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Synthesis of Semiconducting Functional Materials in Solution: From II-VI Semiconductor to Inorganic–Organic Hybrid Semiconductor Nanomaterials**

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This Feature Article provides a brief overview of the latest development and emerging new synthesis solution strategies for II–VI semiconducting nanomaterials and inorganic-organic semiconductor hybrid materials. Research on the synthesis of II–VI semiconductor nanomaterials and inorganic–organic hybrid semiconducting materials via solution strategies has made great progress in the past few years. A variety of II–VI semiconductor and a new family of [MQ(L)_{0.5}] (M = Mn, Zn, Cd; Q = S, Se, Te; L = diamine, deta) hybrid nanostructures can be generated using solution synthetic routes. Recent advances have demonstrated that the solution strategies in pure solvent and a mixed solvent can not only determine the crystal size, shape, composition, structure and assembly properties, but also the crystallization pathway, and act as a matrix for the formation of a variety of different II–VI semiconductor and hybrid nanocomposites with diverse morphologies. These II–VI semiconductor nanostructures and their hybrid nanocomposites display obvious quantum size effects, unique and tunable optical properties.

1. Introduction

Over the past few years, a lot of efforts have been made for the fabrication and control of size and shape of II–VI semiconductor nanostructures, because of their importance in catalysis, electronics, photonics, optoelectronics, sensing, and potential applications in nanodevices.^[1–7] The great interest in II–VI semiconductor nanomaterials stems from the fact that novel properties are acquired at this length scale and, equally important, that these properties change with their size or shape. Many methods have been developed to fabricate II–VI semiconductor nanostructures^[8] such as wet-chemical methods, including solvothermal/hydrothermal method^[9–20] and capping agent/surfactant assisted soft synthesis approach,^[1,21–29] sonochemical methods,^[30–32] templating methods,^[33–36] self-assembly oriented attachment growth,^[37–39] and chemical vapor deposition (CVD) method.^[40–47] On the other hand, hybrid structures consisted of semiconducting organic slabs

and strongly luminescent II–VI semiconductor nanostructures offer favorable perspectives through highly saturated, tunable optical properties, in combination with an easy process-ability from solution and low cost of precursors, which is of importance for high-tech applications such as hybrid organic–inorganic light-emitting diodes and solar cells.^[48–50] In recent years, novel nanostructures of functional II–VI semiconductor chalcogenides, including nanobelts, nanowires, nanosaws, nanocombs and nanowindmills have been synthesized using thermal evaporation method by Wang's group^[42,44,51–60] and Lee's group.^[61–66]

In contrast to the traditional thermal evaporation routes or chemical vapor deposition (CVD) method, even hard template approaches, solution chemistry based so-called “soft” approaches can provide an alternative, convenient, lower temperature, and environmentally friendly pathway for fabrication of advanced inorganic materials with desirable shapes and sizes,^[67] which do not rely on drastic conditions (i.e., high temperature, high pressure etc.), and the reaction was usually initiated under mild conditions or under natural conditions to turn down the heat for the synthesis of materials.^[68,69] Recent advances in soft synthesis of diverse nanomaterials have demonstrated that soft approaches are indeed promising for controllable synthesis of low dimensional nanostructures such as one-dimensional (1D) nanostructures of chalcogens and chalcogenides,^[70] and inorganic nanotubes.^[71]

In this Feature Article, we highlight the latest development and emerging new synthesis solution strategies for the syntheses of II–VI semiconducting nanomaterials and inorganic-organic hybrids semiconductor materials. Due to such a large number of publications in the field of synthesis of semiconductor

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nanomaterials and hybrid semiconducting materials, we have chosen just a small number of particularly representative and instructive literature examples to reflect some new synthetic strategies emerging recently in a pure solvent or in a mixed solvent, which determine the structural, compositional and morphological characteristics of the II–VI semiconductor and semiconducting inorganic-organic hybrids.

2. Synthesis of II-VI Semiconductor and Inorganic–Organic Hybrids in Solution

As one kind of solution-based chemical processes, hydrothermal process has been widely used for the synthesis of a huge range of solid-state compounds such as oxides, sulfides, halides,^[72–75] molecular zeolites, and other microporous phases, since the pioneering work from 1960s to 1980s. In recent years, this approach has been extended for synthesis of various kinds of functional oxides functional oxides,^[76] and non-oxide nanomaterials^[77] with specific shape and size, and even new molecules.^[78]

With the development of hydrothermal process, solvothermal process has emerged in recent years and has received great interests in synthetic chemistry and materials science field. The potential of this technique for preparative solid-state chemistry

has been intensively reviewed.^[79–82] In recent years, exploration of rational solution routes to nanocrystals has been extensively explored.^[76,77] Various non-oxide compound nanocrystals such as metal chalcogenides,^[10,13,14,16,17] phosphides,^[83] and metal nitrides can be synthesized.^[84] The results have demonstrated that the physico-chemical properties of a solvent has strong effects on the reactivity, shapes, sizes, and phases of the particles, since solvent properties such as polarity, viscosity, and softness will strongly influence the solubility and transport behavior of the precursors under solvothermal conditions.

