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Synthesis and formation mechanism of NiO@SnO_2@TiO_2 coaxial trilayered nanocables by electrospinning technique

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[Ni($CH_3COO)_2$+PVP]@[$SnCl_4$+PVP]@[Ti($OC_4H_9)_4$+CH_3COOH+PVP] precursor composite cables have been fabricated through modified electrospinning equipment. NiO@SnO_2@TiO_2 coaxial trilayered nanocables were obtained by calcination of the relevant [Ni($CH_3COO)_2$+PVP]@[$SnCl_4$+PVP]@[Ti($OC_4H_9)_4$+CH_3COOH+PVP] precursor composite cables. The samples were characterized by use of thermogravimetric–differential thermal analysis (TG–DTA), X–ray diffractometry (XRD), Fourier transform infrared spectroscopy (FTIR), Scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS), and Transmission electron microscopy (TEM). Experimental results showed that the core layer is NiO, the middle layer is SnO_2 and the outer layer is TiO_2. Finaly the synthesis mechanism of NiO@SnO_2@TiO_2 coaxial trilayered nanocables was preliminarily proposed.

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Keywords: NiO@SnO_2@TiO_2, Coaxial trilayered nanocables, Electrospinning technology, Synthesis mechanism

1. Introduction

Quasi one–dimensional (1D) nanomaterials–coaxial nanocables have been extensively studied in recent years for potential applications in biomedical sensors, optoelectronic devices, field emission devices and other fields because of its physical and chemical characteristics [1-6]. Many methods have been reported for the fabrication of these unique structures from diverse materials. Recently, a large number of fabrication methods have already been demonstrated for fabrication of coaxial nanocables, such as sol–gel method [7], hydrothermal method [8], template method [9], liquid–phase deposition [10], etc. For instance, CdS@PANI [11]、CdS@TiO_2 [12]、PEG@PCL [13]、InN@In_2O_3 [14] coaxial nanocables has been reported. Apart from the above preparation methods, surface oxide nanowires and a line template are required to achieve a higher synthesis of experimental conditions and a greater number of steps. Electrospinning technique as a simple, convenient, and versatile method has been utilized in the preparation of many one–dimensional nanostructural materials such as long fibers with diameters ranging from tens of nanometers up to micrometers . Recently, this technique was used as an approach to fabricate coaxial trilayered nanocables. For example, Zhang, et al [15] synthesized TiO_2@SiO_2 nanocables through electrospinning technique. Wang, et al [16] reported a simple but effective method of combining solvothermal and hydrothermal reactions to synthesize Y_2O_3:Eu^{3+}@SiO_2 nanocables. Hongyan Chen [17] et al obtained TiO_2@ TiO_2 and PS@PAN nanowire–in–microtube structured fibers via electrospinning technique. To the best of our knowledge, there have been no reports on the preparation of NiO@SnO_2@TiO_2 coaxial trilayered nanocables by electrospinning technique. In this paper, NiO@SnO_2@TiO_2 nanocables were fabricated by calcination of the electrospun nanocables of [Ni($CH_3COO)_2$+PVP]@[$SnCl_4$+PVP]@[Ti($OC_4H_9)_4$+CH_3 COOH+PVP] precursor composite nanocables, and some new results were obtained and this preparation technique can be applied to prepare other coaxial trilayered nanocables.

2. Experimental section

Polyvinyl pyrrolidone (PVP) (Mw = 1 300 000, AR) powder was dissolved in N,N–dimethylformamide (DMF, AR) in a conical flask, then slowly added Ni($CH_3COO)_2\cdot 4H_2O$ and stirred at room temperature, then remaining motionlessly, a viscous precursor composite gel of [Ni($CH_3COO)_2$+DMF+PVP] were obtained. PVP powders was dissolved in DMF, and $SnCl_4\cdot 5H_2O$ was dissolved in CH_3COCH_3, respectively, and stirring for 6 h, then mixed the two solutions, a viscous precursor composite gel of [$SnCl_4$+DMF+PVP] were obtained. PVP powder was dissolved in a mixture of absolute ethanol and acetic acid in a conical flask, and then $Ti(OC_4H_9)_4$ was added slowly. The mixture was stirred to form a homogeneous sol. Thus, a viscous precursor composite gel of $[Ti(OC_4H_9)_4+CH_3CH_2OH+CH_3COOH+PVP]$ were obtained.

