Electronic Supplementary Material (ESI) for RSC Advances

Supporting Information

Synthesis of Pt@NH_2-MIL-125(Ti) as a photocathode material for photoelectrochemical hydrogen production

Chuantao Hou, Qin Xu, Yanjuan Wang, Xiaoya Hu[*]

Email: xyhu@yzu.edu.cn

Experimental Section

NH_2-MIL-125(Ti) was synthesized according to the literature methods.[1] All other reagents were purchased from Aldrich and used without further purification.

Preparation of the Pt@NH_2-MIL-125(Ti): 50 mg of activated NH_2-MIL-125(Ti) was suspended in 10 mL of dry n-hexane as hydrophobic solvent and the mixture was sonicated for 15 min until it became homogeneous. After stirring for 2 h, 0.1 mL of aqueous K_2PtCl_4 solution of different concentrations as the hydrophilic solvent was added dropwise over a period of 15 min with constant vigorous stirring. The resulting solution was continuously stirred for 2 h. After careful filtration, the yellow powder was dried in air at room temperature.

The reduction of K_2PtCl_4 was performed by a photoreduction method. The synthesized sample was suspended in methanol/H_2O (V/V=9:1) and degassed using N_2 for at least 15 min before being placed in front of a 250 W Xe-lamp. After illuminated for 30 min, the sample was further washed by water, and followed by treating in 100 °C for 5 h to yield Pt@NH2-MIL-125(Ti).

Fabrication of NH_2-MIL-125(Ti) and Pt@NH_2-MIL-125(Ti) electrodes: ITO slices were cleaned by immersion in 2 M boiling KOH solution solved in 2-propanol for 20 min, followed by washing copiously with water and dried at 120 °C for 2 h.

An aliquot of 5 μL 1mg/mL as-synthesized NH_2-MIL-125(Ti) or Pt@NH_2-MIL-125(Ti) suspension in water was dropped onto a piece of ITO slice with fixed area of 0.04 cm^2. After drying in air, thin films on ITO were obtained. The thin films are referred as NH_2-MIL-125(Ti) electrode and Pt@NH_2-MIL-125(Ti) electrode, respectively.

PEC experiments general: PEC measurements were performed with a home-built pec system. A 250W Xe lamp was used as the irradiation source. Photocurrent was measured on a CHI 760D electrochemical workstation (CH Instruments, Austin, TX). All experiments were carried out at room temperature using a conventional three-electrode system with the modified ITO electrode as the working electrode, a platinum wire as the auxiliary electrode, and a saturated calomel electrode as the reference electrode.

Characterization: scanning electron microscope (SEM) and energy dispersive X-ray spectrum (EDX) analysis were performed on a scanning electron microscopy (SEM, Hitachi S-4800, Japan) at an acceleration voltage of 15 kV. High-resolution transmission electron microscopy (HRTEM)

and TEM images were performed on Tecnai G2 F30 S-TWIN (FEI, USA) with operating voltage at 200 kV. X-ray diffraction (XRD) patterns of the sample were recorded on a German Brucker AXS D8 ADVANCE X-ray diffractometer. Diffuse reflectance spectra (DRS) was obtained with a UV−vis recording spectrophotometer Cary 5000 (Varian, USA).

