Supporting Information

Controllable Hydrothermal Synthesis of Manganese Dioxide Nanostructures: Shape Evolution, Growth Mechanism and Electrochemical Properties

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Experimental Section

***Synthesis*:** For investigation of the effect of K^+ ions, different amount KCl was added the reaction system. In a typical synthesis procedure: 0.1 mmol of $KMnO_4$ was put into 15 mL of deionized water under stirring to form a homogenous solution. Subsequently, a certain amount of KCl added into the total solution, and then the solytion was transferred into a stainless-steel autoclave with a capacity of 20 mL, sealed and heated at the enactment temperature for 24 h. When the reaction was completed, the autoclave was cooled to room temperature naturally. The resultant product was collected and washed with deionized water, and anhydrous ethanol for several times until the solution was neutral. The final product was dried in a vacuum at 80 °C for 3 h. The synthetic conditions for preparing some typical samples are summarized in Table S1.

Table S1. Summary of the Experimental Parameters and Their Corresponding Morphologies of MnO_2 Obtained under Different Conditions.

Sample number	$KMnO_4$ [mmol]	KCl [mmol]	T [ºC]	Phase	Morphology
S'-1	0.1	0.1	180	α	nanowire (main)
S'-2	0.1	0.9	180	α	nanowire
S'-3	0.1	1.0	180	δ	nanowall (main)
S'-4	0.1	1.9	180	δ	nanowall

Results and Discussions

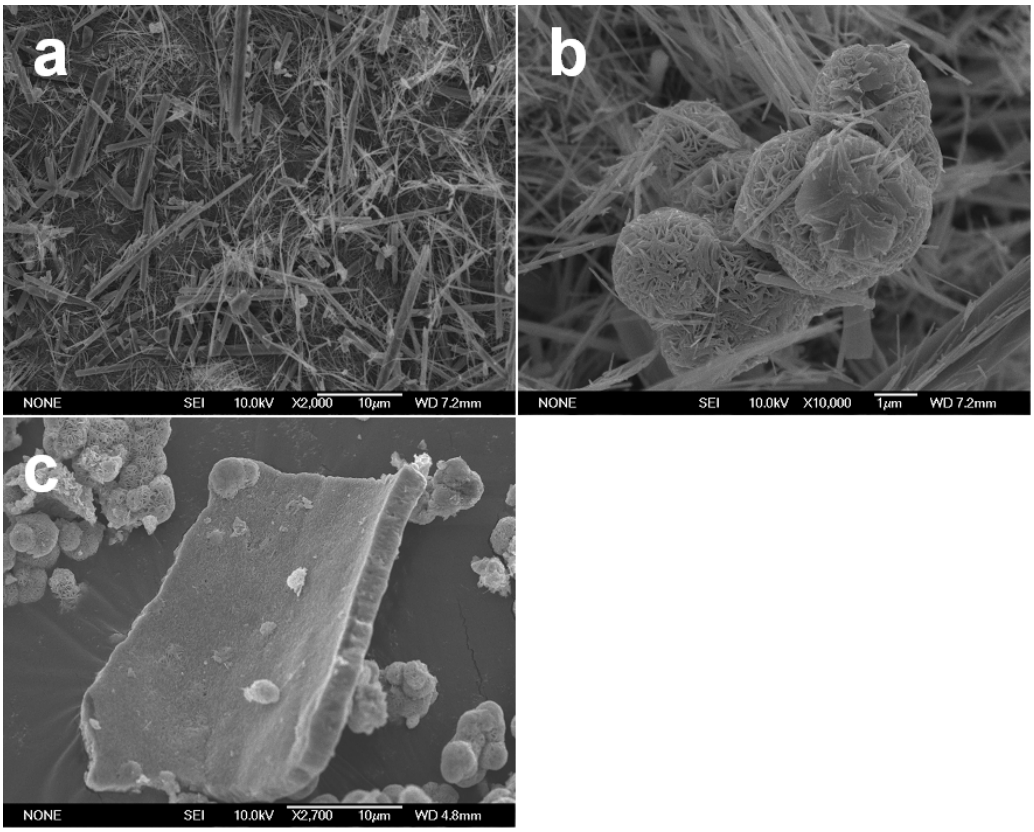

Figure S1. a), b) and c) SEM images of S-2, S-5 and S-7, respectively.

