Self-Supported Metallic Nanopore Arrays with Highly Oriented Nanoporous Structures as Ideally Nanostructured Electrodes for Supercapacitor Applications

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Supercapacitors have attracted great interest as an electrical energy storage system because of their high power density, fast charge–discharge rate, and excellent cycle stability.[1–4] They are attractive alternatives or complements to batteries in electrical energy storage applications, especially in high-power applications. The energy storage mechanism of supercapacitors is widely considered to be a surface phenomenon, through either ionic adsorption–desorption at the electrode/electrolyte interface (electrochemical double-layer capacitors), or fast and reversible surface redox reactions between the electrode and electrolyte (pseudocapacitors).[5,6] Therefore, electrodes with large specific surface areas are beneficial to achieving high supercapacitor performance. Normally, large specific surface area can be expected by applying nanostructured electrodes.[6–13] In particular, highly oriented 1D nanostructure (e.g., nanowire, nanotube) arrays have been considered an efficient electrode structure for supercapacitors.[14–21] The structural features of 1D nanostructure arrays (especially those of high aspect ratio) are not only able to provide a large specific surface area in the electrode for the growth of active materials, but they also provide straight pathways for ion transport as a result of the highly oriented structure.[21,24–29] However, there are two challenging technical issues still existing in the application of 1D nanostructures to supercapacitors: i) the agglomeration of high-aspect-ratio 1D nanostructures; ii) the structural stability of 1D nanostructure arrays (i.e., 1D nanostructure arrays might collapse when they are integrated into the electrode unit of a supercapacitor). Agglomeration decreases the effective specific surface area and increases the ion-transport resistance, both of which impose adverse effects on supercapacitor performance. Since arrayed nanowires or nanotubes with an aspect ratio higher than 5 tend to be agglomerated,[16] most of the 1D nanostructures used for supercapacitor electrodes so far have had a low aspect ratio, so as to avoid agglomeration and to maintain their highly oriented nature.[16,23,29] On the other hand, the collapse of 1D nanostructure arrays in the electrodes of supercapacitor device would also block the straight pathways for ion transport to the surface of active materials. So far most commercial supercapacitor devices still adopt thin-film electrodes rather than nanostructured electrodes, although nanostructured electrodes are highly desirable for achieving much better performance. Therefore, an important goal for nanostructured materials in supercapacitor applications is the design of suitable nanostructured electrodes for high-performance supercapacitors based on the advantageous features of nanostructures.

Anodized aluminum oxide (AAO) membranes have been widely used as a nanoporous template for fabricating regular arrays of 1D nanostructures and surface nanopatterns.[30–36] Unfortunately, the AAO template cannot be used as a supercapacitor electrode because it is an insulator. However, the structural features of the AAO membrane (i.e., highly oriented nanoporous structure and tunable structural parameters) provide a hint for the design of nanostructured electrode for supercapacitors. The structure of nanopore arrays is the negative structure of nanowire arrays (as schematically indicated in Figure 1a). With the same structural parameters (including unit density, diameter, and length), nanopore arrays have the equivalent specific surface area as that of nanowire arrays. Nanopore arrays are actually a porous film unlike nanowire arrays, and the nanopore arrays should not have any agglomeration and collapse like high-aspect-ratio nanowire arrays. Furthermore, nanopore arrays are a self-supported and homogeneous structure; the high aspect ratio of the nanopores may even strengthen the structural stability of nanopore arrays during the device integration process. With such nanopore arrays as a nanostructured electrode, large specific surface area and highly oriented pore structure can be achieved simultaneously. The large specific surface area can ensure high capacitance, while the highly oriented and stable nanoporous structure can facilitate ion transport; thus, high-performance supercapacitors should be highly expected. Therefore, in the present work, we demonstrate the design and application of self-supported metallic nanopore arrays with highly oriented nanoporous structure as ideally nanostructured electrodes for supercapacitor applications. Compared to the supercapacitor-electrode application of 1D nanostructure arrays, nanopore arrays can avoid structural agglomeration and collapse while keeping all the advantageous features.
features of 1D nanostructure arrays, including large specific surface area and unobstructed ion transport for the realization of high-performance supercapacitors.

As shown in Figure 1b, the self-supported metallic (nickel) nanopore arrays with highly oriented nanoporous structure were fabricated using a two-step replication process, including gold layer deposition (Step I), polymer infiltration (II), template removal (III), Ni electrodeposition (IV), and polymer dissolution (V). The AAO template was adopted as the master template. The pore diameter and interpore distance, and pore length of 350 nm, 400 nm, and 350 and 400 nm, respectively. In first step of the replication process, rectangularly ordered arrays of poly(methyl methacrylate) (PMMA) nanopillars were obtained after the removal of the AAO template (Figure 1b, Step II and III), which acts as the initial template. It is worth mentioning that the obtained free-standing PMMA nanopillar arrays must always be kept in solution, otherwise they will tend to agglomerate. The PMMA nanopillar arrays were then adopted as the template for the electrodeposition of Ni with the gold film as the working electrode in the second step of the replication process (Figure 1b, Step IV). Finally, the PMMA nanopillars were dissolved in chloroform, leading to the self-supported Ni nanopore arrays, which represent the negative structure of the PMMA nanopillar arrays (Figure 1b, Step V).

