Sonoelectrochemical synthesis of CdSe nanotubes†

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CdSe nanotubes were successfully synthesized by a sonoelectrochemical technique for the first time; the formation process of the CdSe nanotubes was carefully studied and a sonication-induced roll-up mechanism is proposed.

Since the first identification of carbon nanotubes,[1] inorganic compounds with tubular morphology have received considerable attention.[2] The formation of layered or artificial layered nanotubes was suggested to occur by a roll-up process of a sheet onto itself, a 2D-to-1D structure transformation. The roll-up mechanism, however, was challenged by "TiO_2 nanotubes", which did not have layered structure and were also claimed to be prepared through this roll-up process,[3] although the so-called "TiO_2 nanotubes" were finally confirmed as nanotubes of sodium titanate with a layered structure.[4] Is it possible that non-layered compounds can be prepared into nanotubes through a roll-up process, similar to the way of rolling-up layered compounds? The answer is in the affirmative. Up to now, a few reports have been published on the research of rolling-up non-layered compounds to form nanotubes, such as $Ln(OH)_3$, Bi_2Se_3, $SrAl_2O_4$, *etc.*[5]

Cadmium selenide, one of the most extensively studied IIB–VIA semiconductors,[6,7] does not possess a layered structure. Nanotubes of CdSe are usually synthesized by a template-based route.[8] However, since the template-based methods are relatively complicated and most of the products are polycrystalline nanotubes, it is essential to develop a simple and mild chemical method for the synthesis of single crystalline CdSe nanotubes.

In recent years, sonochemical and sonoelectrochemical techniques have been extensively used in the synthesis of various nanostructured materials. The sonoelectrochemical method is accomplished by applying an electric current pulse to nucleate and perform the electrodeposit, followed by a burst of ultrasonic energy that removes the products from the sonic probe cathode.[9] Although several layered compound nanotubes have been prepared by means of sonochemical and sonoelectrochemical methods,[10] the synthesis of non-layered compound nanotubes using a sonoelectrochemical technique has not been reported.

In this communication, we report on the development of a one-step, non-templated sonoelectrochemical synthesis of single-crystal CdSe nanotubes. Furthermore, based on the direct evidence of the bending and roll-up processes, a sonication-induced roll-up mechanism is proposed. The electrogenerated chemiluminescence (ECL) of the resulting CdSe nanotubes was also studied.

From field emission scanning electron microscopy (FESEM) images of the resulting CdSe products (Fig. 1(a)), it can be seen clearly that the CdSe products have a tubular structure. The enlarged views (top and bottom right insets of Fig. 1(a)) show a broken CdSe nanotube and a CdSe nanotube with open end, respectively. Energy-dispersive spectroscopy (EDS) analysis reveals that the CdSe product is composed of pure CdSe (Fig. 1(b)), only cadmium and selenium elements were detected, and their atomic ratio was almost 1 : 1, in agreement with the chemical composition of CdSe. The XRD pattern as shown in Fig. S1 (ESI†) could be indexed as CdSe cubic phase (JCPDS card no. 19-0191).

To further investigate the morphology and structure of the CdSe product, transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) were employed. Fig. 2(a) shows the general morphology of the products. The clear contrast observed along the length of the worm-like morphology suggests that the CdSe has a tubular structure, and these nanotubes are entangled with each other. Fig. 2(b) shows a magnified image of a CdSe nanotube with an outer diameter of 80 nm and a wall thickness of 10 nm. The CdSe nanotube with a straight part reveals a representative round open tip. It is also worth mentioning that the indicated open tip is not completely seamed. This indicates that the nanotubes were probably formed through a roll-up process. More rarely, but occasionally seen in our intermediate products (see below) are nanoscrolls of other shapes. As shown in Fig. 2(c), the sample has a helical morphology. In addition, a half-tube like morphology is also observed in an intermediate product as shown in Fig. 2(d). These images provide strong evidence for the roll-up mechanism induced by sonication.

