Short communication

Controlled synthesis of NiS nanoparticle/CdS nanowire heterostructures via solution route and their optical properties

Shancheng Yan a,b,∗, Yi Shi b,∗∗, Litao Sun c, Zhongdang Xiao d, Bo Sun d, Xin Xu a

a School of Geography and Biological Information, Nanjing University of Posts and Telecommunications, Nanjing 210046, PR China
b National Laboratory of Solid State Microstructures, School of Electronic Science and Engineering, Nanjing University, Nanjing 210093, PR China
c Key Lab of MEMS of Ministry of Education, Southeast University, Si Pai Lou 2#, Nanjing 210096, PR China
d 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

1. Introduction

Semiconducting nanowire heterostructures with modulated compositions and/or doping are at the forefront of the current scientific revolution of nanoscience, which is increasingly important in the assembly of electronic and photonic devices [1]. Compared with notable progress in the nanowire preparation for the homogeneous systems, the desired one-dimensional (1D) heterostructure formation with well-defined interfaces has been lagging far behind. To date, there have been only a limited number of reports regarding the rational design and successful fabrication of heterostructures within a given 1D nanostructure [2–6]. Especially, the synthesis of single-crystal semiconductor-based heterostructures is still a big challenge, while it is a prerequisite for exploring fundamental nanoscale semiconductor physics and offering technological devices with optimum characteristics [7].

In the case of the CdS, it is with a direct bandgap of 2.42 eV, which is considered to be an excellent material for various optoelectronic applications in the visible range of the electromagnetic spectrum, like nonlinear optical devices, LEDs, and solar cells [8–13]. Nickel sulfide (NiS) has aroused increasing attention because of its applications for cathode materials of lithium batteries because of its high lithium activity, high theoretical capacity (590 mAh g−1), high electronic conduction and low cost [14–18]. Moreover, CdS-based heterostructures were prepared for attempting to improve the efficiency connected with photogenerated electrons and holes or incorporate new properties [19–21]. Therefore, to fabricate 1D heterostructure nanostructures and study their growth behaviors are very necessary.

In the present work, we used the preformed CdS nanowires in succession as 1D nanoscale substrates for the growth of NiS nanoparticles by a solution phase method. In our experiments, we did not need the surface pretreatments to introduce new surface functional groups or additional covalent and/or noncovalent interconnectivity. We think that there is a lot of cation vacancies on the surface of the CdS nanowires synthesized for 2 h, which allows foreign cations to dissolve. To the best of our knowledge, no NiS NP/CdS NW heterostructure has been reported until now. The effects of reaction conditions, such as reaction time, reaction temperature, and reaction solvent were also studied. The detailed formation mechanism of the NiS NP/CdS NW heterostructure has been proposed according to the experimental results. Raman and PL are used to characterize their optical properties. This unique method
was facile and would find significant application in nanowire-based electrochemical power sources, such as electrode materials for lithium ion batteries and fuel cells, electrochromic films, electrochemical supercapacitors [17,18,22].

2. Experimental

All chemicals were of analytical grade and purchased from Nanjing chemical reagent Co., Ltd. and used as received. In a typical synthesis of CdS nanowires, a mixture of 0.064 g S powder and 0.2664 g Cd(CH₃COO)₂. 2H₂O were dissolved consecutively in 40 ml ethylenediamine. The resulting mixture was loaded into a Teflon autoclave with 50 ml volume, which was then filled with en up to 80% of the total volume. The autoclave was sealed and maintained at 200 °C for 2 h. 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 [23]. The NiS NP/CdS NW heterostructures were fabricated by the chemical solution method. 0.0030 g as-prepared CdS nanowires and 0.0050 g NiCl₂. 6H₂O were dissolved in 40 ml anhydrous ethanol. The resulting mixture was loaded into a Teflon autoclave with 50 ml volume. 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.

The samples used for FESEM observations were supported on the aluminum foil substrate. To prepare the samples for TEM measurements, the NiS NP/CdS NW heterostructures in ethanol were subjected to sonication to generate a well-dispersed colloidal solution of the sample, which was then dropped on a TEM grid. TEM (JEOL 2100) equipped with an energy dispersive X-rays analysis (EDXIA) using an accelerating voltage of 200 kV were also 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/1max 2500VL/PC) with monochromatic Cu Kα radiation at 40 kV and 200 mA. The composition of the samples was analyzed with X-ray photoelectron spectroscopy (PHS5000 VersaProbe, ULVAC-PHI). PL measurements were conducted at room temperature using the laser with a wavelength of 325 nm as the excitation source (FLS 920). The power is about 20 mW from the laser. The Raman spectra were obtained on Raman spectrometers excited by the 514.5 nm line of an Ar+ laser (T64000). The power is about 500 mW from the laser. When it reaches the samples by light path, laser power has only a few milliwatts.

