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

Macroporous metal-organic framework microparticles with improved liquid phase separation

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Supporting Information

Notes for the Single X-ray CIF data:

High electron density peaks in the channels were refined as partially occupied Cu and C atoms in order to demonstrate that the cavities of the large cell are not uniformly occupied by Cu residues. It is impossible to put a precise number on the molecular weights of the contents of the cavities, therefore in the CIF only the sum formula of the framework was given. We added a line to the _refine_special_details section of the original CIF explaining this discrepancy. However, Cifcheck's algorithms do not take comments sections into account, but automatically flag up A level alerts.

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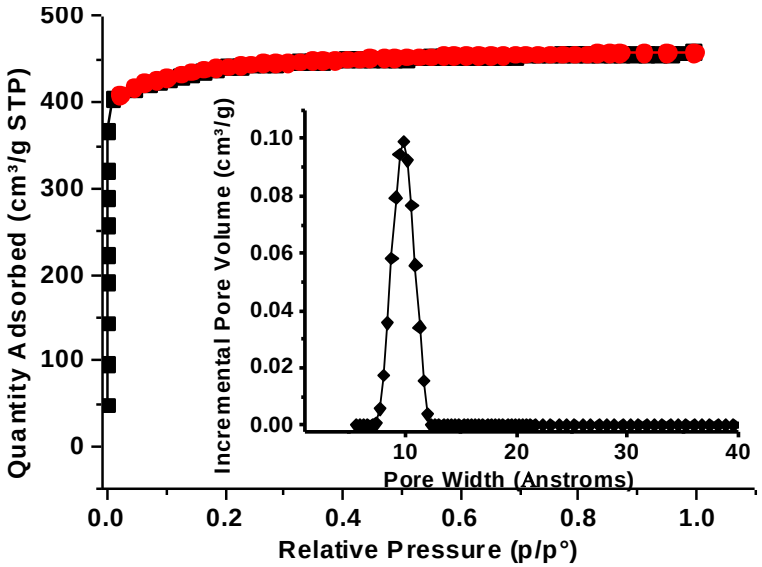

Figure S1. N_2 sorption of HKUST-1 crystals prepared via a solvothermal approach using water:ethanol 1:1 v/v as solvent at 120 ^{o}C. The type I isotherm demonstrates that a microporous material was produced. The inset shows the micropore distribution with a sharp peak around 1 nm which is typical for HKUST-1.

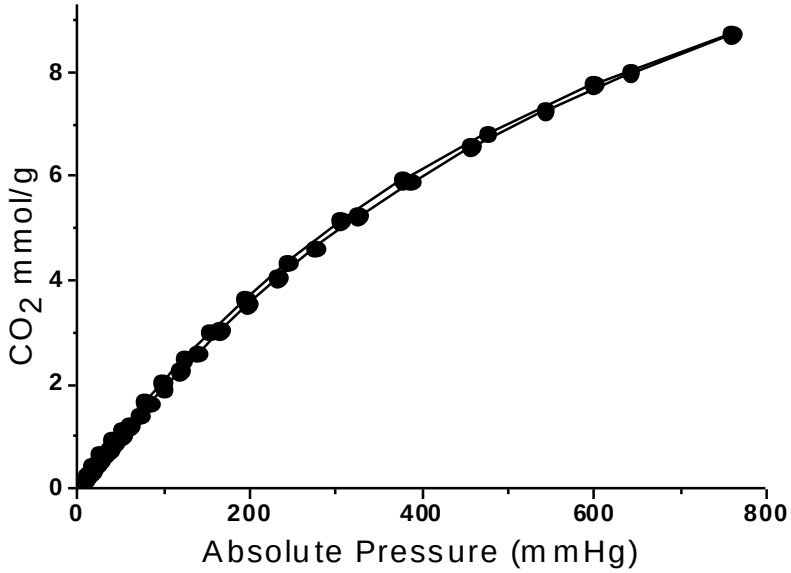

Figure S2. The plot of CO_2 uptake on the modified HKUST-1 particles. The maximum uptake value is 8.73 mmol/g. The CO_2 uptake on the prepared HKUST-1 particle is similar to the uptake on the as-prepared HKUST-1 particles at 9.02 mmol/g.

