

Porosity control in mesoporous polymers using CO₂-swollen block copolymer micelles as templates and its use as catalyst support

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1. Experimental Section

Chemicals: CO₂ (>99.95%) was provided by Beijing Analysis Instrument Factory. F127 (BioReagent) was provided by Sigma. N,N'-methylenebisacrylamide (99+%), water (HPLC Grade), Phenylacetylene (98%) and 1,3,5-trimethylbenzene (98%) were produced by Alfa Aesar. Potassium persulfate (A.R.) was purchased from J&K scientific Co., Ltd. Acrylamide (A.R.) and acetonitrile (A.R.) were provided by Beijing Chemical Reagent Company. The Pd/C catalyst was provided by Baoji Rock Pharmachem Co., Ltd. (5 wt% Pd, Product No. D₅L₃).

Polyacrylamide (PAM) synthesis: In a typical experiment, a desired amount of F127 was added into water (10 g), which was loaded in a stainless-steel autoclave (50 mL). Then the monomer acrylamide (0.4 g), crosslinker N,N'-methylenebisacrylamide (0.05 g) and initiator potassium persulfate (0.05 g) were added into the autoclave. CO₂ was charged into the cell under stirring until the desired pressure was reached. After the mixture was stirred at 60 °C for 30 minutes, the stirrer was stopped and CO₂ was released. The product was obtained after washing with methanol and drying at 40 °C under vacuum for 24 hours.

Characterization of the PAM: The morphologies of the PAM were characterized by a HITACHI S-4800 scanning electron microscope and high-resolution transmission electron microscopy (HRTEM) (FEI Tecnai G2 F20U-TWIN). The porosity properties were gained from nitrogen adsorption-desorption isotherms using a Micromeritics ASAP 2020M system. FT-IR spectra were obtained using a Bruker Tensor 27 spectrometer, and the samples were prepared by the KBr pellet method. The TG measurements were carried out using Shimadzu DTG-60H with N₂ flow of 10 mL/min.

Pd/PAM synthesis: For a typical synthesis of Pd/PAM, 0.119 g PAM prepared at 4.8 MPa was added to 30 mL H₂O, then 0.3 mL Na₂Pd₂Cl₄ solution (0.0564 mol/ L) was added into the above-mentioned solution. After kept stirring for 4 hours at room temperature, 5 mL 2 M HCOONa aqueous solution was dropwise added into the mixture. The mixture was stirred for 6 hours at room temperature, then the precipitates were separated by centrifugation, washed with water and ethanol and dried at room temperature in vacuum for 5 hours.

Characterization of the Pd/PAM: X-ray diffraction (XRD) pattern was performed on a Rigaku D/max-2500 diffractometer with Cu K α radiation (λ = 1.5418 Å) at 40 kV and 200 mA. The loading content of Pd was

determined by ICP-AES (Shimadzu ICPE-9000). The morphology of the catalyst was characterized by HRTEM (FEI Tecnai G2 F20U-TWIN). XPS measurement was performed on the VG Scientific ESCALab220i-XL spectrometer using Al K α radiation.

Catalytic activity of the Pd/PAM: For the hydrogenation of phenylacetylene, Pd/PAM (3 mg), phenylacetylene (0.91 mmol) and 1,3,5-trimethylbenzene (internal standard, 126 μ L, 0.91 mmol) were added into 2 mL acetonitrile. The air in the reactor was replaced by H $_2$ for three times. Then, the mixture was stirred in a 30 $^{\circ}$ C water bath for desired time. The product was analyzed by a gas chromatograph (Shimadzu GC-2010) equipped with a flame ionization detector (FID) and a Rtx-5 capillary column (0.25 mm in diameter, 30 m in length). The identity was ascertained by GC-MS (Shimadzu GCMS-QP2010S).

