ALD RUTHENIUM OXIDE-CARBON NANOTUBE ELECTRODES FOR SUPERCAPACITOR APPLICATIONS

Roseanne Warren[1], Firas Sammoura[1,2], Alina Kozinda[1], and Liwei Lin[1]
[1]University of California, Berkeley, USA
[2]Masdar Institute of Science and Technology, Abu Dhabi, UAE

ABSTRACT

This work presents the first demonstration of atomic layer deposition (ALD) ruthenium oxide (RuO_2) and its conformal coating onto vertically aligned carbon nanotube (CNT) forests as supercapacitor electrodes. Specific accomplishments include: (1) successful demonstration of ALD RuO_2 deposition, (2) uniform coating of RuO_2 on a vertically aligned CNT forest, and (3) an ultra-high specific capacitance of 100 mF/cm^2 from prototype electrodes with a scan rate of 100 mV/s. Advantages of the ALD method include precise control of the RuO_2 layer thickness and composition without the use of CNT-binder molecules. In addition to high capacitance, preliminary results indicate that the ALD RuO_2-CNTs have good stability over repeated cycling. Besides its use in supercapacitors, ALD-RuO_2 has potential NEMS applications: in biosensors and pH sensing [1], as a strong oxidative material in multiple chemical processes [2], and in catalytic reactions for photocatalytic systems [3].

INTRODUCTION

Supercapacitors are electrochemical energy-storage devices that store charge by: 1) reversible adsorption of ions onto high-surface area, porous materials (known as "electric double layer capacitors"), or 2) reversible surface reduction-oxidation (redox) reactions (known as "pseudo-capacitors"). With their high power density and long cycle stability, supercapacitors are well-suited to complement or replace batteries in a wide range of applications, including transportation, renewable energy, and portable electronics [4]. High-performance supercapacitors are characterized by: high specific capacitance, good stability over repeated cycling, and low series resistance.

RuO_2 is considered one of the best pseudo-capacitive materials in terms of charge storage ability and fast, reversible reaction kinetics [4]. Because of its high electrical conductivity (comparable to that of metals), RuO_2 supercapacitors can have low resistive energy losses [5]. In addition, RuO_2 has three available oxidation states as it cycles between its oxide and hydroxide states, enabling RuO_2 electrodes to store large quantities of charge [4]. CNTs are a good supporting electrode material for active RuO_2 pseudo-capacitive layers because CNTs have: 1) high surface area and porosity, 2) good electrical conductivity, and 3) excellent mechanical flexibility and strength [6].

While there have been numerous studies of RuO_2 - CNT composite materials for supercapacitor applications, there is a need for improved synthesis methods to maximize device performance. Current methods for depositing RuO_2 on CNTs include sputtering, electroplating, chemical vapor deposition (CVD), and pyrolysis. These methods are often time-consuming, can yield incomplete surface coverage, and result in poor control over critical properties such as chemical composition and thickness [7, 8]. Due to the high cost of RuO_2, supercapacitor devices should use only the minimum amount of RuO_2. Since pseudo-capacitors store charge by surface redox reactions, the RuO_2 layer in RuO_2-CNT composites can be just a few nanometers in thickness. In this work, we have found that the ALD method is well-suited for creating high-performance RuO_2-CNT supercapacitor electrodes with excellent conformality and precise control over film thickness and chemical composition.

ALD is a form of CVD in which reactant precursors are pulsed sequentially, enabling films to be deposited on the substrate one monolayer at a time. The ALD process enables angstrom-level control over film thickness, and can achieve uniform film coverage even when used with high aspect-ratio geometries. While the ALD process for Ru is well-established, the ALD process for RuO_2 is still poorly understood. In addition to demonstrating a high-performance RuO_2-CNT supercapacitor, the results of this study have potential wide-ranging applicability by furthering our understanding of the ALD RuO_2 process.

