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生物模板法常温合成 CdS 纳米线

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摘要: 采用新型生物模板法常温合成 CdS 纳米线的新方法,并对其结构和性能进行了表征。SAED 分析表明:生物模板表面包覆上了结晶良好的 CdS 纳米颗粒。TEM 照片表明:CdS 纳米线长(4±0.6) μm,直径为(400±55) nm,构成纳米线的 CdS 颗粒尺寸为(5.5±0.3) nm。荧光光谱分析表明:该纳米线具有优异的荧光性质,使其在生物,电子领域有潜在的应用。

关键词: 硫化镉; 纳米线; 生物纳米管; 模板; 室温
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Biotemplating Fabrication of CdS Embedded Bionanowires at Room Temperature

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Abstract: Cadmium Sulfide (CdS) nanowires (NWs) were synthesized by templating bionanotubes self-assembled from bis (*N*-amido-glycylglycine)-1,7-heptane dicarboxylate using cadmium chloride ($CdCl_2$) and sodium sulfide (Na_2S) as Cd and S precursors. The-COOH groups from the bionanotube surface act as chelating agents to coordinate Cd^{2+} ions and facilitate further growth of CdS nanocrystals on the bionanotube. The morphology, structure and composition of CdS embedded bionanowires were characterized by Transmission Electron Microscopy (TEM), High Resolution Transmission Electron Microscopy (HRTEM), Selected Area Electron Diffraction (SAED), UV, steady state Photoluminescence (PL) and Energy-dispersive X-ray spectroscopy (EDS) techniques. The results show that the resulting CdS embedded bionanowires, (4±0.6) μm in length and (400±55) nm in diameter, are coated by CdS nanoparticles with diameter of (5.5±0.3) nm. This work presents an effective direct-growth strategy on biomolecular templates to synthesize monodispersed QD-coated nanowires at room temperature by using coordination between -COOH and Cd^{2+}, which has not accomplished previously by any other non-biotemplating synthetic methods.

Key words: CdS; nanowire; bionanotube; templating; room temperature

0 Introduction

CdS nanocryst als and Ⅱ-Ⅵ semiconductor nanoparticles have been extensively studied due to the unique optical and electrical properties including the broad excitation region, tunable size-dependant

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photoluminescence (PL), high quantum yield, excellent chemical stability, and narrow emission peaks [1-3]. Recently, synthesis of one-dimensional CdS embedded bionanowires (NWs) has received much attention because of its potential application as building block for electronic and optoelectronic devices. There have been two major approaches reported for synthesizing semiconductor NWs chemically: Vapor-liquid-solid (VLS) method and organic solution reaction of precursors in organic solvent at high temperature (over 200 ℃). Both approaches have been well established, however these methods have some drawbacks as well. The VLS technique requires high reaction temperature (usually ~1 000 ℃) and the number of the species of VLS coatings are limited due to the availability of precursor vapors while the second method lacks the control of morphology in synthesized NWs[4-5].

Bio-templating is a promising alternative method for semiconductor NW synthesis since it offers a variety of advantages such as low energy consumption for the synthesis and ease of template bionanotube preparation and CdS coating process[6-8]. Furthermore, a large variety of well-defined bio-templates have been evolved to precisely control metal nanoparticle growth at the micro- or nano- level[9-11]. In order to synthesize CdS NWs that are applicable for building blocks of nano devices, high crystal quality and aspect ratio of the NWs are of great importance due to the critical requirement of the optical properties of the NWs and applications as electronic circuits, nanosensor arrays[12-13]. Despites these advantages, the bio-templating synthesis of semiconductor NWs still needs to improve the yield and the quality of QDs by optimizing reaction steps and the growth speed to become effective for the practical applications.

Some previous works have shown effective synthesis approaches in the growths of inorganic nanocrystals[14-16], semiconductor and metal NWs by employing biomolecular templates and specific mineralizing peptides on the template surfaces. Here, we report the direct nucleation and growth of CdS nanocrystals on the biomolecular nanowires without using the mineralization peptides. The bionanotubes provide coordinating groups (-COOH) to anchor Cd^{2+} and this site subsequently can react with S^{2-} for the completion of CdS growth on the bionanotubes. The whole synthesis process is completed in simple two steps without the uses of catalytic peptides or capping agents, commonly used for various nanoparticle synthesis[17].

