# Electronic Supplementary Information

## Modified Redox Synthesis and Electrochemical Properties of Potassium Manganese Oxide Nanowires

Qiang Wu,*[,a] Haisheng Tao,[a,b] Ke Xie,[a] Ning Liu,[a] Leshu Yu,[a] and Zheng Hu[a]

[a] Key Laboratory of Mesoscopic Chemistry of MOE, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, China

[b] Anhui Key Laboratory of Chemo-Biosensing, College of Chemistry and Materials Science, Anhui Normal University, Wuhu 241000,China

* To whom the correspondence should be addressed. E-mail: wqchem@nju.edu.cn.

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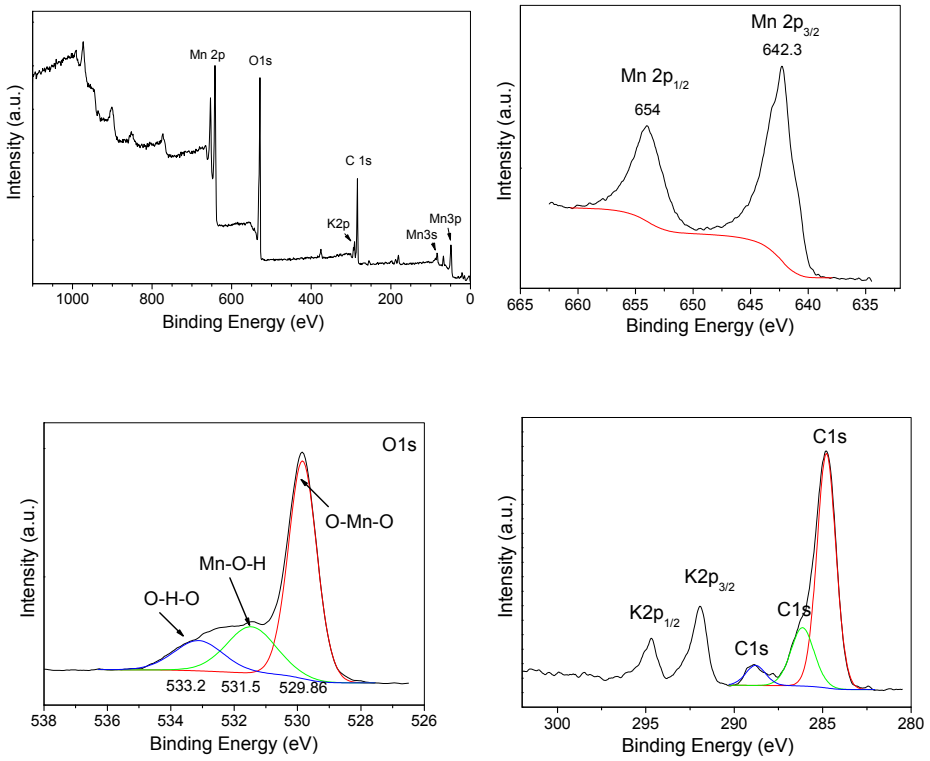
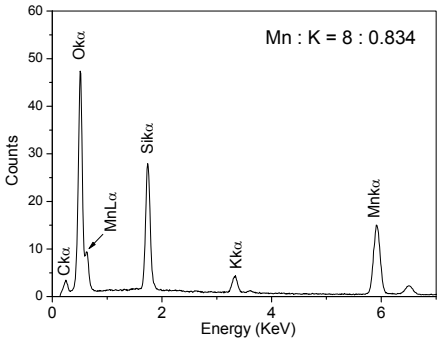
## ESI-1. Composition analysis of KMO nanowires




| Name | Peak BE | Height CPS | At. % | |
|---|---|---|---|---|
| C1s A | 284.79 | 16188.76 | 26.95 | |
| C1s B | 286.14 | 4030.27 | 8.27 | |
| C1s C | 288.79 | 1383.8 | 2.41 | |
| K2p | 291.93 | 5316.01 | 2.38 | |
| O1s A | 529.84 | 42407.59 | 25.33 | 40.93 |
| O1s B | 531.46 | 9071.76 | 9.45 | |
| O1s C | 533.12 | 5902.51 | 6.15 | |
| Mn2p | 642.26 | 27520.1 | 19.07 | |

