

Supporting information for
One nanometer polydopamine layer assisted anatase TiO₂
with highly active visible-light photocatalysis

Wen-Xin Mao ^{a,b}, Xi-Jie Lin ^{a,b}, Wei Zhang ^a, Zi-Xiang Chi ^a, Rong-Wen
Lyu ^{*b}, An-Min Cao ^{*a}, and Li-Jun Wan ^{*a}

*^a Key Laboratory of Molecular Nanostructure and Nanotechnology and Beijing National
Laboratory for Molecular Sciences, Institute of Chemistry, Chinese Academy of Sciences (CAS),
Beijing 100190, P. R. China.*

*^b State Key Laboratory of Fine Chemicals, Dalian University of Technology, Dalian 116024,
China.*

*Corresponding author: anmin_cao@iccas.ac.cn

Materials: Average diameter 30 nm anatase TiO₂ (Alfa Aesar), dopamine hydrochloride (DA, Alfa Aesar), Hexamethylenetetramine (HMTA, Alfa Aesar), Rhodamine B (RhB, Alfa Aesar), commercial P25 TiO₂ (Alfa Aesar), ethanol (Alfa Aesar). All chemicals were used without further purification and all solutions were prepared using ultrapure water (resistance >18 MΩ cm⁻¹).

Preparation of TiO₂@PDA Core–Shell particles: First, a calculated amount of TiO₂ and dopamine hydrochloride (1 mmol TiO₂ and 0.05 mmol DA) was added to 50 ml ultrapure water. Such a small molar ration of TiO₂: DA (20:1) is targeted to make sure that each TiO₂ particle is able to be coated with a uniform PDA layer with an exact thickness of 1 nm. Then, 0.71 mmol HMTA was then added to cause the PDA formation. Because HMTA can hydrolyze in water to give NH₃,^{1, 2} so that the basicity of the solution was changed slowly, which is able to ensure the reacting environment suitable for controlled hydrolysis and this is critical in the synthesis process. After sealing and vortexing for 30 s, the reaction mixture was incubated at 90 °C for 3 h. To isolate the TiO₂@PDA core-shell particles, the reaction mixture was centrifuged at 10000 rpm for 2 min, the supernatant was removed, and the concentrated particles were washed by water and ethanol 2 times each, then were collected at the bottom of the Eppendorf tubes.

Preparation of TiO₂-DA particles: First, a calculated amount of TiO₂ and dopamine hydrochloride (1 mmol TiO₂ and 0.1 mmol DA) was added to 50 ml ultrapure water, and then the mixture was kept in dark place in case of dopamine getting polymerization for 3 h with stirring. The isolating procedure was performed as that of TiO₂@PDA.

Characterization: Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) images were collected on a JEM-2100F (JEOL) operated at 200kV. X-ray diffraction (XRD) measurement was carried out using a Rigaku D/max2500 diffractometer with filtered Cu Kα radiation, and the data were collected from 10° to 80°. The UV-visible absorption spectra of catalysts were obtained by using a UV-visible spectrophotometer (UV-2550, Shimadzu, Japan). BaSO₄ was used as a reflectance standard. The FTIR spectra of catalysts were performed by a TENSOR-27, Bruker, Germany.

Photodegradation performance measurements: The photocatalytic activity of the samples was evaluated in terms of the photodegradation of RhB under visible light irradiation at ambient temperature. 10 mg of catalyst was added into a 30 mL of 10 mg/L dye aqueous solution to undergo a stirring in the dark for 1 h. After reaching a complete adsorption–desorption

equilibrium, it was exposed to visible light irradiation offered by 50 W Xe lamp with a 420 nm cut-off filter under continuous stirring. A small quantity of liquid was sampled at the interval of 15 min to measure variation of the concentration of RhB in the solution. The concentrations of RhB was determined from the absorbance at the wavelength of 554 nm by an UV-visible spectrophotometer (UV-2550, Shimadzu, Japan). The same procedure was also done to P25, p-TiO₂, and TiO₂-DA for comparison. Catalysts were centrifuged out and washed for the recyclable catalysis.

Controlling Experiments: To change the thickness of the PDA layer, we can achieve this by simply adjusting the concentrations of reactants. The details of difference in the utilization of reagents were list in Table S1.

