



# Synthesis and characterization of Co<sub>3</sub>O<sub>4</sub>/RuO<sub>2</sub> composite nanofibers via electrospinning

Sang-Yong Jeong<sup>a</sup>, Hyo-Jin Ahn<sup>b</sup>, Tae-Yeon Seong<sup>a,\*</sup>

<sup>a</sup> Department of Materials Science and Engineering, Korea University, Seoul 136-713, Republic of Korea

<sup>b</sup> Department of Materials Science and Engineering, Seoul National University of Technology, Seoul 139-743, Republic of Korea

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## ABSTRACT

Co<sub>3</sub>O<sub>4</sub>–RuO<sub>2</sub> composite nanofibers (NFs) were synthesized by an electrospinning method. Scanning electron microscopy and high-resolution transmission electron microscopy (HRTEM) examinations show that all the synthesized NFs have uniform surface morphology and their diameters are in the range of ~30–70 nm. X-ray diffraction (XRD) results show that crystalline Co<sub>3</sub>O<sub>4</sub> phase and RuO<sub>2</sub> phase coexist in the composite NF matrix which is confirmed by X-ray photoemission spectroscopy. In addition, the HRTEM energy-dispersive X-ray spectroscopy mapping results show that the Co<sub>3</sub>O<sub>4</sub> and RuO<sub>2</sub> phases are uniformly distributed across the NF matrix.

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## 1. Introduction

One dimensional (1-D) nanostructure materials are of increasing interest because of the unusual and unique properties [1,2]. To produce 1-D nanostructure materials for specific applications, different synthetic methods, e.g., chemical vapor deposition (CVD) [3], hydrothermal synthesis [4], electrodeposition and sol–gel template synthesis in an anodic alumina oxide template [5,6], have been employed. Among these synthetic methods, electrospinning (a drawing process based on electrostatic interactions) has received wide attention because of its simple process and the controllability of the morphology and surface topology of electrospun nanofibers (NFs) [7,8].

Recently, 1-D nanostructured transition metal oxides, such as RuO<sub>2</sub> nanoneedles [9], Co<sub>3</sub>O<sub>4</sub> nanowires [10] and VO<sub>2</sub> nanowires [11], have been widely studied. Composite oxide nanostructures, such as ZnO nanowire–CdO nanocomposites [12], TiO<sub>2</sub>–RuO<sub>2</sub> composite nanorods [13], and WO<sub>3</sub>–TiO<sub>2</sub> composite nanotubes [14], were also synthesized. In addition, some metal oxide NFs [15–17] were synthesized by electrospinning. However, the composite NFs of transition metal oxides have not been extensively investigated. In particular, for Co<sub>3</sub>O<sub>4</sub> and RuO<sub>2</sub> materials which are important for electrochromic [18] and electrochemical applications [19], their composite thin films [20] and nanoparticles [21] were synthesized. However, detailed works on the synthesis of the 1-D nanostructures of Co<sub>3</sub>O<sub>4</sub> and RuO<sub>2</sub> are still lacking. In this work, we synthesized

Co<sub>3</sub>O<sub>4</sub>–RuO<sub>2</sub> composite NFs by electrospinning and characterized their structural properties. The composite NFs are polycrystalline and are composed of uniformly distributed spinel Co<sub>3</sub>O<sub>4</sub> and rutile RuO<sub>2</sub> phases.

## 2. Experiments

Starting metal precursor dissolved in de-ionized (DI) water was prepared using cobalt acetate tetrahydrate (Co(CH<sub>3</sub>CO<sub>2</sub>)<sub>2</sub>·4H<sub>2</sub>O, Aldrich) and ruthenium chloride hydrate (RuCl<sub>3</sub>·xH<sub>2</sub>O, Aldrich). Poly(vinylpyrrolidone) (PVP, Aldrich, Mw = 1,300,000 g/mol) was dissolved in ethanol. Each metal precursor and PVP solutions were subsequently mixed by a volume ratio of 1:1 and continuously stirred at room temperature (RT) for 6 h. Then, the Co metal precursor/PVP and Ru metal precursor/PVP solutions were mixed by controlling the volume of each solution to produce a mixed solution having an atomic ratio (Co:Ru) of 1:1, followed by stirring at RT for 3 h. For comparison, single Co metal precursor/PVP and single Ru metal precursor/PVP solutions were also prepared. The precalculated amounts of the metal precursors were controlled to be ~7 wt.% according to both single and mixed compositions, and the amounts of PVP were kept to be ~6 wt.% of the total weight of the electrospinning solutions at all different compositions. A feeding rate was controlled to be 0.03 ml/h during electrospinning and a Si collector was vertically positioned at 6.5 cm away from the syringe needle under a constant potential of 5.5 kV to collect as-spun metal precursor/polymer NFs. The as-spun NFs were dried in an oven at 80 °C for 12 h. PVP and ligand were then removed from the NFs by calcination at 400 °C for 1 h in air, resulting in the formation of Co-oxide, Ru-oxide, and composite Co–Ru oxide NFs. The morphology and structure of the NFs were examined by field-

