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Letter

Solvothermal route to Fe–N–S–O nanowires

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A B S T R A C T

We report a facile solvothermal method to fabricate novel Fe–N–S–O nanowires with amorphous phase in pure solvent diethylenetriamine. The chemical composition of the nanowires is determined as $Fe_{0.36}S_{0.15}O_{0.26}N_{0.23}$ by inductively coupled plasma-atomic emission spectrometry (ICP-AES) measurement. The nanowires are rather straight along growth direction and are of smooth surface. Nevertheless, the nanowires are easily soluble in water and rather unstable in air and under electron beam irradiation. Moreover, we investigate the influence of molar ratio of starting materials and sulfur sources on the final structure and morphology of the products. It is found that the wire-like morphology is gradually destroyed with increase of the molar ratio of $Na_2S_2O_3{\cdot}5H_2O$ and $FeCl_3$.

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1. Introduction

One-dimensional (1D) nanostructures such as nanowires, nanobelts and nanotubes have attracted considerable attention due to their promising applications in electronic and optoelectronic nanodevices [1–16]. Compared with syntheses and potential applications of 1D semiconductor nanowires, metal salts-related nanowires have attracted less attention. Nevertheless, these nanowires have been found to be of novel electronic structures and variable components, which results in numerous potential applications in catalysts, magnetic devices, electric transportation, sensors, additives and solar energy cells to now [17–32]. Among the various synthesis methods, hydrothermal/solvothermal syntheses are the most low-cost, simple, large-scale, and practical routes to metal salts-related nanowires. In this paper, we developed a facile solvothermal route to novel Fe–N–S–O nanowires by direct reaction between $Na_2S_2O_3{\cdot}5H_2O$ and $FeCl_3$ in the pure solvent diethylenetriamine. The morphology and chemical composition of the Fe–N–S–O nanowires are investigated in detail. Moreover, we investigate the effects of other sulfur sources, e.g. thiourea (CH_4N_2S) and sulfur powders (S) on the structure and morphology of the final products, and the probable reaction mechanism is preliminarily proposed.

2. Experimental

The products were fabricated by a facile solvothermal process. All the chemicals are analytic grade and used without further purification. In the experiment, 0.001 mol ferric trichloride ($FeCl_3$), sodium thiosulfate ($Na_2S_2O_3{\cdot}5H_2O$) (the ratio of $Na_2S_2O_3{\cdot}5H_2O$ and $FeCl_3$ is 1:1), and 40 ml diethylenetriamine ($C_4H_{13}N_3$) were added into 50 ml Teflon-lined stainless steel autoclaves and stirred for half an hour. Then, the autoclave is sealed and maintained at 180 °C for 24 h. After the autoclave was cooled to room temperature, black precipitates were found. The precipitates were washed by ethanol several times and dried in vacuum for further characterization (Note: the product is easily soluble in water and oxidized in air). We also investigate effects of other sulfur sources, e.g. thiourea (CH_4N_2S) and sulfur powders (S) on the structure and morphology of the final products. The synthesis condition is similar to that mentioned above and the ratio of sulfur source and $FeCl_3$ is fixed at 1:1. The morphology of the nanowires was characterized using field emission scanning electron microscopy (FE-SEM; FEI XL30 S-FEG). The microstructure and chemical composition of the nanowires was further characterized by transmission electron microscope equipped with energy-dispersive X-ray spectroscopy (TEM; Philips CM200). Bulk composition analysis was conducted using inductively coupled plasma-atomic emission spectrometry (ICP-AES).

3. Results and discussion

The morphologies of the products are first characterized by SEM, as shown in Fig. 1. There are large-scale nanowires with the length up to several tens of micrometers. These nanowires are of smooth surfaces and rather straight along growth direction. The corresponding XRD patterns (not shown here) indicate that the nanowires are amorphous. Because these nanowires are easily oxidized in air and soluble in water, we employ TEM to further investigate the microstructure of the nanowires. Fig. 2a shows the typical TEM image of an individual nanowire. The diameter of the nanowire is ca. 120 nm and exhibits relative smooth surface. The corresponding EDS spectrum indicates that the nanowire mainly consists of Fe, N, O and S elements, as shown in Fig. 2b. Whether the detected C signal comes from the nanowire or the carbon coated copper grid is unknown, and the exact atomic ratio of the light element is difficult to be determined by TEM-based EDS measurement. So, we utilize inductively coupled plasma-atomic emission

