

## Supporting Information

### Chemicals and reagents

Commercial reagents were used as received without any further purification. 1-hexene and platinum on active carbon (Pt wt 1%) were purchased from Acros Organics Co. Ltd. 2-Methyl imidazole was purchased from Aladdin Chemical Co. Ltd. Cis-cyclooctene was bought from Alfa Aesar Co. Ltd. Other reagents were purchased from Shanghai Chemical Reagent, Inc. of the Chinese Medicine Group.

### Characterization

Powder X-Ray diffraction (XRD) patterns were recorded on a Rigaku D/Max 2500 powder diffraction system using Cu K $\alpha$  radiation ( $\lambda=0.1541$  nm). The nitrogen-sorption experiments were performed at -196 °C using a Micromeritics ASAP 2020. Samples were degassed at 180 °C for 6 h prior to the measurements. BET surface area was calculated from the adsorption data in the relative pressure  $P/P_0$  range from 0.05 to 0.25. Pore size distributions were determined from the adsorption branches using the Barret–Joyner–Halenda (BJH) method. Pore volume was estimated at the relative pressure  $P/P_0$  of 0.99. Transmission electron microscopy (TEM) was performed using a FEI Tecnai G2 Spirit at an acceleration voltage of 120 kV. STEM and DF-STEM were performed on Philips Tecnai G220 microscope operating at 300 kV. FT-IR spectra were collected with a Nicolet Nexus 470 IR spectrometer with KBr pellet. The Pt content was determined by PLASAM-SPEC-II inductively coupled plasma atomic emission spectrometry (ICP). Hydrogen sorption studies were done on a Micromeritics 2050 at 273K up to 1 bar. Before starting the adsorption measurements, each sample was activated by heating under vacuum at 473 K for 12 hours unless otherwise noted.

### Synthesis of Pt nanoparticles

Pt nanoparticles were prepared by a glycol reduction method by  $H_2PtCl_6$ . In a typical procedure for the synthesis of ‘unprotected’ Pt NPs under inert atmosphere, a glycol solution of NaOH (50 mL, 0.5 M) was added into a glycol solution of  $H_2PtCl_6 \cdot 6H_2O$  (1.0 g, 1.93 mmol in 50 mL) with stirring to obtain a transparent yellow platinum hydroxide or oxide colloidal solution which was then heated at 160 °C for 3

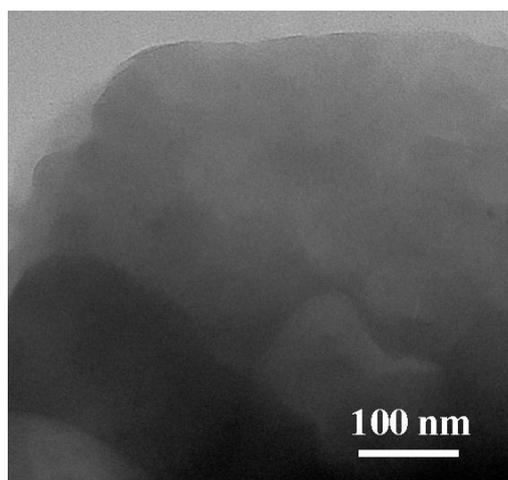
h, with an Ar flow passing through the reaction system to take away water and organic byproducts. A transparent dark-brown homogeneous colloidal solution of the Pt metal nanocluster (Pt: 3.76 g/L glycol, 19.3 mmol/L) was obtained without any precipitate. The obtained Pt nanocluster solution is very stable, no precipitate was observed after standing for several months.