2.1. Synthesis of Semiconductor Nanomaterials in Solution

2.1.1. Pure Solvent System

Solvothermal/hydrothermal approaches have served as powerful tools for synthesis of a variety of nanomaterials.^[84,85] One outstanding characteristic of solvothermal/hydrothermal strategies is that, especially when the starting precursors are exposed to special conditions, often in pure solvent, some quite unexpected reactions will take place, accompanied with the formation of nanoscopic morphologies and new phases, which cannot be achieved by traditional reactions. There are also some review articles provide a brief overview of the current



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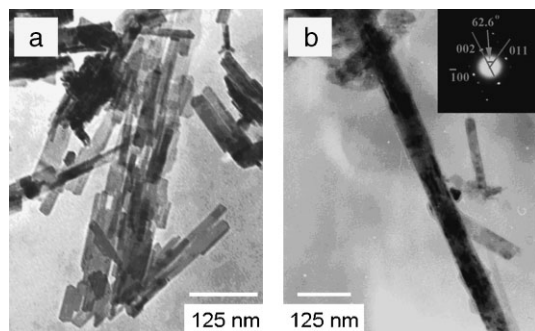


Figure 1. TEM images of a) CdSe nanorods and b) ZnSe nanorods synthesized in *n*-butylamine at 160 °C for 12 h, and at 220 °C for 12 h, respectively. Reprinted with permission from [16]. Copyright © 2002, Wiley-VCH.

studies on the synthesis methods for semiconductor nanomaterials by solvothermal approach,^[86–88] thus, these examples will be not included here.

Pure solvent process has been successfully applied to prepare II–VI semiconductor morphologies via different precursors with various synthesized conditions.^[9–12] It was found that solvent, temperature, and reactant have significant effect on crystal structure and particle size of II–VI semiconductor nanoparticles, including CdS nanorods, ZnSe nanorods, CdS nanowires.^[16,89–101] Furthermore, wurtzite ZnSe and CdSe nanorods can also be synthesized by using *n*-butylamine, i.e., a monodentate amine, as solvent (Fig. 1). The simple polyamines, which contain either polydentate or monodentate, can be elegantly used to act as “*shape controller*” for the synthesis of a variety of semiconductor nanocrystals.^[16] In addition, hydrothermal methods with use of water which is an environmentally friendly solvent, also have been shown to be effective in the architecturally controlled synthesis of semiconductor nanomaterials, for example, circular and hexagonal CdS rings (Fig. 2).^[102,103]

2.1.2. Mixed Solvent System

A solvent used in solvothermal process is usually composed of only one component, thus the reaction is relatively simple and it is easy to control with several controllable parameters such as solvents, temperature, and reaction time. However, whereas some experimental results showed that, in some cases, a mixed solvent, which is composed of two or more components, was much more effective for synthesis of low-dimensional nanostructures with uniform morphologies, or high aspect ratios and or novel nanoarchitectures. Comparatively, the properties of a mixed solvent can be tuned by changing the components and volume ratios, thereby some favorable synthetic conditions for the growth of low-dimensional nanostructures can be achieved. Hence, it should be very interesting and important to further develop an effective mixed solvents process for the synthesis of II–VI semiconductor nanostructures with high aspect ratio. Recent studies have shown that the use of a mixed solvent in some cases has an obvious advantage for the fabrication of ultralong

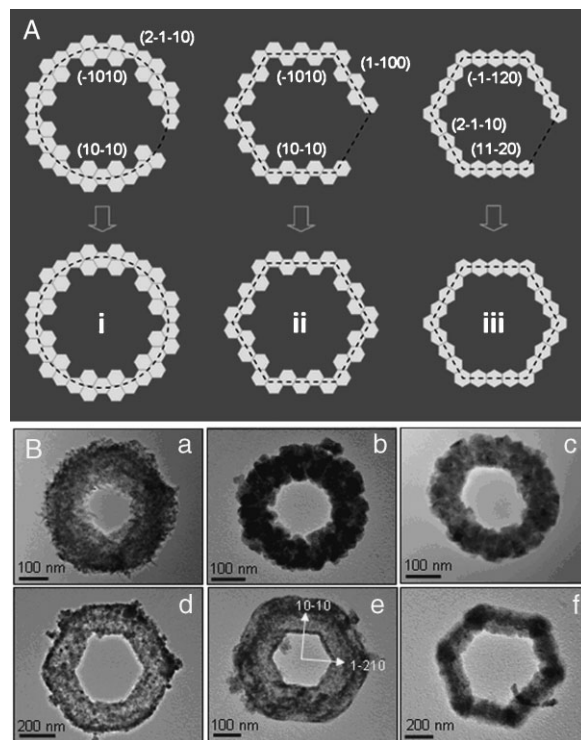


Figure 2. A) Schematic illustration of three novel self-tuning mechanisms for ring formation (viewed along the [0001] axis of the wurtzite CdS crystal). B) TEM images of the type (i) circular CdS rings (a–c) and of the type (ii) hexagonal CdS rings (d–f). Reprinted with permission from [102]. Copyright © 2005, American Chemical Society.