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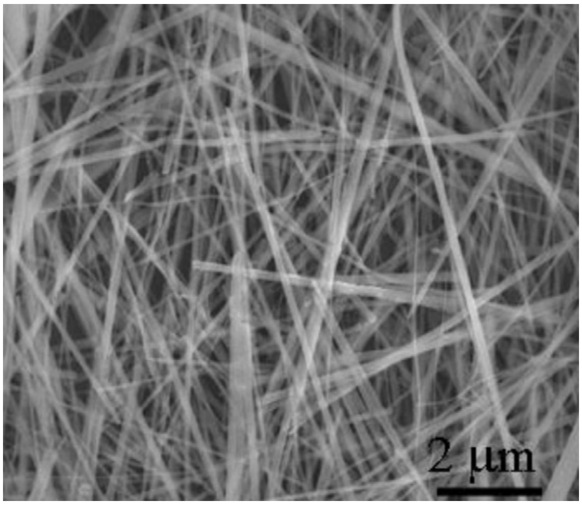

Fig. 1. SEM image of the products.

spectrometry (ICP-AES) to determine the exact atomic ratio of the elements and origin of the detected C element. The results reveal that and the C element is not detected by the ICP-AES measurement and atomic percent of Fe, S, O and N elements is about 36%, 15%, 26% and 23%, respectively. The light element H cannot be detected by ICP-AES. Expect the influence of the H element, the formation of the nanowires can be confirmed as $Fe_{0.36}S_{0.15}O_{0.26}N_{0.23}$. The nanowire is amorphous and unstable under electron beam irradiation, as confirmed by the further TEM measurement. Fig. 2c and d shows the TEM images of the nanowire after electron beam irradiation for 10 min and 20 min, respectively. It is found that the edge and tip of the nanowire are destroyed by electron beam irradiation within 10 min and the whole nanowire is completely decomposed after 20 min. We deduce that electron beam irradiating on the nanowires can produce high temperature on the surface of the sample, resulting in decomposition of the nanowires.

The influence of the molar ratio of $Na_2S_2O_3{\cdot}5H_2O$ and $FeCl_3$ on the final morphologies of the products is also investigated. As shown in Fig. 3a–c, the wire-like morphology is gradually destroyed with increase of the molar ratio of $Na_2S_2O_3{\cdot}5H_2O$ and $FeCl_3$, and is completely disappeared at the molar ratio of 4 between the $Na_2S_2O_3{\cdot}5H_2O$ and the $FeCl_3$ (Fig. 3c). The chemical composition of the final products is almost unchanged, which is confirmed by ICP-AES measurement. We deduce that excess $Na_2S_2O_3{\cdot}5H_2O$ can wrap the as-synthesized products and further restrain the 1D growth of the product. Nevertheless, the exact reaction mechanism is unclear and needs to be further investigated.

We also observe that sulfur sources have significant effects on the morphology and structure of the final products. Here, we use thiourea (CH_4N_2S) and sulfur powders (S) as alternative sulfur sources. The formation of both final products is FeS_2, though the morphology and stability of the structure is different. It is found that some microparticles with quasi-spherical and cubic morphologies are obtained using thiourea as precursor, as shown in Fig. 4a. These microparticles with average size of 3 μm are poor crystalline and are not stable in the electron beam irradiation in SEM instruments. Nevertheless, microparticles with regular cubic shape are produced using sulfur powders as precursor (Fig. 4b). The obtained mircoparticles have average size of 1 μm and are rather stable at irradiation condition. As is well known, thiourea and sulfur powders can slowly release S ions in the pure solvent diethylenetriamine ($C_4H_{13}N_3$)

