Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A

Silica SOS@HKUST-1 Composite Microspheres as Easily-Packed Stationary Phase for Fast Separation

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Supporting Information

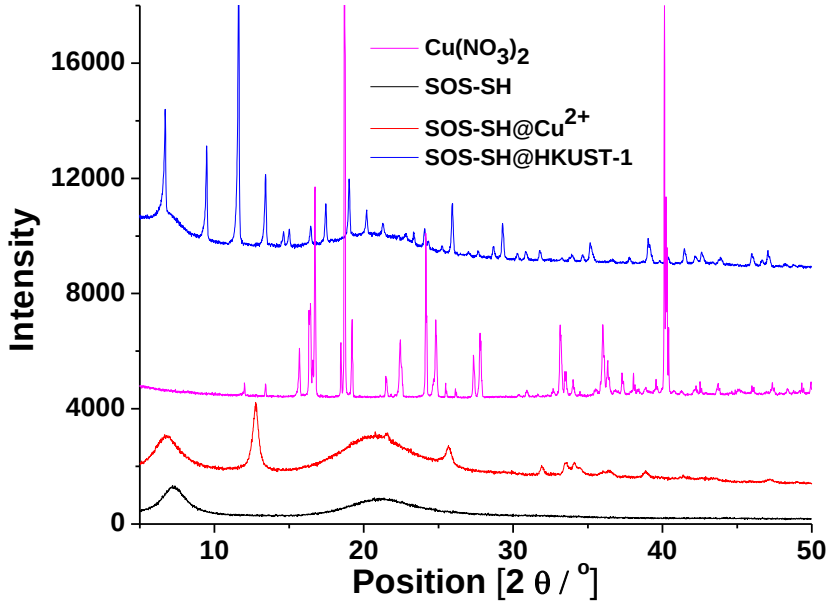

Figure S1. PXRD patterns of the SOS-SH particles, as-purchased $Cu(NO_3)_2$, Cu^{2+} immobilised on SOS-SH particles, and the SOS-SH@HKUST-1 composite particles.

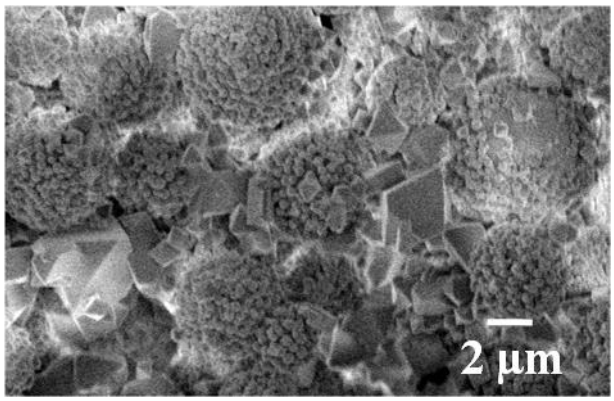

Figure S2. The SEM image showing the poor growth of HKUST-1 on SOS particles without firstly immobilizing Cu^{2+}.

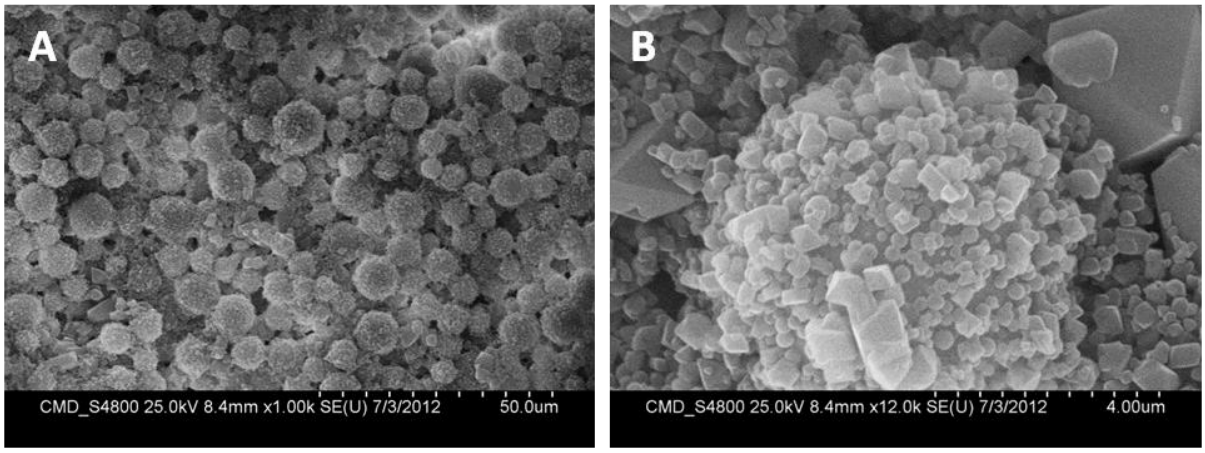

Figure S3. The SEM images of SOS-COOH@HKUST-1 composite microspheres at different magnifications.

