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Highly Dispersed RuO₂ Nanoparticles on Carbon Nanotubes: Facile Synthesis and Enhanced Supercapacitance Performance

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RuO₂/CNT nanocomposites with well-dispersed RuO₂ nanoparticles (diameter <2 nm) on the carbon nanotubes' surface, synthesized through an easy and efficient solution-based method, have been investigated for potential application in electrochemical capacitors (ECs) as electrode materials. The electrochemical results demonstrate that the supporting material of CNT can significantly promote the supercapacitance performance of RuO₂. The RuO₂ nanoparticles in the composite with a RuO₂/CNT mass ratio of 6:7 could achieve a specific capacitance of as high as 953 F g⁻¹. The results also demonstrate that the resulted RuO₂/CNT nanocomposites are superior electrode materials for ECs with a high specific capacitance and significantly enhanced high-power and high-energy capabilities as well as improved cycling performance compared with bare RuO₂. At a power density of 5000 W kg⁻¹, the RuO₂/CNT composite (RuO₂/CNT = 6:7 in wt %) can still deliver an energy density of 16.8 Wh kg⁻¹, which is about 5.8 times larger than that of bare RuO₂ (2.9 Wh kg⁻¹). The much improved electrochemical performances could be attributed to the dispersive action and good electronic conductivity of CNTs as well as the pinning effect for nanosized RuO₂ particles on the CNTs' surfaces.

1. Introduction

Electrochemical capacitors (ECs), also called supercapacitors or ultracapacitors, are rechargeable power sources exhibiting great power densities and long cycle life.^{1–3} Two types of electrochemical capacitors have been widely studied. One is the double-layer EC (DLEC), the other is the redox EC (RDEC). Although the former mainly uses carbon materials,^{4–6} the latter uses certain transition-metal oxides or conducting polymers^{7–11} as electrode materials. Among the transition-metal oxides, ruthenium oxide has been employed as one of the most important electrode materials for RDECs because of its ultrahigh pseudocapacitance (ca. 700 F g⁻¹) and reversibility of accepting and donating protons from an aqueous electrolyte.^{12–16} However, because of the high cost of Ru, the commercial application of RuO₂ as electrode materials in ECs has been restricted. The limitation has encouraged several studies of combining RuO₂ with low-cost materials, such as carbon^{3,17,18} and cheap metal oxides.^{19–21} Carbon nanotubes (CNTs) are one of the best material choices in view of facile fabrication and high electronic conductivity. CNTs are also a promising electrode material of DLECs because of their high accessible surface area, high stability, and high mechanical strength.^{22,23} Zhang et al. reported that CNT arrays exhibit superior rate capability due to their unique structures and high electronic conductivity.⁵ It is expected that the combination of RuO₂ and CNTs can take the advantages of both the high pseudocapacitance of RuO₂ and the stable double-layer capacitance of CNTs, which might result in much enhanced supercapacitance performance.^{3,17,24–26} However, the synthesis of uniform RuO₂ nanoparticles well dispersed on the CNTs' surface has not been well-explored.

In this paper, we report the facile synthesis of a composite of RuO₂ nanoparticles and CNTs. Uniform RuO₂ nanoparticles can be well-dispersed on the CNTs' surface through an easy and efficient solution-based method. The RuO₂/CNT nanocomposites show excellent supercapacitance performance and cycling performance compared with both pure CNT and pure RuO₂ when used as electrode materials for supercapacitors. The RuO₂ nanoparticles in the composite with a RuO₂/CNT mass ratio of 6:7 could achieve a specific capacitance of as high as 953 F g⁻¹ and outstanding cycling performance, which are benefiting from the dispersive action and good electronic conductivity of CNTs as well as the pinning effect for nanosized RuO₂ particles on the CNTs' surfaces.

