

# Manipulating Solar Absorption and Electron Transport Properties of Rutile TiO<sub>2</sub> Photocatalyst via Highly n-Type F-Doping

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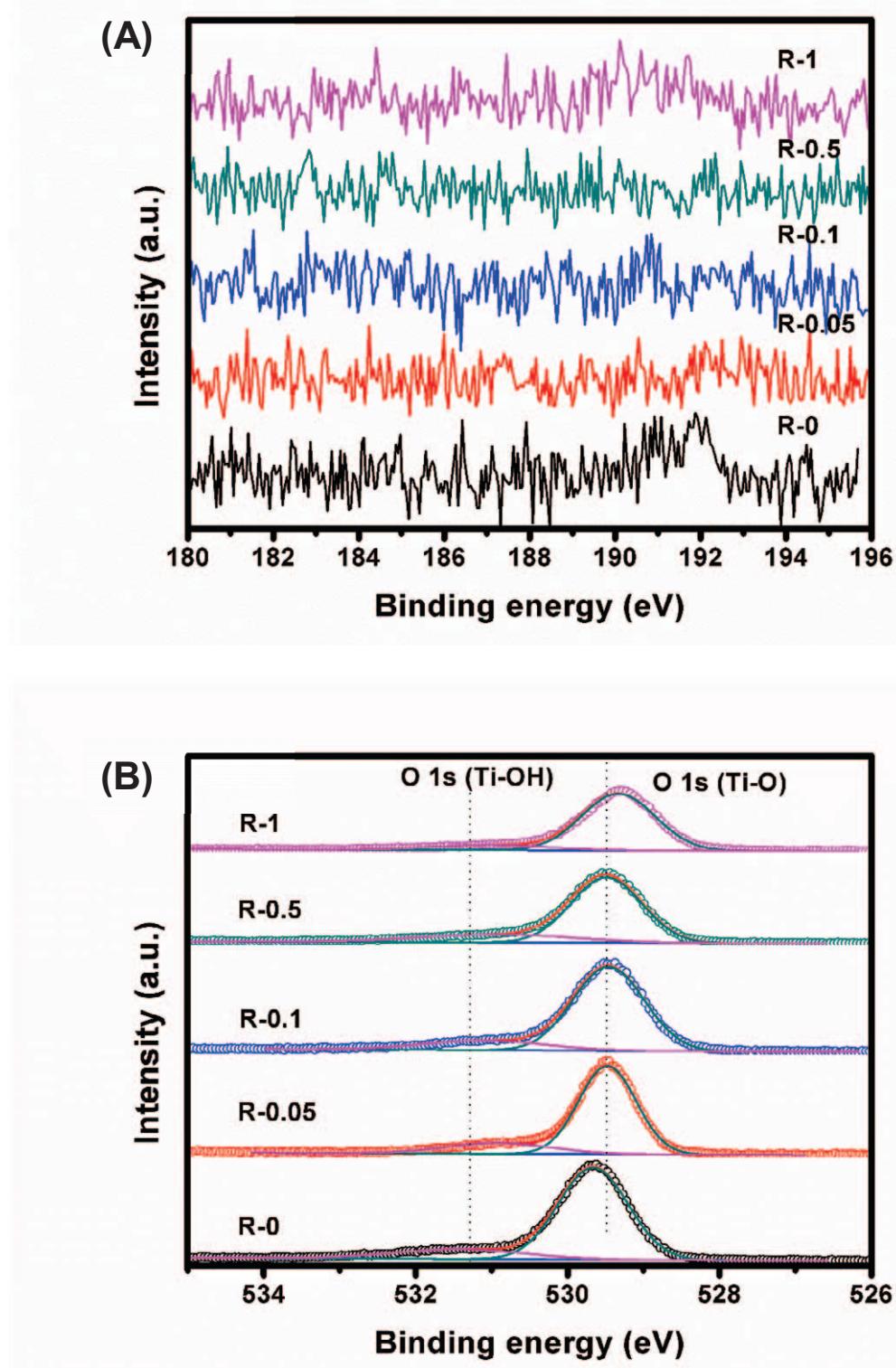
