J Mater Sci (2008) 43:860–864
DOI 10.1007/s10853-007-2190-9

Production of beads like hollow nickel oxide nanoparticles using *colloidal-gel* electrospinning methodology

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Received: 23 July 2007 / Accepted: 24 September 2007 / Published online: 31 October 2007

Abstract In the present study *colloidal-gel* electrospinning technique is proposed to produce new shape of nickel oxide hollow nanoparticles. In the colloidal-gel process, a colloidal precursor was prepared by dissolving nickel acetate tetra hydrate in ethanol at 352 K. The precursor was mixed with poly(vinyl acetate)/*N*, *N*-dimethylformamide (14 wt%). The polymer-precursor mixture was electrospun at relatively low voltage depending on the concentration of nickel acetate in the precursor. The obtained mat was dried under vacuum at 353 K for 24 h, and then sintered at 827 K for 3 h. The XRD and SEM results indicated that the proposed methodology produces pure nickel oxide hollow nanoparticles with beads-like form.

Introduction

In recent years, nanostructured materials have been actively studied due to both scientific interests and potential applications. Among them, much attention has been focused on the research field of nanoscale oxide particles of transition metals, which are gaining continuous importance for various applications such as catalysts, passive electronic components, and ceramic materials [1]. Nickel oxide (NiO) is a very important material extensively used in catalysis [2], battery cathodes [3, 4], gas sensors [5], electrochromic films [6], and magnetic materials [7]. Several researchers have prepared NiO nanoparticles by various methods like sol–gel [8], surfactant-mediated synthesis [9], thermal decomposition [10], and polymer-matrix assisted synthesis [11]. It is noteworthy mentioning that the reported methods produced nearly one shape of nickel oxide nanoparticles; namely cubic. Also, some of them suffer from the lack of homogeneity in the produced nanoparticles [12]. Here, we offer new methodology for production of homogenous hollow nickel oxide nanoparticles having beads-like form via modification of the traditional sol–gel electrospinning technique.

In this study, mixture of colloidal solution and polymer has been electrospun rather than the real-solution/polymer mixture in the ordinary sol–gel electrospinning process. The colloidal solution (precursor) was prepared by mixing nickel acetate tetra hydrate and ethanol at 352 K (i.e., at the boiling point of ethanol). At this temperature ethanol can carry big amount of nickel acetate (up to 50 wt%) without precipitation of nickel acetate particles. The precursor was mixed with 14% (wt) poly(vinyl acetate) (PVAc) solution (solvent was *N*,*N*-dimethylformamide (DMF)) with ratio of 3:2. After good mixing the mixture was electrospun and dried under vacuum at 353 K for 24 h. Scanning electron

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microscope (SEM) images showed that the obtained nanofibers are necklace-like shape. EDX data indicated that concentration on nickel at the beads is higher than elsewhere in the nanofiber. Therefore, these beads might be considered as nickel acetate nanoparticles. Beads like nanoparticles of pure nickel oxide were obtained after sintering the nanofibers at 823 K for 3 h, as indicated by the SEM and XRD results. The obtained nanoparticles were hollow, as shown in the SEM image.

Experimental

Nickel (II) acetate tetra hydrate (Aldrich Co., USA), *N*,*N*-dimethylformamide (Aldrich Co., USA), ethanol (A.R. quality, Hayman Ltd., UK), and PVAc (M.w = 500,000, Aldrich Co., USA) were used as received without further purification. The nickel acetate was dissolved in ethanol at 352 K. The dissolution time depended on the required concentration; it was 5, 7, 10, and 13 min for 20, 25, 35, and 50% (wt), respectively. PVAc (14 wt%) solution was prepared in DMF by stirring at room temperature for 24 h. The prepared precursors were added to PVAc/DMF (60 wt% precursor) and vigorously mixed for 30 min at room temperature. Therefore, the concentrations of nickel acetate in the final mixtures were 12, 15, 21, and 30% (wt), respectively. Electrospinning process was achieved via DC high-voltage power supply (Chungpa Emt Co., South Korea) at voltage of 10, 8, and 5 kV for 12, 15, and 21% nickel acetate mixtures, respectively. The nanofibers were collected on aluminum sheet, the distance between the tip and the collector was 15, 17, and 20 cm for 12, 15, and 21% mixtures, respectively. The obtained mat was dried at 353 K in vacuum dryer for 24 h, then sintered at temperature of 827 K for 3 h.

