Bismuth Triiodide Sheets Assisted Solution Synthesis of Cadmium Sulfide Binary Crystals and Branched Nanowires

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ABSTRACT

We report here on a solution-phase procedure for the synthesis of CdS binary crystals and branched nanowires (NW). These branches are perpendicularly aligned on both sides of the trunk along a 2D plane. This is attributed to the adoption of the BiI_3 sheet as a template, which was used to confine the growth of CdS NWs. The perpendicular alignment is dominated by both the electrostatic force of the Bi-I layer and the lattice match between the (001) plane and the (110) plane of wurtzite CdS. This 2D feature growth of branched NWs shows great potential in assembling NWs.

Keywords: Cadmium Sulfide, binary crystals nanowire, branched nanowire, Bismuth Triiodide sheets, synthesis

1 INTRODUCTION

Assembling nanowires (NW) and tailoring nanostructures into branched NWs are two approaches to increase the structural complexity of NWs and enable greater functionality [1-3]. As one of the most important II-VI group semiconductors, CdS NWs have been widely synthesized and demonstrate desirable potential in optoelectronics [4-8]. It is crucial to fabricate CdS branched NWs to further tune their properties and exploit their applications [9]. CdS multi-pod nanostructures have been synthesized through a thermal evaporation process [10,11]; and CdS tetra-pod nanostructures with rigidly geometrical shapes were obtained by a solution method [12-14]. Note that using those methods all the branches of each multi-pod nanostructure only grew on the same crystal nucleus. The alignment of the branches along the trunk is imperative to the effective assembly of NW devices. Jung, et al. reported the synthesis of CdS branched NW heterostructures via sequential seeding of gold nanocluster catalysts in a metal-organic chemical vapor deposition process [15]. Yao et al. synthesized the pine-like branched NWs via a solvothermal approach [16]. However, the random distribution and poor alignment of the branches on the trunk limit their further application in nanodevice fabrication and integration.

In this report, we demonstrate a low-temperature solution-phase approach for synthesis of CdS binary crystal and branched NWs. These branches are parallel to each other and perpendicular to the NW trunk. The planar confinement of growth was realized by introducing bismuth triiodide (BiI_3) sheets as 2D templates. BiI_3 was selected due to its layered structure as well as its orderly aligned polar Bi-I bonds exposed on the surface [17]. To lower the reaction temperature, we adopted a solution reaction system which employs an organic solvent with a boiling point higher than 300°C. Cadmium acetate dihydrate [$Cd(CH_3COO)_2{\cdot}2H_2O$] and S powder were used as the Cd source and S source correspondingly.

2 EXPERIMENTAL SECTION

BiI_3 (99.999%, Alfa Aesar)/ethanol solution was coated on the Si substrate and dried naturally. The mixture of Cadmium acetate dihydrate [$Cd(CH_3COO)_2.2H_2O$, 0.2 g, 99.999%, Alfa Aesar] and Dotriacontane ($C_{32}H_{66}$, 5 g, 97%, Alfa Aesar) was treated at 160 °C for 2 h before the substrate covered with BiI_3 was introduced. The reaction lasted for 24 h at 185 °C after adding sulfur powder (S, 99.9%, 0.15 g, Alfa Aesar); the substrate was pulled out and coated with BiI_3 sheets. Then the substrate was put into the mixture again. The products were pulled out in 24 h and washed in isopropanol at 160 °C for 30 min, and dried at 200 °C for 0.5 h.

The morphology and internal structure of the CdS binary crystals and branched NWs were analyzed using an FEI Sirion XL30 field emission scanning electron microscope (SEM) equipped with an energy-dispersive X-ray (EDX) spectrometer, and a FEI Tecnai F-20 transmission electron microscope (TEM).

