

Template-free synthesis of mesoporous polymers

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1. Experimental Section

Materials: [C_nmim][BF₄] (>98% purity) were provided by Lanzhou Greenchem ILS, LICP, CAS. Acrylamide (A. R. grade) was produced by Beijing Chemical Reagent Company. N,N'-methylenebisacrylamide (laboratory grade) was obtained from Alfa Aesar. Potassium persulfate (K₂S₂O₈) (A. R. grade) and p-chloronitrobenzene (p-CNB) were supplied by Sinopharm Chemical Reagent Co., Ltd. The Pd/C catalyst was provided by Baoji Rock Pharmachem Co., Ltd. (5 wt% Pd, Product No. D5L3). Palladium chloride (PdCl₂) (>97% purity) was produced by Sinopharm Chemical Reagent Co., Ltd. H₂ (99.99% purity) was provided by Beijing Analytical Instrument Factory.

PAM synthesis and characterization: The polymerization was performed in 25 mL flask with a magnetic stirrer inside. For the polymerization of acrylamide, 0.750 g of the monomer acrylamide, 0.012 g of the crosslinker N,N'-methylenebisacrylamide and 0.012 g of the initiator potassium peroxydisulfate were dissolved in 18 mL [C_nmim][BF₄] and the mixture was stirred to form a homogeneous solution. The solution was stirred under N₂ atmosphere at 60 °C for 4 h to polymerization, and then cooled down to room temperature with methanol to terminate the reaction. The product was washed by acetone for several times and dried at 50 °C for 24 h.

The morphology of the PAM was characterized by a HITACHI S-4800 SEM and TEM JeoL-1010 operated at 100 kV. The mesoporosities were determined by N₂ adsorption-desorption isotherms using a Quadrasorb SI-MP system. FT-IR spectra were obtained by a Bruker Tensor 27 spectrometer. The thermogravimetric analysis

(TGA) measurement was carried out with a heating rate of 20 °C/min using PerkinElmer Pyris 1 under N₂ flow of 50 mL/min to estimate thermal stability. X-ray photoelectron spectroscopy (XPS) data were obtained with an ESCALab220i-XL electron spectrometer from VG Scientific using 300W AlK α radiation. The base pressure was about 3 \times 10⁻⁹ mbar. The binding energies were referenced to the C1s line at 284.8 eV from adventitious carbon.

Pd/PAM synthesis, characterization and catalytic activity: PdCl₂ (0.010 g) and the PAM synthesized in [C₄mim][BF₄] (0.20 g) were added into a flask containing 100 mL ethanol. The colloidal sol of the polymer-anchored palladium is prepared by an alcohol reduction method. The mixture was stirred at 70 °C for 24 h. After centrifugation, the product was dried at 50 °C for 24 h. Pd/PAM was obtained after cooling. XRD analysis was performed on the X-ray diffractometer (ModelD/MAX2500, Rigaku) with Cu Ka radiation. XPS measurement was performed on the VG Scientific ESCALab220i-XL spectrometer using Al Ka radiation. The loading content of Pd in PAM was determined by ICP-AES (VISTA-MPX).

For the hydrogenation reaction, p-chloronitrobenzene (0.31 g), ethanol (10mL), and Pd/PAM (10 mg) were placed in a 20 mL stainless steel reactor. The reactor was evacuated and filled with H₂ (three times). The stirrer was started with a rate of 300 rpm. H₂ was added to the suitable pressure and kept to be constant during the reaction, which was monitored by a pressure transducer (Foxboro/ICT model 930). After reaction for a certain time, the products were separated from the catalyst by centrifugation (1200 rpm). The products were analyzed by a high performance liquid chromatography (HPLC) with Shimadzu LC-15C pump, Shimadzu UV-Vis SPD-15C detector at 295 nm and a Supelcosil LC-18 5 μ m column at 35 °C. Methanol/water solution (60/40 V/V) was used as the mobile phase at flow rate of 1.0 mL/min.