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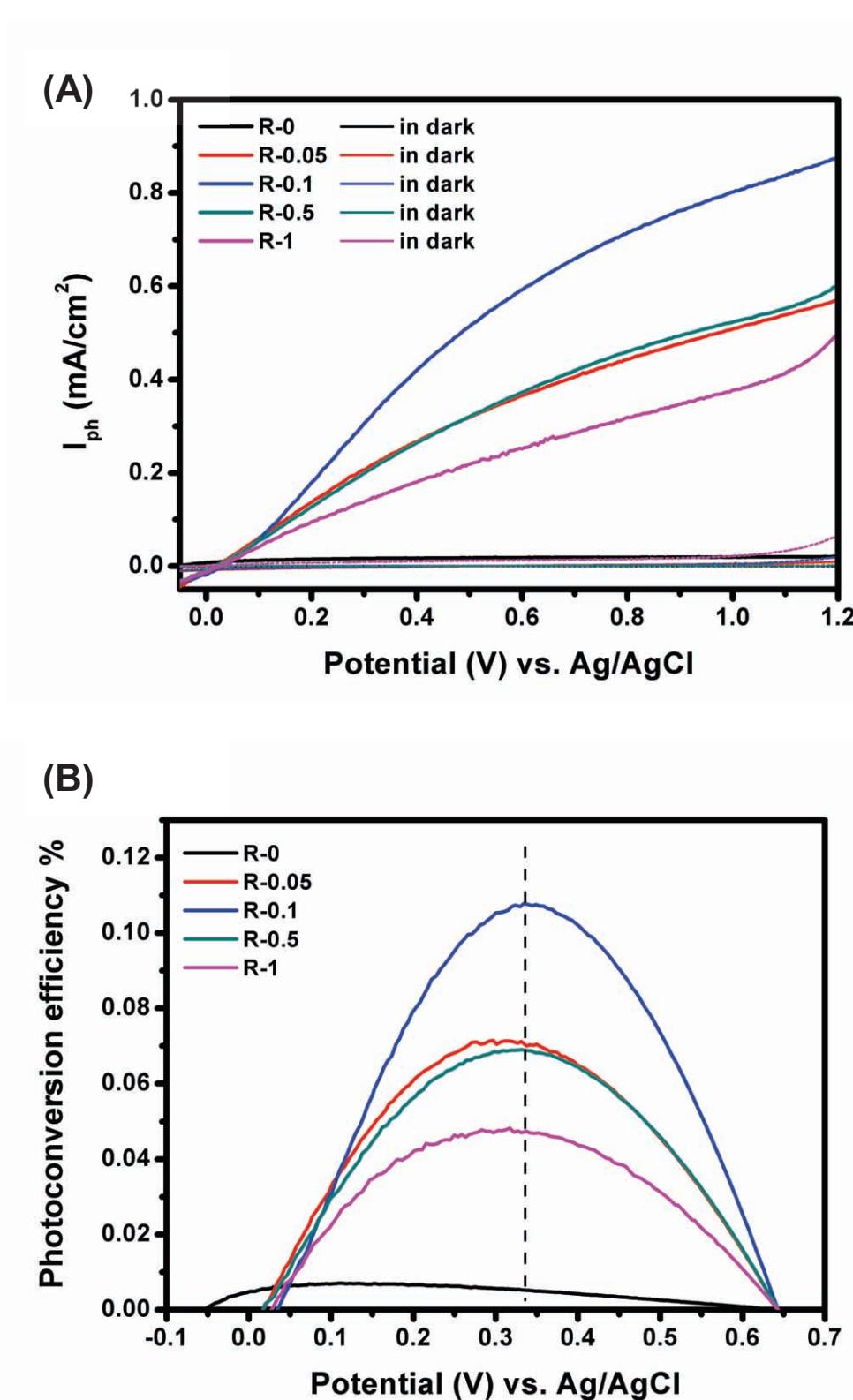


**Fig. S1** XPS spectra of (A) B 1s and (B) O 1s from the rutile single crystal TiO<sub>2</sub> with different F:Ti molar ratios of reaction precursors.

