Thermolysis of Dialkyl Dithiophosphates in Porous Anodic Alumina Template: A Versatile Route to Produce Semiconductor Metal Sulfide Nanowires

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A facile and versatile method characterized by thermolysis of metal dialkyl dithiophosphates in porous anodic alumina templates was proposed for producing semiconductor metal sulfide nanowires. Highly crystalline nanowires of binary metal sulfide ME (M = Cd, Pb, or Zn) have been prepared and characterized by X-ray diffraction and electron microscopy (SAED, SEM, and TEM).

Recently, the investigation of one-dimensional (1D) semiconductor nanostructures has attracted much more attention owing to their novel properties and the potential applications in nanodevices.[1] As one series of the most important semiconductors, metal sulfides occupy a special position as they have a unique combination of physical and chemical properties suitable for the applications in solar cells and optoelectronic and electronic devices.[2] Considerable efforts have been made on the synthesis of metal sulfide nanowires,[3–7] among which the template-mediated techniques were demonstrated to be very effective.[7] This synthesis protocol involves the restricted growth of desired material within a porous host structure such as porous anodic alumina (PAA) film, and the pores of the PAA act as the templates that determine the shape, size, and, in many cases, the orientation of the produced materials. When a suitable template has been selected, the key of this technique is how to generate desired materials with crystalline structures in the tiny pores facilely and effectively, under moderate conditions to avoid the destroying the porous structure. Several processes, such as chemical bath deposition,[8] sol–gel deposition,[9] photochemistry deposition,[10] and electrochemistry deposition,[11] have been utilized to grow metal sulfide nanowires in template materials. However, these methods are often complicated to some extent and it is still a challenge to establish a mild, general, and efficient method to fabricate 1D semiconductor nanowires with highly crystalline structures.[9]

Thermolysis of single-source precursors has been investigated as an important approach to produce a range of semiconductor materials either as thin films or as nanocrystalline materials.[12,13] The molecular reactant as precursor is required to have all the elements needed for the resultant and precisely defined structure to ensure adequate stability under ambient conditions and controllable thermolytic reactions.[12] The use of single-source precursors with preformed element constitution provides a convenient reactive intermediate for growth under lyothermal conditions and seems suitable for producing nanomaterials in templates. Herein, we proposed a novel versatile route which joints the precursor strategy with template-mediated technique to produce metal sulfide nanowires conveniently. The readily available compounds named metal dialkyl dithiophosphates (abbreviated as MDTPs, and in this report M = Cd, Zn, and Pb), which are stable in ambient conditions but liable to decomposed to generate crystalline metal sulfide when heated as low as 160 °C, were realized to be appropriate single-source precursors. Accordingly, crystalline nanowires of semiconductor metal sulfides such as CdS, ZnS, and PbS were prepared simply by heating MDTPs precursors filled in PAA templates.

A typical synthesis to produce CdS semiconductor nanowires was described in brief as following: A PAA template with a pore size of about 100 nm was plated on the bottom of a flask under reduced pressure for 20 min, and then immersed into 10-mL methanol solution containing 0.06 g of cadmium di-*n*-butyl dithiophosphate.[14,15] The pores of the template were then filled with the precursor solution. Taking the template out, and heating it at 200 °C for 3 h, the CdS semiconductor nanowires were then formed in template. Aligned CdS nanowire arrays could be achieved by partially removing the PAA template with aqueous solution of sodium hydroxide, well-isolated CdS nanowire could be achieved by fully dissolving the template. Similar processes were conducted to produce ZnS and PbS nanowires.

The 1D structure of the prepared material was elucidated by SEM and TEM. Figure 1a shows the general SEM image of the brush-like morphologies of the as-prepared CdS nanowires on the partially dissolved template. The surface layer has not been completely removed which results in the sticking together of the CdS nanowires. In a local view as shown in Figure 1b, we can see highly dense nanowire arrays, in which the nanowires are continuous and arranged parallel to one another with a uniform

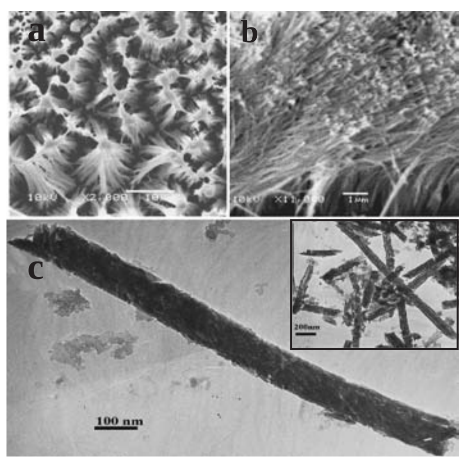

Figure 1. SEM images of uniform CdS nanowire arrays. (a) General view, (b) Local view, and (c) TEM image of the individual CdS nanowires. The upper right inset is an image of multi-CdS nanowires.