nanowires or nanoribbons of transition metal sulfides.^[104–106] Closed PbS nanowires with regular elliptic or parallelogrammic morphologies and nanorods were synthesized by a solvothermal approach in the presence of poly[*N*-(2-aminoethyl)acrylamide] in a mixed solvent of ethylenediamine and water (3:1, v/v) in the range of 110–150 °C.^[107] Liu *et al.* demonstrated a facile solution-phase method for the synthesis of single-crystal, high aspect ratio, and ultrathin nanowires of hexagonal-phase Cu₂S by thermal decomposition of Cu₂S-C-NEt₂ in a mixed surfactant solvent of dodecanethiol (DT) and oleic acid (OA) at 160 °C as shown in Figure 3.^[105] The growth of Cu₂S nanowires was believed to be attributed to the

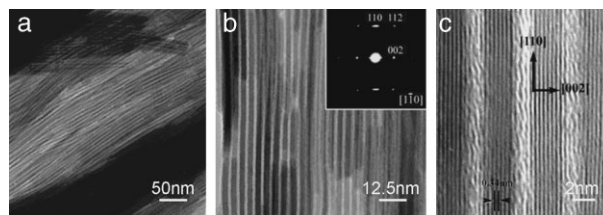


Figure 3. a) Low-magnification, b) high-magnification, and c) high-resolution TEM images of Cu₂S nanowire bundles. The black zone in (a) represents a denser region of the nanowires. The inset in (b) shows the SAED pattern recorded from a thin region. The lattice spacing of 0.34 nm corresponds to the (002) crystal plane of hexagonal-phase Cu₂S. Reprinted with permission from [105]. Copyright © 2005, American Chemical Society.

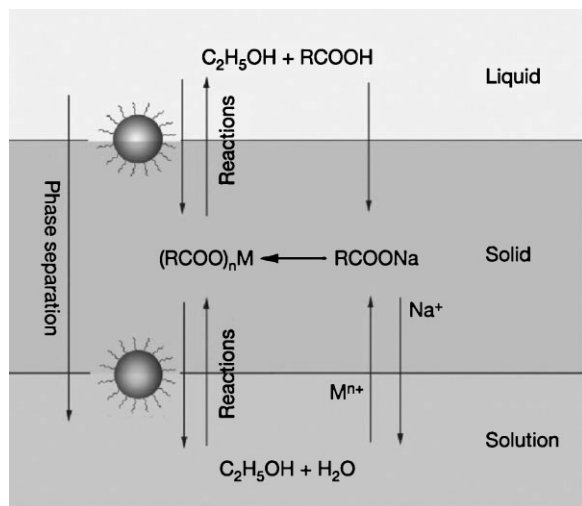


Figure 4. Scheme of liquid–solid–solution (LSS) phase transfer synthetic strategy. Reprint with permission from [108]. Copyright© 2005, Nature Publishing Group.

synergistic effect of the solvent OA and the adsorbent affinities of DT. Furthermore, uniform and high aspect ratio CdS nanowires with an average diameter of 25 nm and lengths of 20–40 μm can be solvothermally synthesized in a mixed solvent of ethylenediamine and dodecanethiol.^[106]

Li and co-workers have developed a liquid-solid-solution synthetic strategy to obtain various functional monodisperse nanocrystals (Fig. 4).^[108] In these procedures, water, ethanol and linoleic acid have been adopted as the continuous solution, II–VI semiconductor nanocrystals, including CdS, ZnS, CdSe, and ZnSe can be synthesized.^[109] The success of this method largely depends on the effective complexation of linoleate on the surfaces of nanocrystals in a water-ethanol mixed-solution system. In addition, there are also other reports to synthesize anisotropic II–VI semiconductor nanoparticles using mixed-surfactant systems for nanocrystal growth.^[110,111] Therefore, it is worth noting that mixed solvent process was an effective preparation route that can be applicable to the synthesis of low dimensional II–VI semiconductor nanostructures. On the other hand, these reported synthesis routes almost are two-phase or three heterogeneous solution as well as these reactions are determined by their interface.

