Supporting Information

Palladium decoration directed synthesis of ZIF-8 nanocubes with efficient catalytic activity for nitrobenzene hydrogenation

Experimental

Materials

$Zn(NO_3)_2·6H_2O$ (≥99.0%), cyclohexane was purchased from Sinopharm Chemical Reagent Co., Ltd. 2-methylimidazole (97%), nitrobenzene was purchased from Alfa Aesar. Brij®C10 was purchased from Aldrich. $PdCl_2$ and Na_2PdCl_4 were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). All chemicals were used as received without further purification.

Preparation of the H_2PdCl_4

$PdCl_2$ 1.77g, 1.7 ml concentrated hydrochloric acid (12mol/L) and 8.3 ml deionized water are added to the glass bottle with cover in 50 °C water bath. After stirring for 12 h, 1mol/L H_2PdCl_4 is obtained.

Preparation of the $Pd(MIM)_4$

1 mL, Na_2PdCl_4 (1mol/L) and 1 mL, 2- methylimidazole (4mol/L) was mixed together under stirring and acetone was then added to precipitate the product.

Synthesis of Pd/ZIF-8 nanocubes in reverse micelles

In a typical procedure, Brij®C10 (3.42 g), cyclohexane (15 mL) and an aqueous solution of $Zn(NO_3)_2·6H_2O$ (1 mL, 1 mol/L) were mixed under stirring at 37°C to form a transparent reverse micelle solution A. Then H_2PdCl_4 (100 µL, 1mol/L) was added into it to form a brown transparent reverse micelle solution B. Similarly, Brij®C10 (3.42 g), cyclohexane (15 mL) and an aqueous solution of 2-methylimizadole (1 mL, 4 mol/L) were mixed under stirring at 37 °C to form a transparent reverse micelle solution C. Then solution C was rapidly added into solution A under stirring. The color disappeared and the mixture turned turbid. After two hours the nanocrystals were separated with ethanol, centrifuged, and washed with ethanol several times.

Synthesis of Pd Nps/ZIF-8 via H_2 reduction

The as-synthesized Pd/ZIF-8 was placed in a porcelain boat under hydrogen atmosphere at 80°C in a tube furnace. After 2 h, the product was collected for further characterization.

Catalysis Studies

The hydrogenation of nitrobenzene using the Pd NPs/ZIF-8 catalyst was carried out in a magnetically stirred in a well-stirred glass pressure vessel (48 mL) at 30 °C. Dispersed in 5 mL ethanol, the catalysts (i.e., Pd/ZIF-8, Pd Nps/ZIF-8 and commercial Pd/C) (5mg Pd) were mixed with 1 mmol substrate in the pressure vessel. H_2 flow was applied into the vessel for several minutes to remove oxygen. The vessel was then pressurized by 1.0 bar H_2. Take one point every 15 minutes and the reaction conversion was analyzed by gas chromatographic. Toluene was used as an internal standard. Because the correction factor of nitrobenzene and aniline to toluene is

very close, we can calculate the conversion rate directly by peak area normalization method within the allowable error range.

The calculation formula of conversion is: $[(C_0 - C_r)/C_0] * 100\%$

The calculation formula of selectivity is: $[C_p/(C_0 - C_r)] * 100\%$

The calculation formula of yield is: conversion*selectivity.

where C_0 is the initial concentration of nitrobenzene, and C_r and C_p are the concentration of reactant nitrobenzene and aniline, respectively, at a certain time after the catalytic reaction.

