Research Article

Ferromagnetic Behaviors in Fe-Doped NiO Nanofibers Synthesized by Electrospinning Method

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Ni1−xFexO nanofibers with different Fe doping concentration have been synthesized by electrospinning method. An analysis of the phase composition and microstructure shows that Fe doping has no influence on the crystal structure and morphology of NiO nanofibers, which reveals that the doped Fe ions have been incorporated into the NiO host lattice. Pure NiO without Fe doping is antiferromagnetic, yet all the Fe-doped NiO nanofiber samples show obvious room-temperature ferromagnetic properties. The saturation magnetization of the nanofibers can be enhanced with increasing Fe doping concentration, which can be ascribed to the double exchange mechanism through the doped Fe ions and free charge carriers. In addition, it was found that the diameter of nanofibers has significant impact on the ferromagnetic properties, which was discussed in detail.

1. Introduction

Diluted magnetic semiconductors (DMS) have been intensively studied due to their high potential for applications in spin-dependent semiconductor electronics [1]. Practical spintronic materials should have high Curie temperatures, high spin polarization of charge carriers, and compatibility with semiconductors [2, 3]. Lots of experiments were carried out to study the fascinating properties of the oxide-based DMSs (e.g., ZnO, TiO2, SnO2, In2O3, etc.) with various transition metal (TM) ions doped [4–7]. But, compared to the TM-doped oxide-based materials mentioned above, it is more feasible to realize the p-type doping in NiO system.

Recently, one-dimensional nanofibers have received intensive attention due to their excellent magnetic, optical, electric, and chemical properties [8]. The low-symmetry structure will affect their peculiar magnetic properties [9]. In the recent study of DMS materials, nanoparticles, films structure of NiO have already been prepared by sol-gel techniques, hydrothermal route, and Pulsed lase deposition [10–12]. Unfortunately, the investigation of the Fe-doping effect on ferromagnetism of one-dimensional DMS fibers is very limited. Thus, it is necessary to study the influence of low dimensional structure on NiO-based system. Among all the methods of making one-dimensional nanostructure magnetic materials, electrospinning is a simple, versatile, and convenient approach with the characteristic of easy control and low cost [13].

Our previous works have already reported the room-temperature FM behavior of the Fe-doped NiO nanoparticles [12, 14]. Although pure NiO exhibits insulating character and antiferromagnetic order at room temperature, introduction of Fe ions will break the symmetry of the system in NiO, showing the room-temperature ferromagnetism [15, 16]. Therefore, it is anticipated that Fe-doped NiO nanofiber would exhibit ferromagnetism.

In this work, we prepared Fe-doped NiO nanofibers (NFO) and observed remarkable FM properties at room temperature. The result may be attributed to the double exchange mechanism through the doped Fe ions and free charge carriers.

2. Experimental Procedure

2.1. Preparation of Fe-doped Nanofibers. Ni(AC)2⋅4H2O and the appropriate amount of Fe(NO3)3⋅9H2O with different
atomic ratios were dropped slowly into the mixed solution (made by 45 mL alcohol and 5 mL water) with stirring. Then 2 g PVP powder were added slowly into the solution under stirring, and the sol solution was obtained for electrospinning. The precursor sol solution was loaded into a 10 mL plastic syringe with a syringe needle of which the internal diameter is 0.5 mm. The needle was connected to a DC high-voltage power supply. In our experiment, a voltage of 12 kV was applied between the cooper plate collector and the syringe needle with a distance of 12 cm. The PVP/Ni(CH$_3$COO)$_2$ composite nanofibers were collected on the cooper plate during electrospinning processes. Pure NiO and Fe-doped NiO nanofibers were finally obtained by calcination at 660°C for 3 h in air to remove PVP completely.

2.2. Characterization. X-ray diffraction (XRD) was employed to investigate the crystal structure of nanofibers. And the morphologies of nanofibers were characterized by scanning electron microscope (SEM). The valence state of the Fe ions was analyzed by X-ray photoelectron spectroscopy (XPS) and magnetic properties of the samples were measured by Physical Property Measurement System (PPMS).

