Electronic Supplementary Information (ESI)

Synthesis of Mn_3O_4 Octahedrons and Other Manganese-based Nanostructures through a Simple and Green Route

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Experimental:

Synthesis of Manganese-based Nanostructures: In a typical synthesis, 0.1 g of $KMnO_4$ and 20 mL of 10 g/L CMC were mixed under magnetic stirring. After 5 min stirring, the mixture was transferred and sealed in a 50 mL Teflon-lined autoclave, heated at 140 °C for 6 h, and finally cooled to room temperature. The precipitate was collected by centrifugation (4 000 rpm, 4 min), washed alternately with deionized water and ethanol four times, and dried in air at ambient condition. The details about the experimental conditions for typical samples are listed in Table SI1 and SI2.

Characterizations: Powder X-ray diffraction (XRD) patterns were collected using a Shimadzu XRD-6000 diffractometer with Cu K_α radiation (λ = 1.5418 Å). Scanning electron microscopy (SEM) characterization was performed on a JEOL XL30-ESEM scanning electron microscope. Transmission electron microscopy (TEM), High-resolution TEM (HRTEM) images and the corresponding selected area electron diffraction (SAED) pattern were captured on the JEOL JEM-2100 instrument microscopy at an acceleration voltage of 200 kV.

Electrochemical Measurements: The electrochemical measurements were all carried out on a CHI660B electrochemical work station (CHI co., US) with a conventional three-electrode electrochemical cell. A GC electrode modified with Mn_3O_4 samples was used as working electrode, a saturated calomel electrode as the reference electrode and a platinum plate as auxiliary electrode. All the solutions were purged with nitrogen for 30 min in order to remove the oxygen before electrochemical experiments, and during the whole experimental process the electrochemical cell was kept under nitrogen atmosphere.

The GC electrode, with 3mm diameter was polished with 0.05 μm alumina suspension on a

chamois, further rinsed in absolute ethanol and double distilled water under ultrasonic environment for 2-3 min successively and then dried at room temperature. After dropping the mixture of Mn_3O_4 (2 mg/mL), Cyt c (6 mg/mL) and Nafion onto the surface of the cleaned GC electrode with an injector, the Cyt c/Mn_3O_4/GC electrode was finally obtained after the modified electrode was dried at room temperature. The Mn_3O_4/GC modified electrode was prepared with the same method for subsequent comparison.

Table SI1 The experimental conditions for the different manganese-based nanostructures

Product	$KMnO_4$ (g)	10 g/L CMC solution (mL)	Temperature (° C)	Time (h)
Mn_3O_4 octahedrons	0.1	20.0	140	6
MnOOH nanorods	0.05	2.0	140	16
MnO_2 nanowires	0.1	1.0	200	48
Aggregated $MnCO_3$ nanoparticles in the form of spindles	0.05	10.0	200	12

Table SI2 The detailed experimental conditions for the manganese-based nanostructures

Product	KMnO4 (g)	10 g/L CMC solution (ml)	Temperature (°C)	Time (h)
Mn_3O_4 + MnOOH	0.1	5	140	6
Mn_3O_4 + MnOOH	0.1	10	140	6
Mn_3O_4	0.1	20.0	140	2
Mn_3O_4	0.1	20.0	140	4
Mn_3O_4	0.1	20.0	140	6
Mn_3O_4	0.1	20 (20 g/L)	140	6
Mn_3O_4 + MnOOH	0.1	20.0	120	6
Mn_3O_4 + $MnCO_3$	0.1	20.0	160	6
Mn_3O_4 + $MnCO_3$	0.1	20.0	200	6

