

Coaxially Coated Vertical Carbon Nanofiber Arrays as 3D Multifunctional Electrodes for Battery-Supercapacitor Hybrids

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Objective:

The objectives of this proposed work are: (1) establishment of the fabrication of a set of unique hierarchical electrode materials by combining dissimilar functional nanomaterials in a unique three-dimensional (3D) architecture which forms ternary vertical nanowire arrays; (2) study of their properties for electrical energy storage in a battery-supercapacitor hybrids based on lithium chemistry; and (3) development of scalable production strategies for such high-performance energy storage technologies.

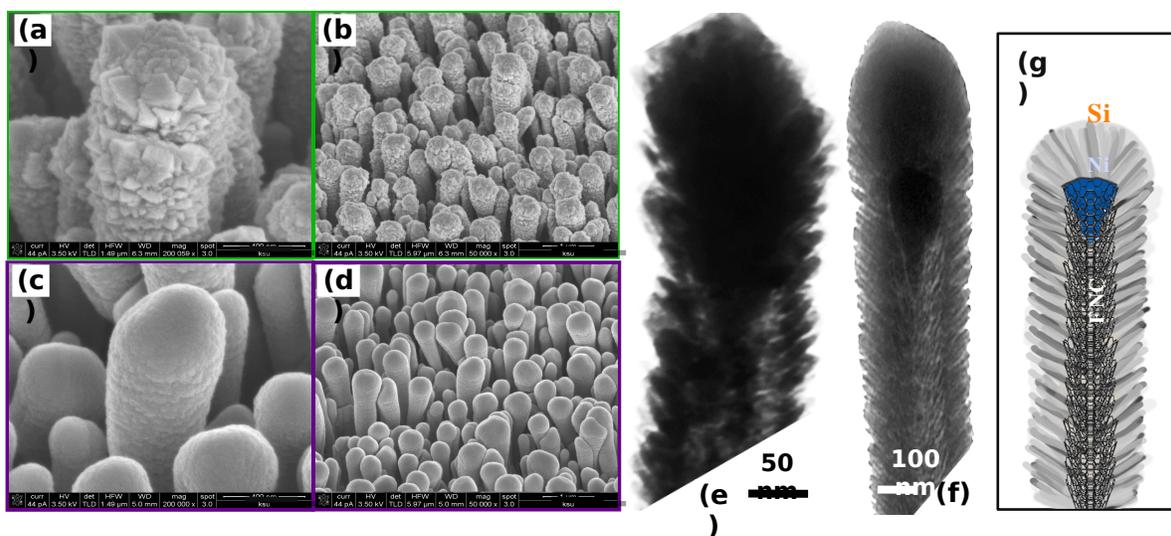


Fig. 1 SEM images of the core-shell structure of (a) & (b): TiO₂; and (c) & (d) Si deposited on vertically aligned carbon nanofibers by ion beam sputtering. TEM images of the nanocolumnar structure of the (e) TiO₂ and (f) Si shells on the carbon nanofibers. (g) Schematic of the hierarchical structure of the Si/VACNF anode. The scale bars are 200 nm in (a) & (c), and 1 μ m in (b) & (d).

Methods:

This work takes an approach of stepwise assembly of nanomaterials with different functionalities in a hierarchical vertical nanofiber array. The proposed ternary structure was fabricated on a nanostructured template, i.e. a vertically aligned carbon nanofiber (VACNF) array that is grown on a proper metal foil with plasma enhanced chemical vapor deposition (PECVD). In the last years, the project has been focused on the study of two types of materials, i.e. TiO₂ as Li-ion battery cathode and Si as Li-ion battery anode. Both of them were deposited on 5 μ m long VACNF arrays by magnetron ion sputtering. The highly conductive VACNFs serve as both a 3D brush-like nano-template and a good current collector. The nanostructured shell significantly reduces the diffusion path length and enables fast reactions for supercapacitors and Li-ion batteries. The combination of the stable VACNF core and conductive polymer outer layer makes

it possible to accommodate the large volumetric change of the shell materials during charge-discharge cycles. Combining these two types of electrodes into a full cell forms an interesting battery-supercapacitor hybrid cell which behaves similar to an asymmetric supercapacitor based on lithium chemistry. Optimum performance with high power, high capacity and long cycle life can be achieved by tuning the charge balance between these two electrodes.

Highlight of Results:

Hierarchical Structure of the Electrodes: After ion sputtering of 500 nm nominal thickness of TiO₂ or Si, the deposits are found to spread along the whole CNF forming tapered shells with ~50 to 200 nm radial thickness (see Fig. 1a-d). Interestingly, the shell is not a solid layer. Instead, it consists of nanocolumns of ~50 to 200 nm in length and 20-30 nm in diameter, which are obliquely anchored on the sidewall of the CNF (see Fig. 1e-g). Such nanocolumnar structure is a result of the low substrate temperature (T_s) relative to the melting temperature of the deposits (T_m), i.e. $T_s/T_m < 0.3$, following the Thornton's Structural Zone Model. The nanocolumnar structure is further enhanced by the glancing incident angle at which the target flux impinges the vertical sidewall of the CNFs. In Li-ion batteries, the nanocolumnar shell on VACNFs form a hierarchical structure which has unique advantages in accommodating the large volumetric expansion/contraction and enhancing the charge-discharge rate. The voids between the nanocolumns allow Li⁺ to access the whole shell through the liquid electrolyte which has a 7 orders of magnitude larger diffusion coefficient than solid Si materials, i.e. $\sim 3 \times 10^{-14}$ cm²/s in bulk Si and 5.1×10^{-12} cm²/s in nanostructured Si vs. $\sim 1 \times 10^{-5}$ cm²/s in organic electrolyte.