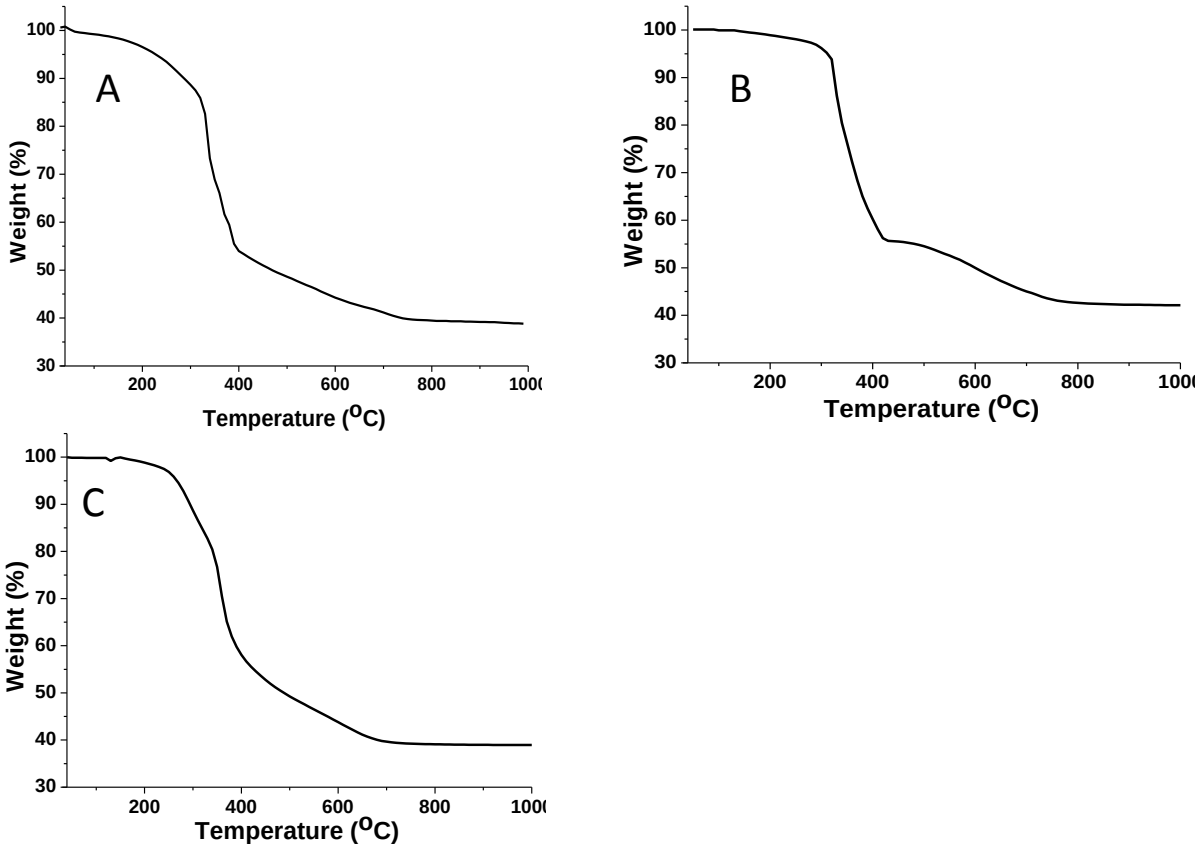

Figure S4. (A) TGA curve of the HKUST-1 synthesized in the absence of SOS particles. Gradual mass loss until 325 ^{o}C (weight 85%), then rapid decomposition until 395 ^{o}C (weight 54%), slow mass loss again until weight 39.4% at 800 ^{o}C. (B) TGA curve of the SOS-COOH@HKUST-1 particles. Slow mass loss until 320 ^{o}C (weight 93%), rapid decomposition until 428 ^{o}C (56%), and then gradual loss to 800 ^{o}C with weight 42.3%. (C) TGA curve of the SOS-COOH particles. Slow mass loss until 240 ^{o}C (weight 97.5%), quick mass loss until 330 ^{o}C (83.2%), rapid decomposition until 395 ^{o}C (58%), and then the weight percentage stable at 39.2% at 800 ^{o}C. Because the decomposition of HKUST-1 and SOS-COOH happened in the overlapping temperature range, it was difficult to calculate the loading of HKUST-1 on SOS particles.

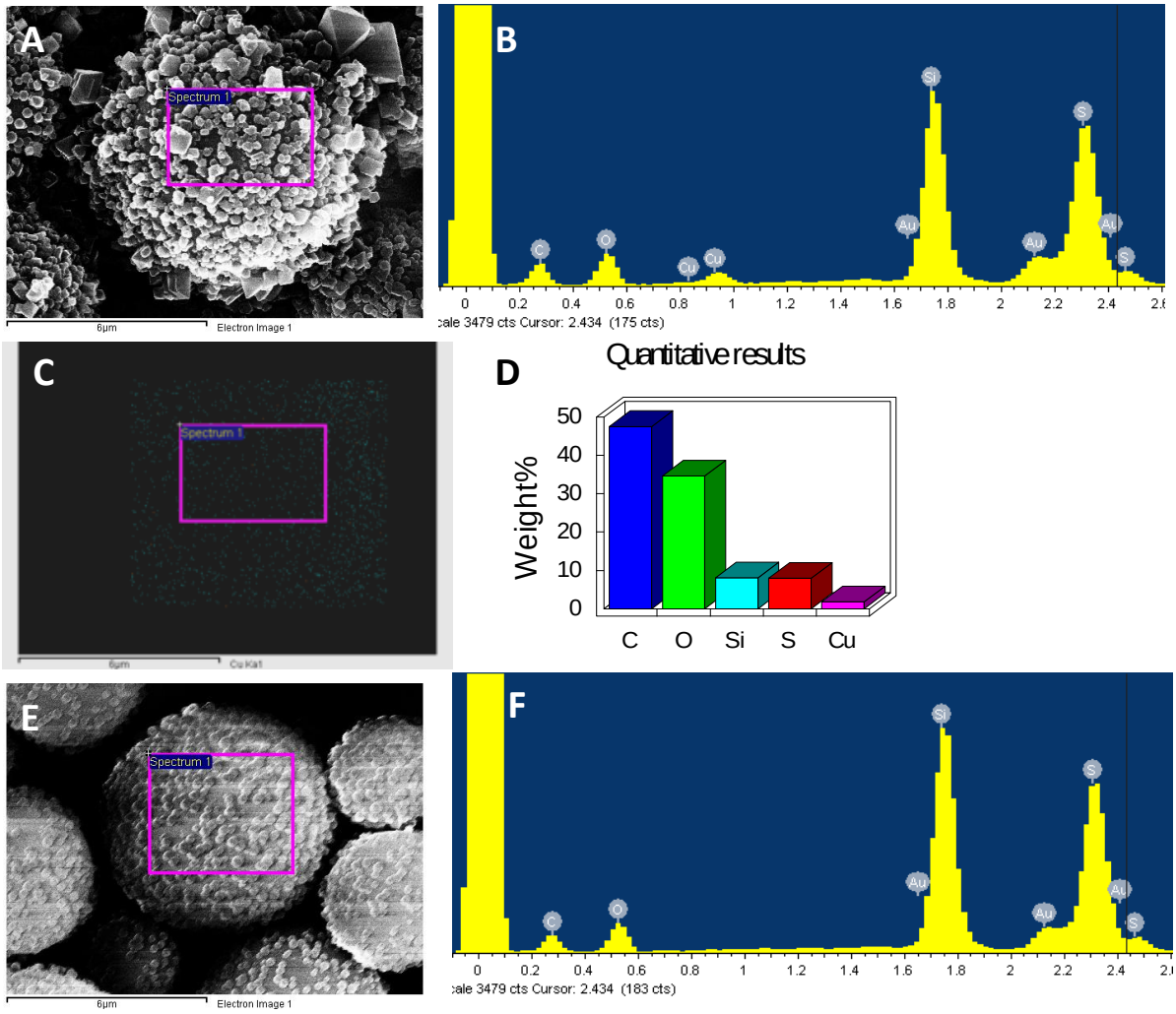

Figure S5. SOS-COOH@HKUST-1: (A) The SEM image and the selected area for element analysis; (B) The element spectrum for the selected area; (C) Mapping of Cu for the selected and larger area, indicating the uniform distribution of HKUST-1 on SOS-COOH particles; (D) The weight ratio of elements calculated by the instrument software. The sample was coated with Au. So Au was removed for the calculation. **SOS-COOH particles:** (E) The SEM image and the selected area; (F) The elemental spectrum for the selected area. This sample was coated with Au as well. Comparing spectrum (B) and (F), one can clearly see the presence of Cu, consistent with the observation of HKUST-1 on SOS-COOH particles.