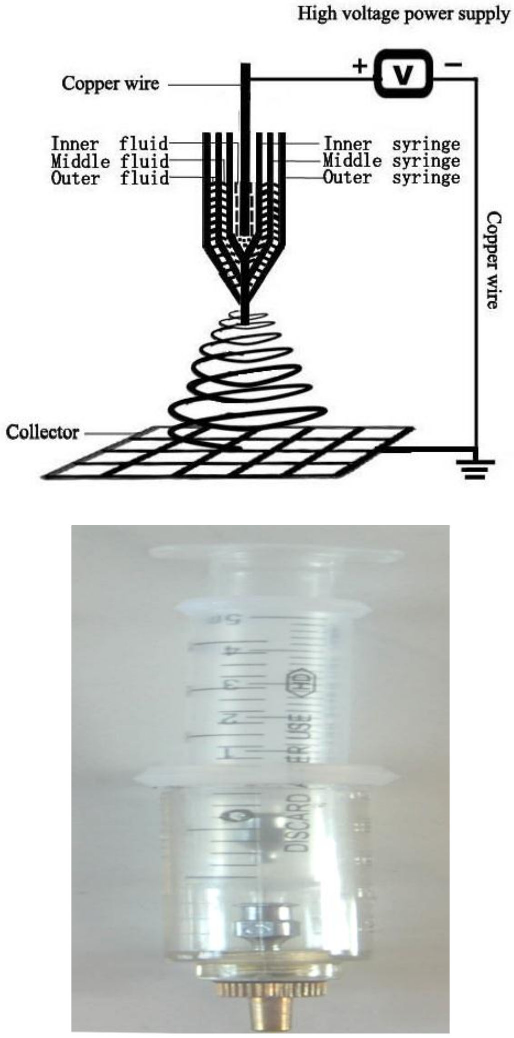

Fig. 1. Schematic diagrams (left) and material object photo (right) of spinneret electrospinning setup for preparation of coaxial trilayered nanocables.

The experimental setup of coaxial trilayered nanocables is illustrated in Fig. 1. The spinneret was assembled by three coaxial stainless steel capillaries and connected to the anode of the high–voltage generator. Aluminum foil was grounded to work as the collector. Three kinds of viscous fluids were fed into the outer, middle, and inner capillaries, respectively. The work distance between the spinneret and collector was 15 cm, and the work voltage was 18 kV. After the electrospinning process, $[Ni(CH_3COO)_2+PVP]@[SnCl_4+PVP]@[Ti(OC_4H_9)_4+CH_3COOH+PVP]$ precursor composite nanocables were collected. The collected precursor composite nanocables were calcined at a heating rate of 1 ℃/min and remained for 8 h at 600 and 800 ℃, respectively. Thus, $NiO@SnO_2@TiO_2$ coaxial trilayered nanocables were obtained when calcination temperature were 600 and 800 ℃.

4. Results and discussion

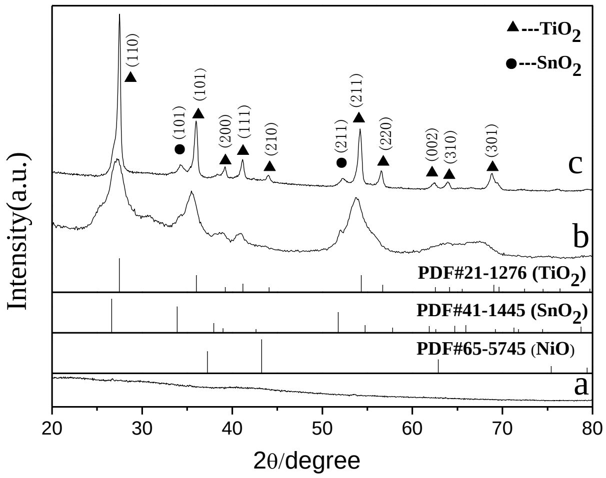

Fig. 2. XRD patterns of the precursor composite cables (a) and samples calcined at 600 ℃ (b) and 800 ℃ (c) for 8 h.