**Fig. S1.** XPS spectra of KMO nanowires. The Mn/K atomic ratio is about 8:1. The assignment of the $O_{1s}$ peaks was referenced the literature [W. F. Wei, X. W. Cui; W. X. Chen, D. G. Ivey, *J. Phys. Chem. C,* 2008, **112**, 15075] and some oxygen species come from the surface hydration. From XPS results, the composition of KMO nanowires is calculated to be $K_{2-x}M_8O_{16}$ (x≈1).




| Element | Intensity | Weight% | At% |
|---|---|---|---|
| C | 3.255 | 4.785 | 8.907 |
| O | 46.291 | 48.063 | 67.170 |
| Si | 26.311 | 11.112 | 8.846 |
| K | 3.440 | 2.489 | 1.423 |
| Mn | 14.364 | 33.551 | 13.654 |

**Fig. S2.** EDX spectrum of KMO nanowires grown on Si substrate. It is revealed that the product consists of Mn, K and O elements (Si signal comes from the substrate, and C from the contaminants). The Mn/K atomic ratio is about 8:0.834, agreeing with the XPS result in the acceptable error range. This result clearly indicates that the product is potassium manganese oxide rather than manganese oxide.

**ESI-2. TEM images of occasionally observed tubelike KMO nanostructures**

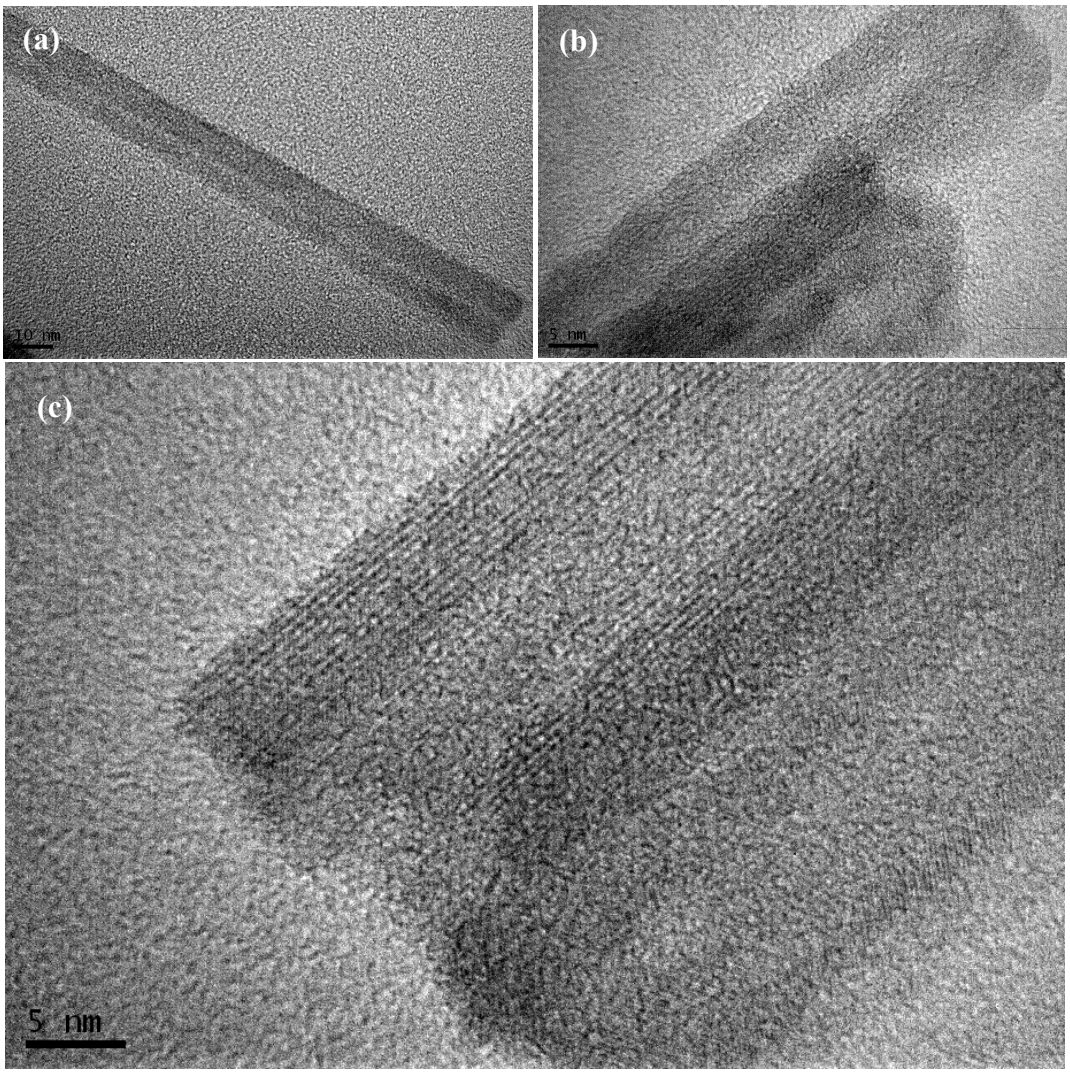



**Fig. S3.** (a) TEM image of a tubelike nanostructure. (b) HRTEM image of tubelike KMO nanostructures occasionally observed in the product. (c) Two parallel tubelike nanostructures with open ends. The yield of tubelike nanostructures in the product is less than 2%.

## ESI-3. $N_2$ adsorption/desorption isotherm of KMO nanowires

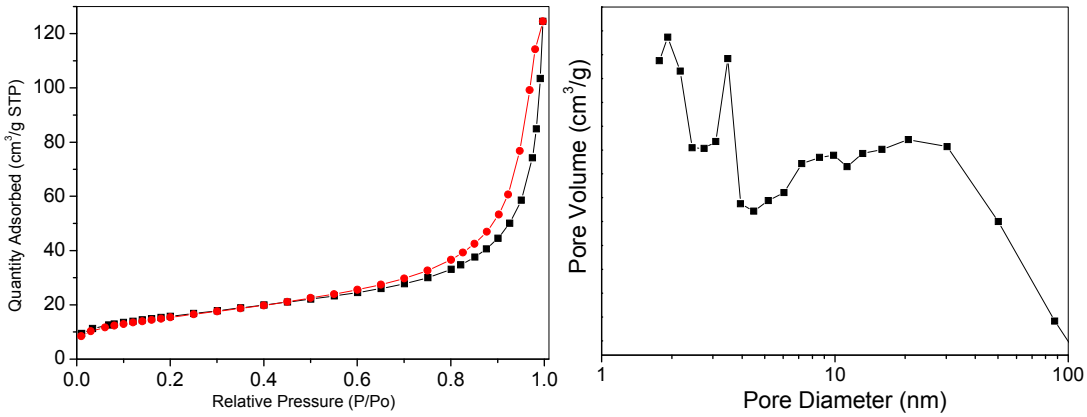



**Fig. S4.** $N_2$ adsorption/desorption isotherm of the KMO nanowires. The BET specific surface area is about 55.6 $m^2/g$. The pore size distribution curve shows that the pore sizes are about 5-60 nm, which may result from the accumulated pores between the nanowires. The pore volume is about 0.19 $cm^3/g$ according to the BJH adsorption and desorption data.

