

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

Synthesis of core-shell-shell structured acid-base bifunctional
mesoporous silica nanoreactor (MS-SO₃H@MS@MS-NH₂) and its
application in tandem catalysis

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Section S1. Synthesis of MS-SO₃H@MS@MS-NH₂ with different particle sizes and catalytic active site concentrations via adjusting the preparation parameters.

(a) MS-SO₃H@MS@MS-NH₂ (d = 40-50 nm, -SO₃H content = 0.47 mmol/g, -NH₂ content = 0.51 mmol/g)

First, 3.0 mL of TEOS and 210 μL of MPTMS was added sequentially into the homogeneous solution composed of H₂O (40 mL), ethanol (8 mL), CTAB (1.5 g) and 25 wt% NH₃·H₂O (160 μL) under vigorous stirring at 60 °C. After continually stirring for 1 h, TEOS (200 μL) was added to create an intermediate shell in order to isolate the inner core shell from the outer shell. The resulting suspension was stirred for an additional 1 h. Then a mixture of TEOS (260 μL) and APTMS (240 μL) was added. The following steps, that is, template removal, amino group protection/deprotection and thiol group oxidation were conducted via the same synthesis route of MS-SO₃H@MS@MS-NH₂ in Experimental section 2.2.

The TEM image of the sample was shown in Figure S2a.

(b) MS-SO₃H@MS@MS-NH₂ (d = 70-90 nm, -SO₃H content = 0.47 mmol/g, -NH₂ content = 0.52 mmol/g)

First, 3.0 mL of TEOS and 210 μL of MPTMS was added sequentially into the homogeneous solution composed of H₂O (40 mL), ethanol (8 mL), CTAB (1.5 g) and 25 wt% NH₃·H₂O (160 μL) under vigorous stirring at room temperature. After continually stirring for 1 h, TEOS (200 μL) was added to create an intermediate shell in order to isolate the inner core shell from the outer shell. The resulting suspension was stirred for an additional 1 h. Then a mixture of TEOS (260 μL) and APTMS (240 μL) was added. The following steps, that is, template removal, amino group protection/deprotection and thiol group oxidation were conducted via the same synthesis route of MS-SO₃H@MS@MS-NH₂ in Experimental section 2.2.

The TEM image of the sample was shown in Figure S2b.

(c) MS-SO₃H@MS@MS-NH₂ (d = 80-100 nm, -SO₃H content = 0.28 mmol/g, -NH₂ content = 0.53 mmol/g)

First, 3.0 mL of TEOS and 100 μL of MPTMS was added sequentially into the homogeneous solution composed of H₂O (38 mL), ethanol (10 mL), CTAB (1.5 g) and 25 wt% NH₃·H₂O (160 μL) under vigorous stirring at room temperature. After continually stirring for 1 h, TEOS (200 μL) was added to create an intermediate shell in order to isolate the inner core shell from the outer shell. The resulting suspension was stirred for an additional 1 h. Then a mixture of TEOS (250 μL) and APTMS (250 μL) was added. The following steps, that is, template removal, amino group protection/deprotection and thiol group oxidation were conducted via the same synthesis route of MS-SO₃H@MS@MS-NH₂ in Experimental section 2.2.

The TEM image of the sample was shown in Figure S2c.

(d) MS-SO₃H@MS@MS-NH₂ (d = 250-300 nm, -SO₃H content = 0.60 mmol/g, -NH₂ content = 0.93 mmol/g)

First, 2.2 mL of TEOS and 220 μL of MPTMS was added sequentially into the homogeneous solution composed of H₂O (36 mL), ethanol (12 mL), CTAB (1.5 g) and 25 wt% NH₃·H₂O (160 μL) under vigorous stirring at 60 °C. After continually stirring for 1 h, TEOS (100 μL) was added to create an intermediate shell in order to isolate the inner core shell from the outer shell. The resulting suspension was stirred for an additional 1 h. Then a mixture of TEOS (500 μL) and APTMS (400 μL) was added. The following steps, that is, template removal, amino group protection/deprotection and thiol group oxidation were conducted via the same synthesis route of

MS-SO₃H@MS@MS-NH₂ in Experimental section 2.2.
The TEM image of the sample was shown in Figure S2d.

