Supporting Information for

Photoactive PANI/TiO_2/Si Composite Coatings With 3D Bio-inspired Structures

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Materials and Methods

Chemicals and instruments: Ethanol, hydrochloric acid, potassium hydroxide (KOH), titanium n-butoxide [$Ti(OC_4H_9)_4$], methylene blue (MB), ammonium persulfate, aniline and polyvinylpyrrolidone k-30 (PVP) were purchased from Beijing Chemical Reagent Plant in the highest available purity and used without further purification. The Si wafers [p-type (100)] were obtained from Youyan Guigu Beijing, China.

Wet etching of the silicon wafer: Firstly, the Si wafer was submerged in a HF (1% electronic grade) aqueous solution for 30 s, to remove the native oxide layer. The wafer was then washed in an ultrasonic bath with deionized water for 5 min and dried under nitrogen gas flow. At last, pyramidal structures were generated by etching the Si wafer in a solution of KOH (pH=14) for 30 min at 85 °C, and washed in an ultrasonic bath with deionized water for 5 min.

Hydrothermal growth of the TiO_2 rods: The Si substrate with pyramidal structures (P-Si) was immersed into 0.075 M $Ti(OC_4H_9)_4$ in ethanol solution for 30 s. Then, the above sample was sintered at 450 °C for 30 min to yield a layer of TiO_2 nanoparticles. Finally, the TiO_2 rods were grown from the TiO_2 nanoparticles in the solution of 10 mL purified water, 10 mL hydrochloric acid (37%) and 0.5 mL $Ti(OC_4H_9)_4$ at 130 °C for 8 h.

Fabrication of PANI nanoparticles on the TiO_2 rods: Aniline (1.82 mL) and hydrochloric acid (1.667 mL) was dissolved in deionized water (50 mL) to form 0.2 mol/L of aniline hydrochloride as one solution. Another solution was prepared by dissolving ammonium persulfate (5.711 g) in deionized water (50 mL). Then 4 g of PVP was added to the mixture of the above two solution. The fabricated TiO_2/ P-Si composite was placed into the resulting solution for 4 h at 20 °C. The composite was then taken out and washed with deionized water. The PANI/TiO_2/P-Si with hierarchical structures was finally obtained when it was dried under a nitrogen gas flow.

Photocurrent measurement: The photoelectric conversion of PANI/TiO_2/P-Si was investigated using electrochemical method. Under the irradiation of 300 W xenon light source, selecting PANI/TiO_2/P-Si as working electrode, a saturated Ag/AgCl electrode and a platinum electrode as the reference and counter electrode, respectively.

Linear sweep voltammetry curves were measured in a glass cell with a quartz window with 0.5 M Na_2SO_4 electrolyte.

Photocatalytic activity measurement: Photocatalytic activities of samples (1.0×1.5 cm^2) were performed by the degradation of MB under the irradiation from 300 W xenon light source. The samples were immersed into 3 mL MB solution (2 mg/mL, neutral condition) and stirred in dark for 30 min to ensure the adsorption equilibrium before the light illumination. After light irradiation, the MB solution was immediately measured with a UV–vis spectrophotometer.

Characterization: Scanning electron microscopy (SEM) measurements were carried out by using a Hitachi S4800 (Japan) microscope. X-ray diffraction (XRD) patterns were recorded by a Rigaku D/Max-2550 diffractometer with Cu Kα radiation (λ = 1.54056 Å) (40 kV, 350 mA) in the range of 20-70° (2θ). Raman measurements were performed at room temperature on a Renishaw micro-Raman system microscope. UV–visible spectra were recorded on a UV–visible spectrometer (Shimadzu UV3600, Shimadzu, Japan). Photocurrent response was recorded using a Gamry instruments framework electrochemical station using the irradiation of a Hal-320 compact Xenon light source. The water contact angle of the sample was determined by using a contact angle analyzer (DCA315, USA). The photocatalytic degradation of MB was conducted under the illumination of a 300 W Xenon lamp.