To investigate the lowest crystallizing temperature and the variety of phases, the precursor composite nanocables and samples obtained by calcining the precursor composite nanocables at different temperatures for 8 h were characterized by XRD, as indicated in Fig. 2. The results showed that the precursor composite nanocables were amorphous in structure, and only a broad peak was located around 22.5 °, which is the typical peak of the amorphous polymer PVP [20]. These results indicate that the precursor composite nanocables are amorphous in structure. When the nanocables were sintered at 600 ℃, observed reflections were indexed to TiO_2 [19]. The diffraction peaks of PVP disappeared. When the nanocables were sintered at 800 ℃, observed reflections were indexed to TiO_2. The crystal became fully developed. The d (spacing between crystallographic plane) values and relative intensities of TiO_2 are consistent with those of PDF standard card (21–1276), and the rutile structure of the prepared TiO_2 was tetragonal system with space group $P4_2/mnm$; observed reflections can be indexed to SnO_2 [20], the d values and relative intensities of SnO_2 were consistent with those of the PDF standard card (41–1445). The structure of the prepared SnO_2 was a tetragonal system with space group $P4_2/mnm$.

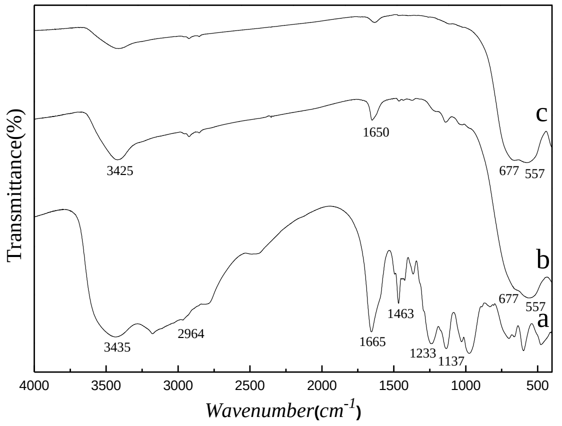

Fig. 3. FTIR spectra of the precursor composite cables (a) and samples calcined at 600 ℃ (b) and 800 ℃ (c) for 8 h.

$NiO@SnO_2@TiO_2$ coaxial trilayered nanocables were further studied by FTIR as shown in Fig. 3. As seen form Fig. 3a, the FTIR spectrum of composite cables indicated that the wide absorption peak at 3435cm^{-1} attributes to the stretching vibrations of O–H of the surface absorbed water. It can be seen from Fig. 3b (600℃) and 3c (800℃), two new absorption peaks at low wavenumber 677 cm^{-1} and 557 cm^{-1} are appeared, which ascribe to the vibration of Sn–O–Sn, Ti–O–Ti and Ni–O–Ni bonds, indicating that the formation of NiO, SnO_2 and TiO_2.

To study the morphology and size of the samples, the samples were investigated by SEM as shown in Fig. 4. In Fig. 4a and 4b, the nanocables surface were smooth with no cross–linking. When the calcination temperature reached 800 ℃, as shown in Fig. 4c, the surface roughness of the sample increased, the porous structure was formed, and the nanocables diameter became significantly smaller and more uniform. From the TEM image obtained by electrospinning technique, when sintered at 600 ℃, the cable clearly revealed its core–in–shell structure in Fig. 6.