\* Corresponding author. Tel.: +82 2 3290 3288; fax: +82 2 3290 3584.  
E-mail address: [tyseong@korea.ac.kr](mailto:tyseong@korea.ac.kr) (T.-Y. Seong).

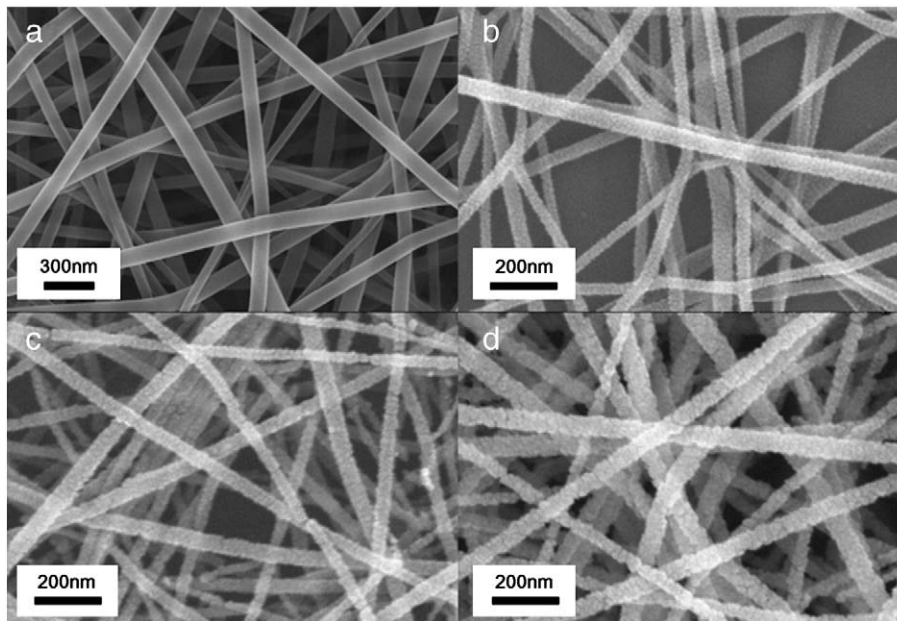


Fig. 1. SEM images of (a) the as-spun composite NFs, (b) calcinated Co-oxide NFs, (c) calcinated composite oxide NFs, and (d) calcinated Ru-oxide NFs.

emission scanning electron microscopy (FESEM, Hitach S-4700), high-resolution transmission electron microscope (HREM, TECNAI G2 F30), and X-ray diffraction (XRD, Rigaku D/MAX2500V with a Cu  $K\alpha$  radiation) analyses. The chemical bonding states of the NFs were studied by X-ray photoelectron spectroscopy (XPS, ESCALAB 250, VG Scientifics using an Al  $K\alpha$  x-ray source). The composition of the NF was characterized by HREM energy-dispersive X-ray spectroscopy (EDS) using a JEOL JEM 2100F microscope equipped with an Oxford INCA energy EDS.

### 3. Results and discussion

Fig. 1 exhibits SEM images of the as-spun and annealed oxide NFs. SEM-energy-dispersive spectroscopy measurement (not shown) exhibited that the composite NFs after calcination at 400 °C contained

nearly the same amount of Co and Ru, namely, an atomic ratio (Co:Ru) of 1:1. Fig. 1(a) shows the as-spun composite NFs (~80–150 nm in diameter). The as-spun single Co and Ru NFs also had similar morphologies and diameters (not shown). Fig. 1(b), (c), and (d) reveal the Co-oxide, composite oxide, and Ru-oxide NFs, respectively, after calcination. It is noted that calcination causes a reduction in their diameters by 53–63%, namely, all the NFs have diameters in the range of ~30–70 nm.