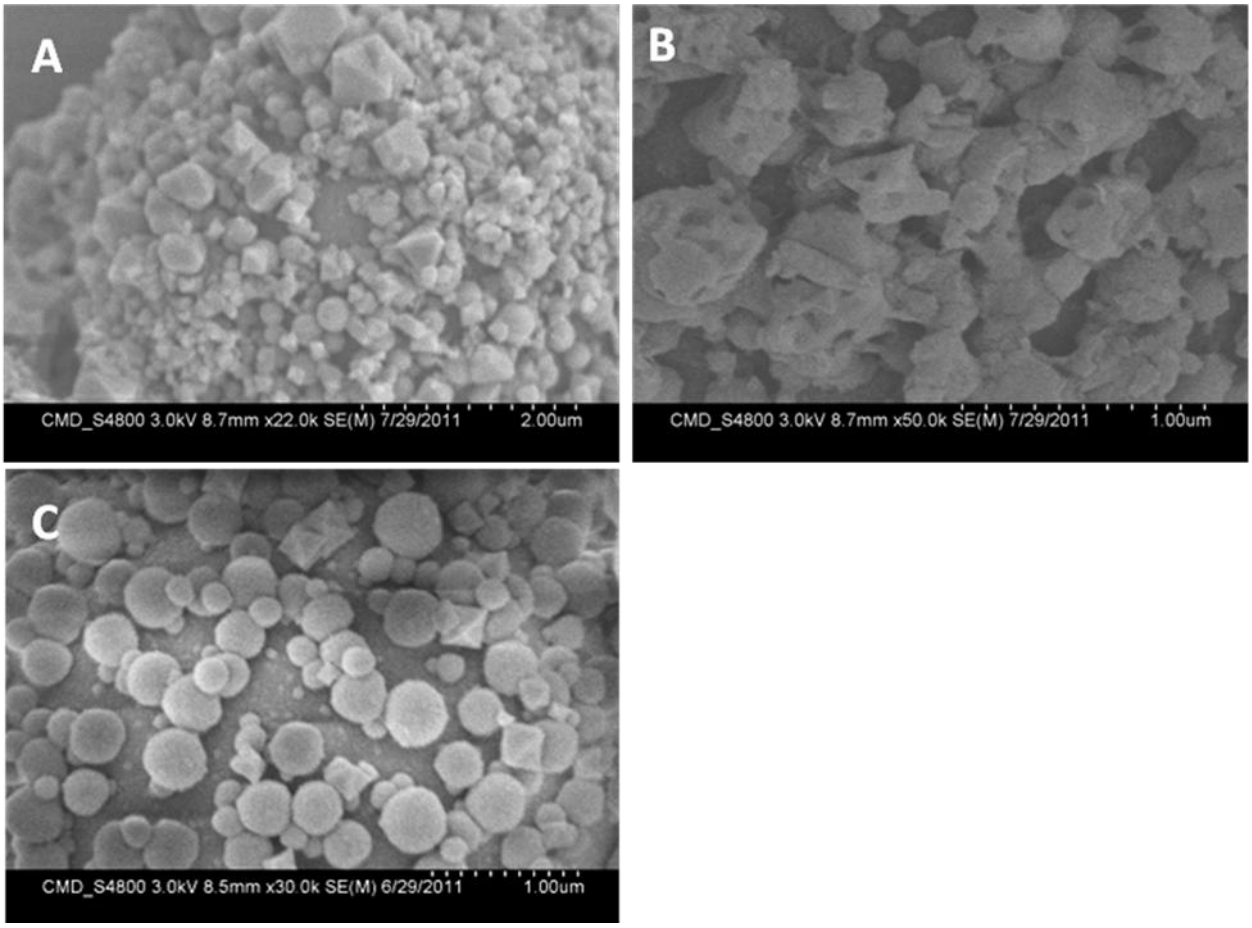

Figure S6. The SEM images at higher magnification showing the HKUST-1 crystalline particles on the SOS-COOH particle surface. (A) The sample prepared using 25 mmol $Cu(NO_3)_2$ without washing as detailed in method 1. (B) The sample in (A) washing once after immobilization of Cu^{2+} ions. (C) The sample in (A) washing twice after immobilization of Cu^{2+} ions.