## ESI-4. Characterization results of the products from other conditions

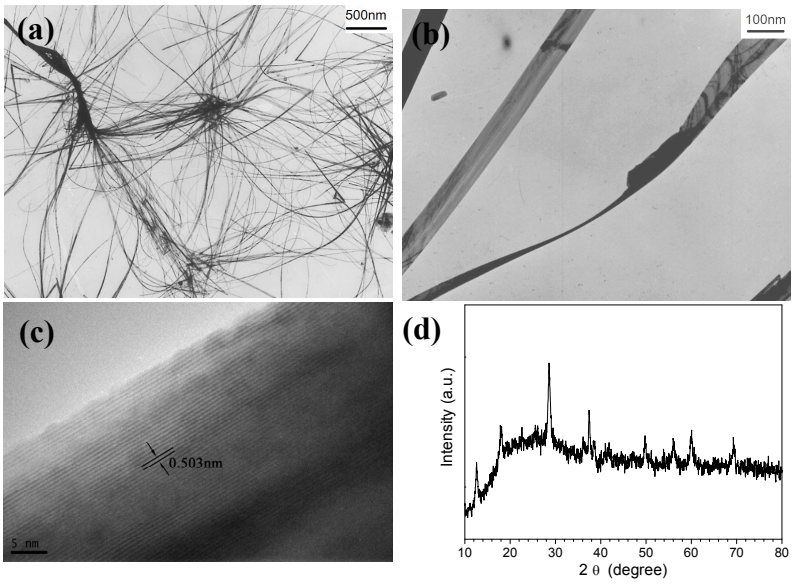



**Fig. S5.** (a-c) TEM images and (d) XRD pattern of the product in the absence of $KBrO_3$. It is seen the nanostructures show beltlike morphology with the composition of $KMn_8O_{16}$ (JCPDS 34-0168), which is different from the phase of the nanostructures obtained with $KBrO_3$/KBr oxidizer.

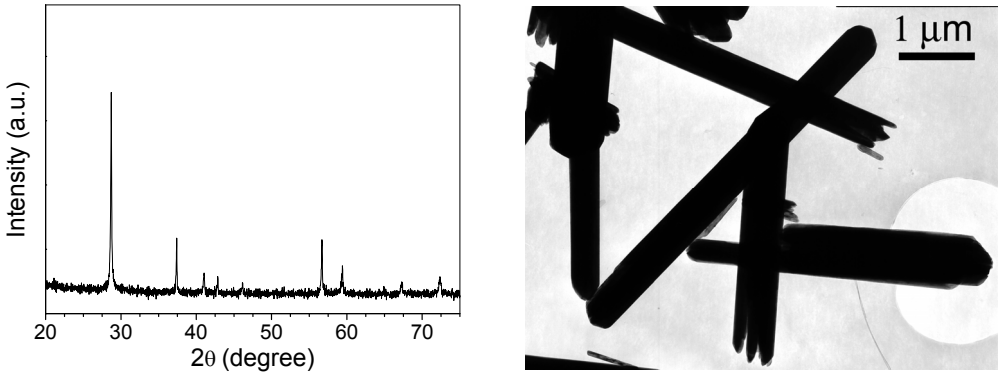



**Fig. S6.** XRD pattern and TEM image of the product synthesized using LiBr as the substitute for KBr. $\beta$-$MnO_2$ nanowires rather than KMO nanowires were obtained.

