Stabilized TiN Nanowire Arrays for High-Performance and Flexible Supercapacitors

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Supporting Information

ABSTRACT: Metal nitrides have received increasing attention as electrode materials for high-performance supercapacitors (SCs). However, most of them are suffered from poor cycling stability. Here we use TiN as an example to elucidate the mechanism causing the capacitance loss. X-ray photoelectron spectroscopy analyses revealed that the instability is due to the irreversible electrochemical oxidation of TiN during the charging/discharging process. Significantly, we demonstrate for the first time that TiN can be stabilized without sacrificing its electrochemical performance by using poly(vinyl alcohol) (PVA)/KOH gel as the electrolyte. The polymer electrolyte suppresses the oxidation reaction on electrode surface. Electrochemical studies showed that the TiN solid-state SCs exhibit extraordinary stability up to 15 000 cycles and achieved a high volumetric energy density of 0.05 mWh/cm³. The capability of effectively stabilizing nitride materials could open up new opportunities in developing high-performance and flexible SCs.

KEYWORDS: Solid-state supercapacitors, flexible, TiN nanowires, polymer electrolyte

Increasing power and energy demands for next-generation portable and flexible electronics such as roll-up displays, photovoltaic cells, and wearable devices has inspired intensive efforts to explore flexible, lightweight, and environmentally friendly energy storage devices.1−4 Flexible solid-state supercapacitors (SCs) represent a new class of energy storage devices that can provide high specific/volumetric energy and power densities for flexible electronics.5−8 Recent efforts have been dedicated to achieve thin, lightweight, and flexible SCs.1,9−12 For example, Kaner et al. developed a class of graphene-based SCs with high power density and excellent cycle stability.1 Wang and co-workers recently developed flexible solid-state SCs based on carbon nanoparticles-MnO₂ nanorods hybrid structure.3 In addition to carbon or metal oxide materials, metal nitrides are emerging as a new and promising electrode material for high-performance supercapacitors due to their excellent electrical conductivity and high capacitance.13−17 Among nitride materials, TiN holds great promise as an electrode material for SCs,18−20 due to its superior electrical conductivity (4000−55500 S/cm)21,22 and mechanical stability.22 However, previous studies found that TiN electrode performed in alkaline electrolyte solution suffered from substantial capacitance loss (28% retention of initial capacitance after 400 cycles18), while the underlying degradation mechanism remains unclear.18,20,23 Fundamental understanding of the mechanism causing the instability of TiN electrode is scientifically important and will provide guidance for experimental efforts to address the limitation. The present experiments reveal not only important insights about the mechanism of TiN degradation but also demonstrate a distinct method that can effectively stabilize TiN nanowire-arrayed electrodes for SCs. Superior electrochemical

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performance was obtained from the TiO2-based solid-state SCs. This work could open up new opportunities in design and fabrication of high-performance and flexible solid-state SC devices.

Free-standing TiN nanowires (NWs) were grown on a carbon cloth by a two-step process (see Methods in the Supporting Information, SI), as illustrated in Figure 1a. TiO2 NWs (Figure 1b). The TiO2 NWs have diameters in a typical range between 100 and 200 nm and lengths about 1.5 μm (Figure S1, SI). These TiO2 NWs were further thermally annealed in ammonia (NH3) at a range of temperatures between 700 and 1000 °C, to convert them to TiN. The color of TiO2 NW film turned from white into black after annealing in NH3 at 800 °C for about 60 min (Figure 1b). SEM images reveal that there is no obvious morphological change in nanowire structure upon thermal treatment between 700 and 1000 °C (Figure 1c,d and Figure S2, SI). Significantly, X-ray diffraction and Raman analyses confirm the transformation of rutile TiO2 to cubic TiN when TiO2 NWs are annealed in NH3 at 800 °C or above (Figure S3 and S4, SI). A high-resolution transmission electron microscopy (TEM) image collected at the NW edge revealed that the NW has a lattice fringes of 0.245 nm, which can be assigned to (111) of the cubic TiN phase (Figure 1d inset), again suggesting the conversion of TiO2 to highly crystalline TiN NWs. Nevertheless, energy dispersive X-ray spectroscopy (EDS) data reveal that the Ti:N:O ratio of 48:41:11. The small amount of oxygen suggests the presence of TiO2 and/or TiOxNy in the TiN NW. Additionally, EDS elemental mapping data show that these elements are uniformly distributed in the NW (Figure S5, SI). Furthermore, X-ray photoelectron spectroscopy (XPS) studies were carried out to determine the changes of surface chemical composition and oxidation state of these samples, as a function of NH3 annealing temperature (Figure S6, SI). XPS survey spectra of TiO2 NWs that annealed in NH3 confirm the presence of N, while no N signal is found for the pristine TiO2 NWs, as expected. The core level N1s spectra collected from TiO2 NWs annealed in NH3 at various temperatures show a broad peak, which can be further deconvoluted into two synthetic peaks. The binding energies of the synthetic peaks centered at 396.5−396.8 eV and 397.6 eV are consistent with the reported values for Ti−N and Ti−N−O, respectively. The relative ratio between the Ti−N and the Ti−N−O peak intensity increases with the increase of annealing temperature, indicating that the degree of nitridation is depending on the annealing temperature. The Ti 2p detail spectrum of the pristine TiO2 exhibits the Ti 2p3/2 binding energy of 459.3 eV that is consistent with typical values reported for TiO2 (ca. 458.6−459.3 eV). Upon annealing in NH3, multiple peaks are evolved at lower binding energies, which can be assigned to be Ti−N (2p3/2 = 455.6−455.9 and 2p1/2 = 461.4−461.8), Ti−N−O (2p3/2 = 457.1−457.5 eV and 2p1/2 = 463.1−463.5 eV), and Ti−O (2p3/2 = 458.7−459.3 eV and 2p1/2 = 464.4−465.0 eV). As the annealing temperature increases, the binding energy of Ti−O shifts toward lower energy due to the formation of Ti3+ as a result of nitridation. The relative peak intensity of Ti−N to Ti−O increases gradually as the increase of annealing temperature, which is consistent with the N 1s spectra. These results reveal that the surfaces of NH3-treated TiO2 NWs are composed of Ti−N−O, Ti−N, and Ti−O chemical states.

