## **Supporting Information**

Xiao Yu,<sup>a</sup> Ling Xin,<sup>a,c</sup> Yong Liu,<sup>\*c</sup> Wenxia Zhao,<sup>b</sup> Baojun Li,<sup>c</sup> Xiang Zhou<sup>c</sup> and Hui Shen<sup>a</sup>

<sup>a</sup>Institute for Solar Energy Systems, School of Physics, Sun Yat-sen University, Guangzhou 510275, China.

<sup>b</sup>Instrumental Analysis & Research Center, Sun Yat-sen University, Guangzhou 510275, China. <sup>c</sup>School of Materials Science and Engineering, State Key Laboratory of Optoelectronic Materials and Technologies, Sun Yat-sen University, Guangzhou 510275, China. *E-mail: liuyong7@mail.sysu.edu.cn* 

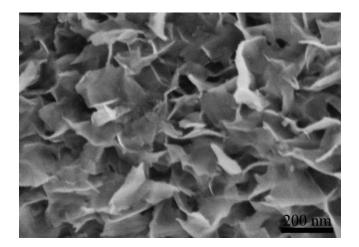
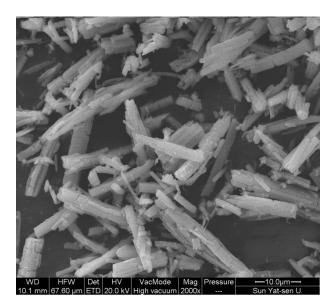
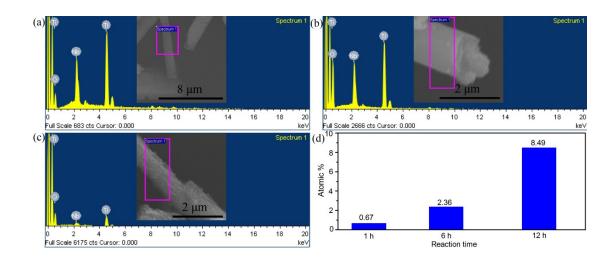


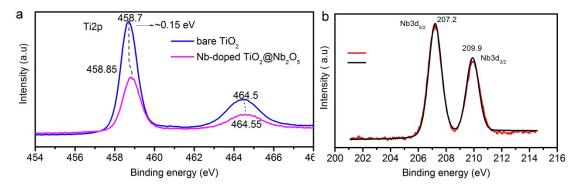
Fig. S1 High-magnification FESEM images of  $Nb_2O_5$  nanosheets in the Nb-doped  $TiO_2@Nb_2O_5$  sample.



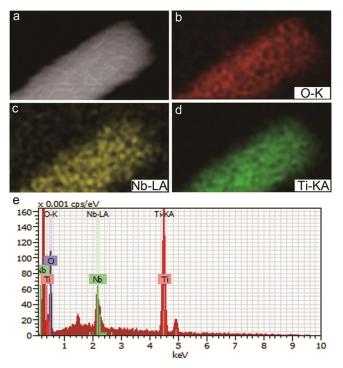
**Fig. S2** FESEM of bare  $TiO_2$  rods.



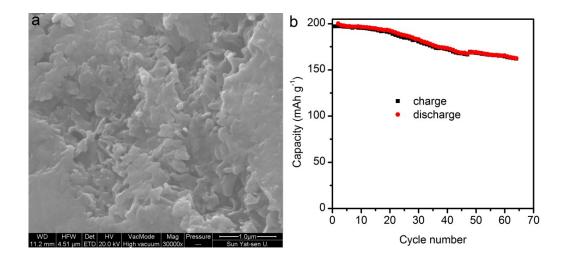
**Fig. S3** The time-dependent EDX spectrum of Nb-doped  $TiO_2@Nb_2O_5$  heterostructures that obtained by hydrothermal treatment at 150 °C for (a) 1 h, (b) 6 h, and (c) 12 h, respectively. (d) Histogram of Nb dopant concentration in above samples with different reaction time.



**Fig. S4** (a) High-resolution Ti 2p spectra of bare  $TiO_2$  and Nb-doped  $TiO_2@Nb_2O_5$ , showing a ca. 0.15 eV shift to higher binding energy, (b) Nb  $3d_{5/2}$  XPS spectra of Nb-doped  $TiO_2@Nb_2O_5$  coreshell heterostructures.



**Fig. S5** Images of elemental mapping and the EDS spectrum of Nb-doped  $TiO_2@Nb_2O_5$  core-shell heterostructures by SEM mapping analysis. All the elements (O, Ti and Nb) are homogeneously distributed in the Nb-doped  $TiO_2@Nb_2O_5$  core-shell heterostructures as shown in the upper images and the EDS spectrum shows the presence of O, Ti and Nb elements.



**Fig. S6** (a) The Nb<sub>2</sub>O<sub>5</sub> nanosheet aggregates produced without the addition of Ti precursor; (b) the cycling performance of bare Nb<sub>2</sub>O<sub>5</sub> electrodes.

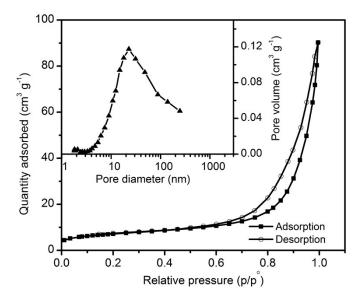


Fig. S7 Nitrogen adsorption-desorption isotherms for Nb-doped  $TiO_2@Nb_2O_5$  core-shell heterostructures. Inset shows the corresponding pore size distribution.

<b>Table S1</b> Resultant values of equivalent circuit for both the Nb-doped $TiO_2@Nb_2O_5$ and bare $TiO_2$ nanorod electrodes after and before cycle.						
samples	$\begin{array}{c} R_e\!/\Omega \\ (before) \end{array}$	$\begin{array}{c} R_b / \Omega \\ (before) \end{array}$	$\begin{array}{c} R_{sf+ct}\!/\Omega \\ (before) \end{array}$	Re/Ω (after)	Rb/Ω (after)	$\begin{array}{c} R_{sf+ct}\!/\Omega \\ (after) \end{array}$
Nb-doped TiO <sub>2</sub> @Nb <sub>2</sub> O <sub>5</sub>	3.1	14.8	8.2	3	4.4	4.1
bare TiO <sub>2</sub>	3.7	25.1	21.7	3.5	17.7	14.3