Supporting Information

Surper-Large Dendrites Composed of Trigonal PbO₂ Nanoplates with Enhanced Performances for Electrochemical Devices

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The chemical equations involved for PbO₂ formation during electrochemical deposition can be described as follows:¹⁻⁴

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\begin{align*}
H_2O & \rightarrow OH_{ad} + H^+ + e \\ (1) \\
\text{Pb}^{2+} + OH_{ad} & \rightarrow \text{Pb(OH)}^{2+} \\ (2) \\
\text{Pb(OH)}^{2+} + H_2O & \rightarrow \text{PbO}_2 + 3H^+ + e \\ (3)
\end{align*}
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References


(4) D. Devilliers, T. Baudin, M.T. Dinh Thi and E. Mahé, *Electrochimica Acta*, 2004, 49, 2369-
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


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 MPb(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 PbO₂ dendrites composed of nanoplates.

Figure S5. N₂ adsorption-desorption isotherm curves for (1) super-large PbO₂ dendrites composed of trigonal nanoplates and (2) small PbO₂ 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$_2$SO$_4$ recorded a scan rate of 75 mV/s.