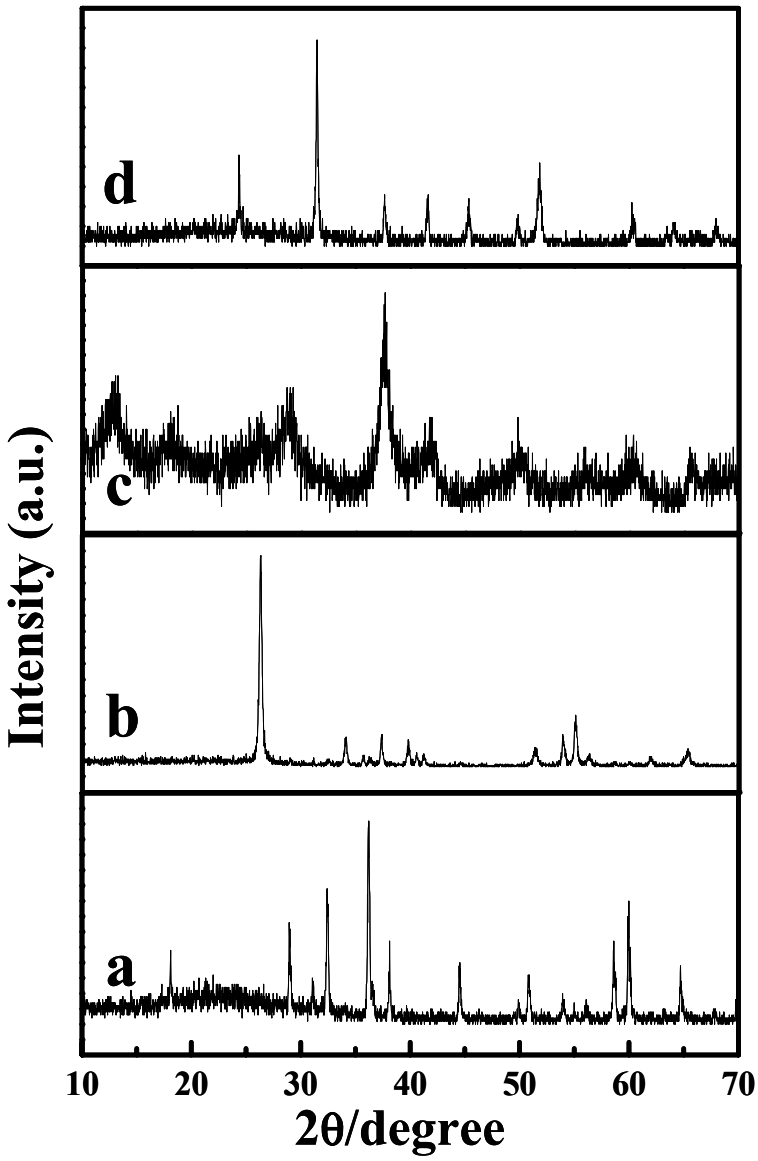

Fig. SI1 XRD patterns of the obtained manganese-based nanostructures: (a) Mn_3O_4 octahedrons; (b) MnOOH nanorods; (c) MnO_2 nanowires; (d) Aggregated $MnCO_3$ nanoparticles in the form of spindles.