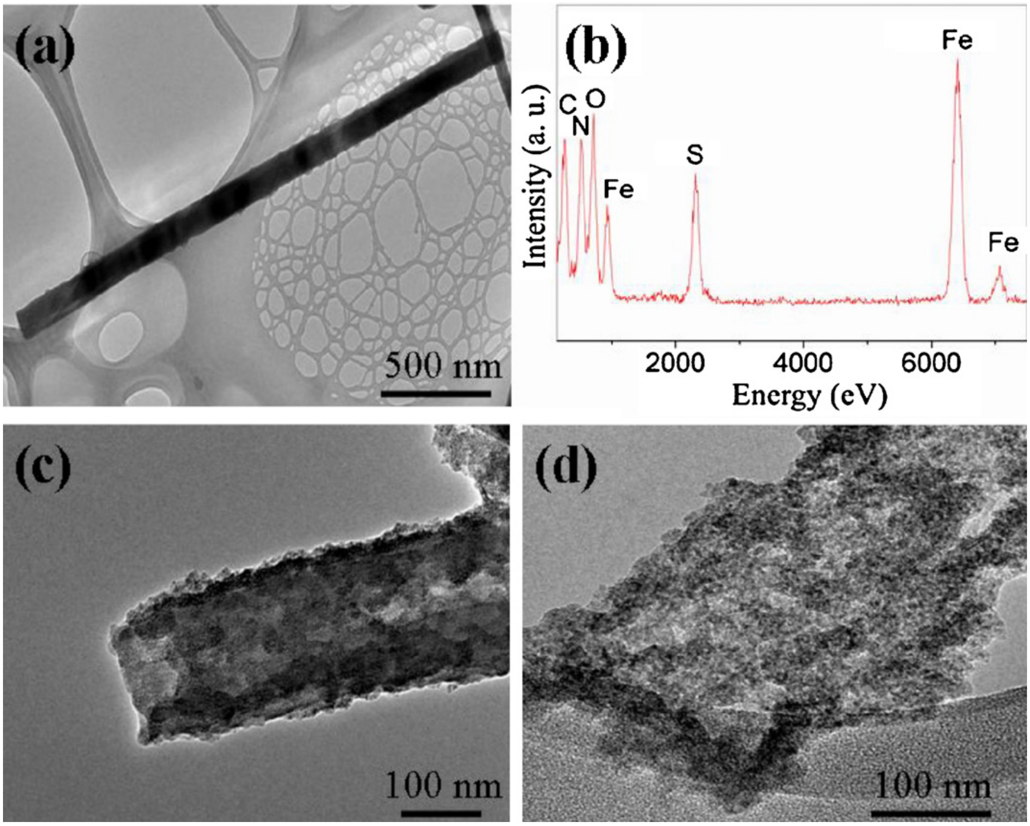

Fig. 2. (a) TEM image of an individual nanowire. (b) EDS spectrum of the nanowire. (c and d) TEM images of the nanowire after electron beam irradiation for 10 min and 20 min, respectively.

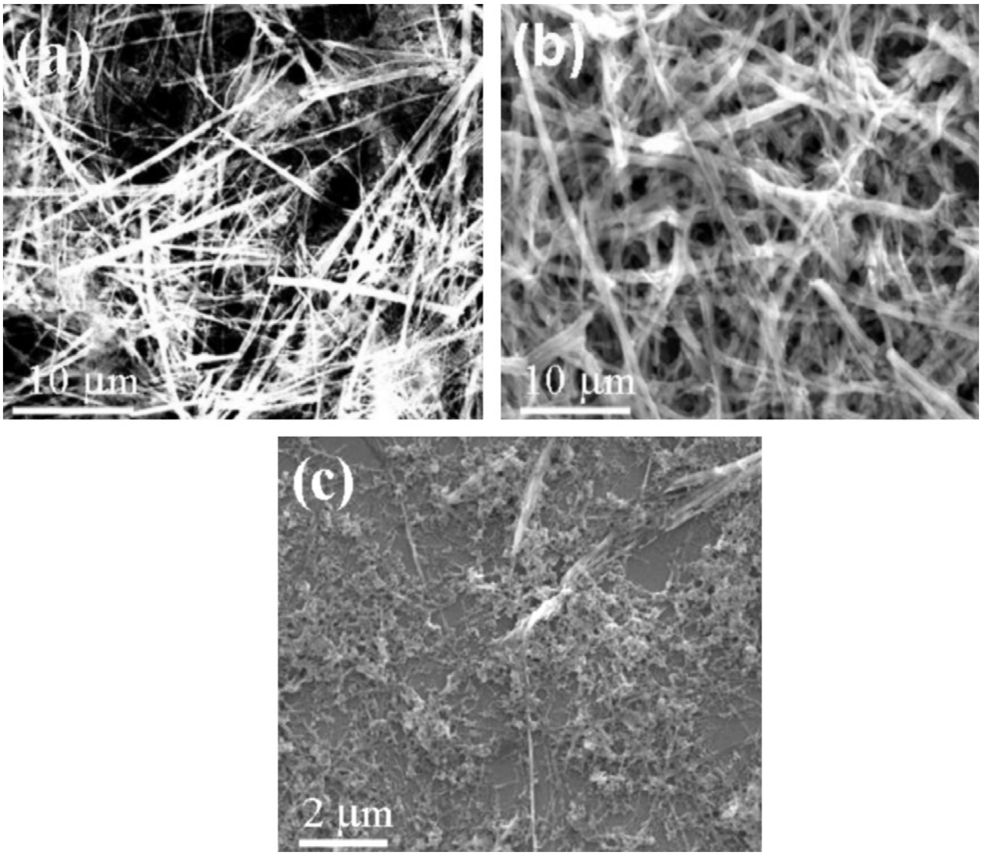

Fig. 3. SEM images of the products obtained at different molar ratios of $Na_2S_2O_3{\cdot}5H_2O$ and $FeCl_3$: (a) 2:1; (b) 3:1; (c) 4:1.