1 Experimental

1.1 Chemicals and regents

Analytic grade reagents of nonanedioic acid, 1-[3-(dimethylamino) propyl]-3-ethylcarbodiimide hydrochloride, 1-hydroxylbenzoltriazole, glycine-glycine-benzyl ester, dimethylformalmide, triethylamine, citric acid, NaOH, HCl, $CHCl_3$, CH_3OH, $CdCl_2 \cdot 2.5H_2O$ and Na_2S were purchased from Sigma-Aldrich and used without any further purification. All aqueous solutions were prepared with deionized H_2O (Milli-Q water, R >18.2 MΩ·cm) and thoroughly bubbled by nitrogen to prevent oxidation.

1.2 Synthesis of Bionanotube Templates

Bionanotube templates in this report for the growth of CdS NWs were prepared from a glycine-based peptide monomer, bis(*N*-α-amidoglycylglycine)-1,7-heptane dicarboxylate. These peptide monomers (10 mmol·L^{-1}) were self-assembled into nanotubes in a pH value of 5.5 citric acid/NaOH solution after 1 week. These bionanotubes were grown in diameter of 100~400 nm, and the bionanotubes with an average diameter of 400 nm were separated with centrifugation and size separation columns. Details of the monomer synthesis, the self-assembly procedure, and the size separation are described in previous publications[12,18]. After the bionanotubes were washed thoroughly with deionized water and followed by centrifugation for several times, these bionanotubes were redispersed in a phosphate buffer solution (pH=7.4) in a centrifuge tube. The resulting bionanotubes were used as templates for the immobilization of Cd^{2+} and the subsequent CdS nanocrystals growth.

1.3 Preparatoin of CdS embedded bionanowires

The assembly strategy of CdS nanocrystals (NCs) on the bionanotube is based on *in situ* two-step

deposition procedure as illustrated in Fig.1. Under bubbled N_2 condition, 0.5 mL cadmium chloride solution (7.0 mmol·L^{-1}) was added dropwise to 0.5 mL bionanotube-containing solution to coordinate Cd^{2+} ions onto bionanotubes via electrostatic interaction. After stirred for 1 hour, the mixed solution was incubated for another 4 days in refrigerator at 4 ℃. Then, the excess Cd^{2+} ions were removed by centrifugation (14 000 r·min^{-1} for 60 min) and rinsed by deionized water three times. In the second step, 0.5 mL of freshly prepared oxygen-free Na_2S solution (2.0 mmol·L^{-1}) was added dropwise to this solution with vigorous stirring under N_2. The CdS NCs were formed on the bionanotube gradually during the following 48 hours incubation in refrigerator at 4 ℃. Furthermore, these CdS NWs were ready for the optical and microscopic characterizations after purified by repeating centrifugation (14 000 r·min^{-1} for 60 min) and rinsing by de-ionized water three times for the removal of excess Cd^{2+} and S^{2-} ions since the residual ions could contaminate the coating.

1.4 Instruments

Absorption spectra were recorded by a Cary 50 Probe UV-Vis spectrophotometer in the wavelength range of 350 ~600 nm. The samples for PL characterization were prepared by transferring a 100 μL buffer solution containing CdS NWs onto a 10 mm ×10 mm Si(100) wafer, and then the sample was dried by spinning-coating. The steady-state photoluminescence (PL) emission spectra of these samples were recorded by a Jobin Yvon-Spex Fluorolog spectrophotometer equipped with a Xenon lamp as an excitation source at 367 nm. All measurements were performed at room temperature. Transmission Electron Microscopy (TEM) samples were prepared by dropping 10 μL of the sample solution on carbon-coated 80 μm (300 mesh AL) copper grids. Excess solutions were removed by filter papers. All TEM/HRTEM images and Selected Area Electron Diffraction (SAED) patterns were recorded with a JOEL JEM-2100 microscope operating at an acceleration voltage of 200 kV, equipped with a field emission gun. Energy-dispersive X-ray spectrometer (EDS) analysis was performed using a Thermo Noran EDX system attached to the JOEL JEM-2100 micro scope.

