



Preparation and characterization of electro-spun $\text{RuO}_2\text{--Ag}_2\text{O}$ composite nanowires for electrochemical capacitors

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ABSTRACT

We synthesized $\text{RuO}_2\text{--Ag}_2\text{O}$ composite nanowires by means of an electrospinning method and investigated the capacitance, high-rate performance, and cycle number dependence of the composite nanowire electrodes. In order to synthesize optimum $\text{RuO}_2\text{--Ag}_2\text{O}$ composite nanowires, the relative mole ratio of Ag precursor to Ru precursor varied from ~ 0.1 to ~ 0.3 . X-ray diffraction, X-ray photoelectron spectroscopy, scanning electron microscopy, and high-resolution transmission electron microscopy results show that crystalline $\text{RuO}_2\text{--Ag}_2\text{O}$ composite nanowires ($\sim 40\text{--}70$ nm in diameter) are formed upon calcinations. Cyclic voltammetry results show that among the samples, the $\text{RuO}_2\text{--Ag}_2\text{O}$ composite nanowires fabricated with the mole ratio of ~ 0.2 give the highest capacitance, excellent high-rate performance, and excellent retention of capacity ($\sim 97\%$).

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1. Introduction

Energy storage devices, such as batteries, fuel cells, solar cells, and electrochemical capacitors, are of significant technological importance because of the development of electronic devices, e.g., mobile phones, electric vehicles, displays, and laptop computers [1,2]. Electrochemical capacitors, which store electric energy by means of two different energy storage mechanisms of electrostatic (electrochemical double layer capacitors, EDLC) and faradaic charge transfer (pseudo-capacitors), have characteristic features, such as high power density, high energy density, and long cycle life [3,4].

Recently, one-dimensional nanostructures are of increasing interest because of their unique electrical, physical, and optical properties, and various applications, such as catalysts, electronics, optics, biondiagnostics, and energy storage devices [5,6]. For energy devices, electrochemical capacitors have been fabricated using different one-dimensional nanostructures. For example, Li et al. reported that Ni-embedded carbon nanofibers produced a specific capacitance of 164.0 F/g in 6 mol/L KOH electrolyte at a scan rate of 2 mV/s [7]. Hyun et al. synthesized $\text{MnO}_x\text{--RuO}_2$ nanofibers by a co-electrospinning method to fabricate electrochemical capacitors and showed that the nanofibers having a high porosity and a

high surface area yielded a specific capacitance of 208.7 F/g at a scan rate of 10 mV/s [8]. Chen et al. reported on the fabrication of electrochemical capacitors using In_2O_3 nanowires/carbon nanotube electrodes synthesized by pulsed laser deposition and vacuum filtration methods, giving a good retention of capacity ($\sim 88\%$) up to 500 cycles and a capacitance of 64 F/g [9]. However, the electrochemical properties of one-dimensional nanostructured electrodes for electrochemical capacitors have not been widely investigated hitherto. In addition, among the various synthesis methods, an electrospinning method was known to be one of the effective ways, which is capable of a large-scale production of nanofibers [10,11].

In this work, we synthesized $\text{RuO}_2\text{--Ag}_2\text{O}$ composite nanowire electrodes for electrochemical capacitors by an electrospinning method and investigated their electrochemical properties. In order to optimize the electrochemical properties, the RuO_2 -based composite nanowires were fabricated as a function of the amount of Ag_2O . RuO_2 was chosen as a host electrode because it has a high specific capacitance and high conductivity [12,13].

2. Experimental procedures

$\text{RuO}_2\text{--Ag}_2\text{O}$ composite nanowire electrodes were synthesized by an electrospinning method. First, a precursor solution of $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ (Aldrich) was dispersed in N,N -dimethylformamide (DMF, Aldrich) for 12 h. Poly(vinylpyrrolidone) (PVP, Aldrich, $M_w = 1,300,000\text{ g/mol}$) was also dissolved in N,N -dimethylformamide (DMF, Aldrich) for 12 h. Then, to form single RuO_2 nanowires, these dispersed solutions were mixed well by stirring at room temperature for 2 h. To fabricate $\text{RuO}_2\text{--Ag}_2\text{O}$ composite nanowire electrodes, AgNO_3 (Aldrich) was added to a mixture of $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ (Aldrich) dispersed in N,N -dimethylformamide (DMF, Aldrich). To fabricate optimum $\text{RuO}_2\text{--Ag}_2\text{O}$ composite nanowire electrodes, the relative mole