Fig. 2 shows HREM images obtained from the Co-oxide, composite, and Ru-oxide NFs. The HREM results reveal that all the NFs are polycrystalline. This is confirmed by transmission electron diffraction (TED) patterns as shown in the inset. The TED pattern from the Co-oxide NFs exhibits discontinuous diffraction rings consisting of diffraction spots, Fig. 2(a). However, those from the composite and Ru-oxide NFs show continuous diffraction rings, Fig. 2(b) and (c), respectively. The TED results indicate that the Co-oxide NFs contain larger nanoparticles (or nano-grains) as compared to the Ru-oxide and composite NFs. The exact reason for the different behaviours is not clearly understood at the moment.

Fig. 3 shows XRD plots obtained from all the NFs after calcination. For all the samples, the XRD results reveal a polycrystalline nature. The Co-oxide NFs are composed of the  $\text{Co}_3\text{O}_4$  phase with a normal spinel structure, while the Ru-oxide NFs consist of the  $\text{RuO}_2$  phase

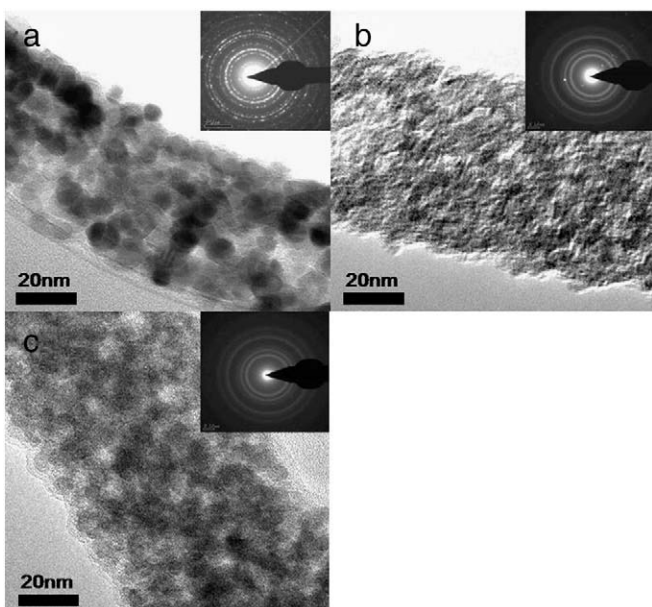


Fig. 2. HRTEM images obtained from (a) the Co-oxide, (b) composite, and (c) Ru-oxide NFs.

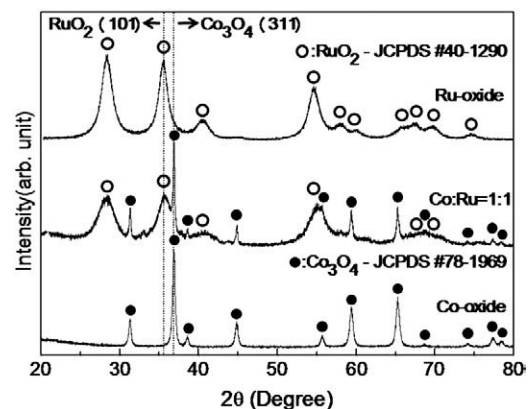


Fig. 3. XRD  $\theta$ - $2\theta$  plots obtained from (a) the Co-oxide, (b) composite, and (c) Ru-oxide NFs.

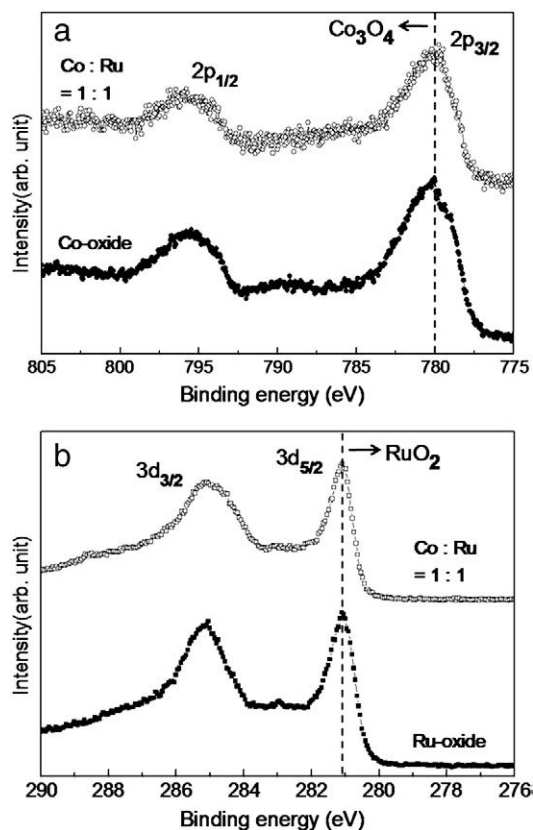


Fig. 4. (a) The Co 2p and (b) Ru 3d core levels for the single and composite oxide NFs.