2. Results

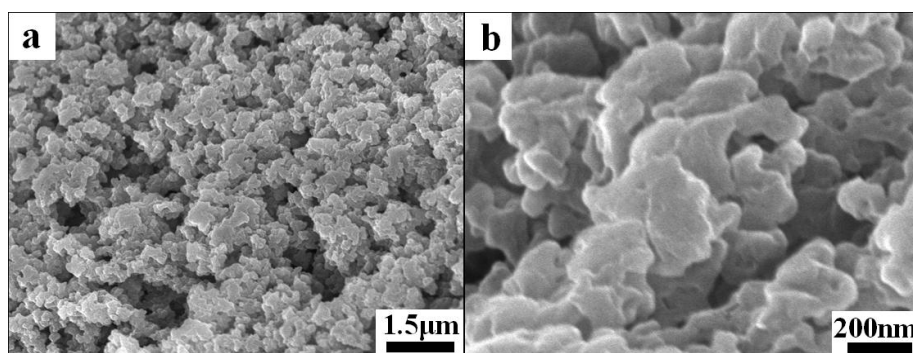


Fig. S1 SEM images of the PAM synthesized in 10 wt% F127 aqueous solution.

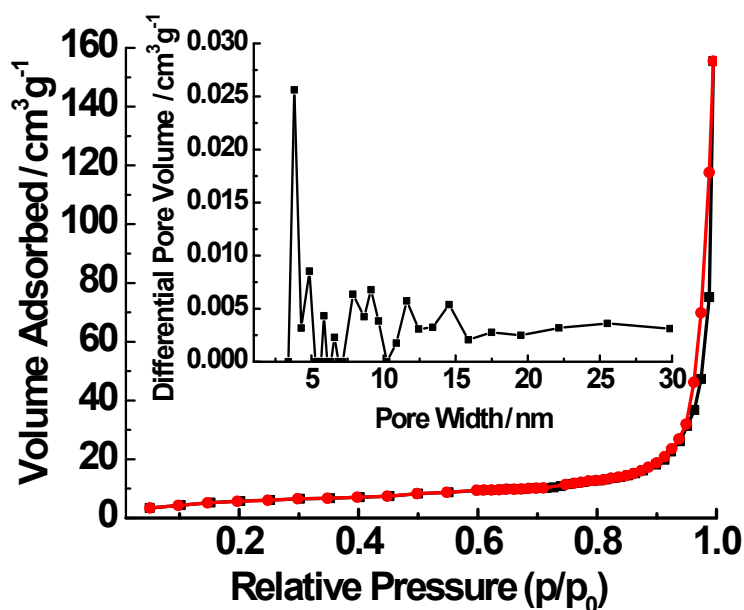


Fig. S2 N $_2$ adsorption-desorption isotherm and mesopore size distribution curve of the PAM synthesized in 10 wt% F127 aqueous solution.

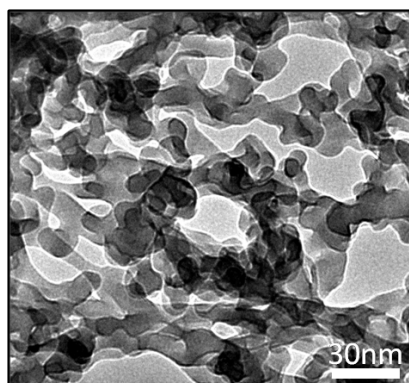


Fig. S3 TEM image of the PAM synthesized in the CO₂-present 10 wt% F127 aqueous solution at 4.8 MPa.

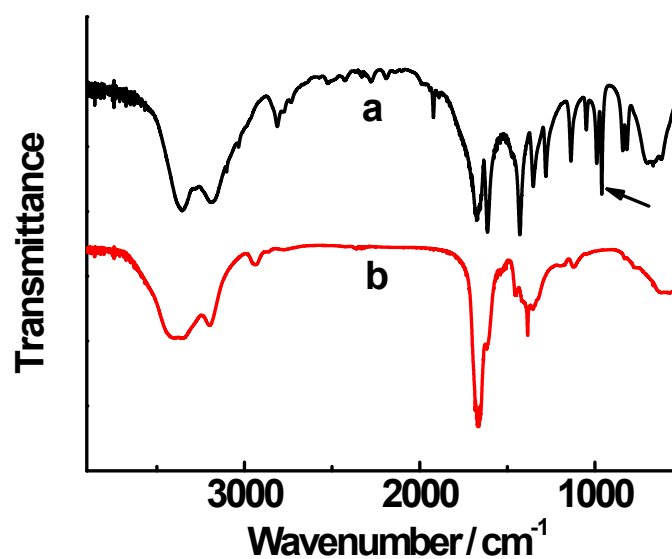


Fig. S4 FT-IR spectra of acrylamide (AM) (a) and the PAM synthesized at 60 °C and 4.8 MPa (b). The absorption peak of =CH₂ appears only in the spectrum of AM (960 cm⁻¹, curve a) and vanishes in the spectrum of PAM (curve b), confirming that monomers have polymerized completely.

