A V$_2$O$_5$/Conductive-Polymer Core/Shell Nanobelt Array on Three-Dimensional Graphite Foam: A High-Rate, Ultrastable, and Freestanding Cathode for Lithium-Ion Batteries

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Lithium-ion batteries (LIBs), the most important and widely used rechargeable batteries, have the advantages of high working voltage, high capacity, low toxicity and long cycling life. Most applications require LIBs with both large energy density and high power density. LIBs with high energy densities rely largely on positive-electrode (anode) materials that need to have large capacities and/or high working voltages. Generally, a further increase in capacity of the positive electrode will require multi-electron insertion and extraction reactions. Currently, the most-studied positive-electrode materials can only reversibly accept one electron and deliver capacities lower than 200 mA h g$^{-1}$. However, vanadium pentoxide, V$_2$O$_5$, can capture multiple electrons and has a high capacity of 294 mA h g$^{-1}$ in the voltage range of 4.0−2.0 V (vs Li/Li$^+$). Because of its layered crystal structure along the c-axis, V$_2$O$_5$ serves as a good host for reversible Li$^+$ insertion/extraction according to the simplified reaction V$_2$O$_5$ + xLi$^+$ + xe$^-$ ↔ Li$_x$V$_2$O$_5$. Moreover, V$_2$O$_5$ has the advantage of low cost and high abundance in the Earth’s crust. Unfortunately, up to now, the performance of the bulk V$_2$O$_5$ LIB electrode has been hindered by its poor cycling stability and rate capability owing to its low Li$^+$ diffusion coefficient (ca. 10$^{-12} \text{cm}^2 \text{s}^{-1}$) and moderate electrical conductivity (10$^{-5}$−10$^{-8} \text{S cm}^{-1}$).

The general approaches to enhancing the energy and power densities include constructing three-dimensional (3D) porous electrodes with a conductive backbone, fabricating nanometer-scale architectures with short ion/electron transportation paths, and coating a conductive layer on active materials. So far, numerous V$_2$O$_5$ nanostructures have been prepared and decent electrochemical performance has been demonstrated in these systems (see a complete list in Table S3 in the Supporting Information). V$_2$O$_5$-based composite materials with nanocarbon have also been reported, for example, V$_2$O$_5$/carbon (porous carbon, carbon nanotubes, and reduced graphene oxide, rGO) and V$_2$O$_5$/conducting polymer. However, in all this work, the V$_2$O$_5$ is in powder form and thus needs to be mixed with additives (e.g., carbon black) and polymer binders, and finally compressed onto a current collector (Al foil). The extra weight of additives, polymer binders, and metal substrates decreases the energy and power density of the whole electrodes.

Recently, a new electrode design strategy has been exploited to fabricate integrated, binder-free, and lightweight LIB electrodes by directly depositing active materials on self-supported 3D porous carbon materials. Among them, chemical vapor deposition (CVD)-derived 3D graphene foam (also called ultrathin graphite foam, UGF) appears to be an excellent backbone for constructing high-rate binder-free electrodes. CVD–UGF has good electrical conductivity (ca. 1000 S m$^{-1}$), a high porosity of ca. 99.7%, a low density (ca. 0.6 mg cm$^{-3}$), and a large specific surface area (ca. 850 m$^2$ g$^{-1}$). However, to date, there is no report on an integrated positive LIB electrode prepared by direct growth of V$_2$O$_5$ nanorays onto UGF.