2. Experimental Section

2.1. Synthesis of RuO₂/CNT Nanocomposites. RuCl₃·3H₂O and sodium hydroxide used in this paper were provided by Beijing Beihua Fine Chemicals Co., Ltd. and used as received. Multiwalled CNTs were used in our experiments (Shenzhen Nanotech Port Co., Ltd.), which were prepared by catalytic decomposition of CH₄ using La₂NiO₄ as catalyst precursor. The nominal diameter, length, and purity are 60–100 nm, 5–15 μm, and >95% with <3% amorphous carbon, respectively. The CNTs were purified by being dispersed in a 6 M HNO₃ solution and heated to 110 °C for 48 h, then filtered and washed with distilled water and ethanol several times. Such CNTs were characterized with contained acidic sites on the surface. To prepare RuO₂/CNT nanocomposites, 10 mg of CNTs was dispersed to 30 mL of distilled water and ultrasonicated for 3 h; then a suitable amount of RuCl₃·3H₂O was added to the CNT solution. NaOH was used to adjust the pH value of the above solution to 7. The mixture was refluxed at 120 °C for 6 h. After the reaction, the suspension and precipitate were separated, dried, and then heated at 150 °C for 6 h.

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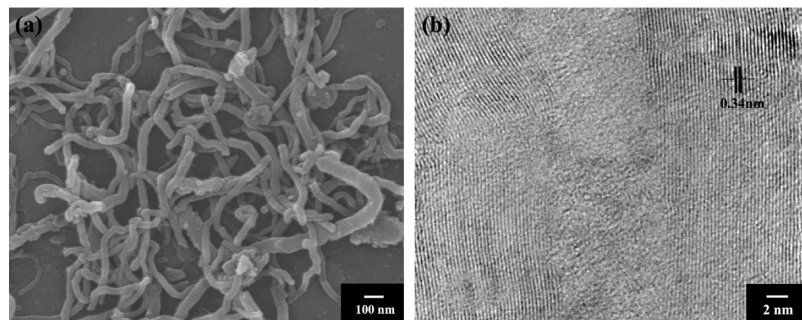


Figure 1. (a) SEM and (b) HRTEM images of the multiwalled CNTs used.