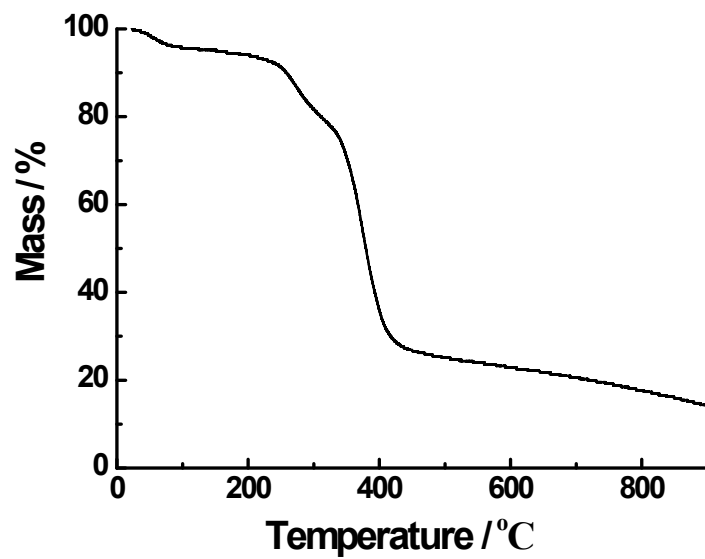


Fig. S5 Thermogravimetric curve of the PAM synthesized at 60 °C and 4.8 MPa.

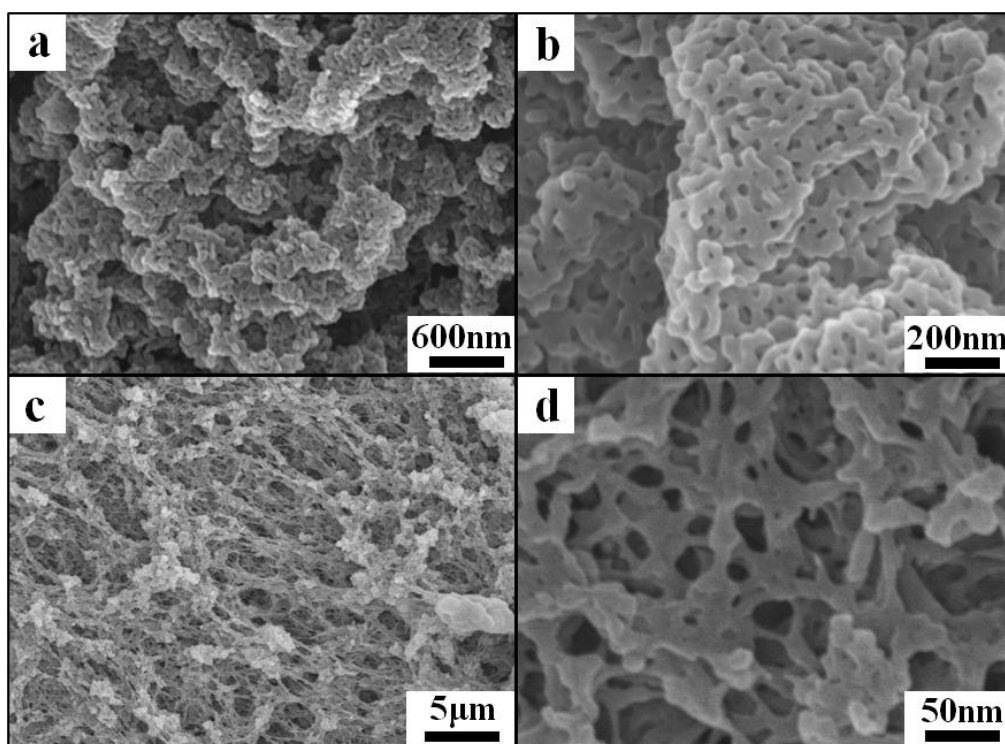
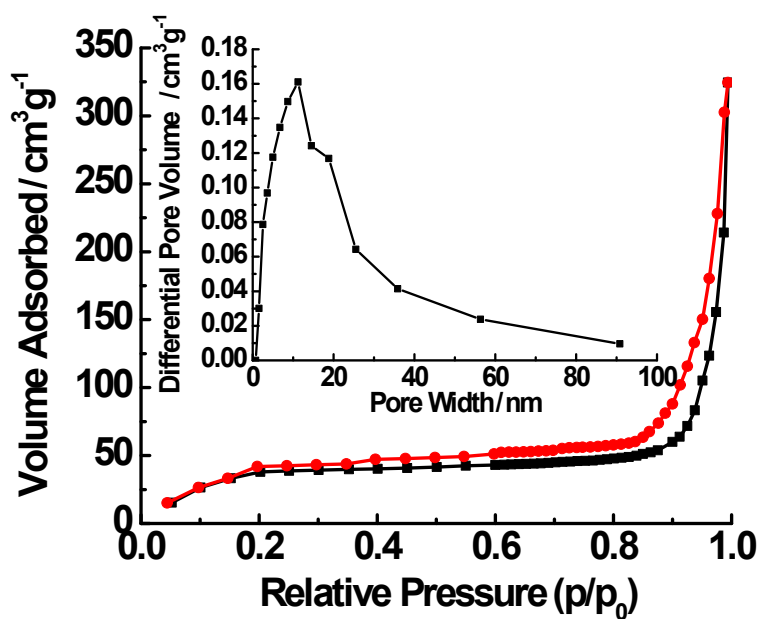


