

# Supplementary Information:

## H<sub>2</sub> Spillover Enhanced Hydrogenation Capability of TiO<sub>2</sub> Used for Photocatalytic Splitting of Water: A Traditional Phenomenon for New Application

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### Experimental

#### Catalyst preparation

The catalyst 1wt% Pt/P25 was prepared using conventional impregnation method. At first, 1 g of commercial P25 (Degussa) was immersed into a given amount of the aqueous solution of H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O. Then the obtained slurry was dried overnight at room temperature. The dried powder was subsequently dispersed into 200 mL deionized water and reduced by 220 mg NaBH<sub>4</sub>. After centrifugation, the catalyst precursor was obtained, which was washed with deionized water for three times and dried at 120 °C for 4 hours. The dry precursor of Pt/P25 was annealed in 8% H<sub>2</sub>/N<sub>2</sub> atmosphere (100 mL/min) at 200, 400, 500 or 700 °C for 4 h, respectively. The final catalysts are denoted as Pt/P25-x, x represents the treatment temperature.

For comparison, the Pt/P25-400-N<sub>2</sub> was prepared in the same way except that the Pt/P25 was annealed in N<sub>2</sub> at 400 °C for 4 h. Meanwhile, the Pt/TiO<sub>2</sub>(H<sub>2</sub>) sample was also prepared by pre-hydrogenation of the P25 at 400 °C in 8% H<sub>2</sub>/N<sub>2</sub> atmosphere (100 mL/min) for 4 h, and the post-loading of Pt on the pre-hydrogenated P25, using the same impregnation method as described above.

#### Catalyst characterization

The images of HRTEM and TEM were taken by using JEOL-JEM-2100F electron microscope operating at 200 kV. Before measurement, the samples were ultrasonically suspended and deposited onto an ultrathin carbon film coated on the Cu grids.

The X-ray powder diffraction (XRD) was performed on a D/max 2500v/pc (Rigaku) diffraction instrument operating at 200 mA and 40 kV, using Cu K $\alpha$  as radiation source ( $\lambda=0.15418$  nm). The data of  $2\theta$  from 20 to 80° were collected with the stepsize of 0.02°.

UV-vis diffuse reflectance spectra (UV-vis DRS) of the catalysts were recorded on a Lambda 750S UV-vis-NIR spectrometer (Perkin-Elmer) equipped with an integrating sphere. The DRS spectra were collected in 200–800 nm against barium sulfate.

H<sub>2</sub>-TPR measurements were performed on the TP-5079 TPDRO setup (supplied by the Tianjin Xianquan Instrument Company) equipped with a thermal conductivity detector (TCD). A mixture of 8 vol.% H<sub>2</sub> in N<sub>2</sub> was used as reductant at a flow rate of 30 mL/min. The tests were carried out from room temperature to 900 °C at a heating rate of 10 °C/min.

X-ray photoelectron spectra (XPS) were recorded on a PHI-1600 ESCA spectrometer using Mg K $\alpha$  (1253.6 eV) as radiation source. The base pressure was about  $5 \times 10^{-8}$  Pa. The binding energies were calibrated using C 1s peak at 284.6 eV as standard and quoted with a precision of  $\pm 0.2$  eV.

The electron paramagnetic resonance (EPR) spectra were measured with a Bruker A320 spectrometer operating at X band frequency (9.77 GHz) and a 100 kHz field modulation. The spectra of the samples were recorded at 100 K by calibrating the spectrometer with a DPPH standard at  $g = 2.0036$ .

Photoluminescence (PL) emission spectra were collected on the Fluorolog3 photoluminescence spectrometer (Horiba Jobin Yvon, Japan) at room temperature. The excitation wavelength is 325 nm, and the spectral range is from 350 to 600 nm.

#### Hydrogen production measurements

Photocatalytic hydrogen evolution was carried out in a Labsolar-III AG system (Beijing Perfectlight Technology Co., Ltd). In a typical photocatalytic experiment, 0.05 g catalyst was suspended in 100 mL aqueous solution containing 50 vol.% methanol. The reaction temperature was maintained at 7 °C. The amount of H<sub>2</sub> evolved was determined by a gas chromatograph (Beifen 3420).

The light source in the above experiments was a 300 W Xe arc lamp with an AM 1.5 G filter (Beijing Perfectlight Technology Co., Ltd). Data were taken approximately every hour during the simulated solar irradiation.

