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One-pot fabrication of hollow SiO_2 nanowires via an electrospinning technique

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ABSTRACT

Hollow SiO_2 nanowires (NWs) were one-pot fabricated via an electrospinning method. Their morphologies, structures, and chemical compositions were investigated by means of scanning electron microscopy (SEM), high-resolution transmission electron microscopy (HRTEM), X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS). In order to fabricate optimum hollow SiO_2 NWs, the relative volume ratio of tetraethyl orthosilicate (TEOS, an alkoxide precursor) to ethanol (solvent) was systematically controlled from 0.02 to 0.36. SEM, HRTEM, XRD, and XPS results indicate that amorphous SiO_2 hollow NWs can be one-pot synthesized by using the volume ratio of 0.18 under a constant voltage of 8.0 kV.

1. Introduction

Over the past two decades, nanostructured materials have received increasing attention in academic fields as well as industry fields because of their unique physical and chemical properties. Recently, one-dimensional nanostructures such as nanowires, nanorods, nanobelts, and nanotubes are of increasing interests owing to various applications such as energy storage devices, photonics, electronics, and biodiagnostics [1–3]. Up to now, many researchers have developed various synthetic methods of one-dimensional nanostructures, e.g., template-directed synthesis, self-assembly, phase separation, nanolithographic technique, electrospinning method, etc [4]. Among these various methods, an electrospinning method is considered one of the powerful tools for the fabrication of one-dimensional nanostructures with several advantages such as relatively simple, cost effective, and production on a large scale [5,6]. There are several parameters which could affect the morphology of the resultant nanowires formed by electrospinning. For example, the morphology of nanowires such as random-type, core–shell-type, and mats-type could be controlled by manipulating main injection parameters of polymer solutions, applied voltages, temperatures, and ambient conditions [7].

SiO_2 materials have been extensively studied because of various applications such as dental composites, glasses, optical materials, anti-reflective coatings, and catalysts [8,9]. Moreover, one-dimensional SiO_2 nanowires (NWs) are of growing interest because of their unique properties. Liu et al. reported on the synthesis and characterization of SiO_2 nanofibers (NFs) for dental composite applications via electrospinning [9]. Ding et al. reported that the morphology and phase of electro-spun TiO_2–SiO_2 composite NFs depended on the calcination temperature and the content of precursors [10]. Zhan et al. synthesized hollow SiO_2 NFs with hierarchical walls by a co-electrospinning method using triblock copolymer as porous directing agent [11]. However, despite the potential importance of hollow NWs for applications such as gas storage and energy conversion, one-pot

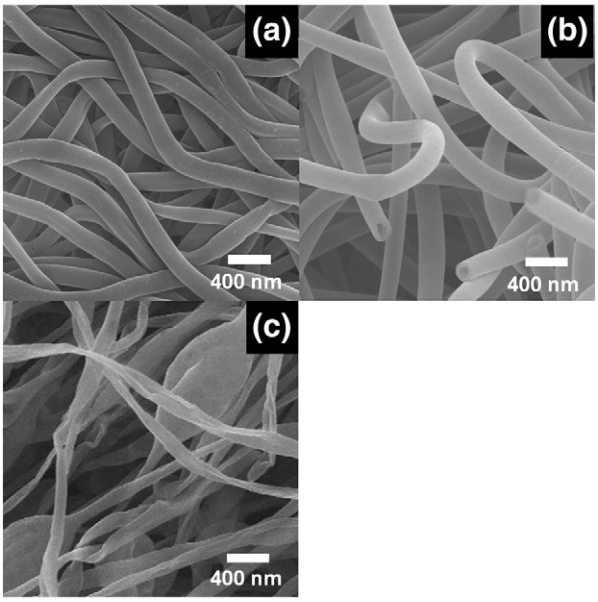

Fig. 1. SEM images of (a) sample A, (b) sample B, and (c) sample C before calcination.

