Electronic Supporting Information

for

Synthesis of Highly Monodispersed Ga-soc-MOF Hollow Cubes, Colloidosomes and Nanocomposites

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Experimental Section:

Chemicals and Materials. $Ga(NO_3)_3 \cdot xH_2O$ (99.9%, Aladdin), dimethyl sulfoxide (DMSO, 99.7%, Acros), acetonitrile (CH_3CN, 99.5%, Vetec), polyvinylpyrrolidone (PVP, MW=40000, Sigma-Aldrich), N,N-dimethylformamide (DMF, 99.8%, Vetec), $HAuCl_4 \cdot 3H_2O$ (98%, energy chemical), sodium borohydride ($NaBH_4$, ≥98.0%, Aldrich), triethylamine (TEA, 99%, Sigma-Aldrich), tetramethylammonium nitrate (TMAN, 96%, Sigma-Aldrich), Maleic acid (MA, 99%, Aladdin), Sorbitan Trioleate (Span-85, TCI), dioctyl sulfosuccinate sodium salt (AOT, >95.0%, TCI), and HCl (36-38%, Beijing Chemical Factory). All of the chemicals and solvents were used as received without further purification.

3,3',5,5'-azobenzenetetracarboxylic acid (H_4-ABTC) ligand was synthesized following the published procedure.[1]

Synthesis of Ga-soc-MOF cubes. A precursor solution was prepared by mixing $Ga(NO_3)_3 \cdot xH_2O$ (15.0 mg, 0.059 mmol), H_4-ABTC (10 mg, 0.028 mmol), 0.01 mL of MA (0.86 M in deionized water) and 0.2 mL of PVP (0.01 M in DMF or DMSO) in 0.5 mL of DMSO and 1.0 mL of CH_3CN. The mixture was heated to 120 °C and held for 1 h on a hot plate with continuous stirring. The products were harvested by centrifugation and washed with anhydrous ethanol two times.

Synthesis of Ga-soc-MOF hollow cubes. Solid Ga-**soc**-MOF cubes (0.5 mg, 5.4×10^{-4} mmol) and PVP (200 mg, 5×10^{-3} mmol) were mixed in 1.0 mL of deionized water under magnetic stirring. After 2 h, HCl solution (1.09 M, 0.2-0.3 mL) was added and the mixture was vigorously stirred for another 10 h. The precipitates were collected by centrifugation and washed with anhydrous ethanol several times. All the experiments were carried out at room temperature (about 25 °C).

Synthesis of Ga-soc-MOF colloidosomes. $Ga(NO_3)_3 \cdot xH_2O$ (25.0 mg, 0.098 mmol), H_4-ABTC (10 mg, 0.028 mmol), 0.05 mL of triethylamine (0.72 M in deionized water) 0.05 mL of AOT (0.22 M in deionized water) and 0.05 mL of Span-85 were mixed in 0.5 mL of DMSO, 0.2 mL of CH_3CN and 0.2 mL of deionized water. The mixture was stirred at room temperature for 12 h, and then heated to 120 °C and held for 3 h on a hot plate with continuous stirring. The products were harvested by centrifugation and washed with anhydrous ethanol two times.

Synthesis of Au@Ga-soc-MOF nanocomposite. Ga-**soc**-MOF cubes (1.0 mg, 10.1×10^{-3} mmol) was dispersed in deionized water (0.5 mL), followed by the addition of PVP (10 mg, 2.5×10^{-4} mmol). After stirring for 30 min, an aqueous solution of $HAuCl_4\cdot3H_2O$ (1.0 mL, 0.3 mM) was added and the mixture was stirred for 10 min. Afterwards, an aqueous solution of $NaBH_4$ (1.0 mL, 3 mM) was added and the mixture was vigorously stirred for another 10 min. The products were collected by centrifugation and washed twice with anhydrous ethanol. All the experiments were carried out at room temperature (about 25 ^oC).

Catalytic Study on 4-Nitrophenol. The catalytic reaction was monitored by UV-vis spectroscopy. 4-nitrophenol (0.03 mL, 0.010 M) was mixed with freshly prepared $NaBH_4$ solution (0.12 mL, 0.10 M). Then, the Au@Ga-**soc**-MOF nanocomposites (50 μL, 1.0 gL^{-1}) were added to the reaction system. The reaction was conducted in a quartz cuvette with an optical path length of 1.0 cm. The absorbance spectral was recorded in the range of 280 to 500 nm.

Characterization.

Power X-ray diffraction (XRD) measurements were performed on a D8 focus diffractometer with graphite monochromatized Cu Kα radiation (λ = 0.15405 nm). Thermogravimetric analysis (TGA) were recorded on Thermal Analysis Instrument (SDT 2960, TA Instruments, New Castle, DE) with a heating rate of 10°/min in an air flow of 100 mL/min. The morphology of the samples were characterized by a field-emission scanning electron microscope (FE-SEM, S-4800, Hitachi) equipped with an energy-dispersive X-ray (EDX) spectrometer. Transmission electron microscopy (TEM) images were obtained on a FEI Tecnai G2 S-Twin with a field emission gun operating at 200 kV. Fourier transform infrared spectra were measured on a Vertex PerkinElmer 580BIR spectrophotometer (Bruker) with KBr pellet technique. The UV-vis adsorption spectra were measured on a Hitachi U-3100 spectrophotometer. Gas sorption isotherm measurements were carried out on an Autosorb IQ instrument. The samples were fully exchanged with ethanol, and degassed at 150 ^oC for 8 h before gas adsorption measurement.

