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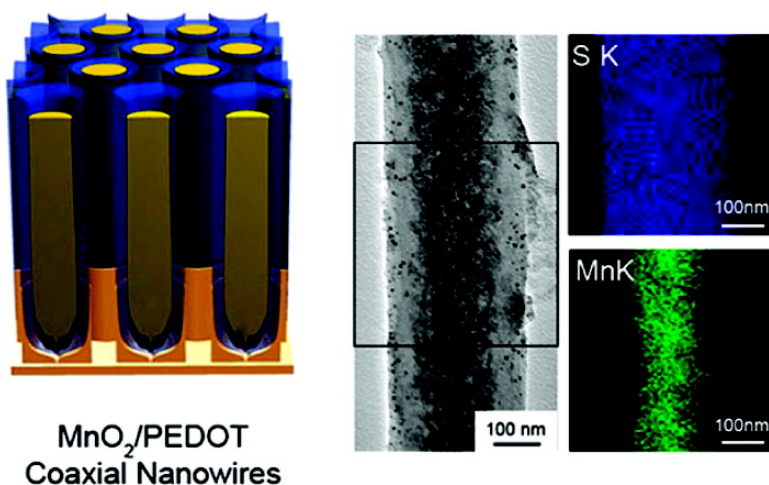
MnO/Poly(3,4-ethylenedioxythiophene) Coaxial Nanowires by One-Step Coelectrodeposition for Electrochemical Energy Storage

Ran Liu, and Sang Bok Lee

MnO₂/PEDOT
Coaxial Nanowires

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MnO$_2$/Poly(3,4-ethylenedioxythiophene) Coaxial Nanowires by One-Step Coelectrodeposition for Electrochemical Energy Storage

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One-dimensional (1D) nanostructured materials have been intensively investigated as building components in electrochemical energy storage[1] and solar energy conversion[2] devices because they provide short diffusion path lengths to ions and excitons, leading to high charge/discharge rates[1] and high solar energy conversion efficiency.[2] More recently, coaxial nanowires have attracted greater attention in this field due to their added synergic properties (e.g., high conductivity)[3a] or functionalities (e.g., core/shell p-n junction)[3b,c] arising from the combination of different materials.[3] Various materials such as semiconductor/semiconductor, metal/ metal oxide, and metal oxide/metal oxide, have been employed as core/shell in coaxial nanowires.[3] However, there have been few studies on the coaxial nanowires with transition metal oxide and conductive polymer, although both of them are important electroactive materials used in electrochemical energy storage.[4] The combination of these two materials at 1D nanostructures may exhibit excellent electrical, electrochemical, and mechanical properties for electrochemical energy storage. To date, only a few reports have been published on the synthesis of metal oxide/ conductive polymer with core/shell structures.[5] In all of these reports, a stepwise synthetic approach was adopted: metal oxide nanoparticles,[5a] nanostrands,[5b] or nanotubes[5c] were first synthesized and subsequently coated chemically by conductive polymers as shells.

In this paper, we introduce a simple one-step method to synthesize MnO$_2$/poly(3,4-ethylenedioxythiophene) (PEDOT) co-axial nanowires by coelectrodeposition in a porous alumina template.[6] MnO$_2$ is one of the most popular electrochemical energy storage materials because of its high energy density, low cost, environmental friendliness, and natural abundance,[7] but it has poor conductivity.[4c] PEDOT has merits of excellent conductivity, high stability, and mechanical flexibility,[8] but it provides low electrochemical energy density. Electrodeposition is used here because it is a simple yet versatile method in controlling structures and their composition by tuning applied potentials and electrolyte ingredients.[9] In this report, MnO$_2$/PEDOT coaxial nanowires are found to be promising electrochemical energy storage materials. The core MnO$_2$ provides high energy storage capacity, while the highly conductive, porous, and flexible PEDOT shell facilitates the electron transport and ion diffusion into the core MnO$_2$ and protects it from structurally significant collapsing and breaking. These combined properties enable the coaxial nanowires to have very high specific capacitances at high current densities.