3 RESULTS AND DISCUSSION

SEM analyses indicate that only a few CdS branched NWs were formed without introducing BiI_3 sheets during the synthesis. The number of branched NWs increased after introducing BiI_3 sheets which suggests that the formation of branched NWs is related to the BiI_3 sheets (Figure 1a). Each of the branched NWs has thin branches on both sides of a thick NW trunk. All the branches on the same NW trunk aligned themselves along a 2D plane (Figure 1b). Interestingly, there is a 90° angle between the trunk and the branches (Figure 1c). The energy-dispersive X-ray (EDX) spectrum on the as-synthesized sample reveals that these branched NWs consist of Cd and S with an atomic percent proportion of 1:0.98, respectively (Figure 1d). Note that Bi and I elements were not detected. The morphology of CdS

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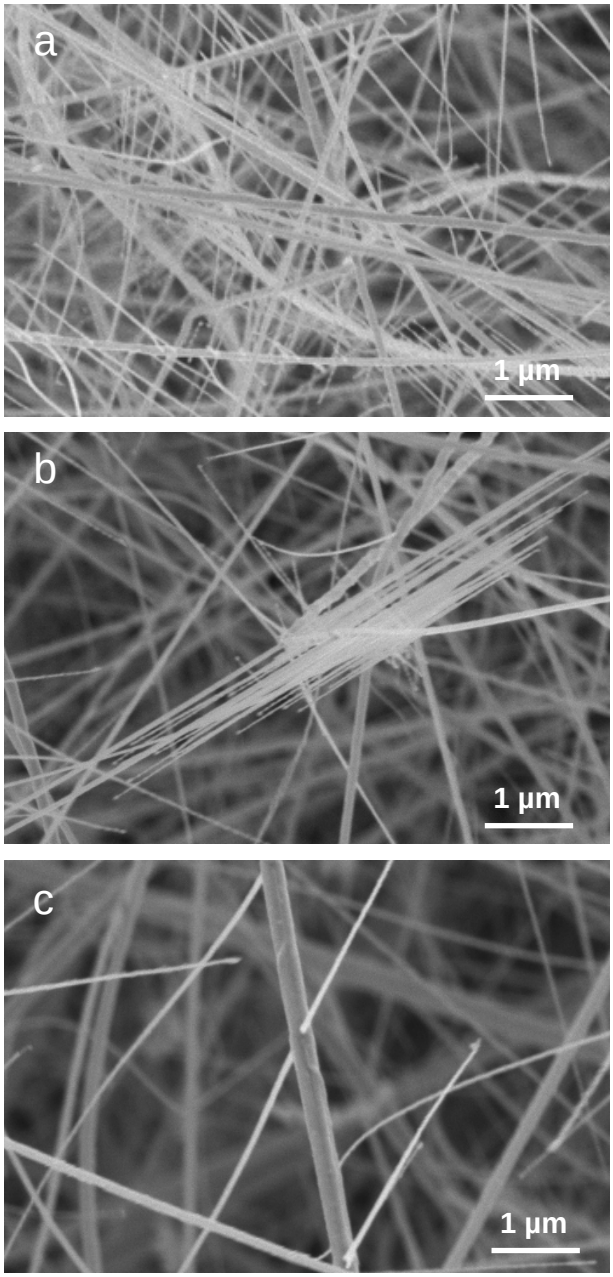
branched NWs is distinct from the CdS multi-pod nanostructure with randomly aligned branches, as well as the CdS tetra-pod nanostructure with an angle of 109.5º between two fingers [10-14]. This indicates that the formation of 2D branched NWs is not only different from the radial growth achieved by a thermal evaporation process but also from the zinc blende/wurtzite phases twinning occurred in the solution-based synthesis of CdS NWs. Due to the low reaction temperature (185 °C), our method for growing branched NWs differs from the seeded growth which is based on the SLS mechanism [18, 19]. The former is affected by the BiI_3 sheets.



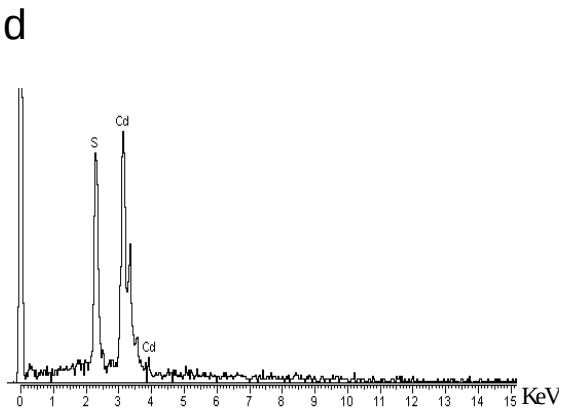
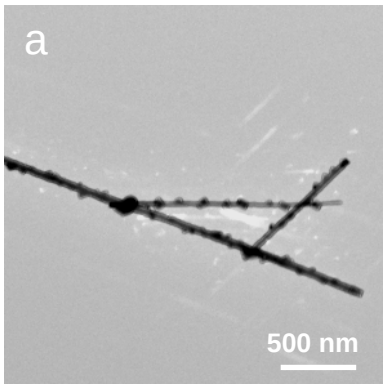


Figure 1: (a)-(c) are three representative SEM images of the branched NWs synthesized with the reaction time of 24 h after introducing the BiI_3 sheets. (d)) is an EDX spectrum of branched CdS NWs.