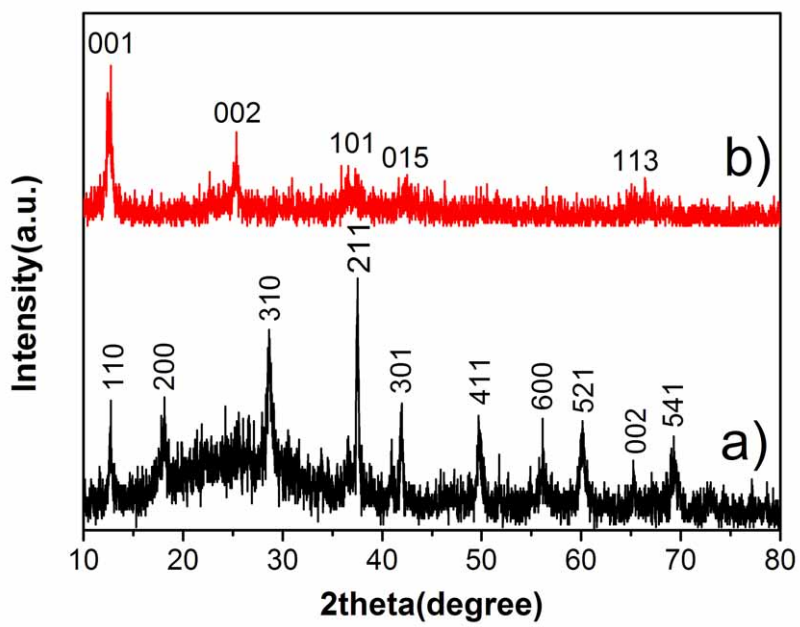

Figure S2. XRD patterns of as-prepared MnO_2: (a) S-2, and (b) S-5, respectively.

It was unexpected that XRD did not detect the composition of the mixture, S-2 and S-5, which may be attributed to the sensitivity of XRD is not so high. It is well known that the material with content less than 5% cannot be detected by this method. So the β-MnO_2 in S-2 and α-MnO_2 in S-5 were undetectable by XRD due to the low content and poor crystallinity. However, it is clearly can be seen the product consist of different types of MnO_2 investigated by SEM technique (Figure S1). In addition, it can estimate that the content of less phases do not exceed 5%.

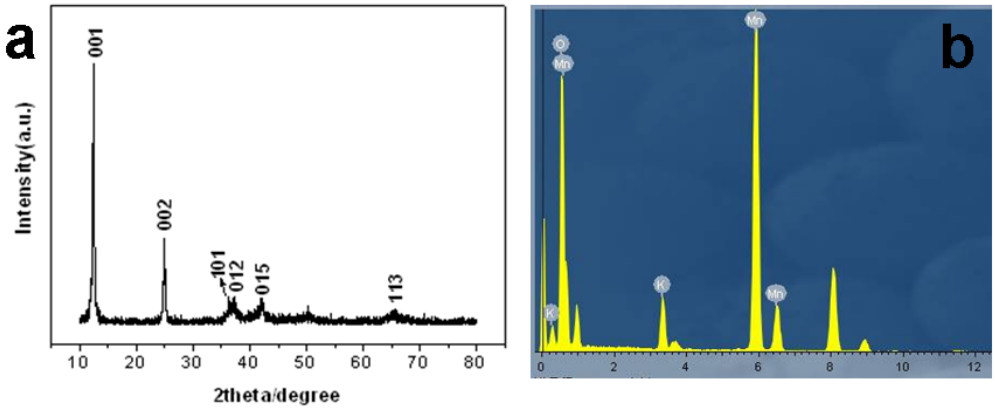

Figure S3. a) XRD pattern and b) EDS pattern of S-8, δ-MnO_2 nanowall.

