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Letter

# Solution-based synthesis of ZnO nanoparticle/CdS nanowire heterostructure

Shancheng Yan[a,b], Dong Hu[a], JianSheng Wu[a], Xin Xu[a], Jun Wang[a], Zhongdang Xiao[b,*]

[a] School of Geography and Biological Information, Nanjing University of Posts and Telecommunications, Nanjing 210046, PR China
[b] State Key Laboratory of Bioelectronics (Chien-Shiung Wu Lab), School of Biological Science & Medical Engineering, Southeast University, Si Pai Lou 2#, Nanjing 210096, PR China

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ABSTRACT

The heterostructure of ZnO nanoparticle (NP)/CdS nanowire (NW) was successfully fabricated by a two-step chemical solution method. The first, CdS nanowires were synthesized by a simple solvothermal route. The second, ZnO nanoparticles were grown on the surface of CdS nanowires in a chemical solution of $Zn(CH_3COO)_2 \cdot 2H_2O$ and anhydrous ethanol at 200 °C. The heterostructure of synthesized ZnO NP/CdS NW was characterized by transmission electron microscopy (TEM). The effects of reaction conditions, such as different reaction time of CdS nanowires synthesized and deposition reaction time were investigated. Moreover, the formation mechanism of the ZnO NP/CdS NW heterostructure has been phenomenologically discussed.

## 1. Introduction

One-dimensional (1-D) nanostructures, such as nanowires, nanotubes, and nanobelts have been synthesized by a wide range of semiconductors and used as building blocks for novel electronic and optoelectronic devices in the past several decades [1–3]. Especially, for their fascinating properties and potential applications in the field of nanoscale science, one-dimensional (1D) heterostructures including coaxial core–shell, axially modulated, and alloyed nanowires are been particular interested [4–10]. CdS ($E_g = 2.42$ eV at room temperature) and ZnO ($E_g = 3.2$ eV at room temperature) are important wide band gap II–VI semiconductor materials, which attract much attention because of their unique properties and wide range of applications in sensors, lasers, waveguides, photocatalysts, and optoelectronic devices [11–18]. On account of this, compositional control has been applied in ZnO-included heterostructures to improve the efficiency connected with photogenerated electrons and holes or incorporate new properties [19–23]. However, there were few reports concerning the effects of the structural correlation on the formation of CdS-based heterostructures, which was essential for the design and preparation of complicated nanocomposites [24].

In this study, we used the preformed CdS nanowires in succession as 1D nanoscale substrates for the growth of ZnO nanoparticles by a solution phase method. In our experiments, we need not surface pretreatments to introduce new surface functional groups or additional covalent and/or noncovalent interconnectivity. To our knowledge, no ZnO NP/CdS NW heterostructure has been reported until now. The effects of reaction conditions, such as the reaction time of CdS nanowires synthesized and the deposition reaction time, were also investigated. This method was facile and will find significant application in nanowire-based solar cells.

## 2. Experimental

All chemicals were of analytical grade and purchased from Nanjing chemical reagent Co., Ltd. and used as received. In a typical procedure, a mixture of 0.064 g S powder and 0.2664 g $Cd(CH_3COO)_2 \cdot 2H_2O$ were dissolved consecutively in 40 ml ethylenediamine. The resulting mixture was loaded into a 50 ml Teflon-lined autoclave, which was then filled with ethylenediamine up to 80% of the total volume. The autoclave was sealed and maintained at 200 °C for 2 h [25]. After the reaction completed, the autoclave was cooled to room temperature naturally, the resulting solid products were filtered off, washed with absolute ethanol and distilled water several times, and then dried in vacuum at 60 °C for 4 h. The ZnO NP/CdS NW heterostructure was fabricated by the chemical solution method. 0.0030 g as-prepared CdS and 0.0050 g $Zn(CH_3COO)_2 \cdot 2H_2O$ were dissolved in 40 ml anhydrous ethanol. The resulting mixture was loaded into a 50 ml-Teflon-lined autoclave. The autoclave was sealed and maintained at 200 °C for 24 h. The autoclave was cooled to room temperature naturally. Finally, the resultant products were centrifugalized, washed with deionized water and ethanol to remove the ions probably remained, and dried at 60 °C in air.