References:

1. Y. L. Liu, J. F. Eubank, A. J. Cairns, J. Eckert, V. C. Kravtsov, R. Luebke and M. Eddaoudi, *Angew. Chem., Int. Edit.* 2007, **46**, 3278.

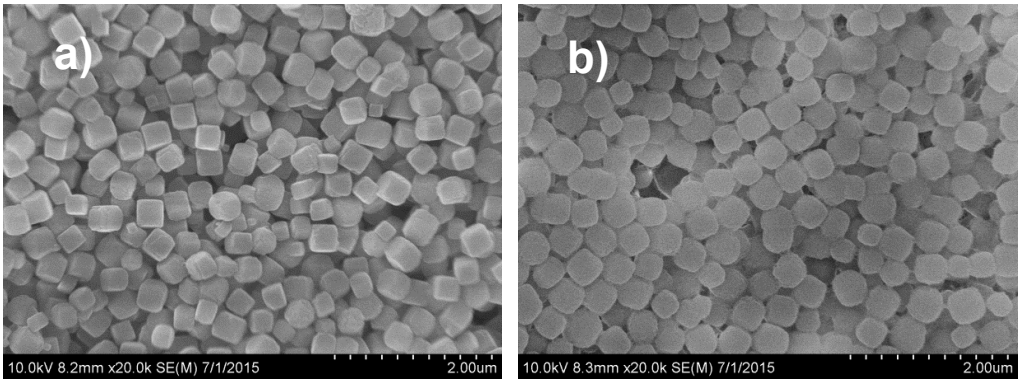


Figure S1. SEM images of Ga-**soc**-MOF particles synthesized in the absence of (a) PVP, and (b) MA.

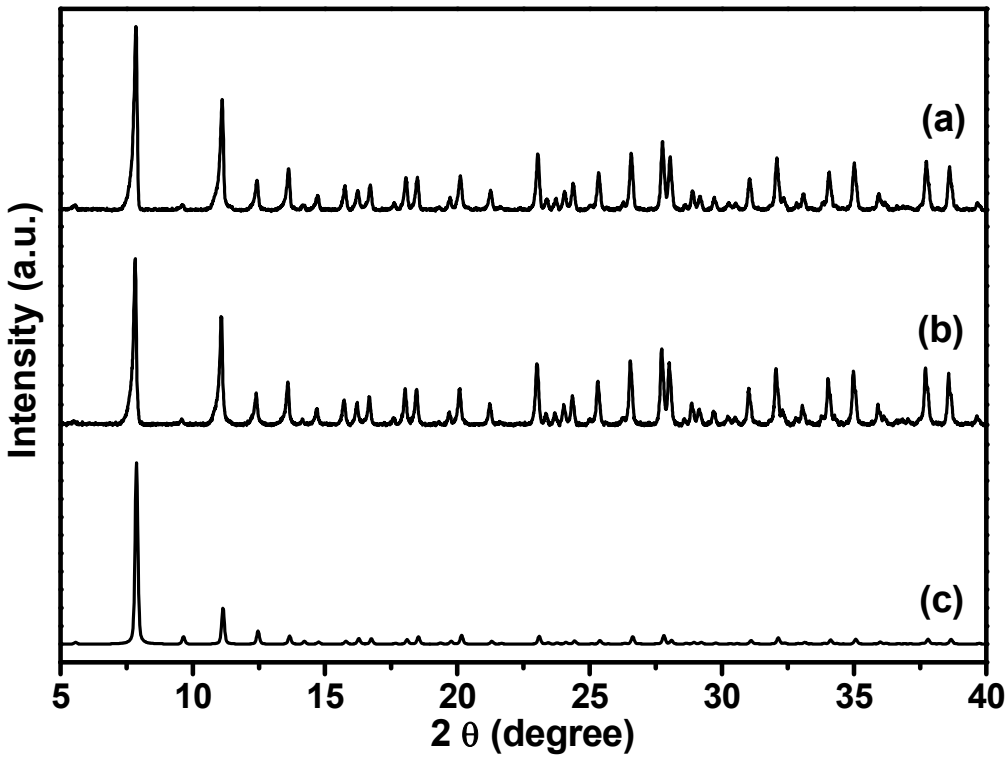


Figure S2. XRD pattern for (a) Ga-**soc**-MOF cubes, (b) Ga-**soc**-MOF colloidosomes, and (c) calculated XRD pattern for In-**soc**-MOF.