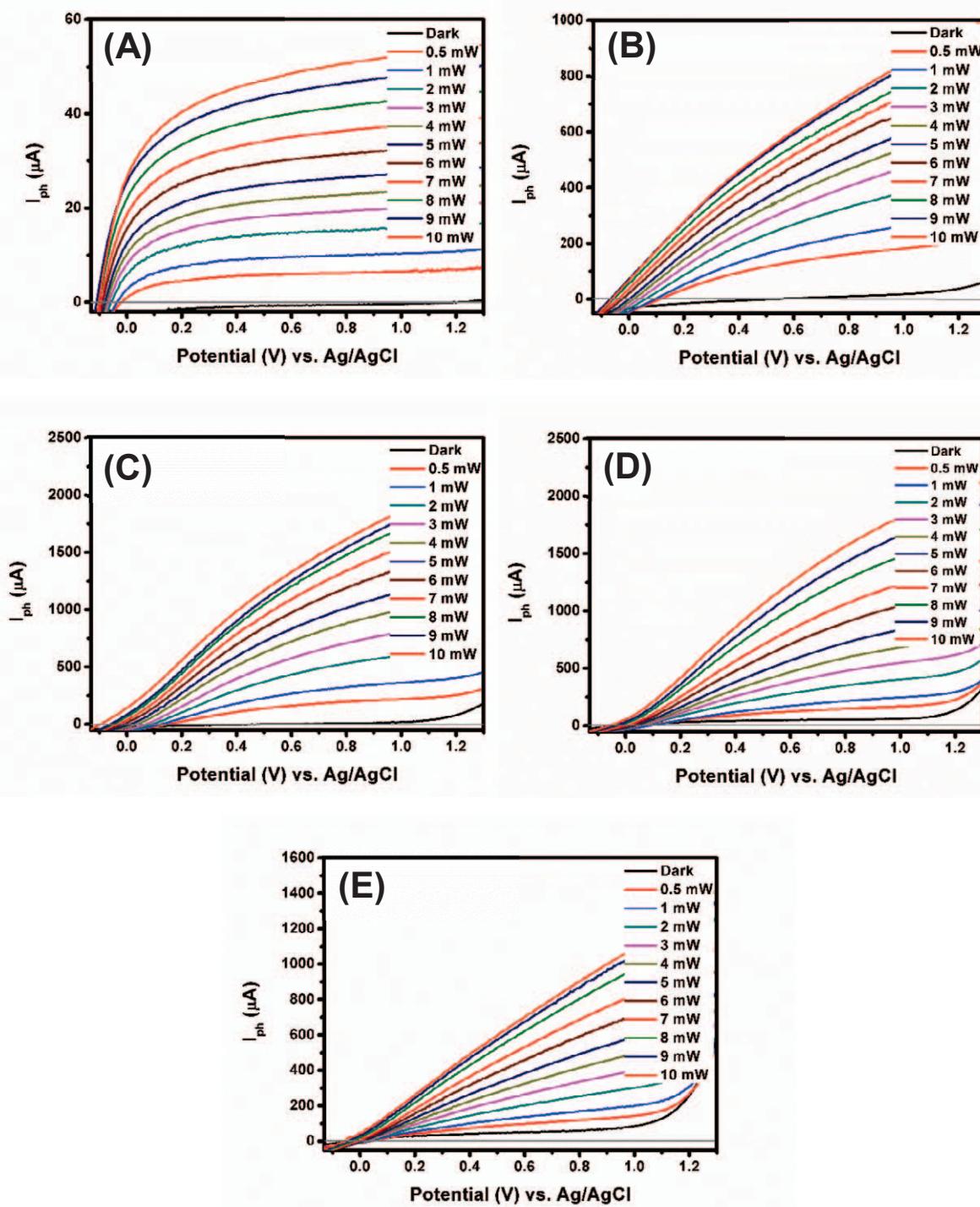
The photoconversion efficiencies of pristine and F-doped TiO<sub>2</sub> films were calculated using the equation