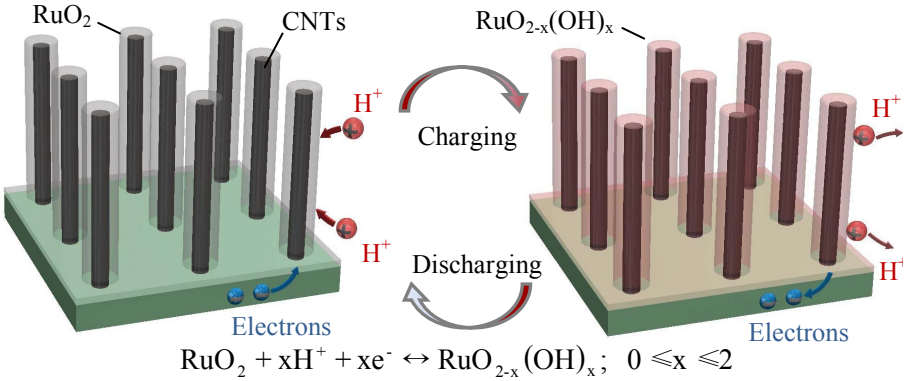

Figure 1: Conceptual illustration of the ALD RuO_2-coated CNTS on a conductive substrate. During charging, the RuO_2 surface adsorbs protons from the electrolyte and a current flows into the CNTs to create a $RuO_{2-x}(OH)_x$ surface layer, where $0 < x \leq 2$. During discharging, the reaction is reversed.

CONCEPT

Figure 1 shows a conceptual illustration of our device design. A forest of vertically-aligned CNTs is covered with a layer of RuO_2 several nanometers thick deposited by ALD. As the device charges, the active RuO_2 layer absorbs protons from the electrolyte and electrons flow into the device from an external circuit as the RuO_2 layer is converted to $Ru(OH)_2$ by a surface redox reaction. When discharging, stored electrons flow out of the device to an external circuit and protons are released into the electrolyte as $Ru(OH)_2$ is converted back to RuO_2 in the reverse redox reaction. In our device, the high strength and mechanical flexibility of the CNT forest is important for relieving mechanical stresses in the RuO_2 layer that arise from repeated cycling through redox states.

EXPERIMENT

Vertically-aligned, multi-walled CNTs are grown by chemical vapor deposition in a horizontal tube furnace with ethylene gas as the carbon-source. The CNTs are grown on a molybdenum- and oxide-coated silicon wafer, using aluminum and iron as catalyst layers [9]. Following the CNT growth, RuO_2 is deposited on the CNTs using a Cambridge Fiji F200 Plasma ALD with ruthenium bis(ethylcyclopentadienyl) ($Ru(EtCp)_2$) and oxygen as precursors. In our experiment, the ALD deposition temperature was varied from 300°C to 400°C.

Imaging of the RuO_2-coated CNTs was done using an FEI Nova NanoSEM 650 scanning electron microscope (SEM) and an FEI Technai 12 transmission electron microscope (TEM). Materials characterization was done using a Siemens D5000 X-ray diffractometer (XRD), and a PHI 5400 X-ray photoelectron spectrometer (XPS) was used for glancing incident XPS (GIXPS) measurements. Both XRD and GIXPS measurements were taken of thin-film ALD-RuO_2 samples deposited on silicon substrates under the same conditions as the ALD RuO_2-coated CNTs. Electrochemistry measurements were conducted using a three-electrode test set-up in 0.5 M H_2SO_4 electrolyte with an Ag/AgCl reference electrode, Pt counter electrode, and a Gamry Reference 600 potentiostat.

RESULTS AND DISCUSSION

A cross-sectional SEM image of the RuO_2-coated CNTs (Figure 2a) shows that the CNT forest is approximately 5 μm tall with large pore spaces available for the electrolyte to penetrate into the dense matrix of CNTs. A close-up SEM image (Figure 2b) shows that the CNTs are uniformly coated by the ALD process. A TEM image (Figure 2c) shows that the ALD coating is approximately 20 nm thick and has good adhesion to the CNT surface.