2 Results and discussion

As illustrated in Fig.1, the synthesis strategy consists of simple two steps. Pre-synthesized bionanotubes from self-assembled peptide monomers, bis (N-amidoglycylglycine)-1,7-heptane dicarboxylate, was adjusted to pH value of 7.4 by phosphate buffer. Hence, -COOH groups from the bionanotubes are deprotonated at this pH value and the resulting -COO^- groups can coordinate with Cd^{2+} ions in the first step in Fig.1. After the excess unbound Cd^{2+} ions were removed by centrifugation and rinsing procedures, S^{2-} ions were added from the precursor, Na_2S (2 mmol·L^{-1}), in the second step in Fig.1 and the transparent solution containing Cd^{2+}-coordinating bionanotubes slowly turned the color of solution to light yellow. This color change suggests the formation of the CdS NWs in the solution.

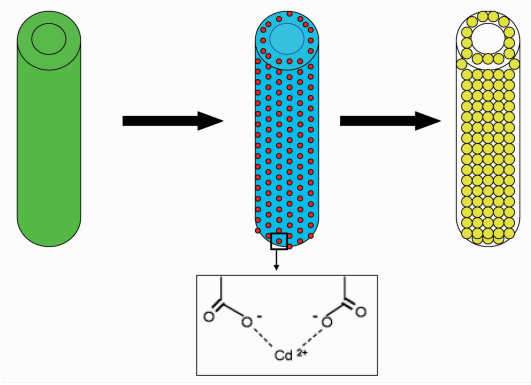

Fig.1 Schematics for in situ synthesis of CdS embedded bionanowires by using bionanotubes as templates

Fig.2 (a) shows a typical TEM image of the resulting CdS NWs and an enlarged image of the selected area in Fig.2 (b), respectively. These TEM images of CdS NWs clearly show uniform CdS NC coating on the surface of bionanotubes and the size of the CdS NCs on the bionanotubes are highly monodispersed. The CdS NCs have an average diameter of 5.5 nm with a narrow size distribution on the basis of the TEM images. The average diameter of CdS NCs matches the distance between the two

adjacent -COO^- binding sites along the bionanotube axis, 6.4 nm [12], which suggests that the -COO^- groups may coordinate Cd^{2+} nucleation and the size of resulting CdS NCs is limited by this spacing. The CdS NCs on the bionanotube were further characterized by high-resolution TEM (HRTEM) (Fig.2(c)).

The HRTEM image of CdS NCs shows a lattice fringe of d =0.332 nm, corresponding to the (111) plane of CdS in the face-centered cubic (fcc) structure[6]. In order to confirm the coating of CdS NCs on the surface of bionanotube, selected area electron diffraction (SAED) was conducted. In Fig.2 (inset), SAED pattern of CdS NCs on the bionanotube shows crystalline faces of (111), (200), (220) and (311). The elemental composition of the CdS NWs is further validated to contain C, O, P, S, Cu and Cd in the EDX spectrum of Fig.3. The appearance of C and O element should be attributed to the bionanotube, whereas N may come from phosphate buffer and Cu is from the TEM grid.

