1-D coordination polymer template approach to CdS and HgS aligned-nanowire bundles

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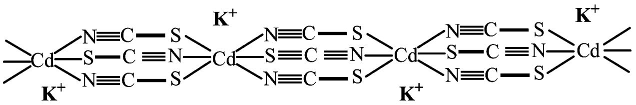
A 1D inorganic coordination polymer template route was firstly developed to synthesize metal sulfide aligned-nanowire bundles. Based on this strategy, CdS and HgS aligned-nanowire bundles with high yields were successfully prepared in a water system at room temperature using $KCd(NCS)_3$ as a soft template. The results revealed that the morphologies of the MS (M = Cd, Hg) aligned-nanowire bundles were uniform with lengths of several microns and the diameters of each single wire were *ca.* 10–30 nm and 60–80 nm for CdS and HgS, respectively.

The realization of technologically useful nanomaterials depends not only on the quality of the nanocrystals (*e.g.*, size and shape) and their surface chemistry, but also on their spatial orientation and arrangement.[1] Recent research on metal and semiconductor nanostructures is expanding rapidly into the assembly of nanoparticles in two (2-D) and three-dimensional (3-D) ordered superstructures.[1,2] A range of methods, including solvent evaporation of hydrophobic colloids,[1b] molecular cross-linking in colloidal aggregates,[3] and biotemplate-directed synthesis,[4] have been reported and they usually require the synthesis of initial nanoparticles with uniform size. One-dimensional (1-D) nanostructures are of particular interest because of their potential in fundamental research and industrial applications.[5] The synthesis of 1-D nanostructure arrays, especially the creation of aligned 1-D nanostructures is considered to be a definitive step towards the fabrication of advanced electronic and opto-electronic nanodevices.[6] Commonly, the aligned 1-D nanostructures usually require solid templates, such as porous alumina,[7] polymer nanotubes,[8] and patterned catalysts,[9] to control the directional growth. Recently, Zhao and co-workers[10] reported a self-supported pattern of radially aligned Ag_2S nanorods in a water system. However, the development of universal, mild, and effective routes for creating novel aligned 1-D nanostructures remains a key research challenge. In this paper, we demonstrate a new room-temperature approach to metal sulfide aligned-nanowire bundles in water system using a simple 1-D inorganic coordination polymer as soft template. Herein, as the example, we report the design strategy and synthesis of MS (M = Cd, Hg) aligned-nanowire bundles with high yields using $KCd(SCN)_3$ as template.

NCS^- anion and its related species such as NCO^-, $NCSe^-$, CN^-, N_3^-, *etc.*, a class of good linker ligands in supramolecular chemistry and coordination chemistry, have been extensively studied in the past several decades.[11] Their versatile coordination modes lead to numerous 1-D, 2-D and 3-D coordination polymers with novel structures. Among them, $Cd(SCN)_3^-$ anion has a 1-D structure and can form supramolecules with many ions such as Na^+, K^+, Me_4N^+, Et_4N^+ *etc.* in water solutions. Single crystal analyses[12,13] of these complexes revealed that adjacent Cd atoms are linked by bridging SCN^- ligands to form an infinite 1-D polymeric chain as follows:



It is thought that if metal sulfide nanoparticles form in a solution containing $Cd(SCN)_3^-$, they may adsorb to the electron-rich $Cd(SCN)_3^-$ chains and grow along the chain direction to form 1-D nanostructures. Because the chains in $KCd(SCN)_3$ are arranged along one direction,[12,13] nanowires formed in this supramolecular system may be directed along this direction to produce well-aligned nanowire arrays. Our experiments show that $Cd(SCN)_3^-$ functions well as the chain director in the formation of MS nanowire bundles.

Experimental

Step I: Formation of the $Cd(SCN)_3^-$ template

$CdCl\cdot 2.5H_2O$ (0.228 g, 1 mmol) was stirred with KSCN (0.292 g, 3 mmol) in water (100 mL) for 15 minutes at room temperature to yield a clear solution (pH = 6.5).

Step II: Synthesis of CdS nanowire bundles

Under stirring, $(NH_4)_2S$ (0.02 M, 50 mL) and $CdCl_2$ (0.02 M, 50 mL) solutions were added dropwise respectively at about the same speed (to keep the ratio of $NCS^-:Cd^{2+}$ at *ca.* 3) into the above solution during a 10 min time span. The mixture (pH = 6.5–7) was stirred for 2 days and filtered. The final product was washed with water thoroughly and then dried under vacuum.