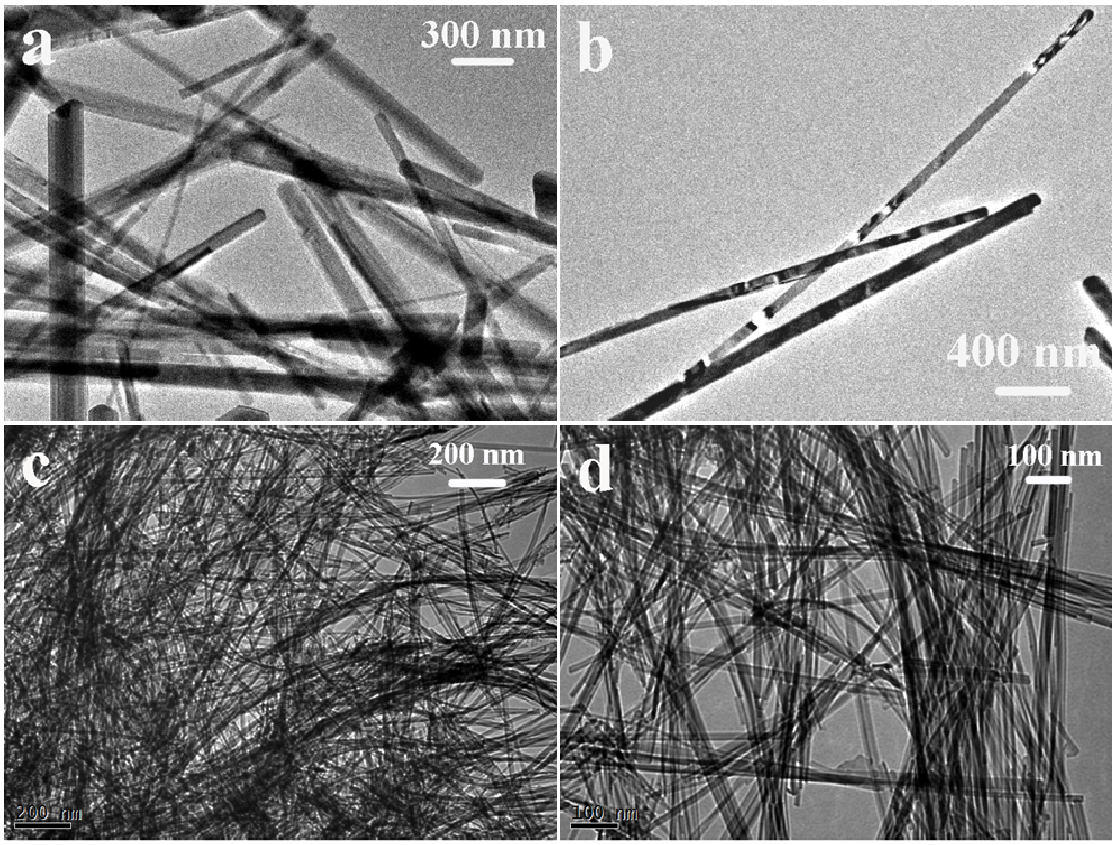

Fig. SI2 TEM images of (a, b) MnOOH nanorods and (c, d) MnO_2 nanowires

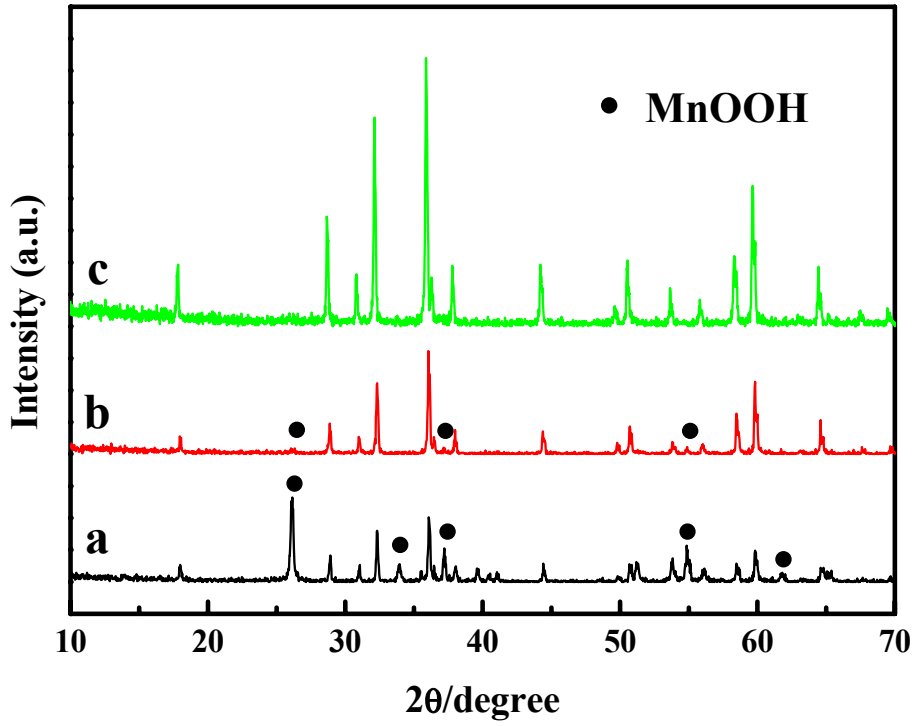

Fig. SI3 XRD patterns of the products prepared with 0.1 g of $KMnO_4$ and (a) 5 mL of 10 g/L CMC solution; (b) 10 mL of 10 g/L CMC solution and (c) 20 mL of 20 g/L CMC solution under hydrothermal conditions at 140 °C for 6 h. The diffraction peaks signed with "•" can be indexed as MnOOH and the other diffraction peaks can be indexed as Mn_3O_4.