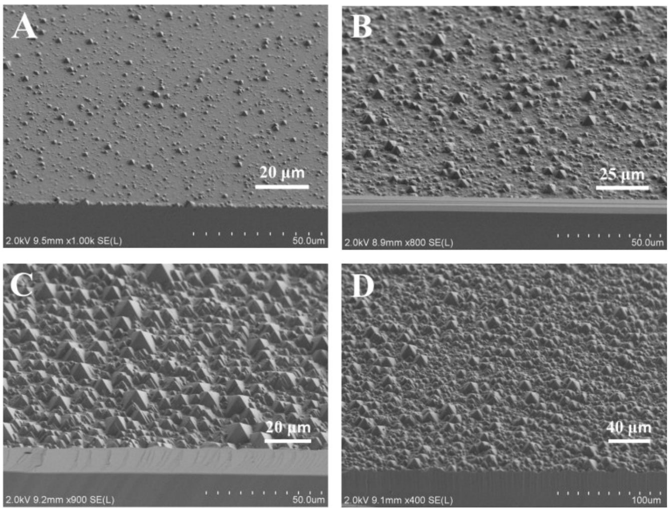

Fig. S1 Cross-sectional (45^{o} tilt view) SEM photographs of P-Si fabricated with KOH etching time: (A) 5 min, (B) 15 min, (C) 30 min and (D) 35 min.

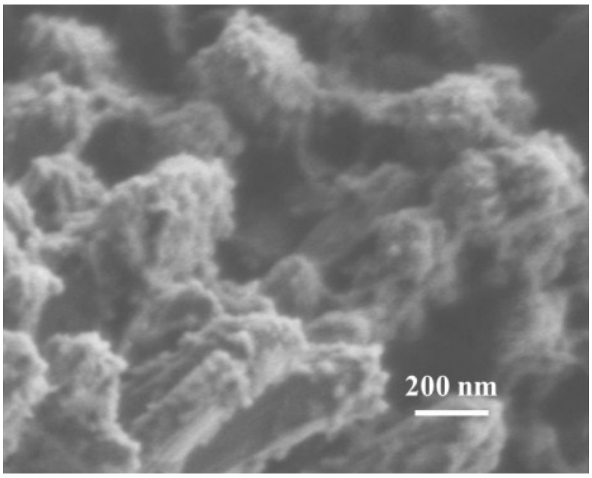

Fig. S2 SEM image of PANI/TiO_2 on the Si.

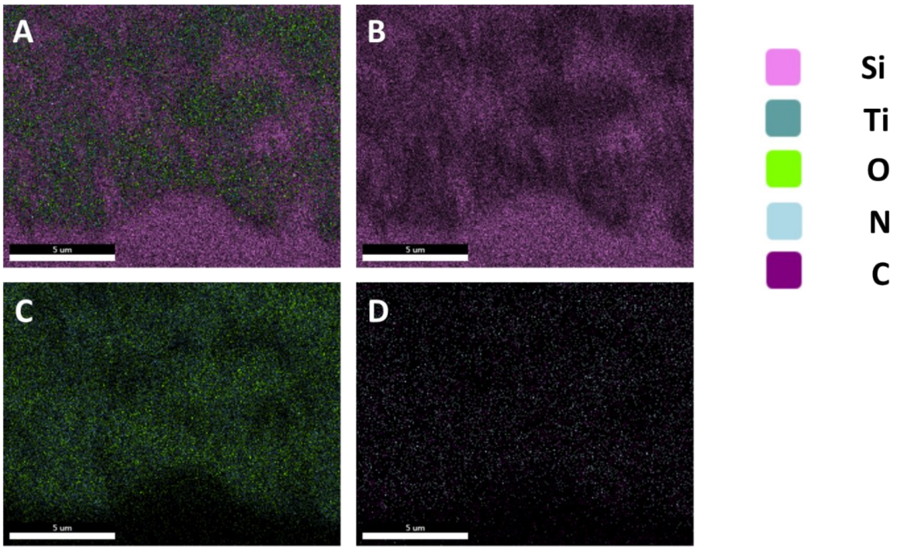

Fig. S3 (A) Si, Ti, O, N and C EDS map, (B) Si EDS map, (C) O and Ti EDS map, and (D) C and N EDS map of PANI nanoparticles/TiO_2 rods/Si pyramids.

