Letter

$Cu_{5.5}FeS_{6.5}$ nanotubes—a new kind of ternary sulfide nanotube

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A new kind of ternary sulfide nanotubes, $Cu_{5.5}FeS_{6.5}$ nanotubes, was synthesized in autoclaves at 195 °C, and it was found that armchair, zigzag and complex arrangements exist in the nanotubes.

The discovery of carbon nanotubes has greatly stimulated the study of nanoscopic structures.[1] Nanotubes are envisaged for potential applications in several areas, such as catalysis, composite materials and nanowires, up to artificial muscles and intramolecular junctions.[2] Several types of nanotubes have been synthesized. Arc discharge or high temperature treatment of molecular precursors have been applied to synthesize nanotubes of simple materials such as C,[1] $B_xC_yN_z$,[3] or BN.[4] Fullerene-like nanocages and nanotubes of MS_2 sulfides ($M = Mo,W$) can be obtained *via* high temperature reactions of the corresponding oxides with H_2S.[5,6] Different types of nanoscopic tubules were obtained at low temperatures using templating reactions with organic surfactants. This approach has led to hollow tubules of oxides such as SiO_2[7] and V_2O_5.[8] Tubular MoS_2 has also been prepared by the decomposition of $(NH_4)_2MoS_4$ within the pores of an alumina membrane, followed by dissolution of the templating oxide in aqueous NaOH.[9] Recently, a solvothermal method has been developed in our lab to produce carbon nanotubes.[10] But up to now, nanotubes of ternary compounds have not been reported. Here, we report a new kind of ternary inorganic nanotube, $Cu_{5.5}FeS_{6.5}$ nanotubes,[11–14] which was prepared in autoclaves at 195 °C.

EDX analysis (Fig. 1) of the nanotubes indicated that they were made up of Cu, Fe and S; the average atomic ratio of Cu : Fe : S was 5.46 : 1 : 6.59 (the deviation was lower than 6%), which satisfied the stoichiometry of $Cu_{5.5}FeS_{6.5}$. The carbon in the EDX spectrum originated from the amorphous carbon film on the Ni TEM grid. Elemental analysis of the samples only found a negligible amount of carbon in the samples.

Some mineralogists reported that $Cu_{5.5}FeS_{6.5}$ has a hexagonal structure, while others maintained that it has a trigonal structure.[11,12] In fact, what they disputed were only minor differences in structure, which could not be differentiated from the XRD patterns of $Cu_{5.5}FeS_{6.5}$. Fig. 2 shows a schematic of the structure of $Cu_{5.5}FeS_{6.5}$. It can be seen that $Cu_{5.5}FeS_{6.5}$ has a layered structure characterized by S_2 pairs and MS_4 tetrahedrons.[12] The $Cu_{5.5}FeS_{6.5}$ nanotubes are thought to be formed by rolling the basal planes into a cylindrical structure.

Fig. 3(a) and (b) show TEM images of the $Cu_{5.5}FeS_{6.5}$ nanotubes. The nanotubes are generally quite straight with an average diameter of about 50 nm; the thickness of the walls of the nanotubes varies from 5 to 20 nm. Fig. 3(c) shows a HREM image of the walls of the thick-walled nanotube in Fig. 3(b), which indicates that the layers of the walls of the nanotube are well stacked and that the average distance between the neighboring fringes is about 5.4 Å. The dark shadow in Fig. 3(c) originates from the wall of another nanotube shown in Fig. 3(b). We failed to obtain an HREM image of the thin-walled nanotube, which indicates that the crystallinity of the thick-walled nanotube is relatively better than that of the thin-walled nanotube. Generally speaking, the crystallinity of the nanotubes was not good; both HREM

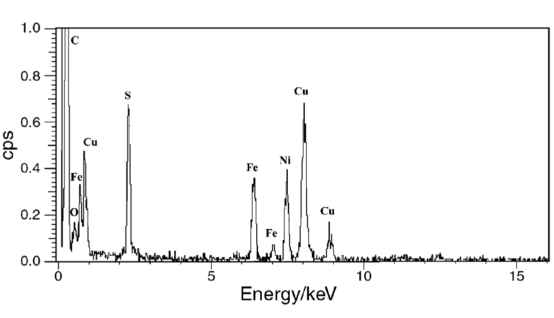

Fig. 1 EDX spectrum of a $Cu_{5.5}FeS_{6.5}$ nanotube.

