

## Electronic Supplementary Information

# **Controllable fabrication of TiO<sub>2</sub> anatase/rutile phase junctions by a designer solvent for promoted photocatalytic activity**

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## 1. Experimental section

### 1.1 Materials and reagents.

Tetrabutyl titanate (TBOT  $\geq$  99% purity) was obtained by Shanghai Aladdin Biochemical Technology Co., Ltd, China. The commercial P25 TiO<sub>2</sub> was purchased from Beijing Entrepreneur Science & Trading Co., Ltd, China. choline chloride (ChCl), lactic acid, oxalic acid, absolute ethanol and methyl alcohol were supplied from Sinopharm Chemical Reagent Beijing Co., Ltd, China.

### 1.2 DES and TiO<sub>2</sub> Preparation

DESs were prepared by mixing two hydrogen-bond donors (lactic acid and oxalic acid) and hydrogen-bond acceptor (ChCl) with a molar ratio of donor to acceptor of 1:1 at 70 °C for 2-4 h until clear, transparent, homogeneous target liquids appeared. Moreover, the molar ratios of two hydrogen-bond donors of lactic acid to oxalic acid change from 6:1 to 1:10.

The TiO<sub>2</sub> was prepared as follows. First, 1 mL TBOT was added dropwise into the mixture solvent containing 15.5 mL ChCl/lactic acid/oxalic acid DES and 0.5 mL distilled water under vigorous stirring. Then the obtained mixture was poured into a 25 mL Teflon-lined stainless steel autoclave. The autoclave was put into an oven and heated at 180 °C for 18 h. After naturally cool down to the room temperature, the white precipitate was obtained via centrifugation, washing thoroughly with absolute ethanol and distilled water, and drying at 60 °C for 5 h.

### 1.3 Hydrogen evolution test

The photocatalytic H<sub>2</sub> evolution experiments were performed in a 20 mL quartz vessel sealed with a silicone rubber septum at an ambient temperature under atmospheric pressure. First, 1 mg as-prepared anatase/rutile junction TiO<sub>2</sub> was suspended in 10 mL double distilled water containing 20 vol% methanol as the sacrificial electron donor. Then, the sample solutions were thoroughly deaerated by bubbling nitrogen for 30 min. Next, each sample solution was irradiated by a 500 W mercury lamp (the light intensity was 0.020 W) at room temperature with continuous stirring. Finally, the evolved gases were analyzed by injecting 1 mL of headspace gas

into the gas chromatograph (FULI 9750, thermal conductivity detector, nitrogen as the carrier gas, 5A° molecular sieve column) and quantified using an external standard calibration plot.

#### *1.4 Photoelectrochemical measurements*

Photoelectrochemical performance measurements were carried out in a standard three-electrode PEC cell, with TiO<sub>2</sub>, saturated calomel electrode, and Pt wire as the working electrode, reference electrode, and counter electrode, respectively. A 0.5 M Na<sub>2</sub>SO<sub>4</sub> solution was used as the electrolyte and a 300W Xenon lamp was used as the light source. Electrochemical impedance spectroscopy (EIS) was carried out under 300 W Xenon lamp illumination at open circuit voltage over a frequency range of 0.1-100000 Hz with a bias voltage of 0.5 V.

#### *1.5 Characterizations of DESs and catalysts*

Fourier transform infrared (FT-IR) spectra were measured by Nicolet IS50 FT-IR spectrometer. The crystal structures of the samples were tested by X-ray diffraction (XRD, Bruker D8, Germany) equipped with Cu K $\alpha$  radiation. Raman spectra were carried out on a LabRAM HR800 confocal microscope Raman spectrometer. Scanning electron microscopy (SEM) images were detected on a Hitachi S4800 scanning electron microscope operating at 5.0 kV. Transmission Electron Microscopy (TEM) and High-Resolution Transmission Electron Microscopy (HRTEM) analyses were measured by JEM 2010 EX instrument. Photoluminescent (PL) spectra were obtained by an FLS-920 Edinburgh fluorescence spectrometer.

#### *1.6 Method of structure optimizations*

All the DFT calculations were operated using the Gaussian 09 program. The M062X/6-31+G (d,p) method has been used for structure optimizations. The subsequent frequency calculations at the same level verify the optimized structures to be at ground states without imaginary frequencies (NImag=0).