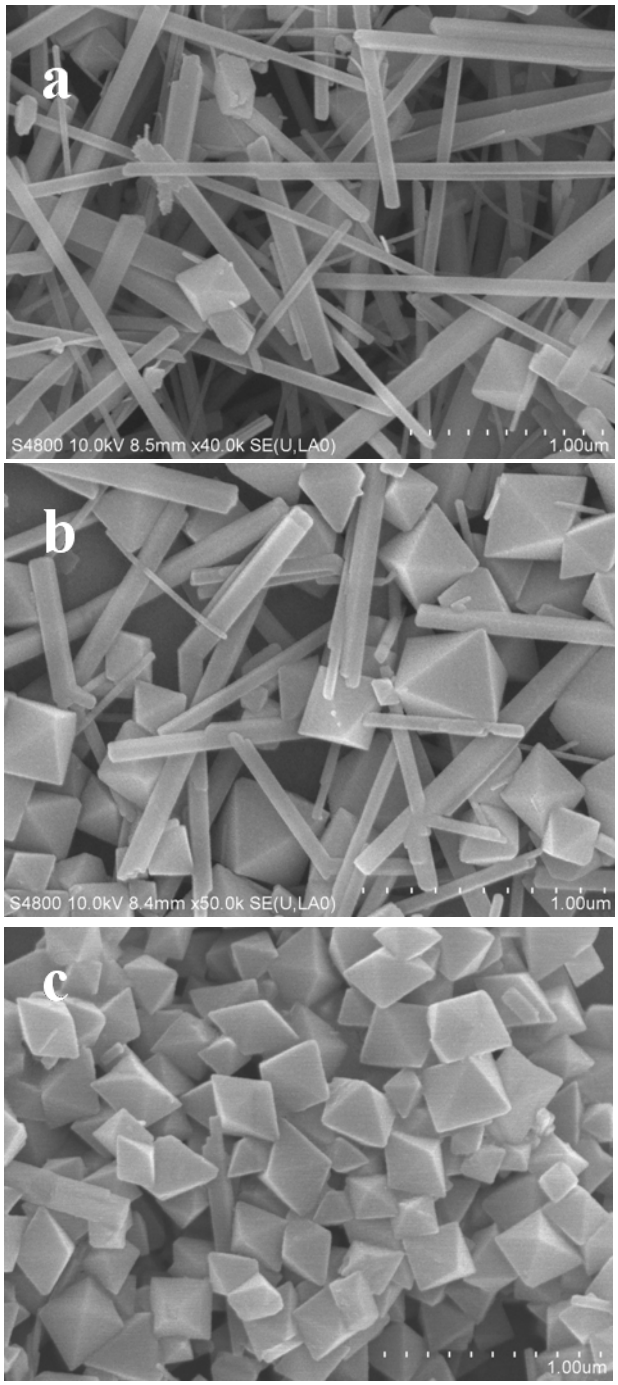

Fig. SI4 SEM images of the products prepared with 0.1 g of $KMnO_4$ and (a) 5 mL of 10 g/L CMC solution; (b) 10 mL of 10 g/L CMC solution and (c) 20 mL of 20 g/L CMC solution under hydrothermal conditions at 140 °C for 6 h.

