

## Template-free synthesis of single-crystalline cadmium nanotubes

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By pyrolysis of CdS powder in inert gas, single-crystalline cadmium nanotubes growing in the form of a heap, were produced for the first time in high yield.

Since the discovery of carbon nanotubes in 1991,<sup>1</sup> tubular one-dimensional (1-D) nanomaterials have attracted intense interest from scientists in various fields such as chemistry, physics, material science and so on, because the nanotubes exhibit unique physical and chemical properties and have wide potential applications in nanoelectronics, chemical sensors, batteries and other fields.<sup>2</sup> Various nanotubes made from layer compounds, for example, graphite,<sup>1</sup> boron nitride,<sup>3</sup> metal disulfides ( $\text{MX}_2$ ,  $\text{M} = \text{W}, \text{Mo}, \text{Ti}, \text{Nb}, \text{Ta}, \text{Re}, \text{Bi}$ ;  $\text{X} = \text{S}, \text{Se}$ ),<sup>4</sup> have been studied extensively; In addition, nanotubes constructed from non-layer compounds can be obtained under appropriate reaction conditions. Thus far, there are many reports on the developments of new nanotubes of metal oxides<sup>5</sup> (e.g.  $\text{TiO}_2$ ,  $\text{Ga}_2\text{O}_3$ ,  $\text{In}_2\text{O}_3$ ,  $\text{ZnO}$ , and rare earth oxides), metals<sup>6</sup> ( $\text{Ni}$ ,  $\text{Fe}$ ,  $\text{Co}$ ,  $\text{Au}$ ,  $\text{Te}$  and  $\text{Bi}$ ), sulfides<sup>7</sup> ( $\text{PbS}$ ,  $\text{CdS}$  and  $\text{CdSe}$ ), some semiconductor compounds ( $\text{GaN}$ ,<sup>8</sup>  $\text{InP}$ )<sup>9</sup> and other materials.<sup>10</sup> Recently, much attention has been focused on the synthesis and study of metal nanotubes which show different physical properties in terms of surface plasmon,<sup>11</sup> transport<sup>12</sup> and magnetic behavior<sup>6a</sup> from their corresponding bulk materials. In addition to  $\text{Te}^{6d}$  and  $\text{Bi}^{6e}$  nanotubes, which are prepared without using any template, other metallic nanotubes reported so far are synthesized through a template route. For example,  $\text{Ni}$ ,<sup>6a</sup>  $\text{Co}$ ,  $\text{Fe}^{6b}$  and  $\text{Au}^{6c}$  nanotubes are fabricated from a nanoporous template of nanopore alumina or polycarbonate membranes. Very recently, Xia *et al.*<sup>13</sup> developed a general approach that constructs metal nanotubes as well as other nanostructures with hollow interiors by means of a replacement reaction between the surface of a nanoscale template (e.g. Ag nanowire) and an appropriate salt precursor such as  $\text{HAuCl}_4$ ,  $\text{PdCl}_2$ . In a typical procedure, the desired metal is coated on the surface of a 1-D nanomaterial to form the core-sheath structure by the corresponding metal salts reacting with the template; subsequently, the template is removed by selectively etching in an appropriate solution and 1-D nanostructures with hollow interiors are generated. By adopting this method, highly crystalline metallic nanotubes of Au, Pd, and Pt<sup>13</sup> are obtained using Ag nanowires as a sacrificial template. However this method can not be used to produce nanotubes made from active metals such as Zn, Cd *etc.* In this communication, we present a template-free pyrolysis route to produce single crystalline cadmium nanotubes.

The Cd nanotube was grown in a standard CVD apparatus consisting of a tube-like high temperature furnace with a quartz tube (length: 120 cm; diameter: 2.5 cm) and an independent temperature controller. A quartz boat with 0.5 g CdS powder was placed at the center of the furnace. Before increasing temperature,  $\text{O}_2$  in the reaction system was eliminated completely by flushing with Ar gas at  $100 \text{ ml min}^{-1}$  for 2 h. Then the reaction was carried out at  $700\text{--}1000^\circ\text{C}$  for 4 h. After the reaction, wool-like silvery white products were found in the region of  $50\text{--}300^\circ\text{C}$ .

