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Amine-Functionalized MIL-101(Cr) with Imbedded Platinum Nanoparticles as A Durable Photocatalyst for Hydrogen Production from Water

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Catalyst Preparation: NH_2-MIL-101(Cr) was prepared using a method published by Chen[10c] with a small modification. Chromic nitrate hydrate (800 mg, 2 mmol), 2-aminoterephthalic acid (360 mg, 2 mmol) and sodium hydroxide (200 mg, 5 mmol) were added into 15 mL deionized water. The mixture was stirred at ambient temperature for 5 minutes, and then the mixture was transferred to 50 mL Teflon-lined stainless steel autoclaves, and heated 16 h at 433 K. After the reaction, the products were extracted by centrifugation and washed with water and methanol, respectively. Finally, the products were dried under vacuum and activated by calcination for 6 h at 473 K.

Anatase TiO_2: Tetra-n-butyl titanate monomer (1.0 mL) was added into 15 mL ethanol. The mixture was stirred at ambient temperature for 5 minutes, and then the mixture was transferred to 50 mL Teflon-lined stainless steel autoclaves, and heated 12 h at 473 K. After the reaction, the products were extracted by centrifugation and washed with ethanol. Finally, the products were dried under vacuum.

Pt/NH_2-MIL-101(Cr): The activated NH_2-MIL-101(Cr) (0.2 g) was suspended in H_2O (20 mL) and sonicated for 20 min until it became highly dispersed. Then 3.98 mL (Pt: 1.5 wt. %) of aqueous H_2PtCl_4 solution (3.861 mM) was added and stirred at room temperature for 8 hours. After the reaction, the products were extracted by centrifugation and washed with water. Finally, the products were dried under vacuum and followed by 1h H_2 reduction at 473 K. The Pt/NH_2-MIL-101(Cr) with different level of Pt loading (0.5, 1.0, 1.5, 2.0, 3.0 wt. %) were prepared. 1.5 wt.% Pt loaded SiO_2 and TiO_2 were also prepared by the similar method.

Photocatalytic activity test: The photocatalytic activity test for H_2 production was carried out in an aqueous solution. A sample (10 mg) was suspended in H_2O (4 ml) and TEOA (1 ml) mixture containing 1 mM RhB in a Pyrex reaction vessel (30 cm^3), sealed with a rubber septum, and bubbled with argon gas for 30 min. Subsequently, the sample was irradiated from the side using a Xe lamp (500 W; SAN-EI ERECTRIC CO., ltd. XEF-501S) through the glass filter (> 420 nm) with magnetic stirring at ambient pressure and temperature. The evolved H_2 gas was monitored using a Shimadzu GC14B gas chromatograph equipped with MS5A column (H_2).

Characterization: X-ray powder diffraction patterns were recorded using a Rigaku RINT2500 diffractometer with Cu Kα radiation (λ = 1.5406 Å). Nitrogen adsorption measurements (BET) were performed using BELSORP-max system (BEL Japan, Inc.) at 77 K. Samples were degassed under vacuum at 473 K for 24 h prior to data collection. Transmission Electron Microscopy (TEM) images were obtained using a Hitachi H-800 electron microscope equipped with an energy-dispersive X-ray (EDX) detector, operated at 200 kV. Photoluminescence measurements were carried out on a flurolog-3 spectrofluorometer (Horiba). UV-vis diffuse reflectance spectra of samples were collected using a Shimadzu UV-2450 spectrophotometer. The reference was $BaSO_4$, and the absorption spectra were obtained using the Kubelka-munk function.