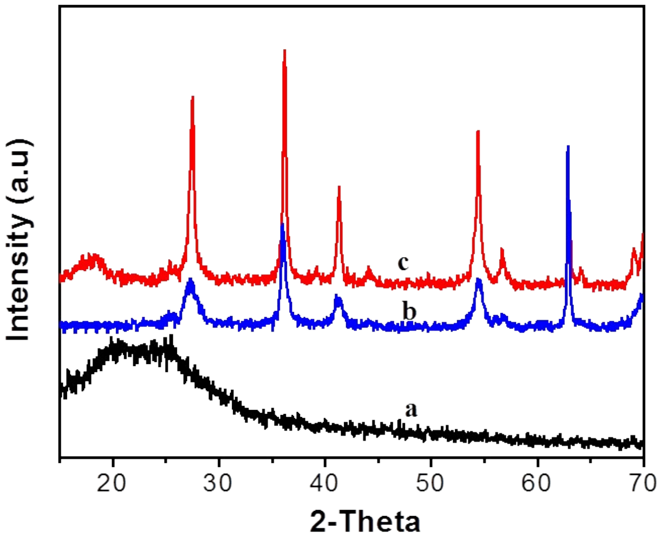

Fig. S4 XRD patterns of (a) pure PANI, (b) pure TiO_2 and (c) PANI/TiO_2.

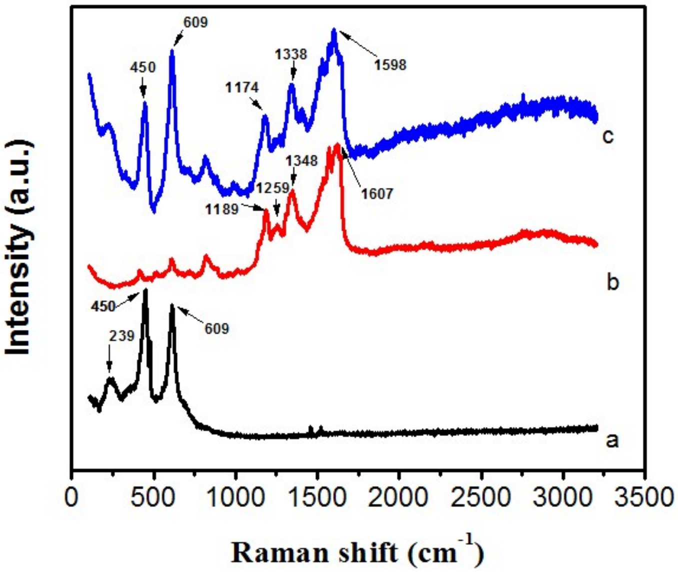

Fig. S5 Raman spectra of (a) pure TiO_2, (b) pure PANI and (c) PANI/TiO_2.

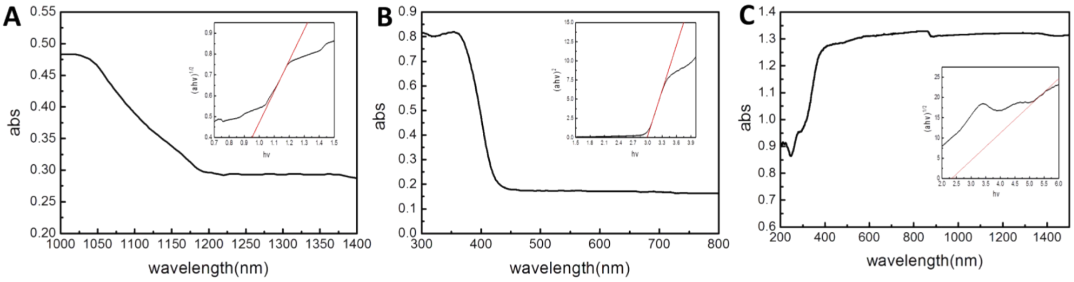

Fig. S6 UV–vis diffuse absorption spectra of (A) pure Si, (B) TiO_2 and (C) PANI (inset: the band gaps of the pure Si, TiO_2 and PANI samples).

Following the equation $\alpha h\nu = A(h\nu - E_g)^{n/2}$,[R1] where α, ν, E_g and A are the absorption coefficient, the light frequency, the band gap, and a constant, respectively, the band gaps of the prepared pure Si, TiO_2 and PANI can be estimated from the intercept of the tangents to the plots shown in the inset of Fig. S6.

[R1] H. B. Fu, C. S. Pan, W. Q. Yao, Y. F. Zhu, Journal of Physical Chemistry B, 2005, 109, 22432-22439.