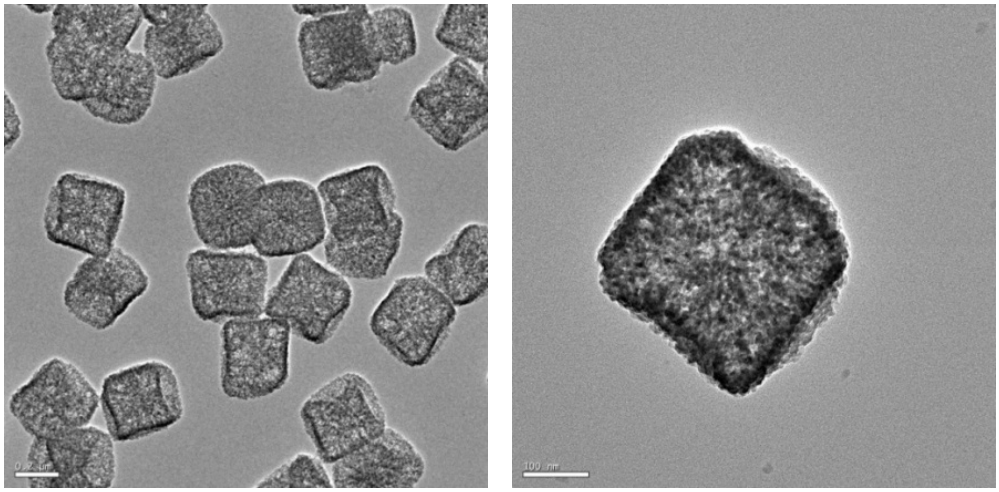


Figure S3. TEM images of Ga-**soc**-MOF cubes after reacting with 0.25 mL of HCl (1.09 M) for 10 h.

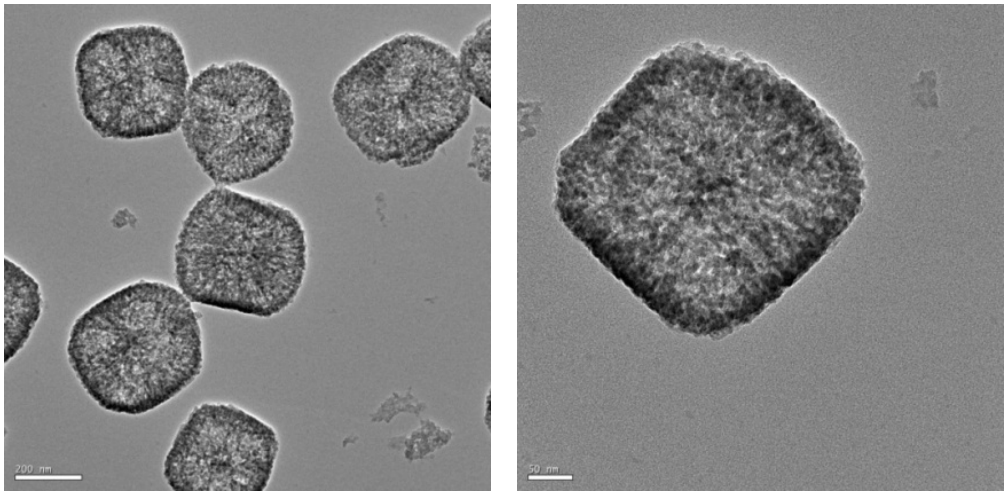


Figure S4. TEM images of Ga-**soc**-MOF cubes after reacting with 0.28 mL of HCl (1.09 M) for 10h.