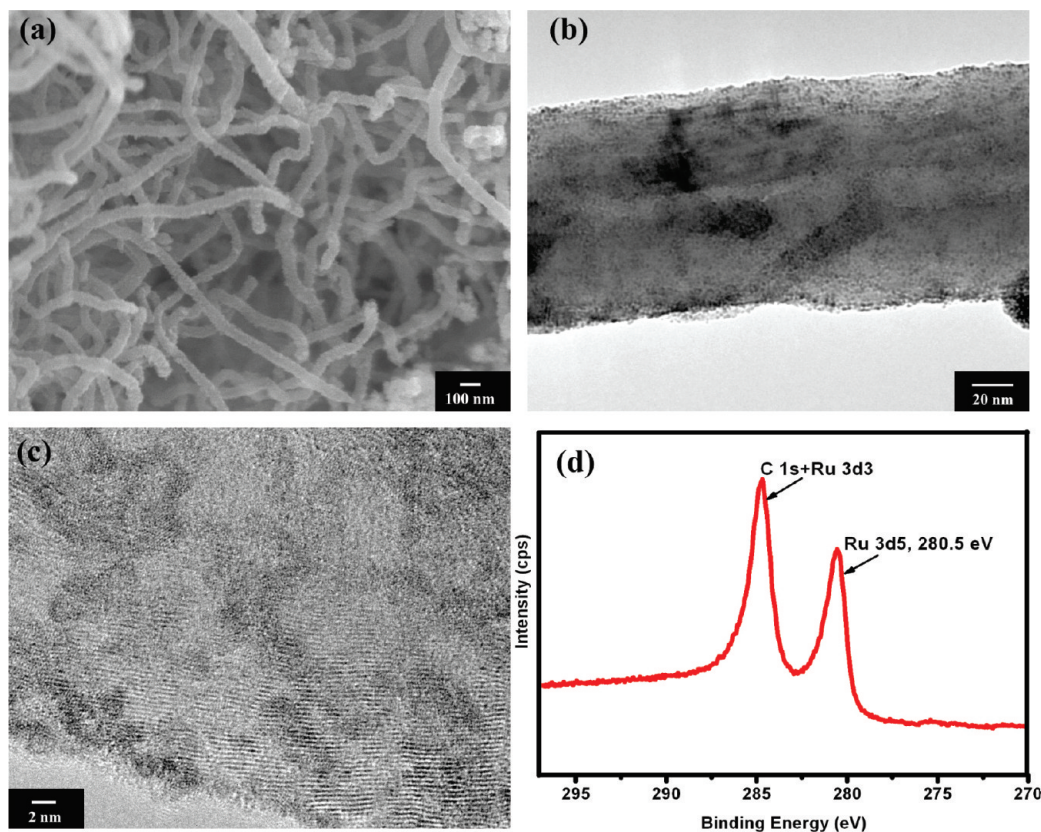


Figure 2. (a) SEM, (b) TEM, and (c) HRTEM images and (d) XPS spectrum of the as-prepared RuO₂/CNT nanocomposites (RuO₂/CNT = 6:7 in wt %).

2.2. Preparation and Characterization of Supercapacitor Electrodes. The products were characterized by scanning electron microscopy (SEM, JEOL JSM-6701F) and transmission electron microscopy (TEM, JEOL JEM-1011). X-ray photoelectron spectroscopy (XPS) was obtained with a VG ESCALab220i-XL electron spectrometer using 300 W Mg K α radiation. Thermogravimetric (TG) analysis was carried out using a PerkinElmer model Pyris 1 thermal analysis equipment under air atmosphere. Electrochemical measurements were carried out on an Arbin BT2000 system and a Parstat 2273 advanced electrochemical system. The working electrodes were prepared by pressing a mixture of active materials, carbon black, and teflonated acetylene black (TAB) binder at a weight ratio of 8:1:1 onto a nickel mesh.

3. Results and Discussion

Figure 1a shows a field emission SEM image of the CNTs used in our experiments. The CNTs are randomly entangled and cross-linked. The nanotubes have a diameter of 60–100

nm and length of several micrometers to several tens of micrometers, which are consistent with the nominal data provided by the supplier. Figure 1b shows a typical HRTEM image of the multiwalled CNTs used. The interplanar spacing of the pure CNTs was measured to be 0.34 nm, corresponding to the crystal lattice distance of multiwalled CNTs.

Figure 2a shows a typical SEM image of the as-prepared RuO₂/CNT nanocomposites. It can be seen that a nanotube structure is still retained after introducing RuO₂. However, the surfaces of the nanotubes became much rougher than pure CNTs, indicating the growth of RuO₂ nanoparticles on the surfaces. TEM observations were used to give more detailed structure information of the nanocomposites. Figure 2b clearly shows that the CNTs are coated with RuO₂ nanoparticles, and these particles are very small and highly dispersed on the whole surfaces of the CNTs. Figure 2c is a high-resolution TEM image of the composite nanotube, which clearly shows the lattice fringes of the CNTs as well as the highly dispersed RuO₂ nanoparticles with an average diameter of about 2 nm; no

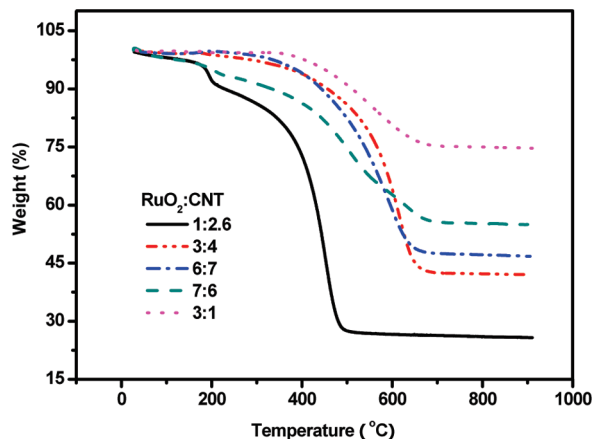


Figure 3. TG results of as-prepared RuO₂/CNT nanocomposites with different RuO₂/CNT mass ratios under air atmosphere.

crystalline RuO₂ lattice fringes could be observed due to the poor crystallinity of the as-grown RuO₂ nanoparticles. It should be noted that whether the RuO₂ coating is also attached to the internal surface of the CNTs besides the external surface needs more investigation.