After this two-step replication process (Figure 1b), large-area, self-supported Ni nanopore arrays with a highly oriented nanoporous structure and a rectangular pore arrangement were successfully obtained (Figure 2d–f). The arrangement (rectangular), diameter (350 nm), and interpore distance (400 nm) of the obtained Ni nanopore arrays are exactly identical to those of the master AAO templates. The length of the Ni nanopores (pore length) could reach up to ~8.4 µm according to the cross-section SEM view in Figure 2f; thus, the aspect ratio of the Ni nanopore arrays is approximately 24. It is worth noting that it is almost impossible to realize such a high aspect ratio in free-standing 1D nanostructure arrays without any agglomeration, which unambiguously highlights the superior character of our nanopore arrays. The specific surface area of Ni nanopore arrays is calculated to be nearly 59 times that of the non-nanostructured electrode (i.e., the specific surface area of 1 cm² footprint area with such nanopore arrays was calculated to be nearly 59 cm²). For nanopore arrays with the same structural parameters, including the density of nanowire per unit substrate area, the diameter of nanowire, and the length of nanowire, the specific surface area should be equal to that of nanopore arrays if there is not any collapse and agglomeration in the nanowire arrays. As mentioned above, both pore diameter and pore length of the AAO templates are tunable. The AAO template with larger specific surface area can be easily realized with either large pore diameter (low aspect ratio) or large pore length (high aspect ratio). Considering that the Ni nanopore arrays are replicated from the AAO template, the structural parameters of the Ni nanopore arrays greatly depend on the structural parameters of the utilized AAO template, which include the pore diameter, interpore distance, and pore length. Therefore, Ni nanopore arrays with larger specific surface area could also easily be realized by adopting the proper AAO template as the initial template in the replication process.

To explore the advantages of the Ni nanopore arrays as nanostructured electrodes for supercapacitor applications, manganese dioxide (MnO₂)—one of the most attractive materials for supercapacitors—was deposited as the active material onto the obtained Ni nanopore arrays through anodic deposition. Here, Ni nanopore arrays with a pore diameter, interpore distance, and pore length of 350 nm, 400 nm, and 1.3 µm, respectively, were utilized as nanostructured electrodes. The footprint area of the Ni nanopore arrays was 0.5 cm². In this case, the effective specific surface area of the Ni nanopore arrays for MnO₂ deposition was calculated to be 10 times that of the non-nanostructured electrode (i.e., the specific surface area was calculated to be about 5 cm²). Figure 3 shows SEM images of bare Ni nanopore arrays and the corresponding Ni nanopore arrays after being coated with different amounts of MnO₂. The mass loadings of MnO₂ range from 80 to
400 µg/cm². The cross-section SEM image of the MnO₂@Ni nanopore arrays clearly shows the uniform coating of MnO₂ on the wall of the nanopores (Figure S2, Supporting Information). Nanopores with larger diameters can offer not only larger specific surface area but also a larger area for the coating of active materials, which is helpful for increasing the mass loading of active materials per unit substrate area. The highly oriented nanoporous structure could be maintained after being coated with even more active materials (e.g., MnO₂ loading from 80 to 400 µg/cm² in our case), which is also attributed to the larger pore diameter. The remaining highly oriented nanoporous structure could effectively facilitate the ion transport in electrodes. Although agglomeration could also be avoided by increasing the diameter of the nanowire without changing any other structural parameters (i.e., length and arrangement), increasing the diameter of the nanowire will result in a larger specific area and a smaller interwire spacing at the same time. After the deposition of active materials, a randomly porous structure will easily form due to the smaller interwire spacing. The interwire spacing of the Ni nanopore arrays became smaller after being coated with MnO₂ (Figure S3c, Supporting Information). When the mass loading of MnO₂ reached 240 µg/cm² (Figure S3c, Supporting Information), the original structure of the Ni nanowire arrays was replaced by a randomly porous structure. Such a randomly porous structure generates a large ion-transport resistance, thus resulting in poor rate capability when applied to a supercapacitor. As shown in Figure 3a–d, the pore diameter of Ni nanopores becomes smaller as the MnO₂ mass loading increases. When the mass loading of MnO₂ reached as high as 400 µg/cm², the pore diameter of the Ni nanopores after MnO₂ coating is about 150 nm. Hence, the hybrid structure maintains the highly oriented nanoporous structure as the original Ni nanopore arrays (Figure 3d and Figure S2, Supporting Information). Such a highly oriented nanoporous structure (which remains so even after being coated with active materials) can promote the transport of electrolyte ions and improve the rate capability of supercapacitors.