2. Results and Discussion

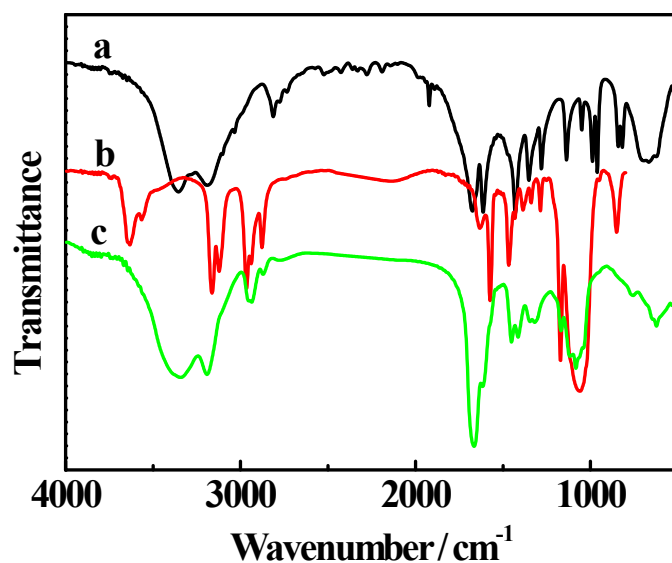


Fig. S1 FT-IR spectra of acryamide (a), [C₄mim][BF₄] (b), and the PAM synthesized in [C₄mim][BF₄] (c). The absorption peak of =CH₂ of AM (960 cm⁻¹) vanishes in the spectrum of PAM, confirming that monomers have polymerized completely. The C–H ring stretching vibrations of the imidazolium in [C₄mim][BF₄] at 3165 and 3110 cm⁻¹ are invisible in the spectrum of PAM, indicating there is no residual IL in the polymer.

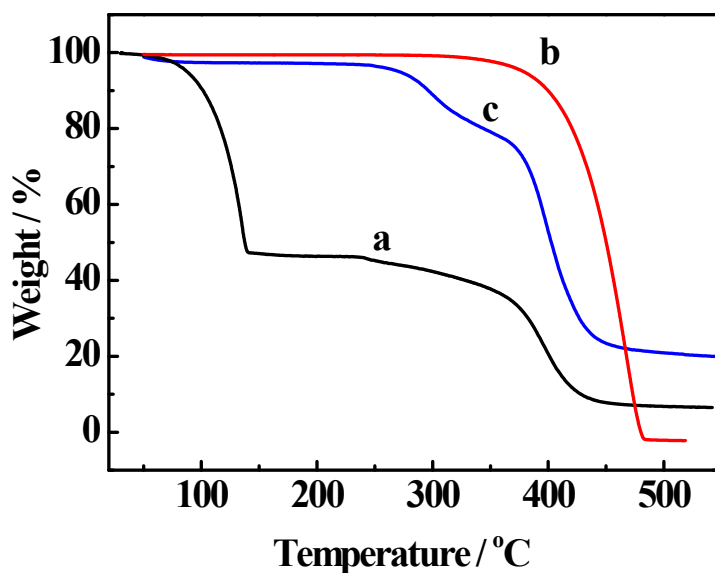


Fig. S2 TGA curves of acryamide (a), [C₄mim][BF₄] (b), and the PAM synthesized in [C₄mim][BF₄] (c). It indicates that the monomers are polymerized completely and the PAM could keep stable up to 270 °C.

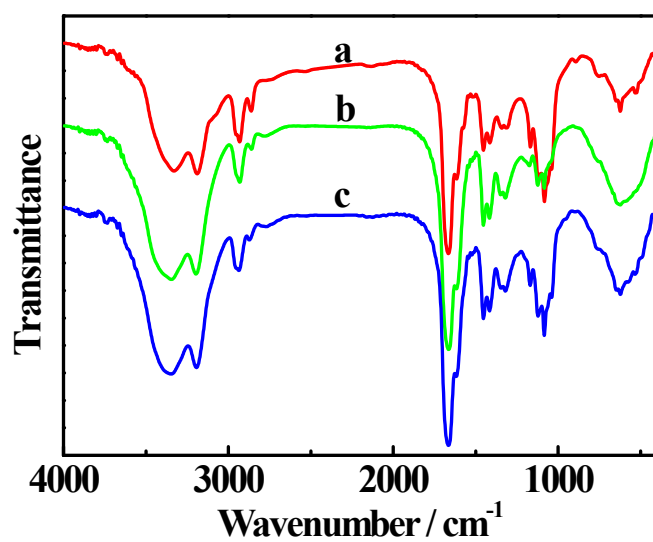


Fig. S3 FT-IR spectra of the PAMs synthesized in [C₆mim][BF₄] (a), [C₈mim][BF₄] (b), and [C₁₀mim][BF₄] (c).