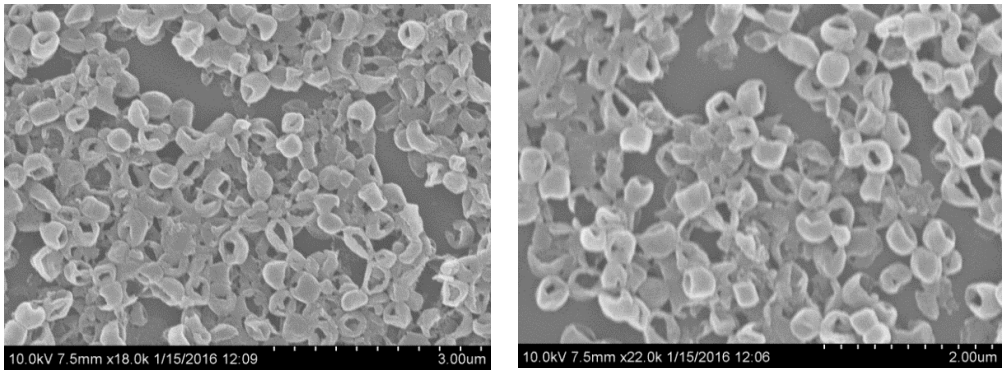
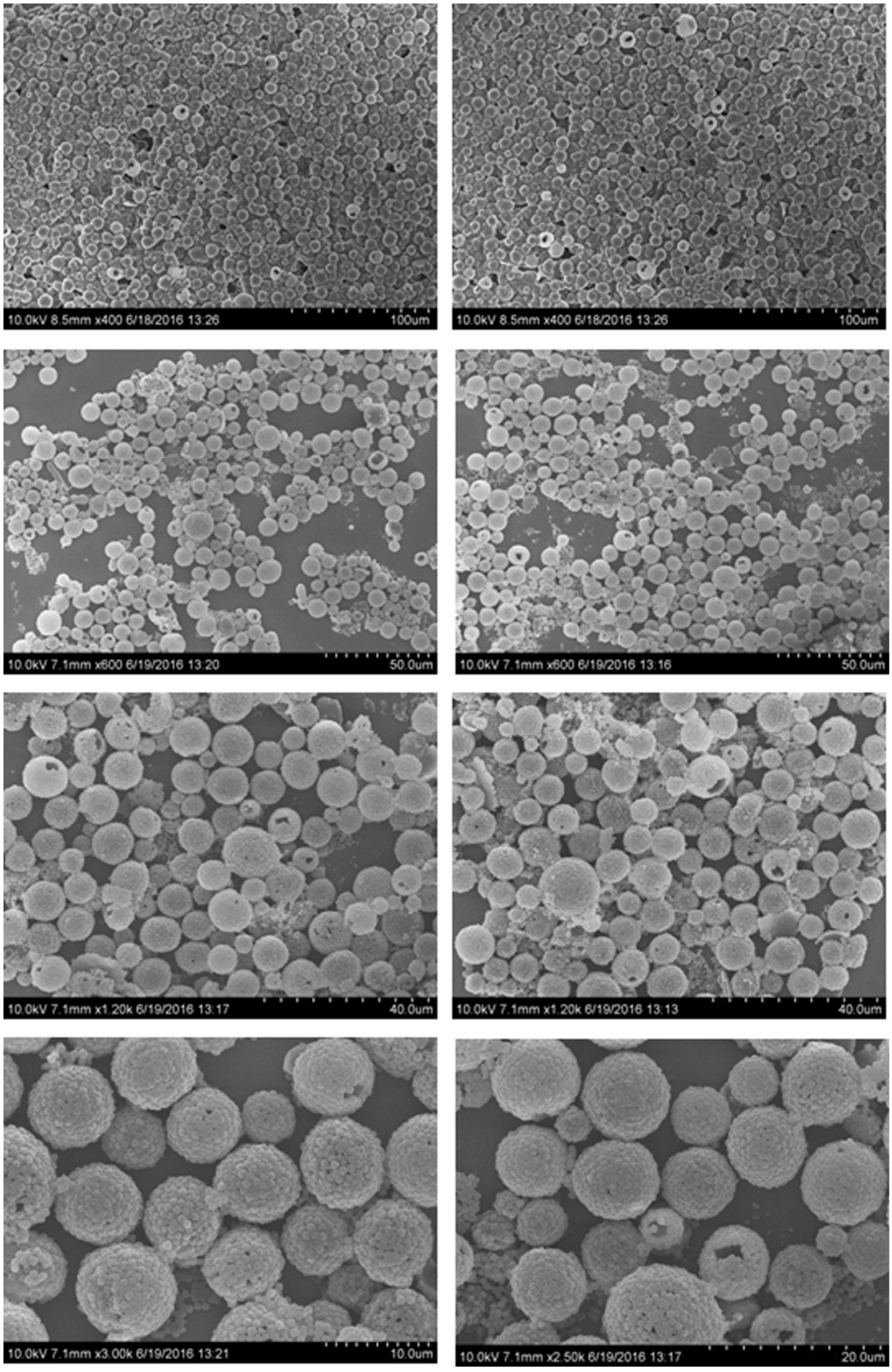