As expected, metallic nanopore arrays with large specific surface area and highly oriented nanoporous structure are beneficial for high-performance supercapacitors. The electrochemical properties of the MnO₂@Ni nanopore arrays were studied by performing cyclic voltammetry (CV) using a three-electrode configuration with a platinum foil as the counter electrode and Ag/AgCl as the reference electrode in an electrolyte of 1 M Na₂SO₄ aqueous solution. Figure 4a exhibits CV curves at scan rates ranging from 2 to 1000 mV/s with a MnO₂ mass loading of 80 µg/cm². Obviously, the CV curves at different scan rates all show a symmetrically rectangular shape, indicating an ideally capacitive behavior and fast charge–discharge characteristics. The absence of redox peaks indicated that the supercapacitors are charged and discharged at a pseudo-constant rate over the entire voltammetric cycles. Moreover, for MnO₂@Ni nanopore arrays, the symmetrically rectangular shape of CV curves was maintained even when a scan rate of 1000 mV/s was applied (Figure 4a), without any significant distortion, demonstrating a highly reversible system with excellent rate capability. The specific capacitance (Cₛ) was calculated to be 672 F/g at 2 mV/s with a MnO₂ mass loading of 80 µg/cm². The charge storage mechanism for MnO₂ in supercapacitors is widely considered to be surface redox reactions, and the charge is stored in the first few nanometers. The charge storage process can be separated into: 1) the surface adsorption of electrolyte ions on surface,

\[
\text{MnO}_2^{\text{(Surface)}} + X^+ + e^- \rightleftharpoons \text{MnOOX}^{\text{(Surface)}}
\]  

where X is Li⁺, Na⁺, K⁺, or another cation, and 2) the intercalation/de-intercalation of electrolyte ions in the bulk,

\[
\text{MnO}_2^{\text{(Bulk)}} + X^+ + e^- \rightleftharpoons \text{MnOOX}^{\text{(Bulk)}}
\]
According to the above equations, both ions and electrons take part in the charge–discharge process. Therefore, transport of the electrolyte ions to the interface of the active material and electrolyte is one of the critical factors in determining the power performance and energy efficiency of supercapacitors.\[14–18\] The previously reported high-surface-area nanoporous electrodes normally have random pore structures and wide pore size distributions, which would generate high ion-transport resistance during fast charge–discharge processes, thus leading to poor rate capabilities.\[10\] In the case of metallic nanopore arrays with highly oriented nanoporous structures, the high $C_p$ can be attributed to both the large conductive surface area and the highly oriented nanoporous structure. The large specific surface area of Ni nanopore arrays can provide a large contact area between the current collector and the active material to greatly shorten the electron-transport path length, while the highly oriented porous structure can facilitate fast electrolyte ion-transport during fast charge–discharge processes. The CV curves at a scan rate of 100 mV/s of samples with different MnO$_2$ mass loadings are shown in Figure 4b. When the mass loading of MnO$_2$ is increased from 80 to 400 µg/cm$^2$, the CV curve maintains a symmetrical rectangular shape, even at the scan rate of 200 mV/s (Figure S7, Supporting Information). The $C_p$ of MnO$_2$@Ni nanopore arrays could reach 382 F/g at 2 mV/s with a MnO$_2$ mass loading of 400 µg/cm$^2$. The larger specific capacitance at lower mass loading indicates the importance of low ion-transport resistance and short electron-transport path length to the performance.

Figure 3. SEM images of a) bare Ni nanopore arrays and b–d) Ni nanopore arrays after being coated with different mass loadings of MnO$_2$: 80 (b), 240 (c), and 400 (d) µg/cm$^2$.

Figure 4. a) CV curves of MnO$_2$@Ni nanopore arrays with a MnO$_2$ loading of 80 µg/cm$^2$ at different scan rates; b) CV curves of MnO$_2$@Ni nanopore arrays with different MnO$_2$ loadings at a scan rate of 100 mV/s; c) GCD profiles of MnO$_2$@Ni nanopore arrays with a MnO$_2$ mass loading of 80 µg/cm$^2$; d) cycling stability of MnO$_2$@Ni nanopore arrays (80 µg/cm$^2$) as a function of cycle number at a scan rate of 50 mV/s.
while the high specific capacitance at high mass loading further emphasizes the importance of the two critical factors in the performance of supercapacitors.