Characterization

The phase of the products was characterized by X-ray powder diffraction (XRD, Panalytical X'pert PRO diffractometer with Cu-Kα radiation). Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images were taken on a Hitachi S-4800 microscope with a field-emission electron gun and a TECNAI F-30 high-resolution transmission electron microscope operating at 300 kV, respectively. The surface area of the as-synthesized carbon nanostructures was measured by the Brunauer–Emmett–Teller (BET) method using nitrogen adsorption and desorption isotherms on a Micrometrics ASAP 2020 system. The pore size distribution plot was obtained by the Horvath-Kawazoe method. Thermogravimetry analysis (TGA) was performed simultaneously on a SDT-Q600 Thermoanalyzer. GC analyses were performed with a FuLi 9790II, equipped with a split/splitless injector, a capillary column (KB-5, 30 m×0.32 mm×0.33 μm) and a flame ionization detector. The high resolution low energy ion scattering spectrum (LEISS) was tested on Ion-TOF Qtac100 low energy ion scattering analyzer. The ion source is He^+ with kinetic energy of 5 keV, ion current of 1600 $pAcm^{-2}$ and scattering angle of 145°. X-ray photoelectron spectrometry (XPS) measurements were carried out by using a PHI Quantum-2000 photoelectron spectrometer (Al K_α with 1486.6 eV operating at 15 kV, 35 W and 200 μm spot size) and an Omicron Sphera II hemispherical electron energy analyzer. (Monochromatic Al K_α with 1486.6 eV operating at 15 kV and 300 W). The base pressure of the systems was 5.0×10^{-9} mbar.

X-ray absorption spectroscopy (XAS) measurements

The X-ray absorption spectra at the Pd K-edge was recorded at room temperature in transmission mode using ion chambers at beam line BL14W1 of the Shanghai Synchrotron Radiation Facility (SSRF), China. The station was operated with a Si(311) double crystal monochromator. During the measurement, the synchrotron was operated at energy of 3.5GeV and a current between 150-210 mA. The photon energy was calibrated with the first inflection point of Pd K-edge in Pd metal foil. The as-obtained XAS data were processed using WinXAS version 3.11. Reliable parameter values, such as bond distances, coordination numbers, etc., were determined via multiple-shell R-space fitting of Pd spectra.

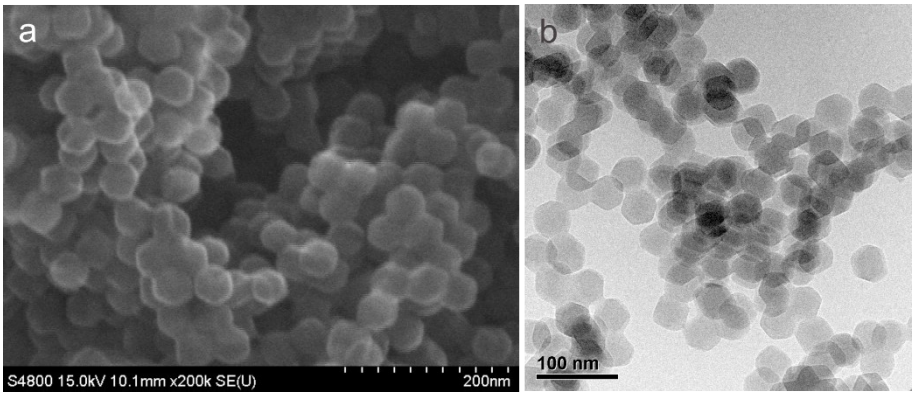

Figure S1. (a) SEM image and (b) TEM image of the as-synthesized ZIF-8 nanocrystals.