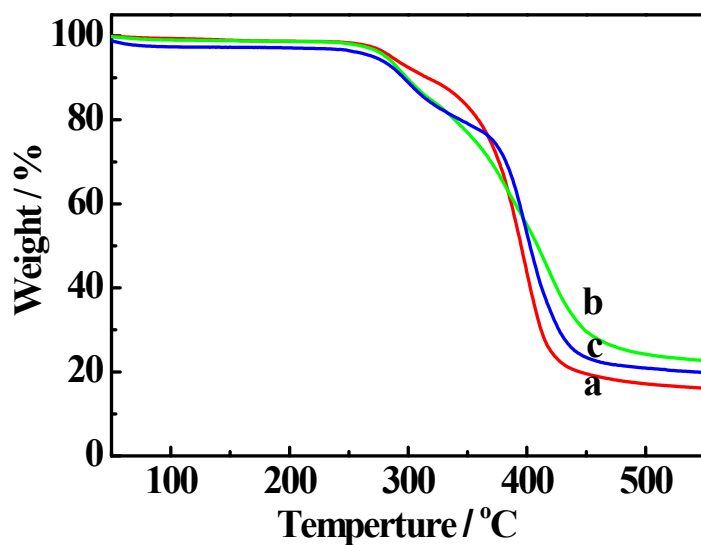
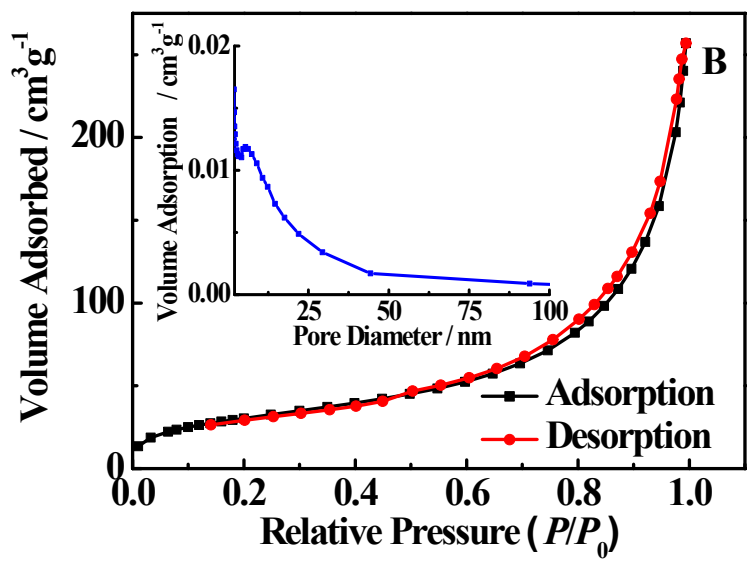
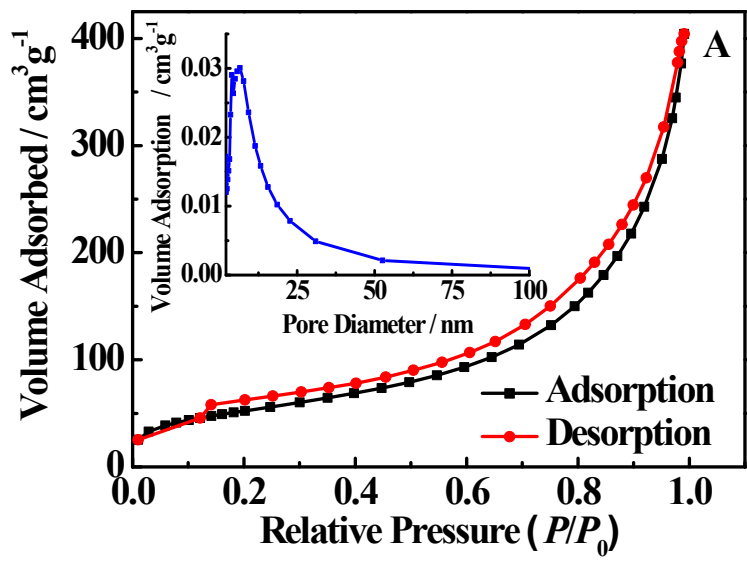


Fig. S4 Thermogravimetric curves of the PAMs synthesized in [C₆mim][BF₄] (a), [C₈mim][BF₄] (b), and [C₁₀mim][BF₄] (c).



