Supporting Information

Surper-Large Dendrites Composed of Trigonal PbO_2 Nanoplates with Enhanced Performances for Electrochemical Devices

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The chemical equations involved for PbO_2 formation during electrochemical deposition can be described as follows:[1-4]

$$H_2O \rightarrow OH_{ad} + H^+ + e \quad (1)$$

$$Pb^{2+} + OH_{ad} \rightarrow Pb(OH)^{2+} \quad (2)$$

$$Pb(OH)^{2+} + H_2O \rightarrow PbO_2 + 3H^+ + e \quad (3)$$

References

(1) J. Lee, H. Varela, S. Uhm and Y. Tak, *Electrochem. Commun.*, 2000, **2**, 646-652.

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(3) A. B. Velichenko, D. U. Girenko and F. I. Danilov, *J.Electroanal. Chem.*, 1996, **405**, 127-132.

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2377.

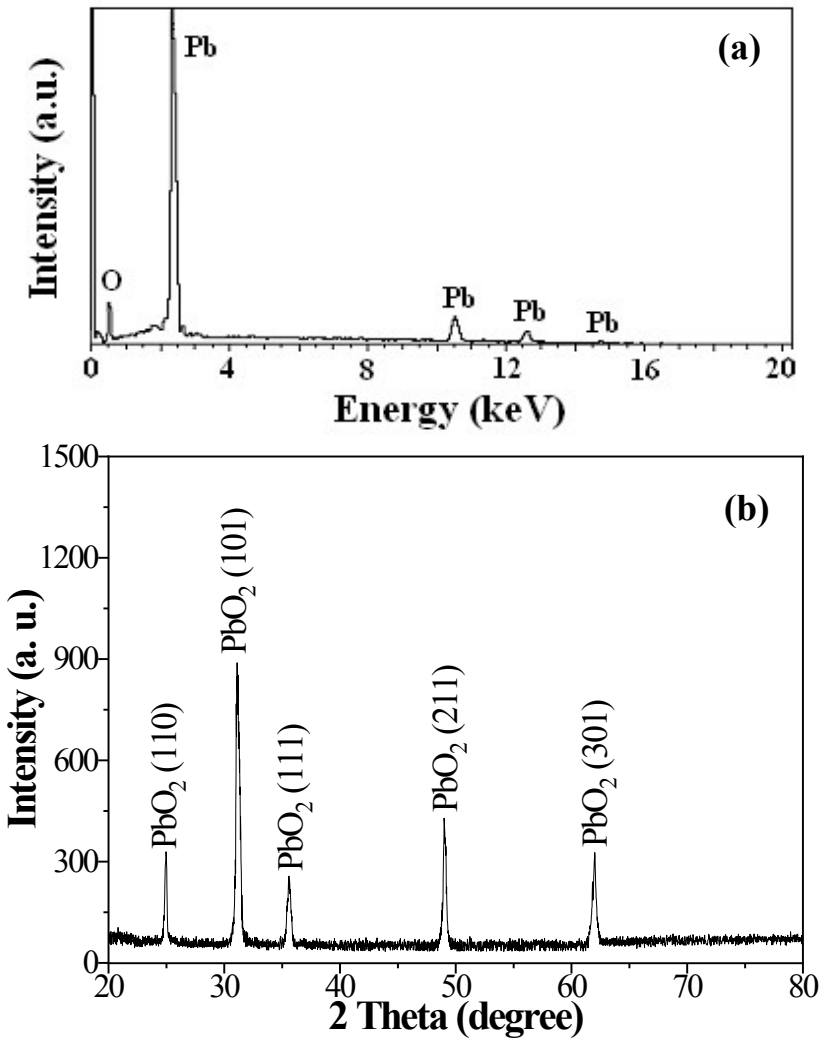

Figure S1. (a) EDS and (b) XRD patterns of super-large PbO_2 dendrites composed of trigonal nanoplates.