Figure S5. SEM images of Ga-**soc**-MOF cubes after reacting with 0.3 mL of HCl (1.09 M) for 10 h.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100um
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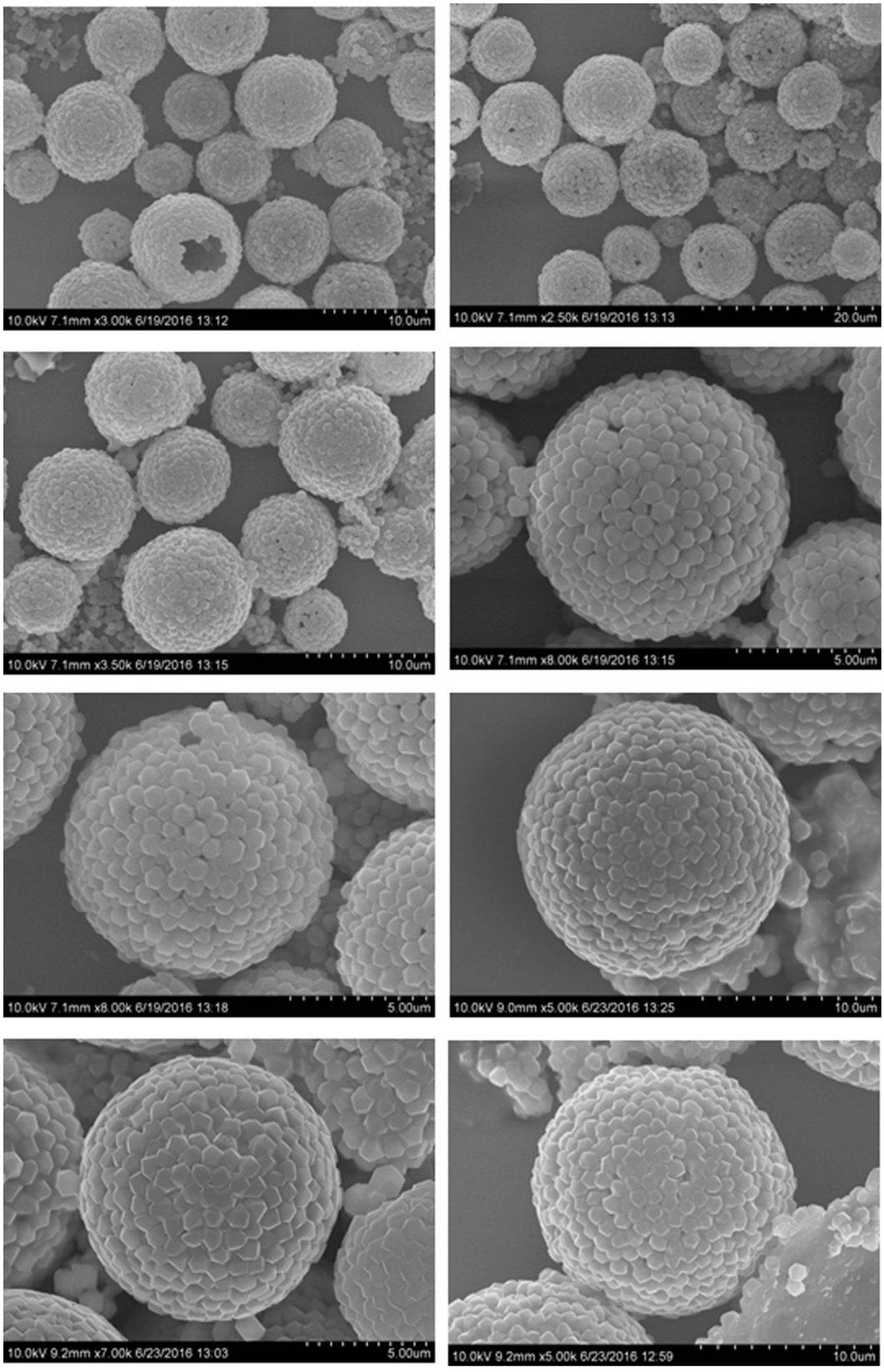
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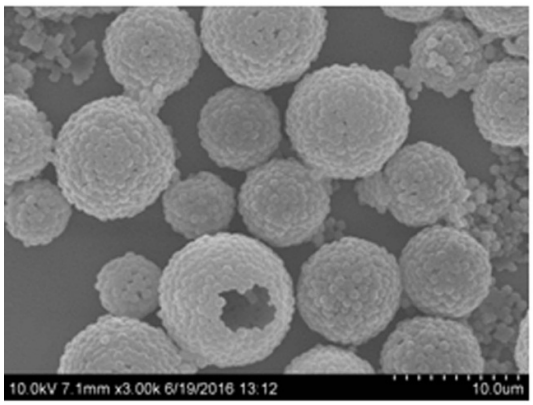
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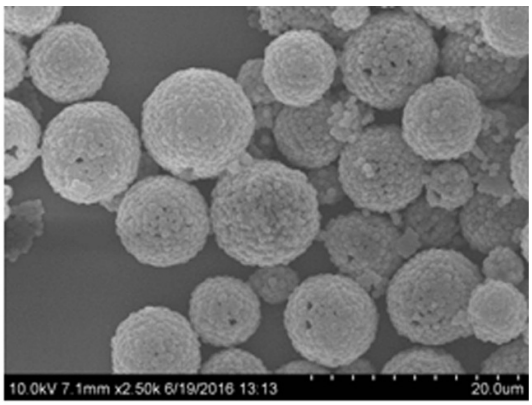
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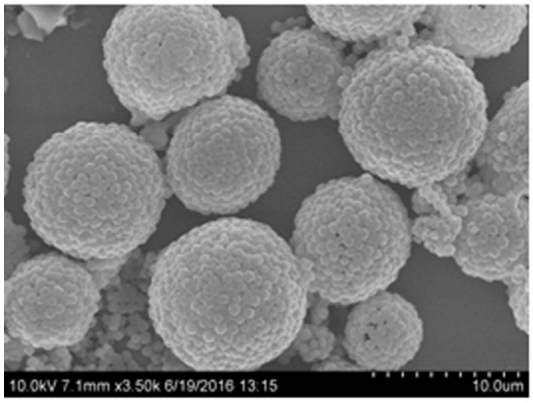
