All Metal Nitrides Solid-State Asymmetric Supercapacitors

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Supercapacitor is relatively new technology compared to batteries but is regarded a highly promising alternative device for electrochemical energy storage, due to its capability of fast energy delivery (up to tens of seconds) and ultralong cycle life (typically $10^5$ cycles).\(^1\)-\(^4\) However, the bottleneck of supercapacitor is the relatively low energy density compared to batteries, particularly when carbon materials are utilized as the electric double-layer capacitive electrode.\(^5\)-\(^7\) Asymmetric supercapacitors (ASCs) can improve the energy density by providing increased voltage of the full devices according to $E = \frac{1}{2} \Delta V$.\(^8\)-\(^12\)

Recently, research on ASCs has been focused mostly on metal oxides because of their high pseudocapacitance through fast reversible redox reactions with ions from electrolyte. However, metal oxides usually suffer from low electrical conductivity and unreliable stability during long cycles. Metal nitrides, in the contrary, show much improved sustainability and superb electrical conductivity (4000–55 500 S cm\(^{-1}\)\(^5\),\(^11\),\(^14\)) and thus become attractive as SC electrode materials. Among all the reported metal nitrides in energy storage, TiN and Fe\(_2\)N received particular attention due to their high capacitance (Fe\(_2\)N as lithium ion battery anode: $\approx 900$ mAh g\(^{-1}\); TiN as supercapacitor cathode: $\approx 150$ F g\(^{-1}\)) and electrical conductivity.\(^15\),\(^16\) Various types of TiN nanostructures have been employed as supercapacitive electrode such as nanoparticle,\(^13\) nanotube,\(^17\)-\(^19\) mesoporous microsphere,\(^20\) and nanosheets.\(^21\) However, TiN was found to be easily oxidized in aqueous solutions

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\text{TiN} + 2\text{H}_2\text{O} \rightarrow \text{TiO}_2 + \frac{1}{2}\text{N}_2 + 4\text{H}^+ + 4\text{e}^-; \text{TiN} + 2\text{O}_2 \rightarrow 2\text{TiO}_2 + \text{N}_2
\]

Therefore, to circumvent the oxidation problem of TiN, researchers combined TiN with more stable materials. They include carbon coating,\(^22\)-\(^24\) carbon nanotube encapsulation,\(^25\),\(^26\) graphene wrapping,\(^27\)-\(^30\) and forming core-shell structures with TiO\(_2\),\(^31\) VN,\(^32\) and MnO\(_2\),\(^33\) as well as decoration with polymers such as polypyrrole,\(^34\) polyaniline,\(^35\),\(^36\) and PEDOT.\(^37\) Those methods showed high efficiency in enhancing TiN cycling and rate properties. Fe\(_2\)N has been reported as anode for lithium-ion batteries\(^38\),\(^39\) in conjunction with carbon-related materials. But, the absence of evident charge–discharge voltage plateau\(^38\) indicates its capacitive property and suitability as the supercapacitor electrode material.

Due to the large surface area, high conductivity, and light-weight property, graphene becomes an effective substrate for SCs electrode.\(^40\) Compared to the stacked graphene layers obtained from solution synthesis, vertically aligned graphene nanosheets (GNSs) on current collectors (such as carbon fiber) are more advantageous as the later allows a maximum usage of the high surface area. This increased surface area will lead to a high capacitance since a supercapacitor device essentially relies on the available active surface sites for charge absorption (for double-layer capacitor) or redox reactions (for pseudocapacitor). Recently, such GNS substrates have been applied to SnO\(_2\) and ZnO-based electrodes to improve LIB performance.\(^41\),\(^42\)

