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Atomic Layer Deposition of Co_3O_4 on Carbon Nanotubes/Carbon Cloth for High-Capacitance and Ultrastable Supercapacitor Electrode

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ABSTRACT

Co_3O_4 nanolayers have been successfully deposited on a flexible carbon nanotubes/carbon cloth substrate by atomic layer deposition (ALD). Much improved capacitance and ultra-long cycling life are achieved when the CNTs@ Co_3O_4 /CC is tested as a supercapacitor electrode. The improvement can be from the mechanically robust carbon cloth/CNTs substrate, the uniform coated high capacitance materials of Co_3O_4 nanoparticles, and the unique hierarchical structure. The flexible electrode of CNTs@ Co_3O_4 /CC with high areal capacitance and excellent cycling ability promises a great potential for developing high-performance flexible supercapacitors.

1. Introduction

One of the main focuses of recent research on supercapacitors is to develop a class of flexible/bendable/wearable energy storage devices with high energy density and long cycling life(1, 2). Typically carbon-based materials, such as graphene/CNTs paper and 3D graphene foam, have been utilized for electrodes of flexible supercapacitors because they are electrically conductive and mechanically robust to certain extent(3). Compared with the flexible graphene or CNTs, commercial available carbon cloth (CC) has also received considerable attention since it costs much less and is durable than metal foil or metal foams(4). In order to realize high energy storage by the devices made of flexible carbon materials, transition metal oxides (such as MnO_2 , Co_3O_4 , Fe_2O_3 , and NiO) are usually incorporated, whereby they contribute capacitance by undergoing redox reactions(5-7). However, metal oxides often show very poor electric conductivity and limited cycling ability, which presents a big barrier for their wide applications as high-energy supercapacitor electrodes(8). To address this issue of transition metal oxides, one approach is the direct growth of nanostructured transition metal oxides on flexible carbon substrate, since the nano-sized materials can provide a larger surface to volume ratio thus ensure better electrode/electrolyte contact(9). In addition, the electrode is binder free which can also contribute to better electrochemical performance and an overall higher energy density. Another approach is to combine transition metal oxides with carbonaceous materials or conducting polymers or even nanosized Au or Pt layers, thus the overall conductivity of the electrode is improved and better electric contact of the metal oxides is expected(10, 11). Typically, surface conductive coating on transition metal oxides and core/shell structures (with conductive core/metal oxide shell) have demonstrated to be effective in resulting in high-performance metal oxides-based electrodes(12). Despite of these efforts, it is still a big challenge to develop truly flexible supercapacitors with nanosized transition metal oxides being assembled on conducting substrate and with high capacitance and excellent cycling stability.

Recent research work on atomic layer deposition (ALD) has demonstrated its potential in developing nano-thin film of high uniformity and conformability on different substrates(13-16). The well-controllable thickness (down to angstrom level) of ALD transition metal oxide layers would be ideal for optimised electrochemical performance. Tremendous research works have been carried out on ALD surface coating for

stable lithium-ion battery electrodes(17, 18). For supercapacitors, little work has been reported on the application of active materials developed by ALD(19). To the best of our knowledge, nobody has studied ALD nanolayers of Co_3O_4 in developing high-performance flexible supercapacitor electrode.

In this work for the first time we report a unique hierarchical structure of ALD Co_3O_4 nanolayer successfully deposited on CNTs in flexible carbon cloth (CNTs@ Co_3O_4 /CC). In the hierarchical structure, CNTs/CC serves as a stable 3-dimensional conductive network for nanostructured transition metal oxides. Compared with conventional CC, CNTs/CC provides a higher surface area, better electric conductivity and therefore higher capacitance. The coverage of CNT surface by ALD Co_3O_4 enables a better electric contact and increases the overall capacitance as a result of the additional Faradic reaction. The intrinsic layer-by-layer characteristics of ALD can prevent the Co_3O_4 from decomposition, deformation and depletion in long-time cycling tests. Indeed, an areal capacity of $\sim 347.2 \text{ mF/cm}^2$ is achieved with the hierarchical CNTs@ Co_3O_4 /CC structure, which is ~ 10 times higher than that of CNTs/CC alone. Furthermore, the hierarchical structure shows ultrastable cycling ability, as no capacity fading is observed even after 50 000 cycles of charge-discharge at high current. ALD Co_3O_4 with different cycles have also been studied and showed promising electrochemical performance. The flexible electrode of CNTs@ Co_3O_4 /CC with high areal capacitance and excellent cycling ability promises a great potential for the next-generation high-energy flexible energy storage devices.