### **Synthesis of Pt@ZIF-8**

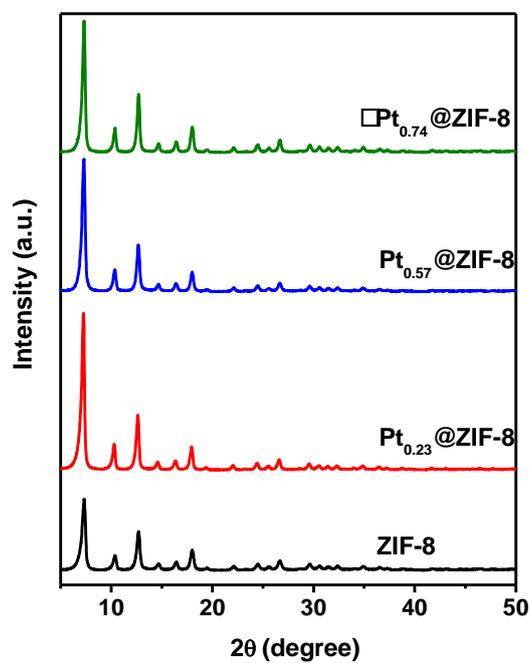
For Pt<sub>0.74</sub>@ZIF-8, 0.3 mL ‘unprotected’ Pt NPs were added into 80 mL methanol containing 406 mg 2-methyl imidazole. The resulted solution was ultrasonicated for 10 mins. After the solution cooled to room temperature, 20 mL methanol with 734 mg Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O was added and the resultant solution was kept stirring for 8 hours at room temperature, and left for another 16 hours. The product was collected by centrifugation, washed several times with methanol, and vacuum-dried overnight at 333 K. For Pt<sub>0.57</sub>@ZIF-8 and Pt<sub>0.23</sub>@ZIF-8, 0.2 mL and 0.1 mL Pt NPs were used instead.

### **Catalytic hydrogenation of alkenes**

Hydrogenation of alkenes (1-hexene or cis-cyclooctene) was carried out in ethanol solution in a static hydrogen atmosphere (1 bar). In a typical experiment, the catalyst was loaded in a reactor and residual air in the reactor was expelled by flushing several times with hydrogen. Ethanol was added in the reactor. Alkene was then added in the reactor. After the reactor was again flushed one time with hydrogen, the reaction was allowed to proceed at 1 atm of hydrogen with a balloon and 293 K for 24 hours. Samples were taken away from the reactor, centrifuged and the filtrate was analyzed using a gas chromatograph (Agilent, 6890N) equipped with a HP-5 column (Agilent) and FID. All the catalyst to substrate molar ratio was 1:20000. For recycling experiments, the used catalysts were separated with centrifugation followed by washing completely with ethanol, and the catalysts were vacuumed at 293 K for 12 hours before reaction.



**Fig. S1** Representative TEM image of Pt<sub>0.74</sub>@ZIF-8 under low magnification.



**Fig. S2** XRD patterns of ZIF-8 and Pt<sub>n</sub>@ZIF-8 composites.

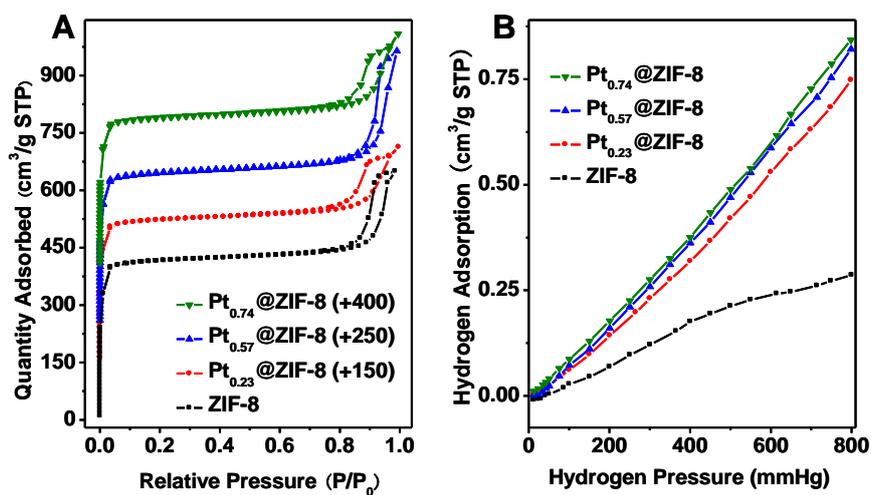


Fig. S3 (A) Nitrogen sorption isotherms, and (B) H<sub>2</sub> adsorption capacity at 273 K for ZIF-8 and Pt<sub>n</sub>@ZIF-8 composites.