In general, to prepare the samples for TEM measurements, synthesized ZnO NP/CdS NW heterostructure in ethanol was subjected to sonication to generate a well-dispersed colloidal solution of the sample, which was then dropped on a TEM grid. TEM (Tecnai G2 S-TWIN) equipped with an energy dispersive X-ray analysis (EDXA) using an accelerating voltage of 200 kV was used to characterize the as-prepared products. The crystalline phases of the products were determined by powder X-ray diffraction (XRD) on a diffractometer (D/max 2500VL/PC) with monochromatic Cu Kα radiation at 60 kV and 300 mA.

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* Corresponding author. Tel.: +86 25 83790820; fax: +86 25 83795635.
*E-mail address:* zdxiao@seu.edu.cn (Z. Xiao).

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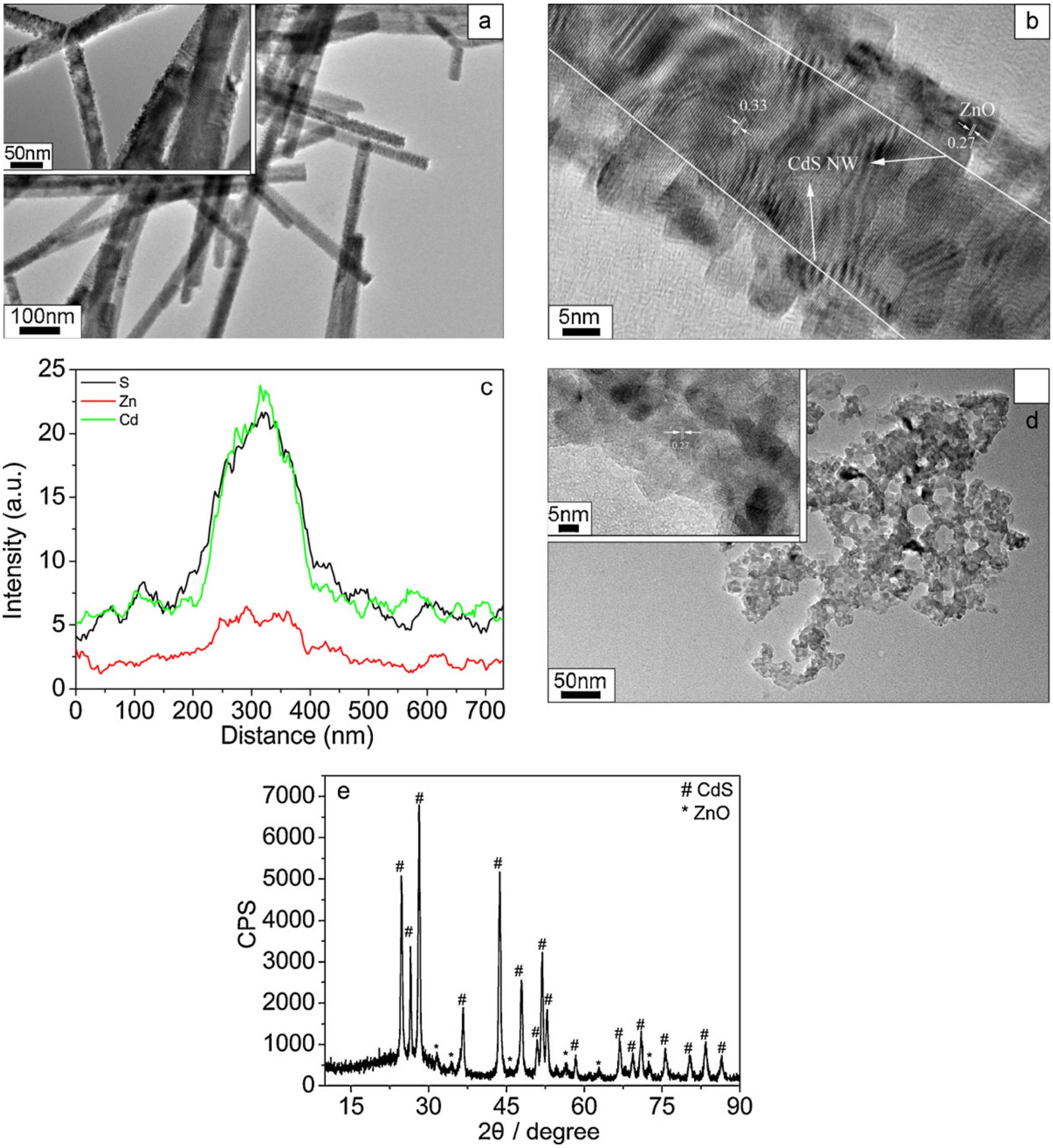

**Fig. 1.** (a) TEM image of the ZnO NP/CdS NW heterostructure. The CdS nanowires were synthesized at 200 °C for 2 h. The reaction time is 24 h for ZnO NP/CdS NW heterostructure. (b) The corresponding HRTEM image (c) EDX line scanning reveals the uniform distribution of Zn, S, and Cd along the cross-section. (d) The ZnO nanoparticles were synthesized at 200 °C for 24 h without adding CdS nanowires. Inset is its HRTEM image (e) XRD pattern of the ZnO NP/CdS NW heterostructures.