In this Communication, we report lightweight, freestanding V$_2$O$_5$ nanoray-based positive electrodes prepared by growing a V$_2$O$_5$ nanobelt array (NBA) directly on 3D UGF, followed by coating the V$_2$O$_5$ with a mesoporous thin layer of the conducting polymer poly(3,4-ethylenedioxythiophene) (PEDOT). This is an “all-in-one” highly integrated electrode. We highlight the following features: i) The 3D porous CVD-UGF acts as both a lightweight scaffold for the growth of V$_2$O$_5$ NBAs, and an efficient current collector. ii) To our best knowledge, it is the first time that a V$_2$O$_5$ nanoray has been fabricated directly on various substrates (including GF, carbon cloth, and indium tin oxide (ITO)/glass). The nanoray architecture is considered more desirable than powder nanostructures in terms of shorter Li$^+$ diffusion paths and more direct electron transport. Moreover, the array architecture is favorable for accommodating the strain caused by the Li ion insertion/extraction and alleviating the nanostructure deterioration. iii) One key point of this work is the conductive PEDOT layer coating without any additional surfactant (such as p-toluenesulfonic acid, p-TSA). This thin
homogeneous layer facilitates the electron transfer around the $V_2O_5$ and also preserves the whole array structure during long-term cycling. More importantly, the introduction of PEDOT can decrease the polarization of electrodes and prolong the discharge plateau above 3.0 V, resulting in an increased proportion of high-voltage capacity and energy density. With these merits, our 3D UGF$^{-}$/$V_2O_5$/PEDOT core/shell NBA exhibits superior high-rate capability and cycling stability. Our results push the promising $V_2O_5$-nanostructure LIB electrode an important step forward into practical applications.

Figure 1a–c show the fabrication process of the integrated UGF$^{-}$/$V_2O_5$/PEDOT core/shell NBA electrode. The CVD-derived UGF is directly used as a 3D porous scaffold for the solvothermal synthesis (SS) of $V_2O_5$ nanobelts, which are coated by a PEDOT shell via a facile electro-deposition (ED) method. The obtained UGF exhibits a continuous and interconnected 3D network with branches of 60–100 µm and macropores of 150–500 µm, and no evident cracks are observed (Figure 1d and Figure S1a in the Supporting Information). The UGF is self-supported and needs no additional structural supporting agent such as poly(methyl methacrylate) (PMMA), which would otherwise reduce the electrical conductivity of the UGF.$^{[17]}$ In our case, the as-prepared UGF is very light, with a density of ca. 0.6 mg cm$^{-2}$, much lower than metal foams (e.g., 10–15 mg cm$^{-2}$ for nickel and copper foams). After the solvothermal synthesis, the UGF is uniformly covered by a quasi-vertically aligned array of $V_2O_5$ nanobelts. Interestingly, the nanobelts form an “arrow-tail”-like hierarchical structure that is made of ca. 4 secondary belts interconnected along the common axis, each with a thickness of ca. 15 nm (Figure 1f and Figure S1b, Supporting Information). In the array structure, each nanobelt is in contact with the UGF and thus can participate in the electrochemical reactions. The sample exhibits a greenish yellow color after loading of $V_2O_5$ nanobelts (Figure 1g). After electro-deposition (ED) of PEDOT, the color of the sample changes to black (Figure 1i). Importantly, the PEDOT thin layer is deposited homogeneously on the surface of each $V_2O_5$ nanobelt, and the hierarchical structure is also maintained (Figure 1h). Noticeably, both the UGF$^{-}$/$V_2O_5$ and UGF$^{-}$/$V_2O_5$/PEDOT samples have sufficient mechanical...
stability and good flexibility (Figure S2, Supporting Information); The samples can be bent without any protective case and will not break, nor will the array layer peel off during repeated bending. Hence, they can be applied as freestanding electrodes without the need for conventional polymer binders, additives, and metal substrates. We have also fabricated the V$_2$O$_5$/PEDOT core/shell NBA on other conductive substrates, including ITO glass and carbon cloths (Figure S3, Supporting Information), which proves the versatility of our synthesis method.

The detailed microstructure of the sample at different stages was analyzed using transmission electron microscopy (TEM) and high-resolution TEM (HRTEM). The ultrathin membrane structure of the CVD–UGF can be seen from the low-resolution TEM image (Figure 2a). The corresponding selected area electronic diffraction (SAED) pattern is a hexagonal pattern characteristic of graphitic samples.$^{[19]}$ The lattice spacing of ca. 0.34 nm corresponds to the (002) planes of graphitic carbon (JCPDS 75–1621) (Figure 2b). Figure 2c shows the hierarchical structure of one of the V$_2$O$_5$ nanobelts, in which the secondary belts are interconnected with each other (the dark lines correspond to the joint axes). The measured lattice spacing of 0.57 nm in the HRTEM image (Figure 2d) is in good agreement with the (200) interplanar distance of the orthogonal V$_2$O$_5$ phase (JCPDS 41–1426). Furthermore, the HRTEM analysis and the fast Fourier transform (FFT) pattern reveal that the V$_2$O$_5$ nanobelts are single crystalline. The growth mechanism of the V$_2$O$_5$ nanobelts is suggested to be a “self-assembly” processes along the preferred crystallographic orientation.$^{[23]}$ It was also simulated by chemical bonding theory of single-crystal growth that V$_2$O$_5$ prefers to form nanobelts along the $b$-axis.$^{[24]}$