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ratio of the Ag precursor to the Ru precursor mixture was controlled as ~ 0.1 , ~ 0.2 , and ~ 0.3 (referred to here as samples A, B, and C, respectively). The precursor solution was poured into a syringe (10 ml) equipped with a 23 gauge needle, which was connected to a DC power supply (Powertron Co., Ltd., Korea). The feeding rate of the solutions was fixed to be 0.01 ml/h during electrospinning and a Si substrate was vertically placed at a distance of ~ 15 cm from the syringe needle under a high voltage of 11 kV in order to collect as-spun nanowires. The as-spun nanowires were dried at 80°C for 2 h in an oven and then annealed at 400°C for 1 h in air, resulting in the formation of single RuO_2 and $\text{RuO}_2\text{-Ag}_2\text{O}$ composite nanowires. The morphologies of the samples were characterized by field emission scanning electron microscopy (FESEM: Hitachi S-4100) and high-resolution electron microscopy (HREM: a Phillips CM20T/STEM Electron Microscope equipped with energy dispersive X-ray spectroscopy (EDS)). X-ray diffraction (XRD: an Rigaku Rint 2500 with a $\text{Cu K}\alpha$ radiation) was used to examine the structural properties of the samples. X-ray photoemission spectroscopy (XPS) examinations were made using a VG Scientific (ESCALAB 250) X-ray photoelectron spectrometer with an Al $\text{K}\alpha$ X-ray source ($\sim 1486.6\text{ eV}$) under a base pressure of 2×10^{-9} Torr. The electrochemical behaviors of the samples were studied in a conventional three-electrode system using Potentiostat/Galvanostat (PGST302N by Eco Chemie, Netherlands). The electro-spun $\text{RuO}_2\text{-Ag}_2\text{O}$ composite nanowire electrode, Pt gauze, and Ag/AgCl (sat. KCl) were used as working electrode, counter, and reference electrode. We prepared slurries consisting of electro-spun $\text{RuO}_2\text{-Ag}_2\text{O}$ composite nanowires (70 wt%), acetylene black (20 wt%), and polyvinylidene fluoride (PVDF) (10 wt%) dissolved in *n*-methyl pyrrolidinone (NMP). The electrodes were fabricated by coating the slurry onto a glassy carbon electrode and then were annealed at 80°C for 20 min in an oven. The electrolyte was a 0.5 M H_2SO_4 solution. The performance of the electrochemical capacitors fabricated using these electrodes was characterized by a cyclic voltammetry technique at scan rates of 10, 30, 50, 100, and 200 mV/s in the range of 0.0–1.0 V at room temperature.

3. Results and discussion

Fig. 1 shows powder XRD data obtained from single RuO_2 nanowires, samples A, B, and C. For all the samples, there are diffraction peaks at 28.0° , 35.0° , and 54.2° , corresponding to RuO_2 phase with tetragonal structure (space group $\text{p}4_2/\text{mnm}$ [1 3 6]) (JCPDS

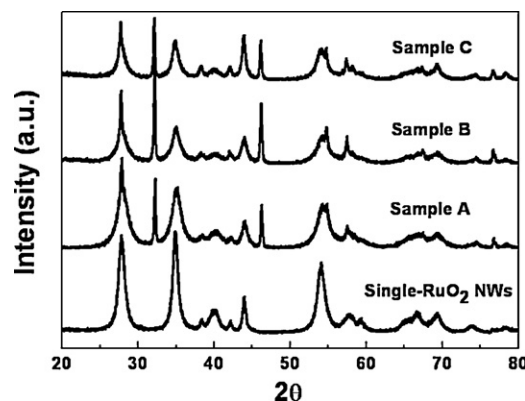


Fig. 1. Powder XRD data obtained from single RuO_2 nanowires, samples A, B, and C. The relative mole ratio of the Ag precursor to the Ru precursor was ~ 0.1 , ~ 0.2 , and ~ 0.3 for samples A, B, and C, respectively.

card No. 43-1027). In addition, extra diffraction peaks are observed at 32.7° and 47.0° , corresponding to Ag_2O phase with cubic structure (space group $\text{pn}3\text{m}$ [2 2 4]) (JCPDS card No. 43-0997). The XRD results indicate that $\text{RuO}_2\text{-Ag}_2\text{O}$ composite nanowire electrodes are formed.