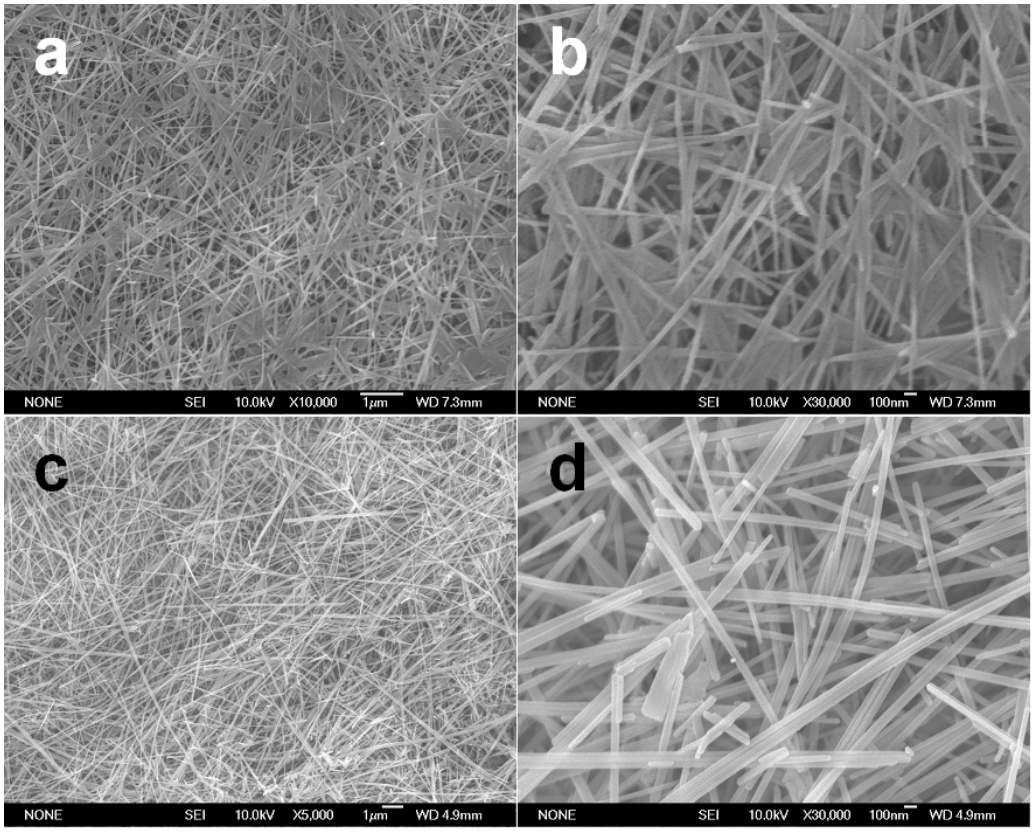

Figure S4. a), c) Low- and b), d) high-magnification SEM images of S-14 and S-15, α-MnO_2 nanowires, respectively.