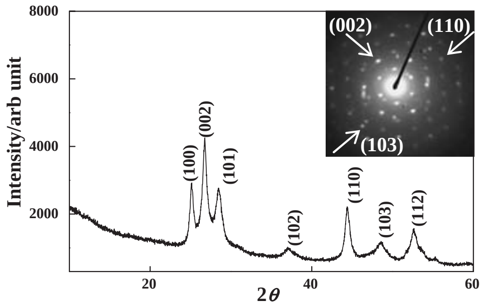

Figure 2. X-ray diffraction and SAED pattern of CdS nanowires.

diameter. Figure 1c shows the typical TEM image of an individual CdS nanowire freed from the template, in which a straight and uninterrupted wire structure can clearly be seen. The diameter of the nanowire is about 90 nm which is close to the pore size of the PAA template, and it is rather uniform at different positions. As expected, it is the PAA template that induces the morphology of the deposited CdS nanowires.

The phase and crystallized structure of the synthesized nanowires were confirmed by XRD and SAED analyses. A typical XRD pattern is shown in Figure 2. All peaks can be indexed as the hexagonal phase (Wurtzite structure) of CdS within the experimental error. The (002) diffraction peak is unusually strong compared to the bulk hexagonal CdS, indicating a preferential growth direction in the sample. The selected area electron diffraction pattern shown in the right inset of Figure 2 also reveals the formation of crystalline CdS. The diffraction spots correspond to the (002), (110), and (103) diffraction planes of a hexagonal CdS crystal, which are consistent with the XRD result. The result reveals that with the use of metal dialkyl dithiophosphate as the single source precursor, crystalline nanowires of metal sulfides can be facilely attained under relative low temperatures.

A number of dialkyl dithiophosphate–metal complexes, which can easily be acquired by the reaction of dialkyl dithiophosphate ligand with metal ions, provide the possibility for the expanding of the method.[15] It is feasible to prepare other metal sulfide nanowires by the thermolysis of the corresponding metal dithiophosphate compounds. For example, ZnS and PbS nanowire arrays were synthesized by decomposing zinc di-*n*-octyl dithiophosphate and lead di-*n*-dodecyl dithiophosphate filled in the PAA template, respectively. The SEM general and local views are shown in Figure 3 which is similar to the as-prepared CdS nanowire arrays mentioned above. Other semiconductor metal sulfide nanowires such as α-Ag_2S and MoS_2 can also be prepared in the same manner.

In conclusion, a facile and versatile synthetic strategy characterized by the thermolysis of metal dialkyldithiophosphates in PAA templates has been demonstrated to prepare the aligned or isolated semiconductor metal sulfide nanowire. Crystalline CdS, PbS, and ZnS nanowires with uniform diameter and length have been successfully acquired via this method. The selection of metal dialkyl dithiophosphates as single-source precursors provides a convenient reactive intermediate for the template-growth of crystalline metal sulfide nanowire materials under relatively mild conditions. It is believed that the simplicity, versatility, high efficiency, and low cost of the method will greatly stimulate their application in modern science and industry.

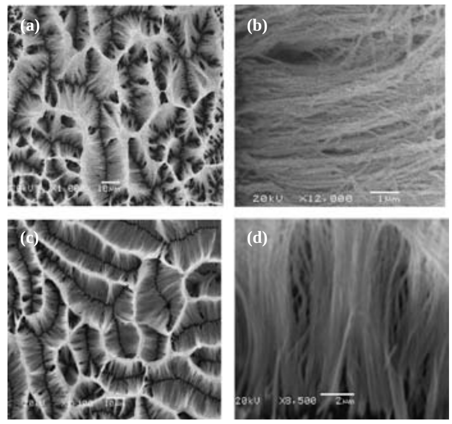

Figure 3. SEM images of uniform PbS (top) and ZnS (bottom) nanowire arrays. (a), (c) General view. (b), (d) Part view.

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