

## Electronic Supplementary Information (ESI)

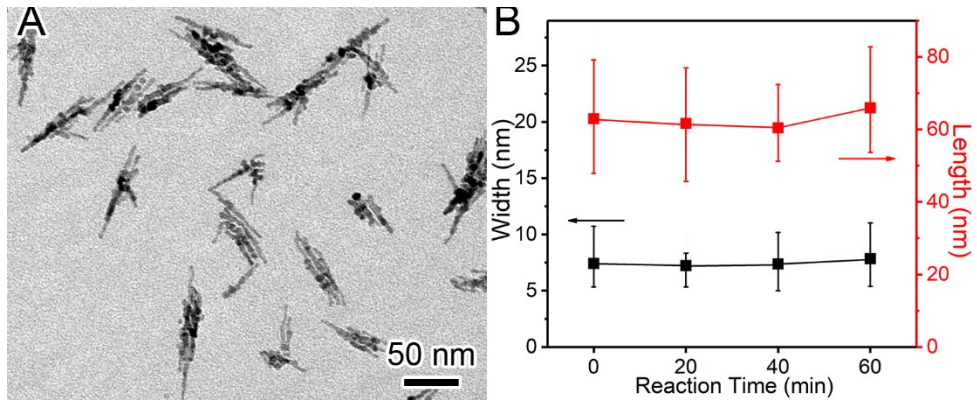
# Fluorine-Assisted Structural Engineering of Colloidal Anatase TiO<sub>2</sub> Hierarchical Nanocrystals for Enhanced Photocatalytic Hydrogen Production

Lan Peng,<sup>a, c</sup> Yiding Liu,<sup>\*,b, c</sup> Yongjie Li,<sup>a</sup> Feng Teng<sup>a</sup> Aiwei Tang,<sup>\*, a</sup>  
Yadong Yin<sup>c</sup>

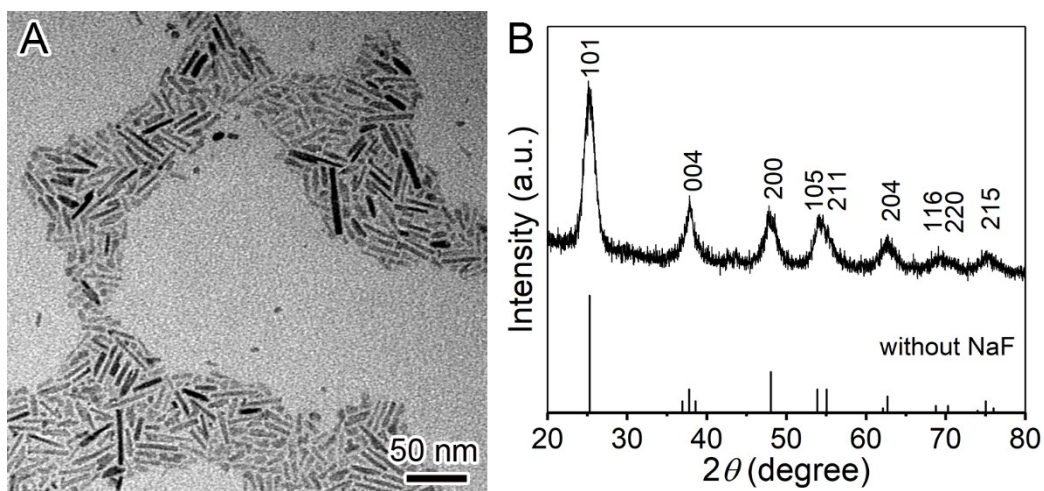
<sup>a</sup>Key Laboratory of Luminescence and Optical Information (Ministry of Education), School of Science, Beijing JiaoTong University, Beijing 100044, China. Email: [awtang@bjtu.edu.cn](mailto:awtang@bjtu.edu.cn)

<sup>b</sup>School of Chemistry and Chemical Engineering, Southwest Petroleum University, Chengdu 610500, China. Email: [yiding.liu@swpu.edu.cn](mailto:yiding.liu@swpu.edu.cn)

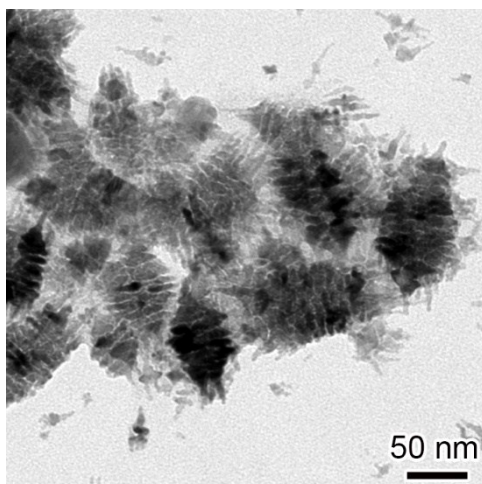
<sup>c</sup>Department of Chemistry, University of California, Riverside, California 92521, United States.