To advance the understanding of the interplay between TiN chemical composition and their electrochemical performances, we studied the effect of nitridation temperature on the electrochemical properties of TiN NWs. Cyclic voltammograms (CV) collected from TiO2 and TiN NWs exhibit rectangular shapes, indicating good capacitive behavior (Figure 2a). Significantly, in comparison to pristine TiO2 NWs, the TiN samples exhibit much higher current density. The TiN sample prepared at 800 °C (denoted as TiN-800) yields the highest current density. The specific capacitances of these electrodes are calculated based on their CV curves and plotted as a function of scan rate (Figure 2b). The TiN-800 sample also achieves the highest specific capacitance of 123 F/g at the scan rate of 10 mV/s, which is almost 10 times higher than the value of pristine TiO2 sample. This value is also substantially larger than the values reported for other TiN nanostructures, including nanoparticles (78 F/g, 1 M KOH), TiN-carbon nanotube composite (11.5 F/g, 7.5 M KOH),27 and TiN nanorods (40 F/g, 2 M KOH).28 Furthermore, the TiN-800 sample shows an excellent rate capability with a 64% retention of the initial capacitance when the scan rate increase from 10 to 400 mV/s (Figure S7, SI). This is the best rate capability ever reported for TiN nanostructures,18,20,23,27,28 and it is even comparable to rate-capability obtained from carbon nanostructures with a large surface area.29-31 The excellent capacitance and rate-capability of TiN NW electrodes can be attributed to their unique structural features, including that (1) the highly conductive and macroporous carbon cloth enables efficient charge transport and accessible diffusion of the electrolyte; (2) the direct connection between TiN NWs and carbon fibers without the need of a binder can effectively facilitate the interfacial charge transfer; (3) the free-standing 1D structure offers a large surface area for surface reactions as well as enables fast intercalation/deintercalation of ions; (4) the highly crystalline TiN NWs
have a much higher electrical conductivity than TiO2 NWs and, thus, are favorable for charge transport.

The electrochemical properties of TiO2 and TiN NWs were further studied by galvanostatic charge−discharge measurements. The charge/discharge curves of TiN electrodes collected at a current density of 1.8 A/g are symmetric, indicative of their good capacitive behavior (Figure S8a, SI). Moreover, the iR drop for the TiN samples decrease as the increase of annealing temperatures, as a result of improved electrical conductivity when the degree of nitridation increased. The specific capacitance of TiN-800 sample measured at this current density reaches 117.5 F/g, which is substantially larger than the values reported for other TiN nanostructures as well as other extensively studied supercapacitor electrodes including single-walled carbon nanotubes, graphene, and VN nanostructures, at the same current density. Importantly, the TiN electrodes show excellent specific capacitances even at a higher current density of 5 A/g (Figure S8b, SI), suggesting the electrodes can be used in devices that involve a fast charging/discharging process.