Surface morphology was studied by JEOL JSM-5900 SEM equipped with energy dispersive X-ray (EDX), (JEOL Ltd., Japan). The phase and crystallinity were characterized by using Rigaku X-ray diffractometer (Rigaku Co., Japan) with Cu Kα radiation over a range of 2θ angles from 20 to 70°. The viscosity and the electrical conductivity of the polymer/precursor mixture were measured by DV III Ultra programmable Rheometer (Brookfieled Co., USA) and EC meter CM 40 G Ver 1.09 (DKK TOA Co., Japan), respectively.

Results and discussion

Figure 1 shows the SEM and EDX results for nanofibers obtained with 15% nickel acetate mixture. As shown in Fig. 1, the obtained nanofibers have necklace-like shape. EDX have been performed at three points, the results show the concentrations of nickel, oxygen, and carbon at the chosen points. As shown in the EDX results, maximum nickel percentage was obtained at the bead (25.58%). This percentage decreases at the points far away from the bead center; 9.25% at a point just beside the bead and 5.64% at the middle point between the two chosen beads. This indicates that nickel acetate slightly dissolves in ethanol at 352 K and the excess solid salt changes to nanoparticles dispersed in an ethanol liquid saturated with nickel acetate. In other words, the prepared nickel acetate/ethanol solution can be considered colloidal solution.

Figure 2 shows schematic diagram describing the formation steps of necklace-shape nanofibers. As presented in the diagram, after mixing the precursor and the PVAc/DMF solution, the acetate groups in the PVAc polymeric chain anchor in the nickel acetate nanoparticles surface due to the dipole nature of the nickel acetate [13]. The applied electric field in the electrospinning process leads to stretch of the spherical nanoparticle, so it turns into ellipsoidal shape in the nanofibers obtained.

The beads transformed to pure nickel oxide nanoparticles after sintering, as shown in the results of SEM (Fig. 3) and XRD (Fig. 4). Figure 3a shows SEM images for the obtained necklace-shape nanofibers corresponding to 15% nickel acetate mixture after sintering at 823 K for 3 h. As shown in the figure, there are traces of nickel oxide nanofibers due to dissolution of the ethanol, which is saturated with nickel acetate in the polymeric chain; this was also concluded from the EDX results (Fig. 1, point (3)). It is noteworthy mentioning that the obtained nanoparticles were hollow and not solid ones, as shown in Fig. 3b; this figure shows the SEM image of slightly crushed beads.

The typical XRD pattern of NiO nanoparticles obtained after heat treatment at 823 K for 3 h is presented in Fig. 4. The standard peaks of the nickel oxide were obtained in the XRD spectra with no other peaks. The existence of strong and sharp diffraction peaks at 2θ values 37.25, 43.30, and 62.90° corresponding to (111) (200), and (220) crystal planes indicated the formation of phase pure nickel oxide at this temperature. The average crystallite size of the prepared nickel oxide calculated from XRD using the Debye–Scherrer formula is about 51.06 nm.