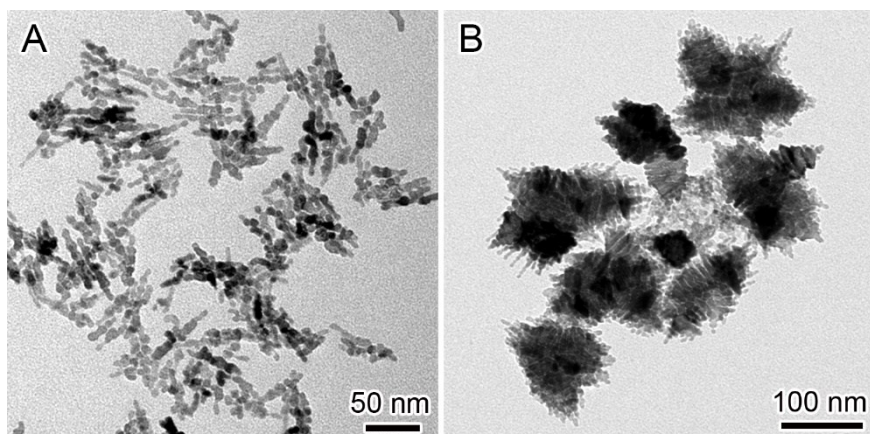
**Figure S1.** The effects of heating time on the morphology of the hierarchical TiO<sub>2</sub> nanocrystals. (A) TEM image of TiO<sub>2</sub> nanocrystals with 1 hour extended heating at 270 °C, (B) plot of the change of width (black line) and length (red line) of TiO<sub>2</sub> nanorods versus heating time.



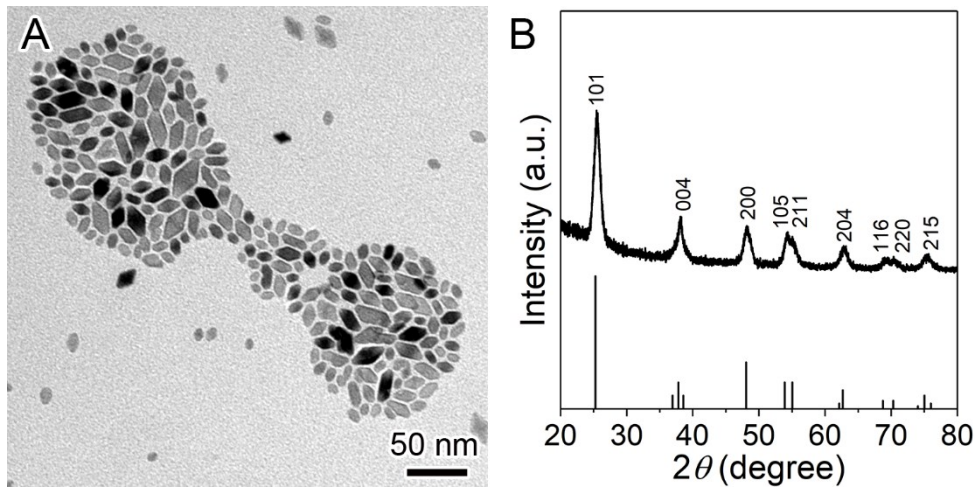
**Figure S2.** (A) TEM image and (B) XRD pattern of  $\text{TiO}_2$  nanorods synthesized in pure OA without NaF at  $270^\circ\text{C}$ .



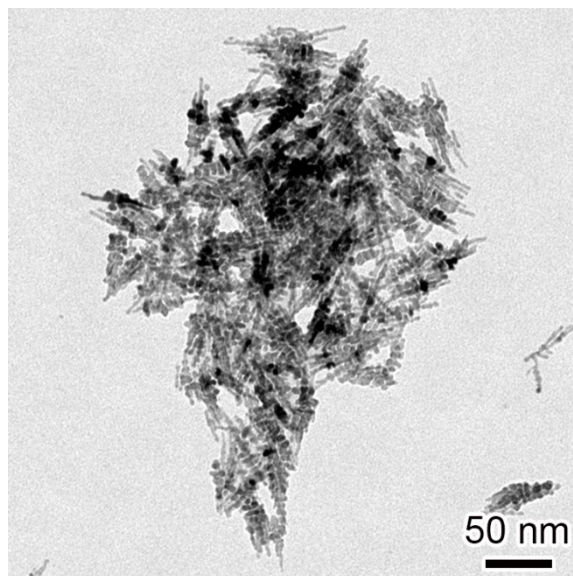
**Figure S3.** TEM image of  $\text{TiO}_2$  nanocrystals synthesized at  $270\text{ }^\circ\text{C}$  with 5 mmol NaF.