Recently, a series of mixed homogeneous solvent reaction systems, such as binary mixed solvents of diethylenetriamine (DETA) and deionized water, has been explored to synthesize various morphologies of II–VI semiconductor nanostructures.^[112–114] Uniform flexible wurtzite ZnS nanobelts decorated with a ZnS-diethylenetriamine (DETA) hybrid intermediate can be prepared by a mild solvothermal reaction using a mixed solvent made of diethylenetriamine (DETA) and water (Fig. 5).^[112]

Complex wurtzite ZnSe microspheres with hierarchical fractal structure (Fig. 6), which show strong quantum size effect, can also be simply prepared by a mild solvothermal reaction in a diethylenetriamine (DETA) – deionized water

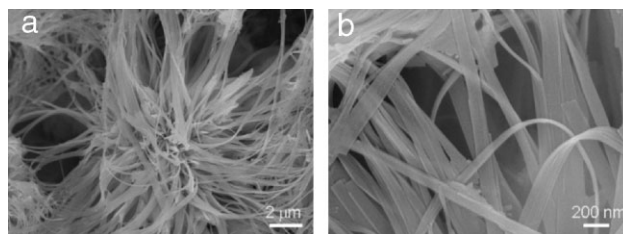


Figure 5. a), b) FE-SEM images of the ZnS nanobelts prepared at 180 °C for 12 h, $V_{\text{DETA}}:V_{\text{DIW}} = 2.5:1$. Reprinted with permission from [112]. Copyright © 2005, Wiley-VCH.

(DIW) binary solution.^[113] Moreover, wurtzite CdS and CdSe nanostructures with complex morphologies such as urchin-like CdS nanoflowers, branched nanowires and fractal nanotrees, which exhibit effective photocatalytic performance in the photodegradation of *acid fuchsine* at ambient temperature, can also be synthesized via a facile solvothermal approach in a similar mixed solution.^[114] Furthermore, this solvothermal reaction in a mixed binary solvent system can be extended for the synthesis of well-defined wurtzite ZnSe ultrathin nanobelts,^[115] wurtzite ZnS architectural structures,^[116] and various CdS nanostructures.^[117]

2.1.3. Capping Agents/Surfactant Assisted Soft Synthesis

Capping agents/surfactant assisted synthesis has been widely explored for fabrication of nanorods, nanotubes, and more complex nanostructures. In their original creative work, Murray et al. reported the synthesis of high quality CdSe nanoparticles based on the high-temperature nucleation and growth of nanoparticles from organometallic precursors.^[21] By injecting a solution of dimethylcadmium and selenium in

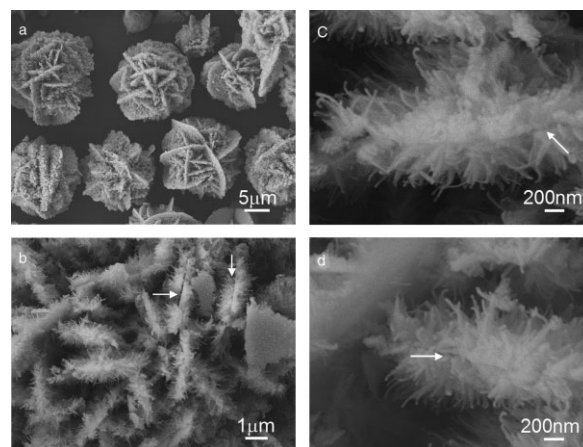


Figure 6. SEM images of the products prepared by the solvothermal reaction at 180 °C for 12 hours, $V_{\text{DETA}}:V_{\text{DIW}} = 1:3$. a) A general view image, and b), c), and d) the higher magnification images, showing the detailed surfaces of the fractal ZnSe microspheres. White arrows in b) indicate the twinning nanosheets with a gap in the middle part of the microsheets. White arrows in c) and d) indicate that the nanofibers are standing on the microsheets. Reprinted with permission from [113]. Copyright © 2006, Wiley-VCH.

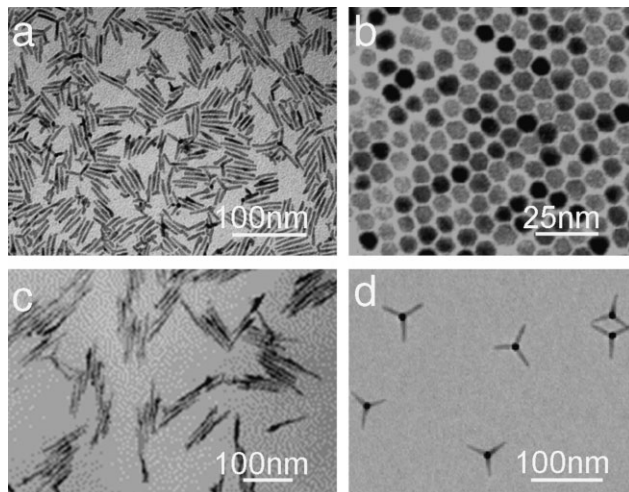


Figure 7. a) TEM micrograph of CdSe nanorods. Reprinted with permission from [22]. Copyright © 2000, American Chemical Society. b) TEM micrograph of CdSe quantum dots. Reprinted with permission from [1]. Copyright © 2000, Nature publishing group. c) TEM micrograph of CdSe tadpole-shaped nanocrystals. Reprinted with permission from [23]. Copyright © 2002, American Chemical Society. d) TEM images of CdSe/CdS nanotetrapods with different lengths of the arms grown from 4.0 nm zb-CdSe seeds. Reprinted with permission from [118]. Copyright © 2007, American Chemical Society.