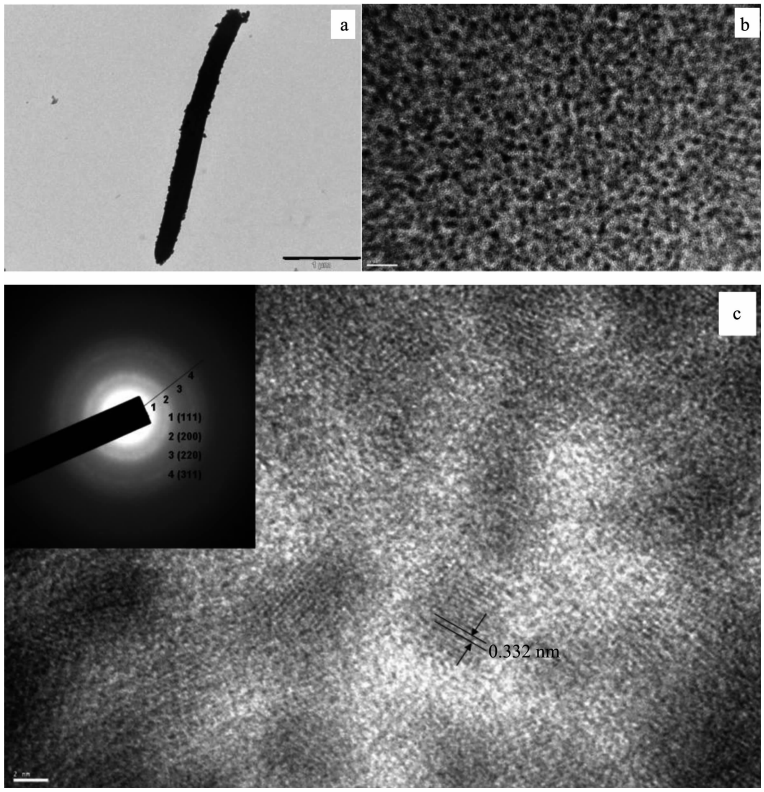

Fig.2 (a) TEM image of a typical CdS NWs, scale bar: 1 μm; (b) enlarged image of selected area in (a), scale bar: 20 nm; (c) HRTEM image of selected area in (b), scale bar: 2 nm; (Inset) ED pattern of the nanowires

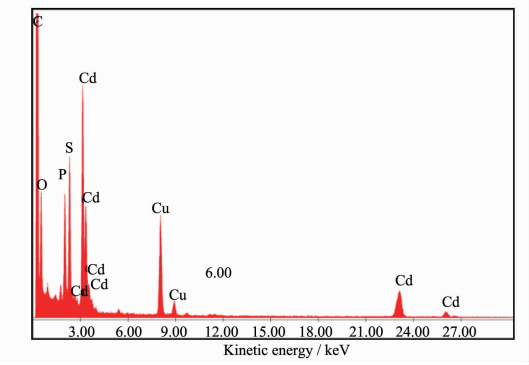

Fig.3 EDS spectrum of CdS embedded bionanowires

The UV-Vis spectroscopic measurement (Fig.4) of CdS NWs shows an absorption peak at 438nm. This peak is blue-shifted about 77 nm from the absorption peak of bulk CdS crystals at 515nm. The absorption peak at 438 nm matches the peak of CdS NCs in a diameter of 5.3 nm [19]. The HRTEM image in Fig.2(b) also shows that the size of CdS NCs on the bionanotube is around 5.5 nm, and this agreement indicates that the absorption peak at 438 nm is from the independent CdS NCs and there is no electronic

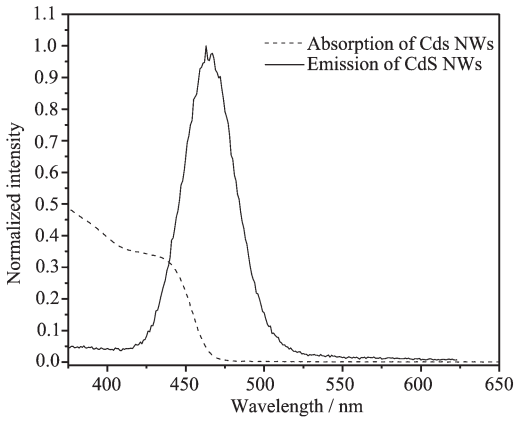

Fig.4　Room temperature UV-Vis and PL spectra of CdS embedded bionanowires

coupling between these NCs. The steady state photoluminescence spectrum reveals that the CdS NWs display its emission peak at 463 nm in Fig.4. This peak also represents the intrinsic emission of the CdS NCs in a diameter of 5.5 nm coated on the surface of bionanotubes. A blue-shifted wavelegnth of 187 nm from bulk CdS crystals ($\lambda_{em} \approx 650$ nm) also provides concrete evidence that quantum-confinement of CdS NCs is in effect on the bionanotube templates. With the procedure in Fig.1, CdS NCs were successfully produced on bionanotubes and the CdS NWs showed the characteristic photoluminescence of CdS NC domains. It is worth noting that 605 nm emission peak is absent in the CdS NW emission spectrum mostly originated from the transition of electrons between trapped surface states and the valence band of CdS. This transition is observed when the CdS contains a large number of surface defects and the spectra in Fig.4 shows that CdS NCs synthesized by this method have less defects due to the low growth speed in the second step in Fig.1[20]