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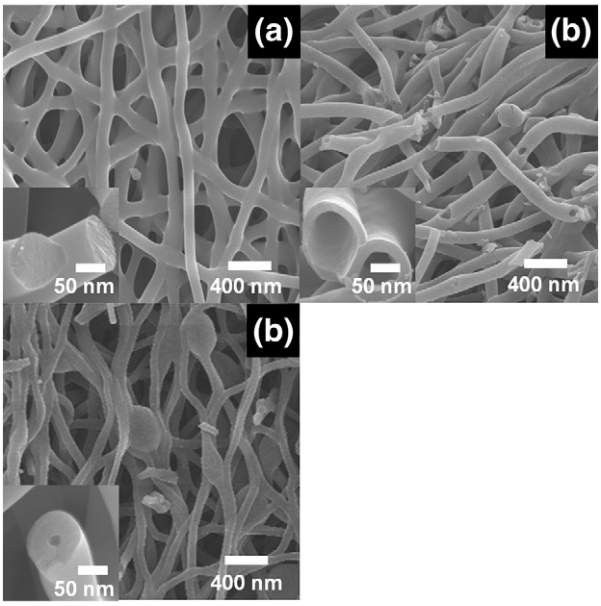

Fig. 2. SEM images obtained from (a) sample A, (b) sample B, and (c) sample C after calcination at 400 °C.

fabrication of hollow SiO_2 NWs has not been extensively investigated so far. Thus, in this work, we one-pot fabricated hollow SiO_2 NWs by changing polymer solution parameters, namely, by controlling the relative volume ratio of tetraethyl orthosilicate (TEOS) to ethanol (solvent) from 0.02 to 0.36, and investigated their structural properties and chemical compositions.

2. Experiments

Hollow SiO_2 NWs were one-pot fabricated by an electrospinning method. Poly(vinylpyrrolidone) (PVP, Mw = 1,300,000 g/mol, Aldrich) was dissolved in ethanol (Aldrich) for 1 h. Then, tetraethyl orthosilicate (TEOS, Aldrich) (as alkoxide precursor) was mixed with the above-dispersed solution for 3 h at room temperature. In order to synthesize hollow SiO_2 NWs, the relative volume ratio of TEOS (alkoxide precursor) to ethanol (solvent) was systematically controlled to be 0.02, 0.18, and 0.36 (referred to be here as samples A, B, and C, respectively). In electrospinning conditions, a feeding rate was fixed at 0.04 ml/h for sample A, 0.02 ml/h for sample B, and 0.02 ml/h for sample C. A distance between a Si collector and a syringe needle was at 5.5 cm under a constant voltage of 10.0 kV for sample A, 8.0 kV for sample B, and 8.0 kV for sample C. The humidity was monitored to be ~20%. The as-spun NWs were dried for 3 h at room temperature. The resulting hollow SiO_2 NWs were obtained by calcination at 400 °C for 2 h in air. The morphology of the samples was characterized by scanning electron microscopy (SEM, Hitach S-4700) and high-resolution transmission electron microscopy (HRTEM, a TECNAI-F20 microscope). The crystallinity and the chemical bonding states of the samples were characterized by X-ray diffraction (XRD, Rigaku D/MAX2500V) and X-ray photoelectron spectroscopy (XPS, ESCALAB 250).

3. Results and discussion

Fig. 1 shows SEM images of as-spun samples which are comprised of precursors and PVP polymer composite NWs before calcination at 400 °C. The diameters of the NWs are measured to be in the range ~160–~190 nm, ~213–~243 nm, and ~100–~160 nm for sample A, sample B, and sample C, respectively. It is generally known that the viscosity of solutions plays an important role in the morphology formation of NWs during electrospinning. As for sample A with a high viscosity (Fig. 1(a)), the solvent molecules are well dispersed over the entangled polymer molecules. For sample C with a lower viscosity (Fig. 1(c)), the solvent molecules tend to cluster due to surface tension, leading to the formation of as-spun NWs with beads [7]. For sample B (Fig. 1(b)), the SiO_2 hollow NWs without beads are successfully fabricated during electrospinning.