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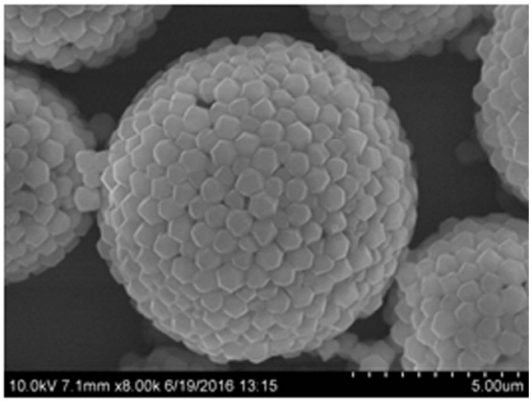
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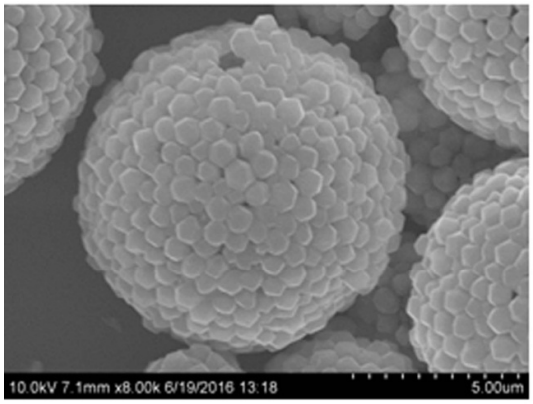
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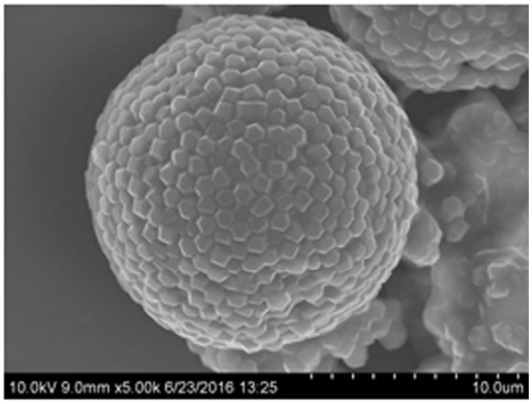
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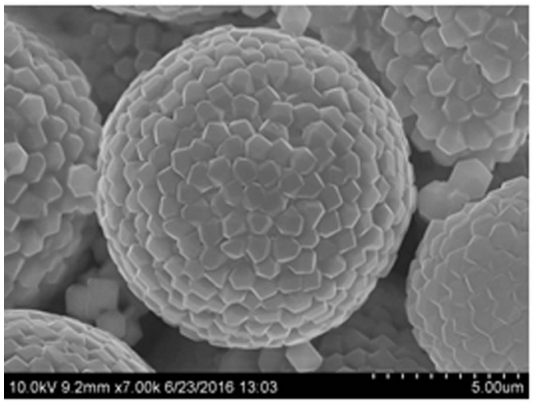
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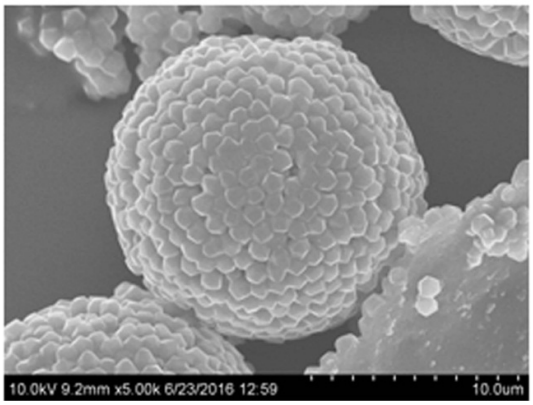
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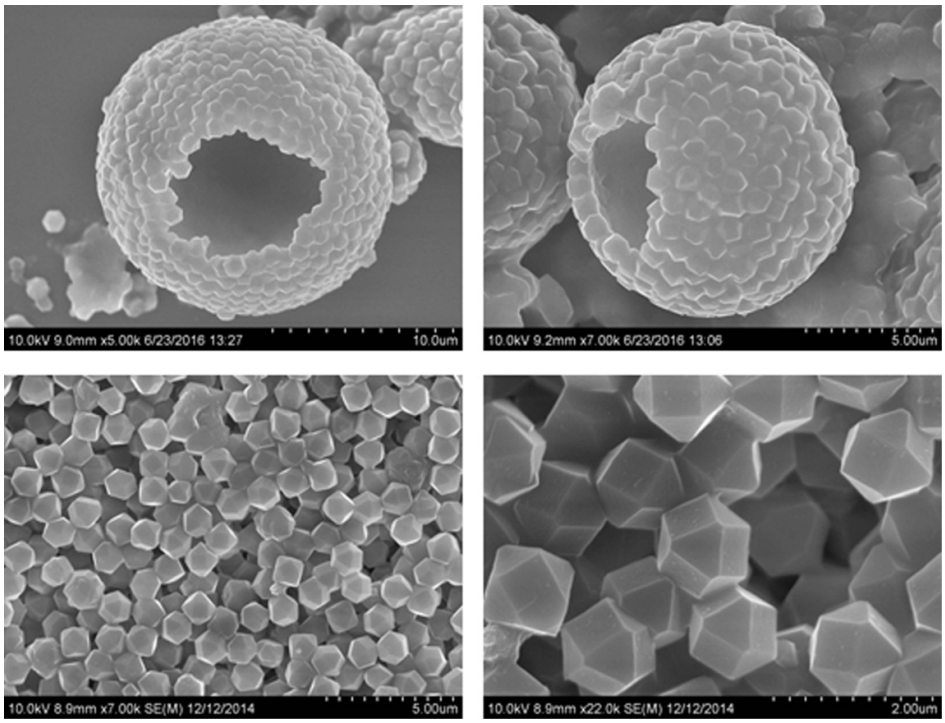