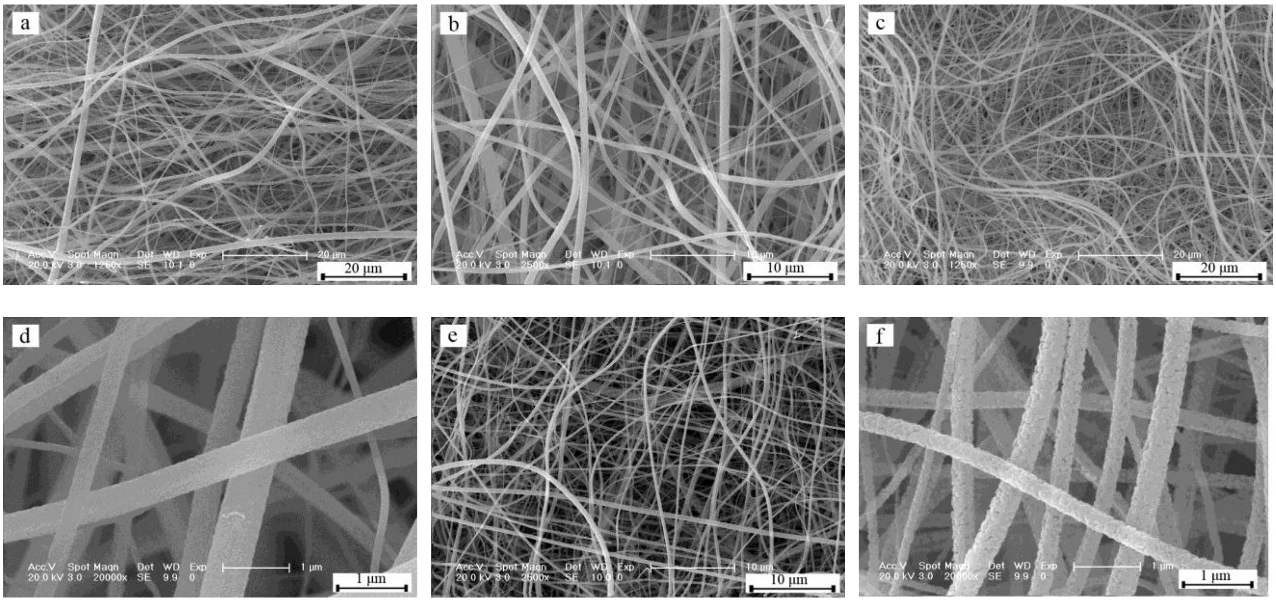

Fig. 4. SEM images of the precursor composite cables (a and b) and samples calcined at 600 ℃(c and d) and 800℃(e and f) for 8 h.

To determine the coaxial trilayered nanocables component further, energy dispersive spectroscopy (EDS) of the samples was manifested in Fig. 5. The presence of O, Ni, Sn, Ti corresponds to coaxial trilayered nanocables and no other impurity peaks occur, indicating the pure coaxial trilayered nanocables were obtained. Au peak is from the conductive film of Au.