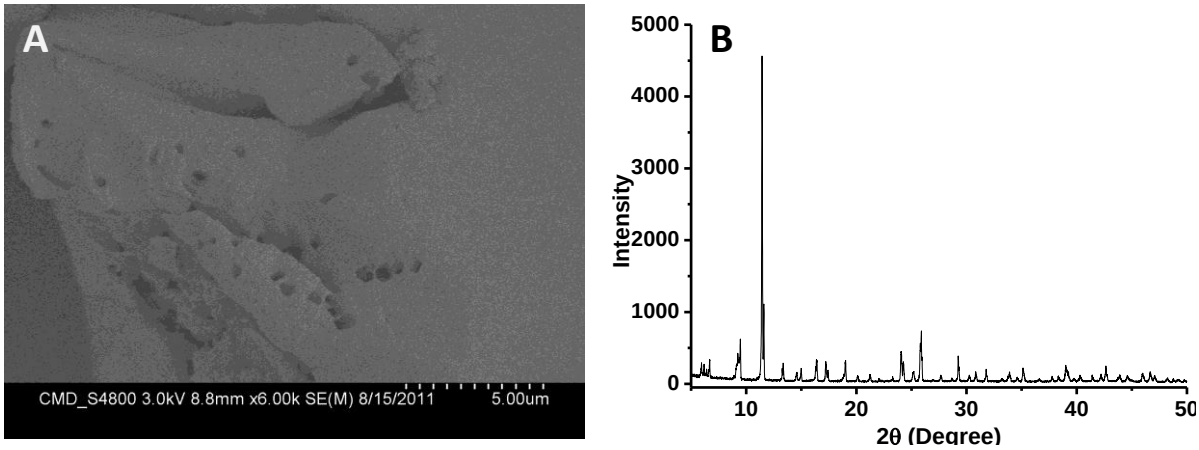

Figure S3. The SEM image (A) and the PXRD pattern (B) for the HKUST-1 particles modified at 120 ^{o}C.