Half-cell Performance: The hierarchical electrode structure indeed showed dramatic enhancements in the electrode performance. For Si/VACNF anodes, three important properties have been demonstrated: (1) An extremely high specific Li storage capacity of ~3,000 to 3,500 mAh/g_{Si} (normalized to the Si mass) has been obtained, matching the maximum reported experimental value for amorphous Si. (2) The specific capacity was almost invariant as the C-rate was increased from C/2 to 5C, and even slightly increased as the C-rate was further increased to 8C. Such high charge-discharge rate and the anomalous increase at high C-rates was not observed in other studies with Si nanowires and other nanostructured Si anodes. (3) More importantly, the electrode is remarkably stable with >99% Coulombic efficiency over 500 cycles. For TiO₂/VACNF core-shell electrodes, the specific Li storage capacity was about 197 mAh/g_{TiO₂} (normalized to the TiO₂ mass), also matched the theoretical full capacity of TiO₂, but is significantly lower than that of Si anode. High-power characteristics similar to Si/VACNF was obtained. The electrode remained stable even at 32C rate over hundreds cycles.

Battery-supercapacitor Hybrid: By combining the

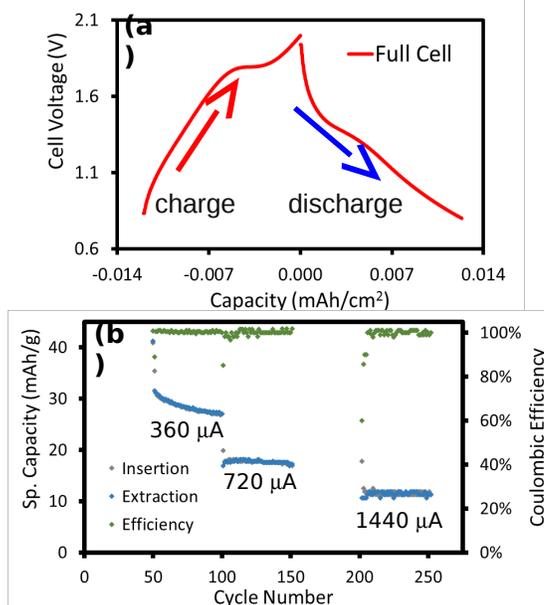


Fig. 2 (a) The representative charge-discharge curve of a full cell consisting of a 18-mm dia. TiO₂/VACNF cathode (0.42 mg TiO₂) and a 18-mm dia. Si/VACNF anode (0.25 mg Si) at 180 µA charge-discharge current. (b) The specific capacity (normal to the total mass of TiO₂ and Si) during Li insertion/extraction and the corresponding Coulombic efficiency over long cycles at different currents.

TiO₂/VACNF cathode and Si/VACNF anode, we have demonstrated a full Li-ion battery cell which behaves as an asymmetric supercapacitor. From the half-cell tests, the 18-mm diameter TiO₂/VACNF cathode has a total Li storage capacity of 83 μAh (197 mAh/g_{TiO₂} multiplied by 0.42 mg TiO₂) at a current of 45 μA (~C/2 rate) as the electrode is charged and discharged between 1.0 and 2.5 V. The capacity drops to 61 μAh (146 mAh/g_{TiO₂} multiplied by 0.42 mg TiO₂) as the current is increased to 180 μA (~2C rate). In contrast, the 18-mm diameter Si/VACNF anode provides 800 μAh (3,200 mAh/g_{Si} multiplied by 0.25 mg Si) at a current of 180 μA (~C/4 rate) as the electrode is charged and discharged between 0.050 and 1.5 V. Importantly, the capacity only drops by ~7% to 746 μAh (2,985 mAh/g_{Si} multiplied by 0.25 mg Si) as the current is increased by 25 times to 4.5 mA (~5C). However, in the full cell, two additional requirements are imposed: (1) the currents at both electrode have to be equal and (2) the full-cell capacity is limited by the electrode with smaller capacity. In this study, TiO₂ was selected as the anode materials due to its higher specific capacity (~200 mAh/g) than other cathode materials such as LiCoO₂ (130 mAh/g) and LiFePO₄ (170 mAh/g). In addition, TiO₂ is known for its high-rate capability due to the fast pseudocapacitive surface reaction based on Li chemistry.

Fig. 2a shows the charge-discharge behavior of the full cell. Clearly, the cell performance is limited by the TiO₂ cathode. At this condition, only 31.3 μAh Li storage capacity is obtained with the full cell during charge-discharge between 0.8 and 2.0 V, accounting for ~51% of the full capacity of the TiO₂ cathode and only ~3.9% of the full capacity of the Si anode. The cell remains stable over 250 cycles with the average coulombic efficiency as high as 99%. However, as the charge-discharge current is increased, the capacity drops similar to other Li-ion batteries. At 180 μA discharge (charge) current, the cell presents 52.3 (67.8) Wh/kg specific energy and 318.4 (424.2) W/kg specific power.

Field Impacts:

The core-shell hierarchical structure provides an effective way to integrate multiscale components for the Li-ion battery electrodes, which efficiently enhances both the charge collection and Li⁺ transport. Thus much higher specific power and stability has been obtained, which is particularly useful to enable the long life and high power rate of the high-capacity Si anodes. The full cell combining a TiO₂/VACNF cathode and a Si/VACNF anode has demonstrated encouraging new approaches to developing high-power battery-supercapacitor hybrids based on Li chemistry. Both the power rate and energy capacity were found to be limited by TiO₂ due to the much higher specific capacity of Si (by 10 times). Such full cells already surpass the energy storage capacity of conventional supercapacitors. Optimizing the mass (and charge) ratio between the TiO₂ cathode and the Si anode will result in the highest cell performance.

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References

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