tributylphosphine into a mixture of hexylphosphonic acid (HPA) and trioctylphosphine oxide (TOPO) at 340–360 °C, uniform CdSe nanorods and quantum dots can be selectively synthesized (Fig. 7a and b).^[1,22] Peng and Alivisatos *et al.* systematically studied the shape evolution of CdSe nanoparticles of various other morphologies, including arrows, pine trees, teardrops, and tetrapods *etc* (Fig. 7c).^[1,22–29] They have even demonstrated that seeded growth of nanocrystals offers a convenient way to design CdSe/CdTe, CdSe/CdS nanoheterostructures with complex shapes and morphologies by changing the crystalline structure of the seed (Fig. 7d).^[28,118] Besides the reports from these groups, there are reports of several other studies to synthesize II–VI semiconductor nanoparticles using this capping surfactant soft approach.^[93,119,120]

2.2. Synthesis of Inorganic–Organic Semiconductor Hybrids

2.2.1. II–VI Inorganic–Organic Hybrids $MQ(L)_{0.5}$ System

Recent development demonstrates that unique hybrid II–VI semiconductors can be synthesized by incorporating segments (e.g., slab, chain) of a II–VI semiconductor MQ and organic spacers (*L*) in one structure via coordinate or covalent bonds (Fig. 8).^[121–124]

While possessing uniform and periodic crystal structures, the resultant three-

dimensional networks $[MQ(L)_{0.5}]$ (*M* = Mn, Zn, Cd; *Q* = S, Se, Te; *L* = diamine, deta) hybrid structures, exhibit a very large blue shift in their optical adsorption edge due to a strong quantum confinement effect (QCE) induced by the internal sub-nanostructures.^[17,18,121] These compounds exhibit significantly enhanced electronic and optical properties,^[121,125–130] including tunable band gap as a result of strong quantum confinement effect (blue shifts up to ~2 eV) and high band-edge absorption (e.g., 10–20 times higher in 3D-ZnTe(en)_{0.5} compared to bulk GaAs) (Fig. 9).^[126] Theoretical calculations on 3D-ZnTe(en)_{1/2}^[127] and 3D-ZnSe(en)_{1/2}^[128] using density functional theory within local density approximation (LDA) as well as optical measurements^[125] have verified that the observed large blue shifts in the band-edge absorption are primarily due to the strong quantum confinement effect in the II–VI semiconductor fragments of these hybrid materials. Especially, a new series of inorganic-organic II–VI hybrid semiconductors with a general formula of 2D-[(M₂Q₂)(L)] (*M* = Zn, Cd; *Q* = S, Se; and *L* = ea, pa, ba, aa, and ha) have been designed and synthesized by Li *et al.*^[131] These compounds are composed of double atomic layers of M₂Q₂ separated by organic monoamines. Optical absorption experiments show that all double-layer compounds exhibit a blue shift in their absorption edge (0.6–1.2 eV), due to the quantum confinement effect. However, the extent of such a blue shift is significantly less than that of the single-layer 2D-[(MQ)(L)] systems (1.0–2.0 eV) as a result of the difference in their layer thickness.^[131] These unique family of II–VI based nanostructured inorganic-organic hybrid semiconductors exhibit nearly zero uniaxial thermal expansion in the temperature range of 95–295 K.^[132]

Recently, uniform and well-defined [ZnSe](DETA)_{0.5} hybrid nanobelts have been synthesized by solvothermal reaction in a mixed solvent system (Fig. 10).^[133] It has been realized for the first time that such [ZnSe](DETA)_{0.5} nanobelts with a band gap 4.6 eV can be synthesized via tuning the composition of a ternary solution made of diethylenetriamine (DETA), hydrazine hydrate, and deionized water. The suitable amount of hydrazine hydrate is essential for the formation of elegant and uniform [ZnSe](DETA)_{0.5} nanobelts. This synth-

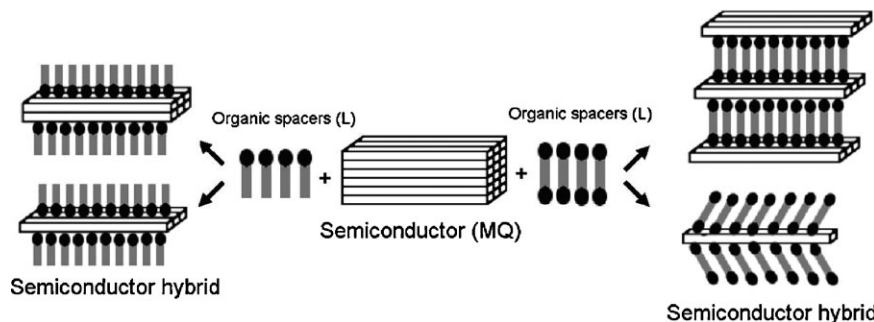


Figure 8. Illustration of the structure of unique hybrid II–VI semiconductors. Reprinted and modified with permission from [124]. Copyright © 2003, American Chemical Society. (Courtesy of Prof. Jing Li in Rutgers University and Prof. Xiaoying Huang in Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences for their allowing to modify this plot).