The chemical composition of the ruthenium oxide nanoparticles is determined using XPS. Figure 2d shows the Ru 3d and C 1s spectra of the RuO₂/CNT nanocomposites. Usually, the Ru 3d₅ spectrum is used for identifying the electronic states of Ru because the Ru 3d₃ spectrum and C 1s spectrum are generally overlapped. The Ru 3d₅ peak of the as-prepared nanocomposites is located at 280.5 eV (Figure 1d), which confirms the successful deposition of RuO₂ into CNTs.²⁷ Thermogravimetric (TG) analyses were carried out to determine the chemical compositions of as-prepared RuO₂/CNT nanocomposites. Figure 3 shows the TG results of the RuO₂/CNT nanocomposites with different RuO₂/CNT mass ratios of 1:2.6, 3:4, 6:7, 7:6, and 3:1. Only one significant weight loss was found around 500 °C in the TG curves, except for the one of the nanocomposite with low RuO₂ content, which exhibited a slight weight loss at about 200 °C due to the removal of adsorbed water and crystal water. The large weight loss at about 500 °C is due to the removal of CNTs from the nanocomposites. After 700 °C, the TG traces are stable with no further weight loss, indicating the complete removal of CNTs. Therefore, the mass ratio of RuO₂ to CNT in the RuO₂/CNT nanocomposites can be calculated based on the TG results. It was found that the RuO₂/CNT mass ratios of the five RuO₂/CNT nanocomposites were 1:2.6, 3:4, 6:7, 7:6, and 3:1.

The electrochemical performances of the RuO₂/CNT nanocomposites as electrode materials for supercapacitors were tested using cyclic voltammograms (CVs) and galvanostatic charge–discharge (GCD) in 1 mol L⁻¹ H₂SO₄. Figure 4a shows the CV curves of acid-treated CNTs, pristine RuO₂ nanoparticles prepared in a controlled experiment in the absence of CNTs, and the RuO₂/CNT nanocomposites with different RuO₂/CNT mass ratios of 1:2.6, 3:4, 6:7, 7:6, and 3:1. It is clear that all the materials are exhibiting an almost rectangular shape, which is a typical capacitor-like behavior. The specific capacitance is increased with the content of RuO₂ in the composites, which is consistent with the fact that the pure RuO₂ has a much larger specific capacitance (ca. 648 F g⁻¹) than that of the pure CNTs (ca. 43 F g⁻¹). In the RuO₂/CNT nanocomposites with a RuO₂/CNT mass ratio of 3:1, a specific capacitance of 592 F g⁻¹ can be obtained based on the whole mass of the composite, which is quite comparable to that of pure RuO₂, but 25 wt % of RuO₂ is saved in this way.