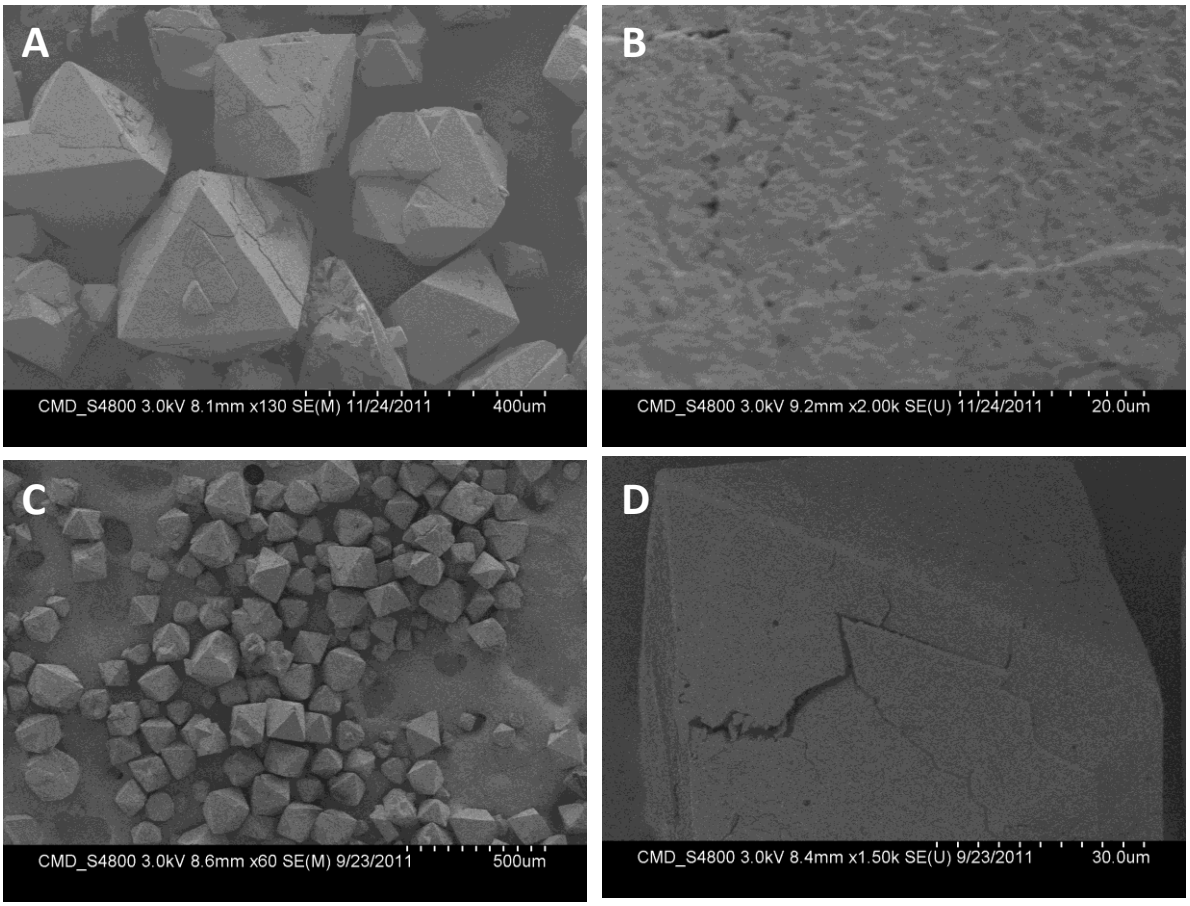

Figure S4. SEM images of the samples prepared from the control experiments for the modification of crystalline HKUST-1 particles. (A&B): the HKUST-1 particles were just heated to 150 ^{o}C without solvent in an autoclave. (C&F): the HKUST-1 particles were modified in methanol but without hydroquinone at 150 ^{o}C under the same autoclave conditions.

All these control experiments showed no macropores generated on HKUST-1 particles.

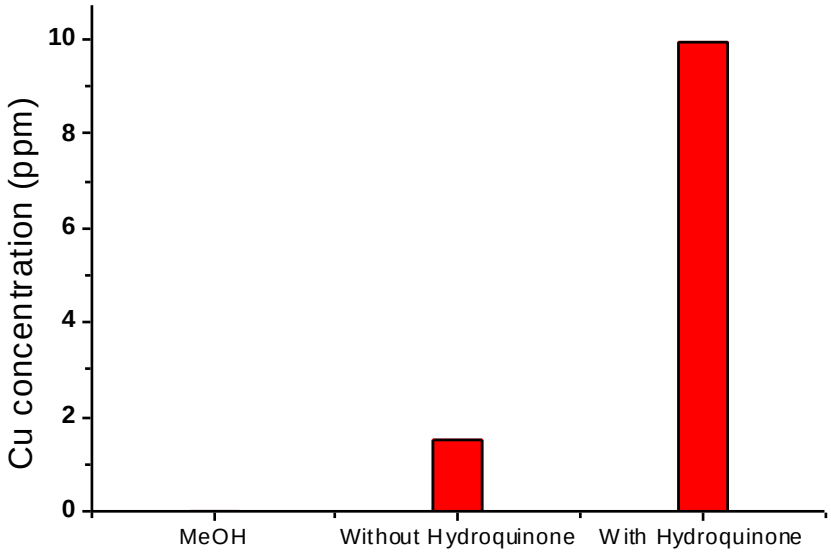

Figure S5. ICP analysis for Cu content in the solutions from the modification reactions in autoclave at 150 ^{o}C for 16 hours. In the case of methanol (MeOH), the solvent was treated under the same solvothermal condition, but with no HKUST-1 and no hydroquinone. The ICP analysis was performed in triplicates for each sample. The measured results are within 5% difference. The average value was used.