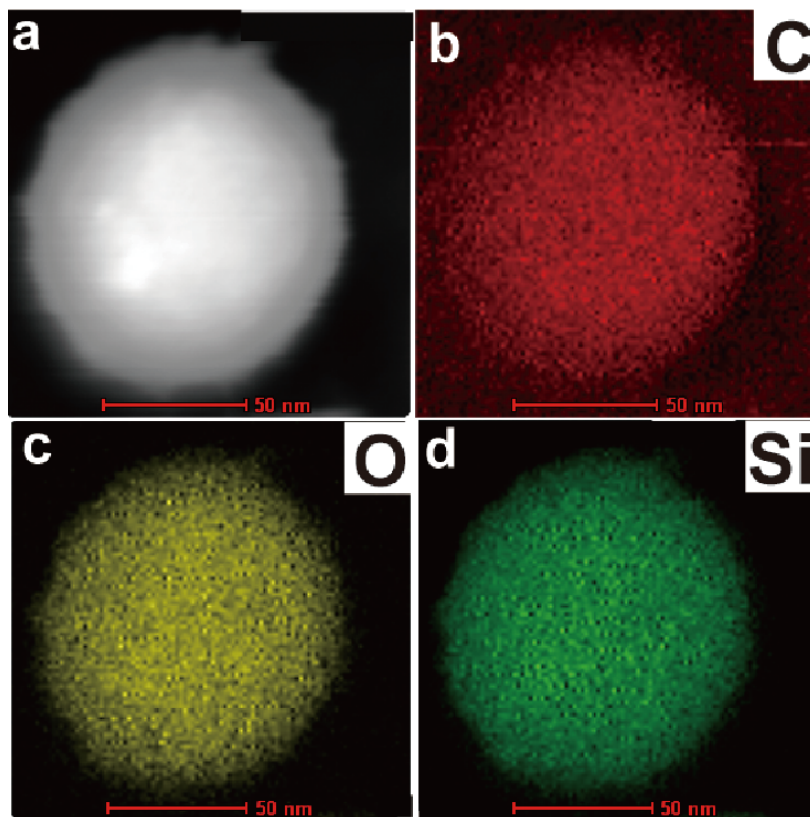


Figure S1. (a) STEM image and (b) carbon, (c) oxygen, (d) silicon EDX elemental mappings of core-shell-shell structured MS-SO₃H@MS@MS-NH₂.

