

# Electrochemical capacitance of nanocomposite films formed by loading carbon nanotubes with ruthenium oxide

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## Abstract

This work reports the supercapacitive properties of composite films of multiwalled carbon nanotubes (MWNT) and ruthenium oxide (RuO<sub>2</sub>). Transmission and scanning electron microscopy, cyclic voltammetry, and electrochemical studies revealed that the nanoporous three-dimensional arrangement of RuO<sub>2</sub>-coated MWNT in these films facilitated the improvement of electron and ion transfer relative to MWNT films. The capacitance was measured for films of different RuO<sub>2</sub> loading, revealing specific capacitances per mass as high as 628 F g<sup>-1</sup>. The energy storage density of the electrode has increased about three times as compared to MWNT treated with piranha solution.

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**Keywords:** Carbon nanotubes; RuO<sub>2</sub>; SEM; TEM; Supercapacitor

## 1. Introduction

Carbon nanotubes (CNTs) are expected to have a wide variety of interesting properties [1] with potential application as nanodevices, field emission display and energy storage devices [2,3]. CNTs have high surface area polarizability, high electrical conductivity and chemical stability, as well as extremely high mechanical strength and modulus, which make them an important material for electrochemical capacitors. Increased demands in electronic communication, electric vehicles, and other devices that require electrical energy at high power levels in relatively short pulses have prompted considerable interest in electrochemical capacitors, also known as supercapacitors or ultracapacitors [4,5]. Electrochemical capacitors can deliver high-power within very short time, and rechargeable batteries, which can store high amounts of energy, have found an increasingly important role in power source applications [6–8]. It has superior rate capability and longer cycle life compared with modern secondary batteries [8]. The largest charge storage capabilities of supercapacitors observed for conducting polymers is (specific capacitance) 450 F g<sup>-1</sup> [9] and transition metal oxides is (specific capaci-

tance) 840 F g<sup>-1</sup> [10–15]. Alternatively, supercapacitors made from high area carbons are attractive for their excellent rates of charge and discharge [16–18]. Rather than storing charge in the bulk of the capacitive material, double-layer supercapacitors store charge in an electrochemical double-layer formed at their interface with the electrolyte. While this mechanism can increase the rate of response by several orders of magnitude, it limits the total amount of charge that can be stored (specific capacitance) 180 F g<sup>-1</sup> relative to redox pseudocapacitive materials [19–22]. Recently, a variety of methods have been reported for producing composites of redox pseudocapacitive materials (ruthenium oxide, polyaniline, poly(*p*-phenylenevinylene), etc.) and double-layer capacitive materials (activated carbon black, carbon aerogels, carbon nanotubes, etc.) [23–33]. The key to increasing energy density of an electrochemical capacitor is to form an electrode containing metal centers capable of providing multiple redox reaction. RuO<sub>2</sub> has been well known as an electrode material showing high performance for electrochemical capacitor because of its multiple oxidation states [34,35]. Even though RuO<sub>2</sub> has a great advantage in terms of a wide potential range of highly reversible redox reactions [36] with high specific capacitance, it is somewhat expensive for commercial electrodes in bulk for electrochemical capacitors. So, dispersion of the RuO<sub>2</sub> in less expensive material is an effective means to decrease costs of electrode material.

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The preparation of hydrous ruthenium oxide/carbon composites has been reported [30,32,37–42]. Miller et al. [30,37], Pekala et al. [38] and Jang et al. [8] prepared the ruthenium/carbon aero-gel by chemical vapor impregnation of ruthenium (III) acetylacetonate into carbon aero-gels. In a different approach, Lin et al. [32] synthesized a similar composite material by adding  $\text{RuO}_2 \cdot \text{H}_2\text{O}$  powder in the sol–gel resorcinol formal dehydration reaction and subsequent carbonization at  $750^\circ\text{C}$  in a nitrogen atmosphere. Ye et al. [39] reported MWNT with  $\text{RuO}_2$  by magnetic sputtering for developing super-capacitor. The capacitance of a MWNT material was reported to increase from 27 to  $295 \text{ F g}^{-1}$  following modification of MWNT with ruthenium oxide [40]. Kim et al. [41] fabricated  $\text{RuO}_2/\text{CNT}$  composite by coating the CNTs with an amorphous  $\text{RuO}_x$  layer using metallorganic CVD followed by post-annealing at  $350^\circ\text{C}$ . Arabale et al. [42] reported the pseudocapacitive behavior of multiwalled carbon nanotubes (MWNTs) functionalized with hydrous ruthenium oxide for supercapacitor application. A specific capacitance of  $80 \text{ F g}^{-1}$  is obtained after ruthenium oxide fictionalization.