The composition of the ALD coating was investigated by GIXPS and XRD measurements. Figure 3a shows the GIXPS spectrum for ALD RuO_2 deposited at 350°C. The results indicate a near-stoichiometric composition (65% O, 35% Ru) within the GIXPS measurement range (top 10 nm of the film). Figure 3b is a plot of the oxygen content of the ALD films measured by GIXPS as a function of deposition temperature. In the range of 300°C to 400°C, we have found that higher deposition temperatures correspond to increased oxygen content of the films.

The ALD process for RuO_2 is believed to occur via the accumulation of subsurface oxygen in a depositing Ru film [10]. In a recent study of ALD growth mechanisms for Ru vs. RuO_2, Methaapanon et al. found that several hundred deposition cycles of Ru were required before RuO_2 layers began to form [11]. The authors proposed that a certain thickness of Ru film is needed before there are enough defect sites to accumulate sufficient quantities of subsurface oxygen to form RuO_2. In our study, XRD measurements of ALD-RuO_2 films deposited at temperatures ranging from 300°C to 400°C show primarily Ru diffraction peaks (Figure 3c). Based on these results, it is likely that an underlying Ru layer is deposited during the ALD process before RuO_2 is deposited as a surface layer. If the surface RuO_2 layer is amorphous or very thin, its XRD signal would not be easily detected compared to the underlying Ru. Ru does not form a native oxide under ambient conditions [12], so we conclude that the surface oxide measured by GIXPS was deposited by ALD. For supercapacitor applications, only a surface layer of RuO_2 is needed for charge storage. The presence of an underlying Ru layer with good electrical conductivity could be beneficial to supercapacitor performance.

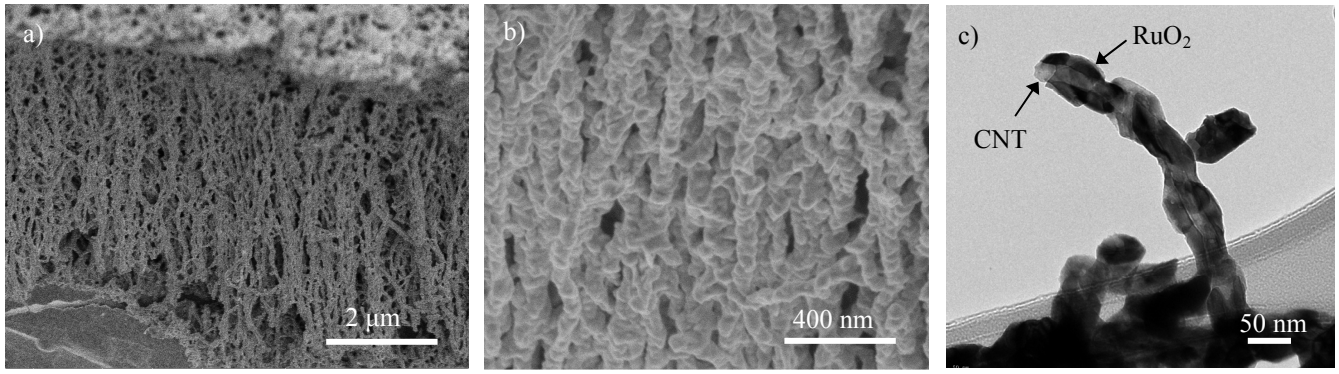

Figure 2: Electron microscope images of the as-fabricated RuO_2-coated CNTs. (a) Cross-sectional SEM image shows that the ALD coating covers the full length of the approximately 5 μm-tall CNTs, (b) Close-up SEM image of the ALD coated CNTs, (c) TEM image of a single RuO_2- coated CNT.