When three different concentrations of cadmium chloride precursor solution, 2 mmol·L^{-1}, 5mmol·L^{-1} and 10 mmol·L^{-1}, were used in the synthesis at the concentration of S^{2-} (2 mmol·L^{-1}) and incubation time of 6 days (4 days for the first step and 2 days for the second step), only part of bionanotube surface was coated by CdS NCs at concentration of 2 mmol·L^{-1} and 5 mmol·L^{-1} (Fig.5 (a)~(b)) while at the high concentration of 10 mmol·L^{-1} entire surface of the bionanotube is coated by CdS NCs (Fig.5 (c)). This result suggests that few Cd^{2+} ions bind on the surface of bionanotube resulting less nucleation centers in the low concentration of Cd precusor. But when the concentration of Cd^{2+} is increased to 10 mmol·L^{-1}, the length of bionanotubes decrease dramatically from (4±0.6) μm (2 mmol·L^{-1}, 5 mmol·L^{-1} and 7 mmol·L^{-1}) to (0.8±0.2) μm with high CdS nanocrystal coating on its surface (Fig.5b). And the yield of final CdS NWs decrease almost 90% as compared with the yield of CdS NWs at the Cd^{2+} concentration of 10 mmol·L^{-1}. Obviously the CdS NWs prepared at the Cd^{2+} concentration of 7 mmol·L^{-1} show the best morphology of resulting CdS NWs since the CdS NCs are packed in the compact arrangement on the whole surface of templating bionanotube.

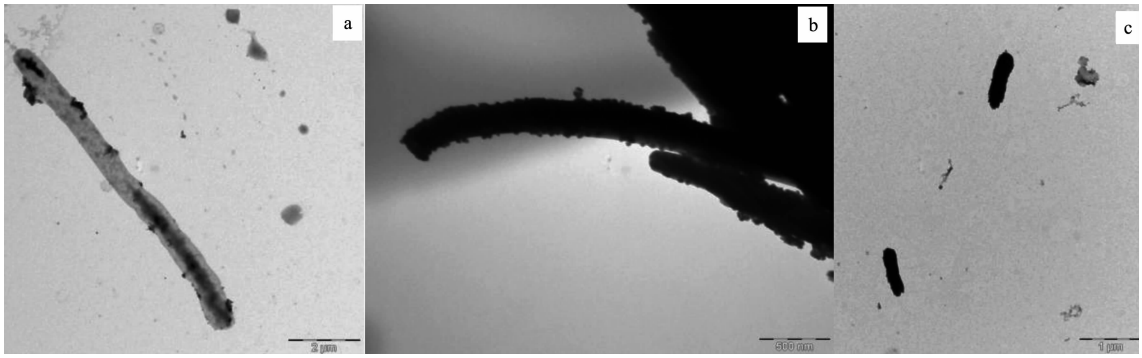

Fig.5　(a) TEM image of CdS embedded bionanowires by using concentration $CdCl_2$ solution of 2 mmol·L^{-1}, scale bar: 2 μm; (b) TEM image of CdS embedded bionanowires by using concentration $CdCl_2$ solution of 5 mmol·L^{-1}, scale bar: 0.5 μm; (c) TEM image of CdS embedded bionanowires by using higher concentration $CdCl_2$ solution of 10 mmol·L^{-1}, scale bar: 1 μm

As a principal step in the whole synthesis procedures, it is worth mentioning that the optimal concentration of Cd^{2+} precursor is 7 mmol·L^{-1}. If the concentration of Cd^{2+} precursor was as low as 2 mmol·L^{-1}, not all -COO^- groups from the bio-nanotube surface are able to coordinate with Cd^{2+} ions due to fewer amounts of Cd^{2+} ions in the mixture solution, which results in less growth centers on the bionanotube surface. Finally, only a small part of the bionanotubes surface is overcoated by formed CdS nanocrystals. On another hand, if high-concentrated Cd^{2+} precursor solution like 10 mmol·L^{-1} is used for incubation with bionanotubes, the bionanotube structures are decomposed by the high concentration Cd^{2+} in the mixture solution and truncated bionanotubes with much shorter length (less than 1 μm) are coated by CdS nanocrystals. The decomposition is because the high concentrated Cd^{2+} ions destroy the hydrogen bonds network between bionanotube monomers by forming -COOCd coordination complex[6].