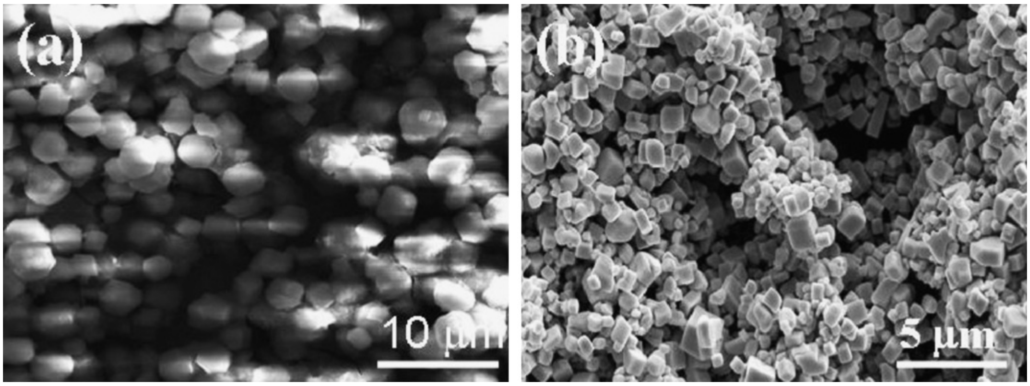

Fig. 4. (a and b) SEM images of the products using thiourea and sulfur as precursors, respectively.

[33], which results in new product FeS_2. The possible reaction processes are listed as follows:

$$Fe^{3+} + 2C_4H_{13}N_3 \rightarrow [Fe(C_4H_{13}N_3)_2]^{3+} \quad (1)$$

$$[Fe(C_4H_{13}N_3)_2]^{3+} + 2S^{2-} \rightarrow FeS_2 + 2C_4H_{13}N_3 \quad (2)$$

$$S_N + 2C_4H_{13}N_3 \rightarrow (C_4H_{13}N_3)_2S_{N-1} + H_2S \quad (3)$$

$$[Fe(C_4H_{13}N_3)_2]^{3+} + 2S^{2-} \rightarrow FeS_2 + 2C_4H_{13}N_3 \quad (4)$$

The solvent $C_4H_{13}N_3$ can first react with Fe^{3+} ions to form relatively stable ligand complexes $[Fe(C_4H_{13}N_3)_2]^{3+}$. Then, thiourea and sulfur slowly releases S^{2-} ion in the solvent $C_4H_{13}N_3$ at moderate temperatures, respectively. The ligand complexes $[Fe(C_4H_{13}N_3)_2]^{3+}$ further react with S^{2-} ions to form final products FeS_2. The difference in the concentration of the released S ions results in the stability and morphology of the final products. Generally, concentration of the S ions released from sulfur is slower than that from thiourea, which results in the products with smaller size and more stable structures. If using $Na_2S_2O_3{\cdot}5H_2O$ as precursor, $Fe_{0.36}S_{0.15}O_{0.26}N_{0.23}$ instead of FeS_2 is obtained, indicating that the reaction mechanism is rather complicated in solvent diethylenetriamine, compared with that using thiourea and sulfur as precursors. Nevertheless, the solubility condition of $Na_2S_2O_3{\cdot}5H_2O$ in diethylenetriamine solvent is unknown, and whether $Na_2S_2O_3{\cdot}5H_2O$ can release S ion or not is also unclear. So, the exact reaction mechanism is unknown and needs to be further investigated.

4. Conclusions

Novel Fe–N–S–O nanowires with amorphous phase were fabricated in pure solvent diethylenetriamine via a facile solvothermal method using $Na_2S_2O_3{\cdot}5H_2O$ and $FeCl_3$ as starting materials. ICP-AES measurement reveals that the chemical composition of the nanowires is $Fe_{0.36}S_{0.15}O_{0.26}N_{0.23}$. The amorphous nanowires are straight along growth direction and are of smooth surface. Nevertheless, the nanowires are rather unstable and gradually decomposed under electron beam irradiation. Moreover, we observe that molar ratio of starting materials and sulfur sources have significant influence on the final structure and morphology of the products. It is found that the wire-like morphology is gradually destroyed with increase of the molar ratio of $Na_2S_2O_3{\cdot}5H_2O$ and $FeCl_3$. Nevertheless, FeS_2 microparticels with different morphology, size and crystallization are obtained using thiourea and sulfur powders as sulfur sources. We deduce that the concentration of S ions released from thiourea and sulfur powders should be responsible for the difference in the final structures and morphologies of FeS_2 microparticles.

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