We report here the analysis of super-capacitive properties of MWNT- $\text{RuO}_2$  composite and the benefits conferred by the excellent nanostructural control offered by these films. Utilization of the ruthenium component in the composite electrodes is an important aspect for practical applications. We demonstrate that the unique structure of MWNT utilizing agglomerated  $\text{RuO}_2$  nanoparticles with optimum quantity provides high electrochemical accessibility which is crucial for its high energy and power density.

## 2. Experimental

MWNT were synthesized on a graphite working electrode by chemical vapour deposition (CVD). A solution of  $0.05 \text{ M Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  was sprayed on working electrode ( $0.1 \text{ cm} \times 2 \text{ cm} \times 0.8 \text{ cm}$ ) and then working electrode was dried in an oven for 30 min at  $100^\circ\text{C}$ . Nickel salts on the working electrode were decomposed under argon flow of 100 sccm for 2 h at  $600^\circ\text{C}$ , and then reduced by hydrogen for 1 h at  $600^\circ\text{C}$  just before CVD. MWNT were directly grown on Ni-loaded working electrode via the decomposition of acetylene under 1 atm of pressure for 3 min at  $600^\circ\text{C}$  in tubular quartz reactor of 1 in. (O.D.) and 35 cm length. The total flow of acetylene and hydrogen was 100 sccm and the ratio of acetylene to hydrogen was 1:9. Once formed, MWNT was impregnated with a ruthenium nitrosyl nitrate solution ( $\text{Ru}(\text{NO})(\text{NO}_3)_x(\text{OH})_y$ ,  $x + y = 3$ ,  $\text{Ru} = 1.5\%$ , solution in dilute nitric acid, Aldrich), and then followed by calcination at  $350^\circ\text{C}$  (30 min) for the formation of a composite electrode. The impregnation of the ruthenium nitrosyl nitrate solution on the as-grown MWNT was repeated several times in order to regulate the deposited amount of  $\text{RuO}_2$ .

The morphological images were examined by scanning electron microscopy (FE-SEM, JSM-6340F, JEOL, Japan). The amount of the impregnated ruthenium oxide into the carbon nanotube material was measured by weight difference. TEM images were obtained using a Phillips CM-30 transmission electron microscope (200 keV). The capacitance was measured

using a conventional three-electrode system (Potentiostat and Galvanostat, EG and G, PAR 273A) using a Pt counter electrode ( $2 \text{ cm} \times 2 \text{ cm}$ ) and an Ag/AgCl reference electrode. Cyclic voltammograms (CV) were obtained in  $1 \text{ M H}_2\text{SO}_4$  using a scanning potentiostat. For charge–discharge studies, a unit cell for electrochemical capacitor was assembled with positive and negative electrodes, which were separated by a polypropylene separator. Galvanostatic charge–discharge tests were performed using an automatic battery cycle (WBCS 3000) at  $0.8\text{--}1.0 \text{ mA cm}^{-2}$  current and a voltage of 0 to  $+0.8 \text{ V}$  depending on the electrolyte. The specific power and specific energy density of electrodes were calculated from data of the charge–discharge cycles.

The as-grown MWNT did not wet even in strong acid and base solution. The wettability of MWNT was tremendously improved with piranha solution treatment, which increased specific capacitance from 10 to  $100 \text{ F g}^{-1}$ . This increase in capacitance is mainly caused by the functional groups formed during piranha solution treatment [43]. The piranha solution is a mixture of  $\text{H}_2\text{SO}_4$  (97%, Matsuno Chemicals Ltd.) and  $\text{H}_2\text{O}_2$  (35%, Junsei). The ratio of  $\text{H}_2\text{SO}_4$  to  $\text{H}_2\text{O}_2$  was 3:1 in volume.