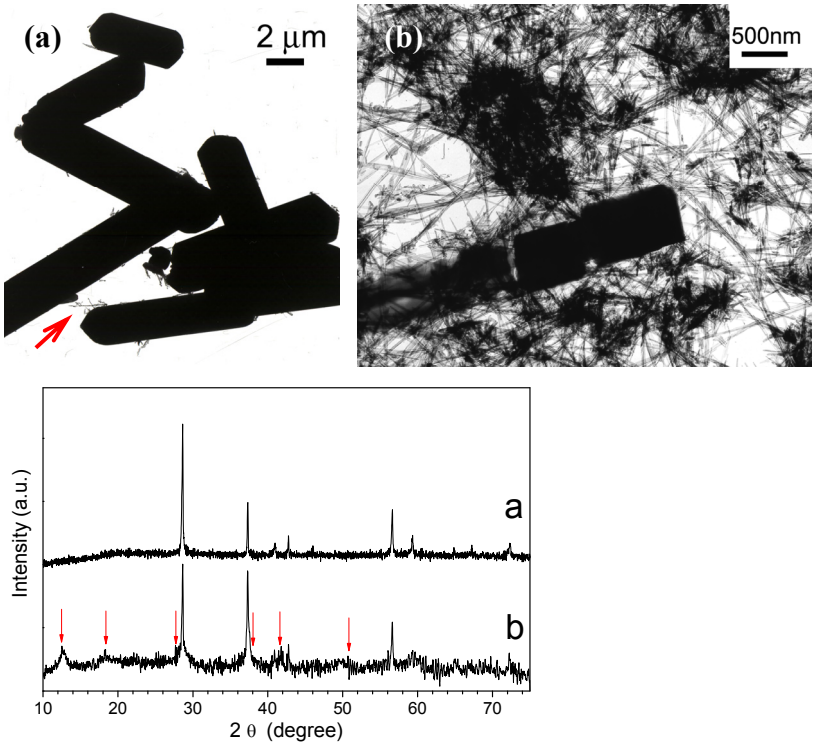



**Fig. S7.** TEM images of the products synthesized with different amount of KBr: (a) 0.03 mol; (b) 0.038 mol. These figures are also shown in main text of Fig. 5C-D. The bottom panel is the corresponding XRD curves. It is seen nanorods in (a) have the compisiton of tetragonal $\beta$-$MnO_2$ (JCPDS 81-2261) and a set of peaks of $K_{2-x}Mn_8O_{16}$ (JCPDS 44-1386) appeared in product (b), corresponding to the thin nanowires in (b). These results indicate the amount of KBr is crucial to the morphologies and composition of the products.