$$\eta = I(1.23 - V)/J_{\text{light}}$$

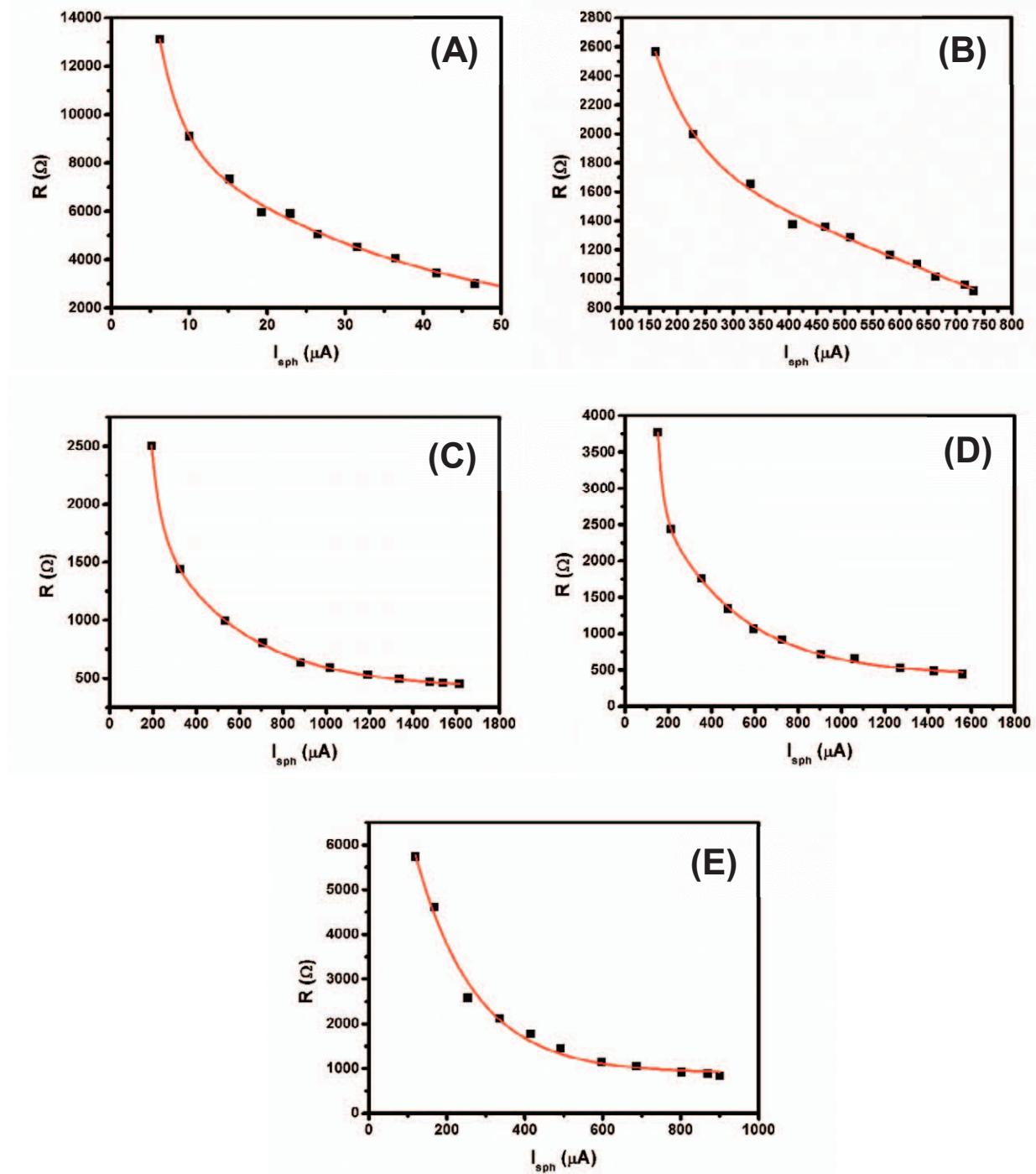
where V is the applied bias vs RHE, I is the photocurrent density at the measured bias and J<sub>light</sub> is the irradiance intensity of 100 mW/cm<sup>2</sup>. The calculated photoconversion efficiency as a function of the applied bias are show in Fig. S2B