3. Results and Discussion

Figure 1 shows the SEM images of the nanofibers before and after calcination. Figures 1(a) and 1(c) show the SEM images of undoped NiO/PVP and Fe-doped NiO/PVP composite nanofibers with smooth surface before calcination. They are several millimeters long with a diameter of approximate 270 nm. Furthermore, in contrast to pure NiO/PVA composite nanofibers, the doping Fe ions in NiO do not influence the morphologies of doped samples. As shown in Figures 1(b) and 1(d), after calcined at 660°C, the diameters of all NiO-based nanofibers shrank drastically to 60–100 nm due to the decomposition of PVP and the transformation from metal salts to metal oxides. Figure 2 shows the XRD patterns of various NiO-based nanofiber samples after calcination. Obviously, all of these samples are pure cubic crystalline NiO phase, and no impurity phase appears.

The existence of the Fe ions in the present NFO nanofibers was verified by the XPS measurements as shown in Figure 3. It can be seen that the spectra consist of Fe 2p$_{3/2}$ (713.2 eV) and 2p$_{1/2}$ (724.5 eV) peaks. The chemical state of the Fe ions may be a mixture of Fe$^{2+}$ and Fe$^{3+}$ as seen from the broad peaks of
Fe 2p. As previously reported [17], in the Fe-doped oxides-based DMS systems, the possible presence of a secondary phase (e.g., metallic magnetic Fe particles) can also be the origin of ferromagnetism. However, no metallic Fe$^0$ (2p$_{3/2}$ binding energy $\sim$ 706 eV and 2p$_{1/2}$ binding energy $\sim$ 719 eV) was observed in the present spectra. Therefore, according to the Fe 2p XPS spectra and XRD results, as for our Fe-doped Ni$_{1-x}$Fe$_x$O nanofibers, suggestion of the secondary Fe metal cluster phase as the origin of ferromagnetism can be ruled out.

As shown in Figure 4, with the increasing of the concentration of the Fe-doping, the samples exhibit obvious FM properties at room temperature. In these type Fe-doped NiO samples, the Ni ions are partially substituted by the Fe ions, which are randomly localized over the host lattice. Thus, this kind of disorder certainly breaks the translation symmetry of the system and the original magnetic order in NiO grains is interrupted. The results are similar with the study of the Li-Fe codoped films [14]. The ferromagnetism in the Fe-doped NiO could be caused by the double exchange through the introduced magnetic Fe ions and the related defects (e.g., Fe$_{Ni}$). That is to say, electrons may weakly trapped in the Fe$_{Ni}$ defect site, where the electron occupies an orbital which overlaps the d shells of both Fe neighbors, enhancing the interaction between Fe ions, resulting the ferromagnetism of the nanofibers. In addition, with the increase of doped Fe ions, the amount of the magnetic Fe ions and the Fe$_{Ni}$ defects will also increase, which will enhance the FM double-exchange interaction.

Moreover, compared with the results of Liu’s group [9], we find the diameter of nanofibers has significant impact on the ferromagnetic properties. We suppose that there are two possible mechanisms of the remarkable FM properties. The first mechanism is associated with the transition of double sublattice to multisublattice states [18]. Yet, this explanation only suits the particles whose diameter is less than 30 nm. The other mechanism is related to the change of the impurity states. With the decreasing size, the impurity states may become much deeper in energy [19], which may enhance the coupling interaction between the 3d spins of Fe ions and the carriers, giving an obvious enhancement of FM properties of the nanofibers. More experiments are carrying on to confirm this assumption.

4. Conclusions

In conclusion, nanofibers were prepared by electrospinning method. XPS spectra reveal that the Fe 2p core-level photoemission spectra consisted of the Fe$^{2+}$ and Fe$^{3+}$ components, and no metallic Fe appeared. All the nanofibers exhibited obvious ferromagnetic ordering at room temperature which
should be ascribed to the double exchange through the introduced magnetic Fe ions and related defects.

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References