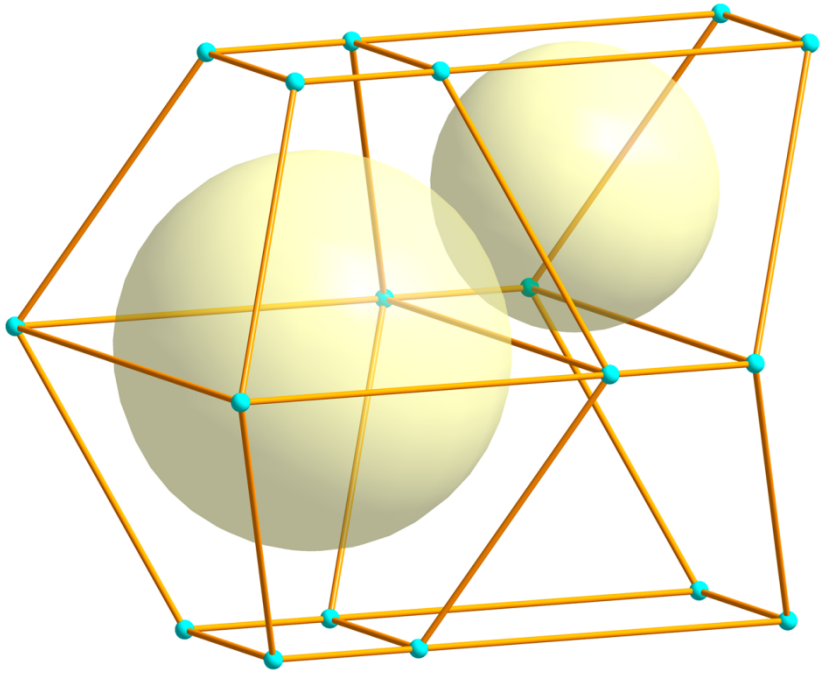

Fig. S1 Perspective view of the two cages with diameters of 12.55 and 6.13 Å in NH_2-MIL-125(Ti).

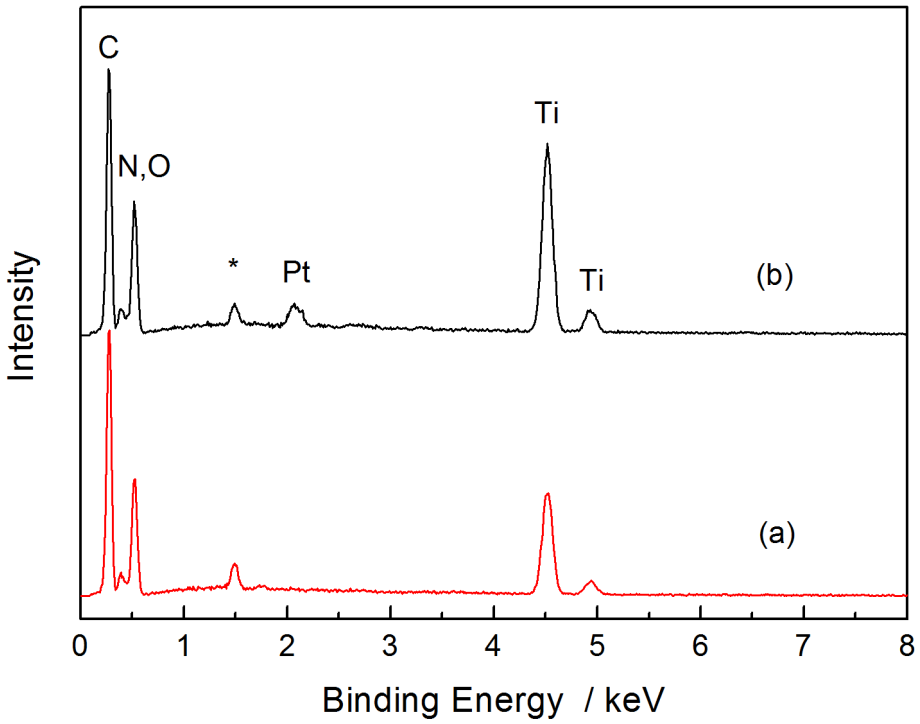

Fig. S2 Energy dispersive X-ray analysis (EDX) of (a) NH_2-MIL-125(Ti) and (b) the synthesized Pt@NH_2-MIL-125(Ti).