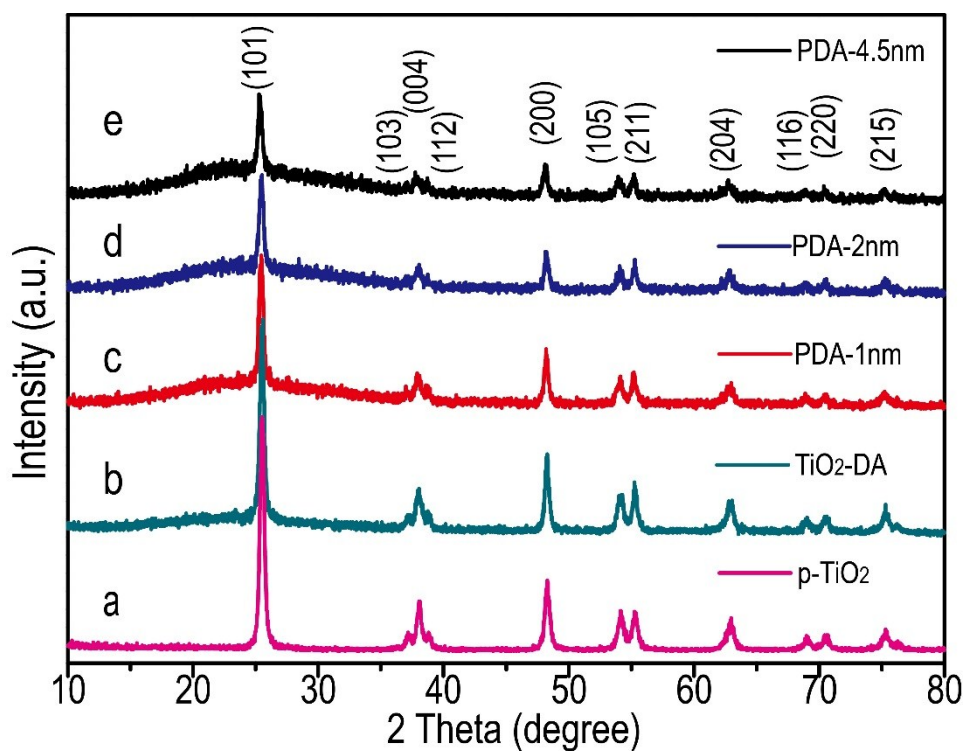


Fig. S1 X-ray diffraction (XRD) patterns of (a) p-TiO₂, (b) TiO₂-DA, TiO₂@PDA with (C) 1 nm PDA shell, (d) 2 nm PDA shell, (e) 4.5 nm PDA shell

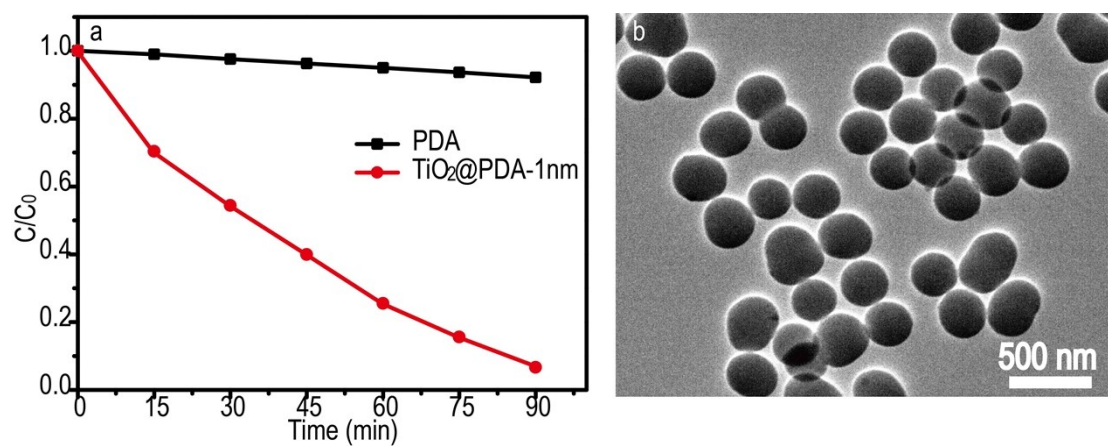


Fig. S2 (a) Evaluation of RhB concentration versus reaction time of PDA nanospheres (black line) and TiO₂@PDA with 1 nm PDA shell (red line), and (b) TEM image of PDA nanospheres.