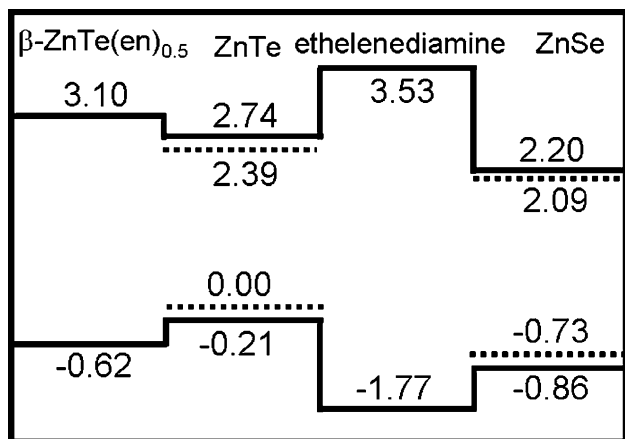


Figure 9. Energy alignments of the conduction and valence band edges for ZnTe, ZnSe, ethylenediamine, and ZnTe(en)_{0.5}. The dashed and solid lines in the inorganic sections are, respectively, for the bulk and isolated slab. The conduction band energies have been adjusted from the LDA values to the appropriate experimental values. Reprinted with permission from [126]. Copyright © 2006, American Physical Society.

esis route in mixed solvent system can even be extended to synthesize of other new nanostructures such as [Fe₁₈S₂₅](TETAH)₁₄ nanoribbons (TETA = protonated triethylenetriamine).^[134]

One-dimensional (1D) MQ(L)_{0.5} nanostructures based on rods, wires, belts, and tubes, as well as semiconductor nanocrystals, have also witnessed an exponential growth of activities and become the focus of intensive research. In comparison with quantum dots and wells, the advancement of 1D MQ(L)_{0.5} hybrid materials has been slow until very recently, how to develop straightforward and low-cost practical routes for preparation of large quantities of 1D MQ(L)_{0.5} hybrid nanostructures still requires great ingenuity.

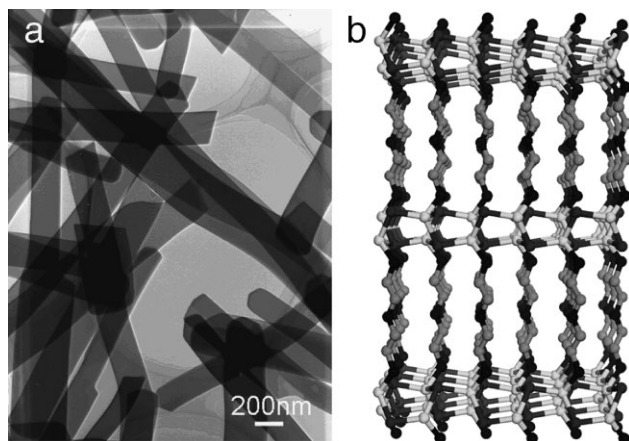


Figure 10. a) TEM images of [ZnSe](DETA)_{0.5} nanobelts prepared in a mixed solution with a volume ratio of V_{N₂H₄·H₂O}:V_{DETA}:V_{H₂O} = 5:14:16. b) Schematic illustration of [ZnSe](DETA)_{0.5} structure. Reprinted with permission from [133]. Copyright © 2005, Wiley-VCH.

2.2.2. Mesostuctured II-VI Inorganic–Organic Hybrids

Previously, Efrima et al. describes a convenient method to produce highly uniform and extremely thin ZnS nanorods and nanowires that self-assemble already in solution into crystalline-like superstructures.^[135] EI-Shall et al. also report a simple, versatile, and rapid (1–3 min) microwave synthetic method of ultra narrow, highly uniform, and confined high quality semiconductor rods and wires, where supercrystalline assembly and alignment as well as confinement have a major effect on their optical and spectroscopic properties (Fig. 11).^[136]