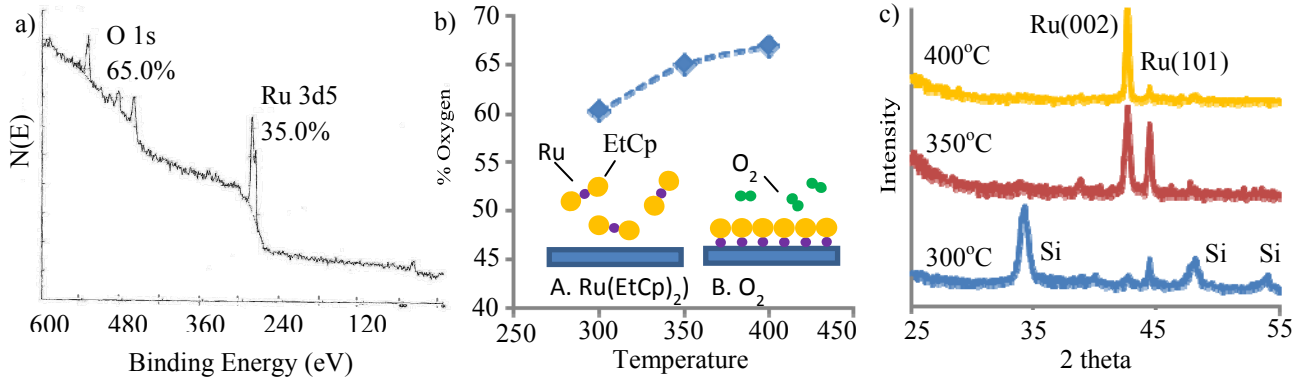

Figure 3: a) GIXPS measurement of ALD RuO_2 thin-film sample deposited at 350°C , (b) Percent oxygen in ALD RuO_2 films as a function of temperature (measured with GIXPS) (Inset) Schematic of the ALD RuO_2 process with alternating $Ru(EtCp)_2$ and O_2 pulses, c) XRD measurement of ALD RuO_2 thin-film samples at 300°C, 350°C, and 400°C deposition.

When tested as a supercapacitor electrode, the ALD RuO_2-coated CNTs demonstrate high capacitive energy storage capability. Figure 4 shows cyclic voltammetry (CV) measurements of the coated CNTs compared to an uncoated CNT sample. A capacitive current of 10 mA/cm^2 for the RuO_2-coated CNTs at a scan rate of 100 mV/s corresponds to a specific capacitance of 100 mF/cm^2, which represents one of the best values in the literature [13, 14]. The high specific capacitance of the RuO_2-coated CNTs can be attributed in part to the quality of the ALD coating. Previous studies have indicated the importance of a hydrous RuO_2 ($RuO_2 \cdot nH_2O$) surface for achieving high supercapacitor performance [15]. From the CV measurements of the RuO_2-coated CNTs, we conclude that the ALD process is well-suited to fabricating such a surface layer. Besides the ALD RuO_2 quality, the high surface area and density of the CNT forest also contribute to the high specific capacitance of our device.

As shown in Figure 4, charge and discharge currents measured by CV for the coated CNTs are approximately fifty times that of the uncoated CNTs. For the uncoated CNT electrode, charge storage is by electric double layer capacitance. The dramatic improvement in supercapacitor performance with the ALD RuO_2-coating is due to the pseudo-capacitive charge storage mechanism of the RuO_2 surface layer. We note that the shape of the CV curve for the RuO_2-coated CNTs in Figure 4 resembles that reported in other studies of RuO_2 supercapacitors [16].

Electrochemical impedance measurements of the RuO_2-coated CNTs are shown in the Nyquist plot in Figure 5. From the x-intercept, we can see that the device has an equivalent series resistance (ESR) of 7.1 Ω, a remarkably low value. This low ESR value can be attributed in part to the conformal nature of the ALD coating which minimizes contact resistance between the active RuO_2 layer and the CNTs [8]. Based on a Randles circuit model of cell impedance [17], the shape of the Nyquist plot suggests that the impedance of our device is dominated by diffusion (Warburg impedance) with low charge-transfer resistance and low double layer capacitance. A low charge-transfer resistance is characteristic of RuO_2 supercapacitors because of their fast reaction kinetics [4].

Repeating chronoamperometry was used to measure the device response to a step-change in applied potential. As shown in Figure 6, the ALD-RuO_2 coated CNTs display rapid charge-discharge characteristics that remain stable over time.