The formation mechanism of PbO_2 dendritic morphology during electrodeposition is discussed as follows:

In order to understand the formation mechanism of PbO_2 dendritic nanostructures, we studied the deposits at different growth stages. Figure S2 shows the evolution process of the morphologies of PbO_2 dendritic nanostructures. From Figure S2(a-c), one can figure out that there is a tendency that PbO_2 nanostructure grows more and more complex. Based on the above results, the possible elementary steps involved in the formation process are expressed as follows. Pb^{2+} ions in

deposition solution firstly form $Pb(OH)^{2+}$, and then PbO_2 will be formed. The electrochemical deposition generally gives rise to the isolated nuclei on the substrate, and these nuclei are randomly and uniformly distributed. With electrodeposition going along, the isolated nuclei will form PbO_2 nanoclusters that act as growth centers or seeds.[1-2] These structures follow an adapted diffusion limited growth pattern model, where particles moving in random walk trajectories stick on a lattice containing a seed particle anisotropically with the seed tips growing preferentially. So the subsequent growth of PbO_2 crystals would preferentially deposit on the preformed nuclei rather than on the substrate surface, which is possibly due to the relatively high activation energy for the surface reaction.[2-3] When the seeds reach certain size, the formation of PbO_2 will be accelerated through the autocatalytic process, which would be facilitated to a highly anisotropic mode to form dendritic feelers on the surface of each nanocluster.[1] In the end, the integrated PbO_2 dendritic structures will be synthesized through the gradual and continued electrodeposition of PbO_2 onto the newly deposited nuclei.

References

(1) L. Wang, Y. Yamauchi, *Chem. Mater.*, 2009, **21**, 3562-3569.

(2) X. Xu, J. Jia, X. Yang, S. Dong, *Langmuir*, 2010, **26**, 7627-7631.

(3) Y. Qin, Y. Song, N. J. Sun, N. Zhao, M. X. Li, L. M. Qi, *Chem. Mater.*, 2008, **20**, 3965-3972.

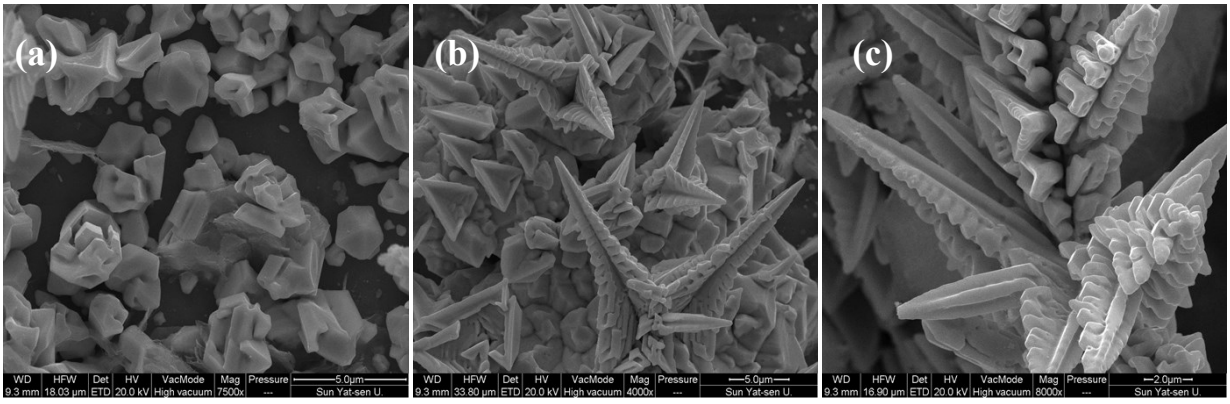

Figure S2. The illustration for the formation process of PbO_2 dendritic nanostructures. The evolvement

sequence is (a)→(b)→(c).

In addition, the effects of other experimental conditions on the morphology were investigated. Here, the various morphologies of PbO_2 were obtained by changing the deposition parameters as shown Figure S3.