Cycling stability is one of the most important characteristics for high-performance electrode materials. Therefore, we examined the cycling stability of the TiN electrodes by CV test at a scan rate of 100 mV/s. As shown in Figure 2c, the pristine TiO2 electrode shows excellent cycling stability for at least 5000 cycles. In contrast, the specific capacitances of TiN electrodes increase gradually in the first 1000−2000 cycles due to self-activation process, and then suffer from drastic loss of capacitance. The activation time for the TiN electrodes was found to be increased with the increase of annealing temperature, suggesting the self-activation could be related to the increased concentration of nitride and oxynitride on the NW surface. The capacitance retentions for the TiN-800, TiN-900, and TiN-1000 samples at 5000 cycles are measured to be 18.6%, 24.5%, and 65.8%, respectively. While these are the best cycling performance reported for TiN nanostructures, it is clear that substantial improvement of TiN electrochemical stability is essential for practical application.

To understand the origin of the instability of TiN NWs, it is important to study the modifications of NW morphology, chemical composition, and electrical conductivity of TiN-800 electrode during the cycling test. Figure 3 shows the core level Ti 2p and N 1s XPS spectra collected for the TiN-800 electrode at different cycles. While the Ti−O peak intensity increases with the number of cycles, the intensities of TiN and Ti−N−O characteristic peaks decrease continuously. Likewise, the nitride...
and oxynitride N 1s XPS peaks also decrease gradually and consequently disappear after 3000 cycles. These results prove that the instability of TiN electrode is due to irreversible electrochemical oxidation reaction in aqueous solution:

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

\[\Delta G = -137.44 \text{KJ/mol}\]

The formation of the electrochemically less active TiO2 layer causes a significant capacitance loss for the TiN electrode. After 3000 cycles, the TiN-800 electrode becomes stable and exhibit a specific capacitance that is comparable to the TiO2 electrode. Moreover, SEM analysis shows that the TiN NWs become amorphous with an obvious increase in wire diameter as a result of cycling and electrochemical oxidation reactions (Figure S9, SI). Structural pulverization is another possible reason for the capacitance loss. Electrochemical impedance spectroscopy (EIS) measurements were performed to study the effect of oxidation and the structural breakdown on the electrical conductivity of the TiN-800 electrode. The Nyquist plots of the TiN-800 electrode display depressed semicircles in the high frequency region after testing for 750, 1500, and 3000 cycles (Figure S10, SI). These EIS data are fitted by an equivalent circuit (Figure S10a, inset) consisting of the bulk solution resistance (R_s), the charge transfer resistance (R_{ct}), the ion diffusion resistance (R_{dl}), and the double-layer capacitance (Q_c). The R_{ct} for the TiN electrode before cycling and after cycling for 750, 1500, and 3000 cycles were calculated to be 1.1, 6.6, 9.2, and 14.9 Ω, respectively. The gradual increase of the TiN electrode resistance supports the formation of TiO2 on TiN surface and/or the structural breakdown of TiN and, thus, the reduction of capacitance.

The above-mentioned results disclose the key to improve the stability of TiN NWs is suppressing the irreversible electrochemical oxidation reactions and structural pulverization. Our strategy of enhancing the stability of TiN electrodes is using solid-state polymer electrolyte. Polymer electrolyte with a limited amount of water not only can effectively suppress the electrochemical oxidation reaction of TiN but also mechanically stabilize the TiN NWs by retaining their structures and contacts during the cycling. Additionally, in comparison to conventional liquid-based supercapacitors, a solid-state device offers a number of desirable advantages such as ease of handling, scalability, improved safety and flexibility, high reliability, wide operation temperature range, and so forth.

Solid-state symmetric SCs based on TiN-800 NWs (denoted as TiN-SC) were fabricated by sandwiching poly(vinyl alcohol) (PVA)/KOH based solid-state electrolyte between two identical TiN-800 electrodes (Figure 4a). The as-fabricated TiN-SCs are highly flexible and have a typical thickness of ~0.8 mm (Figure 4a, inset). To evaluate the feasibility of these solid-state TiN-SCs for flexible energy storage device, we tested their electrochemical properties under bending conditions. Figure 4b shows that the change of the CV curves collected under different bending angles is subtle, confirming that the device has outstanding mechanical flexibility. The electrochemical stability of the TiN-SCs was examined at a scan rate of 100 mV/s. Significantly, the TiN electrode shows greatly improved stability with an extremely high capacitance retention of 82% after 15 000 cycles (Figure 4c), compared to the same TiN electrode tested in 1 M KOH electrolyte solution. The SEM
images reveal that the structural modification of the TiN electrode after 15,000 cycles is minor compared to the one tested in 1 M KOH solution (Figure S11, SI), suggesting the polymer electrolyte can protect the TiN NWs from structural degradation. Furthermore, core level Ti 2p and N 1s XPS spectra confirm that there is no obvious change in the chemical composition of TiN electrode after testing for 15,000 cycles (Figure S12, SI). These results confirm that TiN electrode can be stabilized by using solid-state polymer electrolyte, which effectively suppress the detrimental electrochemical oxidation and structural pulverization.