Results and discussion

Based on the strategy, CdS nanowire bundles were prepared as an example. Fig. 1(a) shows the X-ray diffraction (XRD) pattern (2θ scan) of as-prepared CdS nanowires. All the peaks can

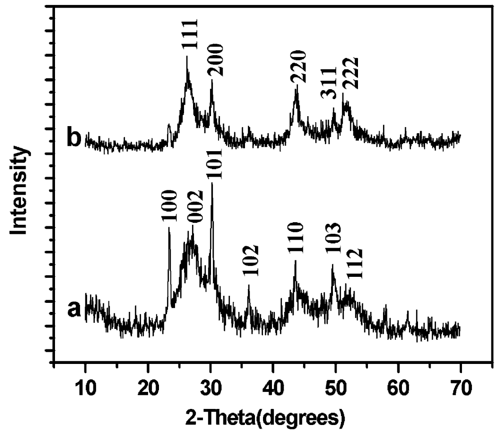


Fig. 1 The XRD patterns of as-prepared CdS (a) and HgS (b) aligned-nanowire bundles.

be indexed to hexagonal CdS with lattice constants comparable to the values of JCPDS 41-1049. Further observation can easily find that the (002) reflection is relatively broad, which is most probably related to the orientation of the CdS nanowires. From the half-width of the XRD peaks, the average nanobuilding unit size is estimated as 22 nm, based on the Scherrer equation ($D = 0.9\lambda/B\cos\theta$, where D is the crystal diameter, λ is the X-ray wavelength 1.541874 Å, and θ is the diffraction angle).

The structure and morphology of the samples were examined by transmission electron microscopy (TEM) and scanning electronic microanalyzer (SEM), and typical TEM and SEM images of the CdS nanowire bundles are given in Fig. 2a and 2b, from which we can see that the products are uniform CdS nanowires with a diameter of *ca.* 10–30 nm and length of several microns for each single wire. The rough surface of the nanowires indicates that they consist of primary crystallites.[14] The yield of CdS nanowire bundles is about 90%.

Fig. 3 shows the UV-Vis and photoluminescence (PL) spectra of as-prepared CdS nanowire-bundles. The nanowires exhibit a well-defined absorption feature at 452 nm, which is considerably blue-shifted relative to the bulk band gap for hexagonal CdS crystals (515 nm), indicating a quantum size effect.[15,16] Under photoluminescent excitation at 346 nm, the CdS nanowires emit blue light at 486.5 nm (Fig. 3, inset), with about 17 nm of blue shift compared with bulk CdS.[17] These features indicate the quantum-confined effects of the CdS nanowire bundles.

Based on the design strategy and the experimental results, a possible formation mechanism is proposed for the CdS nanowires (Scheme 1). With the addition of Cd^{2+} and S^{2-}, immediate solution supersaturation of CdS occurred due to its low solubility in the water system. Most of the CdS nanoparticles formed in the solution then attached to surrounding negatively charged coordination polymer chains. At the same time, the anionic $Cd(NCS)_3^-$ chain adsorbs selectively to positively charged crystal faces which directs the aggregation of the CdS building blocks along one principal axis to produce the chain-like aggregates. As the $Cd(NCS)_3^-$ template is a 1-D linear chain, these interactions are likely to be sufficient to offset the accompanying steric repulsion. The separating surfaces of adjacent particles may have been eliminated after repulsive interactions were overcome as the result of random, Brownian motion-driven particle collisions.[18] Jiggling of nanoparticles by Brownian motion may also allow adjacent particles to rotate to find the low-energy configuration represented by a coherent particle–particle interface. Rotation of particles within aggregates may also be driven by short-range interactions between adjacent surfaces.[19] Diffusion-controlled growth[20] of these CdS nanoparticles then occurs in the aggregates as the amorphous particles are in close proximity and the surface area reduces by particle fusion and structure rearrangement. In aggregation-based growth, reduction in surface free energy is achieved by complete removal of pairs of surfaces.[18] Because the director $Cd(SCN)_3^-$ chains were arranged along one direction and the distances between them were almost equal in this system, which should play a definitive role in the formation of aligned-nanowire bundles. The whole process of the formation of CdS nanowires can be summarized as follows: Primary nucleation → Oriented aggregation → Particle-particle diffusion → Aligned-growth.