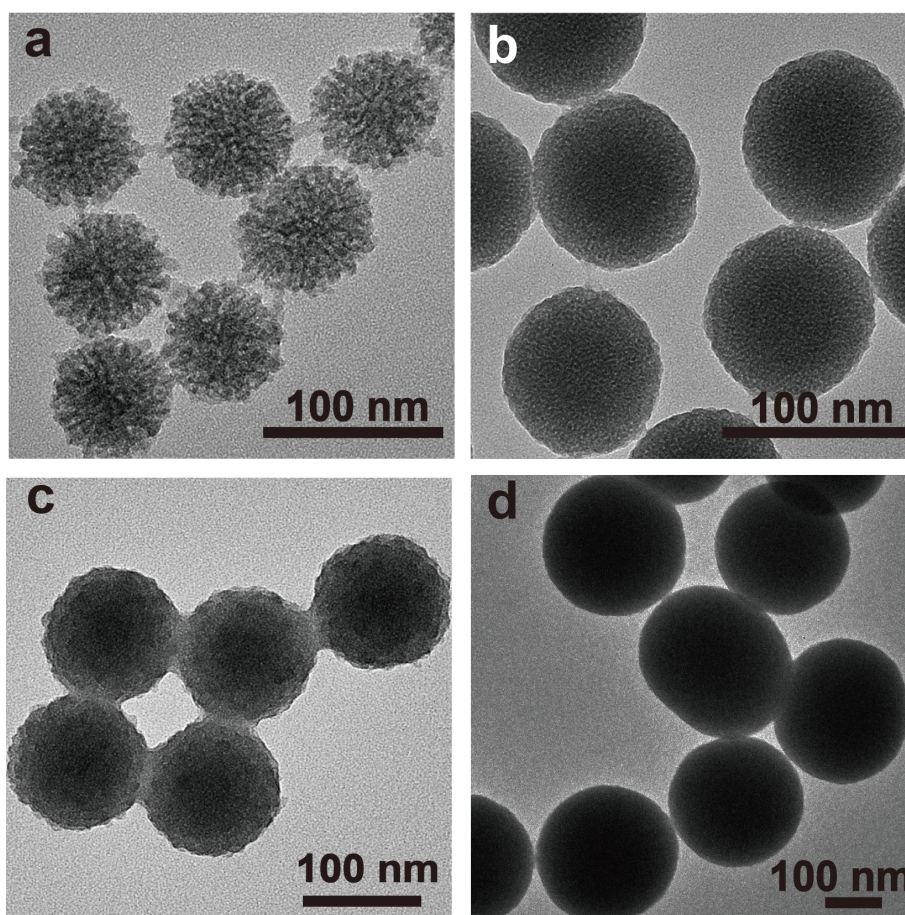


Figure S2. TEM images of MS-SO₃H@MS@MS-NH₂ with different particle sizes and different densities of acid/basic reactive sites via adjusting the ratios of different precursors, the solvent ratio and temperature during the synthesis.

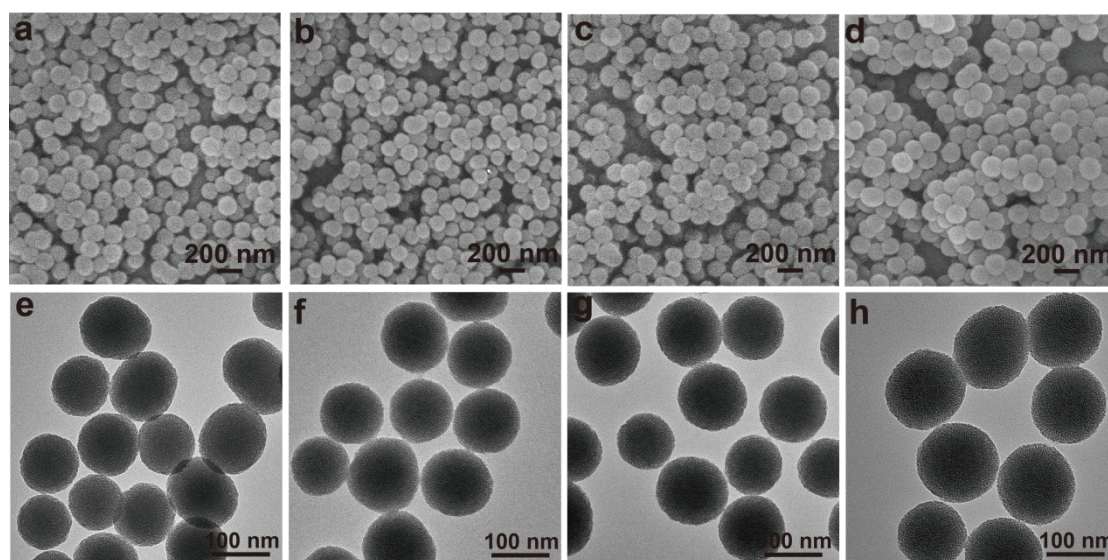


Figure S3. SEM images of (a) MS-SO₃H@MS, (b) MS@MS-NH₂, (c) MS-SO₃H@MS-NH₂ and (d) MS-SO₃H-NH₂. TEM images of (e) MS-SO₃H@MS, (f) MS@MS-NH₂, (g) MS-SO₃H@MS-NH₂ and (h) MS-SO₃H-NH₂.