## **2. Optimized interactional structures of three compositions in DES**

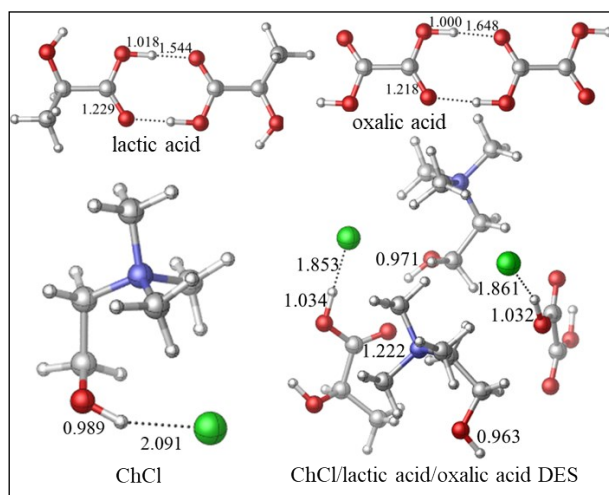
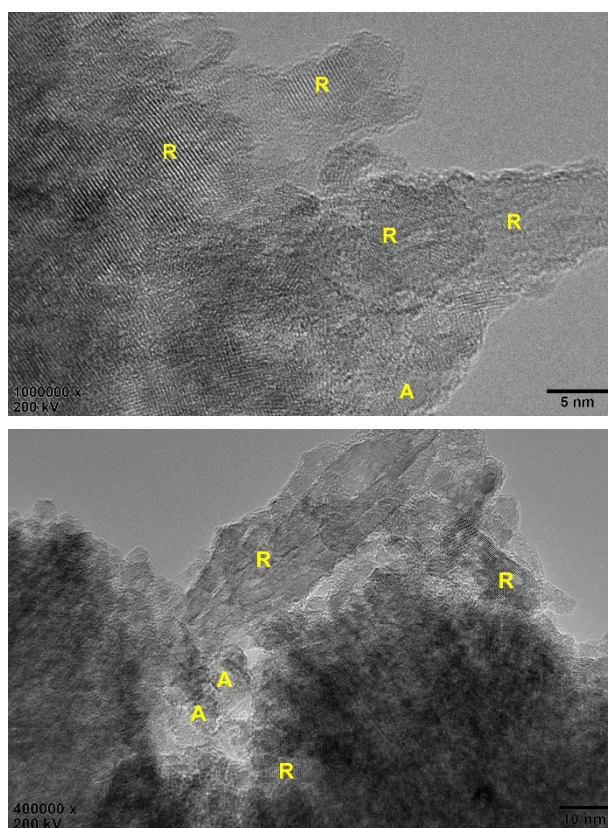


Fig. S1 The optimized interactional structures of three compositions in DES ChCl/lactic acid/oxalic acid by M062X/6-31+G (d,p). White: H; dark grey: C; blue: N; red: O; green: Cl.

### 3. HRTEM images of TiO<sub>2</sub> anatase/rutile phase junction (TiO<sub>2</sub>-AR)



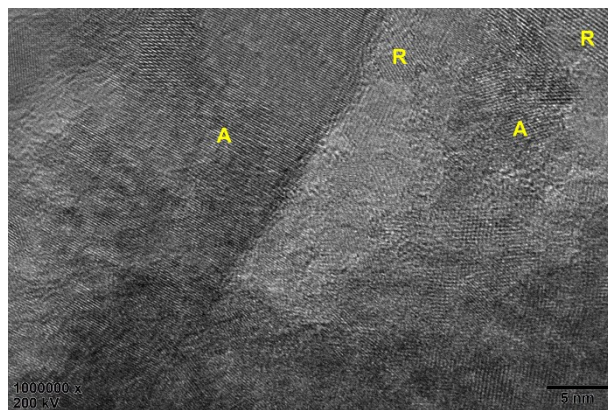


Fig. S2 HRTEM images for TiO<sub>2</sub>-AR sample at 1:4 of lactic to oxalic acid. A: anatase; R: rutile.

#### 4. XRD patterns of TiO<sub>2</sub>-AR sample before and after recycling test

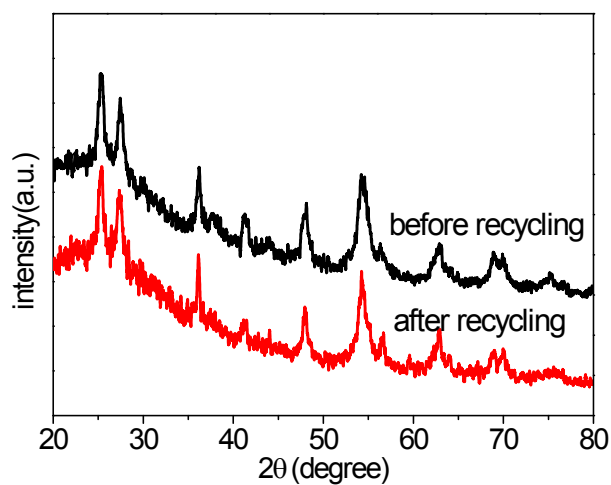


Fig. S3 XRD patterns of TiO<sub>2</sub>-AR sample before and after recycling test.