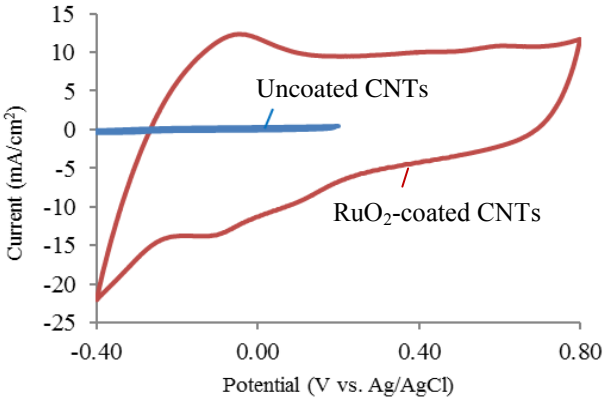

Figure 4: CV measurements of uncoated CNTs and RuO_2-coated CNTs at 100 mV/s scan rate in 0.5 M H_2SO_4 electrolyte with Ag/AgCl reference electrode and Pt counter electrode.

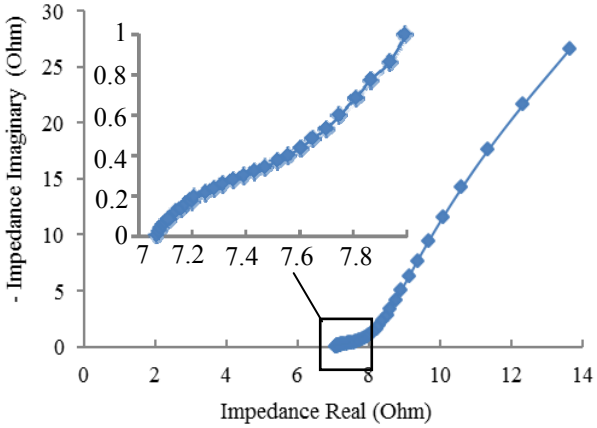

Figure 5: Nyquist plot of the RuO_2-coated CNTs showing a contact resistance (x-intercept) of 7.1 Ω.

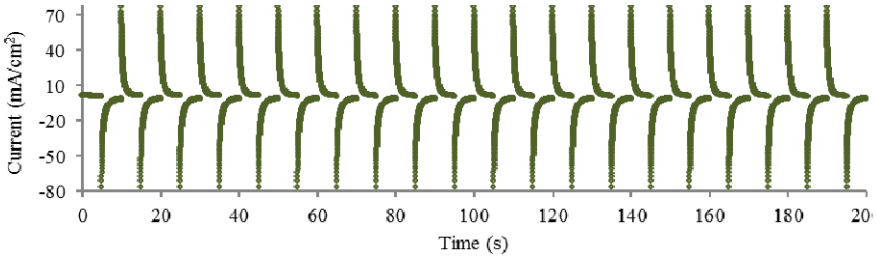

Figure 6: Charge-discharge measurements of the RuO_2-coated CNTs show rapid and consistent supercapacitor cycling as the input potential alternates between 0 and 0.5 V vs. Ag/AgCl.

CONCLUSIONS

In this work we have demonstrated for the first time the application of ALD RuO_2 to supercapacitor energy storage devices. Our results show that ALD RuO_2-coated CNTs can be used as high-performance supercapacitor electrodes. In addition to high specific capacitance, our device has low equivalent series resistance, rapid charge-discharge characteristics, and good stability over repeated cycling. The exceptionally high-performance of the ALD RuO_2-coated CNTs can be attributed to: 1) excellent conformal coverage of the CNTs by the ALD RuO_2 coating, 2) a high-quality RuO_2 surface layer capable of fast, reversible redox reactions, and 3) high surface area of the dense, vertically-aligned CNT forest. We expect that these results can be further improved by optimizing the stoichiometry and thickness of the ALD RuO_2 coating. With the ALD fabrication method, these properties can be controlled with angstrom-level precision to achieve exceptionally high-performance supercapacitor devices.

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