Recently, mesostructured wurtzite ZnS nanowire bundles/amine nanocomposites with remarkable quantum size effects have been synthesized by a mild solution reaction with use of different amine such as *n*-butylamine, ethylamine, and tetraethylene pentamine.^[137] Figure 12A shows the small angle x-ray diffraction of the as-prepared products obtained in *n*-butylamine at different temperature. From the room temperature to 160 °C, obvious diffraction peaks located at low angles which can be indexed as (001), (002), (003) reflections were observed, revealing the formation of mesostructures. The nanowires with well-defined lattice structures are packed along *c* axis and are possibly linked by a layer of amine molecules. With increasing temperature from 80 °C to 160 °C, the diffraction peaks become stronger and the *d*-spacing of the (001) diffractions linearly increased with temperature as shown in Figure 12B. However, the diffraction peaks totally collapsed when the temperature went up to 180 °C for prolonging reaction time up to 48 hours as shown in curve f in Figure 12A, suggesting that the structures already become disordered. This temperature dependent disordering behavior is quite similar to that in a previous report on the

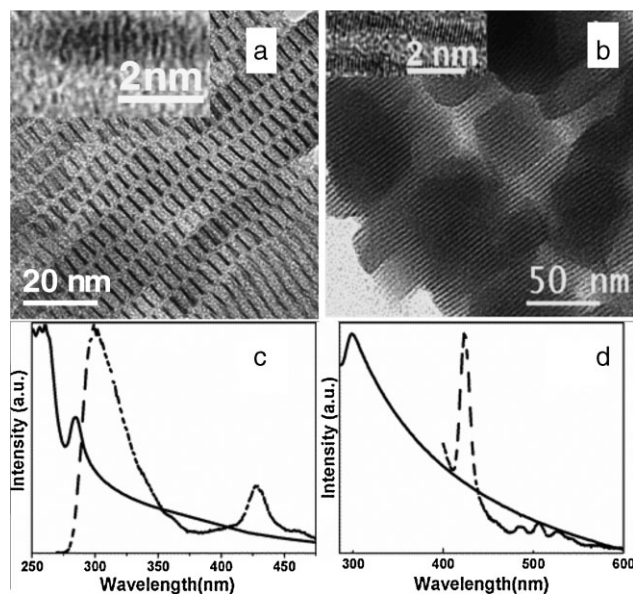


Figure 11. TEM of ZnS a) rods, b) wires (Higher resolution images are shown in the insets) and room temperature UV-visible absorption (solid lines) and PL (dotted lines) of (a) ZnS rods, (b) ZnSe wires. Reprinted with permission from [136]. Copyright © 2006, American Chemical Society.

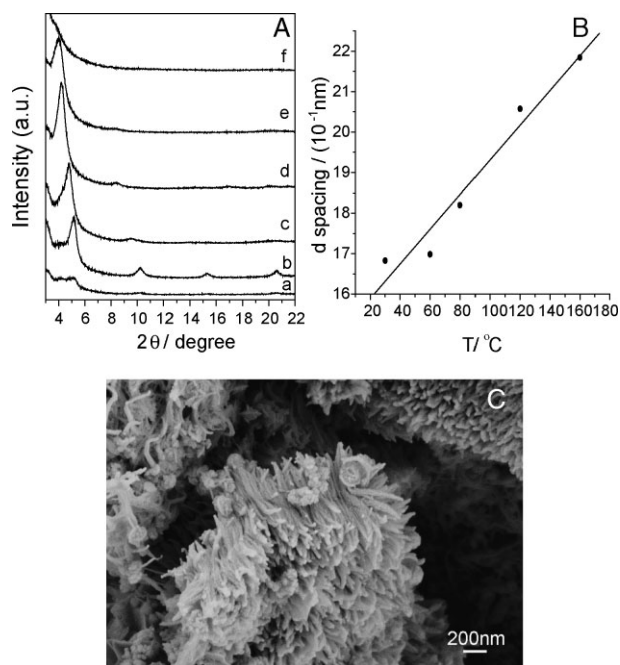


Figure 12. A) Small-angle x-ray diffraction patterns of the wurtzite ZnS nanowires/amine composites obtained with 50 mL *n*-butylamine as structure-directing agents at different temperature. a) 30 °C, Na₂S · 9H₂O, O₂, 12 h. b) 60 °C, Na₂S · 9H₂O, 12 h. c) 80 °C, CS(NH₂)₂, 12 h. d) 120 °C, CS(NH₂)₂, 12 h. e) 160 °C, CS(NH₂)₂, 12 h. f) 180 °C, CS(NH₂)₂, 48 h. B) Plot of the *d*-spacing versus temperature (30–160 °C) in *n*-butylamine system. C) SEM image of ordered arrays of ZnS nanowires prepared in *n*-butylamine at 180 °C after reaction for 12 h. Reprinted with permission from [137]. Copyright © 2007, Wiley-VCH.

mesostructure of tin sulfide-alkylamine by Ozin et al.^[138] However, this unique characteristic of inorganic component with controllable crystallinity in mesostructures is different from the previous metal sulfide mesostructures containing amorphous inorganic component only previously. The results demonstrated that increasing the reaction temperature and or dispersing in acetic acid or sodium hydroxide can destroy the periodic structure and lead to the formation of individual wurtzite nanowires and their aggregates^[137] Both the nanowires/amine nanocomposites and the individual wurtzite nanowires display obvious quantum size effects.^[137]