## 3. Results and discussion

The morphologies and crystalline structures of ZnO NP/CdS NW heterostructure were investigated, which were obtained via a two-step chemical solution process. Fig. 1a shows the TEM image of the ZnO NP/CdS NW heterostructure. The CdS nanowires were synthesized at 200 °C for 2 h. The reaction time was 24 h for ZnO NP/CdS NW heterostructure. The typical TEM image reveals that a huge number of humps cover the surface of CdS nanowires and the side edges are not smooth, which distinguishes them from the original CdS nanowire. The average width is about 32 nm after the reaction on the count of about 100 ZnO NP/CdS NW heterostructures, which is larger than the original CdS nanowires. A high-resolution TEM (HRTEM) image of the ZnO NP/CdS NW heterojunction (Fig. 1b) reveals that crystalline ZnO nanoparticles were grown on a single crystalline CdS nanowire and CdS nanowires have wurtzite crystal phases with atomic plane spacings corresponding to the JCPDS No. 41-1049, and ZnO nanoparticles have hexagonal crystal phases with atomic plane spacings corresponding to the JCPDS No. 36-1451 [26]. The spacing between adjacent lattice fringes is 0.33 nm, which is close to the *d* spacing of the (0 0 2) plane, indicating the [0 0 0 1] direction (*c*-axis) being the preferential growth direction of CdS nanowires. On the other hand, as to the nanoparticle (Fig. 1b), lattice fringes with interplanar spacing of 0.27 nm corresponding to the (0 0 2) planes of hexagonal ZnO are observed. Fig. 1c is corresponding to EDX elemental mapping of Zn, Cd and S for a ZnO NP/CdS NW heterojunction. It is noticeable that the average Zn content ([Zn]/([Cd] + [Zn])) of the individual heterojunction is about 0.21, with a uniform distribution of the elements along the cross-section (Fig. 1c), revealing that the dentiform nanowires maybe of heterostructure. In contrast with ZnO NP/CdS NW heterojunction reaction, a separate experiment was