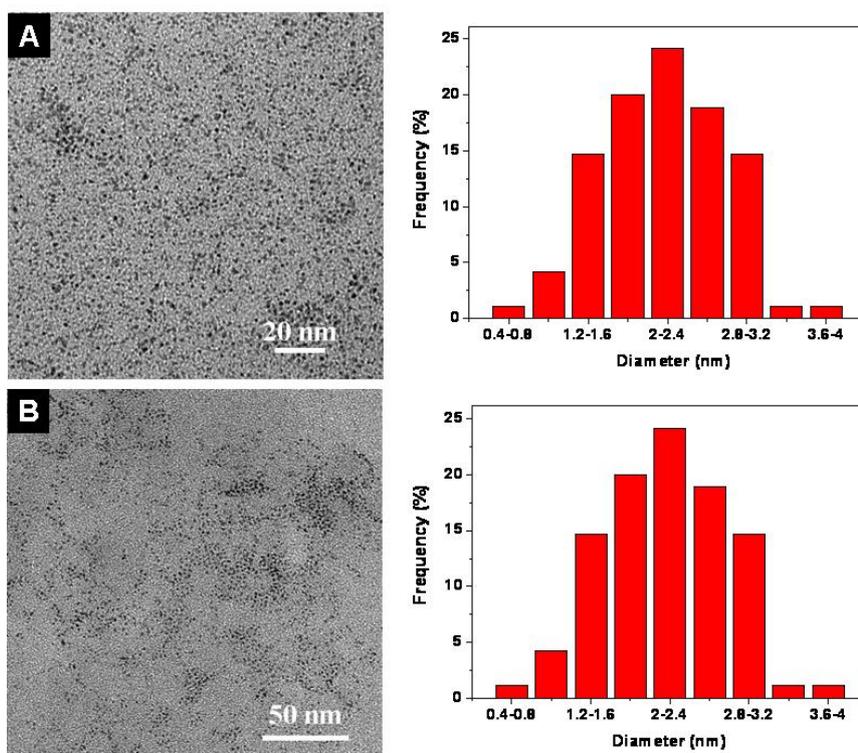


Fig. S4 TEM images of (A) 'unprotected' Pt NPs (average size: 2.08 nm) and (B) imidazole capped Pt NPs (average size: 2.12 nm) and the corresponding particle size distribution histogram.

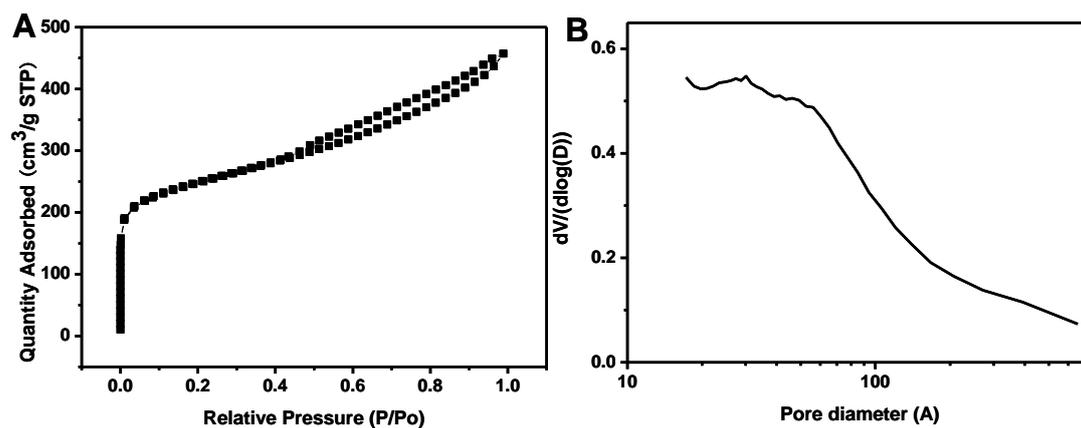


Fig. S5 (A) Nitrogen adsorption isotherm and (B) the corresponding BJH pore size distribution curve of Pt/C.