2. Experimental section

2.1. Material synthesis

CNT/CC is developed by CVD method. At first, a 20 nm thick Ni film was deposited onto the carbon cloth by an electron beam evaporator (Auto 306, HHV). The clean carbon clothes ($2 \times 4 \text{ cm}^2$) were then put in a thermal chemical vapor deposition (TCVD, Lindberg) furnace. Ethanol vapor was introduced into furnace as carbon sources for CNT growth by a mixture of Ar (200 sccm) and H_2 (100 sccm). The growth temperature and time was controlled at 650°C and 10 mins, respectively.

CNT@ Co_3O_4 /CC is made by deposition of Co_3O_4 on CNT/CC by ALD using a SUNALE R-200 ALD reactor (Picosun Oy). The source materials for cobalt and oxygen are dicarbonylcyclopentadienylcobalt ($\text{CpCo}(\text{CO})_2$, 96%, Strem Chemicals) and remote O_2 plasma, respectively.

For O₂ plasma, O₂ (99.999%) was introduced in a remote RF plasma generator with Argon (99.999%) as the carrier gas, and the plasma power was kept at 2500 W. All sources were kept at room temperature. The carrying and purge gas was nitrogen with a purity of 99.999%. Pulse time of cobalt precursor was controlled at 0.1 s, followed by a 6 s N₂ purge step to blow away redundant precursors. The flow of O₂ plasma was 160 sccm and the pulse time was controlled at 16.5s, followed by a 6 s N₂ purge time. The pressure in the reaction chamber was kept in the range from 2 to 6 hPa, and the reaction temperature is kept at 100 °C. **Typical mass loading of Co₃O₄ with 1600 cycles is ~ 0.16 mg/cm².** The as-prepared samples are further annealed in air at 350 °C.

2.2. Characterization

Samples were characterized using scanning electron microscopy (SEM, Zeiss, 5.0-20.0 kV), transmission electron microscopy (TEM, JEOL-2010), X-ray photoelectron spectroscopy (XPS, AXIS Ultra). The mass of electrode materials was measured on an AX/MX/UMX Balance (METTLER TOLEDO, maximum=5.1 g; delta=0.001 mg).

2.3. Electrochemistry measurement

Electrochemical measurements were performed using a workstation (Solartron 1470E) in a three-electrode electrochemical cell at room temperature using 2 M KOH as the electrolyte. The carbon cloth supported nanostructures (~1 cm² area) were used directly as the working electrode. A Pt plate and Ag/AgCl were used as the counter electrode and the reference electrode, respectively. All potentials were referred to the reference electrode. The areal capacitance is calculated by: $C_a = I \cdot t / (\Delta V \cdot S)$, where I is the discharge current, t is the discharge time, ΔV is the voltage drop upon discharging, and S is the geometrical area of the electrode.

3. Result and Discussion

Carbon cloth with typical fibre diameter of ~10 μ m as shown in Figure 1(a) is used in the present work. The CC has commonly been utilized as conductive substrate for flexible electrode/current collector, due to its low cost, high electrical conductivity and mechanical robustness(20-23). After CVD growth of CNTs on CC, as shown in Figure 1(b), the surface of CC is covered with cross-linked CNTs, and the typical CNTs have diameters and lengths in the range of 20-50 nm and more than 10

μ m, respectively. Metal oxides are further coated on the CNTs/CC by ALD, thus a hierarchical structure of CNTs@Co₃O₄/CC is achieved. The Co₃O₄ was deposited using CpCo(CO)₂ and remote oxygen plasma as precursors (experiment procedure is detailed in ESI). The oxygen plasma is utilised not only as an oxygen source, but also as a strong oxidizing agent for the simultaneously functionalization of CNTs, which can avoid pre-treatment of CNTs thus simplifies the fabrication process(24). A typical depositing cycles of 1600 is employed for Co₃O₄. After ALD Co₃O₄, the cross-linked structure of CNTs is maintained and no apparent impurity/damage is enrolled, as can be seen from Figure 1(c). From enlarged SEM image in Figure 1(d), one can see that the CNTs have been coated with a rough layer which is composed of tiny but uniform nanoparticles, indicating that a core-shell structure of CNTs@Co₃O₄ is obtained. HRTEM is further carried out to study the crystalline structure of the CNT@Co₃O₄, as shown in Figure 1(e). The multi-walled CNT is marked with an interlayer spacing of ~0.34 nm, and the lattice fringes of the nanoparticles (with diameter of ~8 nm) with a spacing of ~0.28 nm can be assigned to the (220) planes of cubic Co₃O₄. Previous reports on ALD Co₃O₄ showed its preferential growth directions of (111) or (100) on silicon substrate, yet it can be different if different precursors for Co are used, or a remote O₂ plasma/thermal ALD with O₃ is used as the oxygen source.(25) X-ray photoelectron spectroscopy of Co₃O₄ is further studied. The Co 2p XPS spectrum in Figure 1(f) shows two main peaks located at 780.4 and 795.7 eV, which can be assigned to Co 2p 3/2 and 2p 1/2, respectively, of Co₃O₄ phase(26). From Figure 1(g), the O 1s peak located at approximately at 529.8 eV corresponds to the oxygen species in Co₃O₄(27).