The products were structurally characterized by X-ray diffraction (XRD, Rigaku Dmax2000,  $\text{CuK}\alpha$ ). Their XRD pattern is shown in Fig. 1 with all diffraction peaks indexed to the known wurtzite structure phase of cadmium (JCPDS card No. 5-067). The two peaks are indexed as (002) and (004) of the Cd wurtzite structure, revealing that the nanotubes grew in the (001) direction.

No characteristic peaks from impurities, such as CdS and S, are detected, which indicates that the products are highly pure.

A field emission scanning electron microscopy image (SEM, Hitachi S-4300F) given in Fig. 2a shows the products grown on a Si wafer. The wire-like materials are twisted around each other to form many irregular piles. The energy-dispersion X-ray spectroscopy (EDS, INCA300) attached to the SEM analysis reveals that the products are composed of elemental cadmium (Fig. 2b); the Si signal comes from the Si substrate. As shown in Fig. 2c, which is an SEM image of an individual wire heap, the wire-like materials have a length up to tens of microns and a variable diameter along their length. The diameter range is usually  $30\text{--}200 \text{ nm}$ . These products seem to be like the intestines of animals, which is fully illuminated in the high magnification SEM image in Fig. 2d. Formation of such a structure is due to the physical properties of elemental Cd. Cadmium with a low melting point of  $321^\circ\text{C}$  is a very soft metal and is easily cut with a knife. Therefore, it is

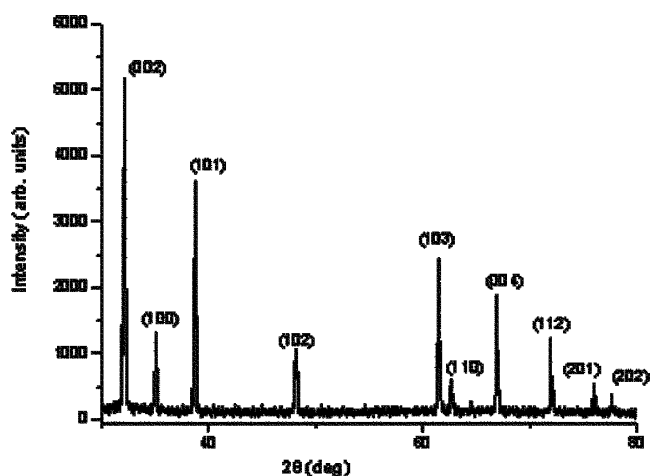


Fig. 1 A typical XRD pattern of cadmium nanotubes.

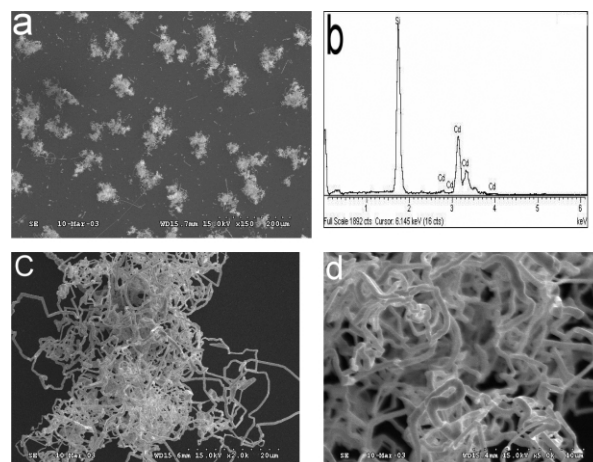
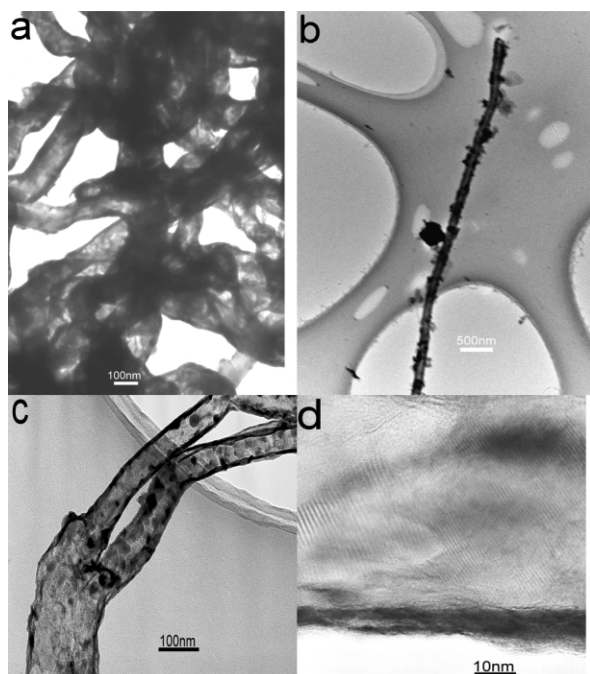


Fig. 2 SEM images of Cd nanotubes: (a) low magnification; (b) EDS which indicates the tube is composed of elemental cadmium; (c) an individual nanotube heap; (d) high magnification.

difficult for the cadmium wires to form a straight structure with a uniform diameter.

