Coaxial Ni$_x$Co$_{2x}$(OH)$_{6x}$/TiN Nanotube Arrays as Supercapacitor Electrodes

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ABSTRACT

Ni$_{x}$Co$_{2x}$(OH)$_{6x}$ as a precursor of intensively studied NiCo$_2$O$_4$ has been directly deposited into self-standing titanium nitride nanotube array (TiN NTA) grid monolithic supports to form a coaxial nanostructured electrode for supercapacitors. With TiN NTA substrates providing a large surface area, fast electron transport, and enhanced structure stability, this Ni$_{x}$Co$_{2x}$(OH)$_{6x}$/TiN electrode exhibits superior pseudocapacitive performance with a high specific capacitance of 2543 F g$^{-1}$ at 5 mV s$^{-1}$, remarkable rate performance of 660 F g$^{-1}$ even at 500 mV s$^{-1}$, and promising cycle performance (about 6.25% capacitance loss for 5000 cycles). Interestingly, the Ni$_{x}$Co$_{2x}$(OH)$_{6x}$/TiN NTA electrode outperforms the NiCo$_2$O$_4$/TiN NTA electrode, indicating that this self-standing Ni$_{x}$Co$_{2x}$(OH)$_{6x}$/TiN NTA monolith is a promising candidate for high-performance supercapacitor applications.

KEYWORDS: Ni$_{x}$Co$_{2x}$(OH)$_{6x}$ · TiN NTA · self-standing electrode · supercapacitors · pseudocapacitive performance

S upercapacitors have attracted tremendous attention because of their high power density and long cycle life.1-5 For pseudocapacitor applications, transition metal oxides/hydroxides are widely investigated,6-9 as they can provide multiple oxidation states for reversible Faradaic reactions. In many reports, Ni(OH)$_2$ and Co(OH)$_2$ have been widely explored owing to their abundance, low cost, and environmental benignity.10-14 Ni(OH)$_2$ possesses high theoretical specific capacitance, but its poor intrinsic conductivity restricts its rate capability.15-17 On the other hand, Co(OH)$_2$ exhibits much higher conductivity.18,19 Consequently, the integration of Ni and Co hydroxides always possesses enhanced specific capacitance and rate capability.16,20-23 Unfortunately, the high rate performance is still unsatisfactory.

To enhance the rate capability of Ni and Co hydroxides, an efficient design is to directly grow the active materials on a nanostructured self-standing current collector.24,25 This monolithic design has apparent advantages as follows:26-29 (i) the nanostructure of the current collector serves a large surface area, which would be favorable for active materials accessible to an electrolyte; (ii) a conductive current collector directly attached to active materials provides fast electron transport, which improves the rate capability; (iii) compared to common slurry-coating technology, where a large area of active surface material is blocked by binders, this design would render auxiliary components such as binder and conductive agents and significantly reduce specific energy density and even specific power density. Among various options for self-standing substrates, titanium nitride (TiN), with excellent electronic conductivity, corrosion resistance, and low cost, is an attractive candidate.30,31 Furthermore, the nanostructured TiN monolithic collector can be a potential choice to enhance the rate capability of Ni and Co hydroxides. However, there are still limited reports on growing Ni and Co hydroxides on a self-standing TiN support.24

Herein, based on TiN nanotube arrays (NTA), we report a self-standing strategy to grow a mixed bimetallic hydroxide [denoted as Ni$_x$Co$_{2x}$(OH)$_{6x}$], which is always used as a precursor to synthesize NiCo$_2$O$_4$.28 NiCo$_2$O$_4$ has been extensively investigated because of its high electrochemical activity,32-35 but to our surprise, the pseudocapacitor performance of its precursor does not arouse...
much attention. In this paper, Ni$_x$Co$_2$(OH)$_6$ was directly grown on titanium nitride nanotube arrays (TiN NTA) by co-electrodeposition to obtain a coaxial nanostructure self-standing monolithic electrode with high rate performance. Compared with NiCo$_2$O$_4$, our findings demonstrate that Ni$_x$Co$_2$(OH)$_6$ materials can deliver superior capacity and rate capability.