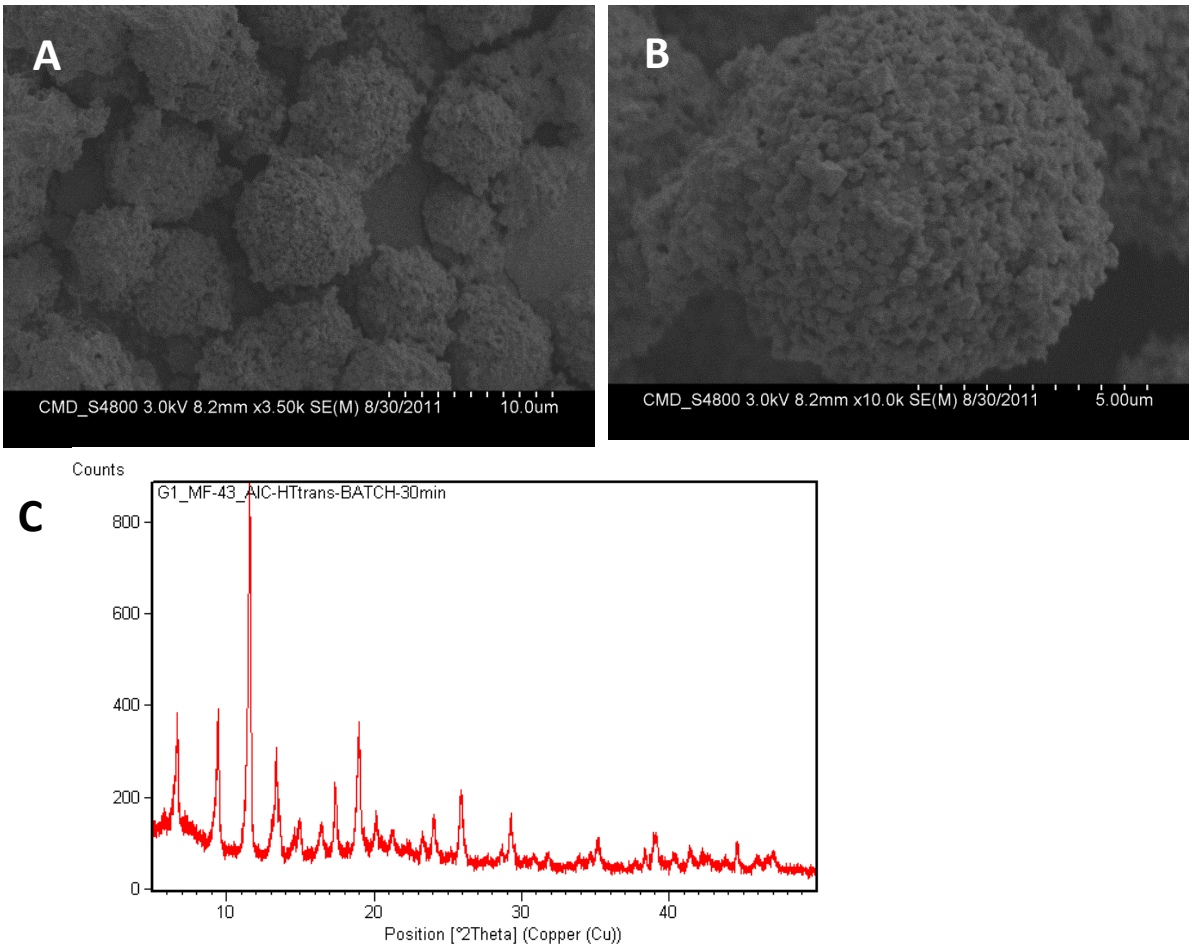

Figure S7. Synthesis of SOS-NH_2@HKUST-1 particles with method 1. HKUST-1 was formed on the SOS particles (SEM images A & B). BET surface area was 367 m^2/g. The PXRD pattern (C) shows the formation of pure phase HKUST-1.

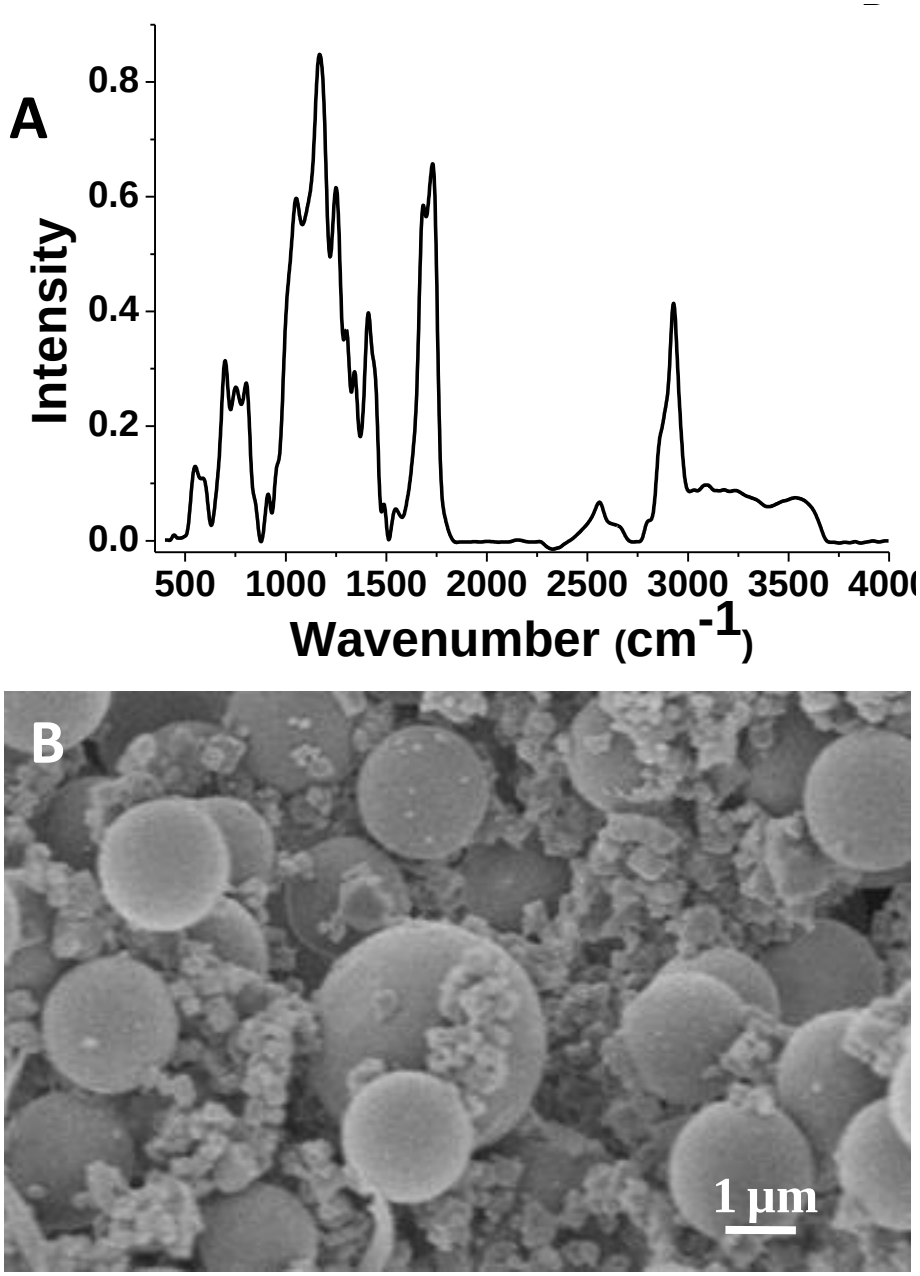

Figure S8. (A) The FTIR spectrum shows strong peaks around 1710 cm^{-1} and 1736 cm^{-1}, demonstrating the successful functionalization of smooth silica spheres with –COOH groups. (B) The SEM shows the morphology of synthesizing HKUST-1 with smooth silica particles via Cu^{2+} immobilization and solvothermal synthesis.