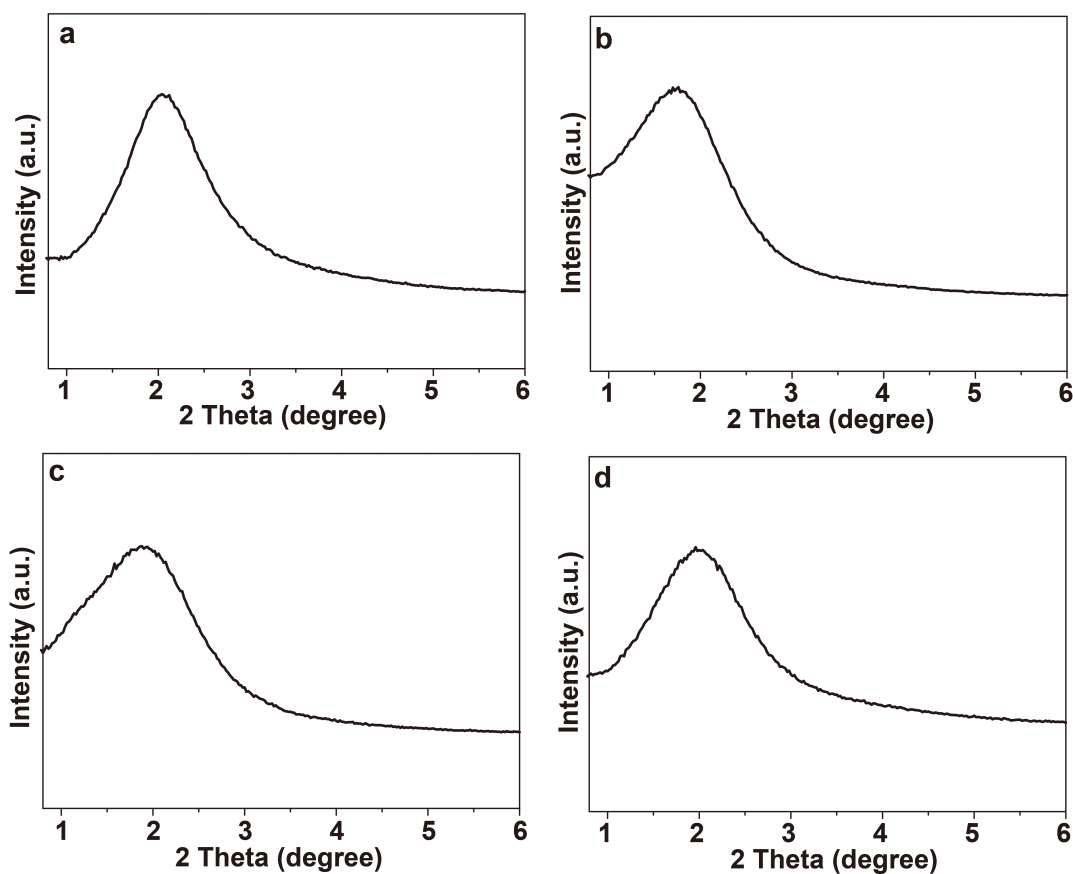


Figure S4. Small-angle XRD patterns of (a) MS-SO₃H@MS, (b) MS@MS-NH₂, (c) MS-SO₃H@MS-NH₂ and (d) MS-SO₃H-NH₂.

Table S1. Physicochemical parameters of the control samples from N₂ adsorption-desorption measurement and elemental analysis.

Sample	BET surface area (m ² /g)	Pore volume (cm ³ /g)	NLDFT pore size (nm)	-SO ₃ H content (mmol/g)	-NH ₂ content (mmol/g)
MS-SO ₃ H@MS	1088	0.92	3.54	0.50	-
MS@MS-NH ₂	886	0.60	3.18	-	0.81
MS-SO ₃ H@MS-NH ₂	946	0.61	3.18	0.52	0.79
MS-SO ₃ H-NH ₂	931	0.63	3.18	0.50	0.79