RESULTS AND DISCUSSION

Synthesis and Structural Analysis. Figure 1a illustrates the process to synthesize Ni$_x$Co$_2$(OH)$_6$/TiN NTA including anodization, calcination in ammonia, and electrodeposition. In our previous reports, Ti foil has been involved to fabricate NTA.36,37 Herein, we chose Ti mesh to prepare TiN NTA (as shown in Figure S1), because Ti mesh has a much larger surface area than Ti foil. Therefore, an improved performance can be expected. After calcination, the obtained pristine TiN NTA possess uniform nanotube arrays with outer diameters in the range 100–120 nm, as shown in Figure 1b. These one-dimensional arrays on a Ti mesh substrate with a fast electron transport network can serve as a favorable current collector. Through optimized electrodeposition, the binary Ni–Co hydroxides are deposited in a well-distributed manner into the TiN nanotube (Figure 1c and d) to form coaxial nanowire arrays. Elemental mapping also reveals a uniform distribution of Ni and Co in the TiN NTA (inset of Figure 1d). This nanostructure ensures (i) improved electronic conductivity owing to the contribution of TiN materials, (ii) enhanced ionic conductivity and favorable access to the electrolyte by avoiding the binder, and (iii) high utilization of well-dispersed active materials on the large surface area of the NTA substrates. Furthermore, the deposited Ni–Co hydroxides inside the NTA are highly porous and form a nanosheet like rippled silk when grown on the TiN film (as shown in Figure S2). This morphology endowed by electrodechemical deposition further improves the surface area of the active materials, facilitating charge storage in the double layer.

To demonstrate the ratio of Ni/Co in the as-prepared samples, XRD analysis was conducted. Figure 2a shows the XRD pattern of the as-prepared Ni–Co
hydroxides. All the diffraction peaks are weak and broad, indicating the low crystallinity, which can be indexed to Ni(OH)\textsubscript{2} (JCPDF: 14-0117) and Co(OH)\textsubscript{2} (JCPDF: 02-0925). These Ni–Co hydroxides change into NiCo\textsubscript{2}O\textsubscript{4} (Figure S3) after calcination, which indicates the molar ratio of Ni and Co in the hydroxides is 1:2.

X-ray photoelectron spectroscopy (XPS) results of Ni\textsubscript{x}Co\textsubscript{2x}(OH)\textsubscript{6x}/TiN NTA are presented in Figure 2b–d. The O 1s spectrum (Figure 2b) shows three oxygen contributions: O1 at 531.2 eV is nickel–oxygen bonds and O2 at 532.1 eV is cobalt–oxygen bonds.\textsuperscript{28,38} The component O3 at 533.9 eV can be attributed to physically and chemisorbed water.\textsuperscript{28} In the Ni 2p XPS spectrum, the main 2p\textsubscript{3/2} peak is fitted with characteristic Ni\textsuperscript{2+} with minor oxidation to Ni\textsuperscript{3+} and two shakeup satellites (denoted as “Sat.”).\textsuperscript{39} The Co 2p spectrum is fitted with Co\textsuperscript{2+} and two shakeup satellites.\textsuperscript{14} The ratio of Ni/Co calculated from the XPS result is about 1:1.9, which corresponds to the XRD result of Ni–Co hydroxides after calcination.

**Electrochemical Characterization.** For electrochemical investigation, we chose an electrolyte mixture (Figure S4) to optimize the capacitance of Ni\textsubscript{x}Co\textsubscript{2x}(OH)\textsubscript{6x} under a stable potential window. The cyclic voltammetry (CV) performance of TiN NTA before and after the deposition of Ni\textsubscript{x}Co\textsubscript{2x}(OH)\textsubscript{6x} at a scan rate of 100 mV s\textsuperscript{−1} is shown in Figure 3a. The CV curve of TiN NTA clearly shows an ideal rectangular shape (also as shown in Figure S5, even at a fast scan rate of 2.0 V s\textsuperscript{−1}). Apparently, after the deposition of Ni\textsubscript{x}Co\textsubscript{2x}(OH)\textsubscript{6x}, a greatly enlarged CV curve with a pair of redox peaks is observed, which can be attributed to the reversible Faradaic redox reactions of Ni\textsubscript{x}Co\textsubscript{2x}(OH)\textsubscript{6x} materials and the double layer capacitance provided by reversible adsorption of electrolyte ions onto the surface of the active materials. In this case, the TiN NTA serves as a
nanostructured current collector, playing an important role in the rate capability but with an insignificant capacitance contribution (further discussed below).