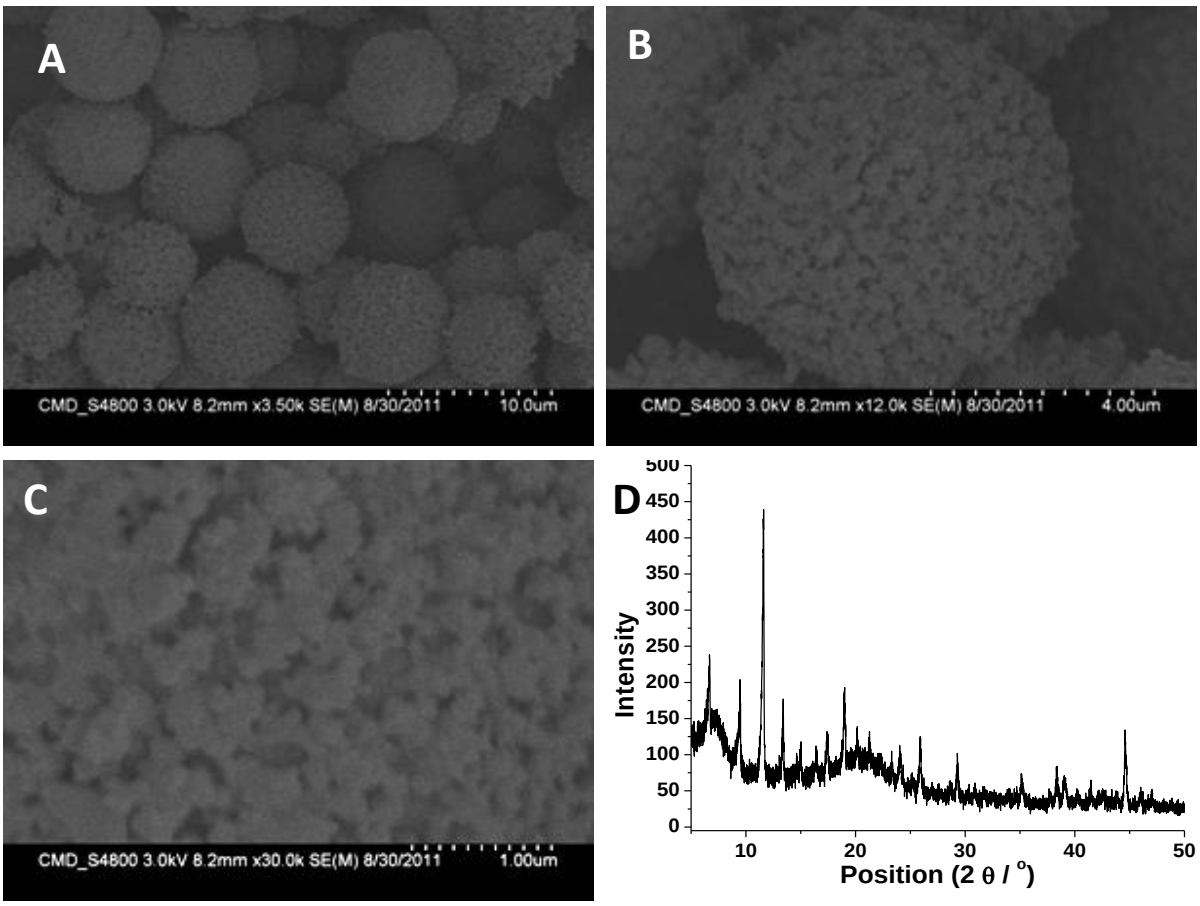

Figure S9. Synthesis of HKUST-1 on SOS-NH_2 particles using the method 2 procedure at room temperature with 3 times repeated synthesis. (A-C) SEM images at different magnification and (D) the PXRD pattern.

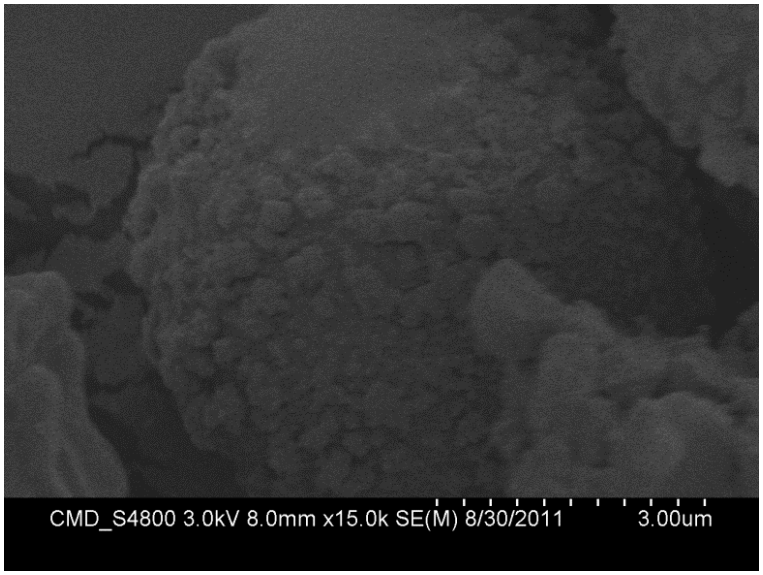

Figure S10. The resulting sample by preparing HKUST-1 film on the SOS-NH_2 particles at 120 ^{o}C.

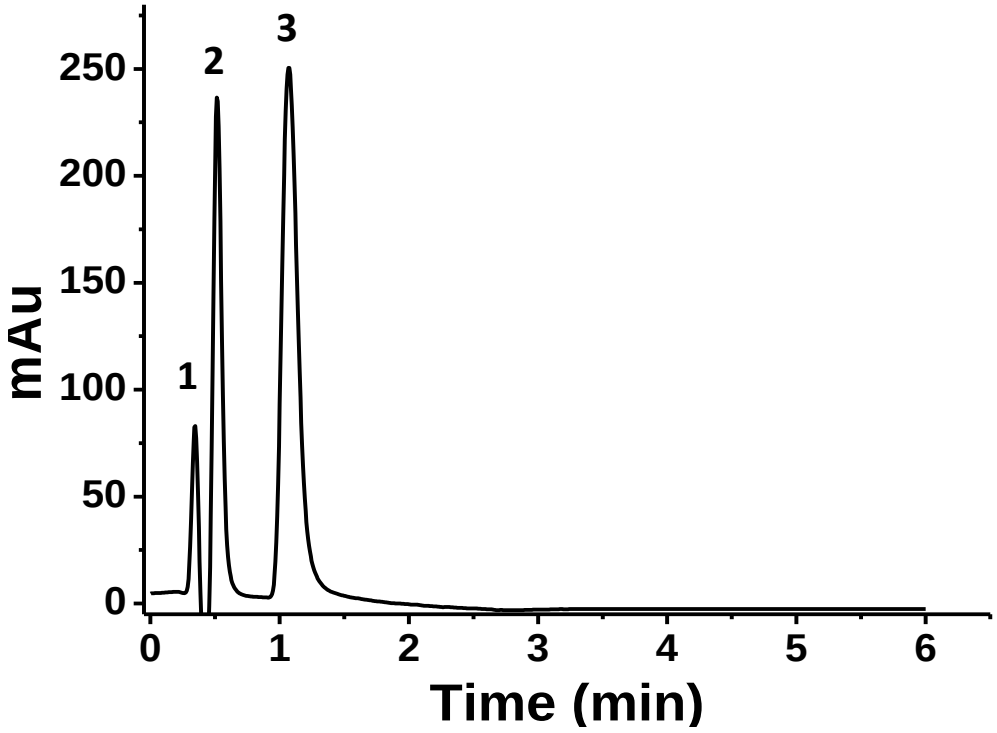

Figure S11. HPLC chromatogram on the SOS-COOH@HKUST-1 packed column for separation of toluene (1), *p*-xylene (2), and thiophene (3) with a mobile phase of heptane:DCM 80:20 v/v at 0.35 cm^3 min^{-1}, back pressure 280 bar.