Before annealing, all the samples consisted of metal precursors and PVP composite nanowires. SEM measurements (not shown) exhibited that their diameters were in the range of ~ 80 to ~ 130 nm for the single RuO_2 nanowires, ~ 80 to ~ 110 nm for sample A, ~ 90 to ~ 140 nm for sample B, and ~ 70 to ~ 120 nm for sample C. After calcinations at 400°C for 1 h, however, the diameters of all the samples became reduced: their diameters range from ~ 40 to ~ 70 nm, as shown in Fig. 2. The inset in Fig. 2(a) exhibits that annealing

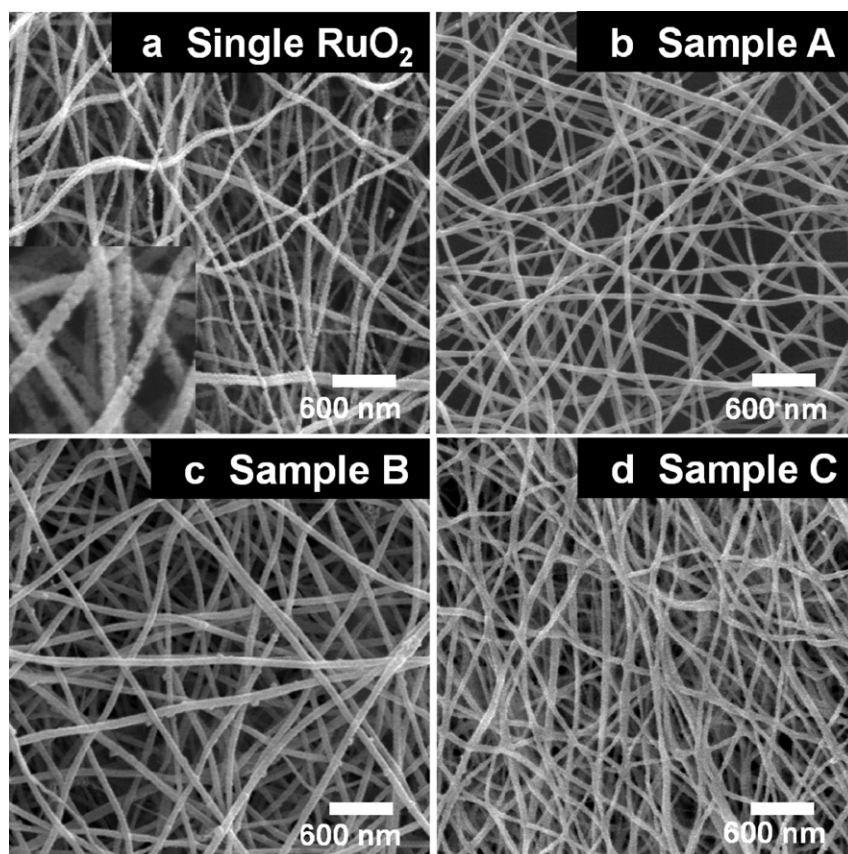


Fig. 2. SEM images obtained from (a) the single RuO_2 nanowires, (b) sample A, (c) sample B, and (d) sample C after calcinations at 400°C for 1 h. The inset in (a) shows an enlarged image, indicating the formation of porous nanowires.