with a tetragonal rutile structure. The composite NFs contain both spinel Co<sub>3</sub>O<sub>4</sub> and rutile RuO<sub>2</sub> phases. It is noted that the Co<sub>3</sub>O<sub>4</sub> (311) and RuO<sub>2</sub> (101) peaks of the composite NFs are located at the same positions as those of the Co-oxide and Ru-oxide NFs, respectively, as marked by the dashed lines. This implies that they are not a Co<sub>x</sub>Ru<sub>y</sub>O<sub>z</sub> ternary phase, but a mixture of Co<sub>3</sub>O<sub>4</sub> and RuO<sub>2</sub> phases, namely, composite NFs form. This is further confirmed by XPS analyses, as described later.

Fig. 4(a) shows the Co 2p core level spectra for the single Co-oxide and composite NFs. Both the Co 2p spectra reveal the 2p<sub>3/2</sub> peak positioned at ~780.0 eV, which is identified to be elemental Co in Co<sub>3</sub>O<sub>4</sub> [22], indicating the presence of the Co<sub>3</sub>O<sub>4</sub> phase. Fig. 4(b) shows the Ru 3d core level for the single Ru-oxide and composite NFs. Both of the Ru 3d spectra exhibit the 3d<sub>5/2</sub> peak positioned at ~281.1 eV, which is identified to be elemental Ru in RuO<sub>2</sub> [23], also indicating the formation of the RuO<sub>2</sub> phase. The XPS results imply that the composite NFs are composed of a mixture of Co<sub>3</sub>O<sub>4</sub> and RuO<sub>2</sub> phases, which is in good agreement with the XRD results (Fig. 3).

Fig. 5 shows TEM-EDS mapping data from the composite NF having an atomic ratio (Co:Ru) of 1:1. The EDS results reveal that Co and Ru atoms are uniformly distributed in the NF. This implies that the grains of Co<sub>3</sub>O<sub>4</sub> and RuO<sub>2</sub> phases are uniformly distributed in the NF matrix. This also confirms that the composite NFs consisting of crystalline Co<sub>3</sub>O<sub>4</sub> and RuO<sub>2</sub> phases are successfully synthesized by means of an electrospinning method.

#### 4. Summary

We synthesized composite nanofibers (NFs) consisting of crystalline Co<sub>3</sub>O<sub>4</sub> and RuO<sub>2</sub> phases by an electrospinning method and their

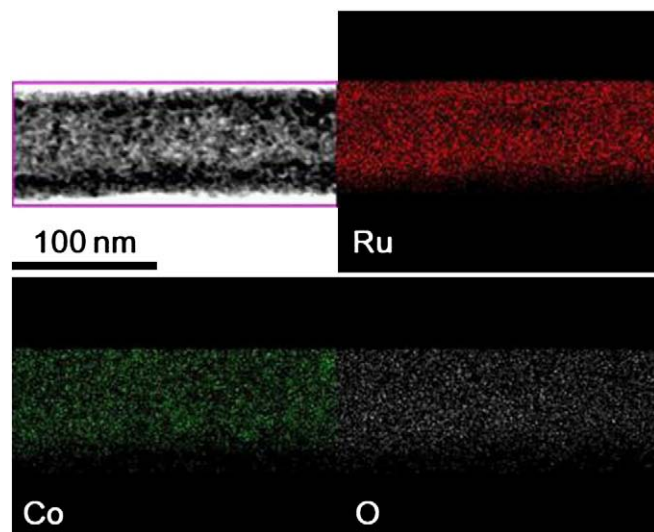


Fig. 5. TEM-EDS mapping data obtained from the composite NF having an atomic ratio (Co:Ru) of 1:1.

surface morphology, structural properties, and chemical compositions were characterized by means of SEM, HREM, XRD, XPS, and EDS. The SEM, XRD and HREM results showed that all the NFs have a crystalline phase and are in the range of ~30–70 nm in diameter. The EDS results exhibited that the Co<sub>3</sub>O<sub>4</sub> and RuO<sub>2</sub> phases are uniformly distributed in the composite NFs. It is shown that the use of the electrospinning method for the synthesis of composite materials having 1-D nanostructures is simple and a powerful process.

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