Water-dissolvable and Reactive $KCdCl_3$ Nanowires: Precursor and Template for Preparation of CdS and CdSe Nanotubes

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CdS and CdSe polycrystalline nanotubes self-assembled from nanocrystals have been successfully prepared using water-dissolvable and reactive $KCdCl_3$ nanowires as precursor and template at room temperature.

Since the discovery of carbon nanotubes in 1991, one-dimensional (1-D) nanostructures such as nanorods, nanowires, and nanotubes, have been the focus of intensive research owing to their unique physical and chemical properties and promising applications. Many strategies have been developed for the preparation of 1-D nanostructures over the past years. Comparatively, the formation of nanotubes is more complex and few effective strategies have been developed. Nanotubes of some materials with a layered structure can be directly prepared under the appropriate conditions. However, nanotubes of other materials without a layered structure were produced by an indirect strategy,[1] in which 1-D templates involving the channels in porous materials,[2–7] 1-D micelles,[8–11] organic and inorganic nanowires,[12–17] etc. were usually used.

In a general preparation process of nanotubes, 1-D nanostructures serve as templates within which different materials are generated in situ by various physical and chemical methods and shaped into duplicated 1-D nanostructures. The 1-D template-based strategy represents an effective, controllable, and reproducible route to the fabrication of nanotubes of many kinds of materials. However, three aspects of problems need to be resolved in many template-based methods: high cost and low output of templates, limited applicability of a specific template, and inconvenience of removing the templates. Water-dissolvable and reactive inorganic nanowires are promising 1-D templates for the fabrication of nanotubes. Very recently, Na_2SO_4 nanowires were developed and used as 1-D template to produce polyelectrolyte and Au nanotubes.[15] However, Na_2SO_4 nanowires were not reactive in the fabrication of polyelectrolyte and Au nanotubes.

Herein, we report the room-temperature fabrication of a new type of water-dissolvable and reactive inorganic nanowire of $KCdCl_3$, and CdS and CdSe polycrystalline nanotubes are prepared using $KCdCl_3$ nanowires as both the precursor and template. One of the advantages of this method is that the preparation of both $KCdCl_3$ nanowires and CdS and CdSe polycrystalline nanotubes self-assembled from nanocrystals can be conducted at room temperature and in air, thus simplicity and low cost can be achieved.

In a typical fabrication procedure for $KCdCl_3$ nanowires, a source solution containing $CdCl_2{\cdot}2.5H_2O$ (0.456 g), KI (0.042 g), and deionized water (3 mL) was added into anhydrous ethanol (30 mL) under magnetic stirring at room temperature. A white product ($KCdCl_3$ nanowires) formed immediately, and the solution was stirred for 20 min. The product was collected by centrifugation and washed with anhydrous ethanol. Then, the $KCdCl_3$ nanowires were dispersed in anhydrous ethanol (20 mL) to act as the precursor and template, which subsequently reacted with chalcogenide ions (S^{2-} and Se^{2-}) to produce CdS and CdSe nanotubes. The sulfur source solution was prepared by dissolving $Na_2S{\cdot}9H_2O$ (0.096 g) into anhydrous ethanol (5 mL); the selenium source solution was prepared by adding Se powder (0.031 g) and $NaBH_4$ (0.060 g) into anhydrous ethanol (5 mL); In a typical fabrication procedure of CdS and CdSe nanotubes, the reaction started and was allowed to proceed for 30 min by adding the sulfur source solution or selenium source solution into the $KCdCl_3$-nanowire template solution under magnetic stirring. The product was collected by centrifugation and washed with deionized water to remove $KCdCl_3$-nanowire template.

X-ray powder diffraction (XRD, Rigaku D/MAX 2550V, Cu Kα) shows that $KCdCl_3$ nanowires are well crystallized with an orthorhombic crystal structure (Figure 1, JCPDS No. 18-0995). Figure 2a shows the transmission electron microscopy (TEM, JEM-2100F) of $KCdCl_3$ nanowires. The $KCdCl_3$ nanowires have typical diameters of 200–300 nm and lengths of 10–50 μm. Figure 2b shows TEM micrograph of a single nanowire, whose corresponding electron diffraction pattern (Figure 2c) indicates that $KCdCl_3$ nanowires are single crystalline in structure.

CdS and CdSe nanotubes were obtained using $KCdCl_3$ nanowires as both the precursor (cadmium source) and template at room temperature. By introducing S^{2-} or Se^{2-} ions to the ethanol solution containing $KCdCl_3$ nanowires, CdS or CdSe formed a shell on the surface of $KCdCl_3$ nanowires as a result of the reaction between $KCdCl_3$ and S^{2-} or Se^{2-} ions and a lower solubility of CdS or CdSe than that of $KCdCl_3$ in solution. The remaining $KCdCl_3$-nanowire template was easily removed by washing with water since $KCdCl_3$ was water-dissolvable. Finally, CdS or CdSe nanotubes were obtained at room temperature by using this simple preparation route.