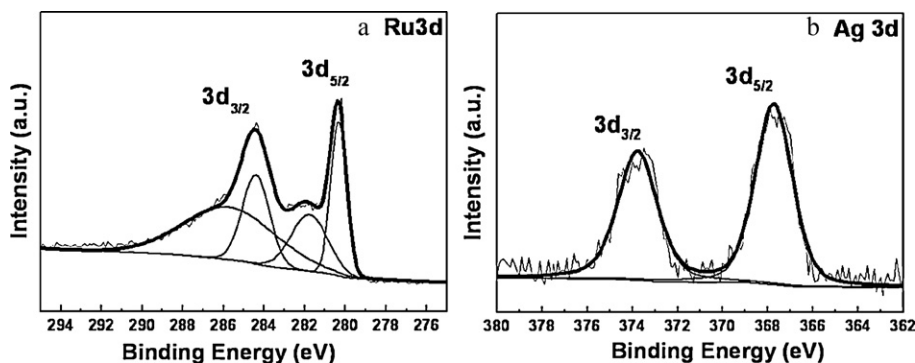


Fig. 3. (a) The XPS spectra for the Ru 3d_{3/2} and 3d_{5/2} photoelectrons at ~284.4 and ~280.3 eV. (b) The XPS spectra for the Ag 3d_{3/2} and Ag 3d_{5/2} photoelectrons at ~373.7 and ~367.7 eV.

causes the surface of the nanowires to get rougher, indicating the formation of porous nanowires. To investigate the chemical bonding states of Ru and Ag atoms, XPS examinations were performed on the annealed samples. Fig. 3(a) shows the XPS spectra for the Ru 3d_{3/2} and 3d_{5/2} photoelectrons at ~284.4 and ~280.3 eV, respectively. This implies that the elemental Ru in the RuO₂ is present as Ru(IV) species. Fig. 3(b) shows the XPS spectra for the Ag 3d_{3/2} and Ag 3d_{5/2} photoelectrons at ~373.7 and ~367.7 eV, respectively. This indicates that the elemental Ag in the Ag₂O is present as Ag(I) species [14,15].

Fig. 4 shows HRTEM images obtained from the samples after annealing. All the electro-spun nanowires consist of small nanoparticles (~2–3 nm in size) and their surfaces are rough, which could increase effective reaction sites. As shown in the insets of Fig. 4(c) and (d), the TEM images reveal somewhat dark band-like contrast at the surface region of the composite electrodes of samples C and D. The dark contrast contains mostly the Ag₂O phase. In order to confirm the distribution of elements, TEM-EDS mapping results were obtained from sample C. The results show that Ru atoms are uniformly distributed across the composite nanowires, but Ag atoms

are mostly distributed in the band-like region of the surface area of the composite nanowires, as shown in Fig. 4(e). The EDS results exhibit that samples A, B, and C consist of Ru- and Ag-oxide phases. This implies the formation of the RuO₂-Ag₂O composite nanowire electrodes with a core-shell structure.

Fig. 5 shows cyclic voltammograms (CVs) of the single RuO₂ nanowires, samples A, B, and C at scan rates of 10, 30, 50, 100, and 200 mV/s in the range of 0.0–1.0 V. The capacitance (C) of all the samples was calculated from the CV data using anodic and cathodic regions by the equation given below [16–18]:

$$C = \frac{q_a + q_c}{2m\Delta V}$$

where m and ΔV are the mass and potential range of the CVs, and q_a and q_c are the charges of the anodic and cathodic regions, respectively. As shown in Fig. 5(a)–(d), the capacitances of the single RuO₂ nanowires, sample A, sample B, and sample C are 58.02, 88.61, 173.25, and 68.33 F/g at 10 mV/s, respectively. The composite electrode shows a higher capacitance than the single RuO₂ nanowire sample, which could be attributed to the formation of the Ag₂O