A lattice-resolved HRTEM image of a CdSe nanotube is given in Fig. 2(e); the clearly marked interplanar *d* spacing is 0.35 nm, which corresponds to that of the {111} lattice planes of cubic CdSe. The nanotube wall is not a perfect single crystal; as indicated by the arrows in Fig. 2(f), many stacking faults and missing layers are present in the nanotube walls. The appearance of defects is mainly due to the high stress and strain present in the nanotubes. The SAED pattern shown in the inset of Fig. 2(b) also reveals that the nanotubes are single-crystalline. The small streaking of the diffraction spots indicates that planar defects are present in the nanotube, in

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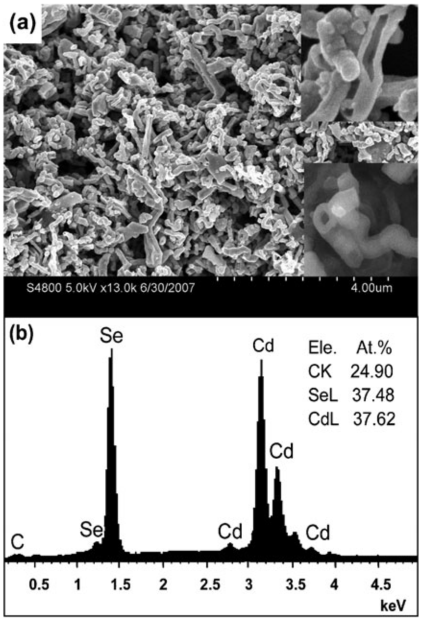

Fig. 1 (a) SEM image of the CdSe products, the insets are magnified images of a broken nanotube (top right) and a nanotube with ringent tip (bottom right). (b) EDS spectrum of the CdSe product.

accordance with the stacking faults and missing layers shown in the HRTEM images.

In order to investigate the growth mechanism of the nanotubes more directly, the evolution of morphology in the sonoelectrochemical process was studied. When the reaction time was shorter than 0.5 h, the products were nanoparticles and curled nanosheets. In Fig. 3(a), a typical curled nanosheet can be seen. As the reaction time was prolonged to 1 h, nanoscrolls prevailed, and the percentage of nanoparticles was decreased. In Fig. 3(b), a nanoscroll in the process of scrolling can be seen. Fig. 3(c) captures a nanoscroll near the end of the roll-up; it has not yet formed a tightly wound tube. According to the magnified image in Fig. 3(d), it is clear that the nanotube is indeed formed by rolling-up of a nanosheet.

Controlled experiments and extensive TEM observations were carried out to verify whether the CdSe nanotubes could be formed without an electrochemical process. When electrodeposition was replaced by adding 2 mL N_2H_4 (85%, as reducing agent), only aggregates of nanoparticles, typically 20–40 nm in diameter, were observed in this ultrasonic process, and no CdSe nanotubes can be obtained (Fig. S2a, ESI†). Gedanken, Hodes and co-workers have prepared CdSe nanoparticles by a sonoelectrochemical method.[7] In their report, they chose Na_2SeSO_3 as the Se precursor, while we used Na_2SeO_3. It is reported that Na_2SeO_3 is more favorable for the preparation of well-crystallized metal selenide.[11] Crystalline CdSe is essential in the preparation of CdSe nanotubes by the roll-up mechanism. So, it can be concluded that the appropriate Se precursor and the combination of electrochemical and sonochemical processes are necessary for the formation of the CdSe nanotubes. In addition, CdSe nanotubes were also synthesized in the absence of poly(vinylpyrrolidone) (PVP) by the sonoelectrochemcial method. However, the obtained nanotubes are coarse and were obtained in a lower yield (Fig. S2b, ESI†). The presence of PVP is favorable for the preparation of CdSe nanotubes. Several recent studies have showed that the existence of an appropriate amount of capping reagents can alter the surface energies of various crystallographic surfaces to promote selective anisotropic growth of nanocrystals.[12]

The ECL behavior of the CdSe nanotubes was studied under conventional cyclic voltammetry (CV). The ECL emission spectrum of CdSe nanotubes is shown in Fig. S3 (ESI†). In the ECL curve, the light emission of CdSe nanotubes shows quite good stability and high intensity which may be attributed to the morphology of the CdSe nanotubes.[13]

Although the growth process of the tubular-like products at the atomic scale has not been completely resolved at this stage, an analogy could be drawn between the growth processes of other layered or non-layered compound nanotubes and that of

