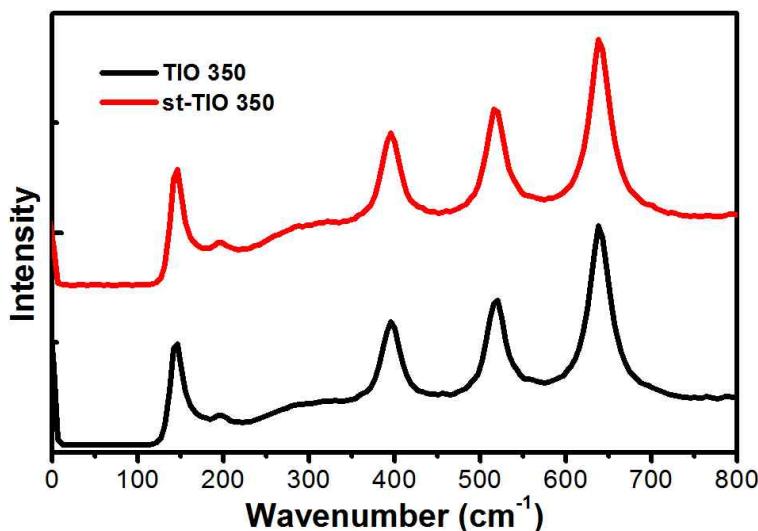


Figure S1. Raman Spectra of st-TIO and TIO.

Surface Area Measurements by the BET Method

Surface area determination was performed by Brunauer-Emmett-Teller (BET) methods using an ASAP 2000 surface area analyzer (Micrometrics Instrument Corp.). Surface-texturing on TIO with a diameter of 350 nm improves the surface area dramatically.

a

Nanostructure	Surface area (m ² /g)
TIO (350 nm)	33.912
St-TIO (350 nm)	124.90
NC-TiO ₂	117.21

b

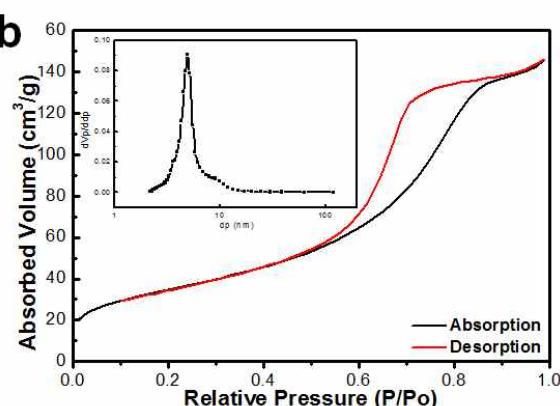


Figure S2. a) Comparison the surface area of nanostructures. b) The N₂ adsorption-desorption isotherm curve of the st-TIO with a diameter of 350 nm.