In this work, we report the fabrication of nanostructured metal nitrides on vertically aligned graphene nanosheets substrate for high-power and ultrastable solid-state ASCs. Atomic layer deposition (ALD) was employed in order to assure the maximum use of the conductive GNS surfaces and have full coverage and tight connection of the active nitride material to the substrate. ALD is proven a powerful tool for nanofabrication and surface engineering of energy materials.\(^43\) We employed solid-state electrolyte to avoid oxidation of metal nitrides.\(^44\)-\(^46\) The ASCs constructed from TiN@GNSs cathode, Fe\(_2\)N@GNSs anode, and poly(vinyl alcohol) (PVA)/LiCl solid electrolyte indeed show an irreversible capacitance of $\approx 58$ F g\(^{-1}\) which is stable up to 20 000 cycles. Moreover, the devices achieve both high volumetric energy density ($\approx 0.55$ mWh cm\(^{-3}\)) and power density ($\approx 220$ mW cm\(^{-3}\)) tested at a high current density of 8 A g\(^{-1}\).

The fabrication process for both electrodes is shown schematically in Figure 1. Thin films of TiO\(_2\) and ZnO with same thicknesses of 20 nm were coated by ALD onto the GNS substrates. To obtain anode precursor, ZnO was first transferred to FeOOH via a solution reaction. Subsequently, the FeOOH@GNS and TiO\(_2@\)GNS samples were thermal annealed in a NH\(_3\) atmosphere for 1 h at 600 and 800 °C, respectively. The morphology of the samples at different fabrication stages are shown by scanning electron microscopy (SEM) images in Figure 2. The GNSs cover homogeneously the surface of carbon fibers (Figure 2a) with an overall height of $\approx 800$ nm and are less...
than 5 nm in thickness (Figure 2b). The smooth surface (Figure 2c) of the original ALD TiO$_2$@GNS becomes porous (Figure 2d) after the annealing process, and the porous structure is expected to enlarge the specific surface area leading to increased capacitance. Regarding the anode, after the ZnO@GNS (Figure 2e, inset) was dipped in 0.5 M Fe(NO$_3$)$_3$ solution for 2 h, the thin film becomes thinner with a thickness \(\approx 10\) nm (Figure 2e), which is FeOOH@GNS according to the previous study.\cite{47} After the ammonia annealing, the FeOOH thin film is converted to Fe$_2$N nanoparticles that are dispersed uniformly on the surface of GNS (Figure 2f) with an average diameter \(\approx 10\) nm.

Transmission electron microscopy (TEM) characterizations were performed in order to reveal the detailed nanostructure and phase of the electrode materials. As cathode, TiN shows the pore size varied from 3 to 10 nm (Figure 3a). High-resolution transmission electron microscopy (HRTEM) reveals the lattice of (111) planes (d-spacings 2.45 Å) and (220) ones (d-spacings 1.48 Å) of TiN (Figure 3f), which is in agreement with the fast Fourier transfer (FFT) generated from the same area (Figure 3e). TEM mapping exhibited the consistent element distribution of Ti (Figure 3c) and N (Figure 3d) with the dark field TEM image in Figure 3b. XRD spectrum of bare GNS after oxygen plasma (see the Experimental Section in the Supporting Information), GNS with 20 nm ALD TiO$_2$, and TiO$_2$@GNS after ammonia annealing were plotted together in Figure 3g. Three typical peaks of graphite were detected in the XRD pattern of bare GNS. After the ALD of TiO$_2$, two weaker peaks of graphene were further weaken and almost disappeared. No obvious peak of TiO$_2$ was observed which may due to the amorphous property of ALD deposited material. As was expected, after high-temperature annealing in ammonia atmosphere, three diffraction peaks at 37°, 44°, and 63° appear and correspond well to the face-centered cubic (fcc) TiN (111), (200), and (220), respectively (JC-PDS, #65-0715) which is identical to previous work.\cite{27,48}