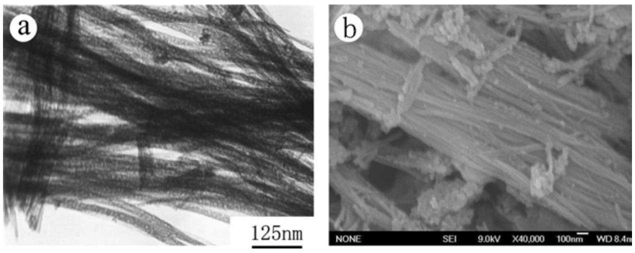


Fig. 2 TEM (a) and SEM (b) images of the as-prepared CdS aligned-nanowire bundles.

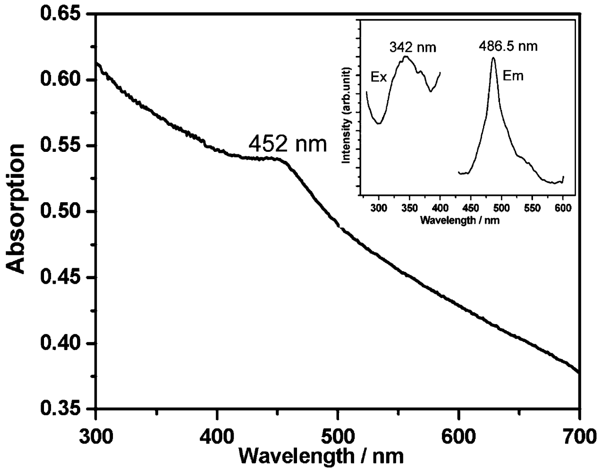
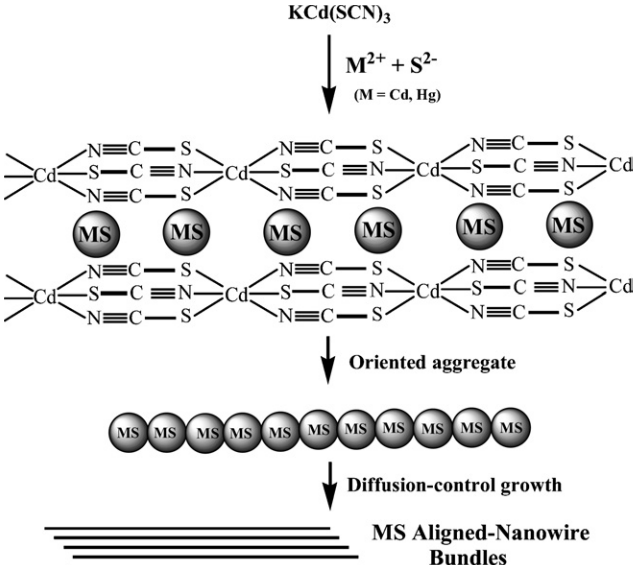


Fig. 3 The UV-Vis and photoluminescence (PL) spectra of as-prepared CdS aligned-nanowire bundles. Inset: PL spectrum.



Scheme 1 The possible formation mechanism of MS (M = Cd, Hg) aligned-nanowire bundles.

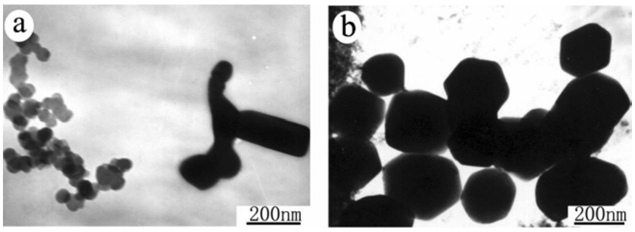


Fig. 4 TEM images of the CdS samples obtained in systems with different ratios of KNCS:$CdCl_2$. a) KNCS:$CdCl_2$ ratio of 4; b) KNCS:$CdCl_2$ ratio of 6.