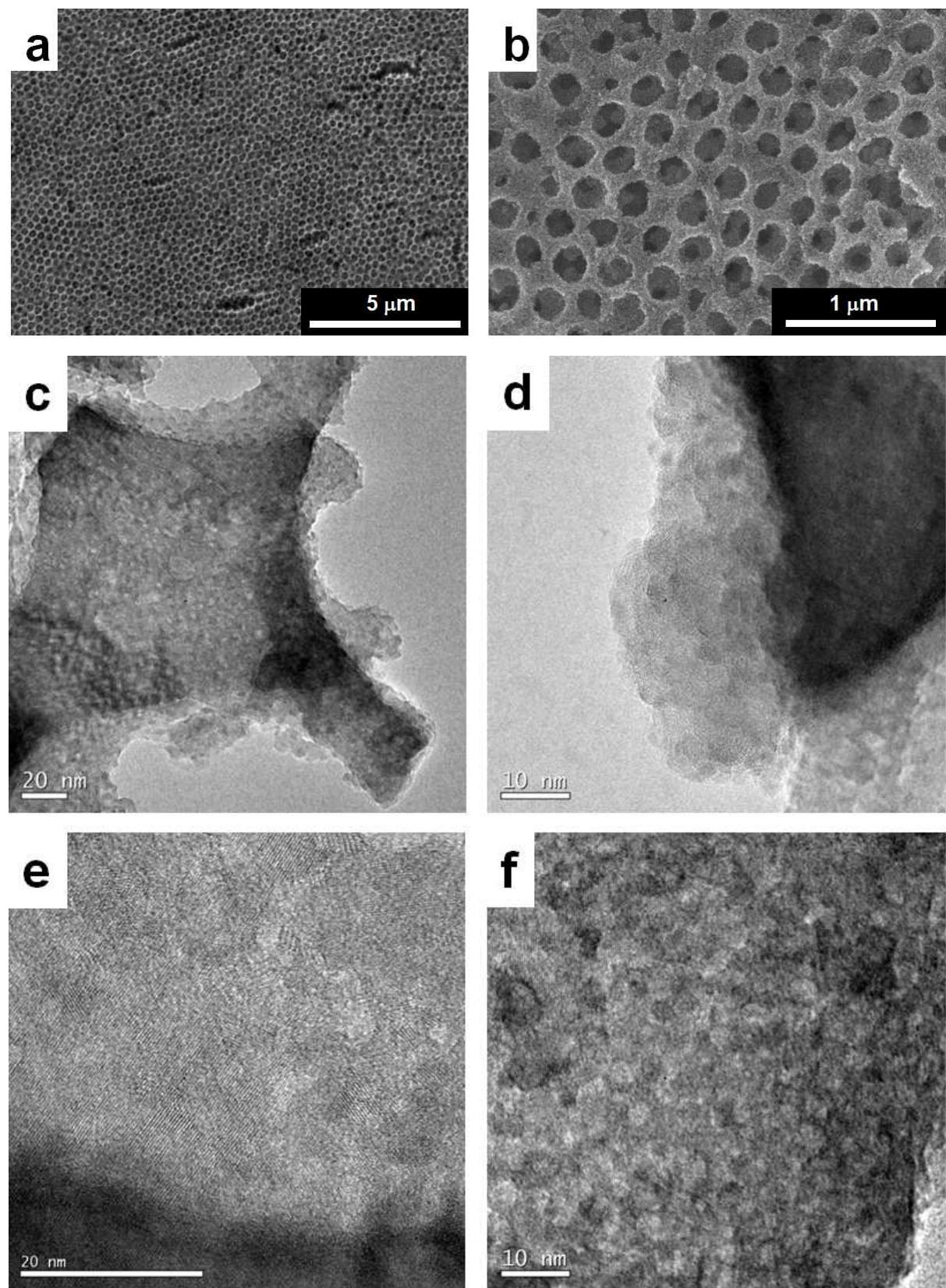
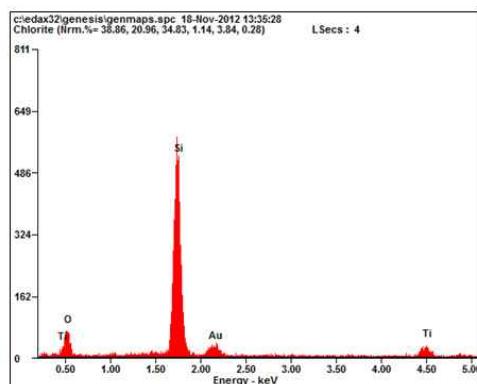


Figure S3. SEM (a and b) and TEM (c-f) images of st-TIO



Element	Wt%	At%
OK	20.53	37.26
SiK	50.98	52.70
AuM	15.74	02.32
TiK	12.74	07.72

Figure S4. EDX analysis of Au/st-TIO on SiO₂/Si substrate

UV-visible cross-sectional area

The absorption cross-sectional area is obtained by the integration of UV-visible absorption curve from 300 to 800 nm and 420 to 800 nm for UV-vis and Visible values, respectively. The structures with a diameter of 350 nm have the highest value of absorption cross-sectional area.

	TIO	st-TIO		Au/st-TIO	
	UV-vis	UV-vis	Visible	UV-vis	Visible
130	148.01	192.45	78.29	-	-
350	143.03	219.80	123.21	289.88	179.88
600	136.39	175.25	115.24	220.34	143.32
P-25	156.21		55.18	-	-