Same characterization was conducted to the anode material. Figure 4a shows the particle morphology of Fe$_2$N with a diameter \(\approx 10\) nm. The Fe$_2$N nanoparticles were detached from the GNS by high-power sonication. TEM mapping of element Fe (blue, Figure 4c) and N (red, Figure 4d) corresponds well to the image profile of Fe$_2$N particles in Figure 4b. Selected area electron diffraction (SAED) pattern (Figure 4e) showed polycrystalline nature of the Fe$_2$N, in which a series of well-defined rings can be assigned to various diffraction planes of (101), (211), (400) of fcc Fe$_2$N. HRTEM image (Figure 4f) showed the clear lattice fringes with d-spacings of 2.11 and 3.45 Å, which conforms well to the crystal face of (101) and (211). To demonstrate the transformation process of the anode material, the XRD spectrum of sample at different fabrication stages was provided in Figure 4g. Through the comparison, it is clear that pure phase of Fe$_2$N was successfully achieved after the transformation reaction of ammonia annealing. The related diffraction peaks of 43°, 56°, 68°, and 75° were indexed to fcc Fe$_2$N lattice of (211), (212), (400), and (213) (JC-PDS, #06-0656), as was reported in previous work.\cite{39,49}
Both the porous TiN cathode and particle Fe$_2$N anode were homogeneously covered/distributed on the thin GNS and were assembled to all-metal nitride asymmetric supercapacitor devices. We consider the benefit of such electrode structures to the device performance as follows. First, TiN$^{[13]}$ and Fe$_2$N$^{[39]}$ are high electrical conductive materials, which would be beneficial to improve the ion and electron transport rates and therefore increase the specific capacitance and rate capability. Second, GNS grown on carbon fibers provides a highly conductive and large surface area ($467 \text{ m}^2 \text{ g}^{-1}$) scaffold for the active materials. Moreover, this vertically aligned graphene effectively avoids the stacking of individual graphene sheets. By applying ALD deposition, electrode materials can fully cover the entire surface of GNS which ensure maximum usage of the substrate surface. Last, the porous TiN thin films and Fe$_2$N nanoparticles are grafted onto GNS by chemical reaction rather than physical mixing. This assures a tight physical connection of both metal nitride materials with the GNS current collector, and also contributes to a long and stable cycling life as well as a high power density.

Before discussing the electrochemical properties of the electrodes, we first consider the possible capacity contribution by the GNS substrate both before and after the ammonia annealing. Previous work $^{[50-53]}$ reported that O in $-\text{C}=-\text{O}$ and $-\text{OH}$ functional groups on graphene surface is easy to be substituted by $-\text{NH}_2$ under high-temperature ammonia annealing conditions. Therefore, as control sample, GNS substrates with same size ($0.6 \times 1 \text{ cm}^2$) were annealed both at 600 and 800 °C with other conditions kept the same (see details in the Experimental Section in the Supporting Information, the control experiment). The cyclic voltammetry (CV) curves in the Supporting Information (Figure S1) showed that the capacity contribution of GNS substrates to the electrodes is less than 0.01% (ratios of area enclosed by the CV curves) both before and after ammonia annealing at 600 or 800 °C. Therefore, in our discussion below, we do not consider the capacitance contribution by the substrates.