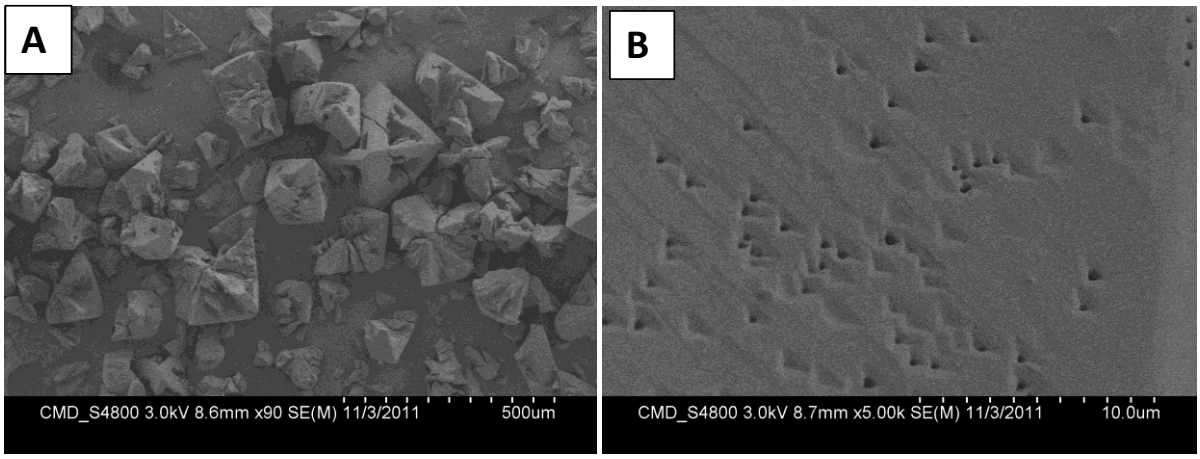

Figure S6. The SEM images at different magnifications show the morphology of HKUST-1 particles modified by addition of 50 µL 1N boric acid aqueous solution (instead of hydroquinone) at 150 ^{o}C for 16 hours.