## 3. Results and discussion

Fig. 1 compares the CV results of a MWNT- $\text{RuO}_2$  composite film with a similarly piranha treated MWNT films. The cyclic voltammograms (Fig. 1a) indicate several important differences between the two films. The first is that the appearance of a broad peak on the CV of composite film, confirming the role of the  $\text{RuO}_2$ . The second point is that the output current of the composite film is about thrice that of the MWNT. Since capacitance can be estimated from the output current divided by the scan

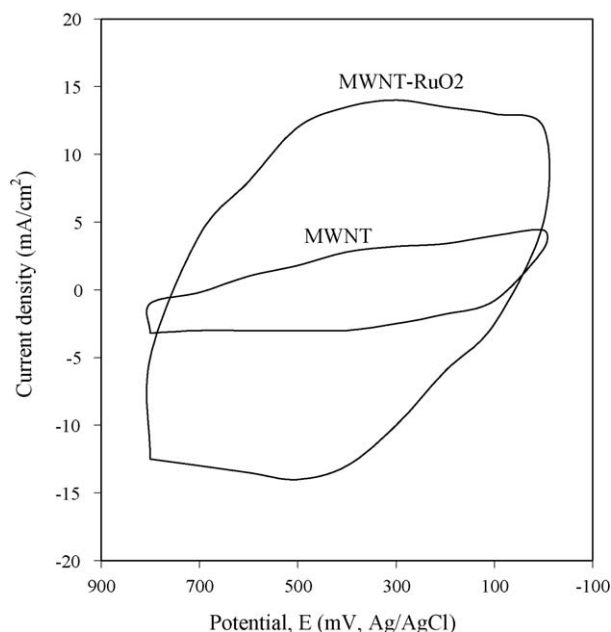


Fig. 1. Plot of current density against potential for piranha treated MWNT and MWNT- $\text{RuO}_2$  electrode at a scan rate of  $10 \text{ mV s}^{-1}$ .

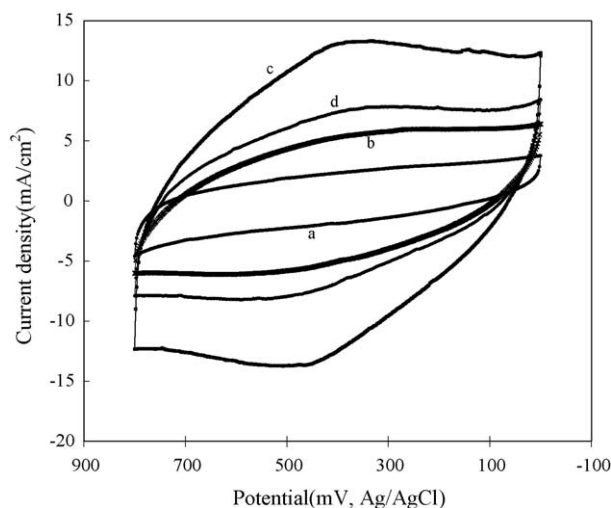


Fig. 2. Cyclic voltammogram of MWNT-RuO<sub>2</sub> electrode at a scan rate of 10 mV s<sup>-1</sup>. (a) MWNT:RuO<sub>2</sub>::1.0:0.0, (b) MWNT:RuO<sub>2</sub>::1.0:0.5, (c) MWNT:RuO<sub>2</sub>::1.0:1.0 and (d) MWNT:RuO<sub>2</sub>::1.0:2.0.

rate, this implies that the capacitance of the composite films is about three times that of the MWNT.

Cyclic voltammograms of an electrode (2 cm × 0.8 cm) of MWNT-RuO<sub>2</sub> were obtained in a conventional three electrodes system at a scan rate of 10 mV s<sup>-1</sup> with different ratios of RuO<sub>2</sub> to MWNT in weight, as shown in Fig. 2. Also, Table 1 shows the specific capacitances of the electrodes of MWNT-RuO<sub>2</sub> from the cyclic voltammograms according to ratios of RuO<sub>2</sub> to MWNT in weight. In case of piranha treated MWNT electrode, the capacitance current is small compare to MWNT-RuO<sub>2</sub> electrode. The capacitance value was calculated using the equation of  $I(A)/(dV/dt)$ , where  $I$  is the capacitive current and  $(dV/dt)$  denotes the scan rate. The optimum impregnation of RuO<sub>2</sub> on MWNT for the specific capacitance of MWNT-RuO<sub>2</sub> electrode was investigated with the results as shown in Fig. 2 and Table 1. The specific capacitance (628 F g<sup>-1</sup>) of the electrodes of MWNT-RuO<sub>2</sub> in case of the ratio of 0.5:1.0 of RuO<sub>2</sub> to MWNT in weight was about three times that (217 F g<sup>-1</sup>) of piranha treated MWNT only. It is most likely that there is a significant increase in the capacitance due to a pseudocapacitance of RuO<sub>2</sub>. The highest capacitance value was obtained with sample MWNT:RuO<sub>2</sub>::1.0:0.5 (Table 1) but in Fig. 2 the highest current is observed for sample MWNT:RuO<sub>2</sub>::1.0:1.0, this is due to presence of different quantity of electrochemically active material (Table 1).