3. Results and discussion

Fig. 1a shows a typical FESEM image of the NiS NP/CdS NW heterostructures synthesized for 24 h at 200 °C. Many nanowire structures can be observed in the product (Fig. 1a). The NiS NP/CdS NW heterostructures are several micrometers in length and about dozens of nanometers in diameter. The crystalline structure of the NiS NP/CdS NW heterostructure was further characterized by TEM. Fig. 1b shows a low resolution TEM image of the NiS NP/CdS NW heterostructure. The typical TEM image in Fig. 1b reveals that the side edges of the NiS NP/CdS NW heterostructures are not smooth, which distinguishes them from the original CdS nanowires. The corresponding image of pure CdS nanowire can be seen in our previous literature [23]. A typical high-resolution TEM (HRTEM) image of the NiS NP/CdS NW heterostructure in Fig. 1c reveals that crystalline NiS 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

![Image](image-url)
NiS nanoparticles have rhombohedral crystal phases with atomic plane spacings corresponding to the JCPDS No. 01-1286. The corresponding XRD pattern of the NiS NP/CdS NW heterojunction is shown in Fig. S1 of the Supporting Information. All curves in Fig. S1 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 NiS. 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 spacing between adjacent lattice fringes is 0.33 nm, which is close to the d spacing of the (001) plane. It is indicated that the [0 0 0 1] direction (c-axis) is the preferential growth direction of CdS nanowires. On the other hand, as to the nanoparticle (Fig. 1c), lattice fringes with interplanar spacing of 0.29 nm corresponding to the (3 0 0) planes of NiS are observed. The misfit-induced interfacial strain may be accommodated by the local curving near-interface junction or compensated by a decrease in the total surface energy due to solvent or surfactant binding [23]. Although the formation of the heterointerface with a large lattice mismatch seems to be explained by the coincidence site lattice model [24], we think that it is more likely to relate to the catalyst-assisted growth in solution and it will be further discussed later. The corresponding EDX analysis of the NiS NP/CdS NW heterojunction is shown in Fig. S2 of the Supporting Information. In Fig. S2, the peaks of Cd, S, Ni, and O are pronounced. It should be noted that the C and Cu are not marked out in Fig. S2. The corresponding SAED pattern of NiS NP/CdS NW heterostructure is shown in Fig. 1d. From the SAED pattern, there are the crystal NiS spots in the pattern, which is different from the pattern of single crystal CdS. In contrast with NiS NP/CdS NW heterojunction reaction, a separate experiment was carried out for NiO crystals. The products are pure NiO nanomaterials shown in Fig. S3 of the Supporting Information. The typical TEM image is illustrated in Fig. S3a. Its corresponding SAED pattern is shown in Fig. S3b. The selected area electron diffraction pattern in Fig. S3d demonstrates a monocrystalline structure of the purely NiO nanomaterials. The marked interplanar spacings of 0.20 nm corresponds well to that of the (002) lattice planes of NiO crystals in the high-resolution TEM (HRTEM) image (Fig. S3c in the Supporting Information).

XPS analysis, as given in Fig. 2, was also employed to determine the chemical composition. Fig. 2a–d displays the full XPS spectrum and high-resolution spectra of the Cd(3d), S(2p), and Ni(2p) regions, respectively. Fig. 2a is the typical survey spectrum of the NiS NP/CdS NW heterostructures, which indicates the presence of Cd, Ni, and S, as well as absorbed C and O on the sample surface. From Fig. 2b and c, it is obvious that the binding energy of peaks Cd(3d5/2) and S(2p3/2) are 404.39 and 160.75 eV, respectively, in agreement with reported values for CdS [25]. The high-resolution XPS in the Fig. 2d gives the binding energies of Ni (2p3/2) to be 854.70 eV which is close to the previous reported value for NiS [26].