**ESI-5. Electrochemical capacitive performance of KMO nanowires and $MnO_2$ nanorods.**

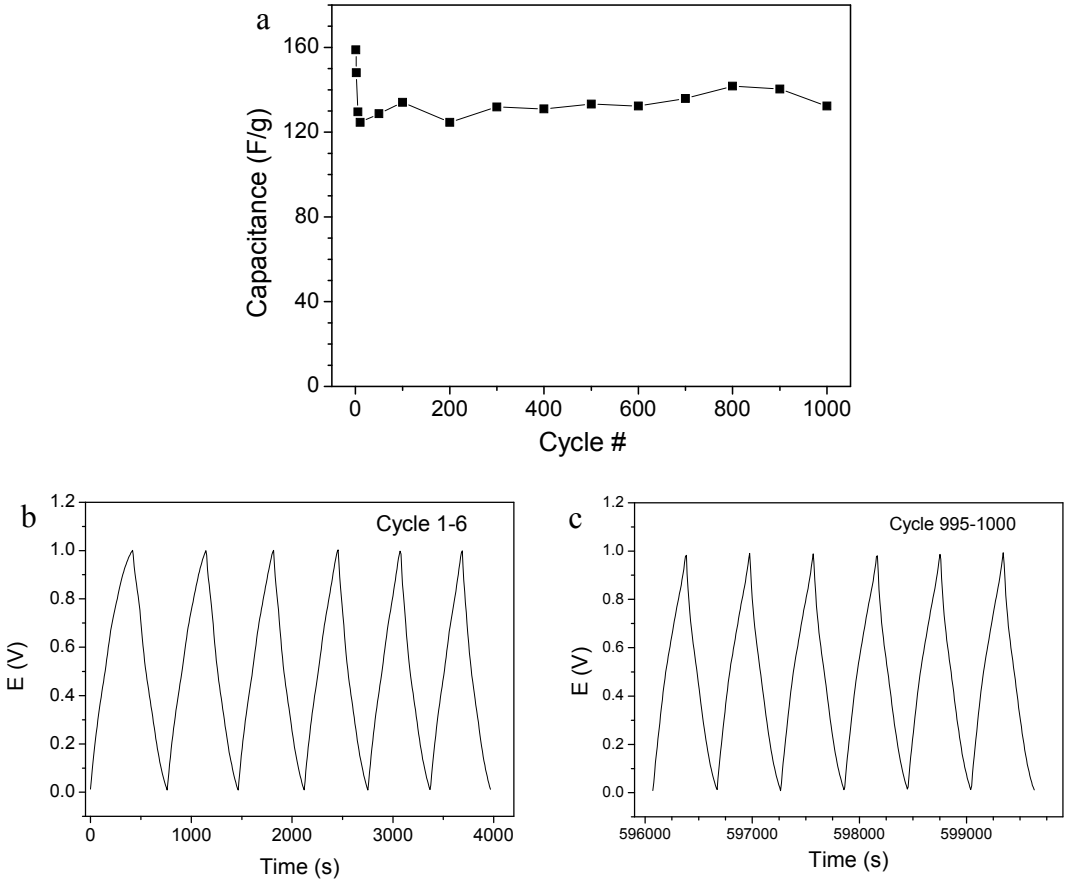



**Fig. S8.** (a) The variation of the discharge specific capacitance of KMO against the cycle number. The capacitance is measured between 0~1.0 V at a specific current of 450 mA $g^{-1}$ in 1M $Na_2SO_4$ solution. It is seen the discharge specific capacitance is about 158.8 F $g^{-1}$ for the first cycle, and decreased to be ~132 F $g^{-1}$ since the fifth cycle and then hold at this level with a ±6% fluctuation due to the temperature variation during the measurement. The larger capacitance for the initial several cycles may result from the pseudo capacitance due to the weak chemical reactions occurred on KMO electrode, which will be decreased after several charge/discharge cycles. After 1000 cycle charge/discharge, the KMO capacitor still has the discharge specific capacitance of 132.3 F $g^{-1}$. (b-c) The charge/discharge curves for cycle 1-6 (b) and cycle 995-1000 (c) indicate the superior stability of KMO nanowires as supercapacitor electrode material.

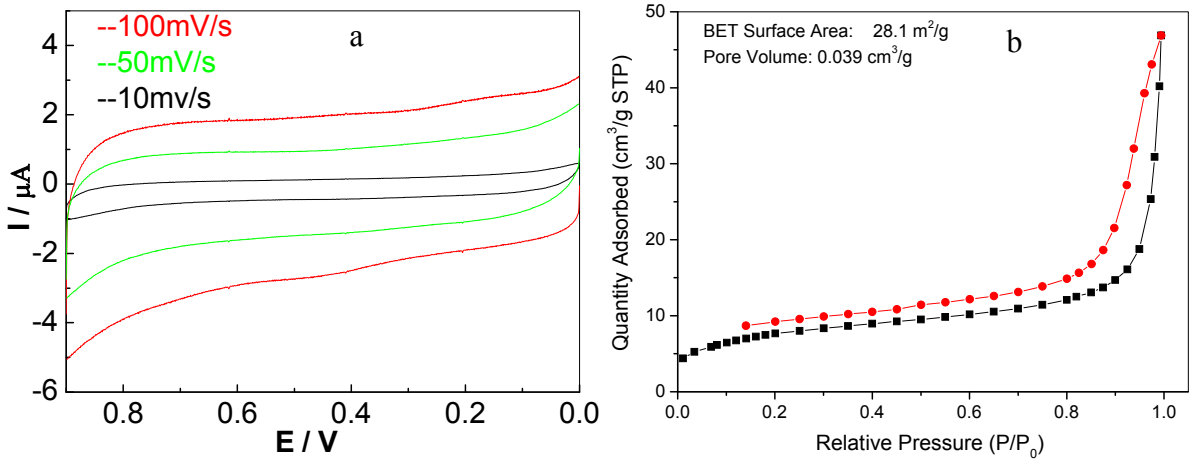