**Figure S4.** TEM image of TiO<sub>2</sub> synthesized with 1mmol NaF in different temperature with extended 1h heating. (A) 200 °C, (B) 300 °C.



**Figure S5.** (A) TEM image and (B) XRD of  $\text{TiO}_2$  nanobipyramids synthesized with 0.8 mmol NaF at 270°C.



**Figure S6.** TEM images of TiO<sub>2</sub> nanocrystals synthesized under typical conditions after phase transfer.

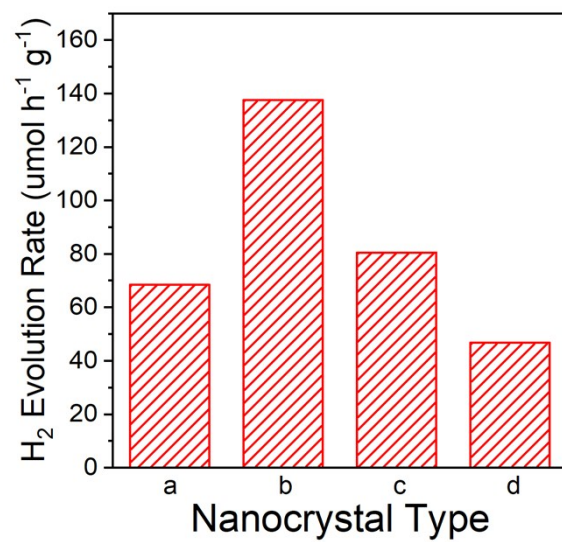
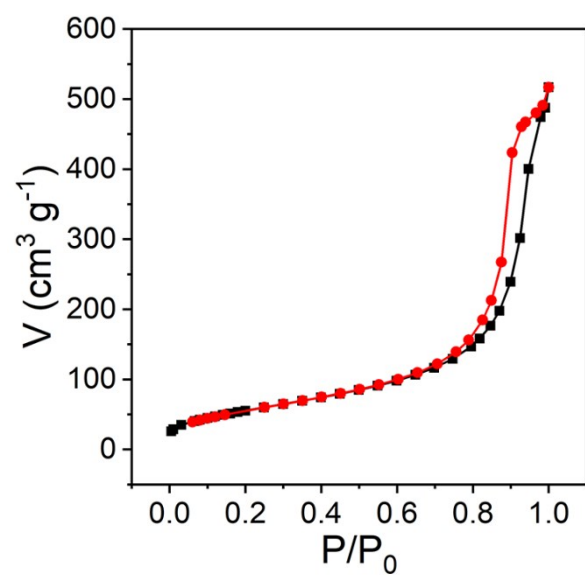
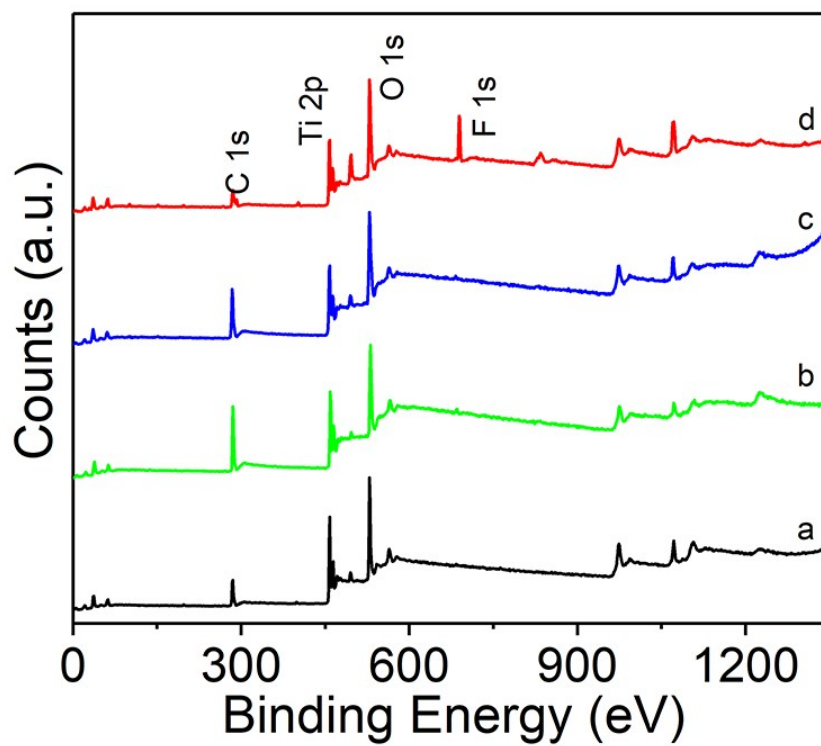