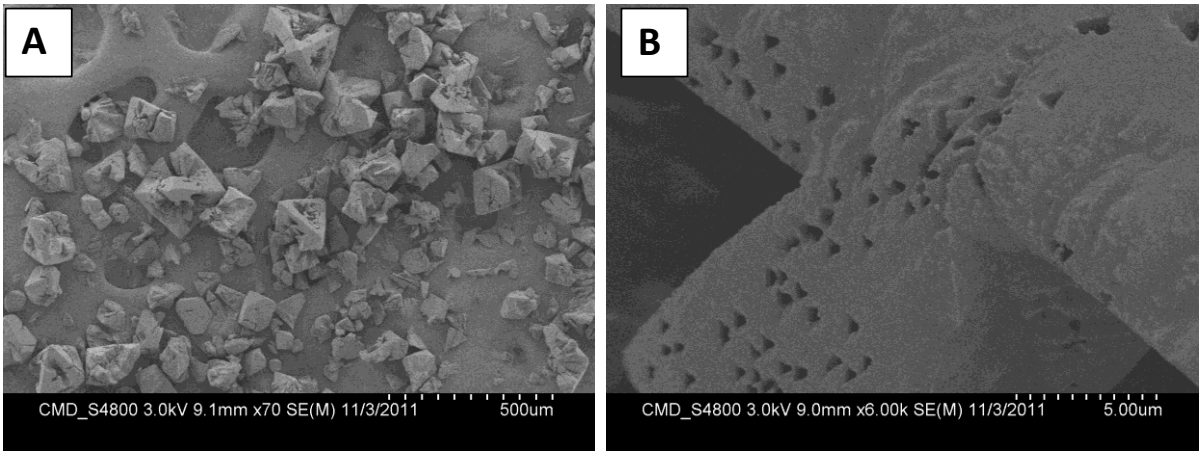

Figure S7 The SEM images at different magnifications show the morphology of HKUST-1 particles modified by addition of 50 µL 1N NaCl aqueous solution (instead of hydroquinone) at 150 ^{o}C for 16 hours.