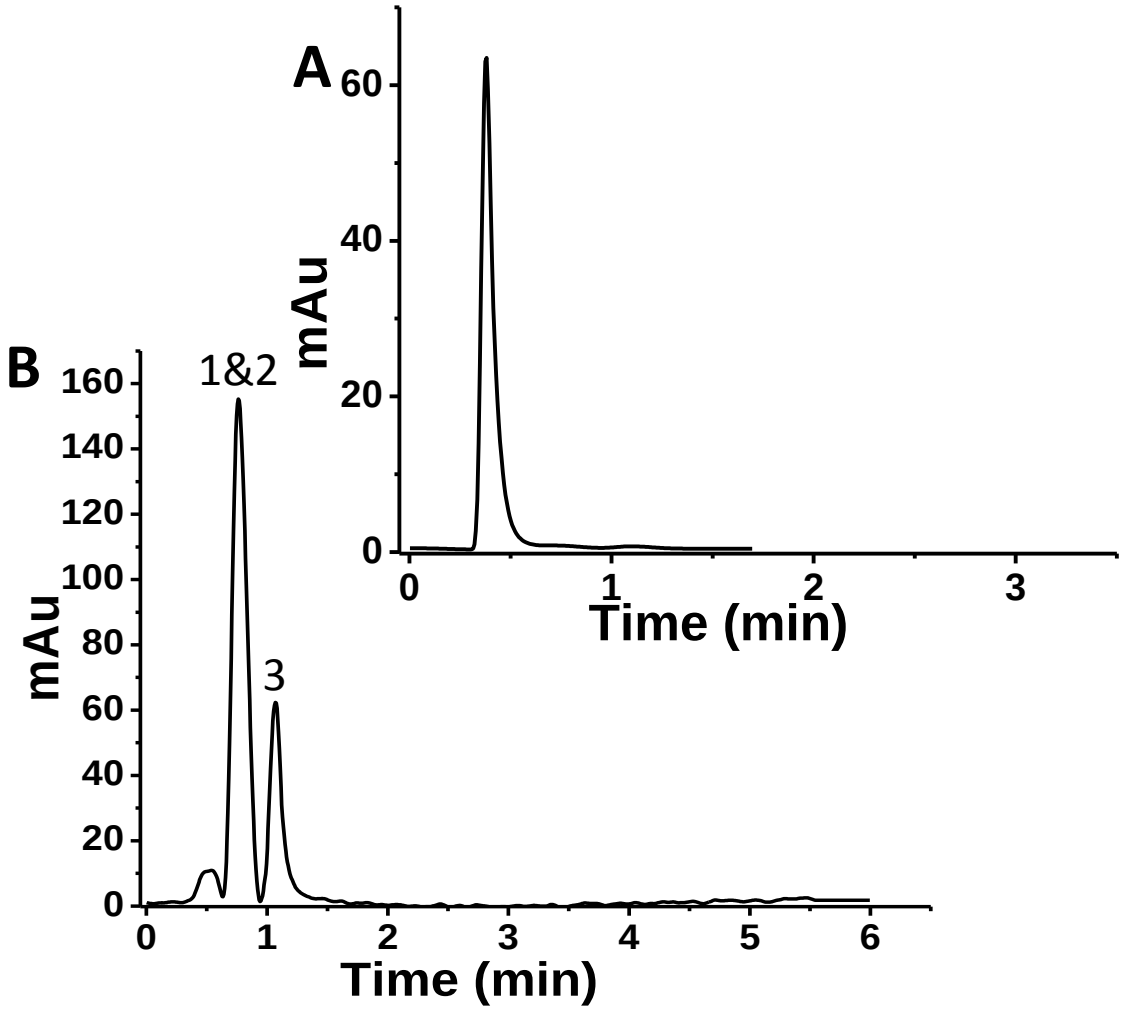

Figure S12. HPLC chromatograms on the (A) SOS-COOH particles packed column and (B) SOS-COOH@HKUST-1 packed column for separation of xylene isomers (injection 1µl, flow rate 0.35 cm^3 min^{-1}, back pressure 145 bar) at 20 ^oC using heptane as the mobile phase. 1. *m*-xylene, 2. *p*-xylene, 3. *o*-xylene.

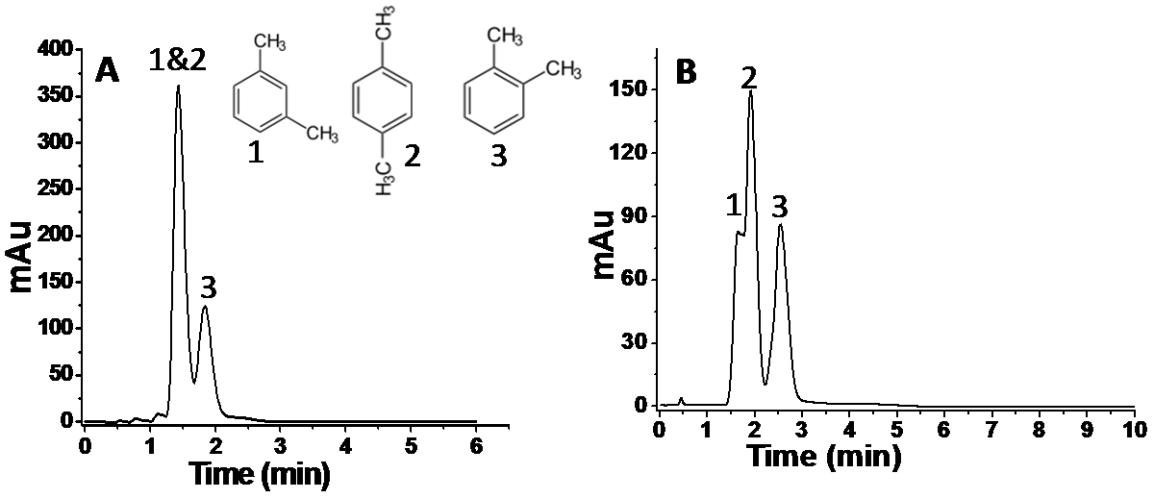

Figure S13. Separation of xylene isomers with DCM-conditioned SOS-COOH@HKUST-1 column for 2 hours (A) and 6 hours (B).