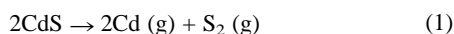
The products are further characterized by transmission electron microscopy (TEM: Hitachi H-800, JEOL-2010F). Fig. 3a shows the general morphology of the products. The clear contrast observed along the length of the cadmium wire-like materials suggests a tubular structure (the outer part is darker than the inner part). These nanotubes are entangled with each other. An individual straight cadmium nanotube with a uniform diameter of 100 nm is shown in Fig. 3b. A very obvious hollow interior is observed. Some fracture pieces, which are also made of elemental Cd by EDS analysis, absorbed to the surface of the nanotube. These Cd pieces originated from the rupture of Cd nanotubes by ultrasound during the procedure of sample preparation. A Y-structure was observed by TEM (Fig. 3c), which is similar to the branched carbon nanotubes reported in the literature.<sup>14</sup>

These Cd nanotubes are sensitive to beam irradiation during the TEM examinations, which is expected due to their low melting points (321 °C). Fig. 3d shows a high resolution TEM image of an individual Cd nanotube. It is observed that after several seconds of intensive electron beam irradiation, the Cd nanotube is partly cracked and has a tendency to transform into a polycrystalline nanowire. But still there is an obvious preferential crystal direction along the length, which indicates that the Cd nanotubes are characteristically single crystalline. This beam sensitivity makes electron diffraction analysis difficult. Nonetheless, our XRD, SEM, TEM, and composition analysis have unambiguously demonstrated that the tubular structures in our sample are metallic Cd nanotubes.



**Fig. 3** TEM images of cadmium: (a) entangled nanotubes; (b) an individual straight nanotube; (c) Y-structure; (d) high resolution.

The Cd nanotube is proposed to grow by means of a vapor–solid process.<sup>15</sup> According to the previous study,<sup>16</sup> the hot CdS gas is composed of Cd gas and S<sub>2</sub> gas at high temperature. Therefore, the chemical reactions we employed in the synthesis of the Cd nanotubes could be described as follows:



During reaction, Cd and S<sub>2</sub> gas flow with the Ar carrier gas to the low temperature region, and some S<sub>2</sub> gas reacts with Cd to form CdS again, which deposits on the quartz tube. At the lower temperature region (< 400 °C), the S<sub>2</sub> has a tendency to polymerize

into S<sub>n</sub> which deposits and does not react with Cd, therefore not all of the Cd changes into CdS.<sup>17</sup> In addition, Cd gas has a much higher partial pressure than S<sub>2</sub> gas; for example, the partial pressures of Cd and S<sub>2</sub> at 900 °C over CdS are 214.6 Pa and 108.0 Pa respectively.<sup>16</sup> Therefore, Cd gas has a higher diffusion velocity. As a result, some Cd can be separated from sulfur and deposited at the low temperature (< 300 °C) region in the form of tubes. The formation mechanism of BN, WS<sub>2</sub> and MoS<sub>2</sub> nanotubes is by rolling layer structures into tubes;<sup>4</sup> the soft template (e.g. surfactants) or solid template (e.g. CNTs, porous alumina) confined growth of non-layer compound nanotubes such as CdS nanotubes,<sup>7b</sup> Ni nanotubes<sup>6a</sup> is also easily understood. These two mechanisms can not account for the tubular formation of cadmium, since cadmium is just a hexagonal material, and no template was used in the growth process. Therefore, subsequent efforts will be made to study the growth mechanism.

In conclusion, the metallic cadmium was obtained for the first time by a simple pyrolysis route, and no template was applied during the growth process. These metallic nanotubes provide a new system for studying the peculiar electronic transformation of 1-D nanomaterials. We expect that this route can be used to prepare Zn nanotubes.

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