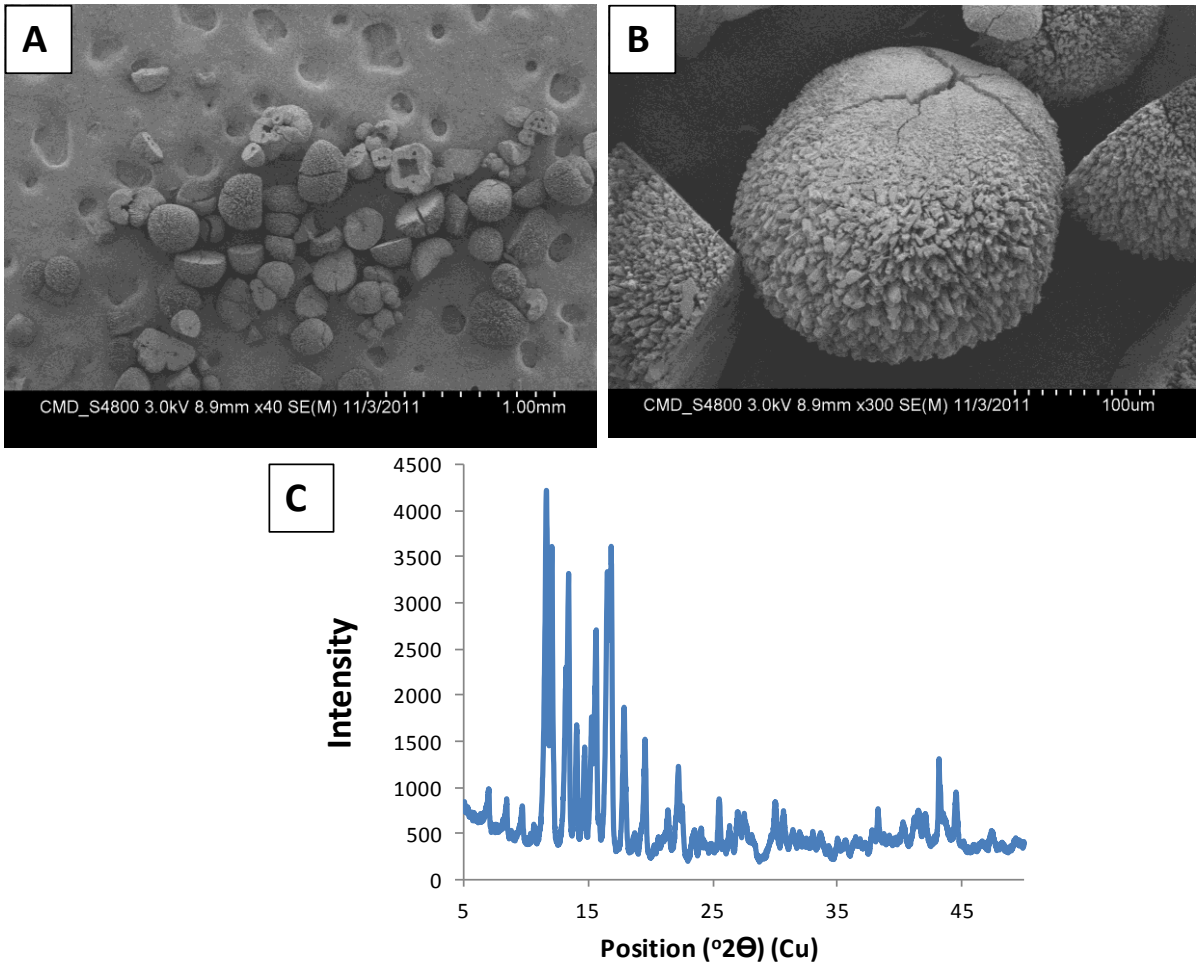

Figure S8. The SEM images (A&B) show the morphology of HKUST-1 particles at different magnifications, modified by addition of 50 µL TMEDA (instead of hydroquinone) at 150 ^{o}C for 16 hours. (C) is the PXRD pattern of the modified HKUST-1 particles.