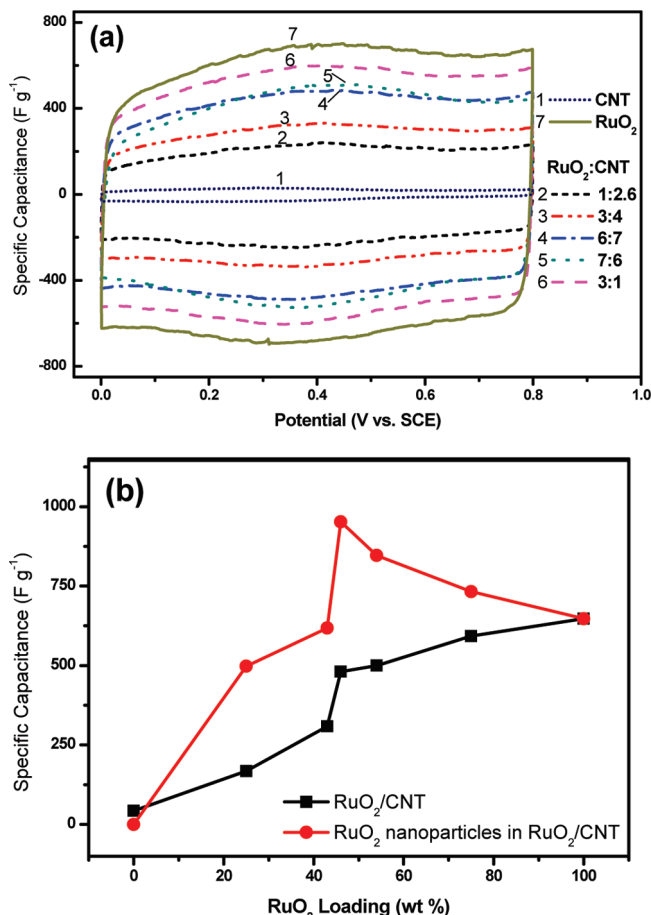


Figure 4. (a) Cyclic voltammograms of pristine RuO₂, acid-treated CNTs, and RuO₂/CNT nanocomposites with different RuO₂/CNT mass ratios at a scan rate of 1 mV s⁻¹. (b) The specific capacitances of the RuO₂/CNT nanocomposites as a function of RuO₂ loading fraction. The specific capacitances in the RuO₂ nanoparticles in the composites are also shown.

Figure 4b shows the specific capacitance of the samples as a function of RuO₂ loading weight in the composites. When the contribution of the double-layer capacitance from CNTs in the composites is eliminated, the specific capacitances contributed by the RuO₂ nanoparticle coatings could be obtained. A maximum specific capacitance of as high as 953 F g⁻¹ was achieved for the RuO₂ in a composite with a RuO₂/CNT mass ratio of 6:7, which is benefiting from the optimized nanostructure with well-dispersed RuO₂ nanoparticles, as shown in Figure 2b. This value is much higher than that of bare RuO₂ (ca. 648 F g⁻¹) and other reported values (500–788 F g⁻¹) of RuO₂²⁸ (see ref 28 and references therein). As far as RuO₂ is concerned, it is the highest capacitance ever measured.²⁸ The results clearly indicate that the presence of the supporting materials of CNTs can increase the capacitance of RuO₂ by a factor of 1.5, which is benefiting from the dispersive action of CNTs for nanosized RuO₂ particles.

In addition to the high specific capacitance, the RuO₂/CNT composite also shows outstanding high-power and high-energy performance compared to pure RuO₂ (see the Ragone plots in Figure 5a). For example, at a power density of 5000 W kg⁻¹, the RuO₂/CNT composite (RuO₂/CNT = 6:7 in wt %) can still deliver an energy density of 16.8 Wh kg⁻¹, which is about 5.8 times larger than that of bare RuO₂ (2.9 Wh kg⁻¹). The good behavior of the RuO₂/CNT nanocomposites might be ascribed to the enhanced electronic conductivity of the whole electrode due to the introducing of CNTs.