Fig. 2 shows the SEM images obtained from all the samples after calcinations at 400 °C. Measurements show that the diameters of the SiO_2 NWs are in the range of ~90–~130 nm for sample A, ~100–~160 nm for sample B, and ~76–~120 nm for sample C, respectively. It is noted that calcination at 400 °C caused the diameters of all the samples to become smaller by ~20–~80 nm. In addition, the cross-section images of the NWs are shown enlarged in the insets in Fig. 2. Sample A contains an array of NWs without hollow structure, Fig. 2(a). Sample B shows hollow NWs, Fig. 2(b). There are holes formed on

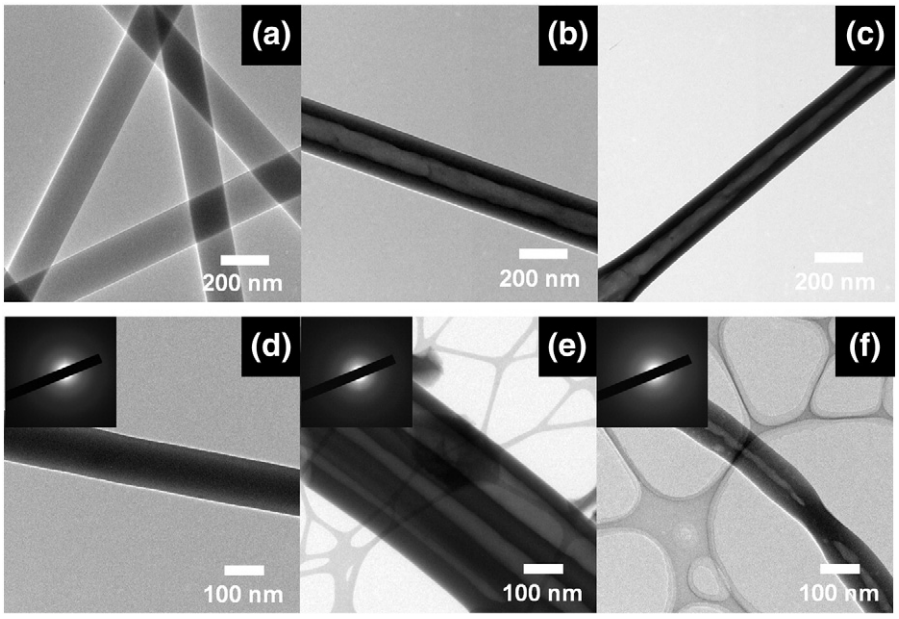

Fig. 3. HRTEM images and TED patterns obtained from sample A, sample B, and sample C before and after calcination, (a)–(c) and (d)–(f).

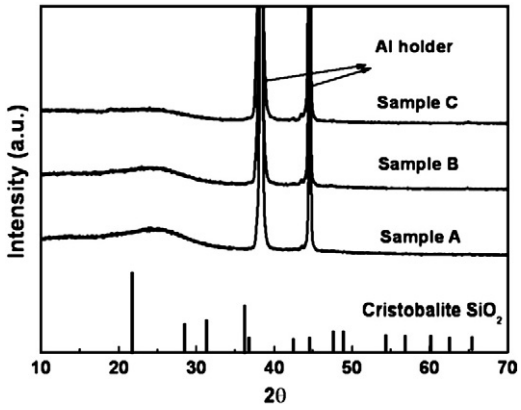

Fig. 4. XRD data from (a) sample A, (b) sample B, and (c) sample C after calcination.

the hollow NWs. Sample C exhibits hollow NWs with beads, whose diameter becomes much reduced, Fig. 2(c).

Fig. 3 shows HRTEM images and transmission electron diffraction (TED) patterns of sample A, sample B, and sample C before and after calcination, Fig. 3(a)–(c) and Fig. 3(d)–(f), respectively. HRTEM images of sample B (Fig. 3(b) and (e)) reveal dark band-like contrast in the edge area of the NWs before and after calcination, which is indicative of hollow nature. However, HRTEM images of sample A (Fig. 3(a) and (d)) exhibit uniform contrast in the whole area of the NWs before and after calcination, which is indicative of dense nature. TED patterns (the insets in Fig. 3(d–(f)) of all the samples reveal a broad diffuse ring around the (000) spot, implying an amorphous characteristic. The SEM and HRTEM results show that amorphous SiO_2 hollow NWs without beads can be synthesized by using the optimized conditions of sample B.

