## **Supporting Information**

## Nano Anatase TiO<sub>2</sub> Quasi-Core–Shell Homophase Junction Induced by a Ti<sup>3+</sup> Concentration Difference for Highly Efficient Hydrogen Evolution

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Figure S1 TEM images of (a)  $TiO_2$ -1:1, (b)  $TiO_2$ -1:2, (c)  $TiO_2$ -1:3, and (d)  $TiO_2$ -1:4.



Figure S2 Size distributions of (a)  $TiO_2$ -1:1, (b)  $TiO_2$ -1:2, (c)  $TiO_2$ -1:3, and (d)  $TiO_2$ -1:4.



Figure S3 Nitrogen adsorption-desorption isotherms of as-prepared catalysts.



**Figure S4** HRTEM images and the corresponding SAED patterns over a single nanocrystal of (a) TiO<sub>2</sub>-1:1, (b) TiO<sub>2</sub>-1:2, (c) TiO<sub>2</sub>-1:3, and (d) TiO<sub>2</sub>-1:4.



Figure S5 XPS survey of as-prepared catalysts and TiO<sub>2</sub>-A.



**Figure S6** Ti 2p XPS spectra of (a) TiO<sub>2</sub>-1:1, (b) TiO<sub>2</sub>-1:2, (c) TiO<sub>2</sub>-1:3, and (d) TiO<sub>2</sub>-1:4 before and after 60 s Ar<sup>+</sup> ion etching. The red and blue dash lines are corresponded to the Ti<sup>3+</sup> and Ti<sup>4+</sup> 2p peaks, respectively.



**Figure S7** (a) Solar-light-driven photocatalytic water splitting for  $H_2$  generation over as-prepared catalysts, TiO<sub>2</sub>-A and P25 without Pt. (b) Cycling measurement of hydrogen generation over TiO<sub>2</sub>-1:3 without Pt under solar illumination.



**Figure S8** (a) XRD pattern of  $TiO_2$ -1:0 and the characteristic diffraction peaks of standard  $TiH_2$  (JCPDS no. 25-0982). (b) XRD pattern of  $TiO_2$ -0:1 and the characteristic diffraction peaks of standard anatase titania (JCPDS no. 21-1272). (c) TEM image, (d) HRTEM image and the corresponding SAED pattern, (e) size distribution of  $TiO_2$ -0:1. (f) Solar-light-driven photocatalytic  $H_2$  evolution performance over Pt loaded  $TiO_2$ -0:1.



Figure S9 Mott–Schottky plots of the catalysts collected at a frequency of 1 kHz in the dark.