**Fig. S9.** Characterizations on the $\beta$-$MnO_2$ nanorods obtained from KCl/$KBrO_3$. (a) CV curves with different scan rates. The capacitance is measured to be 6 F/g at the scan rate of 100 mV/s, which indicates the $\beta$-$MnO_2$ nanorods are not good electrode materials for supercapacitors. (b) $N_2$ adsorption/desorption isotherms. The BET specific surface area is about 28.1 $m^2$/g and the pore volume is about 0.039 $cm^3$/g. This result indicates the $\beta$-$MnO_2$ nanorods have lower surface area and pore volume than the KMO nanowires due to their large sizes and $\beta$ type crystalline structure.

As reported by S. Devaraj et al. (S. Devaraj, N. Munichandraiah, Effect of Crystallographic structure of $MnO_2$ on its electrochemical capacitance properties, J. Phys. Chem. C 2008, 112, 4406-4417), the specific capacitance for different $MnO_2$ samples is found to depend strongly on the crystallographic structure. For the structure with large interlayer separation (~0.7 nm) and large surface area (e.g. KMO), it has large specific capacitance. For the structure with narrow tunnel size (0.19 nm) and small surface area (e.g. $\beta$-$MnO_2$), it provides a very small specific capacitance (9 F/g in this reference) because the narrow tunnel size does not allow intercalation of cations into the structure. Therefore, the poor capacitive performance for $\beta$-$MnO_2$ nanorods is owing to their $\beta$-structure as well as small surface area.