The detailed electrochemical characterization starts with single electrodes in a standard three-electrode testing system with Pt plate as a counter electrode, Ag/AgCl (saturated KCl) as a reference electrode, TiN cathode/Fe$_2$N anode as a working electrode, and 1 M LiCl as an electrolyte. Figure 5a,b shows the CV curves of TiN cathode ($0-0.8$ V vs Ag/AgCl) and Fe$_2$N anode ($-0.8-0$ V vs Ag/AgCl) at...
different scan rates (10, 20, 50, and 100 mV s\(^{-1}\)) separately. Both electrodes show quasi-rectangular shapes at varied scan rates, demonstrating that the majority capacitance should be ascribed to capacitive behavior.\(^{[24]}\) As a comparison, the CV curves of precursor TiO\(_2\) and FeOOH (presented in the Supporting Information, Figure S2) show much smaller curve area. The capacitances estimated from the CV curves for the oxides are about ten times lower than the corresponding TiN and Fe\(_2\)N. CV curves of full device in the range from 0 to 1.6 V at different scan rates are tested in a two-electrode system with TiN as cathode, Fe\(_2\)N as anode, and PVA/LiCl as electrolyte (Figure 5c). The standard rectangle shape verifies a dominating capacitive behavior.\(^{[24]}\) Although there is numerous research work about TiN and Fe\(_2\)N as electrode material for energy storage system applications, the reaction mechanisms were seldom unraveled. Thus, we proposed a possible explanation for the pseudocapacitance with XPS and Raman data as support (see detailed discussion in the Supporting Information). Gravimetric capacitances at different scan rates were calculated based on Figure 5a–c and plotted in Figure 5d. When tested in 1 M LiCl aqueous solution, the individual TiN and Fe\(_2\)N electrodes show high capacitance retention \(\approx 80\%\) and \(\approx 77\%\), respectively, when the scan speed increases from 10 to 100 mV s\(^{-1}\). For the solid-state ASC device, a rather stable capacitance around 60 F g\(^{-1}\) is obtained with less than 2% capacity drop. The improved stabilities of TiN and Fe\(_2\)N in solid electrolyte should be the reason for the higher rate performance of the device compared to that of single electrodes tested in the aqueous electrolyte. Figure 5e shows the galvanostatic charge–discharge curves of the full device between 0 and 1.6 V at four current densities. The linear slopes and triangle shape corroborate the dominating capacitive property of the electrodes in the neutral solid electrolyte, consistent with the CV curves. The single electrodes show similar properties in aqueous electrolyte (Figure S3a,c, Supporting Information). Moreover, both cathode and anode show high stability in 20 000 cycles at 4 A g\(^{-1}\). As for the full device, the cycling property was tested at bending condition from 5000th to 15 000th cycles and then recovered to natural state in last 5000 cycles (Figure 5f). The capacitance profile is nearly flat with a highly reversible capacitance \(\approx 58\) F g\(^{-1}\) up to 2000 cycles and the bending does not affect much the capacitance. The Coulombic efficiency within 20 000 cycles is maintained at about \(100\%\) (Figure S4a, Supporting Information). More details about the bending test are shown in Figure S4b (Supporting Information). The high capacity retention of the device over 20 000 cycles can be ascribed to the structure stability of the electrode material in the gel electrolyte. To confirm this, the morphology of both cathode and anode of the ASCs after 20 000 cycles was checked with SEM (see Figure S5 in the Supporting Information). It is found that the entire electrode structure is well maintained; both the porous structure of TiN and nanoparticle morphology of Fe\(_2\)N are well kept although slight aggregation of Fe\(_2\)N is observed. This confirms the high structure stability of both electrode materials. Nyquist plots of single electrodes and the full device at different cycling stages were tested in aqueous and gel electrolyte, respectively (see Figure S6 in the Supporting Information). Both the single electrode and full device are highly conductive with small
Fe₂N anode (both synthesized on highly conductive graphene nanosheets), and PVA/LiCl neutral electrolyte. The porous structure of TiN and uniform coverage of Fe₂N nanoparticles on the GNS substrates are important merits that account for the outstanding cycling stability (>98% capacity retention in 20 000 cycles) and rate capability (>99% capacity maintenance when scan rate increases from 10 to 100 mV s⁻¹) of the devices. Five devices are tested and show reproducible results. Typical values of the energy density of ≈15.4 Wh kg⁻¹ (=0.51 mWh cm⁻³) and power density of ≈6.4 kW kg⁻¹ (21.4 mW cm⁻²) are obtained. The strategy of combining ALD with ammonia annealing can be extended to other metal nitrides such as SnN, AlN, Zn₃N₂, and Mg₃N₂ for electrochemical energy storage applications.

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

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