

Microwave Synthesis of Highly Aligned Ultra Narrow Semiconductor Rods and Wires

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One-dimensional nanostructures (rods, wires, tubes, ribbons) have recently attracted considerable attention. These nanostructures represent ideal systems for dimension-dependent optical, electrical, and mechanical properties and are expected to play an important role as building blocks in devices and processes, such as light-emitting diodes, solar cells, single electron transistors, lasers, and biological labels.^{1,2} Many modern methods based on physical and chemical approaches have been developed for the synthesis of controlled size and shape of one-dimensional nanostructures, including, for example, vapor–liquid–solid and the solution–liquid–solid processes, solvothermal, template-assisted, kinetic growth control, self-assembly, and thermolysis of a single-source precursor in ligating solvents.³ In addition to these methods, microwave irradiation (MWI) offers great advantages as the simplest and fastest procedure since selective dielectric heating, due to the difference in the solvent and reactant dielectric constants, can provide significant enhancement in reaction rates. Furthermore, MWI methods are unique in providing scaled-up processes without suffering thermal gradient effects, thus leading to a potentially industrially important advancement in the large-scale synthesis of nanomaterials. Although MWI methods have been demonstrated for the synthesis of a variety of high quality, nearly monodisperse semiconductor nanoparticles,⁴ there are very few reports on the synthesis of one-dimensional semiconductors by MWI.^{3j,k,4} However, all the reported one-dimensional semiconductor nanostructures are wider than the Bohr radius, which limits the expected quantum-confinement effects.

Here we report the development of a rapid microwave-assisted methodology for the synthesis of organically passivated uniform, ultra narrow, crystalline and highly aligned rods and wires of ZnS, ZnSe ($1\text{--}1.2 \times 5\text{--}6$ nm rods, $1\text{--}1.2 \times >350$ nm wires), CdS, and CdSe ($3.5 \times >20$ nm rods, dipods, tripods etc.). We also demonstrate the flexibility of the current approach in controlling the shape and assembly of the semiconductor nanostructures. The stepwise formation of the nanowires from small spherical nuclei to short aligned rods to long assemblies of nanowires is observed by varying the MWI reaction times from 30 to 60 s to 1–2 min to >3 min, respectively. Quantum-confinement effects are manifested in the optical absorption and the photoluminescence (PL) properties of the 1D nanostructures. The uniformity of the rods and the wires is demonstrated by their spontaneous assembly into highly ordered 2D supercrystals.

For the synthesis of sulfides, a single precursor, metal ethyl xanthate,⁵ was used, and for selenides, a mixture of metal acetate and selenourea precursors was used. A mixture of ligating solvents of alkylamines ($\text{C}_6\text{--C}_{18}$) and *N,N*-dimethylformamide (DMF) was used to avoid inhomogeneity of the solution due to the poor solubility of selenourea in alkylamines. To generalize the procedure, the DMF and amine mixture was used also for the synthesis of sulfides. In a typical reaction, 1.14×10^{-2} mol of metal xanthate or a mixture of metal acetate (1.365×10^{-3} mol) and selenourea

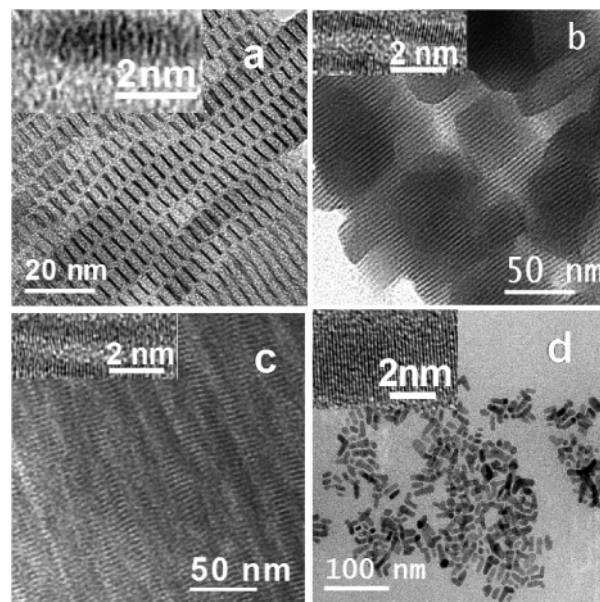


Figure 1. TEM of ZnS (a) rods, (b) wires, (c) ZnSe wires, and (d) CdSe rods. Higher resolution images are shown in the insets.