Fig. S6 SEM images of the PAMs synthesized in 10 wt% F127 aqueous solution at CO₂ pressure of 2.5 MPa (a, b) and 6.9 MPa (c, d).

A:



B:

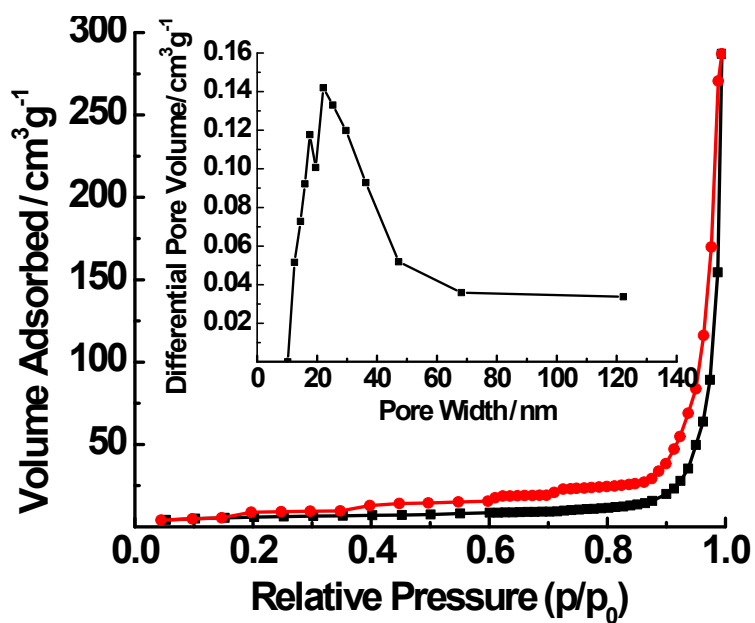


Fig. S7 N₂ adsorption-desorption isotherms and mesopore size distribution curves of the PAMs synthesized in 10 wt% F127 aqueous solution at 2.5 MPa (A) and 6.9 MPa (B).