We further demonstrate that one is able to affect the morphology of the product through adjusting the growth temperature in the experiments. Fig. 3 shows the FESEM images of the samples prepared at various temperatures for 24 h. The morphology of the sample synthesized at 120 °C was observed to be only CdS nanowires (Fig. 3a). The surface of CdS nanowires are smooth according to the high magnification FESEM image (the figures are not given here). As the solvothermal temperature increased, for example 160 °C, some product randomly entangled together. The surface of the CdS nanowires obtained at 160 °C had some nanoparticles (Fig. 3b). As depicted in Fig. 3c, the products obtained at 180 °C were much entangled and more NiS NP/CdS NW heterostructures (Fig. 3c). When the temperature was higher, like 200 °C, the products were composed of NiS NP/CdS NW heterostructures (Fig. 1a). The experimental results revealed that

Fig. 2. (a) Full XPS spectrum of the NiS NP/CdS NW heterostructures synthesized for 24 h at 200 °C; (b–d) high resolution XPS spectra of the NiS NP/CdS NW heterostructures in the Cd(3d), S(2p), and Ni(2p).
the solvothermal temperature of 200 °C was optimum for the formation of the NiS NP/CdS NW heterostructures. It should be noted that the effects of the condition higher than 200 °C temperatures on the products were not checked not only because the NiS NP/CdS NW heterostructures have been obtained at 200 °C but also the autoclave used cannot stand up the higher temperature.

It is found that the ratios of the Ni to CdS in the starting reaction solution significantly affect the morphology and the quality of the NiS NP/CdS NW heterostructures. The FESEM images (Fig. 4) depict this result. When the ratio of Ni to CdS increased to 0.5, the products were a few NiS NP/CdS NW heterostructures (Fig. 4a). The surface of the CdS nanowires had few nanoparticles (the figures are not given here). And no other morphologies but most NiS NP/CdS NW heterostructures were obtained when the ratio was 1:1 (Fig. 1a). Whereas further increased the amount of Ni, for example, the ratio of Ni to CdS was 2:1, the main products were more nanoparticles and some NiS NP/CdS NW heterostructures (Fig. 4b). So, we set the optimal ratio of CdS: Ni at 1:1 for the synthesis of NiS NP/CdS NW heterostructures in our experiments.

Fig. 5 shows a series of FESEM images of the samples prepared at 200 °C for 12, 18, and 48 h, respectively. The morphology of the product prepared at 200 °C for 12 h showed that the product was composed of NiS NP/CdS NW heterostructures (Fig. 5a). The thickness of the NiS NP shell was about 2.1 nm (inset in Fig. 5a is its TEM image). As the reaction time extended to 18 h, the thickness of the NiS NP shell was about 2.8 nm (inset in Fig. 5b is its TEM image). However, the thickness of the NiS NP shell became about 2.2 nm (inset in Fig. 5c is its TEM image) when the reaction time extended to 48 h (Fig. 5c), implying that the growth of NiS NP/CdS NW heterostructures has a complicated mechanism when reaction time is longer than 24 h. Further HRTEM study was carried out to obtain detailed information on the NiS NP/CdS NW heterostructures. It is found that the NiS nanoparticles linked up to form a NiS nanoshell on the surface of the CdS nanowires (Fig. 5d, Arrows refer to the incipient NiS nanoparticles). As solvothermal time increased, for example 72 h, the NiS nanoshell on the surface of the CdS nanowires were also observed (Fig. S4 in the Supporting Information). Continued shell growth eventually lead to the formation of a crystalline shell structure, which is the crystalline growth process (Fig. S4 and Fig. S4 in the Supporting Information). It is well known that there are two most commonly invoked mechanisms of nanocrystal growth. One is Ostwald ripening, the other is oriented attachment. Ostwald ripening is the process by which smaller particles redissolve and larger particles grow by the addition of the redissolved species. The growth of particles is therefore largely controlled by the interaction of the solute species with the
nanostructures growth. In both cases, the driving force is surface energy minimization. Obviously, the growth mechanism from particle shape to shell shape was oriented attachment mechanism.

In our study, we also find that the solvent plays an important role in the formation of the final nanostructure. In our experiments, adding 15 ml water to 25 ml ethanol (Fig. 6a), the products were nanocubes and some CdS nanowires, and without NiS nanoparticles on the surface of CdS nanowires (inset of Fig. 6a). The corresponding TEM image can be seen in the inset of Fig. 6a. The arrows refer to the nanocubes in the inset of Fig. 6a. When the amount of water was increased, e.g., 25 ml water added to 15 ml ethanol, the products were still some NiO nanocubes and some CdS nanowires (Fig. 6b). Further increasing the proportion of water, for example, used water alone as the solvent; the product was composed of the CdS nanowires (Fig. 6c). In its TEM image, the NiO nanocubes were also observed in the product (Fig. 6d). By increasing the proportion of water in synthetic systems, complete different products were obtained. That may be caused by the following reasons. When the solvent was anhydrous ethanol (Fig. 1a), the release rate of Ni²⁺ cations was slow, so the Ni²⁺ cations have much time to adsorb on the surface of the CdS nanowires, which led to form NiS NP/CdS NW heterostructures. In contrast, when the water was added into the solvent, the Ni²⁺ cations were prior dissolved in the water, which led to form separate NiO nanocubes and only CdS nanowires.