After electro-deposition of PEDOT, the V$_2$O$_5$ nanobelts are intimately wrapped by a uniform and mesoporous PEDOT shell with a thickness of about 15 nm (Figure 2e). The HRTEM result and FFT pattern (insets in Figure 2f) reveal that the PEDOT shell is amorphous in nature. As for the V$_2$O$_5$ core, the FFT pattern and lattice fringes (interplanar

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**Figure 2.** TEM characterization. a,b) UGFs. Inset: SAED pattern. c,d) V$_2$O$_5$ nanobelts. Insets: Low magnification TEM image (c) and FFT pattern (d). e,f) V$_2$O$_5$/PEDOT core/shell nanobelt. Insets: HRTEM images and FFT patterns.
distance of 0.57 nm) are similar to that of the pure V$_2$O$_5$ nanobelt shown above. This core/shell heterostructure is also clearly verified by energy dispersive X-ray spectroscopy (EDS) elemental mapping of C, S, V, and O and the EDS spectrum (Figure S4, Supporting Information). More evidence about the phase and composition of the products are provided by the X-ray diffraction (XRD), Raman, and X-ray photoelectron spectroscopy (XPS) results (see Figure S5 and S6 in the Supporting Information, and the associated discussion in the Supporting Information). All in all, it can be concluded that we have successfully fabricated the integrated electrode, using the combination of solvothermal synthesis and electrodeposition.

Detailed electrochemical tests were conducted to investigate the lithium ion storage performance of half-cell coin batteries based on the UGF–V$_2$O$_5$/PEDOT core/shell NBA positive electrode and Li foil negative electrode. As a comparison, all the tests were conducted in parallel to the pure V$_2$O$_5$ NBA sample in order to disclose the important role of PEDOT coating. Figure 3a shows typical cyclic voltammetry (CV) curves at a scan rate of 0.2 mV s$^{-1}$ at the 5th cycle in the voltage range from 4.0 to 2.0 V (vs Li/Li$^+$). Both positive electrodes exhibit three main redox couples, but the peak current densities of the UGF–V$_2$O$_5$/PEDOT electrode are much stronger than those of the UGF–V$_2$O$_5$ one. This higher peak current density indicates that the former has a higher electrochemical reactivity and higher capacity than the latter. Taking the CV curve of the UGF–V$_2$O$_5$/PEDOT core/shell NBA electrode for example, the first reduction peak at ca. 3.36 V is due to the conversion from α-V$_2$O$_5$ into ε-Li$_0.5$V$_2$O$_5$. Then reductions take place at ca. 3.15 V and ca. 2.17 V, corresponding to the formation of δ-LiV$_2$O$_5$ and γ-Li$_2$V$_2$O$_5$, respectively. These reactions are reversible and contribute to a large capacity. Further reduction corresponds to the formation of the irreversible ω-Li$_x$V$_2$O$_5$ ($x > 2$) phase, which is detrimental to the cyclic capacity retention. Thus, we narrowed the voltage range to 4.0–2.0 V (vs Li/Li$^+$). The simplified electrochemical reactions can be expressed as:

$$\begin{align*}
\text{V}_2\text{O}_5 + 0.5 \text{ Li}^+ + 0.5 \text{ e}^- & \leftrightarrow \alpha\text{-Li}_0.5\text{V}_2\text{O}_5 \quad (1) \\
\varepsilon\text{-Li}_0.5\text{V}_2\text{O}_5 + 0.5 \text{ Li}^+ + 0.5 \text{ e}^- & \leftrightarrow \delta\text{-LiV}_2\text{O}_5 \quad (2) \\
\delta\text{-LiV}_2\text{O}_5 + \text{Li}^+ + \text{e}^- & \leftrightarrow \gamma\text{-Li}_2\text{V}_2\text{O}_5 \quad (3)
\end{align*}$$