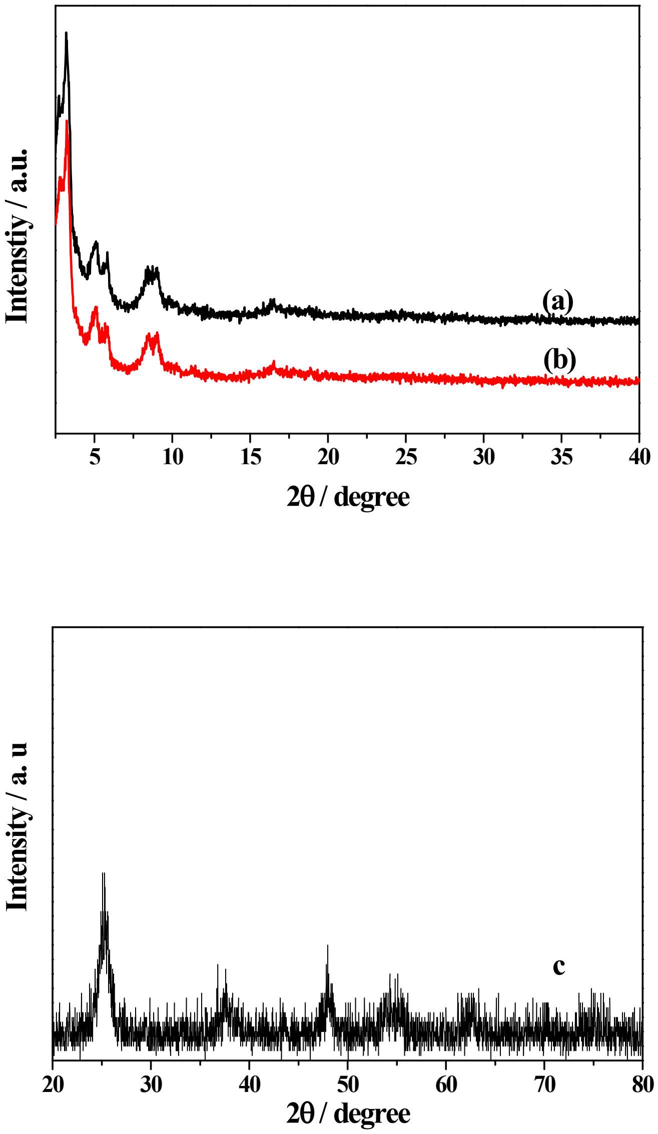

Figure S1. (a) XRD pattern of (a) NH_2-MIL-101(Cr), (b) 1.5 wt.% Pt NPs imbedded NH_2-MIL-101(Cr), and (c) 1.5 wt.% Pt NPs imbedded anatase TiO_2.

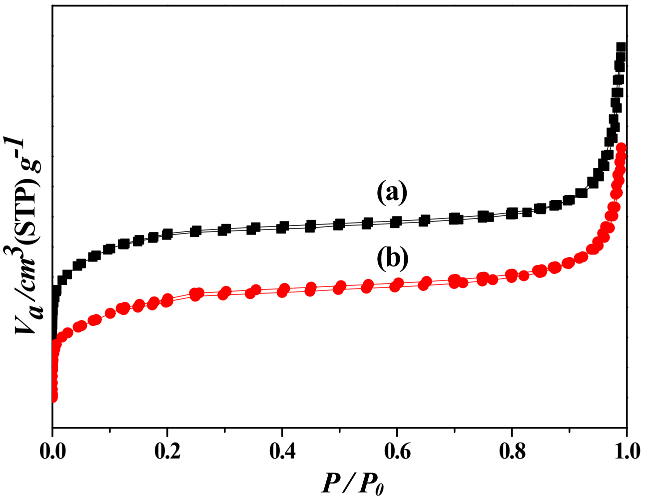

Figure S2. N_2 adsorption-desorption isotherm of (a) NH_2-MIL-101(Cr) and (b) 1.5 wt. % Pt NPs imbedded NH_2-MIL-101(Cr).