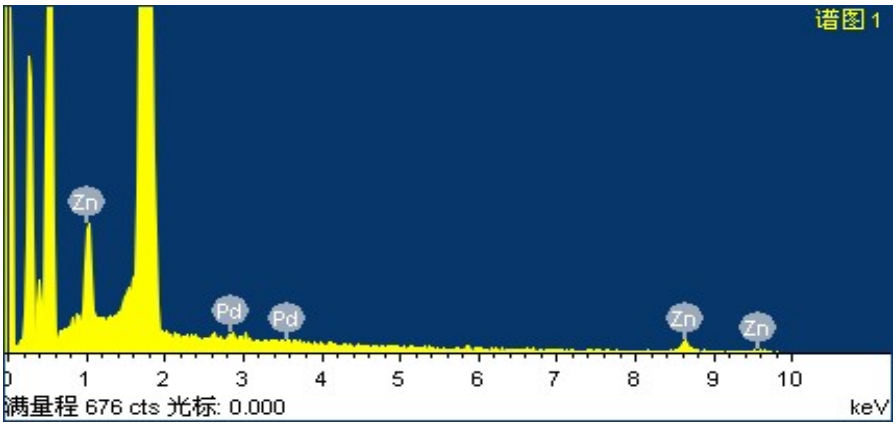

Figure S2. EDS spectra of the as-synthesized Pd/ZIF-8 nanocubes

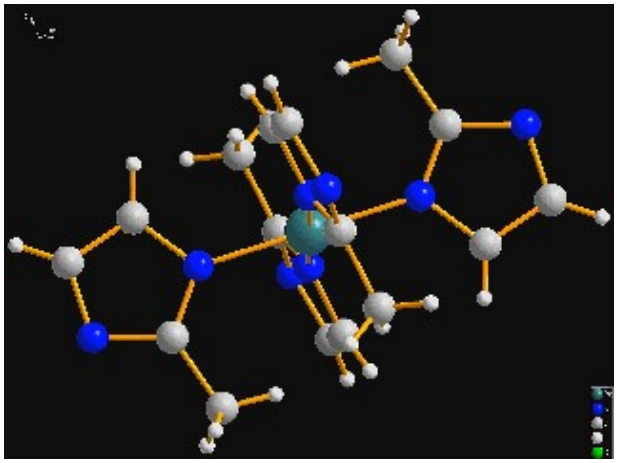

Figure S3. The structure of the reference $Pd(MIM)_4$

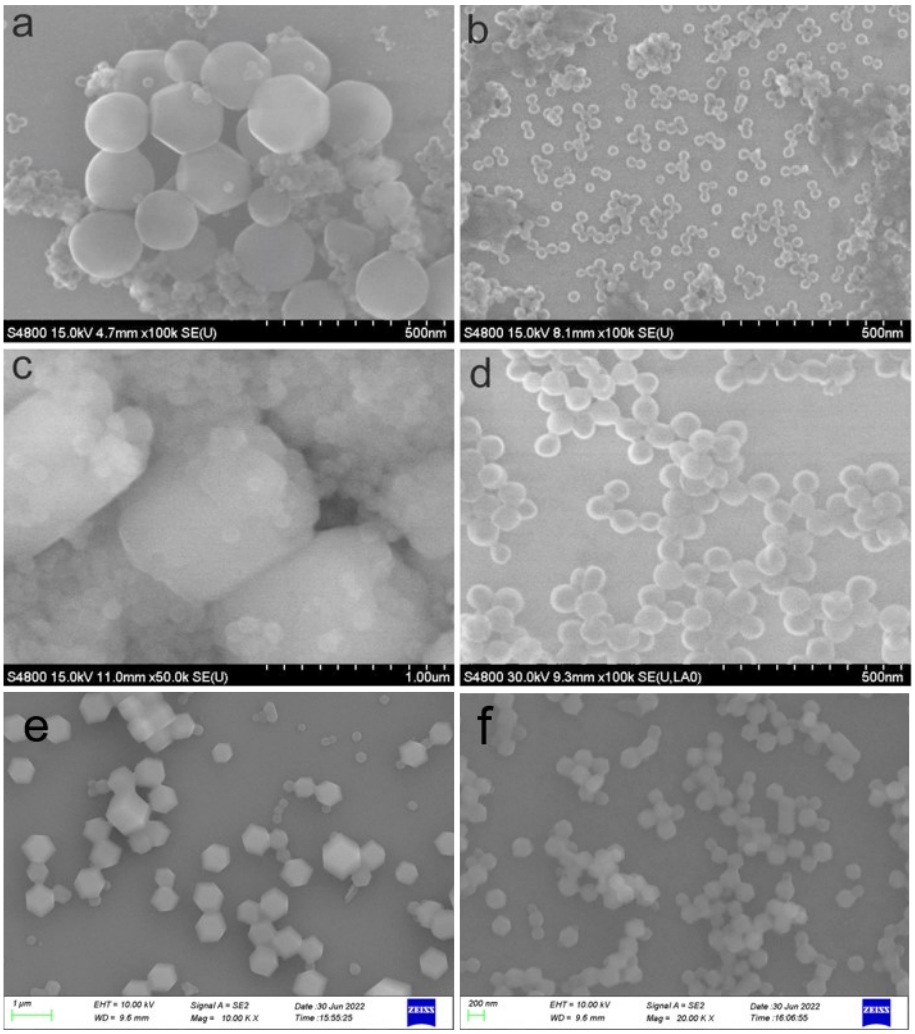

Figure S4. SEM images of different additives (a)100uL 1mol/L HCl, (b)100uL 1mol/L $CuCl_2$, (c)100uL 1mol/L H_2PtCl_6 ,(d)20uL 1mol/L H_2PdCl_4, (e)100uL 1mol/L H_2PdCl_4 in aqueous solution (Pd-ZIF-8-W), (f)without H_2PdCl_4 in