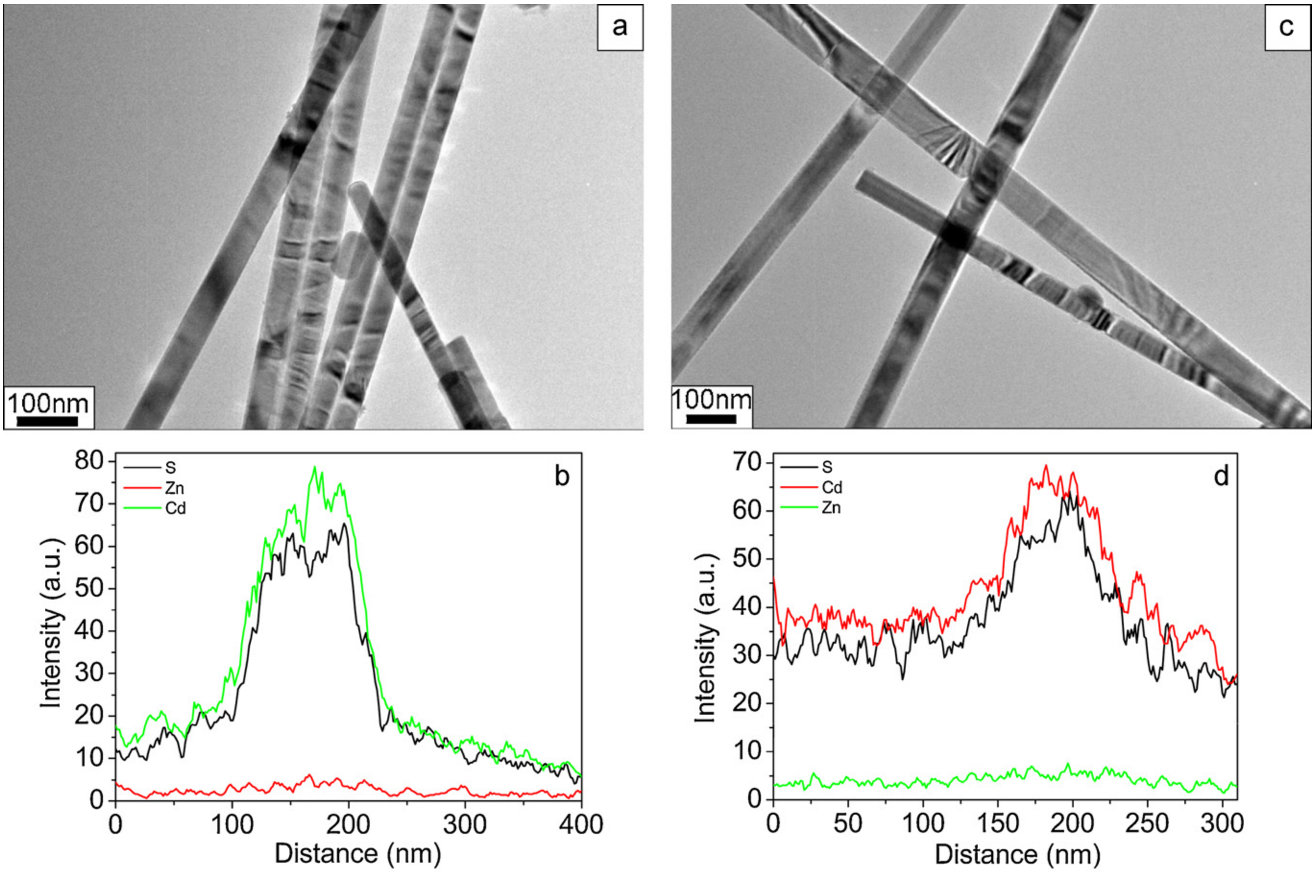

**Fig. 2.** (a) TEM image of the CdS NW without ZnO nanoparticles. The CdS nanowires were synthesized at 200 °C for 12 h. The reaction time is 24 h. (b) EDX line scanning reveals the distribution of S, and Cd along the cross-section without Zn. (c) TEM image of the CdS NW without ZnO nanoparticles. The CdS nanowires were synthesized at 200 °C for 96 h. The reaction time is 24 h. (d) EDX line scanning reveals the distribution of S, and Cd along the cross-section without Zn.

carried out for ZnO nanomaterials. The products are purely ZnO nanoparticles (Fig. 1d). The typical HRTEM image is illustrated in Fig. 1d. The crystal lattice fringes are clearly detected, and the average distance between the adjacent lattice planes is 0.27 nm that also corresponds well to the interplanar distance of the crystal planes of hexagonal wurtzite ZnO, which further proves that ZnO nanoparticles prepared in the present system grew along their *c*-axes [27]. Fig. 1e shows the corresponding XRD pattern of the ZnO nanoparticle (NP)/CdS nanowire (NW) heterojunction. All curves in Fig. 1e obviously show two sets of strong diffraction peaks, indicating that the as-synthesized products are composite materials with high crystallinity. Those marked with "#" can be indexed to CdS, while the others marked with "*" can be indexed to ZnO; no other crystalline impurities are observed. In addition, there is no remarkable shift of all diffraction peaks, implying that the change of the lattice parameters of CdS nanocrystals should be negligible.

The effects of CdS synthesized by different reaction time on hetero-nanostructure were also studied. The CdS nanowires synthesized at 200 °C for 12 h and 96 h were, respectively further used as original CdS nanowires in the above reaction. An interesting phenomena was presented in Fig. 2, that was there were no ZnO nanoparticles adsorbed on the surface of CdS NW synthesized at 200 °C for 12 h and 96 h, respectively (Fig. 2a and c), though the reaction time was also 24 h. It indicated that the CdS nanowires synthesized by different reaction time affected the experimental result. It explains that the property of the CdS nanowires synthesized by different reaction time is different. The detailed explanation can be seen in the following text. Their corresponding EDX line scanning data further show no trace of the Zn element in the CdS nanowires (Fig. 2b and d), which also indicates that the ZnO were not grown on the CdS nanowires surface.