It is clearly shown in the CV curves that the introduction of PEDOT on the surface of V$_2$O$_5$ nanobelts effectively enhanced the electrochemical reactivity of the reactions in Equation 1 and 2. The PEDOT network has an electrical conductivity of ca. 400 S cm$^{-1}$ (measured by four-point probe). Therefore it is anticipated that the homogeneous conductive coating can improve the charge transfer and collection, and also diminish the polarization. These factors are expected to improve the capacity. Indeed, the capacity enhancement is confirmed by the charge–discharge curves in Figure 3b (300 mA g$^{-1}$ is equivalent to 1 C, which is
defined as discharging the entire capacity of \( Li_2V_2O_5 \) in 1 h at a current density of 300 mA g\(^{-1}\). Three discharge plateaus (ca. 3.4, 3.2, and 2.3 V) are noticed for both electrodes, which is consistent with the CV result. Apparently, the UGF–V\(_2\)O\(_5\)/PEDOT core/shell NBA electrode exhibits lower charge voltage plateaus and higher discharge voltage plateaus than the UGF–V\(_2\)O\(_5\) NBA sample. This would correspond to a higher energy density of the UGF–V\(_2\)O\(_5\)/PEDOT NBA electrode. A ca. 98% initial coulombic efficiency can be obtained for the UGF–V\(_2\)O\(_5\)/PEDOT electrode. The efficiency remains close to 100% during the following cycles, which implies an excellent reversibility of the electrode (Figure S7a,b in the Supporting Information).

In order to achieve high power densities, a high rate capability is essential. Figure 3c shows the high-rate (1–80 C) capability properties for both NBA electrodes. (Typical discharge curves at different current densities are shown in Figure S7 in the Supporting Information) Evidently, the UGF–V\(_2\)O\(_5\)/PEDOT core/shell NBA electrode exhibits lower charge voltage plateaus and higher discharge voltage plateaus than the UGF–V\(_2\)O\(_5\) NBA sample. This would correspond to a higher energy density of the UGF–V\(_2\)O\(_5\)/PEDOT NBA electrode. A ca. 98% initial coulombic efficiency can be obtained for the UGF–V\(_2\)O\(_5\)/PEDOT electrode. The efficiency remains close to 100% during the following cycles, which implies an excellent reversibility of the electrode (Figure S7a,b in the Supporting Information).

One of the key features of our integrated \( V_2O_5 \) electrode is a high capacity in the high-voltage range. A higher discharge voltage plateau is favorable for the energy density of the batteries, as it means more energy that the electrodes can release. The UGF–V\(_2\)O\(_5\)/PEDOT core/shell NBA electrode delivers a specific capacity of 297 mA h g\(^{-1}\) at 1 C rate, which is comparable to those in the literature (see Figure 3c and Table S3 in the Supporting Information). However, the discharge capacity in the high-voltage regime (3.0–4.0 V) is greatly improved in the core/shell NBA system; the high-voltage capacity accounts for ca. 62% of all the capacity between 2.0 and 4.0 V (vs Li/\( Li^+ \)). This percentage is much larger than for the UGF–V\(_2\)O\(_5\) electrode without PEDOT coating (ca. 44%). For comparison with all \( V_2O_5 \)-based nanostructure electrodes reported in the literature, a plot of high-voltage capacity percentage versus capacity is constructed in Figure 4a (based on raw data in Table S3). The reason for this improvement could also be ascribed to the enhanced active material utilization of \( V_2O_5 \) and conductivity of the whole electrode brought about by the PEDOT coating.