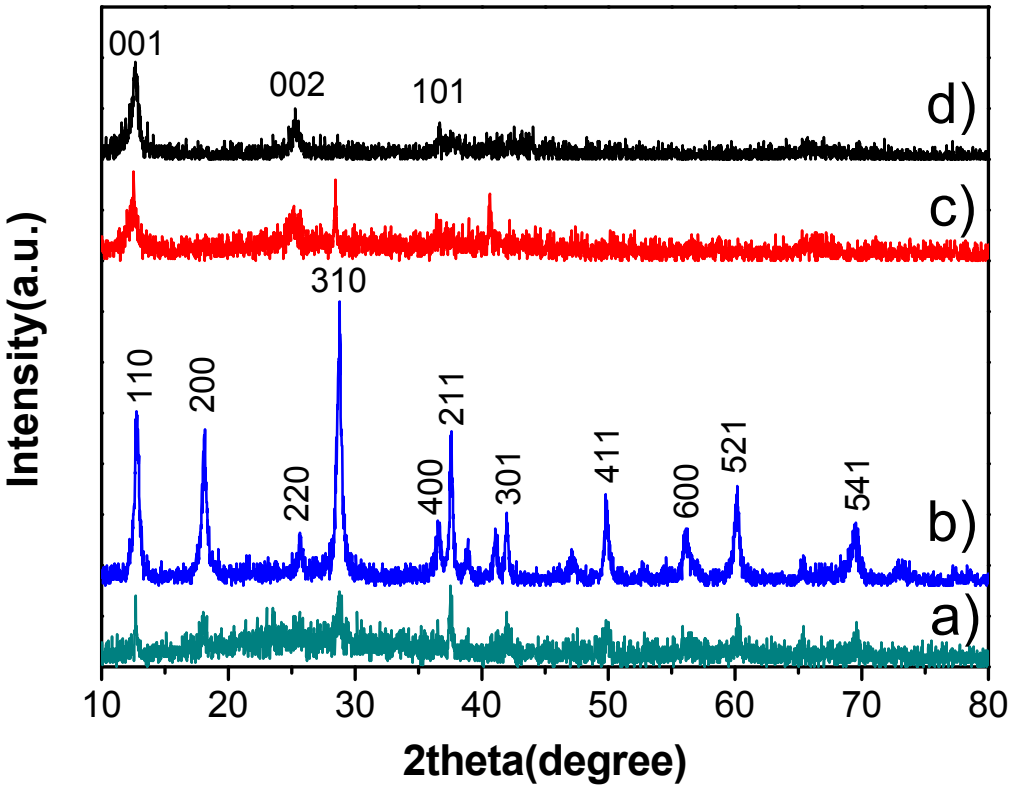

Figure S5. XRD patterns of as-prepared MnO_2 with different amount of KCl: (a) S'-1, 0.1 mmol; (b) S'-2, 0.9 mmol; (c) S'-3, 1.0 mmol, and (d) S'-4, 1.9 mmol, respectively.