Scheme 1 illustrates the growth of MnO$_2$/PEDOT coaxial nanowires. Under a constant potential (typically 0.75 V vs Ag/ AgCl), Mn^{2+} (10 mM manganese acetate) is converted to its higher oxidization state, which can readily undergo hydrolysis to yield MnO$_2$.[7] Simultaneously, EDOT monomer (80 mM) is electropolymerized into PEDOT in the pores of the template.[10] Very interestingly, this coelectrodeposition gives rise to formation of coaxial nanowires.

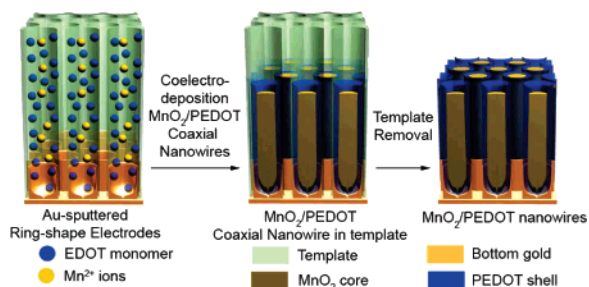**Scheme 1.** One-Step Synthesis of MnO$_2$/PEDOT Coaxial Nanowires

Figure 1a shows the SEM image of free-standing coaxial nanowires grown at 0.75 V after removal of template. Figure 1b shows the TEM image of a single coaxial nanowire. Although the core MnO$_2$ and shell PEDOT can be easily distinguished by their morphologies in TEM images, energy dispersive X-ray spectroscopic (EDS) elemental maps of S and Mn (Figure 1c and d) from the designated area in Figure 1b clearly confirms the coaxial nanostructure. The electron diffraction pattern reveals that the core MnO$_2$ is amorphous (see Supporting information).

We can easily control the structures of coaxial nanowires such as PEDOT shell thickness and nanowire length by varying the applied potential. This should provide us with the ability to tune electrochemical properties of the coaxial nanowires. Since the onset growth potential of MnO$_2$ (0.5 V) is lower than that of PEDOT (0.75 V), MnO$_2$ nanowires can be selectively grown below 0.6 V, while PEDOT nanowires are grown at the potentials above 0.85 V due to the higher growth rate of PEDOT given that the concentration of EDOT monomer is 8 times that of Mn^{2+}. Between these two extreme potentials, coaxial nanowires with various PEDOT shell thicknesses (25−100 nm) can be obtained, as shown in Figure 1e. After the MnO$_2$ cores in these coaxial nanowires are selectively removed by wet etching, PEDOT nanotubes with different wall thicknesses are obtained and clearly observed by TEM (Supporting information). Interestingly, the inner surface morphology of PEDOT nanotubes appears somewhat rough and spiky. It suggests the PEDOT may have grown into the MnO$_2$ core layer. This can be supported further by an EDS line-scan profile on a single coaxial nanowire (Supporting information). Such PEDOT penetrations may play important roles in further improving the core conductivity.