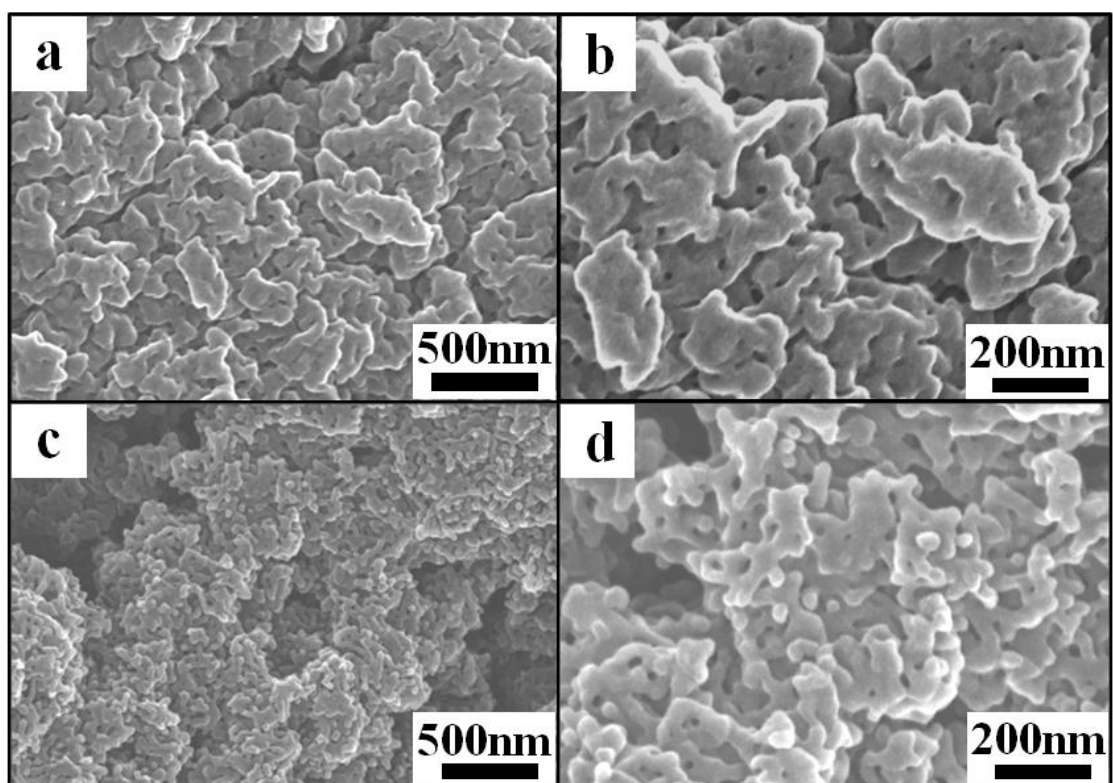
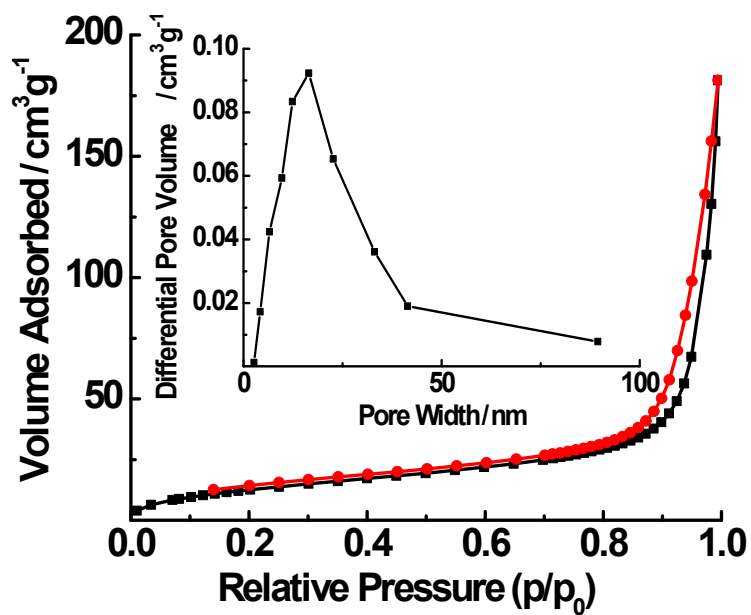


Fig. S8 SEM images of the PAMs synthesized in 2 wt% and 6 wt% F127 aqueous solution at CO₂ pressure of 4.8 MPa.