Other nanocomposites ZnS/CHA (CHA = cyclohexylamine) have also been synthesized via a solvothermal method using CHA as solvent, which yielded uniform and ultralong nanowires with widths of 100–1000 nm and lengths of 5–20 μm.^[139]

2.2.3. Possible Other Hybrid System

Over the past years, an exciting and promising area of materials research that deals with synthesis, characterization, and modification of organic-inorganic hybrid composite materials is rapidly emerging.^[140–148] Hybrid organic-inorganic nanomaterials are of high interest because of the possibility of combining the best properties of the two components and have

been receiving intensive attention. The concept is attractive because it enables the fabrication of materials with new or improved properties by mixing multiple constituents and exploiting synergistic effects. Combining organic materials and inorganic semiconductors into organic-inorganic “hybrids” may thus integrate the favorable properties of *both* classes of materials, forming new and interesting hybrid semiconductors. These hybrid materials are likely to combine the electronic, magnetic, and optical properties, rigidity, and thermal stability of inorganic frameworks with the structural diversity, flexibility, processability, and other preferred properties (e.g., light weight) of organic molecules to further enhance and improve their functionalities and performance.^[149–152] Equally intriguing is the possibility to design functional materials^[153] with mechanical and thermal characteristics,^[154,155] unique optical,^[156] or electronic properties,^[157] catalytic activity^[158] or selective permeation.^[159]

Hybrid structures composed of semiconducting organic polymers and strongly luminescent semiconductor nanocrystals also offer favorable perspectives through highly saturated, tunable emission and absorption, in combination with an easy processability from solution and low materials cost, which is of importance for several high-tech applications such as hybrid organic-inorganic light-emitting diodes and solar cells.^[160–162] The incorporation of nanoparticles into polymers is a design approach that is used in many cases of materials science.^[163,164]

On the other hands, Nurmikko et al. describe a novel hybrid organic/inorganic nanocomposite in which alternating monolayers of J-aggregates of cyanine dye and crystalline semiconductor quantum dots are grown by a layer-by-layer self-assembly technique.^[165] They demonstrate near-field photon-mediated coupling of vastly dissimilar optical excitations in the two materials that can reach efficiencies of up to 98% at room temperature. In addition, some new organic-inorganic hybrid semiconductors based on metal halide units,^[166] or novel semiconductor-dye hybrids^[167] with unique electronic and optical properties also shows special structural and optical related properties.

Another field of the most interesting combination for hybrid materials is that of metal (or semiconductor) and semiconductor materials. Banin et al. report on selective growth of metal tips onto semiconductor elongated nanocrystals.^[168] The growth of the metal presents interesting fundamental questions concerning the chemistry of the process, and with regards to the nature of the unique metal-semiconductor nanoscale interface in the particle. Furthermore, they also show a novel asymmetric metal-semiconductor (Au-CdSe) hybrid nanostructure.^[169,170] This unique structure was preceded by the symmetric structure. Buhro et al. also report heterojunction formation in ZnSe-ZnTe quantum wires grown by the solution-liquid-solid (SLS) mechanism.^[171] Park et al. have successfully demonstrated an SLS approach for making CdS and CdSe nanorods and nanorod heterostructures with controlled sequences of these two materials.^[172] Bawendi et al. also report synthesis of monodisperse samples of CdSe nanorods with CdTe tips with using the mechanism of rod

nucleated growth to form CdSe/CdTe nanobarells, which is particularly well suitable for internal exciton separation and carrier transport.^[173]

3. Conclusion and Outlook

In summary, recent advances have demonstrated that solution strategies either in pure solvent or in mixed solvent can not only determine the crystal size, shape, composition, structure and assembly properties, but also the crystallization pathway, and act as a matrix for the formation of a variety of different II–VI semiconductor and hybrid nanocomposites with various sizes and diverse morphologies.

These II–VI semiconductor nanostructures and hybrid nanocomposites display obvious quantum size effects and their optical properties could be finely tuned. Especially, the reported mixed solvent approach offers an elegant and effective alternative for tuning semiconductor electronic and optical properties, and it would be a general and highly desirable method for the synthesis of these highly technological important II–VI semiconductor and hybrid nanocomposites, even can be rapidly extended to prepare other transition metal semiconductor and hybrid nanocomposites. However, it has to be pointed out that the soft chemistry reaction in a solvent or in a mixed solvent is just at its infancy and far beyond its maturity even though some progresses have been achieved.

Further systematic studies and interdisciplinary efforts are definitely needed to explore the physico-chemical properties of a mixed solvent and the synergistic effect of solvents on the shape, phases, and the detailed nanostructures in these reaction media in order to rationally design and synthesize functional micro-/nanostructured materials with high quality and new properties.

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