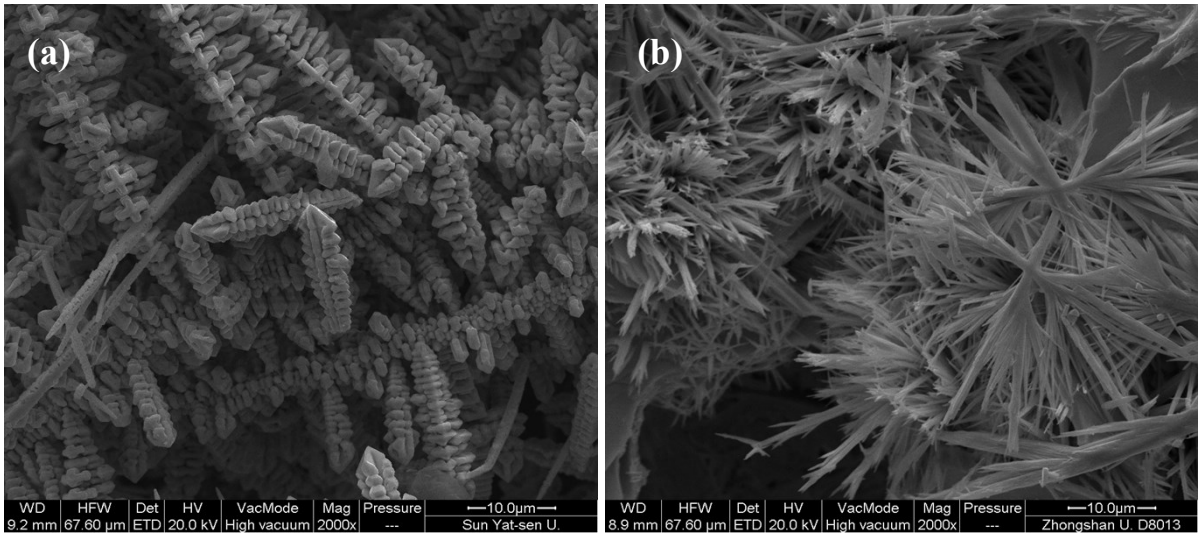

Figure S3. SEM images of PbO_2 under different conditions: (a) 0.01 M$Pb(NO_3)_2$+0.2 M HBO_3 at 5.0 mA/cm^2; (b) 0.1 M $Pb(NO_3)_2$+1.0 M HBO_3 at 10.0 mA/cm^2.

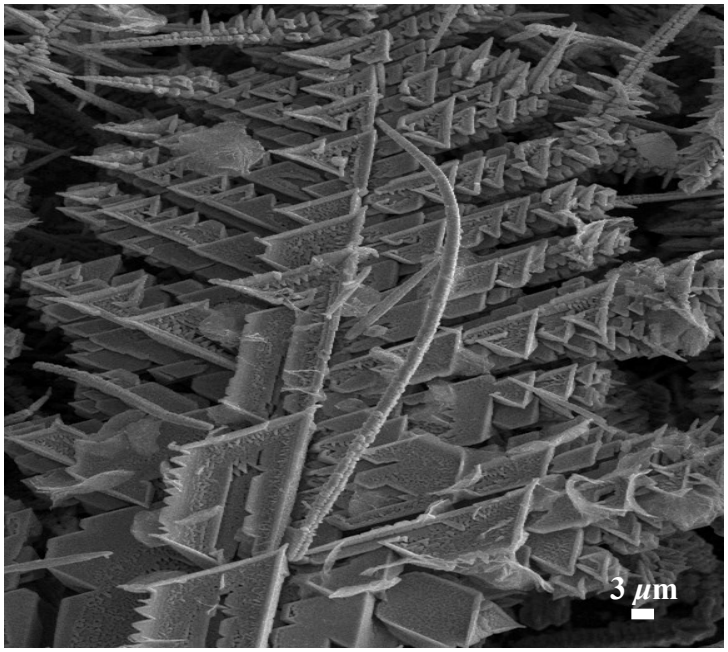

Figure S4. SEM image of small PbO_2 dendrites composed of nanoplates.