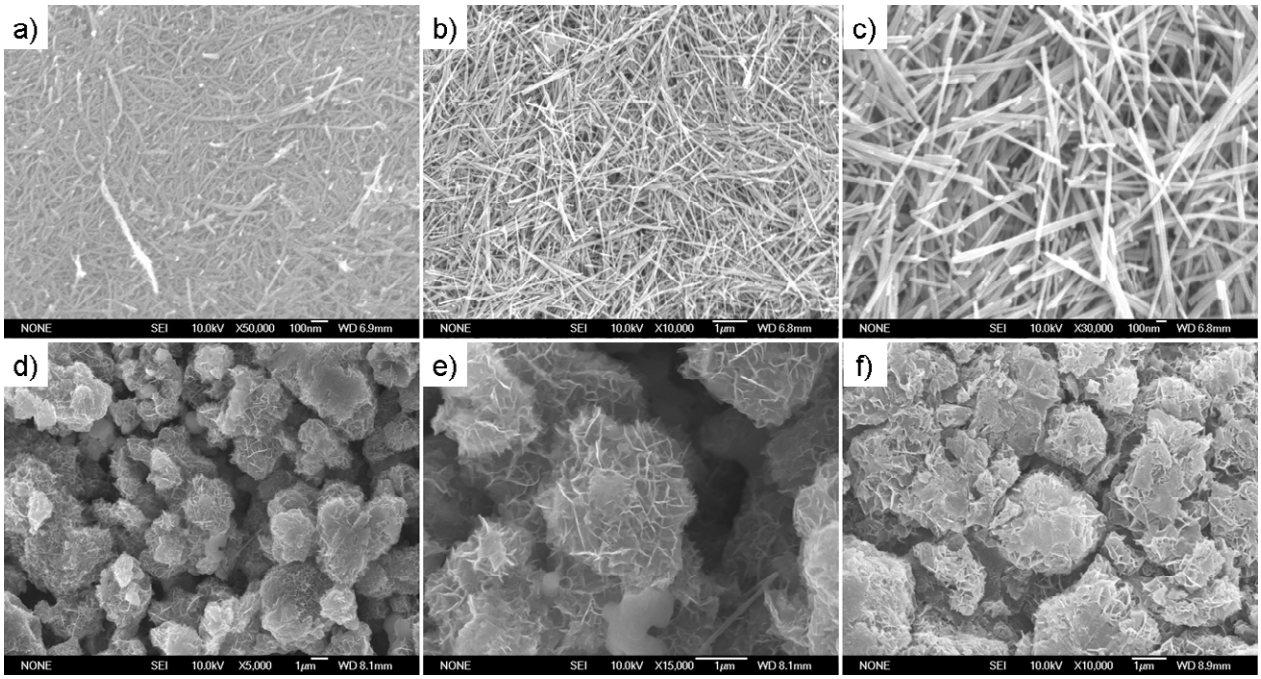

Figure S6. SEM images of as-prepared MnO_2 with different amount of KCl: (a) S'-1, (b and c) S'-2, (d and e) S'-3, and (f) S'-4, respectively.

