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TiN@VN nanowire arrays on 3D carbon for high-performance supercapacitors

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We hybridize core-shell-structured metal-nitride nanowires with a 3D carbon substrate. Such electrode demonstrates high volumetric capacitance and good cycling stability, owing to the synergistic integration of titanium nitride and vanadium nitride, as well as the vast surface area and conductive network provided by the microporous 3D carbon structure.

Supercapacitors are energy storage devices offering high power density and low cost.^[1-5] Their performance critically relies on the choices of 1) active materials that ideally should exhibit high and stable electrochemical activities (thus pseudo-capacitance) and high conductivity to ensure low charge transfer impedance, and 2) electrode structures that ideally should be highly conductive for efficient charge transport and large surface area to achieve high power density.

As compared to the commonly used metal oxides, metal nitrides are the emerging active materials for high-performance supercapacitors because of their both high pseudo-capacitance and superior electrical conductivity.^[6-17] Among them, titanium nitride (TiN) and vanadium nitride (VN) has attracted considerable attention.^[18-21] However, the capacitance of these metal nitrides declines quickly in alkaline electrolyte solution due to their ineluctable transformation to oxides (TiO₂ or vanadium oxide (VO)) which is much less conductive and capacitive. To improve the poor cycling stability of TiN, solid-state electrolyte was used to prevent the oxidation of TiN, however, with sacrifice in performance as compared with liquid electrolyte.^[22]

Recently, graphene foam has been used as three-dimensional (3D) electrodes for supercapacitors.^[23,24] Such 3D carbon scaffold provides large surface area for abundant loading of active materials whereby enhancing the specific capacitance. Comparing to the conventional 2D electrodes, 3D

architecture is obviously able to offer much larger areal or volume power density.^[25-39] But graphene foam is fragile and grown by costly chemical vapor deposition (CVD). In addition, its macroporous (>100 μm) structure is occupied by much void spaces which is undesirable for achieving high power density.

Herein, we hybridized core-shell-structured metal-nitride (TiN@VN) nanowires with a 3D carbon substrate. This hybrid electrode demonstrates high volumetric capacitance and good cycling stability. The high capacitance is attributed to the exceptional electrochemical properties of TiN and VN, as well as the vast surface area and conductive network provided by the microporous 3D carbon structure. The improved stability is resulted from preventing transformation of TiN into poorly conductive TiO₂ by the thin shell of vanadium nitride (VN).

Figure 1. Fabrication of 3D carbon@TiN@VN electrode. The scale bars = 0.5 cm

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Fig. 2 SEM images of 3D carbon substrate (A), TiO₂ nanowires on 3D carbon (B and C), TiN@VN nanowires on 3D carbon (D). TEM images of TiN@VN nanowire (E and F). Elemental mapping of Ti (G) and V (H) elements on the TiN@VN nanowire.

The fabrication process is illustrated in Fig. 1. Firstly, the commercially available cotton pad was dip-coated with graphene oxide (GO) solution (5 mg mL⁻¹), followed by annealing at 1000 °C in the argon atmosphere in order to reduce GO and carbonize the cotton. The resulting carbon structure exhibits a high conductivity (~47 ohms cm⁻²) and highly resistant to acid or alkali conditions. As revealed by scanning electron microscopy (SEM), the 3D carbon is interwoven of carbon nanofibers and microporous (Fig. 2A). TiO₂ nanowires (~100 nm in diameter, ~2 μm in length) array (NA) were then densely grown on the carbon substrate (Fig. 2B and C) through a hydrothermal method reported elsewhere.^[22] Subsequently, an ultrathin layer (a few nm) of vanadium oxide (VO) was coated conformally around individual TiO₂ nanowires using another hydrothermal procedure (Fig. 2D and E).^[40] Finally, annealing in ammonia atmosphere at 850 °C for 3 h converted TiO₂@VO to TiN@VN nanowire arrays. All the Bragg peaks in X-ray diffraction (XRD) pattern of the annealed sample can be unambiguously indexed to TiN (JCPDS No.38-1420) and VN phase (JCPDS No.35-0768) (Fig. S1 in ESI). The high-resolution transmission electron microscopy (TEM) TEM (HRTEM) reveals the perfect crystalline structure of the outer VN shell with an interplanar distance of ~0.235 nm corresponding to the (111) plane of VN (Fig. 2F). The boundary between core-shell and the different crystalline orientation of TiN are clearly visible. The hybridized core-shell structure (TiN nanowire homogeneously coated with an ultrathin VN shell) was further confirmed by elemental mapping of Ti and V (Fig. 2G and H).

Cyclic voltammograms (CV) between 0.2 V and -0.6 V of the 3D carbon@TiN@VN electrode was measured in a three electrode system at various scan rates in 1 M KOH electrolyte (Fig. 3A). One pair of redox peaks can be clearly resolved at -0.1 V and -0.22 V, respectively, which correspond to the transformation between the II, III and IV ionization states of

vanadium.^[41,42] From the charge-discharge voltage profile (Fig. 3B), the volumetric specific capacitance (C_s) is calculated according to the equation $C_s = (I \times \Delta t) / (V \times \Delta V)$, where I is the constant discharge current, Δt is the discharge time, V is the volume of the electrode, ΔV is the voltage difference between the voltage after ohmic drop at the beginning of discharging and the voltage at the end of discharging.^[43] The specific capacitance of 3D carbon@TiN@VN electrode is found to be as high as ~0.64 F cm⁻² (RSD = 7.3%, n=5) (corresponding to volumetric C_s of ~6 F cm⁻³, RSD = 3.1%) at the current density of 1 mA cm⁻². The mass capacitance is ~198.3 F g⁻¹ at a current density of 5 A g⁻¹. Even at a high current density of 10 mA cm⁻², the C_s still reaches 0.52 F cm⁻², suggesting the feasibility for fast charging/discharging.