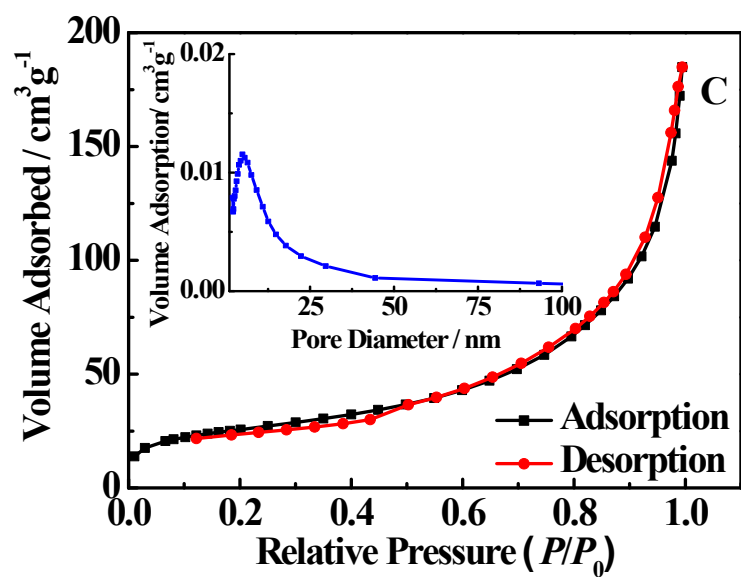


Fig. S5 N₂ adsorption-desorption isotherms and mesopore size distribution curves (the insets) of the PAMs synthesized in [C₆mim][BF₄] (A), [C₈mim][BF₄] (B), and [C₁₀mim][BF₄] (C).

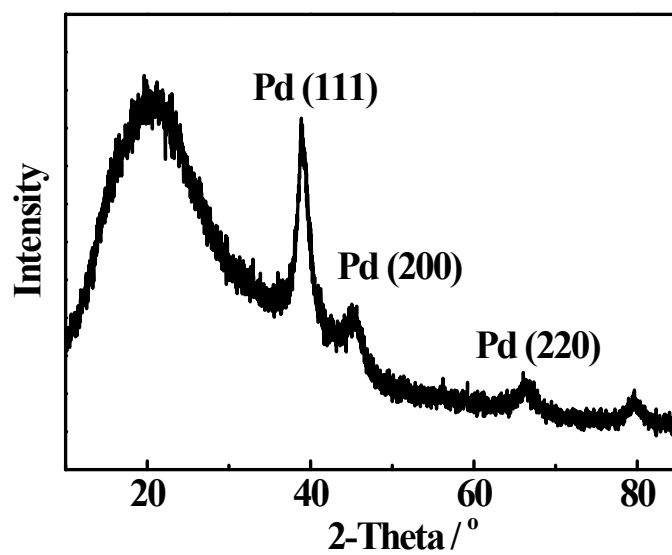


Fig. S6 X-ray diffraction pattern of the Pd/PAM catalyst.

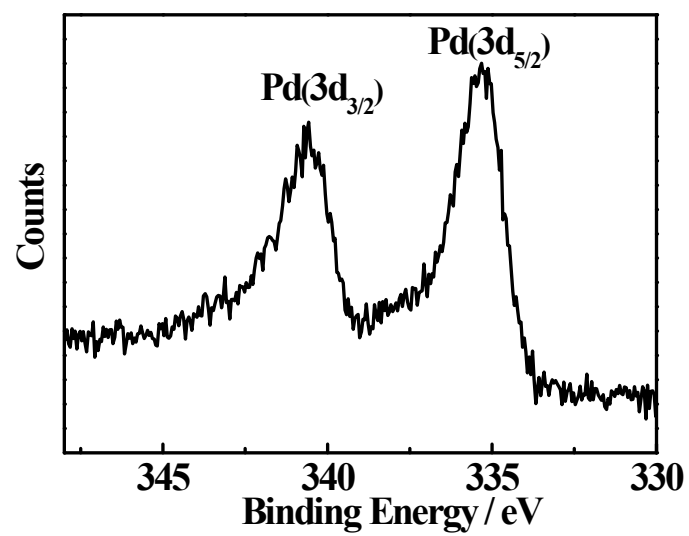


Fig. S7 X-ray photoelectron spectroscopy of the Pd/PAM catalyst.