Fast and facile preparation of superhigh aspect-ratio Cu–thiourea nanowires in large quantity

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Abstract

Superhigh aspect-ratio Cu–thiourea (Cu(tu)) nanowires have been synthesized in large quantity via a fast and facile method. Nanowires of Cu(tu)Cl·0.5H₂O and Cu(tu)Br·0.5H₂O were found to be 60–100 nm and 100–200 nm in diameter, and could extend to several millimeters in length. It is found to be the most convenient and facile approach to the fabrication of one-dimensional superhigh aspect-ratio nanomaterials in large scale so far.

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1. Introduction

Recently, one-dimensional (1D) structures such as wires, rods, belts, and tubes have become the focus of considerable research due to their dimensional anisotropy, and have shown potential applications to nano-electronic and optical devices [1–3]. It is reported widely in previous studies that these nanostructured materials show typical difference in their physical properties from those of the bulk materials [4,5] due to their unique high surface area and low dimensionality [1–3,6,7].

Until now, diverse methods have already been explored for the synthesis and fabrication of one-dimensional morphologies, such as nanolithography techniques [8], template-assisted method [9], vapor–liquid–solid (VLS) preparation, colloidal micellar preparation [10,11], electrochemical processes [12], solvothermal methods [13–15], etc. Recently, more importance to the preparations of high aspect-ratio, ultrathin nanowires of various materials was realized, and many efforts have been focused in this area [16–20].

Herein, we present a fast and simple method, a one-step route to prepare large-scale and superhigh aspect Cu(tu)Cl·0.5H₂O and Cu(tu)Br·0.5H₂O nanowires. These obtained nanowire complexes with high yield can form even within several seconds. To the best of our knowledge, it might be considered as the most simple, low-cost and convenient approach to obtain superhigh aspect ratio nanowires.

It is noticeable that thiourea complexes are starting materials in chemical spray pyrolysis processes which were used to produce thin films of binary and ternary sulfides [21]. A series of thiourea–chloric copper (I) complexes have been synthesized not only because of the appearance of unusual stoichiometries, but also because the planar thiourea molecule is an excellent geometric probe for the electrons used by this ligand in complex formation [22]. A number of copper (I) thiourea complexes have been prepared and reported in the literature over the last 40 years [23–27]. Among these literatures, researches on thiourea–chloric copper (I) seemed plentiful while studies on thiourea–bromic copper (I) were rare [23–27]. Among the reported copper (I) thiourea complexes, most of which were crystals with regular geometrical shapes, and most attentions have been focused on the structure and thermal properties of these complexes. Up to now, this is the first time that the idea of paying more attention to preparations and characterization of 1D nanostructured copper (I) thiourea complexes is brought forward.

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2. Experimental

Typically, an aqueous solution of 0.1 M CuCl₂ was prepared by dissolving a certain amount of cupric chloride dehydrates into superpure water. The 0.1 M thiourea aqueous solution was added to that cupric solution at room temperature without stirring. The mixture was then allowed to stand for a while and a mass of white precipitation formed gradually within 30 s. Then the resulting precipitation was collected by filtration and washed with absolute ethanol and distilled water. Finally it was dried under vacuum at 60 °C.

When the thiourea solution was poured into the CuCl₂ solution, the system immediately turned color from blue gradually into green. The addition of thiourea to CuCl₂ solution results in the reduction of Cu²⁺ to Cu⁺, leading to copper (I) complexes in the aqueous solutions. About 10 s later, white precipitation can be observed clearly. A great deal of white precipitation formed completely after 30 s.

The morphology of the samples was characterized by scanning electron microscopy (SEM, XL30 ESEM FEG) and transmission electron microscopy (TEM, JEOL 2000).

3. Results and discussion

As shown in Fig. 1A, SEM image of the resulting Cu(tu)Cl·0.5H₂O (deduced from the elements analysis) displays uniform wirelike shapes with superhigh aspect-ratio in a quite large scale, and these nanowires can extend even to several millimeters in length. It is also observed with high magnification in SEM and TEM (Fig. 1B) measurements that the nanowires are 60–100 nm in diameter and the surface of the nanowires is very smooth. In addition, the nanowires tend to extend themselves in directions with comparative tropism rather than agglomerating themselves into interconnected nanowire networks.

The structure of the resulting nanowires was also investigated by X-ray diffraction (XRD) measurement. X-ray power diffraction (XRD) spectroscopy was performed on a Japan Rigaku D/Max-II B X-ray diffractometer with CuKα radiation (λ=0.154178 nm). The XRD pattern of the sample was shown in Fig. 2. All the diffraction peaks in the figure can be indexed to the cube structure with cell unit constants a=10.7 Å. Two obvious bands appear with maximum intensity at 8.3 and 11.7, representing Bragg’s reflections from (100) and (110), respectively.