Table 1. Comparison of UV-visible cross-sectional area

Photoelectrochemical (PEC) Measurement

The PEC measurements were done for the TiO_x, st-TiO_x and Au/st-TiO_x structures using Ag/AgCl(KCl sat.) and Pt mesh as a reference electrode and counter electrode, respectively, in a 0.24 M Na₂S and 0.35 M Na₂SO₃ electrolyte solution with the pH adjusted to ~12. A Newport solar simulator was used to illuminate sunlight at AM 1.5. The power of the solar simulator was measured to be 80 mW/cm². The electrochemical data were measured using a Princeton Applied research VersaSTAT3 potentiostat. Linear sweep voltammograms were obtained by increasing the voltage from -0.6V to 1.1 V with a scan rate of 0.01 V/s under illumination of AM 1.5. Chronoamperometry measurements were obtained at + 0.5V while the simulator was switched on and off alternatively every 10 seconds, manually using the shutter. The PEC performances of structures only in the visible range were acquired by the solar simulator coupled with a UV cutoff filter ($\lambda > 420$ nm).

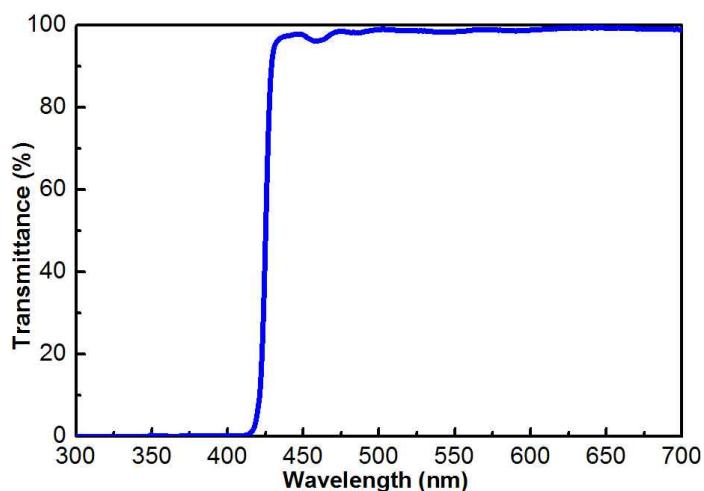


Figure S5. Transmittance spectrum of the UV cutoff filter



Figure S6. Experimental setup for PEC measurements

Incident Photon Conversion Efficiency (IPCE) Measurements

IPCE measurements were performed using the PV measurement system to obtain more detailed photoresponses of the TiO, st-TiO, and Au/st-TiO as a function of wavelength of light. Si solar cell was used as reference cell and the sample was measured from wavelength of 300 nm - 800 nm which gives the exact performance of our structure in the UV-visible region. Interestingly, in addition to the great photocurrent generated in the UV region, st-TiO and Au/st-TiO showed a broad photocurrent spectrum with a notable intensity covering a range of 400 - 700 nm and a maximum at 530 nm, respectively, whereas TiO did not have a similar photocurrent response in the range of 400 - 700 nm. These data provide clear evidence that our structure shows increased plasmon-enhanced photo-conversion efficiency achieved by light trapping of Au/st-TiO structures in the visible region.

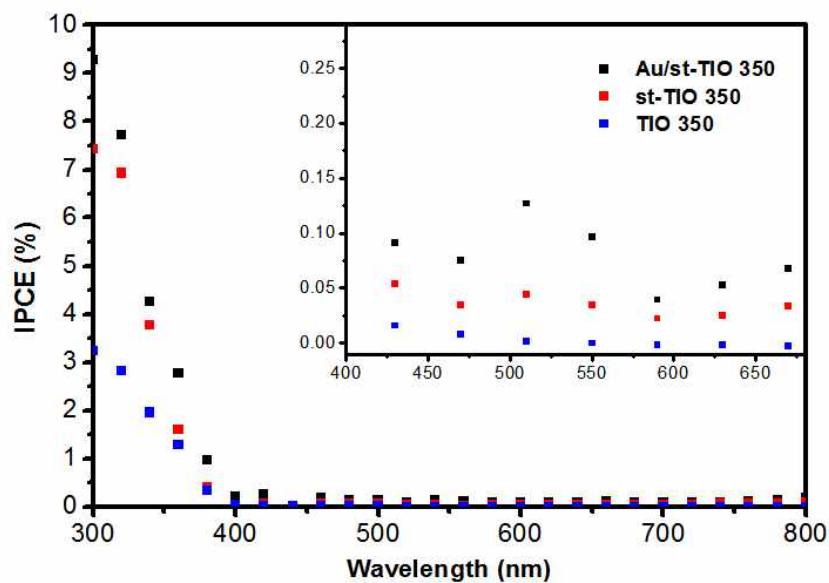


Figure S7. IPCE measurement of Au/st-TIO, st-TIO and TIO under UV-visible range illumination (300-800 nm). The inset is the zoomed-up image of IPCE data showing the increment of Au/st-TIO and st-TIO in the visible region.