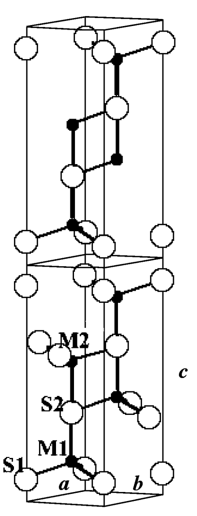

Fig. 2 The schematic structure of $Cu_{5.5}FeS_{6.5}$.

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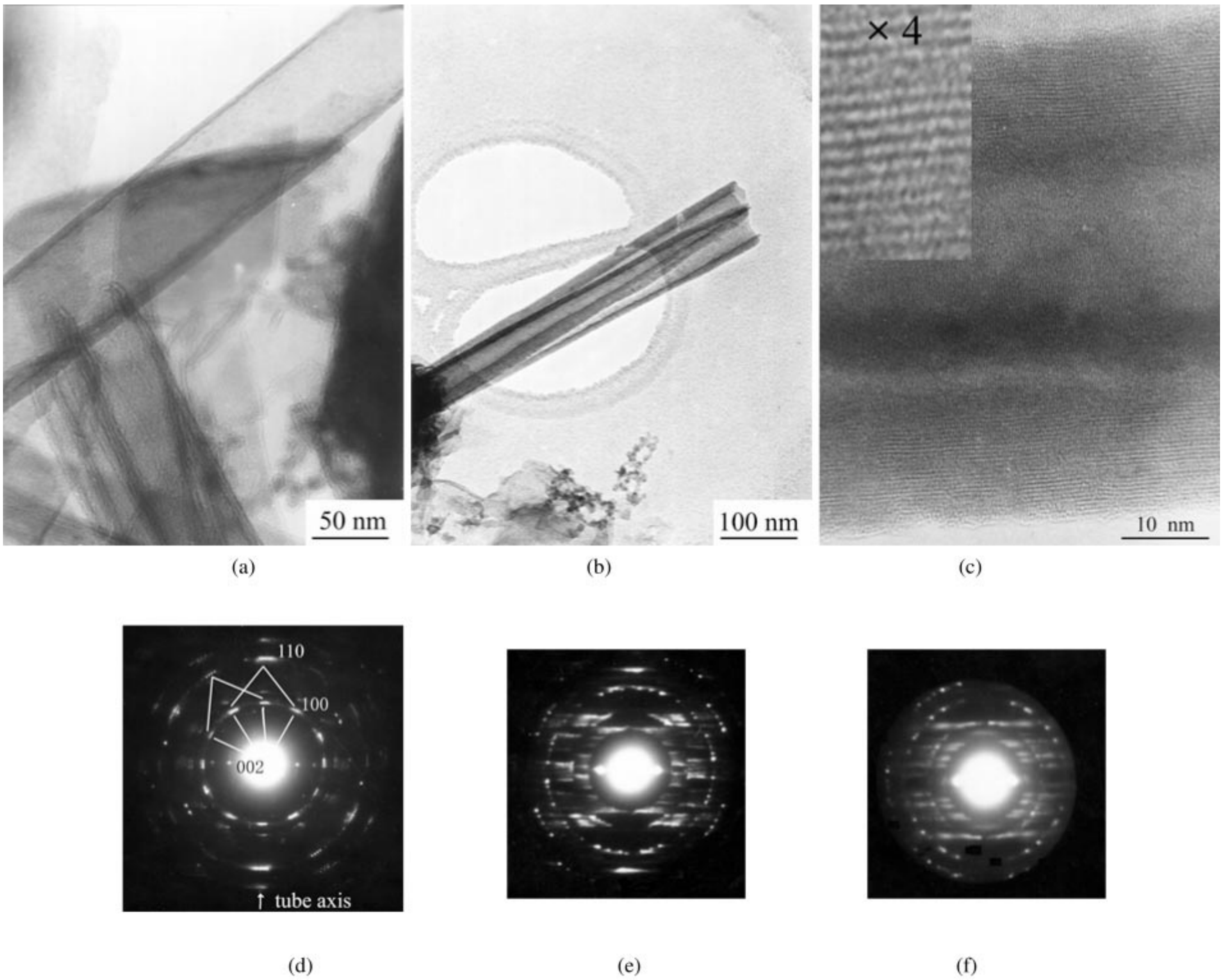