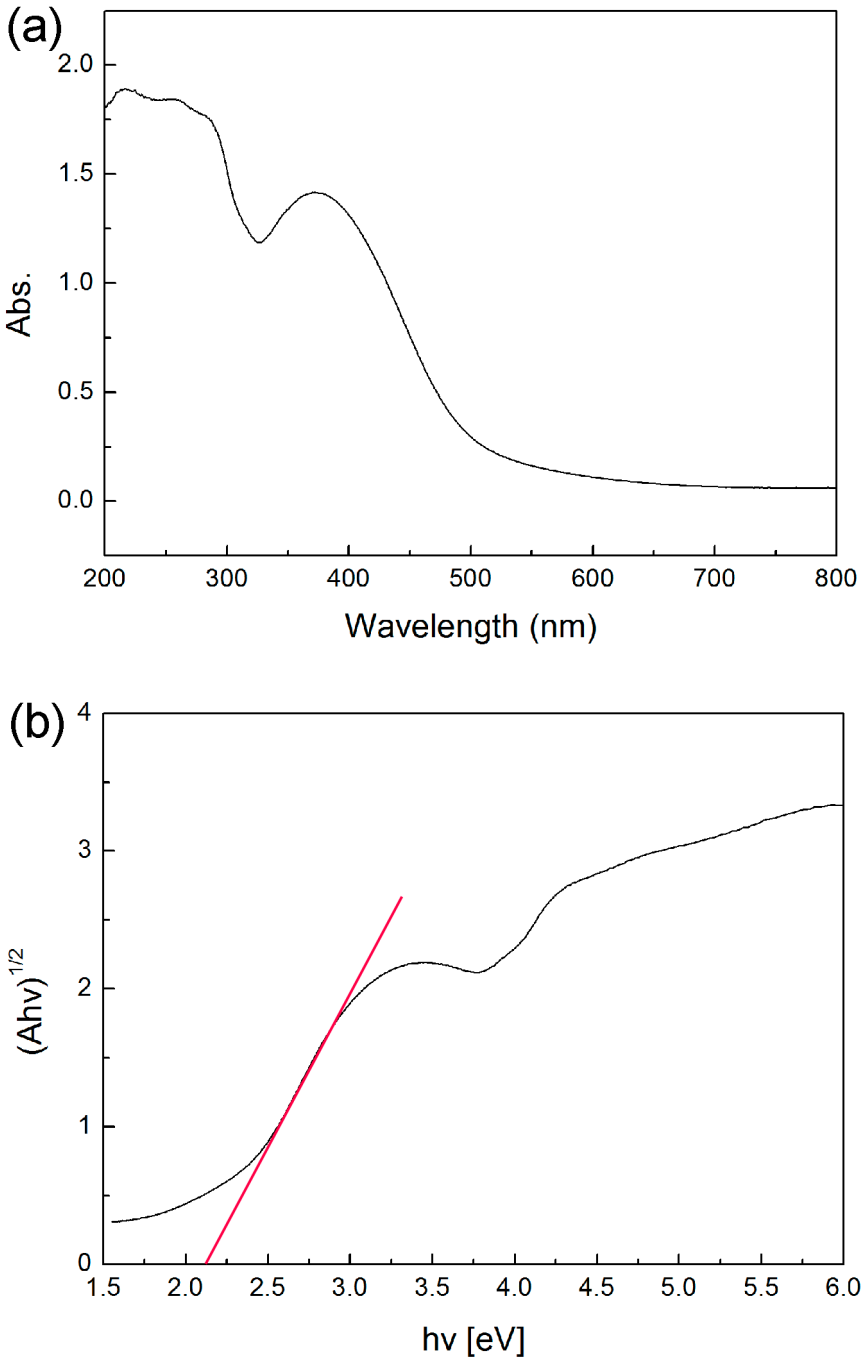

Fig. S3 The diffuse reflective spectra (DRS) of NH_2-MIL-125(Ti), and calculation of band gap in NH_2-MIL-125(Ti) of 2.2 eV.