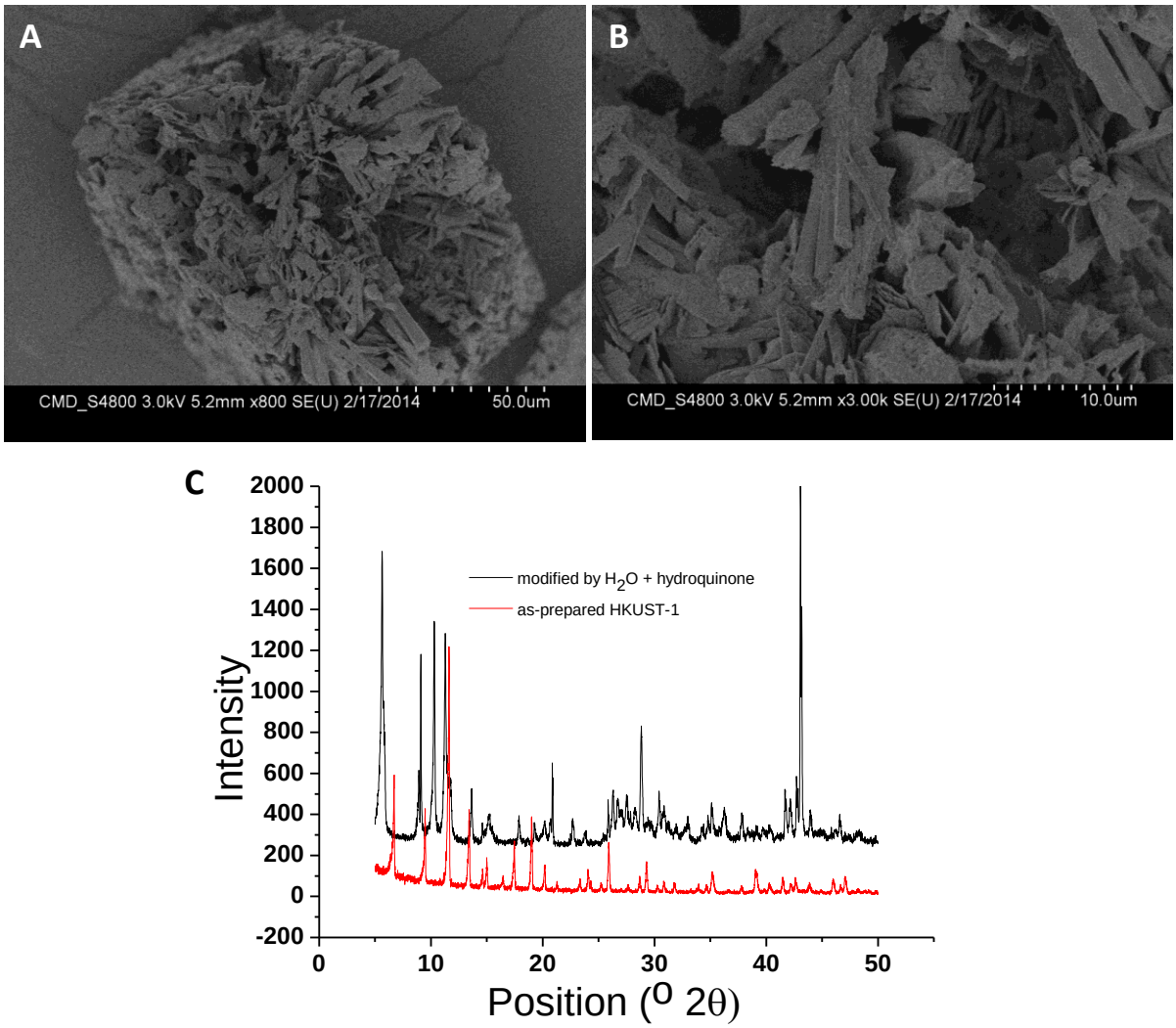

Figure S9. The HKUST-1 crystalline microparticles (prepared from water/ethanol mixture) were modified by water and hydroquinone (20 mg HKUST-1 + 2 cm^3 H_2O + 100 mg hydroquinone) in an autoclave at 150 ^oC for 16 hours. The same condition as used in the study, except that methanol was replaced by H_2O. (A) & (B) show the porous structure after modification. The XRD patterns in (C) shows that the structure is not of HKUST-1, probably a mixture of Cu_2O and other crystalline materials.

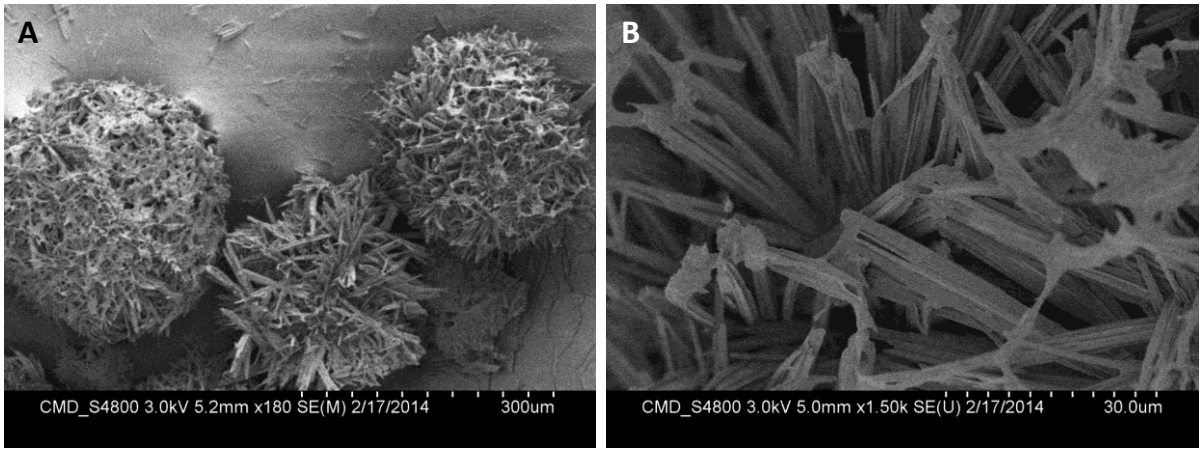

Figure S10. The HKUST-1 crystalline microparticles (prepared from water/ethanol mixture) were modified by water without hydroquinone (20 mg HKUST-1 + 2 cm^3 H_2O) in an autoclave at 150 ^oC for 16 hours. The SEM images (A) & (B) show the porous structure after modification, with the assembled nanofibers.