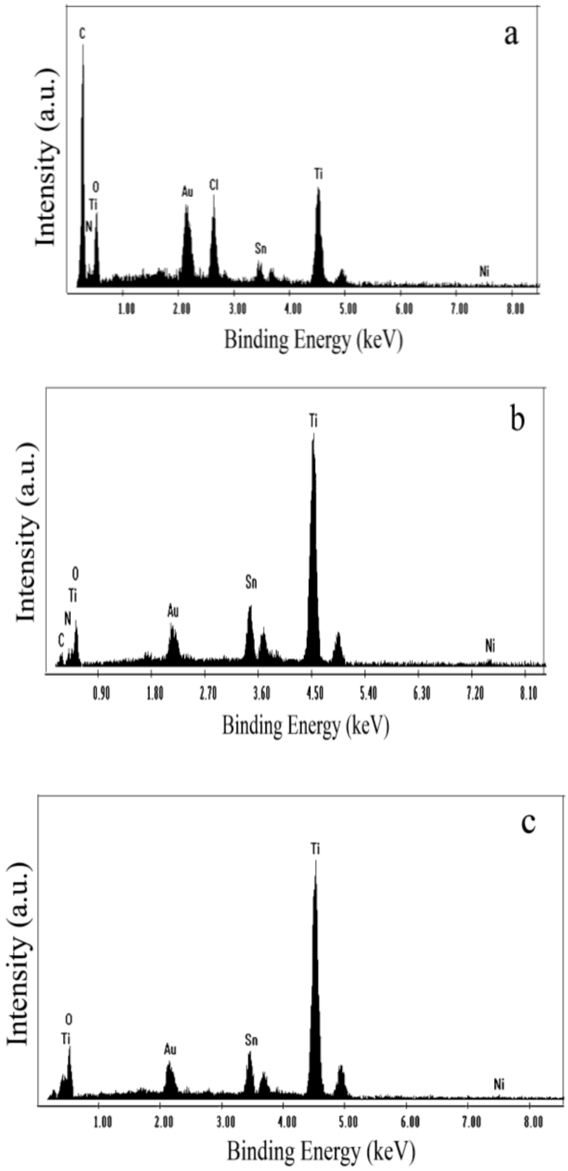

Fig. 5. EDS images of the precursor composite cables (a) and samples calcined at 600 ℃(b) and 800 ℃(c) for 8 h.

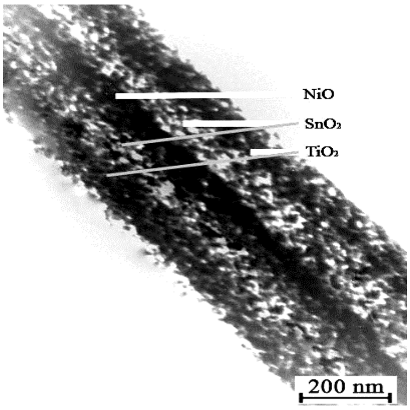

Fig. 6. TEM image of samples calcined at 600 ℃

Electrospinning technique was used to prepare coaxial trilayered nanocables in this paper. Due to the different viscosities and flow rates of the internal, middle, and outer spinning, the role of force in the high voltage field, the inner layer, the middle layer, and outer fluid, is defined as the high stretching frequency of the compound taylor cone formation. This formation is a spinning process that forms a thin outer shell of fluid in the middle layer and in the inner layer covering the fluid surface in the stretch through high frequency bending and lashing deformation. Moreover, the formation is cured to form the core–in–shell structure of the precursor composite nanocables. We prepared the precursor composite nanocables for the sintering process with high temperature, organic material combustion, oxidation of $Ti(OC_4H_9)_4$, $SnCl_4$ and $Ni(CH_3COO)_2$, and crystal phase transition, which the resulting combination between the three oxides becoming more resistant. The sintering process in the precursor composite nanocable, the core layer, the middle layer, and the shell allowed for the development of a well–maintained coaxial trilayered structure, with complete decomposition of organic and crystal formation, eventually forming coaxial trilayered nanocables.

Fig. 7. Illustrative diagram of formation mechanism of coaxial trilayered nanocables.

4. Conclusion

In summary, we successfully prepared coaxial trilayered nanocables using the electrospinning technique, a simple and low–cost approach utilized in the preparation of numerous 1D nanostructural materials as well. We simplified the synthesis of the previous steps in the preparation of nanocables and experimental conditions. The results showed that the obtained product were $NiO@SnO_2@TiO_2$ coaxial trilayered nanocables. The coaxial electrospinning technique can prepare nanostructured materials for further research in a novel manner, which may be functional ceramics, semiconductors, sensor materials, photoelectric conversion materials, catalytic materials, and nonlinear optical materials play a significant effect. The present work provides a new route to fabricate coaxial trilayered nanocables.

Acknowledgments

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