To understand the growth mechanism of branched nanostructures, we carried out a synthesis experiment with a reaction time of 12 h after introducing the BiI_3 sheets. Tiny residual BiI_3 sheets were found on the as-synthesized NWs (Figure 2a). As the reaction time was increased up to 24 h, the NW branches formed in the locations of the tiny BiI_3 sheets. These NW branches aligned perpendicularly on the side of a straight NW trunk are shown in Figure 2b. Further TEM characterization demonstrated that some of the NW trunks and individual NWs have a binary crystal structure as shown in Figure 2c and 2d. A selected area electron diffraction (SAED) pattern taken from the trunk confirms that [0001] is the preferred growth direction for the wurtzite CdS NW (inset of Figure 2c) [20]. The twin diffraction points marked by the circle reveal that the SAED pattern was formed by superimposing two sets of diffraction points. This further confirms that the trunk was composed of two parallel aligned NWs with the same growth orientation. Also, in Figure 2e, some NWs demonstrated a parallel growth phenomenon which may ultimately lead to the formation of binary crystalline NWs or the binary crystal trunk.



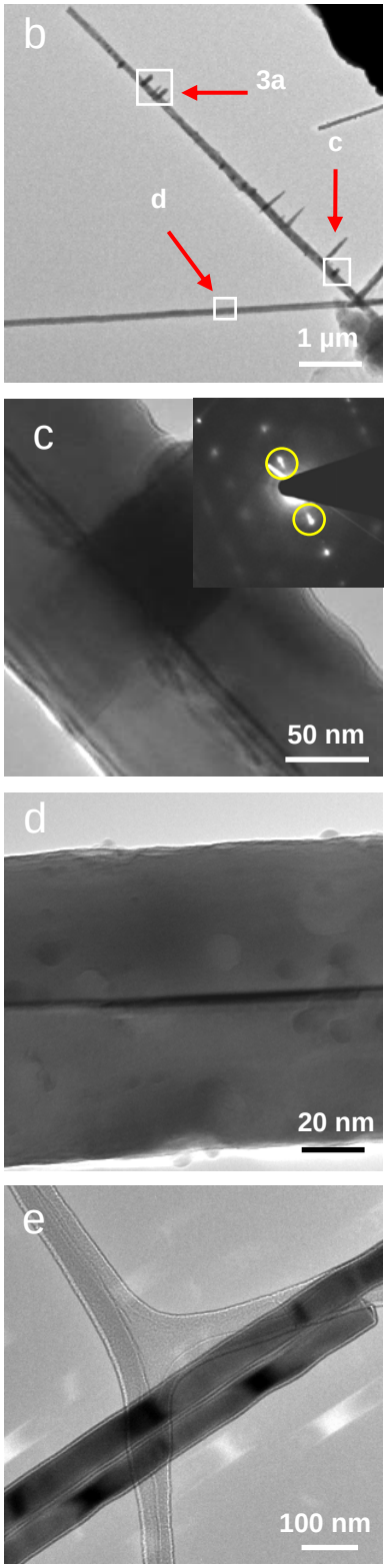


Figure 2: (a) TEM image of the CdS NWs synthesized with the reaction time of 12 h after introducing the BiI_3 sheets. (b) TEM overview of the 2D branched CdS NWs synthesized with the reaction time of 24 h after introducing the BiI_3 sheets. (c), and (d) are high resolution TEM images of the areas marked on image (b). Inset of (c) is an electron diffraction pattern recorded from the trunk as shown in (c). (e) is a TEM image of two parallel aligned NWs grown for 24 h after introducing the BiI_3 sheets.