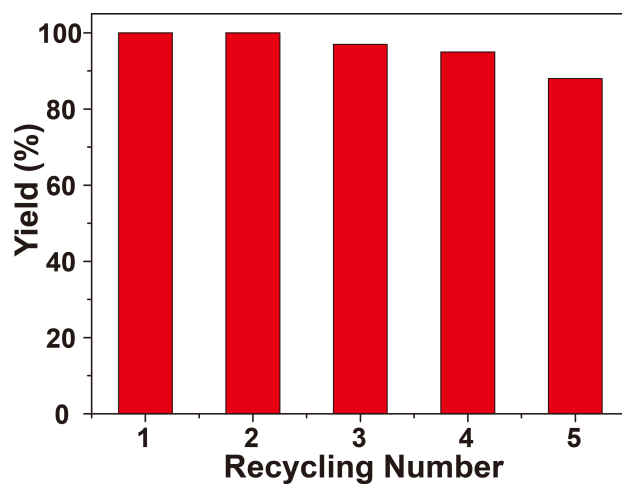


Figure S5. Recycling test of MS-SO₃H@MS@MS-NH₂ in the reaction between benzaldehyde dimethyl acetal and ethyl cyanoacetate.

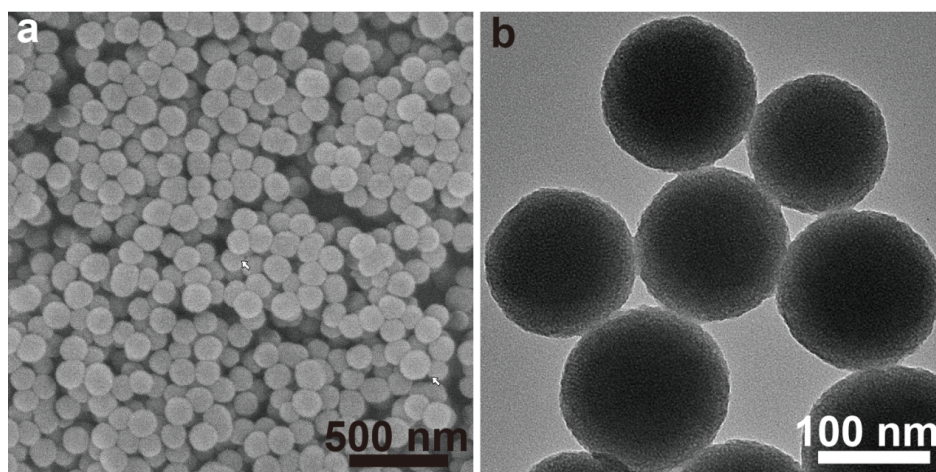


Figure S6. TEM image of MS-SO₃H@MS@MS-NH₂ as bifunctional catalyst after being used repetitively for 5 times.

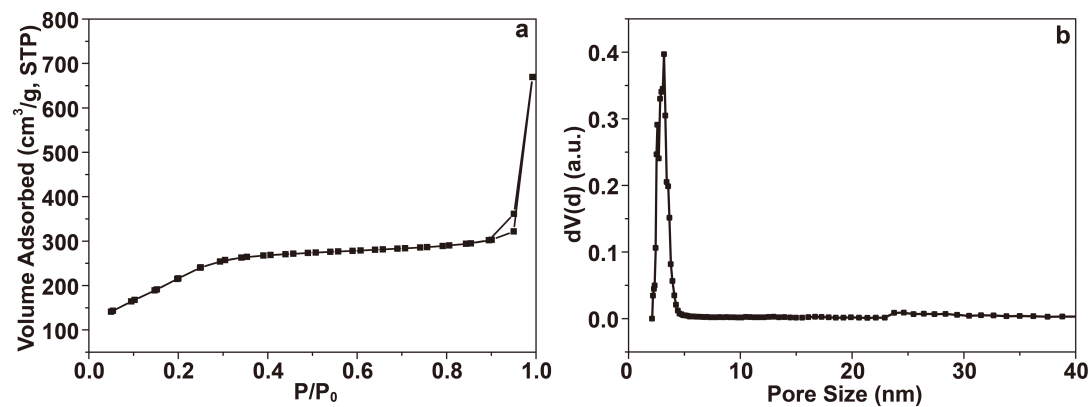


Figure S7. (a) N₂ adsorption-desorption isotherm and (b) NLDFT pore size distribution of MS-SO₃H@MS@MS-NH₂ after being used repetitively for 5 times. (BET surface area: 833.5 m²/g; Pore volume: 0.52 cm³/g; NLDFT pore size: 3.18 nm).