In the electrospinning process, a polymer solution held by its surface tension at the end of a capillary tube is subjected to an electric field. Charge is induced on the liquid surface by an electric field. Mutual charge repulsion causes a force directly opposite to the surface tension. As the intensity of the electric field is increased, the hemispherical surface of the solution at the tip of the capillary tube elongates to form a conical shape known as the Taylor cone [14]. When the electric field reaches a critical value at which the repulsive electric force overcomes the surface tension force, a charged jet of the solution is ejected from

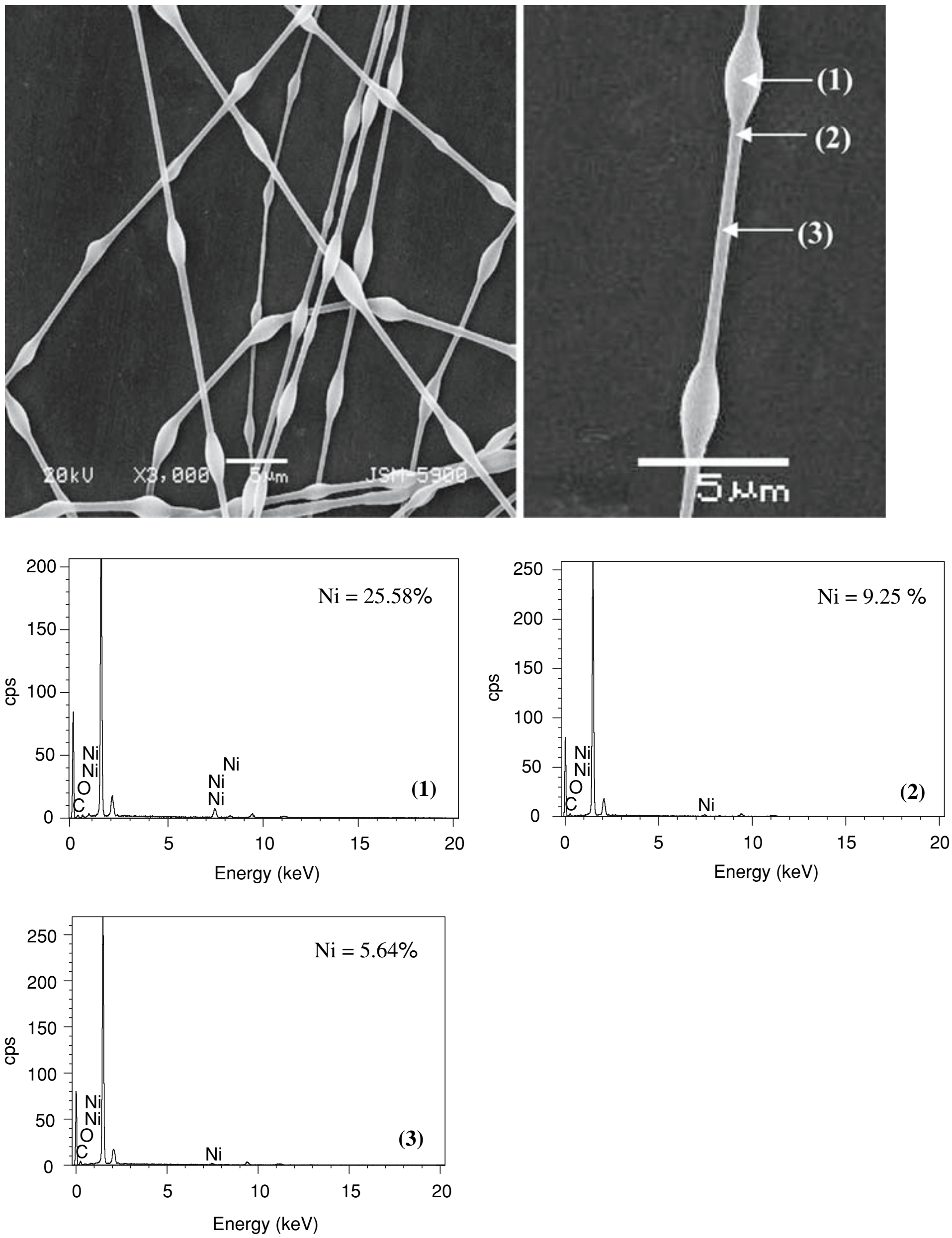

Fig. 1 SEM and EDX results for 15% nickel acetate mixture. The EDX figures show the nickel, carbon, and oxygen concentrations at the points (1), (2), and (3) in the SEM image