We found that the part near the tip of the trunk does not have the binary crystalline nanostructures (Figure 3a). This suggests that the binary crystal nanostructure of the trunk was converted into a single crystalline structure during its elongation and the branches were formed on the trunk with or without the binary crystals nanostructure. Interestingly, the branch that formed on the single crystalline trunk has a polyhedral shape at both tips. A high resolution transmission TEM (HRTEM) image reveals that the CdS branch is single crystalline. The spacing of the lattice fringes along the growth orientation was 0.67 nm (Figure 3b). This confirms that the growth is along the [0001] direction of wurtzite CdS [14]. We found no Bi attached to the body or the tip of any NW. This suggests that the formation of the trunk or the branches is attributed to the epitaxial growth of CdS crystal.

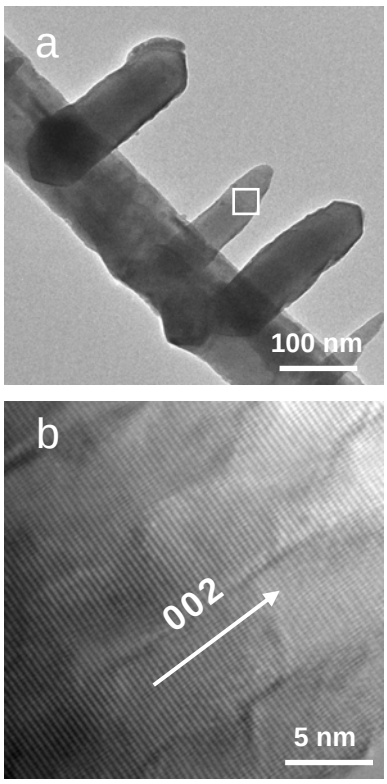


Figure 3: (a) is high resolution TEM images of the areas marked on Figure 2b. (b) is a HRTEM image taken from the area marked by a rectangle on (a).

It is obvious that in our reaction system, BiI_3 sheets provided the induced force between the 2D plane (the surface of BiI_3 sheet) and the reactants to assist the

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formation of a binary crystals nanostructure and branched NWs. Based on the structural phenomena that the size of the branches is much smaller than that of the trunk, we propose that the formation of branched NWs is attributed to a two-step growth. First, as shown in Figure 4, the CdS NWs result from anisotropic growth along the c-axis of wurtzite structures. Second, when BiI_3 sheets were added, some CdS NWs were covered by the BiI_3 sheet. As Cd^{2+} cations were absorbed on both sides of the BiI_3 sheet, CdS branches prefer to be formed on the sides of the trunk after alternative deposition of S and Cd^{2+} cations. During the growth of CdS branches along the [0001] direction, there is a lattice mismatch between the (001) plane of the branches and the (110) plane of the trunk. However the effect of this mismatch is indistinctive. This is largely attributed to the pre-alignment of Cd^{2+} cations and S by the electrostatic force of the Bi-I layer.

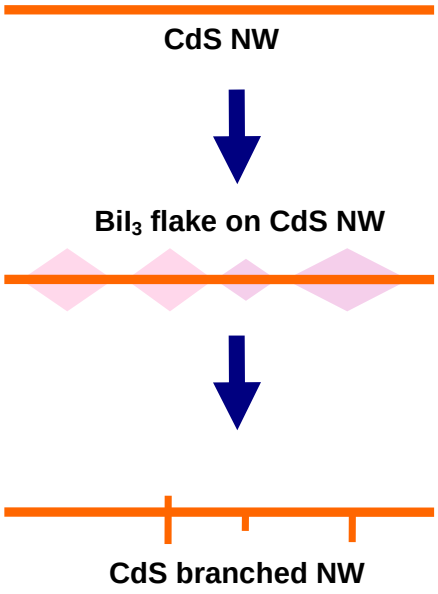

Figure 4: Schematic diagrams of the growth of branched CdS NW assisted by the BiI_3 sheets on the CdS NW.

4 CONCLUSION

In this study, 2D confined growth was demonstrated by the synthesis of CdS NWs with binary crystals and branched features. This growth is attributed to the coordination between the CdS crystal anisotropic growth and the electrostatic force of the Bi-I layer. Further study is under way to synthesize orderly aligned complex nanostructures with various chemical compositions using the 2D template. This may ultimately lead to the fabrication and assembly of nanodevices by the method introduced here.

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