Figure S6. Highly uniform Ga-**soc**-MOF tetrakaidecahedron building blocks and Ga-**soc**-MOF hollow colloidosomes

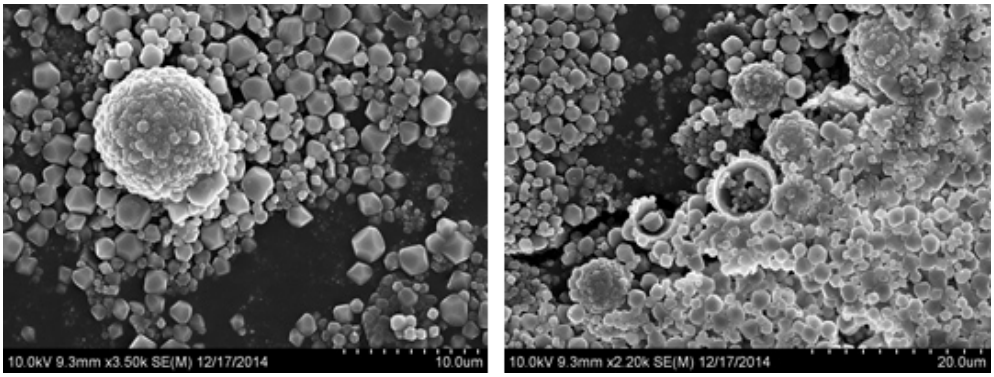

Figure S7. SEM images of Ga-**soc**-MOF colloidosomes synthesized with TMAN.

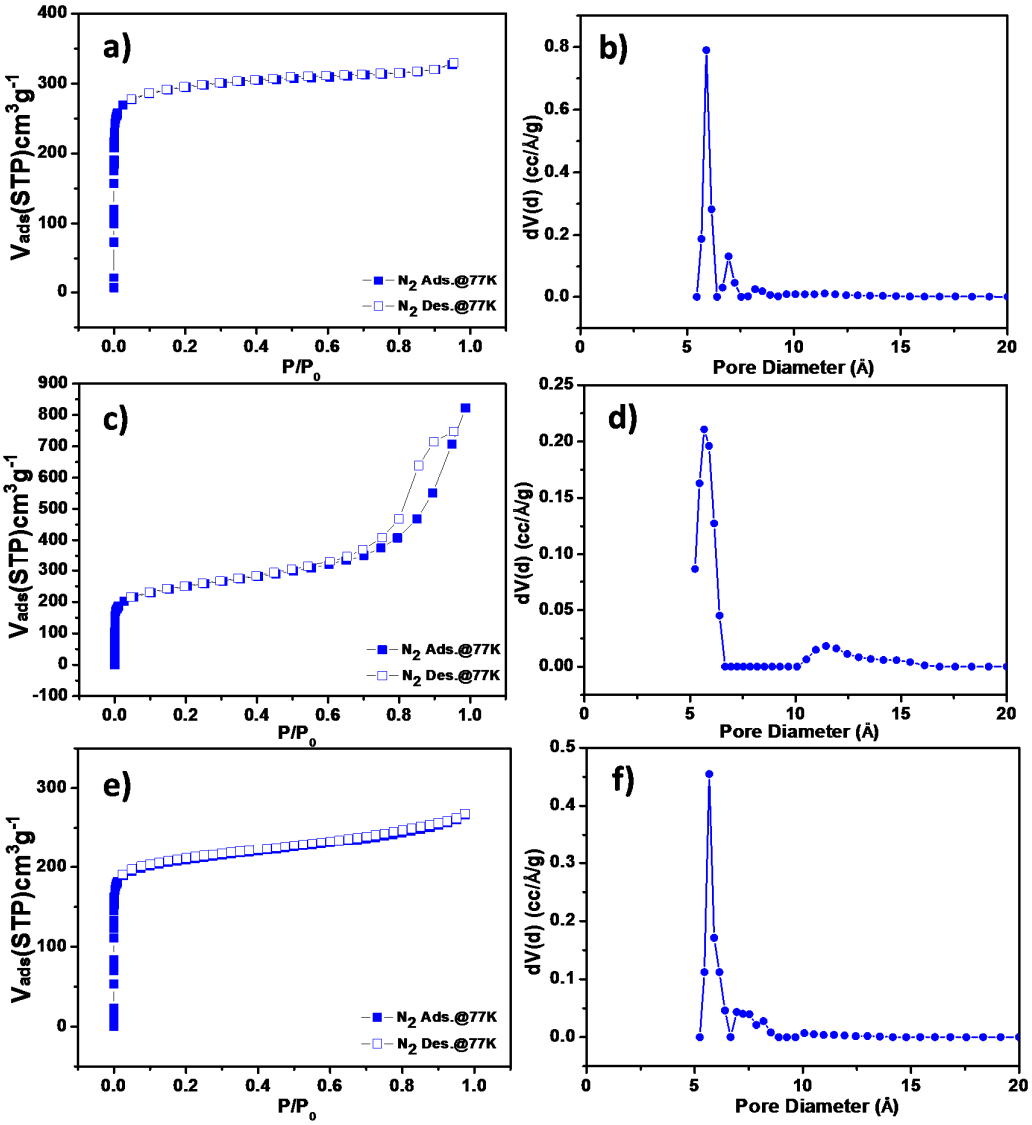

Figure S8. N_2 adsorption−desorption isotherms for Ga-**soc**-MOF hollow cubes, solid cubes and colloidosomes.