(a) (b) (c)

(d) (e) (f)

Fig. 3 (a and b) TEM images of $Cu_{5.5}FeS_{6.5}$ nanotubes; (c) HREM image of the walls of the nanotube in Fig. 3(b); (d) ED pattern of thick-walled nanotubes, the camera length is 100 cm; (e and f) ED patterns of thin-walled nanotubes with quasi-armchair arrangement and with quasi-zigzag arrangement, the camera length is 80 cm.

images and electron diffraction (ED) patterns were not easy to obtain. Fig. 3(d) shows a typical ED pattern of thick-walled nanotubes; the ED pattern has been indexed according to the structure of $Cu_{5.5}FeS_{6.5}$.[11,12] The 001 diffraction is relatively easy to observe on the negative and not dispersive, but is difficult to see in the printed image. The tube axis in Fig. 3(d) is perpendicular to the direction of the spot elongation. The pattern is a superposition of two hexagonal patterns with a mutual 30° rotation. Taking the theoretical calculated ED patterns of MoS_2 nanotubes and the ED patterns of gold alloyed MoS_2 nanotubes into consideration,[15,16] the ED pattern in Fig. 3(d) indicates that the thick-walled $Cu_{5.5}FeS_{6.5}$ nanotube contains both armchair and zigzag arrangements. However, the dispersion of the spots indicates that chirality still exists in our nanotubes, in contrast to the ED pattern of the gold alloyed MoS_2 nanotubes which displays complete suppression of chirality.[16] The lattice parameters based on the ED patterns [Fig. 3(d)] are about $a = 3.7$ and $c = 10.9$ Å, which agree well with the lattice parameters of $Cu_{5.5}FeS_{6.5}$ ($a = 3.782$, $c = 11.187$ Å) and with the results of HREM image of the walls of the nanotubes [Fig. 3(c)].[11,12] The ED patterns of thin-walled nanotubes were also obtained [Fig. 3(e) and 3(f)], and have characteristics typical of the ED patterns reported for armchair and zigzag nanotubes of MoS_2 and WS_2,[15,17] but the patterns are dispersive and blurry.

In our experiments, when 20 runs were carried out, about 6 successfully produced nanotubes with the yield of nanotubes being about 5–8% in those samples containing nanotubes. Besides the nanotubes, the samples consisted of a few cone-shaped structures and large amounts of irregular particles and flakes. It was found that the composition of the flakes perfectly matched the stoichiometry of $Cu_{5.5}FeS_{6.5}$ and their ED patterns and HREM images were in accord with the structure of $Cu_{5.5}FeS_{6.5}$, too. Although not every run yielded the nanotubes, the flakes were obtained every time. This result is superior to the work of Kojima and Ueno for the production of $Cu_{5.5}FeS_{6.5}$; they performed more than 70 runs but only 28 were successful.[18] Elemental analyses showed that the mean composition of the samples was (atomic ratio) Cu 53.4, Fe 8.9, S 37.6%. Fig. 4 shows the XRD pattern of the samples. Taking

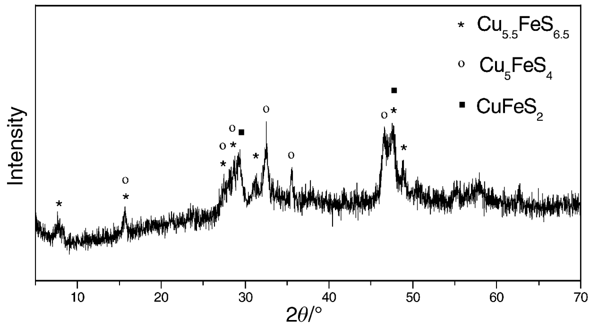

Fig. 4 XRD pattern of the as-prepared sample.