A:



B:

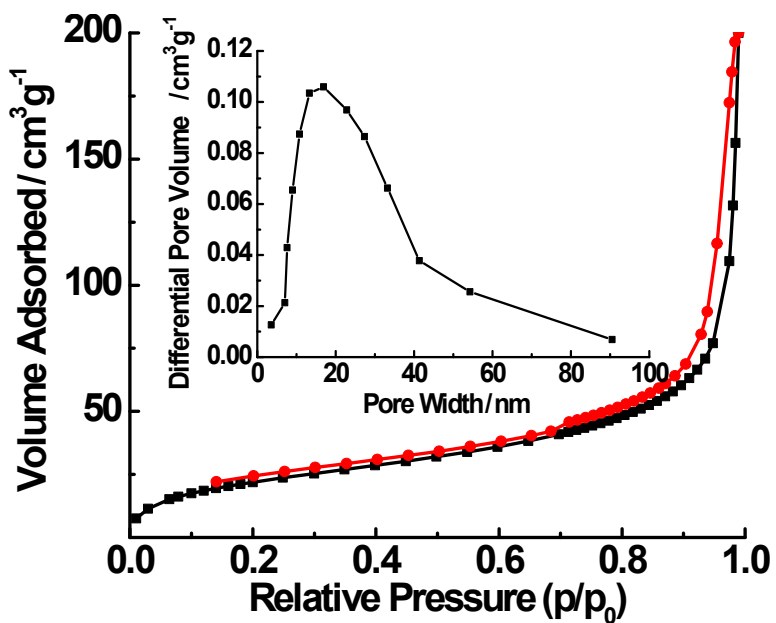


Fig. S9 N_2 adsorption-desorption isotherms and mesopore size distribution curves of the PAMs synthesized in 2 wt% (A) and 6 wt% (B) F127 aqueous solution at 4.8 MPa.

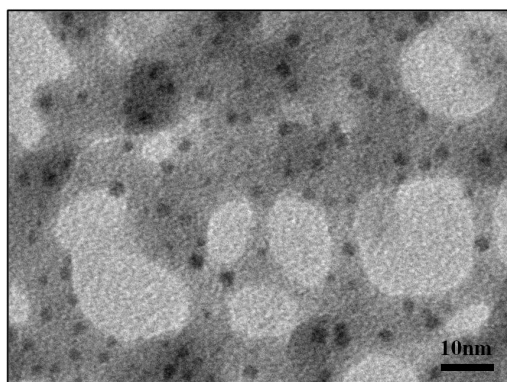


Fig. S10 TEM image of the Pd/PAM catalyst.

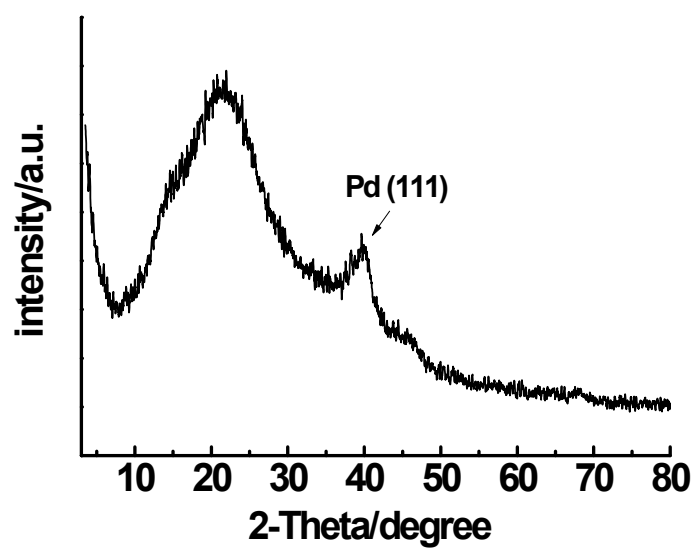


Fig. S11 Wide-angle XRD pattern of the Pd/PAM catalyst.