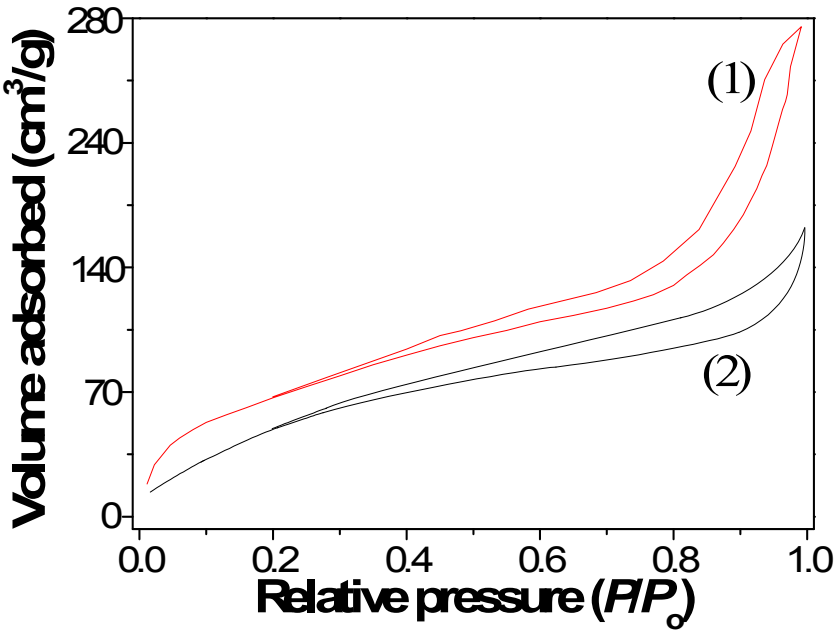

Figure S5. N_2 adsorption-desorption isotherm curves for (1) super-large PbO_2 dendrites composed of trigonal nanoplates and (2) small PbO_2 dendrites composed of nanoplates.

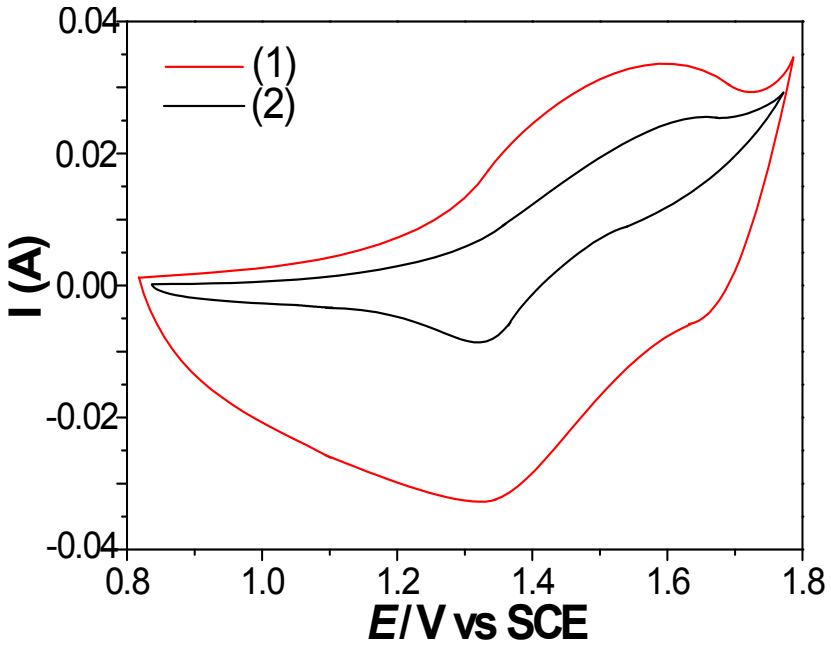

Figure S6. CVs of (1) the super-large PbO_2 dendrites as positive electrode of supercapacitor and (2) the small dendrites in 5.0 mol/L H_2SO_4 recorded a scan rate of 75 mV/s.