To improve our understanding of the templating effects of the $Cd(SCN)_3^-$ chain, comparison experiments were carried out with different ratios of KSCN:$CdCl_2$ in the template formation step. Different $Cd(SCN)_x^{2-x}$ ($x = 3, 4, 6$) can form *via* changing the ratio of KSCN:$CdCl_2$ as 3, 4, 6 in the template formation step (step I) respectively. The experiment results indicate that the morphologies of the final CdS are controlled by the ratios of KSCN:$CdCl_2$ and the nanowires can be obtained only at the presence of $Cd(SCN)_3^-$ chains (KSCN:$CdCl_2$ = 3). When the ratio is *ca.* 4, the final product is a mixture of very short rods and connected spherical particles (Fig. 4a), whereas hexagonal particles can be obtained (Fig. 4b) when the ratio is 6 but the yield is not high and the particle size is sensitive to the addition speed of $(NH_4)_2S$ solution. These results can be well explained according to the coordination modes of NCS^-. If the KSCN:$CdCl_2$ ratio is 4 or 6 in the template formation step, the SCN^- commonly acts as a monodentate ligand to form discrete $Cd(SCN)_4^{2-}$ or $Cd(SCN)_6^{4-}$ anions, which do not exhibit the characteristic structure of a 1-D coordination polymer chain. Previous studies[12,13] also revealed that the $Cd(SCN)_3^-$ chain was formed only when the KSCN:$CdCl_2$ ratio was 3. The above comparison experiments support that no aligned-nanowire bundles can be obtained without the $Cd(SCN)_3^-$ template.

To further test this mechanism, HgS aligned-nanowire bundles were successfully synthesized as another example, using the same $Cd(SCN)_3^-$ coordination polymer chain as template. The preparation procedure is similar to that for CdS aligned-nanowire bundles but using $HgCl_2$ instead of $CdCl_2$ in step II. Because the K_{sp} of HgS is apparently lower than that of CdS, S^{2-} preferentially react with Hg^{2+} to form stable HgS and thus keep $Cd(SCN)_3^-$ chains intact after the addition of $HgCl_2$ and $(NH_4)_2S$ solutions. Stirred in solution, the new-formed HgS nanoparticles adsorb to the $Cd(SCN)_3^-$ chains and grow along the chain direction to produce an aligned-wire bundle morphology.

The XRD pattern (2θ scan) of as-prepared HgS is shown in Fig. 1b, in which the peaks can be indexed to cubic HgS with lattice constants comparable to the values of JCPDS 6-261. From the half-width of the XRD peaks, the average nano-building unit size is estimated as 70.7 nm, based on the Scherrer equation. The TEM and SEM studies revealed that the HgS nanowires were uniform with diameters of *ca.* 60–80 nm and lengths up to 8–10 μm for each single wire, as shown in Fig. 5a and Fig. 5b.

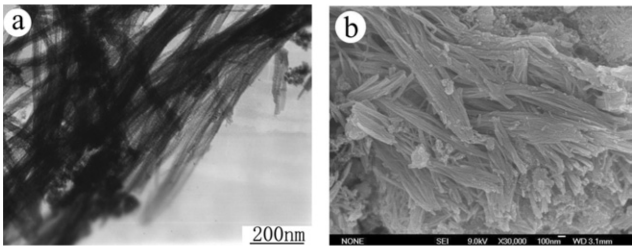


Fig. 5 TEM (a) and SEM (b) images of the HgS aligned-nanowire bundles under 48 hours of stirring in solution.

Attempt to synthesize ZnS aligned-nanowire bundles using the same method should be unsuccessful since the K_{sp} of ZnS is higher than that of CdS. The S^{2-} will preferentially react with Cd(II) in the $Cd(NCS)_3^-$ template to form relatively stable CdS rather than ZnS after the addition of Zn^{2+} and S^{2-}. As a result, the ratio of NCS^- to Cd^{2+} in this system must be changed due to the formation of CdS precipitate and the $Cd(NCS)_3^-$ chain template must collapse. Our experiment on the similar ZnS system only produces CdS particles, showing the above illation to be correct.

Conclusions

In conclusion, water soluble coordination polymers $KCd(NCS)_3$ with 1-D chain structure was firstly utilized as a soft template to synthesize CdS and HgS aligned-nanowire bundles at room temperature. Besides the simplicity compared with solid template and/or surfactant template methods, another apparent merit of this method is the easiness of purification of the final products since the $Cd(SCN)_3^-$ template can be easily washed out by excess water, while most of the surfactants or organic additives are difficult to remove from the nanomaterials. We believe that this strategy can be easily extended to the facile synthesis of other nanomaterials while NCS^- and similar bridging ligands such as $NCSe^-$, N_3^-, NCO^- can effectively link transition metal ions to form 1-D, 2-D, and 3-D structures.

Acknowledgements

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