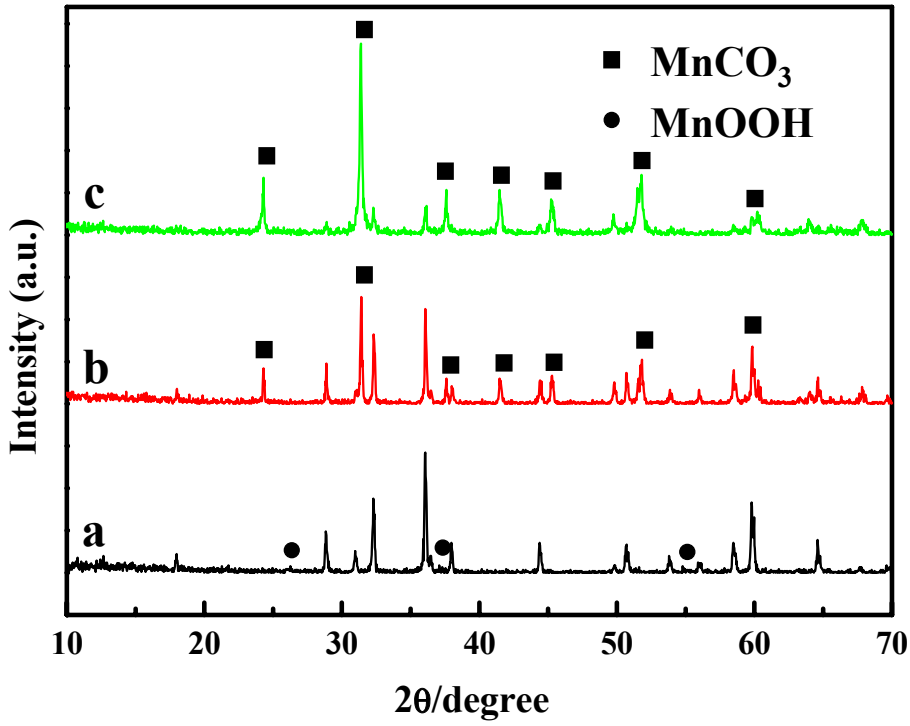

Fig. SI5 XRD patterns of the products prepared with 0.1 g of $KMnO_4$ and 20 mL of 10 g/L CMC solution under hydrothermal conditions for 6 h at (a) 120 °C, (b) 160 °C and (c) 200 °C. The diffraction peaks signed with "•" can be indexed as MnOOH, the diffraction peaks signed with "▪" can be indexed as $MnCO_3$ and the other diffraction peaks can be indexed as Mn_3O_4.

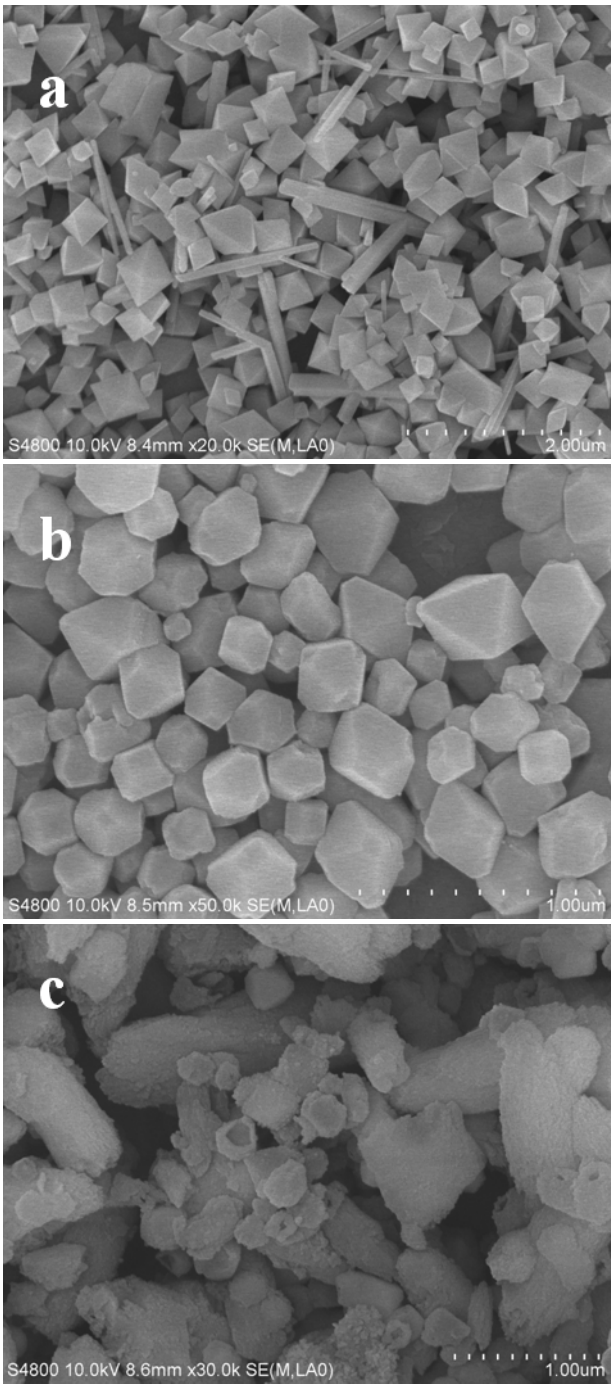

Fig. SI6 SEM images of the products prepared with 0.1 g of $KMnO_4$ and 20 mL of 10 g/L CMC solution under hydrothermal conditions for 6 h at (a) 120 °C, (b) 160 °C and (c) 200 °C.