The effects of reaction time on ZnO NP deposition were investigated by performing TEM analysis on the samples prepared in the longer time, the results were shown in Fig. 3a and c. And therefore, we increase the reaction time to 48 h and 72 h, respectively. The CdS nanowires used as original nanomaterial were still synthesized at 200 °C for 2 h. From Fig. 3a and c, it is found that the surface of CdS nanowires without ZnO nanoparticles. Their corresponding EDX line scanning data also showed no trace of the Zn element in the CdS nanowires (Fig. 3b and d), which further indicates that the ZnO are not grown on the CdS nanowires surface. Generally speaking, with the extension of reaction time, the nanoparticle will grow further. CdS nanoparticles were once deposited on the ZnO nanowire array in a chemical bath containing $CdSO_4$, thiourea, and an aqueous ammonia solution [22]. The deposited CdS has a larger size but lower density, and eventually, all ZnO nanowires are etched, leaving big-sized porous CdS structures after the prolonged deposition time. This experimental result which was not in accordance with our prospective may be caused by other reasons.

On the basis of the TEM observations, we could notice the morphology evolution of the ZnO NP/CdS NW heterostructure depending on the CdS nanowires synthesized by different reaction time and deposition reaction time. Based on the experimental results mentioned above, the growth mechanism of the ZnO NP/CdS NW heterostructure nanowires can be proposed tentatively. Firstly, the dissolved $Zn(CH_3COO)_2\cdot 2H_2O$ in ethanol produces a zinc ion,