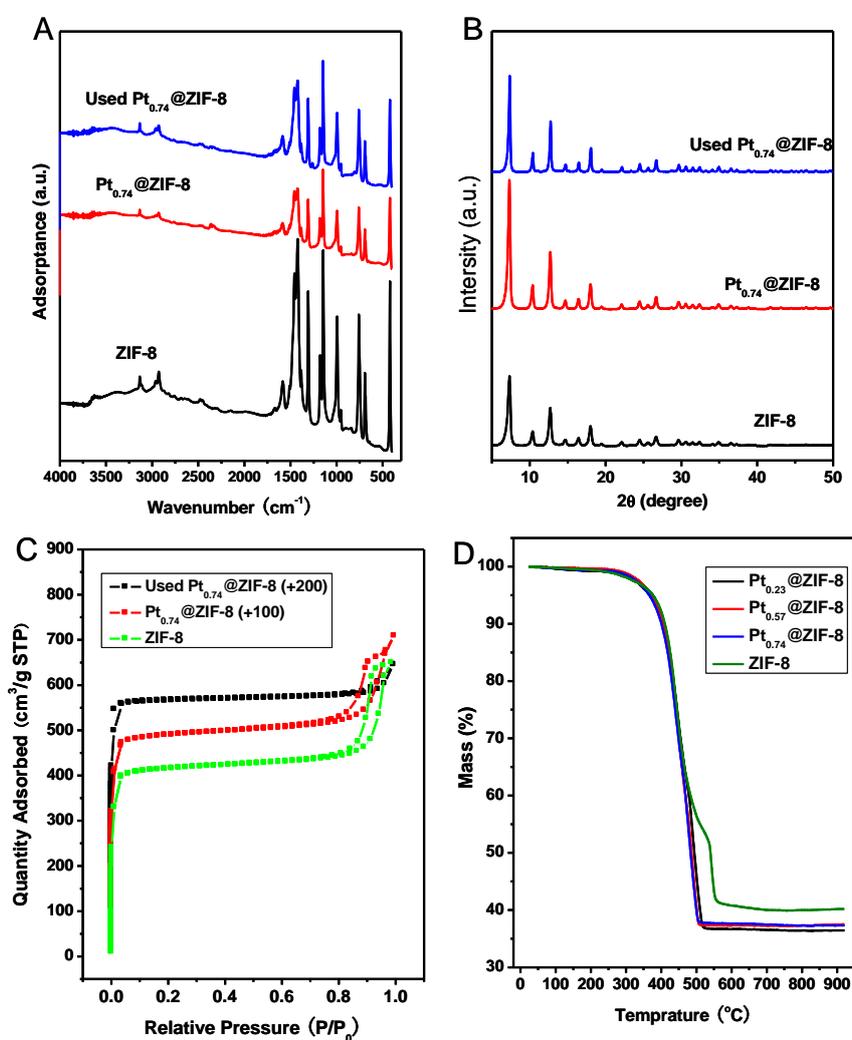


Fig. S6 (A) Fourier transform infrared (FT-IR) spectra, (B) XRD patterns, and (C) nitrogen sorption isotherms of ZIF-8, Pt<sub>0.74</sub>@ZIF-8 and used Pt<sub>0.74</sub>@ZIF-8. (D) Thermogravimetric analysis (TGA) curves of ZIF-8 and Pt<sub>n</sub>@ZIF-8 in air.