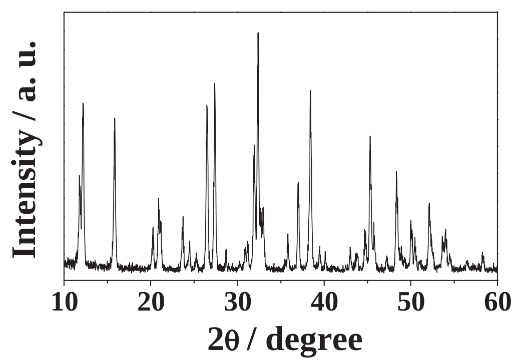

Figure 1. XRD pattern of $KCdCl_3$ nanowires.

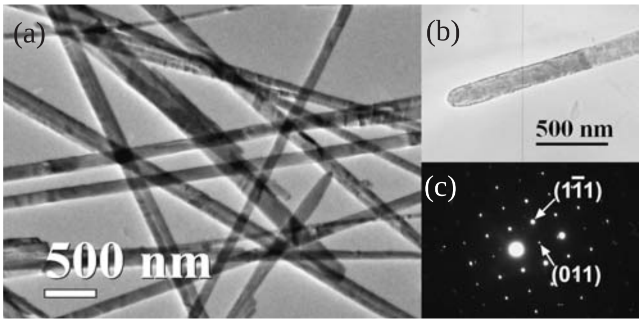

Figure 2. (a) TEM micrograph of $KCdCl_3$ nanowires, (b) TEM micrograph of a single nanowire, and (c) electron diffraction pattern of a single nanowire.

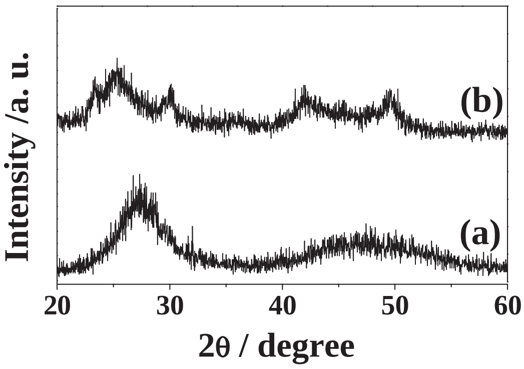

Figure 3. XRD patterns of nanotubes: (a) CdS and (b) CdSe.

XRD patterns of as-obtained samples confirm the formation of crystalline CdS (JCPDS No. 80-0006, Figure 3a) and CdSe (JCPDS No. 88-2346, Figure 3b). No diffraction peaks from the precursor template nanowires are observed. The broadening of the diffraction peaks implies that CdS or CdSe nanotubes consist of very small nanocrystals. Energy dispersive spectroscopy (EDS) results confirm that CdS or CdSe sample consists of cadmium and sulfur (or selenium) with a molar ratio of Cd to S (or Se) of about 1:1, verifying that the formation of CdS or CdSe.

TEM charcaterization shows that the samples of CdS (Figure 4) and CdSe (Figure 5) consist of polycrystalline nanotubes. The sizes of CdS and CdSe nanotubes both in diameter and in length are similar to those of $KCdCl_3$ nanowires. From TEM micrographs, one can see that the ends of CdS and CdSe nanotubes (Figures 4b and 5b) are open. The high-resolution TEM (HRTEM) images (Figures 4c and 5c) reveal that CdS and CdSe nanotubes are formed by the self-assembly of nanocrystals smaller than 10 nm.

In summary, CdS and CdSe polycrystalline nanotubes self-assembled from nanocrystals have been successfully prepared using $KCdCl_3$ nanowire as precursor and template at room temperature. The $KCdCl_3$ nanowires are prepared by adding an aqueous solution containing $CdCl_2$ and KI into anhydrous ethanol at room temperature. The $KCdCl_3$-nanowire template is water-dissolvable and reactive to S^{2-} or Se^{2-} ions, it acts as both the precursor (cadmium source) and template and is easily removed by washing with water. One of the advantages of this method is that the preparation of both $KCdCl_3$ nanowires and CdS or CdSe polycrystalline nanotubes can be conducted at room temperature and in air, thus simplicity and low cost can be achieved.

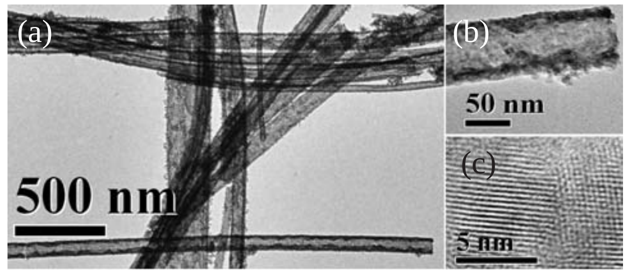

Figure 4. (a) TEM micrograph of CdS nanotubes, (b) TEM micrograph of a single nanotube with an open end, and (c) HRTEM image.

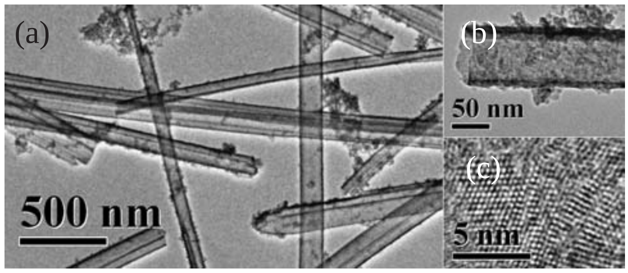

Figure 5. (a) TEM micrograph of CdSe nanotubes, (b) TEM micrograph of a single nanotube with an open end, and (c) HRTEM image.

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