The Co₃O₄ nanoparticles are uniformly distributed on the surface of CNTs. This helps fast ion/electron transport and gives rise to sufficient contact with the electrolyte, which is favoured for electrochemical reaction. Electrochemical test of the CNT@Co₃O₄/CC is carried out in a three-electrode system by using Pt and Ag/AgCl as the counter electrode and the reference electrode, respectively. 2M KOH is used as electrolyte and the CNT@ Co₃O₄/CC is directly used as the working electrode. For comparison purpose, samples with CNTs on CC (CNT/CC) and 1600 ALD cycles of Co₃O₄ on CC (Co₃O₄/CC) are also studied. Figure 2(a) shows the CV curves of the three electrode materials (CNT@Co₃O₄/CC, CNT/CC, Co₃O₄/CC), from which one can see that the CNT@Co₃O₄/CC deliver a much higher capacity than the other two samples, as indicated with a larger enclosed area. From the curves, one can also find that the CNT/CC

shows a nearly rectangular curve with no apparent redox peaks, while both CNT@Co₃O₄/CC and Co₃O₄/CC deliver a pair of redox peaks which can be assigned to the reversible reactions of Co³⁺/Co⁴⁺ associated with anions OH⁻(28). From galvanic charge-discharge curves obtained with a current density of 5 mA/cm², the CNT@Co₃O₄/CC also shows much higher capacity than the other two samples (Figure 2b). The much increased capacitance is attributed to the core-shell structure of CNTs@Co₃O₄, where the CNTs ensure better electric conductivity and more surface area, and the Co₃O₄ provide more redox reactions with the electrolyte thus higher capacitance.

To better illustrate the capacitance improvement, areal capacitances at different current densities of the three samples are shown in Figure 2(c). When the current increases from 1.25 to 10 mA/cm², CNT/CC shows the most stable capacitance retention, yet it also shows the lowest capacitance of ~35 mF/cm². Co₃O₄/CC gives rise to a higher areal capacitance of ~105 mF/cm² at 1.25 mA/cm², but it retains only 31.2% of the capacitance when the current increases 8 times. In comparison, much higher areal capacitance and very good rate capabilities are realized by CNT@Co₃O₄/CC. When the charge-discharge current is at 1.25 mA/cm² the CNT@Co₃O₄/CC can deliver an areal capacitance of 347.2 mF/cm², which is ~10 times of that for CNT/CC and ~3.3 times of that for Co₃O₄/CC. In addition, 65.7% of the capacitance can be maintained when the current density increased to 10 mA/cm². The rate capability demonstrated by the CNT@Co₃O₄/CC is much better than that of Co₃O₄/CC, which further demonstrates the CNTs can ensure fast electron/ion transfer even at high current rates.

Electrochemical impedance spectroscopy of the above three electrode materials are further studied with Nyquist plot showing in Figure 2(d). All the three electrodes have similar bulk resistance in high frequency region (indicated by the intersection of the curve at real part Z'), while the CNT@Co₃O₄/CC shows a little big charge-transfer resistance (as indicated by the diameter of the semi cycle), which may well be due to its multi-phased (CNT-Co₃O₄-KOH) electrode-electrolyte contact for charge transfer (19, 23). In the low frequency region, the Co₃O₄/CC shows the highest diffusion resistance as its slop is the smallest, while both CNT@Co₃O₄/CC and CNT/CC have almost ideal straight lines along the imaginary axis, showing the CNTs are a playing positive role for the fast ion/electrolyte diffusion.