### Supporting figures:

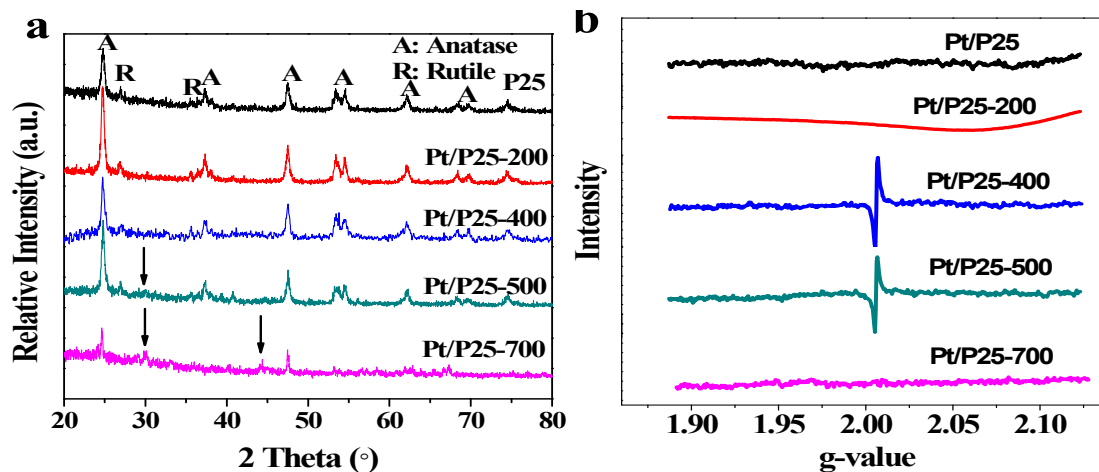


Figure S1. The XRD patterns (a) and EPR spectra (b) of the catalysts Pt/P25 and Pt/P25-x (x= 200, 400, 500 or 700 °C).

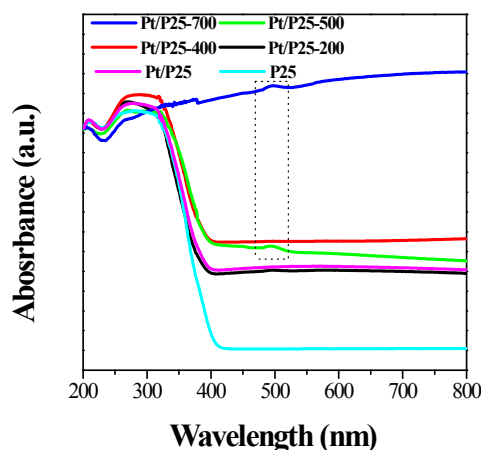


Figure S2. The UV-vis DRS of P25, Pt/P25 and Pt/P25-x normalized at 200 nm (x= 200, 400, 500 or 700 °C).

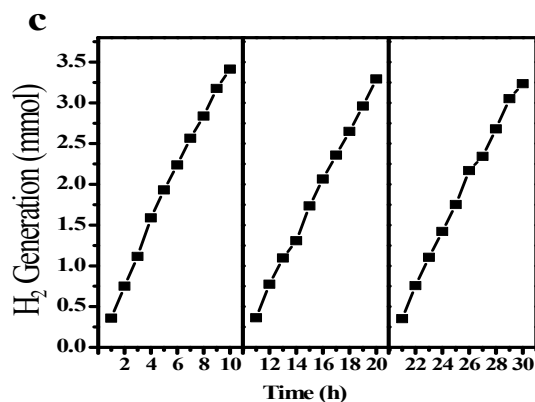
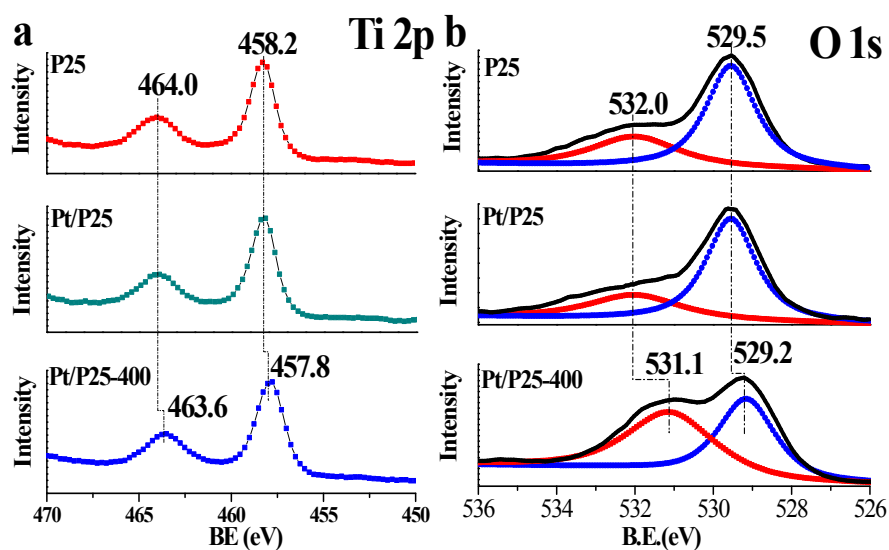
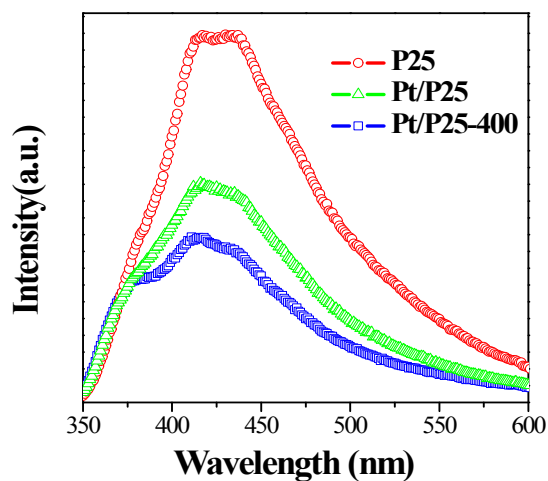


Figure S3. Cyclic measurements of hydrogen production over Pt/P25-400.



**Figure S4.** Ti 2p (a) and O 1s (b) XPS spectra of P25, Pt/P25 and Pt/P25-400; the red and blue dash lines in (b) are the fitting curves.



**Figure S5.** The photoluminescence emission spectra of P25, Pt/P25 and Pt/P25-400.