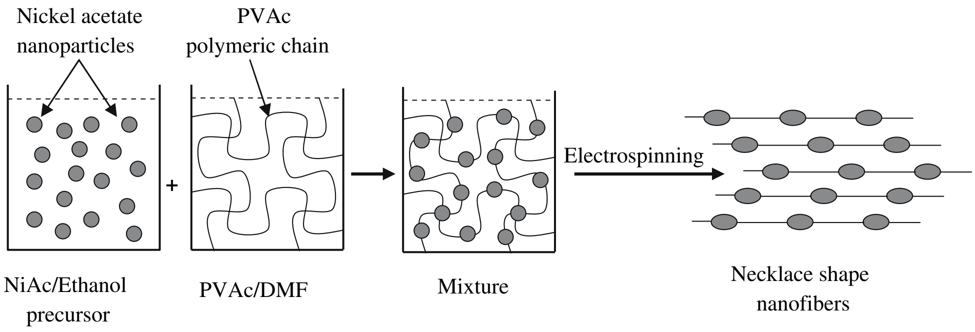

Fig. 2 Schematic diagram describing necklace-shape nanofibers formation steps

the tip of the Taylor cone. Since this jet is charged, its trajectory can be controlled by an electric field. As the jet travels in air, the solvent evaporates, leaving behind a charged polymer fiber which lays itself randomly on a collecting metal screen. Thus, continuous fibers are laid to form a non-woven fabric.

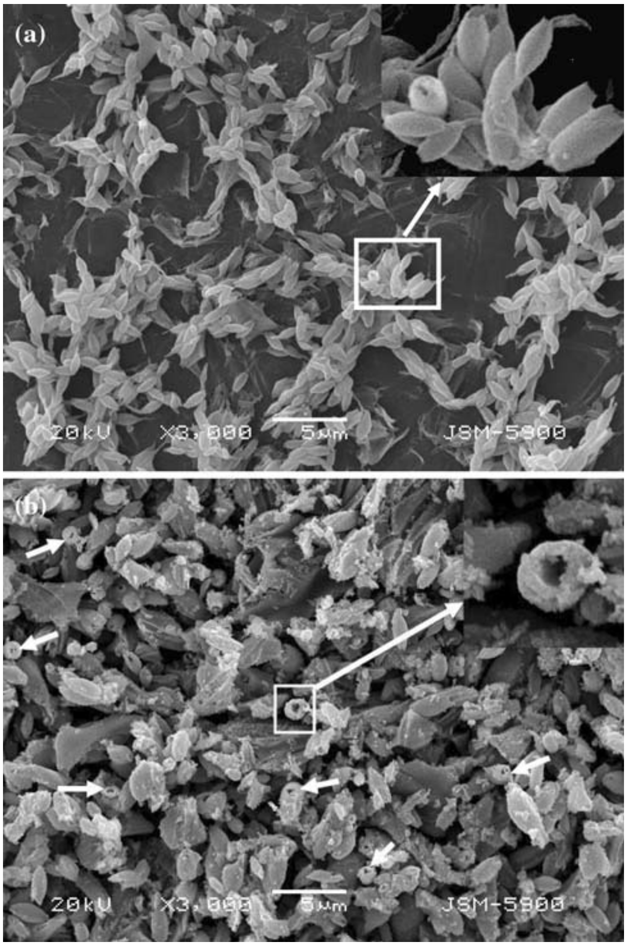

Fig. 3 SEM image for 15% nickel acetate mixture sintered at 823 K for 3 h. (**a**) Nanoparticles as obtained and (**b**) crushed nanoparticles. White arrows point to hollow nanoparticles