For applications in supercapacitor, the long-time cycling stability of the metal oxide-based flexible electrode is also a key requirement, thus the cycling behavior of CNT@Co₃O₄/CC is studied. As indicated in

Figure 3, CNT@Co₃O₄/CC shows a slightly capacitance increase with activation in the first several thousand cycles at the current of 10 mA/cm², where the electrode material gradually become fully-accessed to the electrolyte (29, 30). More importantly, the capacitance is very stable even after 50 000 cycles of charge-discharge. The CNTs@Co₃O₄/CC therefore can deliver much better cycling stability than those of previously reported composite structure of CNT/Co₃O₄ obtained by electrostatic precipitation, hydrothermal and decomposition(31, 32). The excellent cycling ability can well be originated from the densely layer-by-layer deposition of ALD transition metal oxide and the tightly physiochemical bonding with CNTs, thus the metal oxides can maintain the stable mechanical/electronic contact even after long-time cycling(15, 25). In addition, the stable CNTs/CC substrate can also contribute to the long-time cycling ability(33). The excellent cycling ability of the ALD Co₃O₄ demonstrated here promises for much stabilized active material/surface coating of supercapacitor electrodes.

Since ALD cycles of Co₃O₄ can be easily controlled, it is also of interest to study the relationship between the amount of Co₃O₄ and the electrochemical performance. In this work, ALD Co₃O₄ coating with 800 and 2400 cycles are further carried out, compared to the previous 1600 cycles. Figure 4(a-c) show the SEM images of CNTs after 800, 1600, and 2400 cycles of ALD Co₃O₄, and their corresponding TEM images are shown in Figure 4(d-f). From these images, one can see that all the metal oxide nanoparticles are uniformly coated on the surface of CNTs, and the size of Co₃O₄ increases with increasing number of ALD cycles. The thickness of the ALD Co₃O₄ increased from ~5 nm with 800 ALD cycles to ~20 nm with 2400 cycles. The nanosized Co₃O₄ particles (less than 20 nm) facilitate electrochemical reaction with electrolyte(34). The electrochemical behavior of these three electrode samples are showed in Figure 5, where they all illustrate similar redox peaks in CV curves (Figure 5a) and much higher areal capacitance than that of CNT/CC (Figure 5b). One can also see that the areal capacitance increases as ALD cycles increases from 800 to 2400 (Figure 5c). The highest capacitances obtained for the CNT@2400-Co₃O₄/CC is 416.7 mF/cm², which is much larger than previous reported metal oxides/CC composites, such as H-TiO₂/CC, N-Fe₂O₃/CC, and PPy-MnO₂/CC(35-37). The high areal capacitance and excellent cycling stability achieved in present work would pave a good way for metal-oxide based supercapacitors in real application. Nevertheless, in present work, the mass

loading of active material is still not high enough ($\sim 0.5 \text{ mg/cm}^2$) mainly due to the low CNTs loading (33), and an excellent flexible anode (such as Fe_2O_3 and TiN) is also urgently needed for a full-cell configuration, thus future work will be focus on increasing mass loading (specifically CNT) on single electrode and searching of proper anode material for a full-cell flexible supercapacitor.

4. Conclusions

For the first time, Co_3O_4 nanolayers have been successfully deposited on CNTs/CC by ALD for development of flexible supercapacitor electrode. The mechanically robust carbon cloth with CNTs serves as a highly conductive network for nanoparticles of transition metal oxide. ALD Co_3O_4 nanoparticles are shown to contribute to the much improved capacitance of the flexible supercapacitor electrode. Due to the highly uniform and conformal assembling of transition metal oxide nanoparticles in the unique hierarchical structure, the CNTs@ Co_3O_4 /CC demonstrates high areal capacitance and ultra-stable cycling performance. The unique structure of CNT/CC decorated with ALD nanoparticles of transition metal oxide being assembled on the surface and their superior electrochemical performance promise the potential for developing high-performance flexible supercapacitors.

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Figure 1. SEM image of (a) bare carbon cloth, (b) CNT, and (c-d) CNT@Co₃O₄ on carbon cloth. (e) HRTEM image of CNT@Co₃O₄. (f-g) XPS spectrum of ALD Co₃O₄.

Figure 2. (a) CV curves, (b) charge-discharge curves, (c) rate capability, and (d) EIS of the three samples: CNT@Co₃O₄/CC, Co₃O₄/CC, and CNT/CC.

Figure 3. Cycling test of CNT@Co₃O₄/CC with 1600 cycles of ALD Co₃O₄.

Figure 4. SEM and TEM images of CNTs@Co₃O₄/CC with different ALD cycles of 800(a, d), 1600(b, e), and 2400(c, f).

Figure 5. (a) CV curves and (b) charge-discharge curves of Co₃O₄ on CNT/CC with different ALD cycles. (c) areal capacitance of the five samples: Co₃O₄/CC, CNT/CC, and CNT@ Co₃O₄/CC with 800, 1600, 2400 cycles of ALD Co₃O₄.