CV tests of Ni(OH)2 and Co(OH)2 electrodes are carried out at a scan rate of 5 mV s\(^{-1}\) as a fair comparison. As illustrated in Figure 3b, the peaks of the Ni\(_{x}\)Co\(_{2-x}\)(OH)\(_6\) curve are between that of Co(OH)\(_2\) and Ni(OH)\(_2\), which are near 0.2 and 0.15 V, related to a mixed reaction of 1 and 2.16,21

Co(OH)\(_2\) + OH\(^-\) ⇔ CoOOH + H\(_2\)O + e\(^-\)  \hspace{1cm} (1)

Ni(OH)\(_2\) + OH\(^-\) ⇔ NiOOH + H\(_2\)O + e\(^-\) \hspace{1cm} (2)

As shown in Figure 4a, these peaks located within 0.05–0.3 V are clearly observed in all CV curves over the range 5–100 mV s\(^{-1}\). Even at a scan rate of 100 mV s\(^{-1}\), the CV shape has small distortions. This is because TiN NTA provides a conductive framework for fast electron transport and charge separation. Furthermore, TiN NTA on a mesh substrate with a large surface area endows an enhanced contact of Ni\(_{x}\)Co\(_{2-x}\)(OH)\(_6\) with both the electrolyte and current collector, which can further improve the rate capability.

The specific capacitance \(C_s\) of this electrode can be calculated based on the CV curves, and the results are displayed in Figure 4b. As a fair comparison, the \(C_s\) of Ni(OH)\(_2\) and Co(OH)\(_2\) calculated from Figure S6 are also shown in Figure 4b. Obviously, with an increasing scan rate from 5 to 100 mV s\(^{-1}\), the \(C_s\) of Ni(OH)\(_2\) drops quickly (2400 F g\(^{-1}\) at 5 mV s\(^{-1}\), 800 F g\(^{-1}\) at 100 mV s\(^{-1}\)) even when deposited in TiN NTA, which demonstrates that the poor intrinsic conductivity of Ni(OH)\(_2\) limits its electrochemical performance at high scan rates. It is worth noting that 2400 F g\(^{-1}\) is higher than the theoretical capacitance of Ni(OH)\(_2\) (2082 F g\(^{-1}\) within 0.5 V, according to Faraday’s law). This further confirms that double-layer capacitance offers a notable contribution to the total capacitance of electrodeposited materials. On the other hand, the rate capability of Co(OH)\(_2\) is much better (1400 F g\(^{-1}\) at 5 mV s\(^{-1}\), 800 F g\(^{-1}\) at 100 mV s\(^{-1}\)). Compared with the electrodes discussed above, Ni\(_{x}\)Co\(_{2-x}\)(OH)\(_6\) as a combination of Ni(OH)\(_2\) and Co(OH)\(_2\) in situ, exhibits multiple characteristics with both enhanced capacity and rate performance. The capacitance of Ni\(_{x}\)Co\(_{2-x}\)(OH)\(_6\) is impressive at 1665 F g\(^{-1}\) at a scan rate of 100 mV s\(^{-1}\) (equal to 0.18 F cm\(^{-2}\), as shown in Figure S7), which is higher than previously reported Ni and Co hydroxides.40–43 Even under a very high rate of 500 mV s\(^{-1}\), the Ni\(_{x}\)Co\(_{2-x}\)(OH)\(_6\) electrode still reveals a quite considerable capacitance of 660 F g\(^{-1}\) (inset of Figure 4b).