Fig. 1. (A) SEM and (B) TEM images of Cu(tu)Cl·0.5H₂O nanowire.

Fig. 2. XRD pattern of the Cu(tu)Cl·0.5H₂O nanowire.

Fig. 3. (A) SEM and (B) TEM images of Cu(tu)Br·0.5H₂O nanowire.
respectively. Moreover, it is worth noting that the ratio of the intensity of the (100) to the others is much higher, suggesting that the resulting nanowire is mainly dominated by (100) facets, and tend to be growing along the (100) face.

FTIR spectroscopy (data not shown here) was used to detail the structure of resulting Cu(tu)Cl·0.5H2O complex. The characteristic peaks at 3384, 1624 and 696 cm⁻¹ can be assigned to the stretching, in-plane bending and out-plane bending vibrations of N–H in –NH2 group, respectively [27]. The peaks at 1515, 1418 and 1108 cm⁻¹ originated from characteristic vibrations of >N–C=S in thiourea group.

It is quite similar in the case of copper bromide complex to copper chloride–thiourea complex but a little more expeditious (Cu(tu)Br·0.5H2O complex was prepared and purified by a similar way just by using 0.1 mol L⁻¹ CuBr₂ instead of CuCl₂ solution). It only takes ca. 15 s to accomplish the formation of Cu(tu)Br·0.5H₂O complex. A similar morphological of the resulting Cu(tu)Br complex was also observed, as shown in Fig. 3.

The low-magnification SEM image (Fig. 3A) reveals a remarkable orientation at a large area. The smooth surfaces can also be observed along individual wires. Compared with Cu(tu)Cl·0.5H₂O, it can be found that Cu(tu)Br·0.5H₂O nanowires are much thicker than the Cu(tu)Cl·0.5H₂O complex nanowires in diameter, which range from 100 to 200 nm.

XRD measurement of this Cu(tu)Br·0.5H₂O complex was also carried out. The predominant (100), as mentioned above in the case of Cu(tu)Cl·0.5H₂O, can be observed. And the cell unit constant can be estimated as ca. 11.1 Å, which is slightly larger than that of Cu(tu)Cl·0.5H₂O.

Similar FTIR bands, which originated from the characteristic vibrations of thiourea group, can also be seen clearly, confirming the formation of Cu–thiourea complex.

A reaction pathway of the formation of Cu(tu)Cl·0.5H₂O and Cu(tu)Br·0.5H₂O complexes can be proposed according to our results and previous reports [23–27]: (X=Cl, Br)

\[2\text{Cu}_2\text{X}_2 + 2\text{SC(NH}_2)_2 \rightarrow 2\text{CuX} + (\text{NH}_2)_2\text{C}=(\equiv\text{NH})-\text{S}–\text{S}–\text{C}=(\equiv\text{NH}) \times (\text{NH}_2)_2 + 2\text{HX} \]

\[(\text{NH}_2)_2\text{C}=(\equiv\text{NH})-\text{S}–\text{S}–\text{C}=(\equiv\text{NH})(\text{NH}_2)_2 + 2\text{HX} \rightarrow [(\text{NH}_2)_2\text{CS–SC(NH}_2)_2]_2 \times \text{0.5H}_2\text{O} \]

\[\text{CuX} + \text{SC(NH}_2)_2 + 0.5\text{H}_2\text{O} \rightarrow [\text{Cu(SC(NH}_2)_2]_2 \times \text{0.5H}_2\text{O} \]

The influence of molar ratio of thiourea to copper (II) haloid on the yield of those two complexes has also been examined. The results indicate that the maximum yield can be achieved at thiourea:copper (II) = 2.0.

In addition, the Cu(tu)Cl·0.5H₂O and Cu(tu)Br·0.5H₂O nanowires show a high stability towards water, ethanol as well as some acid media, such as HCl etc. Even if standing for a long time, the nanowire structure can not be destroyed. But, they can be dissolved in excessive thiourea solution (when thiourea:copper>4). The unique structure and dissolution, as well as the preferable stability of those two superhigh aspect-ratio nanowires might have potential applications, such as in nanofabrication, for nano-devices, as templates for the nanomaterials' preparation, etc.

4. Conclusions

In conclusion, superhigh aspect-ratio nanowires based upon the copper (II) haloid complexes have been well-prepared via a fast and facile method. The resulting nanowires are a few millimeters in length and 100–200 nm in width. The results described here highlight the potential use of the superhigh aspect-ratio nanowires in the field of nanotechnology. The practical advantages of the superhigh aspect-ratio materials are technically attractive in nanofabrications, and exhibit a significant future towards the application of nanomaterials structured materials.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.matlet.2006.12.003.

References