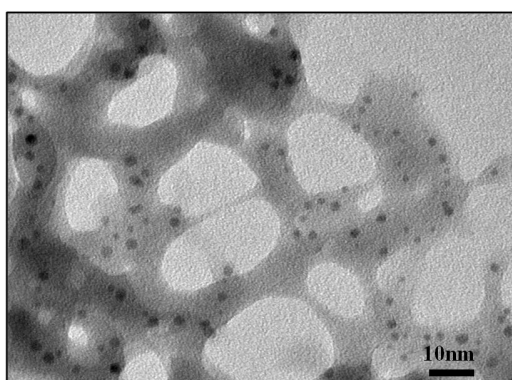


Fig. S12 TEM image of the Pd/PAM catalyst after reused for four times.

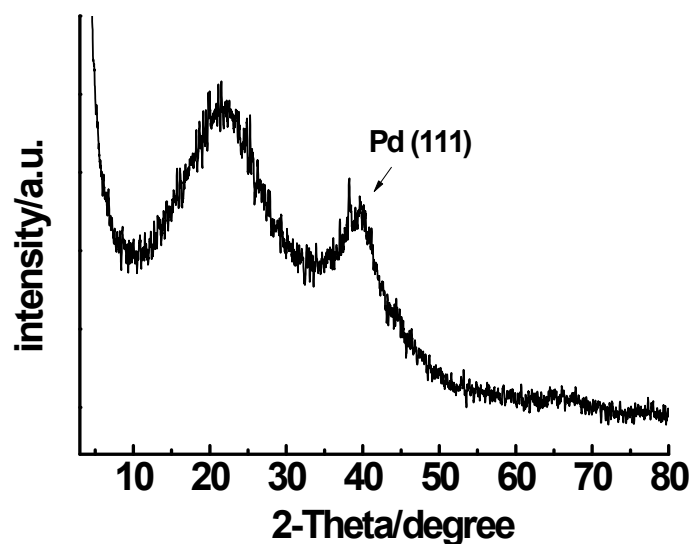


Fig. S13 Wide-angle XRD pattern of the Pd/PAM catalyst after reused for four times.

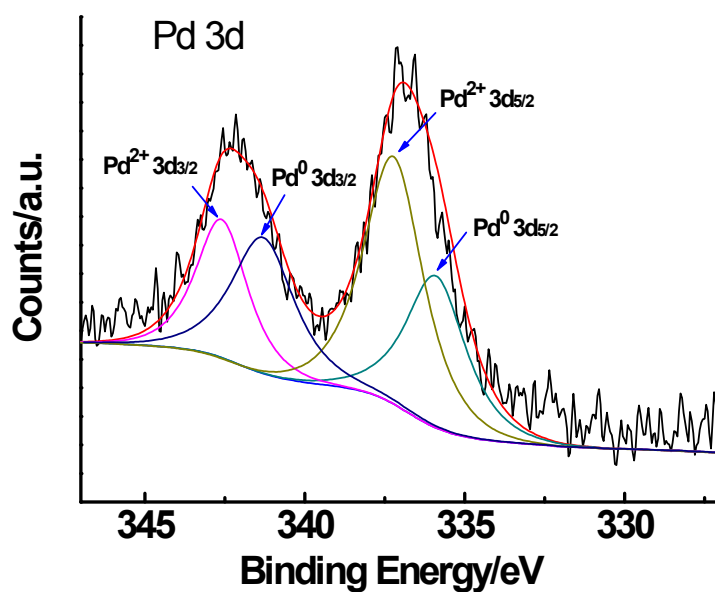


Fig. S14 X-ray photoelectron spectroscopy of the Pd/PAM catalyst. The Pd 3d peak splits to two peaks components, indicating two chemical states of Pd on the surface of PAM, i.e. Pd⁰ (Pd 3d_{5/2}, 335.9 eV; Pd 3d_{3/2}, 341.3 eV) and Pd²⁺ (Pd 3d_{5/2}, 337.3 eV; Pd 3d_{3/2}, 342.7 eV).¹

Reference

- 1 Z. -L. Wang, J. -M. Yan, H. -L. Wang, Y. Ping and Q. Jiang, *J. Mater. Chem. A*, 2013, **1**, 12721–12725.