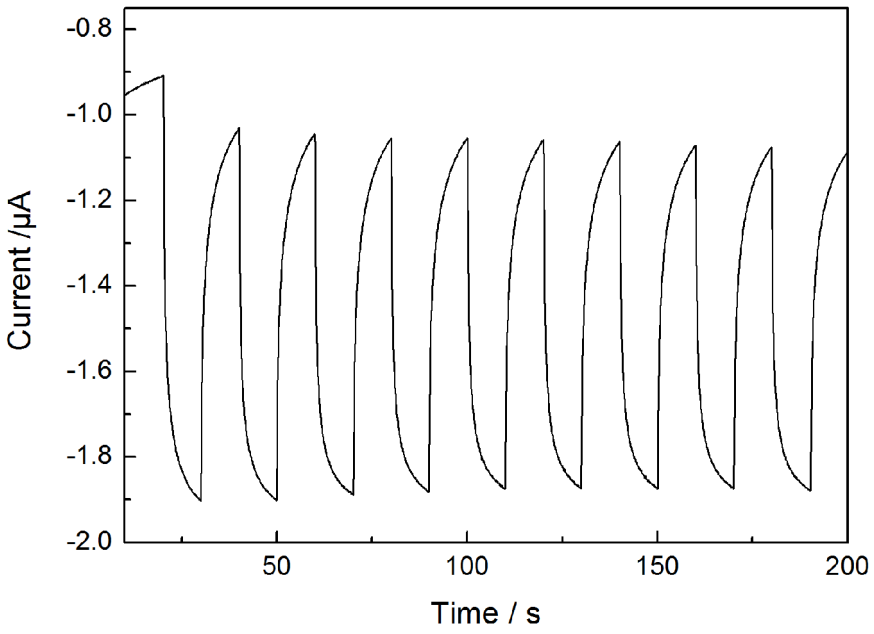

Fig. S4 Photocurrent responses of the Pt@NH_2-MIL-125(Ti) electrode with a potenial of -0.1 V versus NHE in 0.1 M Na_2SO_4 under chopped irradiation for 200s.

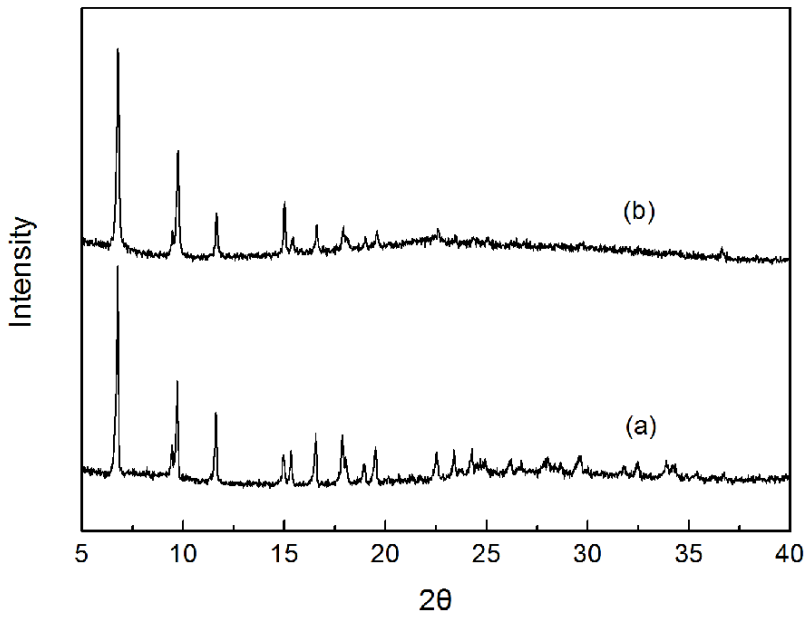

Fig. S5 XRD patterns of (a) powder Pt@NH_2-MIL-125(Ti) and (b) the Pt@NH_2-MIL-125(Ti) thin film on ITO after 1 h PEC operation.

Reference

1 C. Zlotea, D. Phanon, M. Mazaj, D. Heurtaux, V. Guillerm, C. Serre, P. Horcajada, T. Devic, E. Magnier, F. Cuevas, G. Ferey, P. L. Llewellyn, M. Latroche, *Dalton Trans.* 2011, **40**, 4879.