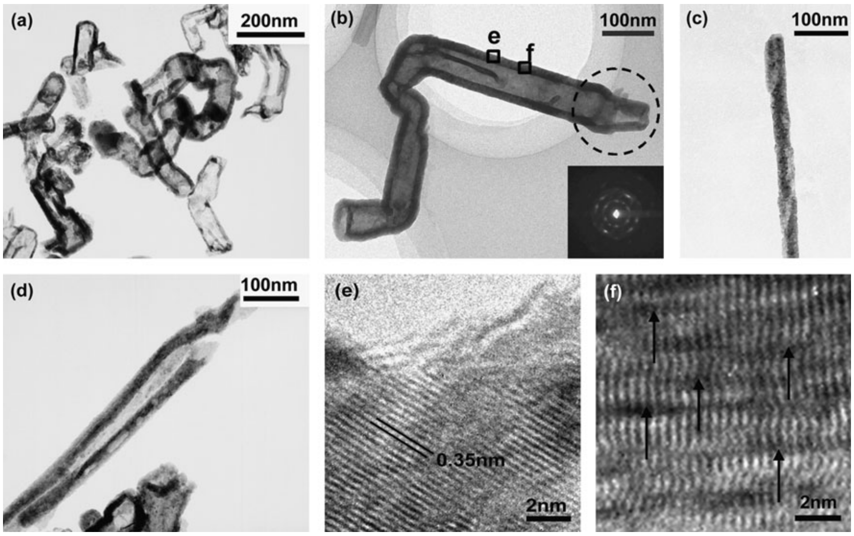

Fig. 2 (a) TEM image of CdSe nanotubes. (b) Magnified image of a typical CdSe nanotube (SAED in inset). (c) Helical nanoscroll. (d) Half-tube nanoscroll. (e) and (f) HRTEM images corresponding to the marked regions in (b); in (e), lattice spacing as discussed in the text is indicated; the arrows in (f) point out stacking faults and antiphase boundaries.

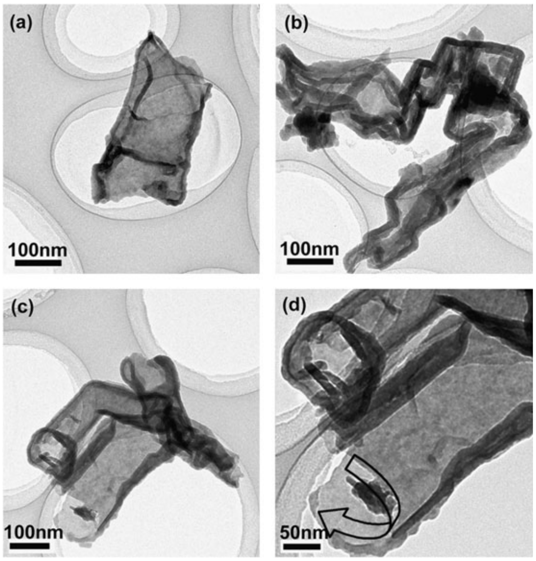

Fig. 3 TEM images showing the rolling-up of CdSe nanosheets to form nanotubes during the sonoelectrochemical synthesis procedure. (a) A curled nanosheet. (b) A nanoscroll in the process of scrolling. (c) A nanoscroll near the end of the roll-up. (d) Magnified image of (c).

CdSe nanotubes.[2,10] We postulate that the formation mechanism of CdSe nanotubes might also involve rolling from its 2D CdSe nanosheet structure.

First, CdSe nanostructures were formed by electrodeposition onto the sonic probe cathode. The deposit could be spheroidal or 2D structure. Then, the subsequent sonic shock wave removed this deposit from the probe surface. It is well known that collapsing bubbles produced in liquid solution during sonication can instantaneously generate local spots of high temperature (>5000 K), pressure (>20 MPa), and cooling rates (>1000 K s^{-1}).[9] We believe that the sonochemical treatments provide the required energy for the roll up of the nanosheets to form tubular nanoscrolls. After the 2D nanosheets were ejected from the probe, due to the high surface energy of the ends of the nanosheets, these flexible and unstable nanosheets might easily roll-up in the sonochemical process.[10] The nanosheets formed in the early stages of the sonoelctrochemical reaction (Fig. 3(a)) and the existence of scrolling nanostructures in the middle of the synthesis procedure (Fig. 3(b) and (c)) provide strong evidence for the roll-up mechanism of nanotubes formed in the sonoelectrochemical procedure. In addition, it is noted that the effect of bubble collapse is asymmetric, which could lead to an asymmetric roll-up. This explains why some CdSe nanotubes are not all open-ended and have a twisted structure. Therefore, we believe that the CdSe nanotubes were likely formed by a sonication-induced roll-up mechanism.

In conclusion, we have successfully synthesized single crystalline CdSe nanotubes by a sonoelectrochemical route in aqueous solution at room temperature. The growth progress suggested that the CdSe nanotubes were fabricated by sonication-induced rolling-up of CdSe nanosheets. This method is simple, convenient and environmentally benign. The sonoelectrochemical synthesis of other nanomaterials is being investigated currently.

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