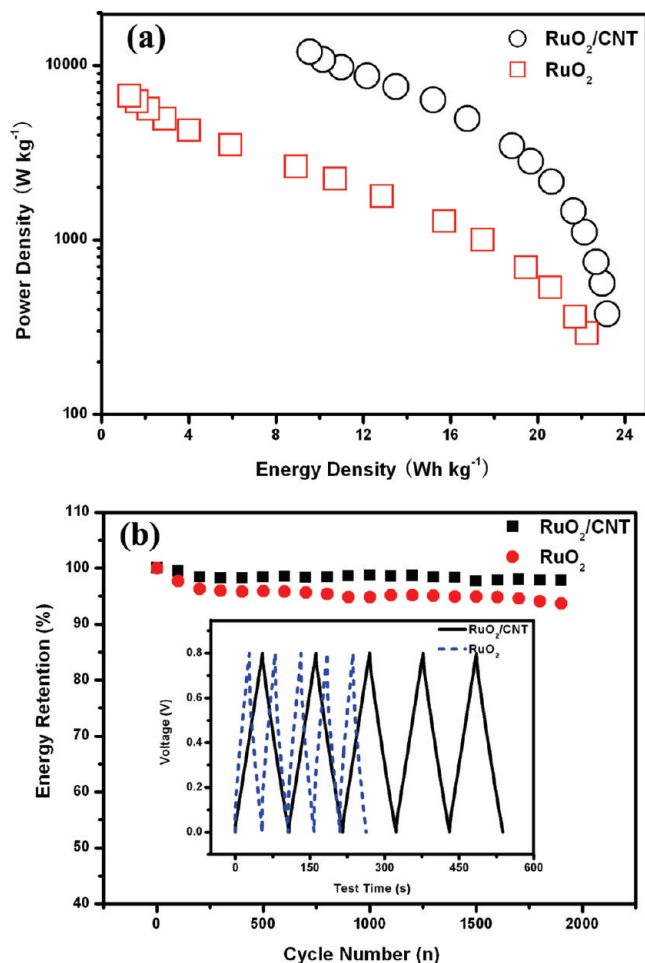


Figure 5. (a) Comparison of Ragone plots and (b) cycling performances for the RuO₂/CNT composite (RuO₂/CNT = 6:7 in wt %) and bare RuO₂. The inset of (b) shows galvanostatic charge-discharge curves of the two samples cycled at 5 A g⁻¹.

Another excellent property of the RuO₂/CNT composite is the improved cycling performance compared with pure RuO₂ (Figure 5b). The superior capacitance behaviors of the RuO₂/CNT composite are further verified by the symmetric and linear galvanostatic charge-discharge curves (inset of Figure 5b) and the longer charge and discharge times. Note that, after 2000 galvanostatic charge-discharge cycles at a current density of 5 A g⁻¹, almost no energy loss is found in the RuO₂/CNT composite (RuO₂/CNT = 6:7 in wt %) (i.e., the capacitance is still about 98% of its initial capacitance). In comparison, the energy retention of bare RuO₂ is only 93% after the 2000 cycles under the same current density. Usually, the RDECs using transition-metal oxides show worse cycling performance than DLECs. In the hybrid ECs using the composite electrode material of RuO₂ (an electrode material for RDECs) and CNT (an electrode material for DLECs), the excellent cycling performance can be attributed to the favorable function of CNTs for pinning nanosized RuO₂ particles and, hence, effectively prevent the aggregation of these nanoparticles during electrochemical cycles, which is similar to that found in lithium storage systems.²⁹

4. Conclusion

In summary, we have demonstrated that the direct growth of RuO₂ nanoparticles on the CNTs' surface provides a simple and convenient method to design superior electrode materials for ECs.

The as-prepared composite nanostructures contain a large number of RuO₂ nanoparticles inlaid on the outer surfaces of the CNTs. Electrochemical test results show that the RuO₂/CNT composite can be used as superior electrode materials for ECs with high specific capacitance and significantly enhanced high-power and high-energy capabilities as well as improved cycling performance compared with bare RuO₂. The improved electrochemical performance can be attributed to the multiple functions of the CNTs, including the following: (i) resulting in a better dispersion of RuO₂ nanoparticles with a small size (<2 nm), (ii) increasing the electronic conductivity of the composite electrodes, and (iii) pinning nanosized RuO₂ particles. The results presented here give clear evidence of the ability of CNTs to improve the electrochemical performance of RDEC electrode materials, such as nanostructured transition-metal oxides.

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