The growth mechanism of coaxial nanowires, although not completely understood, is briefly suggested as follows. We have previously proved that the sputtered ring-shape Au electrodes at the bottom of the pores can direct the growth of PEDOT nanotubes at low overpotential.[11] This may explain the preferential formation of the PEDOT shell. In addition, MnO$_2$ and PEDOT tend to have phase segregation when coelectrodeposited at bulk electrode surface (Supporting information). The phase segregation of these two materials may force the MnO$_2$ to grow in the spaces left by the PEDOT shells as the cores.
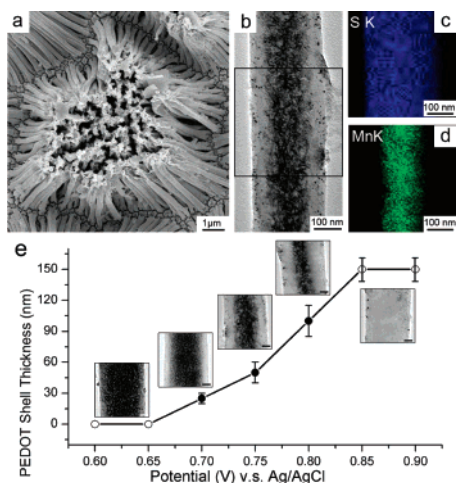
Figure 1. (a) SEM image of MnO_2/PEDOT coaxial nanowires (0.75 V). (b) TEM image from a single coaxial nanowire (0.75 V). (c and d) EDS maps of S and Mn from the boxed area in Figure 1b. (e) PEDOT shell thickness variation with applied potential. Scale bar, 50 nm.
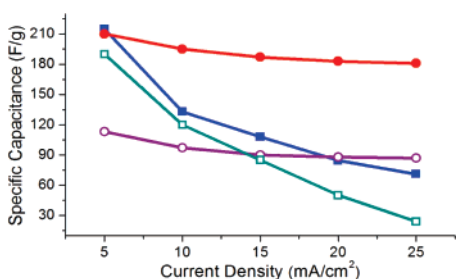
Figure 2. Specific capacitance of MnO_2 nanowires (closed blue square), PEDOT nanowires (open purple dots), MnO_2 thin film (open green square) and MnO_2/PEDOT coaxial nanowires (closed red dots) at difference charge/discharge current densities.

Finally, we investigate electrochemical properties of the coaxial nanowires for an electrochemical supercapacitor, an electrochemical energy storage device required to provide high power while it maintains its energy density (or specific capacitance) at a high charge/discharge rate. Specific capacitance values of coaxial nanowires (grown at 0.75 V), MnO_2 nanowires, PEDOT nanowires, and MnO_2 thin film at different current densities are shown in Figure 2.

Coaxial nanowires not only exhibit high specific capacitance values but also maintain them well at high current density compared to the others. As shown in Figure 2, the coaxial nanowires preserved 85% of its specific capacitance (from 210 to 185 F/g) as the current density increases from 5 to 25 mA/cm^2. These specific capacitance values are comparable to those of electrodeposited MnO_2 films (190−240 F/g), which however decreased significantly with increased current densities (e.g., from 210 to 40 F/g at current density of 1−10 mA/cm^2).[7] The specific capacitance of coaxial nanowires is higher than that of PEDOT nanowires as a result of the inclusion of MnO_2 as cores. The well-maintained specific capacitance is mainly due to short paths of ion diffusion in the nanowires. Therefore, even at high current density (high power demand), the nanowire materials can be fully utilized. The porous nature of the PEDOT shell allows such fast ion diffusion into the core MnO_2 of the coaxial nanowires. In addition, the highly electrical conductive PEDOT shell facilitates electron transport to the core MnO_2, which has low conductivity[4c] that can limit its charge/discharge rate[7] (cyclic voltammogram in Supporting infor-

mation). It also explains the significant decrease of specific capacitance of pure MnO_2 nanowires. With regard to mechanical stability, the solid core MnO_2 and the flexible PEDOT shell prevent, synergistically, the coaxial nanowires from significant collapsing and breaking after removal of the template and the drying process that downgrades their electrochemical performance (Supporting information).

In conclusion, MnO_2/PEDOT coaxial nanowires were fabricated by a one-step coelectrodeposition method. The structures of the coaxial nanowires could be controlled by applied potential. The combination of MnO_2 and PEDOT into 1D nanostructures showed excellent electrochemical and mechanical properties for energy storage applications. The synthetic method presented here will be further investigated for the extension to fabricating other heterogeneous 1D nanocomposite structure with other metal oxides[12] and conductive polymers, which may lead to new types of materials in electrochemical energy storage devices.

Supporting Information Available: Electron diffraction pattern and EDS line-scan, TEM of PEDOT nanotubes, phase segregation, SEM of MnO_2 nanowires, and other detailed electrochemical characterizations. This material is available free of charge via the Internet at http://pubs.acs.org.

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