To confirm these results, electrochemical impedance spectroscopy (EIS) of Ni(OH)\(_2\), Co(OH)\(_2\), and Ni\(_{x}\)Co\(_{2-x}\)(OH)\(_6\) electrodes are measured at a potential of 0.2 V, applying 5 mV ac voltage in the frequency range from 100 kHz to 1 Hz, respectively. As shown in Figure 4c, all the impedance spectra are composed of one semicircle at high frequency and a linear part at
EXPERIMENTAL SECTION

Preparation of TiN NTA. All the chemicals were used as received without further purification. The Ti mesh substrate was anodized in a two-electrode cell (0.1 wt % NH4F/ethylene glycol as electrolyte, Pt as counter electrode) to obtain the precursor of TiN NTA at 60 V under atmosphere for 7 h. The precursor was...
cleaned with ethyl alcohol three times, and then calcined in a tube furnace at 800 °C under ammonia for 1 h. After cooling, TiN NTA was finally obtained. TiN thin films were obtained by directly annealing the Ti mesh substrates under ammonia at 800 °C for 1 h.

Preparation of NiCo2O4/TiN NTA. In a typical process, 2 mmol of Ni(NO3)2·6H2O and 4 mmol of Co(NO3)2·6H2O were dissolved into 40 mL of deionized water to obtain a light pink liquid. Then the co-electrodeposition was conducted at room temperature by a CHI 440A electrochemical workstation with platinum as the counter electrode, a saturated calomel electrode (SCE) as the reference electrode, and TiN NTA as the working electrode. After the co-electrodeposition with a potential at −1.0 V (vs SCE) for 10 s, the sample was carefully washed several times with deionized water. Then the sample was put into a vacuum oven at 120 °C for 8 h. For comparison, Ni(OH)2/TiN NTA and Co(OH)2/TiN NTA were obtained by the same procedure, respectively. The NiCo2O4(OH)x/TiN thin film was prepared by co-electrodeposition on the TiN thin films (mesh substrate).

Characterization. In order to reduce the impact of TiN NTA, we deposited NiCo2O4(OH)x, Ni(OH)2 and Co(OH)2 on stainless steel, which was easily scratched for X-ray diffraction (XRD) analysis. XRD patterns were recorded with a Bruker-AXS Micro diffractometer (D8 Advance) using Cu Ka radiation (λ = 1.5406 Å) from 5° to 95° at a scanning speed of 3° min⁻¹. Morphological information was attained from field emission scanning electron microscopy (Hitachi S-4800). Scanning transmission electron microscope (STEM) and energy dispersive X-ray spectroscopy elemental mapping were obtained from Tecnai F20. X-ray photoelectron spectroscopy was carried out by an ESCALab250-XL electron spectrometer using Al Kα radiation.

Electrochemical Tests. Electrochemical measurements were carried out by a CHI 440A instrument. The three-electrode system includes SCE as the reference electrode, platinum as the counter electrode, and NiCo2O4(OH)x/TiN NTA as the working electrode. In order to obtain a moderate electrolyte with high ionic concentration, we used a 0.1 M KOH and 1.9 M KCl solution. Cyclic voltammetry was tested by a Zahner Zennium electrochemical workstation (Germany).

The specific capacitance (C) of NiCo2O4(OH)x is calculated from the CV curves based on the following equation:

\[ C_{\text{NiCo2O4(OH)x}} = \frac{Q_{\text{NiCo2O4(OH)x/TiN NTA}} - Q_{\text{Ni(OH)2/TiN NTA}}}{\Delta V \times \rho_{\text{NiCo2O4(OH)x}}} \]  

where C (F g⁻¹) is the C, Q (C) is the average charge during the charging and discharging process, ΔV (V) is the potential range, and (g) is the mass of NiCo2O4(OH)x calculated from the charge passed for the deposition.

Conflict of Interest: The authors declare no competing financial interest.

Supporting Information Available: Macroscopic SEM image of TiN NTA, SEM images of NiCo2O4(OH)x/TiN film, XRD of NiCo2O4 CV results, simulation of EIS data. This material is available free of charge via the Internet at http://pubs.acs.org.

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