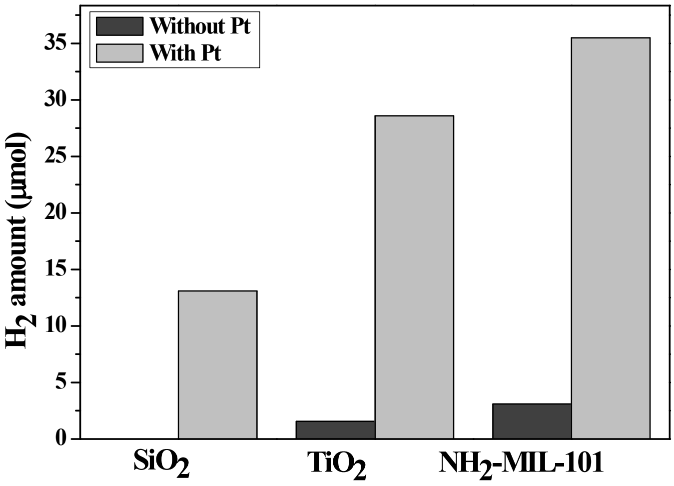

Figure S3. Influence of different catalysts on the H_2 production

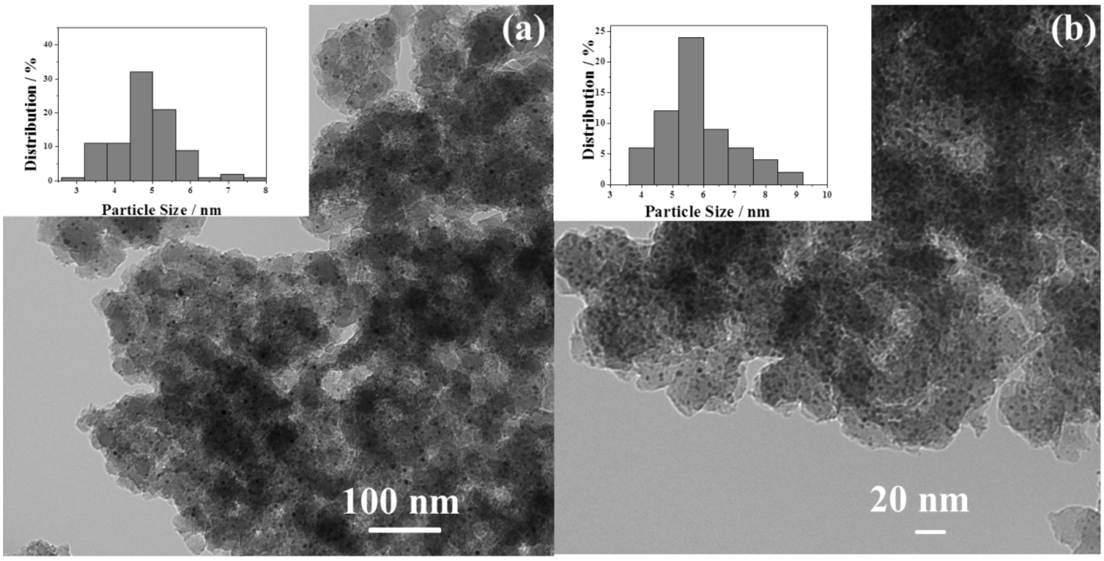

Figure S4. TEM images of (a) 2.0 wt. % Pt NPs imbedded NH_2-MIL-101(Cr), (b) 3.0 wt. % Pt NPs imbedded NH_2-MIL-101(Cr).

