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Convenient arc-electrodeposition technique to synthesize CdS nanotubes at room temperature

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Over the past few years, shape control of nanomaterials has raised significant concerns in the fabrication of one-dimensional (1D) nanomaterials such as nanowires, nanotubes and interesting nanobelts [1]. These 1D nanostructures are ideal systems for investigation of the relationship between the properties (e.g. electrical transport, optical and magnetic behaviors) and dimensionality [2]. For example, considerable progress has been made in the synthesis of 1D semiconductor nanostructured materials due to their unique properties [3]. Especially, much more efforts have been focused on the fabrication of nanotubes. A particularly significant breakthrough in the preparation of MX_2 (M: Mo or W; X: S or Se) nanotubes was made by Tenne and co-workers [4]. Later, various approaches to other nanotubes such as BN [5], vanadium oxide [6], InS [7] and metal Bi [8] have also been reported.

Recently we explored a novel convenient arc-electrodeposition technique to prepare shape-controlled metal nanorods [9], nanorods or nanotubes of metal oxides and hydroxides [10]. The so-called arc-electrodeposition technique is based on the momentary contact of two metallic electrodes on an electrolyte aqueous solution, forming instantaneous circulation between two electrodes and the arc discharge sparks at the point ends of the electrodes. The arc discharge of the electrodes releases great exothermic heat, leading to dissolution of the metallic electrodes in a form of metallic clusters into the aqueous solution. The produced metallic clusters either aggregate into metal nanowires or are oxidized into the corresponding oxides and further grow into nanorods or nanotubes. Herein we extend the arc-electrodepostion technique to prepare CdS nanotubes at room temperature.

The basic experimental setup and procedure for the preparation of the CdS nanotube by the arc-electrodepostion technique at room temperature are similar to those in our previous reports [9, 10]. In the present work, the mixture of Na_2S and KCl aqueous solution was used as electrolyte solution. Two high-purity metallic Cd filaments of 1 mm in diameter were employed as electrodes with the applied alternating current (AC) voltage of 100 V. In the arc-electrodeposition process, the colorless transparent electrolyte aqueous solution turned into yellow gradually, indicating the formation of CdS nanoparticles. The produced solution was allowed to stand for 24 h. The final product was collected by centrifugation, followed by washing using distilled water and ethanol several times. The phase identification of as-prepared product was conducted at room temperature using an X-ray diffractometer (Cu Kα, Philips X'pert system). A transmission electron microscope (Jeol 2010) was employed to observe particle morphology.

Fig. 1 shows the XRD trace of as-prepared CdS nanoparticles using this technique, in which two Cd metallic wires of 1 mm in diameter were employed as electrodes and an aqueous solution containing 0.1 M Na_2S and 0.1 M KCl as electrolyte medium. In this XRD pattern, all the detectable peaks are indexed as those from CdS according to the standard card (JCPDS-ICDD 10-0454). The morphology of the as-prepared CdS was examined by TEM observation. The typical image is shown in Fig. 2a. It can be seen that the CdS nanoparticle obtained using this arc-electrodeposition technique under the conditions mentioned above exhibits a tubular structure in nanoscale. The length of the nanotubes ranges from 50 nm to 80 nm, and the outer diameter is around 10–15 nm with the inner that of 3–8 nm. A magnified TEM image, as shown in Fig. 2b, further reveals this structure.

The formation mechanism of the CdS nanotubes produced by the present arc-electrodeposition technique was proposed as follows:

$$\text{Cd electrodes} \xrightarrow{\text{Arc-electrodeposition}} \text{Cd clusters}$$
$$\xrightarrow{HS^- \text{ or } S^{2-}} \text{Cds clusters} \xrightarrow{\text{Aging}} \text{Cds nanotubes}$$

It is well known that the arc-electrodeposition process produces great exothermic heat, leading to the continuous dissolution of the Cd electrodes in the form of the Cd clusters. The formed Cd clusters were immediately oxidized by HS^- or S^{2-} and further developed into CdS clusters. The formed CdS cluster was aged and grew into the nanotubular structure.

Although the formation mechanism of the CdS nanotube by presence of arc-electrodeposition has not been clearly proved yet, we found that the nucleation and growth process of the produced CdS clusters through the arc-deposition process is strongly affected by the composition of the aqueous electrolyte solution. For example, when 0.1 M Na_2S aqueous solution was employed as electrolyte instead of the mixture of 0.1 M Na_2S and 0.1 M KCl aqueous solutions, it shows that the aged product displays hollow spherical nanostructure with the average particle size of 10–15 nm. The reason for the shape variation of the as-formed CdS

