

Supplementary Information for

Non-Selective Synthesis and Controllable Transformation of Parallel

MnO₂ under Hydrogen Ions

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Experimental section

Preparation templates of MnO_mH_n mesh

The MnO_mH_n mesh was synthesized by a simple and improved hydrothermal method: 40 mL absolute ethanol, 0.06 g urea, 0.467 mL of 50 wt% Mn (NO₃)₂ and 6 mL of 30 wt% H₂O₂ were mixed in turn. After stirring at room temperature for 15 minutes, the mixture was transferred to a 50 mL stainless steel autoclave and heated to 120 °C for 24 h, Finally, the brown precipitate was collected by centrifugation and dried at 80 °C for 12 h.

Effect of acid ions on parallel MnO₂

In a typical synthesis, 20 mg of the MnO_mH_n templates was dispersed in 0.01 mol L⁻¹ KMnO₄ solution (35 mL). Then, 20 μL of concentrated H₂SO₄ was added, stirring slightly at room temperature, the solution was sealed in a 50 mL stainless steel autoclave and heated to 130 °C for 2 h. Following that the autoclave was quickly taken out from the oven and cool quickly with water to avoid further reaction of KMnO₄. Finally, the brown precipitate was carefully washed and collected at 80 °C for 12 h (named as MnO₂-S). As a contrast, HCl and HNO₃ were used to replace H₂SO₄. In detail, 25 μL of concentrated HCl was used and reacted at 120 °C for 2 h (denoted as MnO₂-C); 46 μL of concentrated HNO₃ was employed and reaction at 120 °C reaction for 2 h (named as MnO₂-N).

Effect of H⁺ and K⁺ on parallel MnO₂

Our group has reported that a sufficient amount of H⁺ can form needle-like MnO₂. To investigate whether the effect of H⁺ can be suppressed, the following experiments have been performed: First, 20 mg of the MnO_mH_n templates were dispersed in 0.01 mol L⁻¹ KMnO₄ solution (35 mL), then 400 μL concentrated H₂SO₄ were added to obtain needle-like MnO₂ (named as MnO₂-400). In order to inhibit the structural control of H⁺, K₂SO₄ powder was added before concentrated H₂SO₄, and then stirred and dissolved to form a uniform solution. The amount of K₂SO₄ powder was as follows C_{K⁺} = 0.5C_{H⁺}, C_{K⁺} = C_{H⁺}, C_{K⁺} = 3C_{H⁺}, the obtained samples are called as MnO₂-0.5, MnO₂-1 and MnO₂-3, respectively.

Effect of calcination on loading parallel MnO₂

Typically, the MnO_mH_n templates were calcined in a muffle furnace at 400 °C for 4 h (named as CMnO_x); Then similar loading processes as without calcination were conducted expect for replacing MnO_mH_n with CMnO_x, which named as CMnO_x-2. For comparison, the hydrothermal time has also

been extended to 4 h, the obtained sample was called as CMnO_x-4.

Characterization of parallel MnO₂

The nanostructures and morphology of as synthesized samples were characterized by focused ion beam scanning electron microscope (FIB / SEM, ZEISS AURIGA). The crystal information and chemical composition of the nanostructures were analyzed by powder X-ray diffraction (XRD, D / max 2500 copper K α).

Electrochemical test of parallel MnO₂

In a Na₂SO₄ solution (1.0 M), a three-electrode device was used to test the electrochemical performance. The prepared MnOmHn, CMnO_x and CMnO_x-2 nanopowders were used as working electrodes, respectively. Pt sheets were used as counter electrodes, and saturated calomel electrodes were served as reference electrodes. Typically, a slurry mixed by active materials (70%), carbon black (20%), and polyvinylidene fluoride (PVDF, 10%) in N-methyl-2-pyrrolidone. Then, the slurry was coated evenly on a nickel foam. The as-prepared electrode was put in vacuum oven at 120 °C overnight then uniaxially pressed under 10 MPa. The calculated current densities were based on the total mass of the active material, including the template and parallel MnO₂.