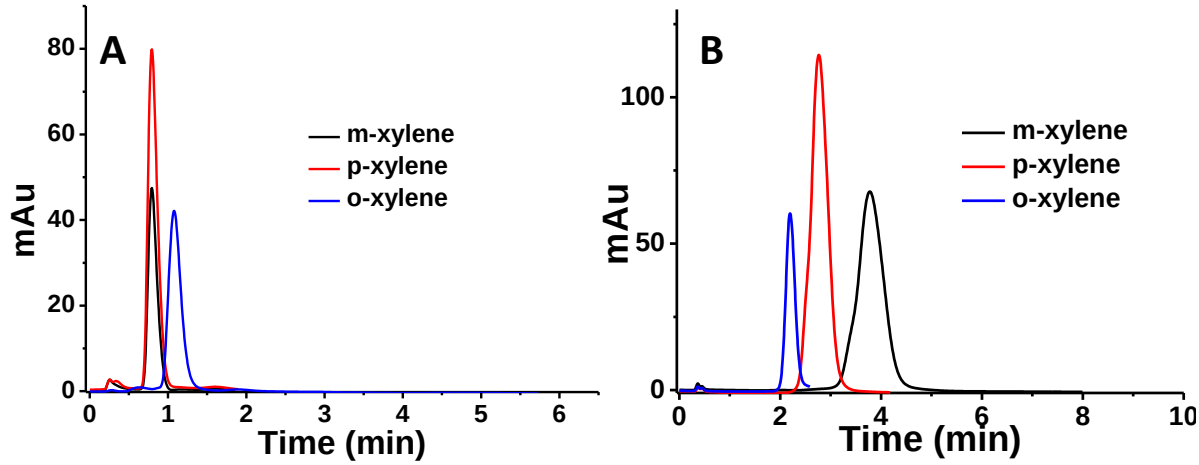

Figure S14. Chromatograms from the individual injections of the test compounds. (A) The column packed with as-prepared SOS-COOH@HKUST-1 particles. (B) The column in (A) conditioned with DCM for 24 hours.

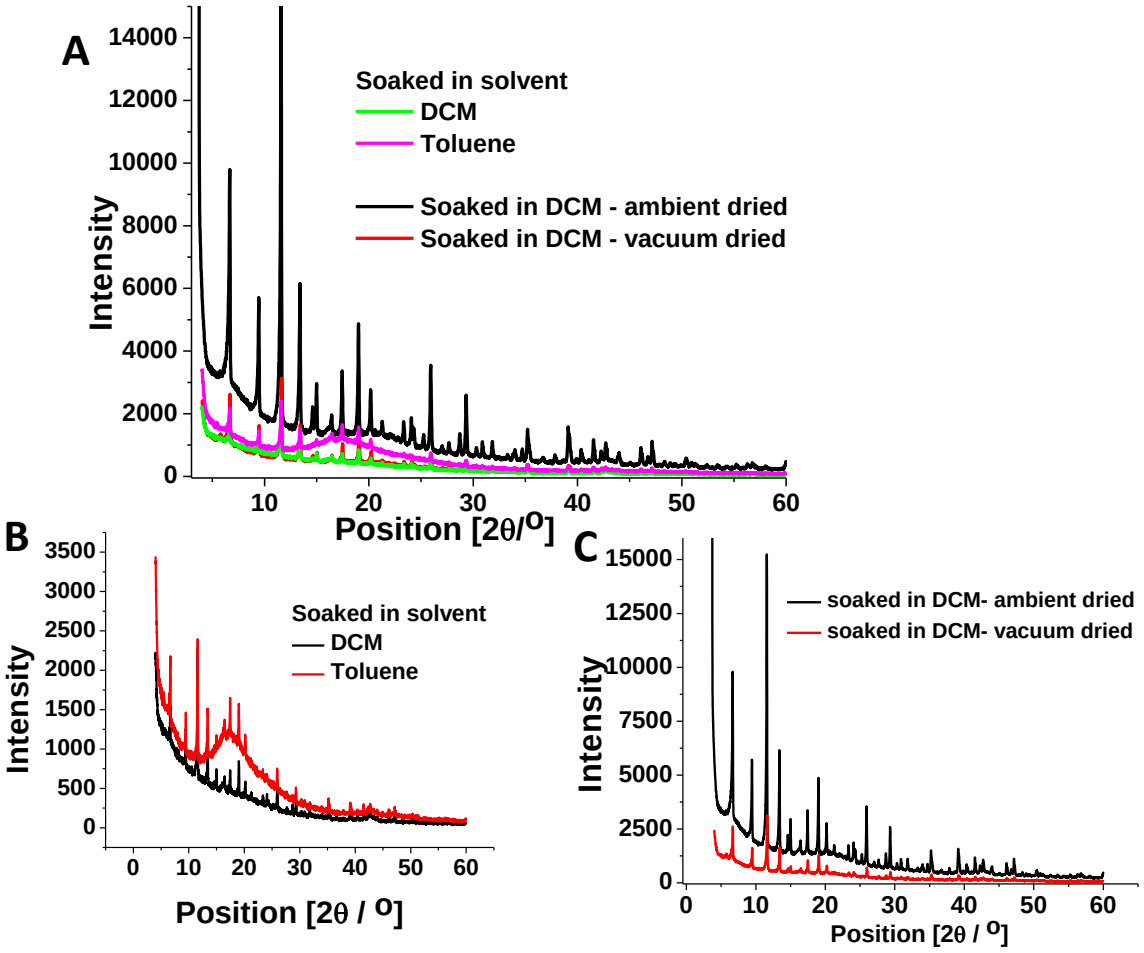

Figure S15. Overlay PXRD patterns of soaked and dry SOS-COOH@HKUST-1 particles (A) showing identical characteristics of crystalline HKUST-1. The PXRD patterns of DCM and toluene soaked SOS-COOH@HKUST-1 (B) are slightly different with the obvious broad peak around 2θ 18° arising from amorphous silica in the DCM-soaked materials. The DCM-soaked materials were dried in two ways (placed in a fume cupboard for 1 hour and thoroughly dried under vacuum). It was believed that some DCM was still trapped in the HKUST-1 with the drying in fume cupboard. The fact that the PXRD patterns are identical (C) suggests the trapping of DCM in the micropores of HKUST-1 does not cause the structure change. The solvent-soaked samples were covered with 6 μm Mylar film in transmission spinner for PXRD measurement (scan range 4 – 60 °, step size 0.0131, scan time 30 minutes).

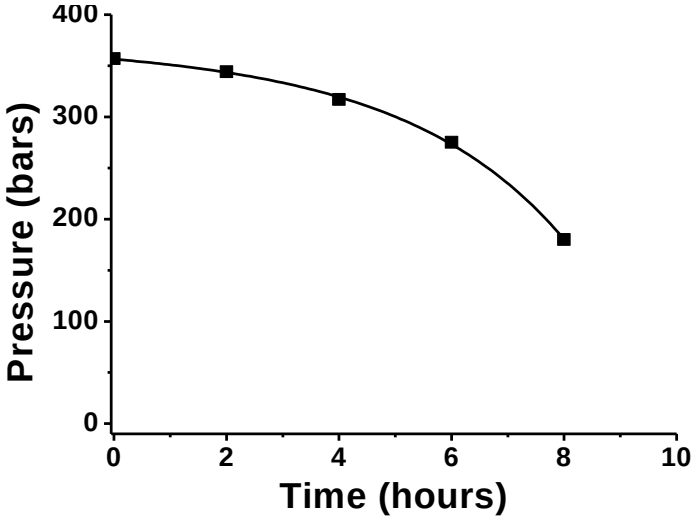

Figure S16. The change of backpressure for the DCM-conditioned column with the time of running heptane as mobile phase.