Table 1  
Specific capacitance of MWNT-RuO<sub>2</sub> electrode from cyclic voltammograms at a scan rate of 10 mV s<sup>-1</sup>

Weight of MWNT (mg)	Weight of RuO <sub>2</sub> (mg)	MWNT:RuO <sub>2</sub>	Capacitance (F g <sup>-1</sup> )
1.20	0.00	1.0:00	217
0.70	0.35	1.0:0.5	628
2.10	2.10	1.0:1.0	467
1.60	2.42	1.0:1.5	362
1.80	3.60	1.0:2.0	370

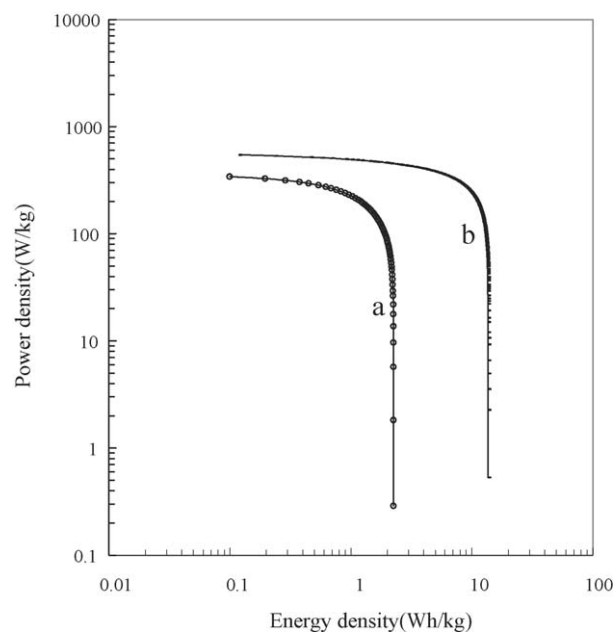


Fig. 3. Plot of power density against energy density for (a) piranha treated MWNT and (b) MWNT-RuO<sub>2</sub> electrode.

Fig. 3 show the plot of power density against energy density for piranha treated MWNT and MWNT-RuO<sub>2</sub> electrode. In the field of capacitor technology, the relation between power density and energy density has practical importance as well as theoretical significance. It is seen from Fig. 3 that the MWNT-RuO<sub>2</sub> electrode could be used in electrochemical capacitors of high energy density.

The morphology of the MWNT-RuO<sub>2</sub> composite films was examined using a scanning electron microscope. RuO<sub>2</sub> was found to coat each individual MWNT and bind the coated tubes together in a nanoporous three-dimensional network (Fig. 4). Fig. 4a is a plan view image in low magnification showing well-dispersed and agglomerated RuO<sub>2</sub> nanoparticles. The nanoparticles of RuO<sub>2</sub> are visible at higher magnification (Fig. 4b). The agglomerated RuO<sub>2</sub> is porous and approximately about 3 nm in size. This indicates that the RuO<sub>2</sub> surface area would be very high because of the porous film and the nanosized particles. The thickness of the electrode of MWNT-RuO<sub>2</sub> is about 10 μm, as shown in Fig. 4c. Fig. 4d shows SEM image of MWNT at higher magnification. MWNT grown on a carbon sheet by CVD is a mixture of straight hollow tubes and coiled hollow or filamentous tubes (Fig. 4d). The thickness of the RuO<sub>2</sub> coating on each tube was observed to reach as much as 250 nm depending on loading conditions employed. It is also interesting to note that the coated MWNT tended to preferentially align parallel to the plane of the film. The structure of the MWNT-RuO<sub>2</sub> composite films was examined using TEM studies on electrode. The RuO<sub>2</sub> particles were finely dispersed on MWNT surface as shown in the TEM images of Fig. 5. The TEM images show finely dispersed RuO<sub>2</sub> on MWNT surface. It is worth noting that the particle size of the dispersed RuO<sub>2</sub> is about 3 nm. RuO<sub>2</sub> nanoparticles are well dispersed over MWNT (Fig. 4). This means that these RuO<sub>2</sub> particles have an effective surface area for an electrochemical capacitor. XRD and EDX spectra (not