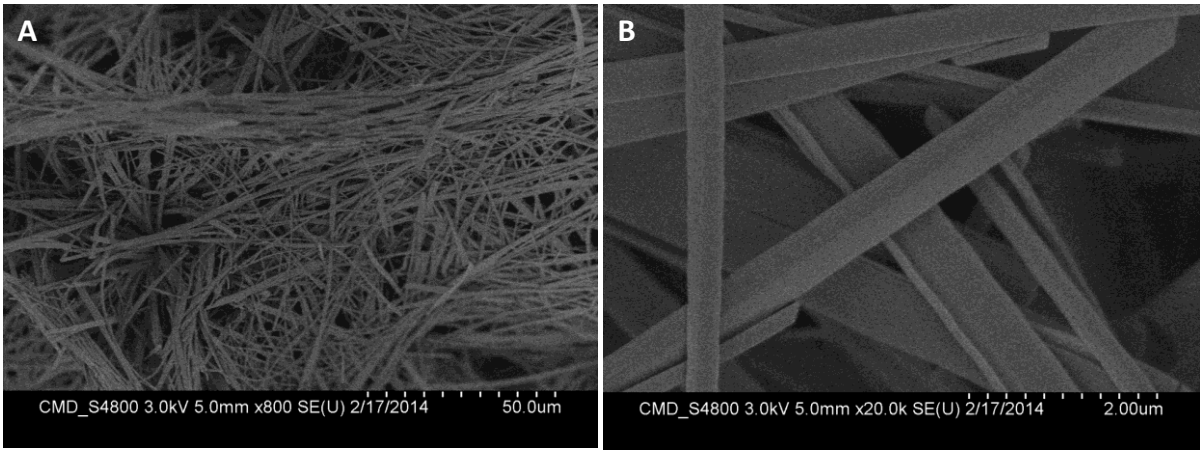

Figure S11. The HKUST-1 crystalline microparticles (prepared from water/ethanol mixture) were soaked in water at room temperature for 16 hours. The microparticles have completely transformed into nanofibers, which have very low surface area around 20 m^2/g.

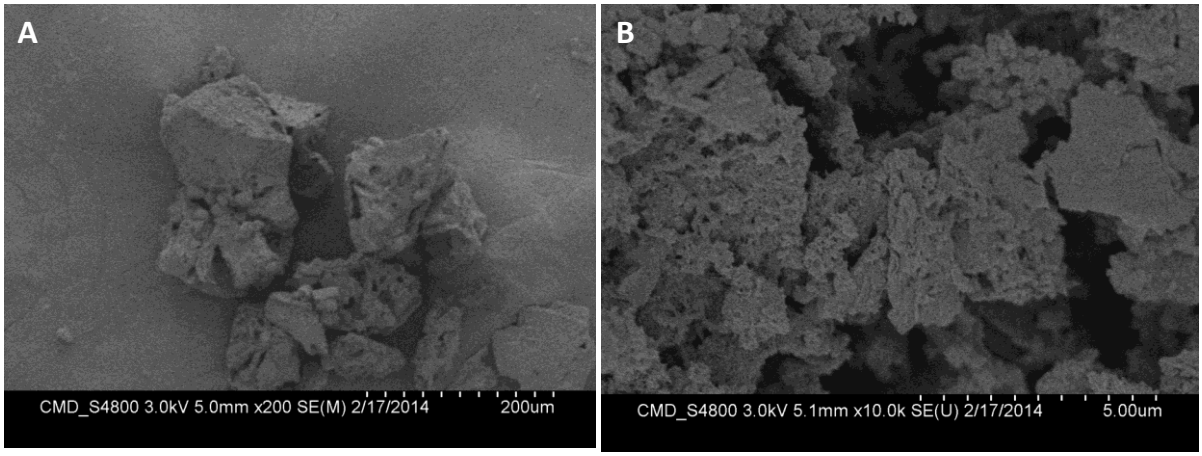

Figure S12. The hydroquinone-modified particles were soaked in water at room temperature for 16 hours. The microparticles largely remained (A) although the structure has been made more porous. Compared with Fig. S11, it seems that the hydroquinone modification has made the HKUST-1 particles more stable when exposed to water.