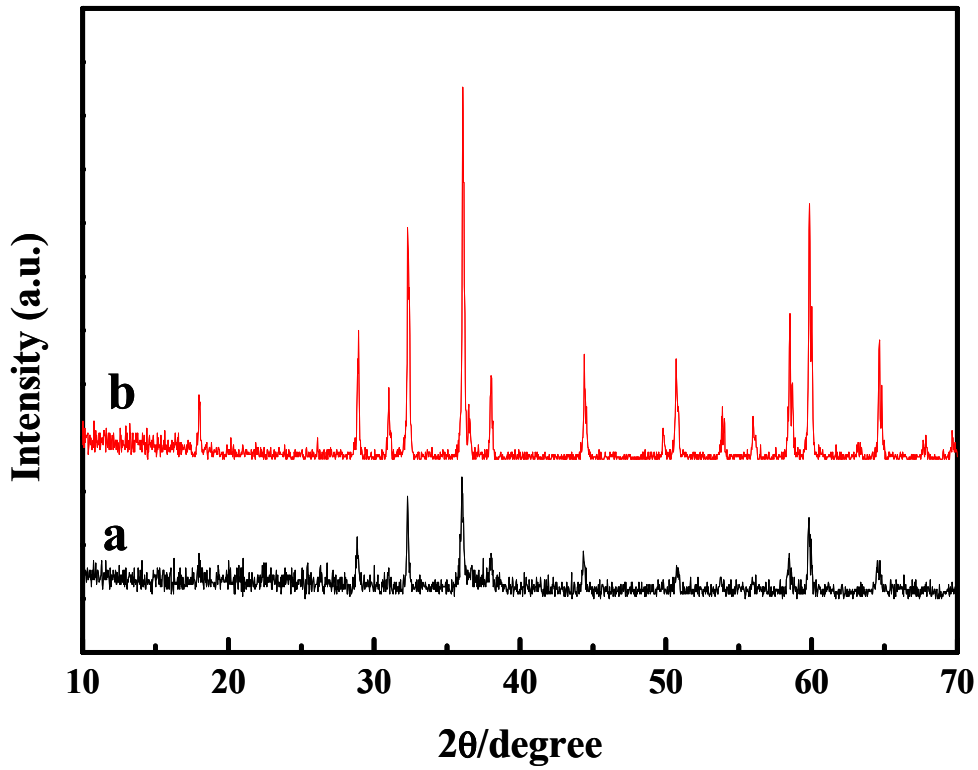

Fig. SI7 XRD patterns of the products prepared with 0.1 g of $KMnO_4$ and 20 mL of 10 g/L CMC solution under hydrothermal conditions at 140 °C for (a) 2 h and (b) 4 h.

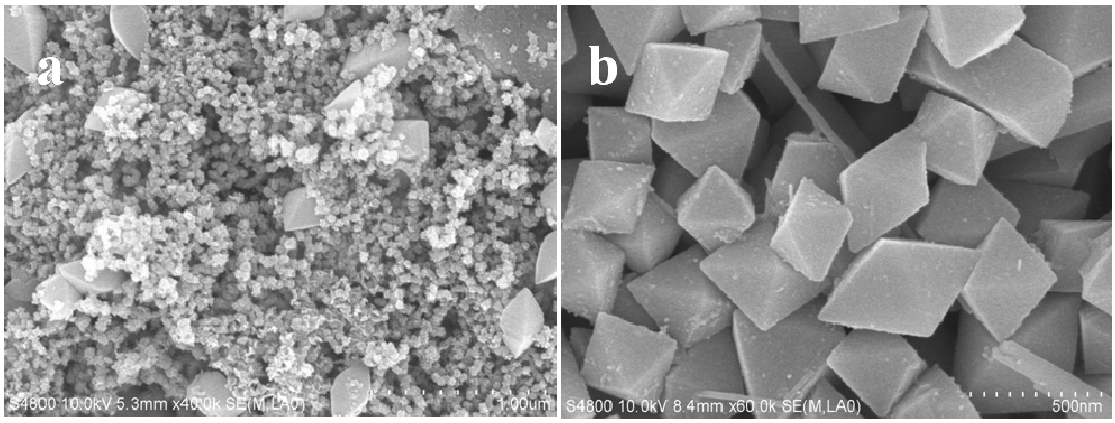

Fig. SI8 SEM images of the products prepared with 0.1 g of $KMnO_4$ and 20 mL of 10 g/L CMC solution under hydrothermal conditions at 140 °C for (a) 2 h and (b) 4 h.

Supplementary Material (ESI) for CrystEngComm