In the present work, the solvothermal temperatures and reaction times were controlled to understand the formation mechanism of NiS NP/CdS NW heterostructures in ethanol. The growth of NiS NP/CdS NW heterostructures could be identified with XRD data, FESEM images, and TEM images. On the basis of the experimental results mentioned above, the growth mechanism of the NiS NP/CdS NW heterostructure nanowires can be proposed tentatively. Firstly, the dissolved NiCl₂·6H₂O in ethanol produces the nickel ion, the free nickel ions are inclined to dissolve in the defects of the CdS nanowires synthesized at 200 °C for 2 h to form NiS [27,28], which does not consume CdS at all. As NiS species accumulate, they aggregate and form their own phase. In order to decrease the interfacial energy, they are pushed out from CdS “embryo” to reduce the interface area and grow through epitaxial mode [29]. Oriented attachment has far been widely observed to occur only among nanocrystals of the same material [30–32]. As solvothermal time increased, notice that the isolated NiS nanoparticles linked together to form NiS nanoshell, which is a thermodynamically driven process. In principle, one-dimensional nanostructures such as nanorods will eventually evolve to the most stable zero-dimensional dot shape if the growth process is diffusion-controlled and no additional precursor is added to the reaction solution [27]. The overall result of this process is that continued shell growth eventually lead to the formation of a crystalline shell structure (Fig. 5c and Fig. S4 in the Supporting Information). All these events are schematically represented in Fig. 7.

To date, it is well known that there are two types of solution routes in the literature for creating nano-objects with heterostructures: seeded growth [33–36] and catalyst-assisted growth [37–40]. For the seeded growth, the second materials epitaxially grow on the suitable crystallographic facet offered by seeds, leading to heterostructure nanomaterials. The fabrication of single-crystal heterostructures is highly difficult in experiment, because the self-nucleation of the second material is difficult to be completely avoided. Meanwhile, accurately controlling the surface states of seed, which is suitable for epitaxial growth of the second materials, is also difficult. Two cases of heterostructures fabricated through seeded growth have been reported in our previous literatures, such as CdS–ZnO [41], and CdS–SnO₂ [42]. In the catalyst-assisted growth, a metal or alloy with a low melting point is used as a catalyst for growing nanowires. This route works at a relatively elevated temperature, at which the metal nanoparticle catalyst shows liquid

Fig. 5. FESEM images of the product synthesized for different reaction time (a) 12 h; (b) 18 h; (c) 48 h and (d) HRTEM image of the product synthesized for 48 h.

growing particles. On the other hand, oriented attachment involves the coalescence of two particles into a single larger one by the fusing of appropriately oriented crystal faces. This mechanism is applicable to particles that are free to move, or when adjacent particles on a surface coalesce, which is favorable for one-dimensional
or quasi-liquid owing to its smaller size and low melt points, dissoc-
iates the dissolved precursor, and absorbs the species that can be
dissolved in the catalyst [29]. It is well known that Ag2S is a kind
of fast ion conductor and Ag cations in Ag2S behave like a "fluid";
therefore, although Ag2S is a stoichiometric compound, there are
a lot of cation vacancies in Ag2S nanocrystals [43]. In our study,
we think that there is also a lot of Cd cation vacancies on the surface
of the CdS nanowires synthesized for 2 h, which allows foreign cations
to dissolve. There are the cation vacancies on the surface of the CdS
nanowires, the NiS nanoparticles only grown on the surface of the
CdS nanowires, which is verified by our experiments. As solvo-
thermal time increased, the isolated NiS nanoparticles linked together
to form NiS nanoshell on the surface of the CdS nanowires. Contin-
ued shell growth leads to the eventual formation of the core–shell
heterostructures (Fig. 5c and Fig. S4 in the Supporting Information).
To find evidence that supports our hypothesis, a supplemental
experiment was carried out. As shown in Fig. S5 of the Suppor-
ting Information, there were no NiS nanoparticle on the surface
of CdS nanowires synthesized at 200 °C for 12 h and 96 h, respec-
tively. 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 previous separate article [44]. So this obser-
vation suggests that the defects of the CdS nanowires are necessary
for synthesis of NiS NP/CdS NW heterostructures. The interfacial
structure is still stable even if the lattice mismatch is quite large,
which unique feature for this method is. In addition, further work
we are planning to do is extending the spectrum of the NiS NP/CdS
NW heterostructures and developing a method for the hierarchical
assembly of the nanoheterostructures.