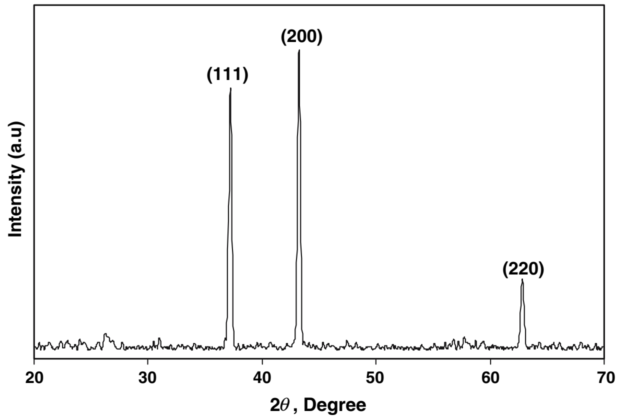

Fig. 4 XRD of the obtained NiO nanoparticles

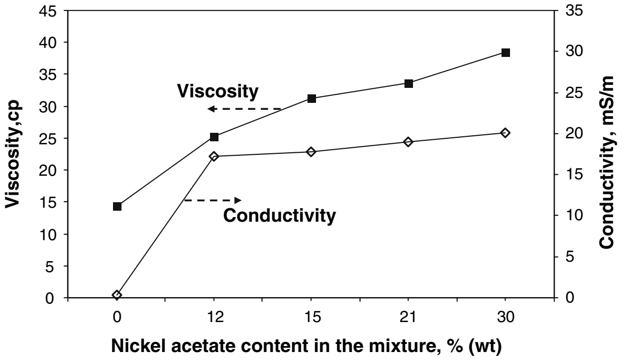

Fig. 5 Effect of the nickel acetate content on the viscosity and electric conductivity of the precursor/polymer mixture

The above description of the process suggests that the following parameters affect the process: solution properties including viscosity, conductivity, and surface tension; controlled variables including hydrostatic pressure in the capillary, electric potential at the tip, and the distance between the tip and the collection screen; and ambient parameters including temperature, humidity, and air velocity in the electrospinning chamber [15]. In a case of nickel acetate/PVAc mixture it was observed that the required voltage decreases with increasing the nickel acetate content, while the optimum distance between the tip and the collection screen increases. This could be a result of increasing the viscosity and electrical conductivity for the mixture with increasing the nickel acetate content, as shown in Fig. 5. Figure 5 shows the effect of nickel acetate content on the viscosity and the electrical conductivity of the mixture. As shown in the figure, both viscosity and electrical conductivity increases with increasing the nickel acetate content in the mixture.

At the normal boiling point of ethanol, 20, 25, 35 and 50% nickel acetate/ethanol colloidal precursor were prepared. In other words, colloidal-gel mixtures of 12, 15, 21, and 30% nickel acetate were obtained. All the colloidal-precursor/polymer mixtures have been successfully electrospun, except the 30% one due to its high electrical conductivity and viscosity. The SEM images obtained corresponding to 12, 15, and 21% mixtures were quite similar, so we offer here the images corresponding to the second one only as a general example.

Conclusion

The present study offers modification of the traditional sol–gel electrospinning technique by exploiting colloidal precursor rather than real solution one. Beside the new shape obtained in this study, the proposed methodology might be used to produce nickel oxide hollow nanoparticles with lower cost (low voltage and small amount of polymer are required) and high yield. The proposed technique might open new avenue to produce other metal oxides nanoparticles by new strategy. Also, the beads in necklace-shape nanofibers might be chemically treated to produce nanoparticles for new compounds having ellipsoidal shape.

Acknowledgement This work is supported by the grant of post-doc program (the second-half term of 2006), Chonbuk National University (CNU), Jeonju 561-756, Republic of Korea.

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