### **Supporting information**

# Boosting Photocatalytic Water Splitting by Tuning Built-in Electric Field at Phase Junction

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## Supplementary Figures and Estimation Method of $\mathbf{S}_{\mathbf{t}}$

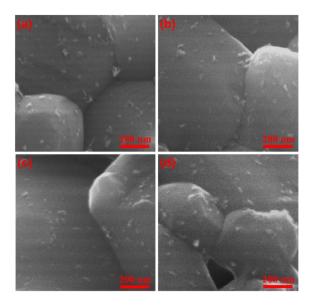


Fig. S1 SEM images of 1% A16/R

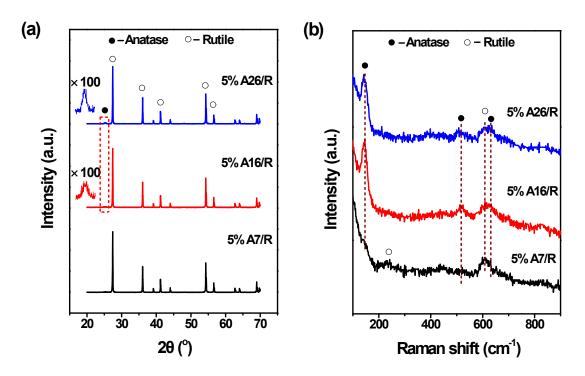


Fig. S2 (a) XRD and (b) UV Raman spectra of 5% A7/R, 5% A16/R, and 5% A26/R samples

Table S1 BET surface areas of R and A/R samples

Sample	R	1% A16/R	3% A16/R	5% A16/R	7% A16/R	5% A7/R	5% A26/R	5% A16+R
BET surface area (m²/g)	4.2	4.6	5.9	8.7	10.9	9.9	6.3	10.6

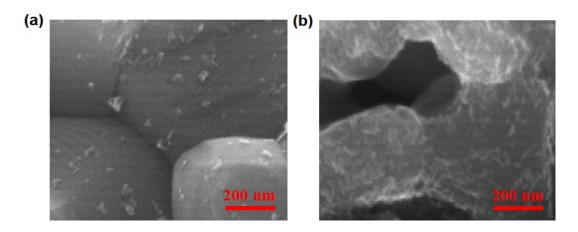


Fig. S3 SEM images of (a) 1% A16/R and (b) 7% A16/R samples

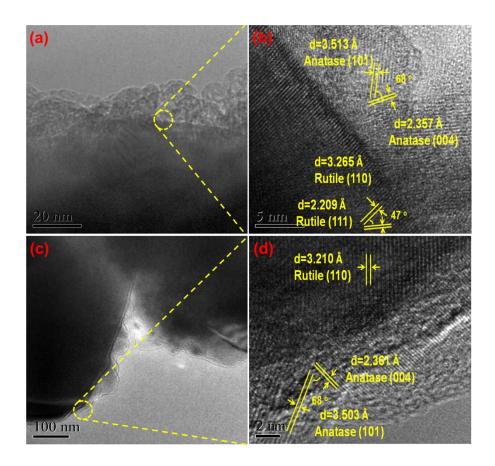


Fig. S4 TEM and HRTEM images of (a, b) 5% A16/R and (c, d) 3% A26/R samples

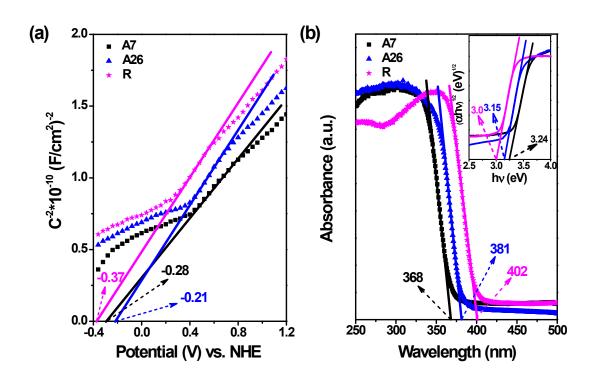


Fig. S5 (a) Mott-Schottky curves and (b) UV-vis diffuse reflectance spectra of A7, A26, and R samples (inset: plots of  $(\alpha hv)^{1/2}$  vs. photon energy)

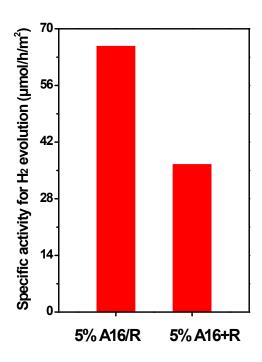


Fig. S6 Photocatalytic  $H_2$  evolution performances per surface area of 5% A16/R and mechanical mixing of 5% A16 with R (5% A16+R)

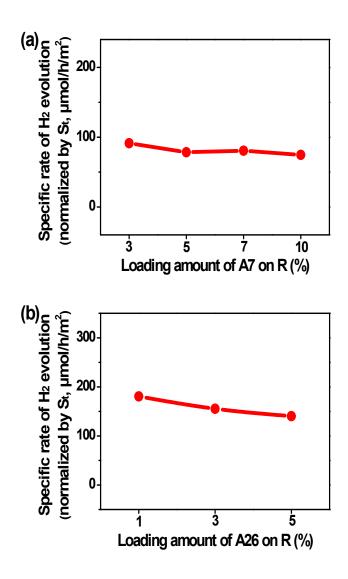


Fig. S7 Specific activity of photocatalytic  $H_2$  evolution (normalized by the total interfacial contact areas between A7 or A26 particles and R) of A7/R and A26/R

The estimation of solar-to-hydrogen (STH) efficiency: STH efficiencies were roughly estimated according to eqn (1). 1, 2 The apparent (or external) STH efficiency, in which all of the incident photons are assumed to be absorbed in a given photocatalyst suspension.

$$P = \frac{c \times h \times n}{\lambda \times t}$$

$$q_p = n/t_{(s)}$$

$$\phi = 2k/q_p$$
(1)

The power of the light P (in Watts) was measured with a FZ-A Irradiatometer (Photoelectric Instrument Factory of Beijing Normal University, China). The average rate of hydrogen production "k" (mol of  $H_2/s$ ) was derived from the amount of  $H_2$  generated from the first 6 hours of illumination. The quantum efficiency " $\phi$ " was calculated by determining the number of moles of hydrogen produced per second, and dividing it by the number of moles of photons absorbed by the system per second (two photons per  $H_2$ ).  $\lambda$  is taken to be 300 nm, h is Planck's constant (in J/s), c is the speed of light (in m/s), n is the number of photons, t is the time (in second),  $q_p$  is the photon flux (number of photons per second).

The estimation of  $S_t$ : It is assumed that each anatase particle is a sphere, and evenly distributed on the rutile. The interfacial contact area ( $S_s$ ) between single A nanoparticle and R particle can be estimated according to average diameter of A measured from SEM. The overall interfacial contact area between A and R ( $S_t$ ) is estimated by  $S_s \times n$ , where n is the number of A particles. The number of A particles is estimated as following: the volume of single A particle on the surface of R and then the mass of single A particle can be calculated according to the average diameter measured from SEM and density of  $TiO_2$  (3.8 g/cm<sup>3</sup>). The actual loading amounts divided by the mass of single A particle is the numbers of A particles (n).

#### References

- 1 K. Maeda, *Chem. Commun.*, 2013, **49**, 8404.
- 2 Z. J. Han, F. Qiu, R. Eisenberg, P. L. Holland and T. D. Krauss, *Science*, 2012, **338**, 1321.