K$_4$Nb$_6$O$_{17}$-type nanotubes

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Since carbon nanotubes were discovered by Iijima in 1991 [1], nanoscale tubular materials have attracted more and more attention due to their unique structure, electronic and optical properties and potential applications in the fabrication of nano-devices. Today, several types of nanotubes, including WS$_2$, MoS$_2$, BN, BCN and titanates [2,3], have been reported. Here we report the preparation of potassium niobate nanotubes at room temperature and the methods to change their interlayer spacing.

Firstly, 0.2g K$_4$Nb$_6$O$_{17}$ powders were added to 100ml HCl (2M) solution and stirred for 4 days to promote ion exchange. The ion-exchanged K$_4$Nb$_6$O$_{17}$ was separated by filtration and dried at room temperature, and was subsequently placed in 10ml aqueous solution of tetra(n-butyl)ammonium hydroxide (TBAOH, 10 wt %) or primary alkyl amines (C$_n$H$_{2n+1}$NH$_2$, n=1, 3, 4, 5, 6, 7, 8, 12, 16) respectively, and stirred for 3 days to form nanoscale tubular products.

Figure 1a is a low magnification TEM image showing a large quantity of potassium hexaniobate nanotubes with a narrow size distribution, which was prepared in the solution of TBAOH. The diameter of the tubular materials is around 20 nm and the length ranges from 500 nm to 2 µm. A HREM image of a nanotube is shown in Figure 1b. The tubular structures consist of multiple walls, similar to carbon nanotubes but with certain special characteristics. No single-wall nanotubes were observed. The inter-shell spacing of the potassium hexaniobate nanotubes is 0.83 nm, corresponding to the distance between the (040) crystal planes of the K$_4$Nb$_6$O$_{17}$ structure. The nanotube is not symmetric. The left hand side wall has five layers and the right hand side wall has six layers. Using SAED analysis, we determined that the axis of nanotubes is oriented along the [100] direction.

The helicity of the potassium hexaniobate nanotubes was further analyzed via HREM imaging and simulations. It was found that the axis direction of some nanotubes deviates from the [100] direction. The formation of variable helicities of nanotubes might result from the presence of defects in the nanotubes.

Figure 2 are TEM images of hexaniobate nanotubes prepared in a primary alkyl amines solution. When CH$_3$NH$_2$ was used, the interlayer spacing of the obtained nanotubes is 0.83 nm, which is similar to that of nanotubes prepared in TBAOH solution. The interlayer spacing was found to increase to 0.19 nm when C$_3$H$_7$NH$_2$ was used (Figure 2b). When C$_4$H$_9$NH$_2$ and C$_5$H$_{11}$NH$_2$ were used, the interlayer spacing of the nanotubes was 2.2 nm and 2.3 nm, respectively (Figure 2c and d). An interlayer spacing of 2.4 nm, 2.5 nm, 2.8 nm, 3.3 nm and 3.6 nm was obtained by using C$_6$H$_{13}$NH$_2$, C$_7$H$_{15}$NH$_2$, C$_8$H$_{17}$NH$_2$, C$_{12}$H$_{25}$NH$_2$ and C$_{16}$H$_{33}$NH$_2$, respectively (Figure 2e ~i).

In summary, we have found a simple route to prepare hexaniobate nanotubes with variable interlayer spacing. Further work is to study the properties of these types of nanotubes.

**Figure 1.** TEM images of (a) many nanotube and (b) a single nanotube.

**Figure 2.** TEM images of nanotubes prepared using C_{n}H_{2n+1}NH_{2}: (a) CH_{3}NH_{2}, (b) C_{3}H_{7}NH_{2},
(c) C_{4}H_{9}NH_{2}, (d) C_{5}H_{11}NH_{2}, (e) C_{6}H_{13}NH_{2}, (f) C_{7}H_{15}NH_{2}, (g) C_{8}H_{17}NH_{2}, (h) C_{12}H_{25}NH_{2} and
(i) C_{16}H_{33}NH_{2}. The interlayer spacings are indicated and increase with the sequence.