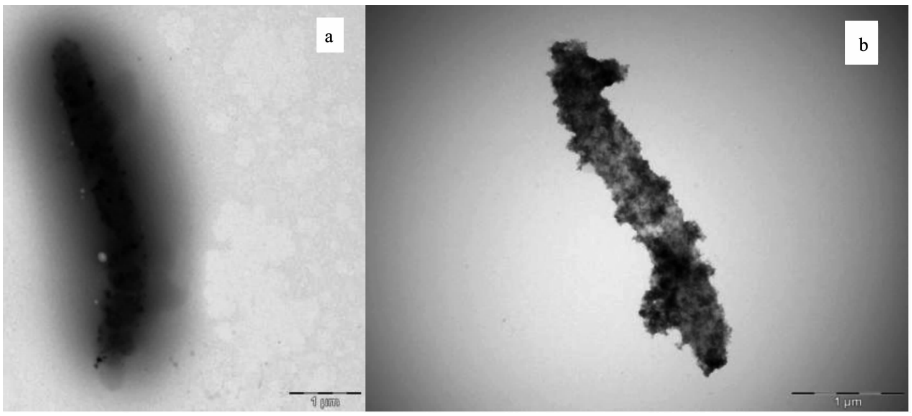

Fig.6 (a) TEM image of CdS embedded bionanowires by using 7 mmol·L^{-1} $CdCl_2$ solution with incubation time of 1 day , scale bar: 1 μm; (b) TEM image of CdS embedded bionanowires by using 7 mmol·L^{-1} $CdCl_2$ solution with incubation time of 2 days, scale bar: 1 μm

To further investigate the direct growth mechanism of CdS NCs on the surface of bionanotubes, we conducted another set of control experiments by varying the incubation time to 1 day and 2 days in the first step of reaction at the fixed Cd^{2+} precursor concentration of 7 mmol·L^{-1}. Fig.6 (a) and (b) reveal the morphology difference of resulting CdS NWs which were characterized by TEM. Compared the 4 day-incubation result in Fig.2(a) with 1 day, 2-day results, it suggests that the coating density of CdS NCs on the bionanotubes increases as the incubation time increases from 1 day, 2 days to 4 days. Longer incubation time helps more Cd^{2+} ions anchored on the bionanotubes for the higher coating density of CdS NCs. Both control experiments with precursor concentration and incubation time changes indicate that the Cd^{2+} ion concentration is a key to control in the direct growth mechanism of CdS NCs on the bionanotubes. Another control experiment reveals that reaction between 7 mmol·L^{-1} $CdCl_2$ and 2 mmol·L^{-1} Na_2S without bionanotubes only produces aggregated CdS nanocrystals with diameter ~20 nm as shown in Fig.7. This result indicates that the coordination between -COOH groups and Cd^{2+} ions plays a critical role to

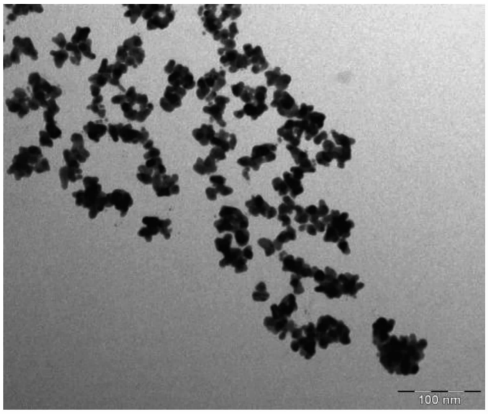

Fig.7 TEM image of CdS nanocrystals from reaction between 7 mmol·L^{-1} $CdCl_2$ solution and 2 mmol·L^{-1} Na_2S solution without bionanotubes as templates, scale bar 100 nm

decide the size of CdS nanocrystals in the whole synthesis procedure of CdS NWs.

It is worth noting that this methodology has several advantages over conventional wet CdS NW synthesis methods such as a simple growth process and high crystallinity. The resulting CdS NCs on the bionanotube maintain discreet quantum confinement even when they are assembled in high density useful feature for future device applications.

3 Conclusions

We have developed a novel bionanotube-templating CdS NW synthesis protocol at pH value of 7.4 and room temperature. The in situ growth mechanism is in two steps: first Cd^{2+} ions from $CdCl_2$ precursor solution are anchored on bionantubes at -COO^- groups via electrostatic interactions. Then, CdS NCs are grown upon the addition of Na_2S solution. Both Cd^{2+} concentration and incubation time are important to control the morphology of resulting CdS NWs. This outcome may lead the potential applications of bionanotubes to serve as the templates for the growths of various metal/semiconductor NWs whose electronic properties depend on the size of NCs on the NWs.

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