aqueous solution (ZIF-8-W). Note: Pd-ZIF-8-W and ZIF-8-W was synthesized by replacing reverse micelle with aqueous solution while other conditions are same.

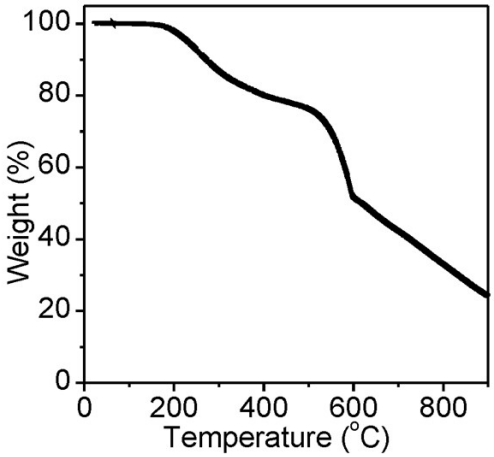

Figure S5. TGA curve of the as-synthesized Pd/ZIF-8.

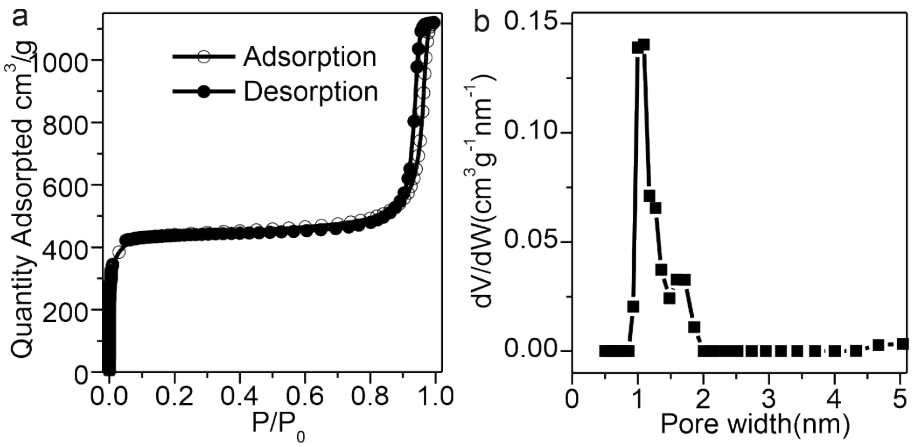

Figure S6. (a) N_2 absorption isotherms, (b)pore-size distribution.

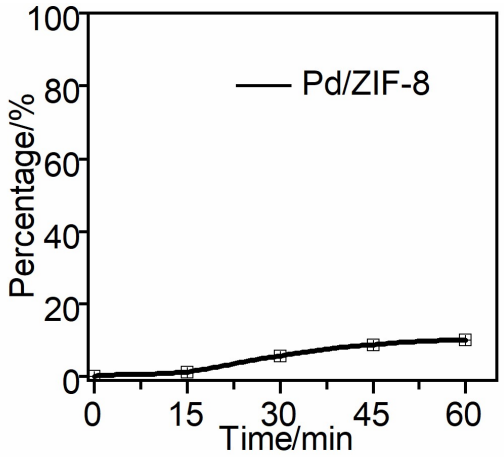

Figure S7. Catalytic performance in nitrobenzene hydrogenation of Pd /ZIF-8.