As a result of the high-rate capability and fast kinetics, our LIB electrodes demonstrate outstanding power densities. The Ragone plot in Figure 4b illustrates the performance of our electrodes (the total mass of the positive electrode was used for the calculation of energy and power densities). Because of the judicious material and structure design, our UGF–V\(_2\)O\(_5\)/PEDOT core/shell NBA electrode indeed shows the merits of both LIB and supercapacitors. For example, an energy density of ca. 238 Wh kg\(^{-1}\) at a power rate of 23 kW kg\(^{-1}\) is achieved, which is higher than that of the UGF–V\(_2\)O\(_5\) counterpart (ca. 131 Wh kg\(^{-1}\) at 23 kW kg\(^{-1}\)) and also other reported \( V_2O_5 \) related materials.\(^{[27]}\) These high-rate values are even much higher than those of reported aqueous-system supercapacitors (usually lower than 60 Wh kg\(^{-1}\)).\(^{[10,28]}\) The comparison in...
Figure 4 unambiguously demonstrates that our UGF−V₂O₅/PEDOT core−shell NBA electrodes indeed have an outstanding performance in terms of both energy and power densities. Finally, our UGF−V₂O₅/PEDOT integrated electrodes exhibit outstanding cycling stability even at high rates. The capacity profiles are nearly flat at discharging rates of both 5 C and 60 C with little decay (Figure 5a,b); a specific capacity of 265 mA h g⁻¹ is maintained at 5 C after 500 cycles, and 163 mA h g⁻¹ after 1000 cycles at 60 C (which is ca. 98% of the highest value). In contrast, the UGF−V₂O₅ NBA electrode without polymer coating shows obvious capacity degradation, with a specific capacity of only 164 mA h g⁻¹ at 5 C after 500 cycles and 52 mA h g⁻¹ at 60 C after 1000 cycles (capacity retention of ca. 60%). The morphologies of the nanobelts from both electrodes after cycling at 60 C for 1000 cycles were checked by SEM and TEM (Figure S8a,b in the Supporting Information). It is observed that the core/shell crossed nanobelt architecture is well preserved without obvious deformation, whereas for the bare V₂O₅ electrode, the nanobelts tend to aggregate and expand (Figure S8c,d, Supporting Information). Such structural stability of the UGF−V₂O₅/PEDOT electrode accounts for its high capacity retention particularly at high current rates. To demonstrate the applications, we show that one coin cell based on the UGF−V₂O₅/PEDOT NBA electrode. Before this test, the cell had been charge/discharge cycled 1000 times at 60 C.

Figure 5. a,b) Cycling performance at high current densities. c) Photograph of 10 green LEDs powered by one coin cell based on the UGF−V₂O₅/PEDOT NBA electrode. Before this test, the cell had been charge/discharge cycled 1000 times at 60 C.

From the comparative results above, it can be inferred that the coating of a mesoporous PEDOT layer in the core/shell structure not only provides a good charge conductive path for the V₂O₅ NBA, but may also act as a soft “armor” to protect the V₂O₅ core from pulverization. As a flexible organic material, the PEDOT shell may accommodate the strain resulting from lithiation/delithiation cycles and stabilize the whole structure during the high-rate cycles. These two functions ideally compensate the drawbacks of V₂O₅ as a LIB cathode. Indeed, our UGF−V₂O₅/PEDOT core/shell NBA electrode outperforms most V₂O₅-based nanostructure electrodes in the literature (see detailed comparison in Table S3). It should be mentioned that the UGF alone shows no capacity in the voltage range of 2.0−4.0 V and that the PEDOT directly deposited on UGF (i.e., UGF−PEDOT) has small but ultrastable capacities of 32 mA h g⁻¹ at 1 C and 15 mA h g⁻¹ at 60 C (Figure S9, Supporting Information). This justifies that the PEDOT is an excellent structural stabilizer for the V₂O₅. In a nutshell, our UGF−V₂O₅/PEDOT core/shell NBA electrodes have an excellent lithium ion storage property with high power density and high energy density, as well as superior high-rate cycling stability.

In summary, we have designed and successfully fabricated a V₂O₅/PEDOT core/shell nanobelt array (NBA) on ultrathin graphite foam (UFG) as self-supported, binder-free positive electrodes. This is the first time that direct growth of V₂O₅ nanoarrays on current collectors has been realized. Such integrated electrodes exhibit ultrafast and stable Li ion storage performance, with higher capacities and improved rate and cycling capabilities than the bare V₂O₅ NBA on UFG. High specific capacities of 265 mA h g⁻¹ at 5 C and 168 mA h g⁻¹ at 60 C are achieved, which can maintain 98% of their values up to 1000 cycles. The key role of the PEDOT shell is explained as facilitating the charge transfer and hence the reaction kinetics, and also preserving the NBA structure.
Supporting Information

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

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