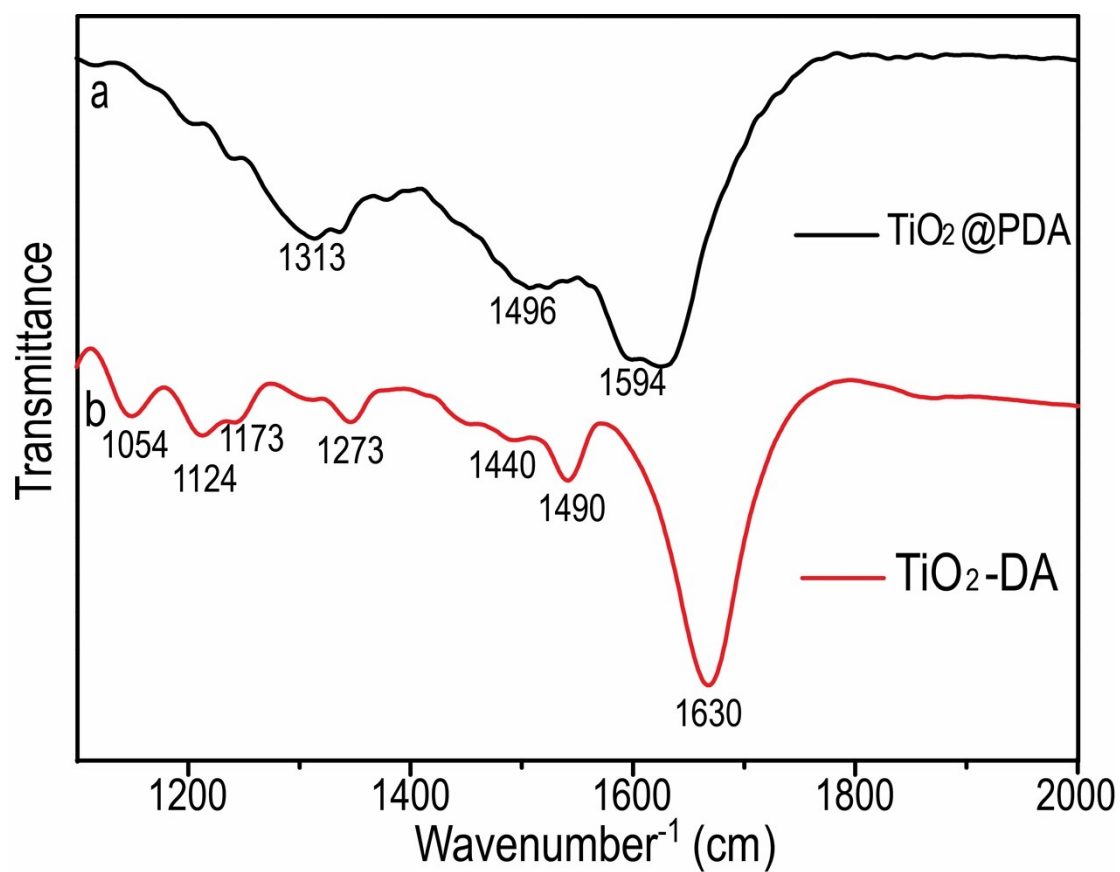


Fig. S3 FTIR spectra of (a) TiO₂@PDA and (b) TiO₂-DA

Tab. S1 Details of controlling experiments

	TiO ₂	DA	HMTA	H ₂ O
TiO ₂ @PDA-1NM	1 mmol	0.05mmol	0.71 mmol	50 ml
TiO ₂ @PDA-2NM	1 mmol	0.1 mmol	0.71 mmol	50 ml
TiO ₂ @PDA-4.5NM	1 mmol	0.2 mmol	0.71 mmol	50 ml

Reference

1. S. Xu and Z. L. Wang, *Nano Res.*, 2011, **4**, 1013-1098.
2. H. Sun, J. He, J. Wang, S.-Y. Zhang, C. Liu, T. Sritharan, S. Mhaisalkar, M.-Y. Han, D. Wang and H. Chen, *J. Am. Chem. Soc.*, 2013, **135**, 9099-9110.