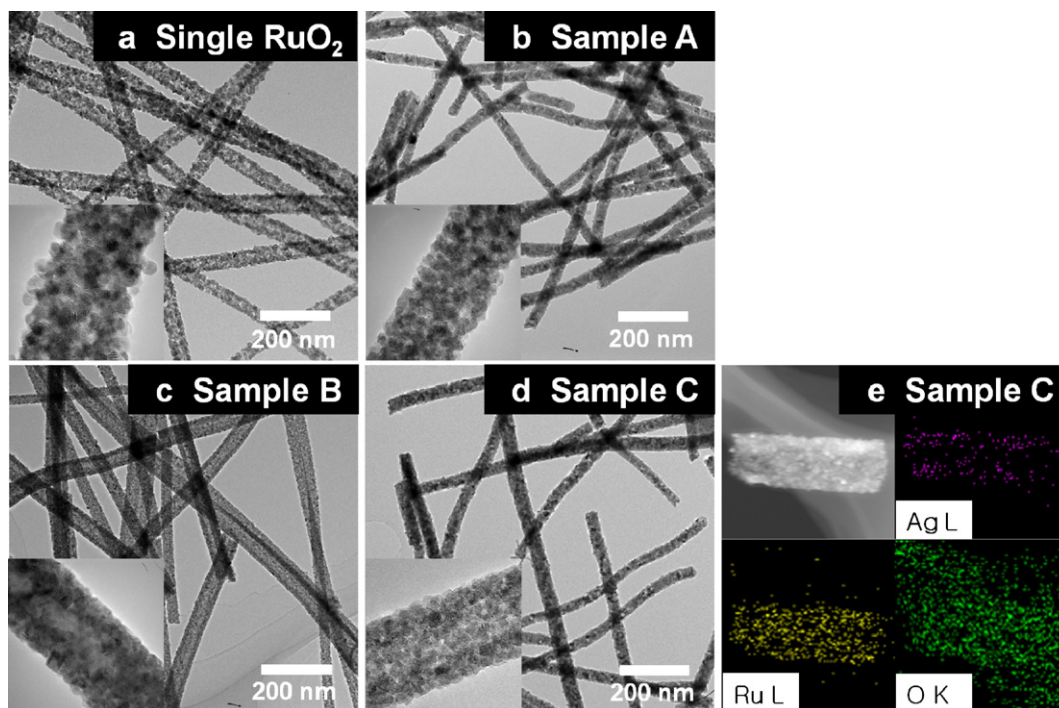


Fig. 4. The HRTEM images obtained from (a) the single RuO₂ nanowires, (b) sample A, (c) sample B, and (d) sample C after calcinations at 400 °C for 1 h and (e) TEM-EDS mapping data obtained from sample C.