Furthermore, it is importantly to make sure the high specific capacitance of the TiN electrode will not be sacrificed by using polymer electrolyte. Figure S13 (SI) shows the galvanostatic charge/discharge curves collected for TiN based supercapacitors with PVA/KOH polymer electrolyte and in a 1 M KOH aqueous electrolyte, at different current densities. In comparison to aqueous TiN-SC, the charge/discharge curves of the solid-state TiN-SC show better symmetry, indicating its superior electrochemical behavior. Significantly, the volumetric specific capacitance of the solid-state device is comparable to the device measured in 1 M KOH solution, at the same current density (Figure 4d). At a current density of 2.5 mA/cm², the volumetric specific capacitance of the solid-state TiN-SC is calculated to be 0.33 F/cm³ (based on the volume of the entire device), which is comparable to the values recently reported for solid-state graphene-based supercapacitors (0.42 F/cm³, PVA/H₃PO₄). Moreover, the TiN-SC has an excellent rate capability, where around 71.6% of initial capacitance is retained even the current density increases by 20 times to 50 mA/cm². This rate capability is also comparable with the value of 75.1% obtained in 1 M KOH solution, indicating that the diffusion of ions in polymer electrolyte is still very efficient. The high-rate capability of the solid-state TiN-SC can also be ascribed to the unique nanostructure with large surface area and high electrical conductivity of TiN NWs, which allow abundant adsorption of ions as well as efficient ion intercalation/deintercalation and charge transport. Noteworthy that the fabrication of solid-state TiN-SCs is binder-free, which enables a low interfacial resistance and fast electrochemical reaction rate compared to the nanoparticle-based electrodes. These results prove that the solid-state TiN-SC maintains its excellent electrochemical performance, while it is effectively stabilized by polymer electrolyte.

Power and energy densities are two important parameters for evaluating the electrochemical performance of a supercapacitor. Figure 4e compares the volumetric power and energy densities of TiN-SC to other reported solid-state supercapacitors. The TiN-SC delivers an energy density of 0.05 mWh/cm³, which is higher than the recently reported multiple walled carbon nanotube-based SCs (0.008 mWh/cm³, PVA/H₂SO₄), single-walled carbon nanotube-based SCs (0.01 mWh/cm³, PVA/H₃PO₄), and slightly lower than the graphene-based SCs (0.06 mWh/cm³, PVA/H₃PO₄). To demonstrate the potential use of these flexible solid-state TiN-SCs, we connected supercapacitor units in series to drive light-emitting-diodes (LED). Each TiN-SC device has the same electrode area of 1 cm² and a potential window of 1.0 V. The electrochemical performances of the tandem TiN-SCs (two or three devices connected in series) were evaluated by charge/discharge measurements (Figure 4f). These tandem devices exhibit an enhanced potential window, which can power red and blue LEDs that have the lowest working potential of 1.5 and 2.5 V, respectively (Figure 4f inset). After charging at 0.5 mA/cm² for 30 s, two devices can power a red LED for more than 15 min, while the three devices can light up a blue LED for more than 6 min. It is expected that the performance of flexible TiN-SCs can be further enhanced by using an ionic-liquid-based gel electrolyte with a wider operation potential, increasing mass loading and optimizing TiN nanostructures, as well as combining with other pseudocapacitive materials.

In summary, we have demonstrated that polymer electrolyte can effectively suppress their electrochemical oxidation reaction and retain their structure, which result in remarkable improvement of the stability of TiN electrode for supercapacitors, without sacrificing their electrochemical performance. The flexible solid-state TiN-SC retains 83% of its initial capacitance after 15,000 cycles. The TiN-SC achieved an excellent volumetric specific capacitance of 0.33 F/cm³ and an energy density of 0.05 mWh/cm³. The demonstration of stabilized metal nitride electrodes could open up new opportunities for flexible solid-state supercapacitors.

ASSOCIATED CONTENT

Supporting Information

Synthetic and analytical methods, capacitive equations, SEM and TEM images, XPS and XRD spectra, CV and charge/discharge curves, and EIS spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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