The galvanostatic charge–discharge (GCD) curves of the as-prepared MnO$_2$@Ni nanopore arrays with a MnO$_2$ mass loading of 80 μg/cm$^2$ at different current densities are shown in Figure 4c. The charging curves are symmetric to their corresponding discharge counterparts, indicating good electrochemical capacitive characteristics and superior reversible redox reaction. Notably, the voltage loss is very low even at a high current density, suggesting low internal resistance, which can be ascribed to the good electrical conductivity of the Ni nanopore arrays and the large contact area between the current collector and active materials (specific surface area). Electrochemical impedance spectroscopy (EIS) plots for the MnO$_2$@Ni nanopore arrays further confirm the results mentioned above. The smaller radius of the semicircle in the high frequency range for electrodes comprising MnO$_2$@Ni nanopore arrays indicates the smaller charge-transfer resistance (Figure S5, Supporting Information). This result also suggests that the nanostructured current collector provides an increased contact area with the active materials, and also enhances the electronic conductivity of the electrode. The $C_{sp}$ calculated from the discharge curves at a current density of 2 A/g was 570 F/g. At a very high current density of 100 A/g, the $C_{sp}$ can still reach 271 F/g (47.5% retention), indicating good rate capability. Such good rate capability can be ascribed to the highly accessible specific surface area, lower ion-transport resistance, and good electric conductivity of the Ni nanopore arrays.$^{[39,45]}$ Furthermore, the cycling performance of the MnO$_2$@Ni nanopore arrays is evaluated by long-time cycling at a scan rate of 50 mV/s with a symmetric two-electrode configuration (as shown in Figure 4d and Figure S8, Supporting Information). The capacitance retention is quite stable, and it maintains 83% of its initial value even after 3000 cycles, which again confirms that the Ni nanopore arrays are an efficient electrode structure for supercapacitors. It should be noted that the performance of the supercapacitor could be further improved through the optimization of the structural parameters of the Ni nanopore arrays and also the electrodeposition conditions of MnO$_2$. For example, templates with hexagonal pore arrangement can increase the density of the nanopores because of the hexagonal closest packing, and thus can achieve a larger specific surface area compared to that of a rectangular pore arrangement; this work is underway.

In summary, we have demonstrated the rational design of nanostructured electrodes for high-performance supercapacitors based on the advantageous features of nanostructures. Self-supported metallic nanopore arrays with highly oriented nanoporous structure are highly desirable nanostructured electrodes for supercapacitor applications. Owing to the promising structural features, such nanopore arrays overcome the drawbacks (agglomeration and collapse) while maintaining all the advantages (large specific surface area and good ion transport) of 1D nanostructure arrays in order to achieve a high-performance supercapacitor. Moreover, self-supported metallic nanopore arrays with promising structural features and tunable structural parameters can be further exploited for various other applications, such as electrodes for batteries and water-splitting devices.

**Experimental Section**

**Fabrication of Ni Nanopore Arrays:** Anodized nanoscale indented aluminum with a rectangular pore arrangement had been previously used as initial templates.$^{[11]}$ After the pore widening process of AAO templates with a 5 wt% H$_3$PO$_4$ solution, a thin gold layer (20 nm thick) was deposited onto AAO templates by electron beam deposition (Kurt J. Lesker PVD225). Then, a PMMA solution was drop-casted onto the AAO template to fill the pores. After drying, the AAO template was selectively removed using a 5 wt% H$_3$PO$_4$ solution. Rectangularly ordered arrays of PMMA nanopillars were obtained with the Au film at the bottom. Subsequently, Ni was electroplated using the pre-deposited Au layer as the working electrode with a current density of 10 mA/cm$^2$. The electrolyte for Ni deposition was an aqueous solution containing 0.38 M NiSO$_4$, 0.12 M NiCl$_2$, and 0.5 M H$_3$BO$_3$. Finally, the PMMA nanostructure was dissolved by chloroform, and self-supported Ni nanopore arrays were obtained.

**MnO$_2$ Deposition:** A thin layer of MnO$_2$ was deposited onto the obtained Ni nanopore arrays using an anodic electrochemical deposition method with a constant potential of +0.8 V for different times. The electrolyte for the deposition was an aqueous solution containing 0.1 M manganese acetate (MnAc$_2$) and 0.1 M sodium sulfate (Na$_2$SO$_4$).

**Characterization:** Morphologies were characterized using SEM (ZEISS AURIGA). Both three- and two-electrode configuration were adopted to determine the electrochemical properties. CV, GCD, and EIS measurements were performed on a Potentiostat/Galvanostat (BioLogic, VSP). CV was carried out at different scan rates of 2, 5, 10, 20, 50, 100, 200, 500, and 1000 mV/s, and GCD curves were obtained at current densities of 2, 5, 10, 20, 50, and 100 A/g.

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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