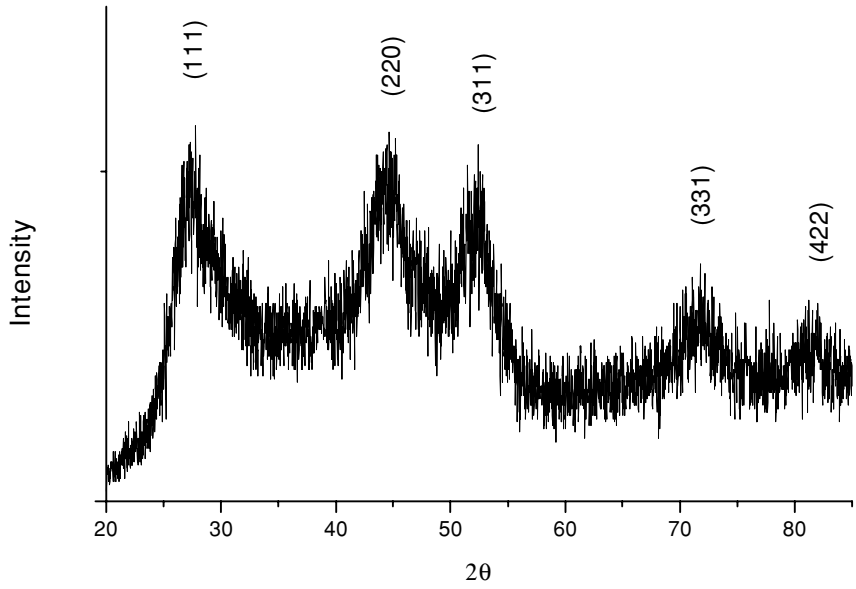

Figure 1 XRD trace of CdS nanotubes prepared using the arc-electrodeposition technique with two Cd metallic wires of 1 mm in diameter as electrodes and mixture of 0.1 M Na_2S and 0.1 M KCl aqueous electrolyte solutions.

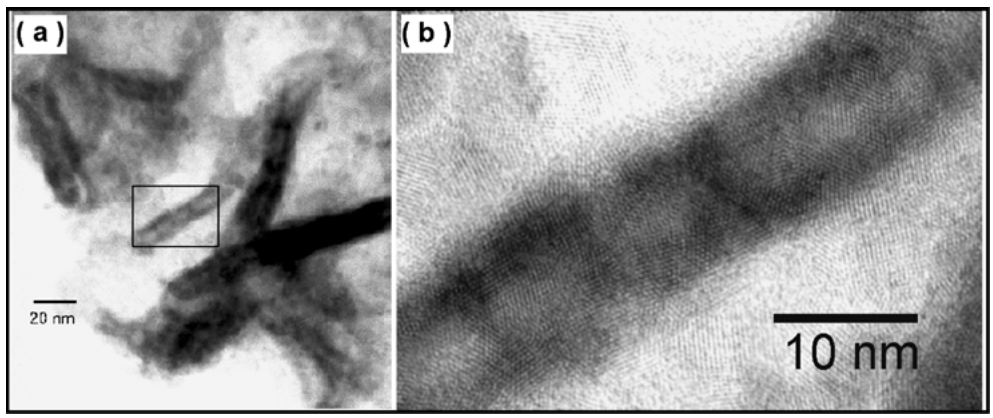

Figure 2 (a) TEM image of the CdS nanotubes prepared using the arc-electrodeposition technique with two Cd metallic wires of 1 mm in diameter as electrodes and mixture of 0.1 M Na_2S and 0.1 M KCl aqueous electrolyte solution; (b) A corresponding magnified image of Fig. 2a.

nanoparticles perhaps results from the difference of ion strength in various aqueous electrolyte solutions. In arc-electrodeposition process, actually the primary metallic Cd clusters are formed rapidly. As well known, the hydrated Cd cluster in solution is not isotropic, but has a well-defined pattern of orientational order which is converted to another distinct pattern by the cluster. Therefore, the extent to which the cluster is observed depends upon many factors, such as the relative magnitude of the solvent polarity or even the ionic strength. As the precipitant, the relative concentration of S^{2-} also plays a very important role during the further oxidation step. Of course, the whole formation step via the arc-electrodeposition technique including the aging and growth of CdS clusters into the nanotube or the hollow spherical nanostructure with different electrolytes is a rather complicated process. We realize that much more work needs to be carried out continuously for determining the real formation mechanisms of the nanotube and the hollow spherical nanostructure.

In conclusion, CdS nanotubes were successfully synthesized using a convenient arc-electrodeposition technique with a mixture of Na_2S and KCl aqueous electrolyte solution. The morphologies of the CdS nanoparticles were strongly affected by the composition of the aqueous electrolyte solution. When Na_2S aqueous electrolyte solution was used instead of the mixture of Na_2S and KCl aqueous solution, the hollow CdS spherical nanostructure was formed.

Acknowledgments

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