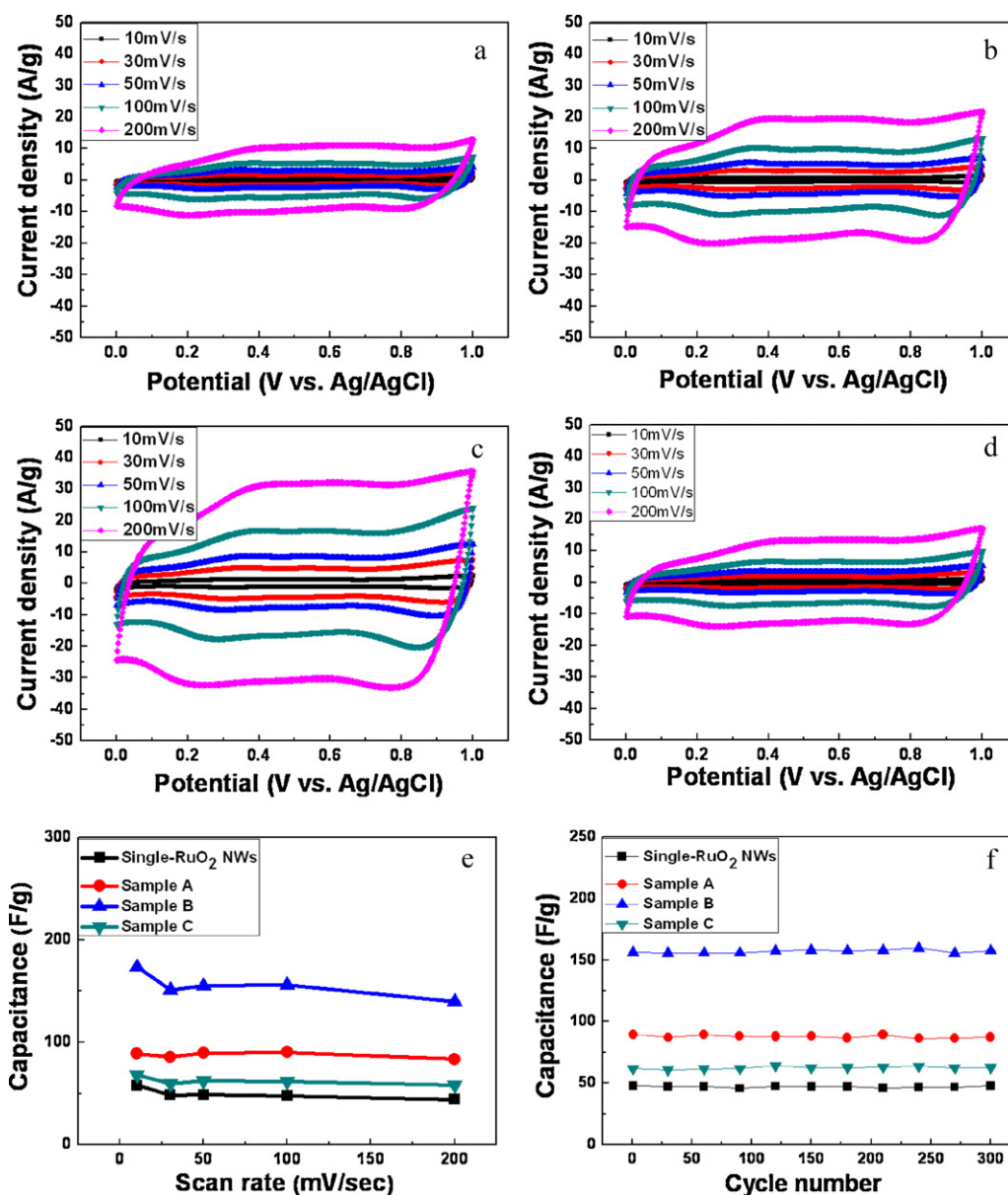


Fig. 5. Cyclic voltammograms of (a) the single RuO₂ nanowires, (b) sample A, (c) sample B, and (d) sample C at scan rates of 10, 30, 50, 100, and 200 mV/s in the range of 0.0–1.0 V. (e) Capacitance measured as a function of the potential scan rate. (f) The cycle number dependence of the capacitance of the electrodes fabricated with the single RuO₂ nanowires, samples A, B, and C.

nano-dots composited within the RuO₂ nanowires. It is noteworthy that sample B gives the highest capacitance among the four samples. In other words, sample B exhibits ~300% higher capacitance than the single RuO₂ nanowire electrodes, indicating that the optimum relative mole ratio of the Ag precursor to the Ru precursor mixture is ~0.2.

To examine the high rate performance of electrochemical capacitors, capacitances were measured as a function of the potential scan rate (Fig. 5(e)), which was calculated using Fig. 5(a)–(d). Although the capacitance of the composite nanowire electrodes decreases slightly with increasing scan rate, the composite electrodes show excellent high-rate performance, which is better than that of RuO₂–carbon composite and RuO₂ powder electrodes [19].

Fig. 5(f) shows the cycle number dependence of the capacitance of the electrodes fabricated with the single RuO₂ nanowires, samples A, B, and C. All the samples exhibit the excellent retention of capacitance (~97%) up to 300 cycles at a scan rate of 100 mV/s.

These results imply that the RuO₂–Ag₂O composite nanowires could represent a potentially important electrode material for the fabrication of efficient electrochemical capacitors. More comprehensive works including the size effects of nanowires are currently in progress in order to optimize the electrode structures for electrochemical capacitors.

4. Summary

RuO₂–Ag₂O composite nanowires were synthesized by an electrospinning method as a function of the relative mole ratio of Ag precursor to Ru precursor ranging from ~0.1 to ~0.3. SEM, XRD and HREM results showed that after calcinations, the composite nanowires consist of RuO₂ and Ag₂O nanoparticles and are in the range ~40–70 nm in diameter. The composite nanowire electrodes fabricated with the mole ratio of ~0.2 showed superior high-rate performance and superior stability, and produced ~300% higher capacitance compared to the single RuO₂ nanowire electrodes. The

results indicate that the RuO₂–Ag₂O composite nanowires could be a potentially important electrode for the fabrication of highly efficient electrochemical capacitors.

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