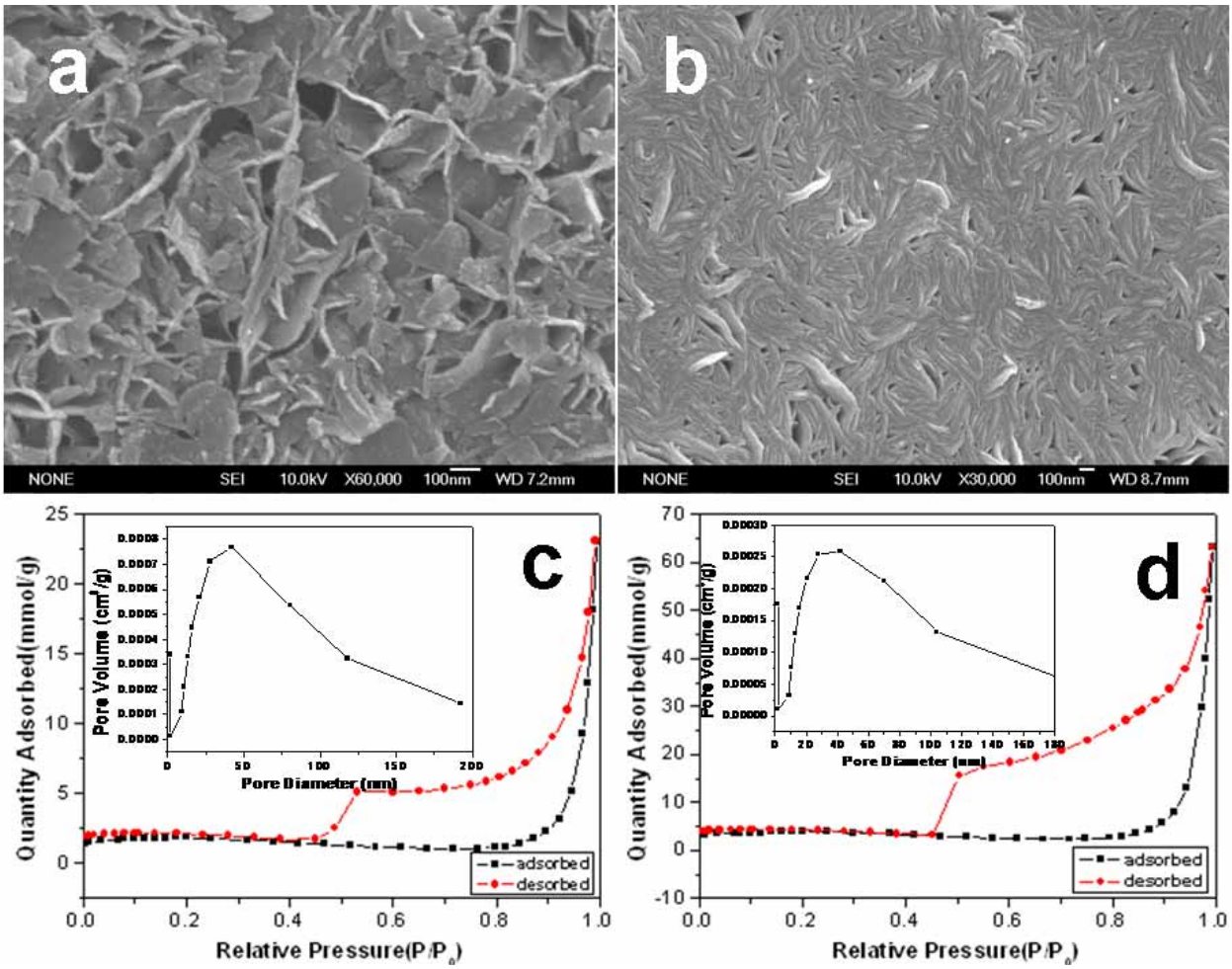

Figure S7. a) and b) SEM images of S-9, δ-MnO_2 nanosheets and S-13, δ-MnO_2 nanowall, respectively; c) and d) N_2 adsorption-desorption isothermal and pore-size distribution curves (inset) of S-9, δ-MnO_2 nanosheet and S-13, δ-MnO_2 nanowall, respectively.

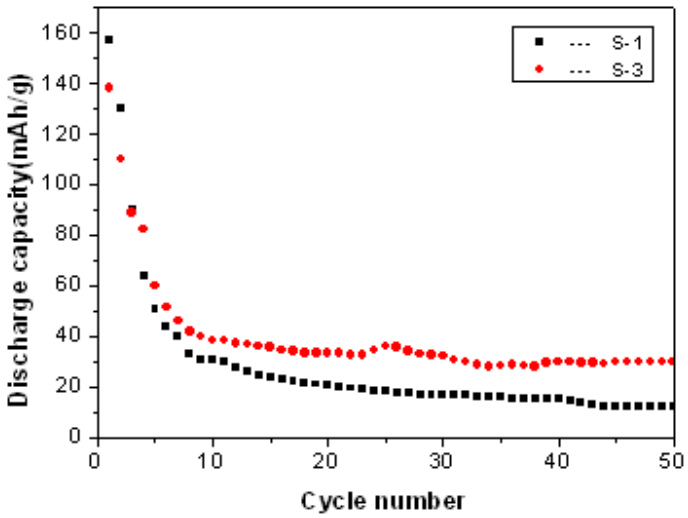

Figure S8. Discharge cycling performance of the electrode made from the as-prepared S-1, β-MnO_2 nanorods and S-3, α-MnO_2 nanowires in the voltage range of 1.5–4.0 V vs. Li/Li^+ at a current density of 50 mA/g. As can be clearly seen, the discharge capacity and cycling stability of as-prepared β-MnO_2 nanorods and α-MnO_2 nanowires are very poor. In detail, the S-1 and S-3 had initial discharge capacities of 138 and 159 mAh/g, respectively. After 50 cycles, the discharge capacities were 17 and 36 mAh/g, respectively. These results may be attributed to the little specific surface area of as-prepared β-MnO_2 nanorods and α-MnO_2 nanowires.