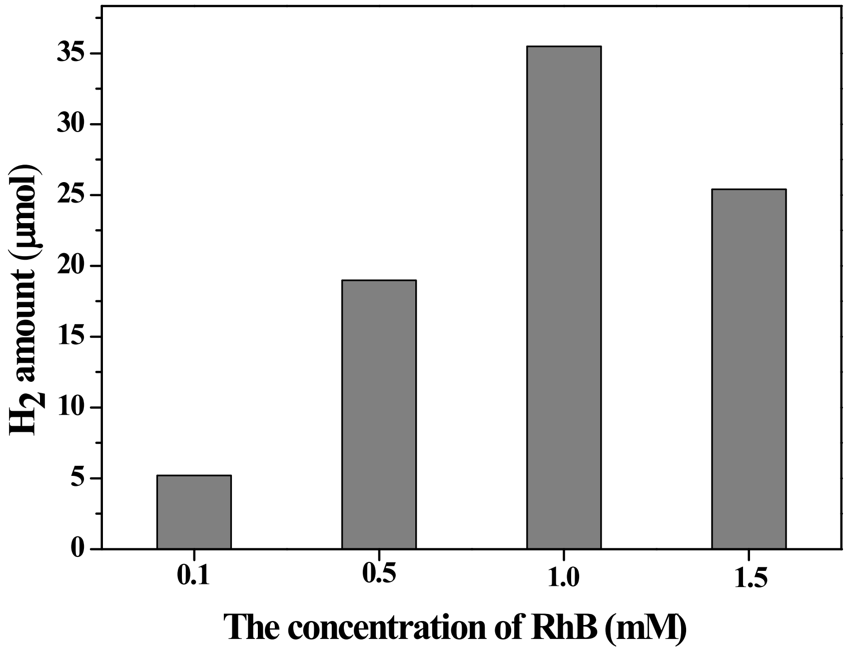

Figure S5. Influence of different concentration of RhB on the H_2 production

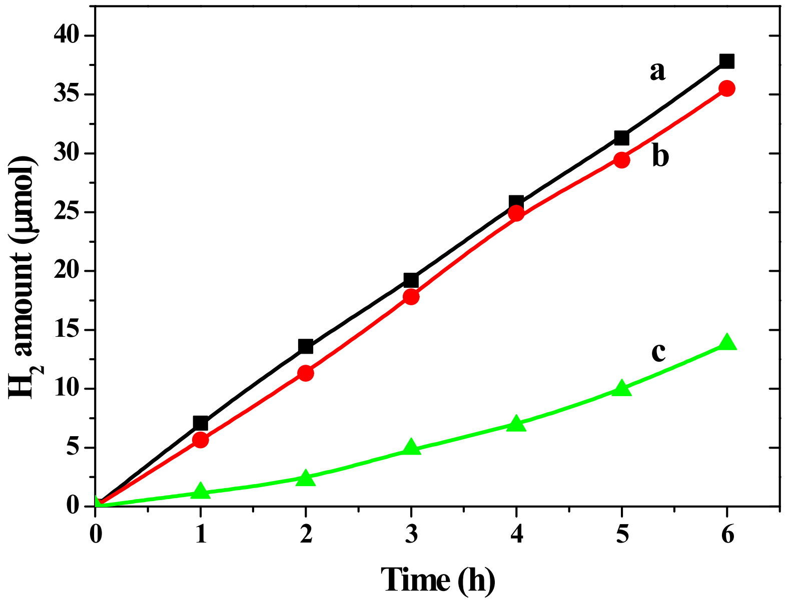

Figure S6. Time course of H_2 formation on 1.5wt. % Pt/NH_2-MIL-101(Cr) under light irradiation with different wavelengths: (a) UV-vis, (b) $\lambda > 420$ nm, and (c) $\lambda > 500$ nm

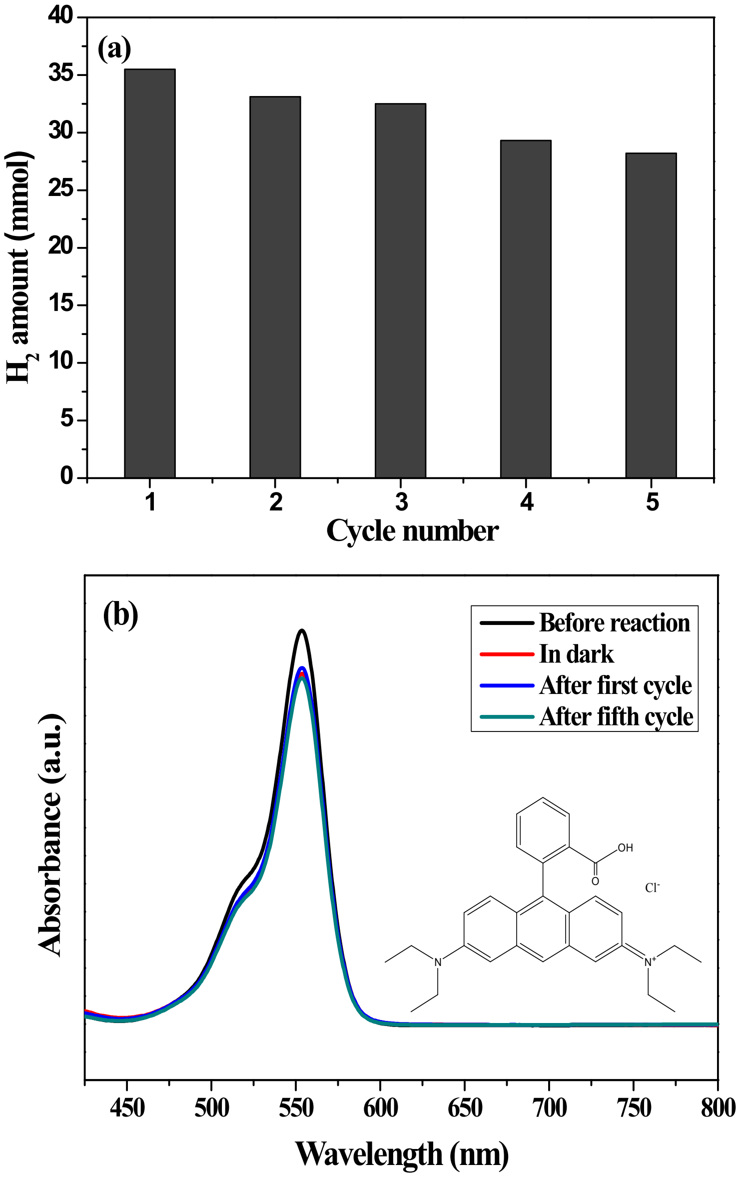

Figure S7. (a) H_2 production in the recycle study over the 1.5 wt. % Pt/NH_2-MIL-101(Cr), (b) UV-visible spectra of supernatant solutions.