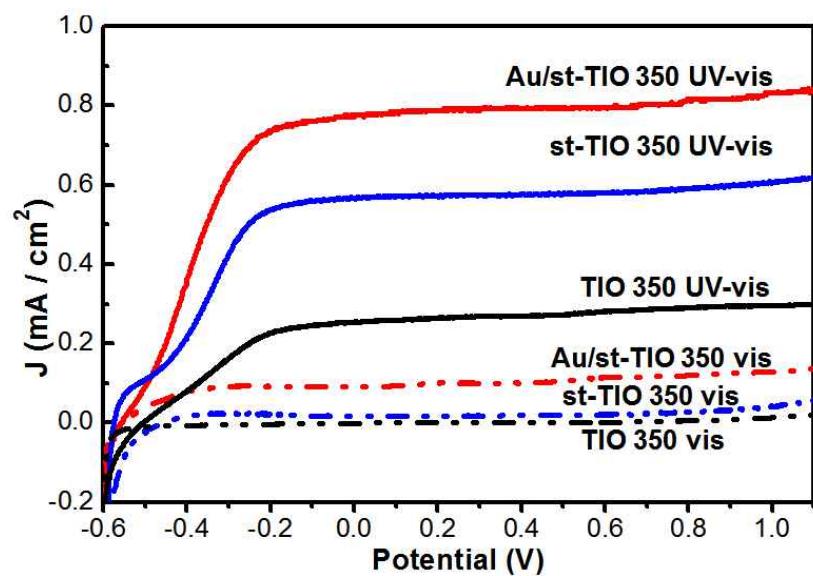


Figure S8. Photocurrent response of Au/st-TIO, st-TIO and TIO with a diameter of 350 nm under UV-visible light illumination (300-800 nm) and visible light illumination (>420 nm).

Efficiency calculations

The amperometric I-t studies on Au/st-TIO as a function of applied over potential at 80 mW/cm² was measured, from which the photocurrent values have been taken for the efficiency measurements. The efficiency of the device was calculated using the following equation

$$\eta \% = \frac{J_p \times (E_{rev}^0 - |E_{app}|)}{I_0} \times 100$$

$$|E_{app}| = E_{app} - E_{m\ ean} - E_{aoc}$$

where J_p is the measured photocurrent in mA/cm², E_{rev}^0 is constant value as 1.23 V for the Ag/AgCl reference electrode, $|E_{app}|$ is the term related to the applied potential calculated through upper equation and I_0 is the intensity of incident light in mW/cm². $E_{m\ ean}$ is -0.196 V for Ag/AgCl reference electrode and E_{aoc} is -0.155 V for Au/st-TIO.

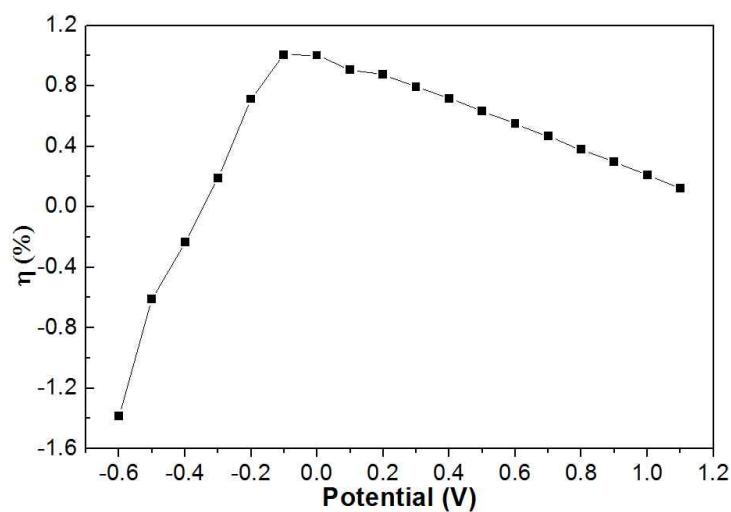


Figure S9. Photoconversion efficiency of the PEC cell with Au/st-TIO electrode as a function of applied potential.