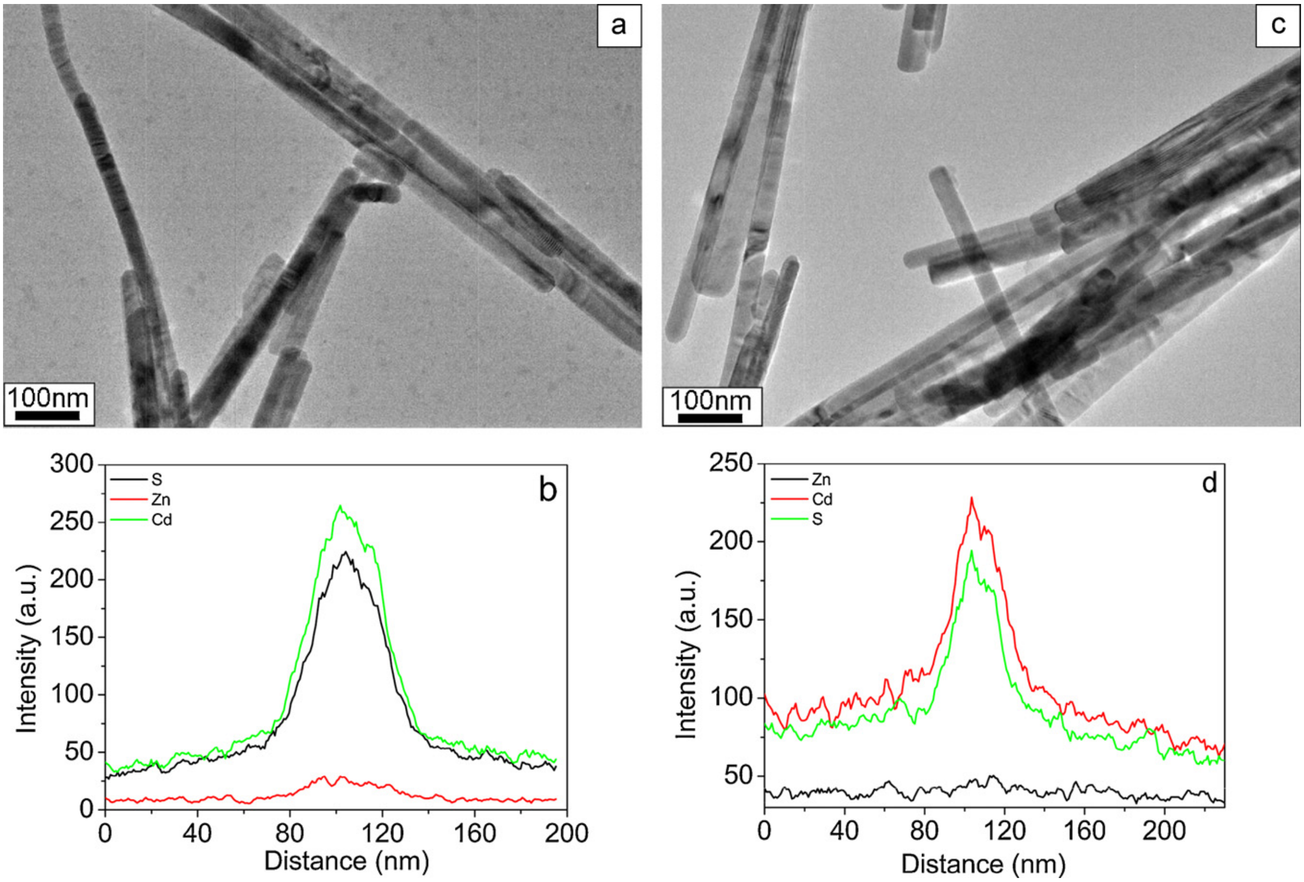

**Fig. 3.** (a) TEM image of the CdS NW without ZnO nanoparticles. The CdS nanowires were synthesized at 200 °C for 2 h. The reaction time is 48 h. (b) EDX line scanning reveals the distribution of S, and Cd along the cross-section without Zn. (c) TEM image of the CdS NW without ZnO nanoparticles. The CdS nanowires were synthesized at 200 °C for 2 h. The reaction time is 72 h. (d) EDX line scanning reveals the distribution of S, and Cd along the cross-section without Zn.

the free zinc ion are inclined to attach to the defects of the CdS nanowires synthesized at 200 °C for 2 h. Then, the ZnO nanoparticles are formed under the solvothermal condition at 200 °C. When the reaction time was increased from 6 h to 24 h, the ZnO nanoparticles would gradually grow up and the thickness of ZnO nanoparticles shell was also increased (Fig. S1 and Fig. 1a). As been well known, controlling the shell thickness is an important issue in core/shell heterostructure nanomaterial synthesis, because this parameter crucially affects the electrical and optical properties of the heterostructures [21]. In this regard, by controlling the reaction time, we can change the ZnO shell thickness relatively easily. The growth in vapor-phase atomic layer deposition is analogous to that in solution-phase process, which is a very powerful thin film growth technique in current semiconductor processing.To further extend the reaction time, such as 48 h or 72 h, an interesting phenomenon appeared: the ZnO nanoparticles disappeared on the surface of CdS nanowires. One reason may be that the crystallinity of CdS nanowires have been improved with the reaction time extended (Fig. 3). Because the crystallinity of CdS nanowires were improved by extended the reaction time, the defects of the CdS nanowires were decreased, which made the ZnO nanoparticles detach from the surface of CdS nanowires. The other reason may be the lattice mismatch which is relative larger between the ZnO and the CdS, which make the ZnO nanoparticles break away from the CdS nanowires. There were no ZnO nanoparticles on the surface of CdS nanowires synthesized at 200 °C for 12 h and 96 h, respectively (Fig. 2). The reason is that the crystallinity of the samples synthesized at 200 °C for 12 h is better than that synthesized at 200 °C for 2 h, which is testified by the XRD pattern (the data is not given here). It also can be seen in our another separate article. It indicates that the free zinc ion is unwilling to attach to the surface of the CdS nanowires with better crystallinity, which makes the ZnO crystal solely grow in solution. The important point of our solution based approach is that it can produce ZnO NP/CdS NW heterostructures depending on the reaction conditions such as original CdS nanowires synthesized by different reaction time. On the whole, the defects of the CdS nanowires are necessary for synthesis of ZnO NP/CdS NW heterostructures, which suggests that the defects give the free zinc ion active region. Of course, this simple methodology described here can be applicable to prepare other heterostructures such as $SnO_2$ NP/CdS NW heterostructures, which can be seen in Fig. S2.

## 4. Conclusions

In summary, ZnO nanoparticle/CdS nanowire heterostructure has been successfully synthesized by a simple two-step chemical solution method. The heterostructure nanowires are composed of CdS nanowires and ZnO nanoparticles grown on the nanowires surface. We have investigated the effects of reaction conditions, such as different reaction time of the CdS nanowires synthesized and deposition reaction time. The morphology evolution of ZnO NP/CdS NW heterostructure has been observed depending on the reaction parameters. The formation mechanism of the ZnO NP/CdS NW heterostructure has been proposed base on the experimental results. The ZnO nanoparticle sensitized CdS NW shows highly potential applications, which could be used as an efficient electrode in solar energy conversion devices based on nanomaterials and nanoarchitecture.

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## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jallcom.2011.04.016.

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