Table S1. Sorption data for the Ga-**soc**-MOF materials.

Property	Solid cubes	Hollow cubes	Colloidosomes
BET surface area (m^2g^{-1})	1154	906	813
Langmuir surface area (m^2g^{-1})	1366	1332	1053
Pore volume (cm^3g^{-1})	0.55	1.27	0.45

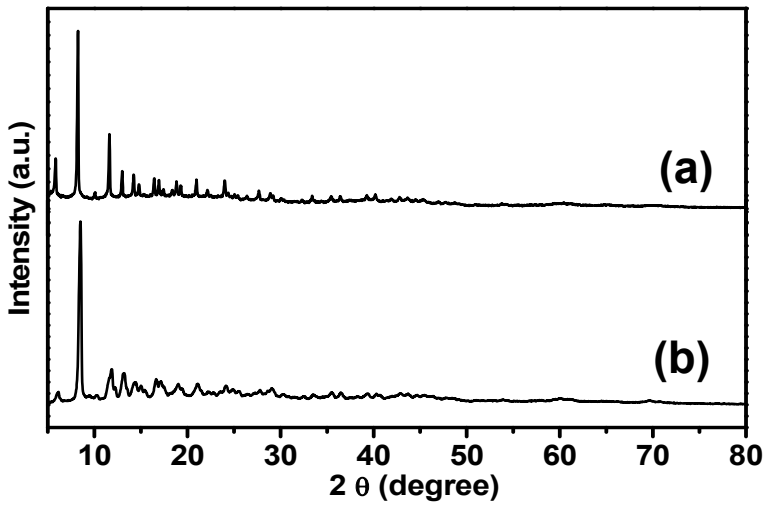

Figure S9. (a) XRD pattern for Ga-**soc**-MOF, and (b) Au@Ga-**soc**-MOF nanocomposite.

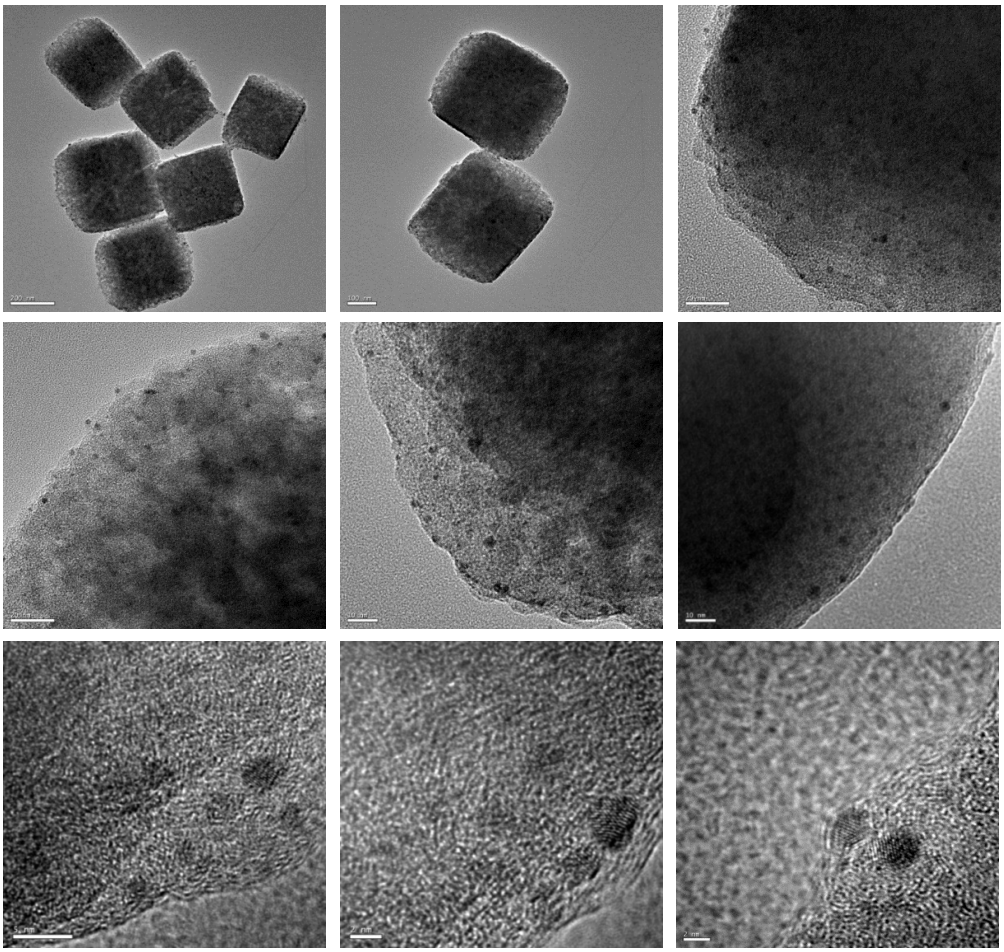

Figure S10. TEM images of as-synthesized Au@Ga-**soc**-MOF nanocomposite with different magnification.