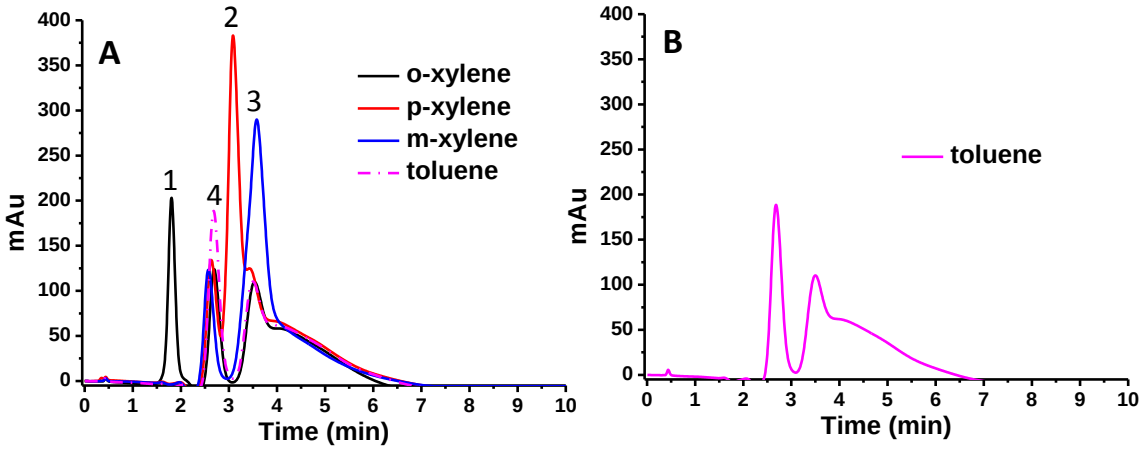

Figure S17. The effect of toluene conditioning on the selectivity of the SOS-COOH@HKUST-1 column for separation of xylene isomers (injection 1µl, flow rate 0.35 cm^3 min^{-1}) at 20 ^oC using heptane as the mobile phase. (A) Individual injections of (1) *o*-xylene, (2) *p*-xylene, (3) *m*-xylene, (4) toluene. (B) UV absorbance is observed for toluene. Toluene eluted as multiple trailing peaks when the column was conditioned with toluene.

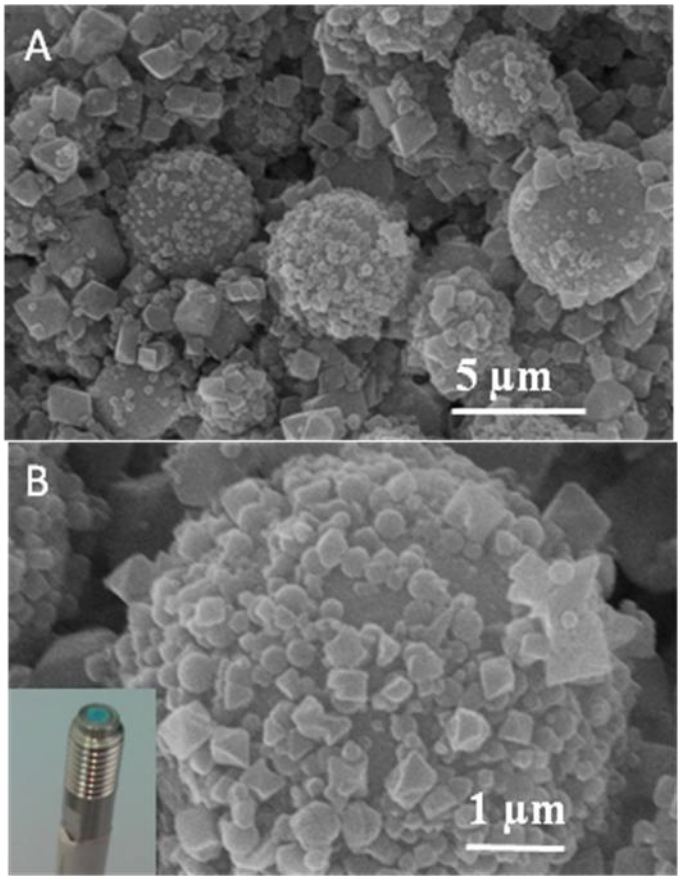

Figure S18. The SEM images at different magnifications (A & B) showing the SOS-COOH@HKUST-1 particles after HPLC testing. The inset in image (B) shows the packed column after testing.

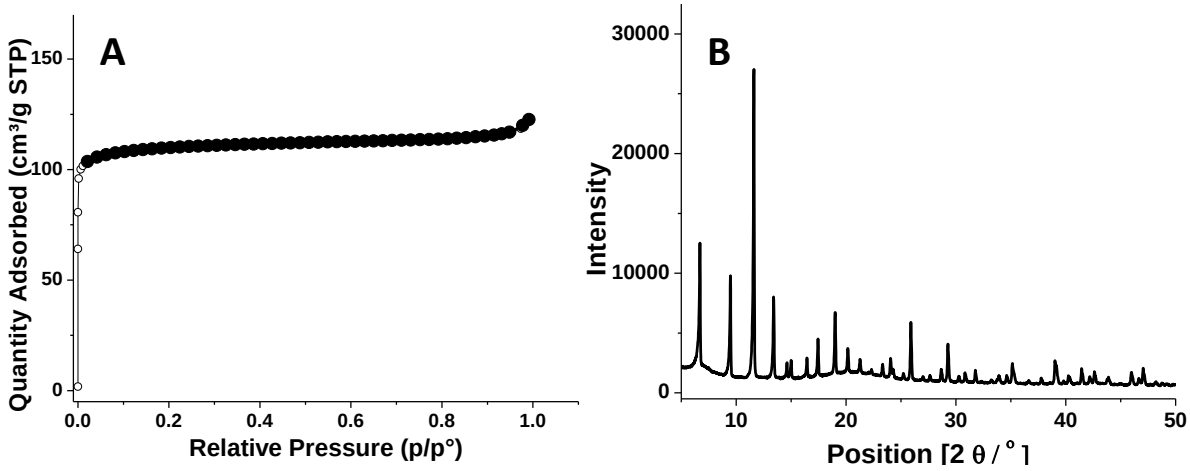

Figure S19. Further characterization data for the SOS-COOH@HKUST-1 particles after HPLC testing. (A) The isothermal plot of N_2 sorption. (B) The PXRD pattern.