Figure S7. Hydrogen evolution rate of (a) nanobipyramidal TiO<sub>2</sub> nanocrystals and hierarchical TiO<sub>2</sub> nanocrystals synthesized with different amount of NaF under low-power light source: (b) 0.8 mmol, (c) 2.5 mmol, (d) 5 mmol.

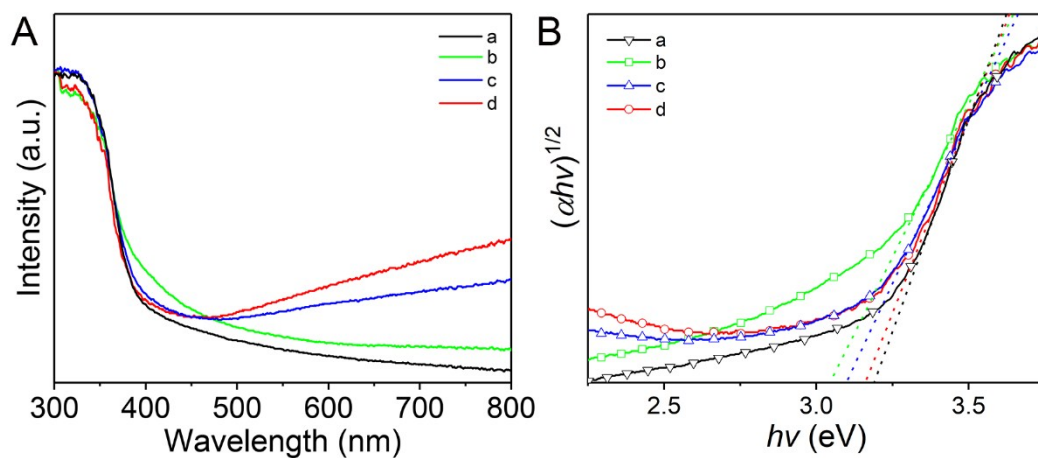




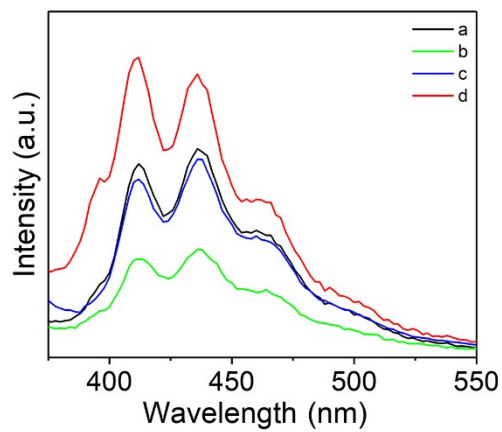
**Figure S8.** Nitrogen adsorption isotherm of TiO<sub>2</sub> nanocrystals synthesized under typical conditions.



**Figure S9.** XPS survey spectra of the (a) bipyramidal TiO<sub>2</sub> nanocrystals and hierarchical TiO<sub>2</sub> nanocrystals synthesized with (b) 0.8 mmol, (c) 2.5 mmol, (d) 5 mmol NaF.



**Figure S10.** (A) UV-Vis diffuse reflectance spectra and (B) Tauc Plots for (a) bipyramidal  $\text{TiO}_2$  nanocrystals and hierarchical  $\text{TiO}_2$  nanocrystals synthesized with (b) 0.8 mmol, (c) 2.5 mmol, (d) 5 mmol NaF.



**Figure S11.** PL spectra of (a) bipyramidal TiO<sub>2</sub> nanocrystals and hierarchical TiO<sub>2</sub> nanocrystals synthesized with (b) 0.8 mmol, (c) 2.5 mmol, (d) 5 mmol NaF measured at room temperature with the excitation of the 300 nm light

**Table S1.** Atomic ratio of (a) nanobipyramidal TiO<sub>2</sub> nanocrystals and hierarchical TiO<sub>2</sub> nanocrystals synthesized with (b) 0.8 mmol, (c) 2.5 mmol, (d) 5 mmol NaF.

	<b>a</b>	<b>b</b>	<b>c</b>	<b>d</b>
<b>% [F]</b>	0.84%	1.53%	2.64%	19.74%