

Electronic Supplementary Information

Hydrothermal preparation, growth mechanism and supercapacitive properties of WO₃ nanorod arrays grown directly on Cu substrate

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The XRD patterns of WO₃ synthesized with different inorganic salts are shown in Fig. S1. It can be seen that different crystalline phases and crystallinity could be obtained with different inorganic salts as additives. Hydrothermal products are a mixture of h-WO₃ and m-W₁₈O₄₉ when rubidium salts are used as additives. The samples are h-WO₃ with poor crystallinity by using Li₂SO₄ and K₂SO₄ as additives. Na₂SO₄ and (NH₄)₂SO₄ could lead to h-WO₃ nano-structures with relative high purity and crystallinity, and there is a obvious (002) peak in the sample with Na₂SO₄ as additive. Based on the experiment mentioned above, the results of XRD patterns are more or less consistent with the SEM images in Fig. 8.

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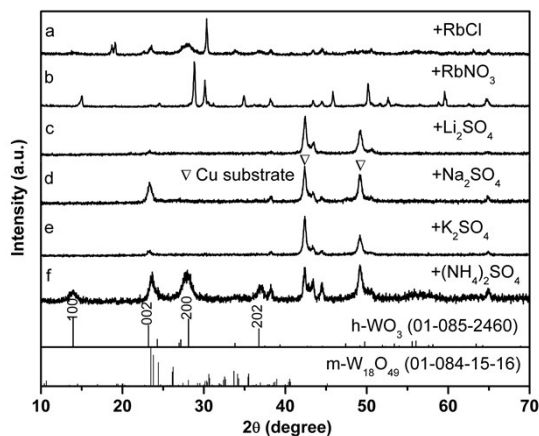


Fig. S1 XRD patterns of the samples synthesized with different inorganic salts: (a) RbCl (6.0×10^{-3} mol), (b) RbNO₃ (6.0×10^{-3} mol), (c) Li₂SO₄ (3.0×10^{-3} mol), (d) Na₂SO₄ (3.0×10^{-3} mol), (e) K₂SO₄ (3.0×10^{-3} mol), (f) (NH₄)₂SO₄ (3.0×10^{-3} mol).

Fig. S2 shows the TEM images of the WO₃ nanorod grown under such hydrothermal conditions (pH value: 2.0, concentration of Na₂WO₄: 0.10 mol L⁻¹, Rb₂SO₄ additive: 3.0×10^{-3} mol, reaction temperature: 180 °C, reaction time: 8 h). It can be seen that the bottom of WO₃ rods grows some WO₃ branches with small size. The morphology of these nanorods might look more like a hierarchical structure. We speculate that these WO₃ branches may appear from WO₃ polycrystalline particles on the side face of WO₃ nanorods in Fig. 10a.

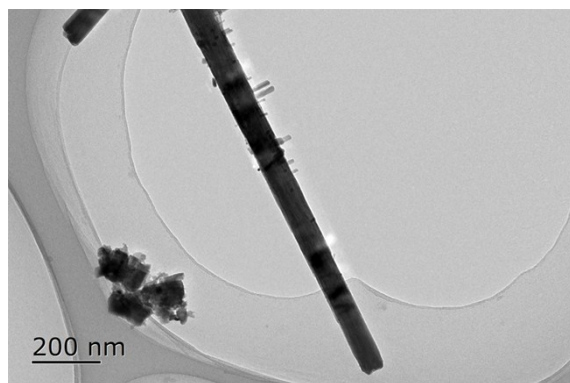


Fig. S2 TEM images of as-prepared WO₃ nanorod.

The Cu substrate and WNRs is to be corroded in a relatively high concentration of H₂SO₄ solution (1 mol L⁻¹) when a positive and negative voltage is applied to the Cu substrate alternately. Fig. S3 shows the cyclic voltammograms of WNRs in 1 mol L⁻¹ Na₂SO₄ electrolyte in the initial cycles. It can be seen that the ions storage

capacity of the WNRs grown on Cu substrate decrease quickly. In addition, a layer of blue floccule will be formed on the interface between the WNRs and H_2SO_4 solution. It might be ascribe to that the Cu substrate and WNRs are corroded by using H_2SO_4 solution as electrolyte.

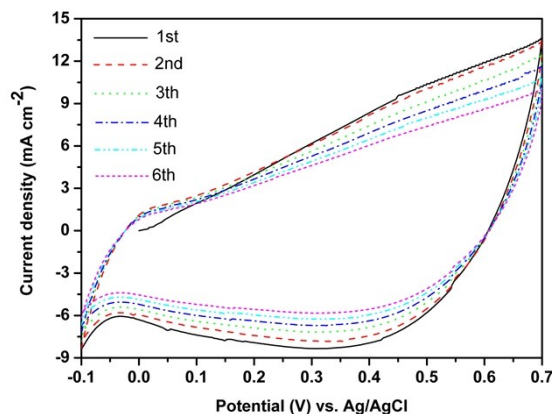


Fig. S3 Cyclic voltammograms of WNRs in $1 \text{ mol L}^{-1} \text{H}_2\text{SO}_4$ electrolyte in the initial cycles.

Fig. S4 shows CV tests of WNRs-3 at different cycles before and after repeated galvanostatic charge-discharge for 1000 cycles at 1 A/g . From Fig. S2 b, it can be seen that the charge-discharge current densities decrease, but not very much. And no significant change in the shape of CVs appears. It might be because the WO_3 nanostructures dissolve into the electrolyte gradually. But for the entire, the WNRs-3 is fairly stable after 10000th cyclic voltammetry and 1000th galvanostatic charge-discharge tests.

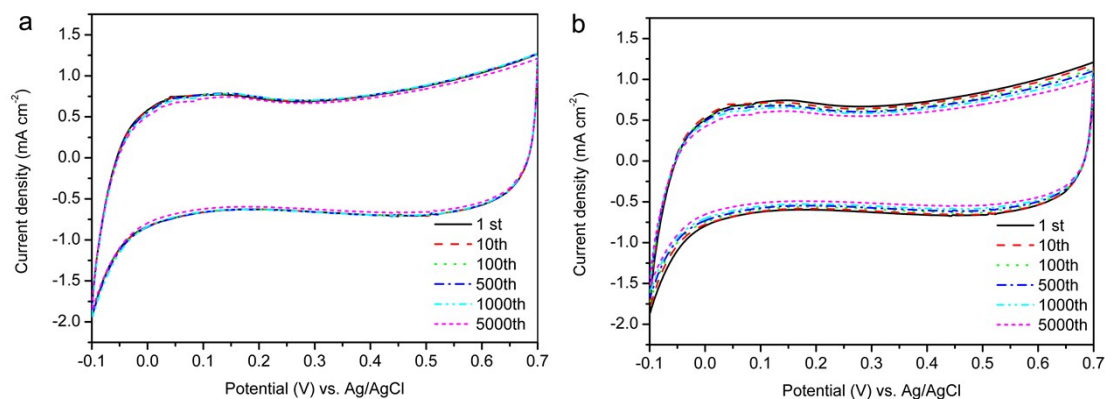


Fig. S4 Cyclic voltammograms of WNRs-3 at different cycles. (a) before repeated galvanostatic charge-discharge. (b) after repeated galvanostatic charge-discharge.