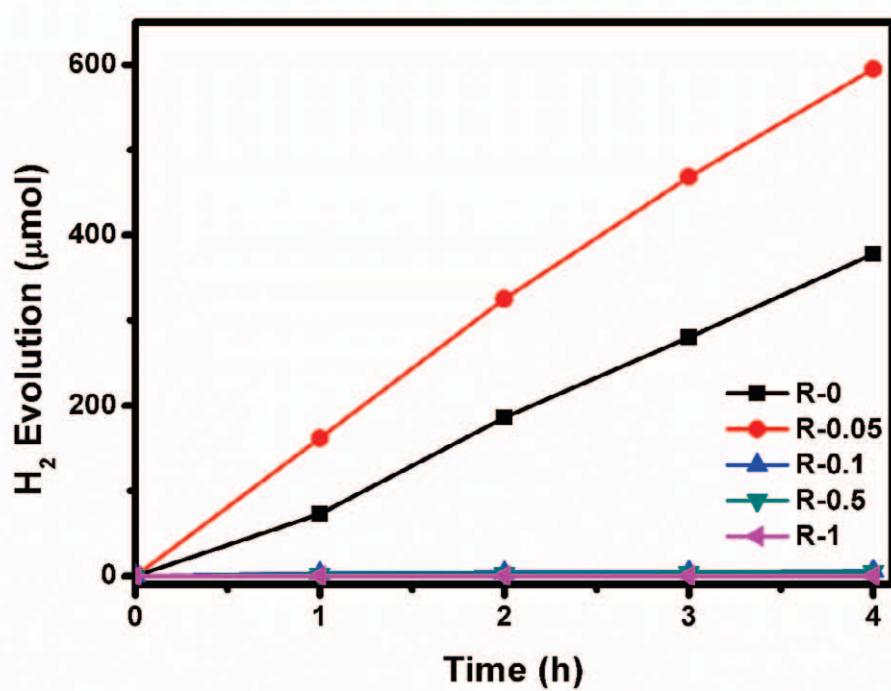
**Fig. S2** (A) Photoelectrochemical (PEC) cell linear sweep voltammetry spectra of the pristine  $\text{TiO}_2$  (R-0) and F-doped (R-0.05 to R-1)  $\text{TiO}_2$  films in a 0.2 M  $\text{Na}_2\text{SO}_4$  solution with a scan rate of 20 mV/s under  $100 \text{ mW/cm}^2$  illumination. (B) Calculated photoconversion efficiencies for the pristine  $\text{TiO}_2$  (R-0) and F-doped (R-0.05 to R-1)  $\text{TiO}_2$  samples, as a function of applied potential vs  $\text{Ag}/\text{AgCl}$ .



**Fig. S3** Photoelectrochemical (PEC) cell linear sweep voltammetry spectra obtained from the rutile  $\text{TiO}_2$  photoanodes with different initial F:Ti molar ratios of (A) 0:1, (B) 0.05:1, (C) 0.1:1, (D) 0.5:1 and (E) 1:1 in 0.2 M  $\text{Na}_2\text{SO}_4$  supporting electrolyte, under different UV light intensities.



**Fig. S4** Relationships between the measured resistance and saturation photocurrent obtained from the rutile  $\text{TiO}_2$  photoanodes with different initial F:Ti molar ratios of (A) 0:1, (B) 0.05:1, (C) 0.1:1, (D) 0.5:1 and (E) 1:1 in 0.2 M  $\text{Na}_2\text{SO}_4$  supporting electrolyte, under different UV light intensities.



**Fig. S5** Time course of evolved  $H_2$  of F-doped  $TiO_2$  samples from water containing 10 vol% methanol as an electron donor under UV-vis light irradiation.