the elemental analyses and standard Cu–Fe–S compounds into consideration,[14] the diffractions at $d = 11.2$ and 5.6 Å strongly indicate the existence of a $Cu_{5.5}FeS_{6.5}$ phase. The XRD pattern can be looked at as a superposition of Cu_5FeS_4 (bornite, orthorhombic), $CuFeS_2$ (chacolpyrite, tetragonal), and $Cu_{5.5}FeS_{6.5}$.[11,12,19] From the XRD pattern, it is confirmed that phases like CuS, $Cu_{1.96}S$, Cu_2S are not present, but it is difficult to rule out the existence of a small amount of other phases like $Cu_{1.81}S$.[19] However, considering that the XRD pattern has a high amount of noise, it is evident that the crystallinity of the samples is not good, which coincides with the poor crystallinity of the $Cu_{5.5}FeS_{6.5}$ nanotubes.

It was found that the nanotubes preferred to grow in a dilute environment and that a too-high initial sulfur loading hindered the formation of nanotubes. Also, the autoclaves should not be loaded to more than 90% of capacity as too-full loading also prevented the formation of nanotubes. Fluctuation of temperature and pressure (produced by designed leakage of the autoclaves) in the reaction usually led to decreased yield of the nanotubes, while the morphology of the nanotubes became irregular, some nanotubes became squiggly and some others were broken. Experiments also indicated that $LiOH \cdot H_2O$ was beneficial for the formation of the nanotubes. This phenomenon is puzzling and the exact explanation is not known, but this chemical probably acts as a mineral nutrient, as did NH_4Cl in the work of Sugaki *et al.*[12] Efforts were made to increase the yield and the crystallinity of the nanotubes by adjusting the reaction conditions (temperature, reaction time, *etc.*), but they were not successful.

Elemental Cu and Fe powders were used in attempts to synthesize the nanotubes, but these also proved unsuccessful. However, the use of elemental Cu and Fe does not seem to prevent the formation of $Cu_{5.5}FeS_{6.5}$ although the yield is not high. As the formation processes of the nanotubes and the $Cu_{5.5}FeS_{6.5}$ phase in this reaction are complicated,[14,18,20,21] the exact mechanism needs further research.

In conclusion, nanotubes of $Cu_{5.5}FeS_{6.5}$ were synthesized in autoclaves at 195 °C and characterized by TEM and EDX. Armchair, zigzag and complex arrangements exist in the nanotubes. The present method is also efficient for the synthesis of $Cu_{5.5}FeS_{6.5}$ phase.

Experimental

A typical preparation procedure is as follows. Carbon steel autoclaves with 25 ml capacity were used to synthesize the nanotubes; they also acted as the Fe source. Thin pieces of elemental copper were fixed to the top part of the autoclaves, which acted as the Cu source. Elemental sulfur (0.1 g, 3.1 mmol), lithium hydroxide monohydrate (0.27 g, 6.4 mmol), and 8 ml of hydrazine monohydrate (86%, v/v) were put into the autoclaves and distilled water was added to fill the autoclaves to 75–80% of the total volume. The autoclaves were kept at 195–197 °C for 6 days and then allowed to cool to room temperature naturally. The precipitates in the autoclaves were removed. The dark-colored floccule suspended in the liquid in the autoclaves was centrifuged and washed with distilled water, dilute hydrochloric acid, and ethanol several times. The final black to slate-gray powders were dried under vacuum at 60 °C for 3 h.

Energy-dispersed X-ray (EDX) analysis results, transmission electron microscope (TEM) images and high-resolution electron microscope (HREM) images were obtained on a JEOL 2010 transmission electron microscope working at an accelerating voltage of 200 kV. EDX analyses of the nanotubes were performed after depositing the sonicated samples on Formvar-coated nickel TEM grids. Elemental analyses of the metal elements in the samples were performed by inductively coupled plasma-atomic emission spectroscopy (ICP-AES), which was carried out on an Atomscan Advantage spectrometer (Therma Jarrell Ash Corp.). The sulfur contents were measured by the combustion method. X-Ray powder diffraction (XRD) patterns were recorded with a MAX 18 AHF X-ray diffractometer (MAC Science Co. Ltd) with Cu-Kα_1 radiation ($\lambda = 1.54056$ Å).

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