Fig. 4 shows XRD data obtained from all the samples after calcination at 400 °C. The XRD results show that for all the samples, there is a broad diffraction peak at 24° in addition to Al-related peaks. This implies that all the samples contain the SiO_2 NWs with amorphous structure, which is in agreement with the TED results (Fig. 3).

To examine the composition and chemical bonding states of Si atoms, XPS measurements were carried out on the samples. Fig. 5 shows XPS spectra of the Si 2*p* core level obtained from the samples. The XPS Si 2*p* core level positioned at ~103.3 eV corresponds to elemental Si in SiO_2 [12]. This indicates that Si in the SiO_2 NWs is present as not Si (II) species but Si (IV) species. The oxidized Si phase in sample A, sample B, and sample C were formed during calcination at 400 °C. The HRTEM, XRD, and XPS results imply that all the samples have the same composition and amorphous phases.

It was shown that sample B synthesized by the volume ratio (0.18) of TEOS (an alkoxide precursor) to ethanol (solvent) exhibited hollow structure during electrospinning. A possible formation mechanism could be related to thermodynamic instability of the solutions used. In other words, under the volume ratio (0.18) of precursor to ethanol at 8 kV, the solution becomes thermodynamically unstable during electrospinning and thus may be separated into an alkoxide precursor-rich phase in the edge region of NWs and a solvent-rich phase in the core region. Thus, hollow SiO_2 NWs can be one-pot fabricated through the process during electrospinning.

4. Summary

We one-pot fabricated amorphous SiO_2 nanowires with hollow structure by an electrospinning method and investigated their morphology, structural properties, and chemical compositions by SEM, HRTEM, XRD, and XPS. Although all the samples have the same chemical composition and structural properties, sample B showed optimum hollow structures without beads. This implies that an electrospinning method could be one of the simplest and most powerful ways for the fabrication of one-dimensional hollow nanostructures.

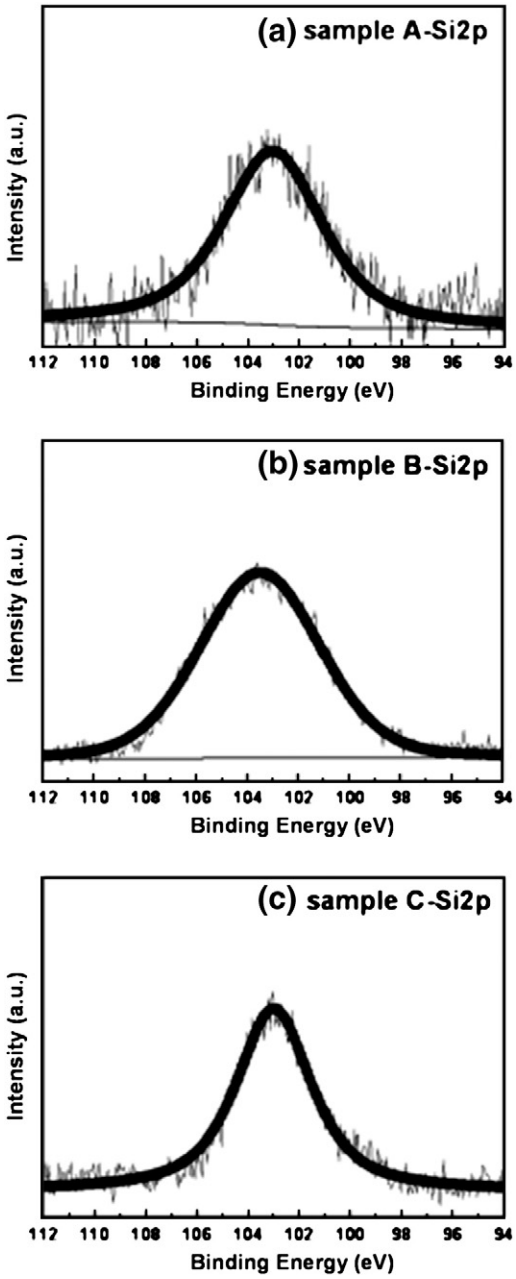

Fig. 5. XPS spectra of the Si 2*p* core level for (a) sample A, (b) sample B (b), and (c) sample.

Acknowledgement

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