Raman spectroscopy is a powerful tool for the investigation of
the doping concentration, lattice defect identification, and crys-
tal orientation properties of the materials. Fig. 8a displays the
room-temperature Raman spectra of the original CdS nanowires
and the NiS NP/CdS NW heterostructure synthesized for 24 h at
200 °C excited by the 514.5 nm line of an Ar+ laser. The peaks at 295
and 592 cm⁻¹ correspond to the first-order (1LO) and the second-
order (2LO) longitudinal optical phonon modes of CdS, which are
polarized in the x–z face and strongly coupled to the exciton along
c axis, respectively [45]. It is noticed that there are two obvious
vibrational modes at 298, and 582 cm⁻¹ for the NiS NP/CdS NW
heterostructure synthesized for 24 h at 200 °C, which is similar to
the literature data [46]. From the Raman spectra, it is interest-
ingly found that the 2LO mode is stronger than the 1LO mode.
Since the strength of exciton–phonon coupled in semiconductors
can be assessed by the intensity ratio of overtone of phonon to
the fundamental (ILO/I1LO). The large intensity ratio of the NW
nanostructures reflects a strong exciton–LO phonon because the
phonon was confined in the transverse directions and the transfer
of the elementary excitation (carriers, exciton, and phonon) in
the longitudinal direction. PL is also acquired to determine the optical
properties of the original CdS nanowires and the NiS NP/CdS
NW heterostructure synthesized for 24 h at 200 °C. Fig. 8b shows
PL spectrum of the original CdS nanowires and the NiS NP/CdS NW
heterostructure synthesized for 24 h at 200 °C with 325 nm laser
excitation under the room temperature. There are two strong emis-
sion peaks with maxima at 413 and 434 nm respectively for the NiS
NP/CdS NW heterostructure, which is also in agreement with the
literature data [45]. It displays three distinct emission bands that
are 405 nm, 459 nm and 502 nm shown in Fig. 8b. The appearance
of an emission peak at 405 nm as shown in Fig. 8b, whose blueshifts
can be ascribed to a high level transition in CdS semiconductor crys-
tallites. Similar band edge emission (459 nm) was also reported on
previous CdS nanowires [47]. The peak appeared around 502 nm
(2.47 eV). This is well known deep-level defect emissions from CdS,
which may be due to radiative recombination involving impurity.

Fig. 6. FESEM images of the product synthesized in different reaction solvents (a)
a mixture of 15 ml H2O and 25 ml ethanol; (b) a mixture of 25 ml H2O and 15 ml
ethanol; (c) 40 ml H2O and (d) TEM image of the product synthesized with 40 ml
H2O.
Fig. 7. A schematic diagram of the growth process of NiS nanoparticles on the surface of the CdS nanowires. (The scheme is for illustration purpose only; scale may vary according to each step.)

Fig. 8. Raman spectrum (a) and PL spectrum (b) of the original CdS nanowires and NiS NP/CdS NW heterostructure synthesized for 24 h at 200 °C, respectively.

and/or defect levels. The origin of this emission is CdS NW related as demonstrated by room-temperature photoluminescence excitation experiments of the other literature [47]. The above results reveal that when the size of the crystal is reduced to the nanoreigon, the atom arrangement inside the crystal lattice may change compared with that of the bulk materials, which would affect the vibrational modes. The significance of the method lies in the potential applicability of the approach to synthesizing other NW-based heterostructure sharing the same cation framework [48–50].

4. Conclusions

In summary, NiS nanoparticle/CdS nanowire heterostructures have been successfully synthesized by a convenient two-step chemical solution method. The heterostructure nanowires are composed of CdS nanowires and NiS nanoparticles grown on the nanowires surface. We have studied the effects of reaction conditions, such as reaction time, reaction temperature, and reaction solvent. The morphology evolution of NiS NP/CdS NW heterostructure has been observed depending on the reaction parameters. The novel catalyst-assisted growth mechanism of the NiS NP/CdS NW heterostructure has been proposed according to the experimental results. Their optical properties are also measured by Raman spectra and PL spectra. The NiS nanoparticle sensitized CdS NW shows highly potential applications, like being used as nanowire-based electrochemical power sources, such as electrode materials for lithium ion batteries and fuel cells, electrochromic films, electrochemical supercapacitors.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.mseb.2012.10.026.

References