Fig. 3 (A) CVs of 3D carbon@TiN@VN electrode at various scan rates. (B) Charge-discharge curves of 3D carbon@TiN@VN at different current densities. (C) Comparison of charge-discharge curves from TiO₂, TiN or TiN@VN nanowires on 3D carbon at 1 mA cm⁻². (D) The cycling stability of the volumetric specific capacitance of 3D carbon@TiN@VN and 3D carbon@TiN at 5 mA cm⁻².

In comparison, the C_s values of 3D carbon@TiN and 3D carbon@TiO₂ electrodes are largely reduced (0.58 F cm⁻² and 0.35 F cm⁻², respectively) (Fig. 3C).

The cycling stability of 3D carbon@TiN@VN electrode was examined by chronopotentiometry at a current density of 5 mA cm⁻². As shown in Fig. 3D, C_s largely retains even after 4000 cycles. The decay of C_s demonstrates two phases: <5% capacitance loss after the first ~2000 cycles; a steeper loss (~14%) in the second phase. In remarkable contrast, the C_s of 3D carbon@TiN electrode degenerates rapidly during cycling, similar to the previous observation.²² As revealed by X-ray photoelectron spectroscopy (XPS) before and after 2000 cycles, such drastic decay is accompanied by the conversion of TiN to TiO₂ (Fig. S2 in ESI). XPS snapshots of 3D carbon@TiN@VN electrode at different cycle numbers show that the VN thin-layer evolves essentially to VO after 1000 cycles as evidenced by the right-shift of the V 2p³ peak (Fig. S3 in ESI).^[44,45] On the other hand, Ti-N peak remains essentially unaltered in the first 2000 cycles while it completely converts to Ti-O peak after 4000 cycles (Fig. S4 in ESI). Consistently, after 4000 cycles, the N 1s peak in XPS spectrum disappears, indicating the complete conversion from nitrides to oxides (Fig. S5 in ESI). As expected, the electrode impedance greatly increases after 4000 cycles because of the poor conductivity of metal oxides (Fig. S6 in ESI). Taken together, the first phase of C_s decay of 3D carbon@TiN@VN is mainly due to transformation of VN shell to VO shell while the second phase is resulted from transformation of TiN core to TiO₂.

The good capacitive performance of our hybrid electrode is attributable to the synergistic integration of two types of metal nitrides. As shown above, TiO₂ nanowires provide low capacitance (Fig. 3c) while TiN nanowires without shell are poorly stable because of their transformation to less conductive TiO₂ (Fig. 3d). It has also been previously shown that CNT@VN composites exhibit poor cycling stability.^[32] The comparison between our electrode and these previous reported electrodes is given in table S1 (ESI). Here, VN shell plays dual roles. Firstly, transition between different ionization states of the mixed-valence vanadium element offers large pseudo-capacitance; secondly, VN shell protects TiN from being oxidized. On the other hand, TiN nanowires firstly serve as the highly-conductive electron collectors, and secondly may contribute to the total capacitance given the thin thickness of VN shell. Furthermore, the microporous 3D carbon substrate provides large (active) surface area and multiplexed conduction networks.

Experimental Section

Preparation of conductive 3D carbon

The cotton was sunk in 5 mg mL⁻¹ graphene oxide (GO) solution for 3 hours. The cotton fibers coated by GO were dried in vacuum oven at 80 °C for 12 hours and repeated 5 times. Then the pretreated cotton was heated in tube oven in the argon at 1000 °C for 1 hour.

Preparation of nanowires array of TiO₂ growth on the 3D carbon (3D carbon @TiO₂)

Nanowires array of TiO₂ was grown on the 3D carbon substrate as literature previously reported.^[1] For example, the 3D carbon substrate was immersed into the 0.2 M titanium isopropoxide of HCl solution and sealed in the autoclave and heated at 150 °C for 20 h. The product was washed completely with DI water and dried in vacuum oven at 80 °C for 12 hours.

Coating an ultrathin layer of vanadium oxide (VO)

3D carbon@TiO₂ was placed in the 12 mM vanadium isopropoxide/isopropanol alcohol solution and sealed in the autoclave and heated at 180 °C for 12 hours. The product was dried in the 80 °C for 12 hours.

Converting TiO₂@VO to TiN@VN

3D carbon@TiO₂@VO was finally converted to 3D carbon@TiN@VN by annealing in tube oven with NH₃ flow at 850 °C for 3 h.

Characterization

The morphology of the samples was examined by field-emission scanning electron microscope (FE-SEM, JSM-6700F) and transmission electron microscope (TEM, Tecnai G² 20). The XRD patterns were obtained using Rigaku D/max 2400 X-ray diffractometer equipped with graphite monochromatized Cu K α radiation (λ = 1.5406 Å; scan rate = 0.02 °s⁻¹). Using a CHI-660D electrochemical workstation (Chenhua), the electrochemical measurements were carried out in a three-electrode system with 1.0 M KOH as the electrolyte solution.

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Entry for the Table of Contents

COMMUNICATIONS

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Page No. – Page No.

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