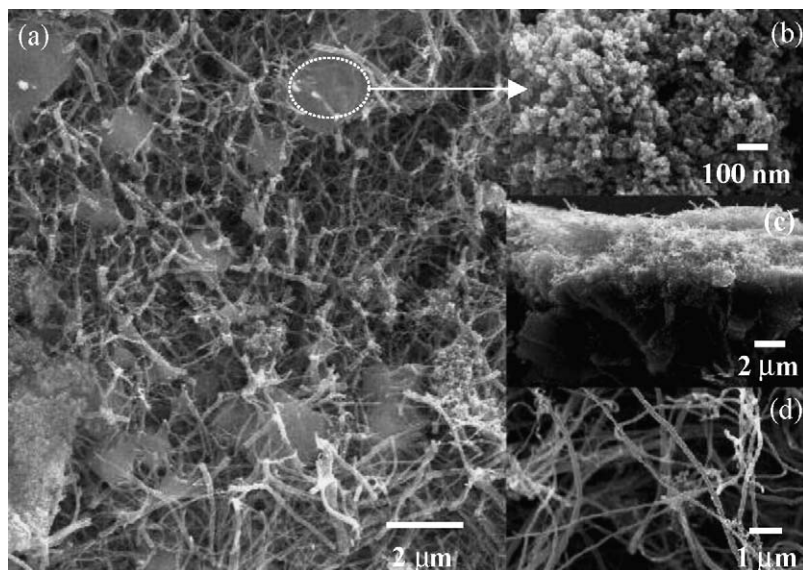


Fig. 4. SEM images of MWNT-RuO<sub>2</sub> electrode: (a) MWNT-RuO<sub>2</sub> electrode, (b) RuO<sub>2</sub> nanoparticles, (c) thickness of MWNT-RuO<sub>2</sub> and (d) MWNT.

shown here) revealed presence and the nanocrystalline nature of the ruthenium oxide particle in MWNT. The structure of the composite film contributes to its improved ionic conductivity, capacitance, and rate of response in three ways. The first is by providing a large surface area of RuO<sub>2</sub> in a porous morphology that allows excellent electrolyte access in three dimensions. Second, since the RuO<sub>2</sub> is coated on each MWNT as a thin layer, the ion intercalation distance is reduced to nanometers. Finally, the conductivity of the MWNTs dispersed throughout the structure increases the electrical conductivity of the composite.

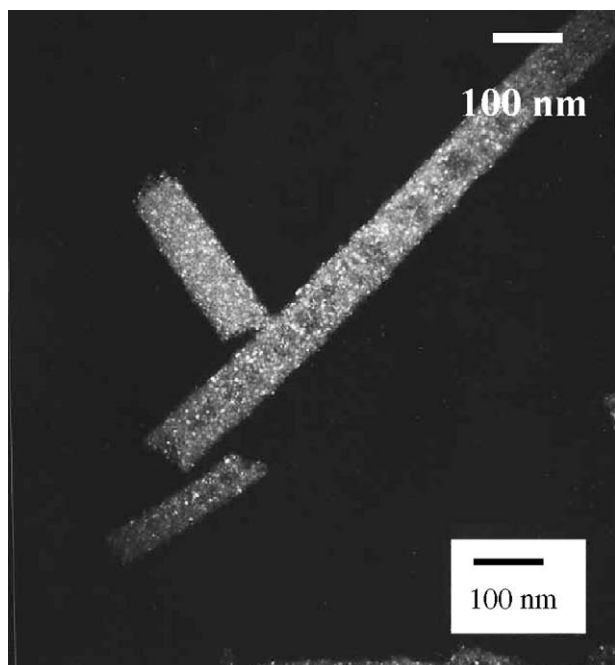


Fig. 5. TEM image of MWNT-RuO<sub>2</sub> electrodes.

#### 4. Conclusions

In summary, we have studied the structure and capacitive properties of composite films made from catalytically grown MWNT and RuO<sub>2</sub>. To achieve both high specific capacitance and high power simultaneously, adding a proper proportion of RuO<sub>2</sub> on MWNT to form a composite electrode may be an effective method. Comparing different ratios, the composition of 1.0:0.5 of RuO<sub>2</sub> to MWNT was the most suitable for electrode materials in electrochemical capacitor. FESEM analysis indicated that it was possible to produce nanocomposite networks of RuO<sub>2</sub>-coated MWNT. CV analysis demonstrated the excellent charge storage and transfer capabilities of these films, a result that is attributed to the high surface area, conductivity, and electrolyte accessibility of the nanoporous structure. These results suggest that nanoporous composites of MWNT and RuO<sub>2</sub> hold great promise for energy storage devices such as supercapacitors.

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