(1.365×10^{-3} mol) was added into a mixture of 0.0124 mol of an aliphatic amine (hexyl or octadecylamine) and 2 mL of DMF, resulting in a clear solution (for long-chain amines, heating in a water bath to $\sim 70^\circ\text{C}$ was necessary). The resulting solution was placed in a conventional microwave oven with the power set to 60% of 650 W and operated in 30 s cycles (on for 10 s, off and stirring for 20 s) for reaction times that varied from 30 s to 3 min. After microwaving, the synthesized rods and wires were flocculated with methanol, centrifuged, and redispersed in a hydrophobic solvent, such as toluene. For all the semiconductors studied, very small spherical or little elongated particles were produced in 30–60 s. In 1–2 min, rods were formed, and in 3 min, ZnS and ZnSe produced wires, whereas for CdS and CdSe, no morphological changes were observed. It is important to note that the relative amounts of rods versus wires can be controlled by the microwaving time, concentration of the reagents, and the chain length of passivating amines. No postsynthesis size-selective precipitation is required.

Figure 1a displays a TEM micrograph of the as-prepared fully developed ZnS rods, with an average diameter of 1 nm and an average length of 5 ± 0.05 nm synthesized in octadecylamine (ODA) with a microwave reaction time of 2 min. The nanorods self-assemble into large arrays of highly ordered 2D supercrystals. At longer reaction times (3 min), wires spontaneously form (Figure 1b) with the same narrow widths as the rods and lengths of more than 350 nm (an aspect ratio of ~ 350).

ZnSe also showed similar behavior; within 2 min of microwave reaction time in ODA, ZnSe nanorods self-assembled into large

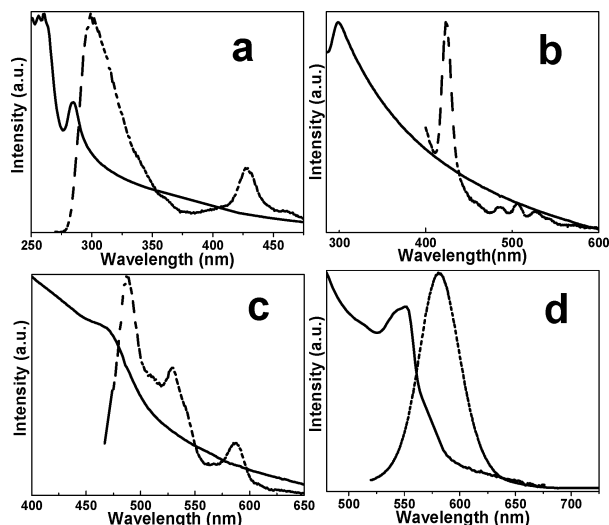


Figure 2. Room temperature UV–vis absorption (solid lines) and PL (dotted lines) of (a) ZnS rods, (b) ZnSe wires, (c) CdS rods, and (d) CdSe rods.

regions of highly ordered 2D supercrystals with 1.2 nm width and 6 nm length, and after 3 min of reaction time, wires were formed (Figure 1c) with the same narrow widths as the rods and lengths of more than 450 nm. It is significant to note that the wires assemble into almost micron long arrays of strictly parallel wires. The wire–wire lateral distance is the same as the rod–rod distance (determined by the chain length of the amine capping agent). CdS and CdSe show similar behavior after 2–3 min microwave reaction time; a mixture of rods, dipods, and tripods was obtained (Figure 1d CdSe, and for CdS, see Supporting Information) with almost the same width (3.5 nm for CdS and 4.5 nm for CdSe) and more than 20 nm in length.

Higher resolution TEM images of individual rods and wires (insets Figure 1a–d) show lattice planes, consistent with wurtzite structure of the individual sulfides and selenides for the 002 planes. The rods are growing through the crystallographic *c*-axis of the wurtzite structure, which is parallel to the major axis of the rods. The growth of the rods is controlled by the fast growth rate along the basal facets compared to the lateral facets. The proposed mechanism involves the adsorption of the amines on both of the long side walls of the rods and only on one side of the head-to-tail spacing between the nanorod tips.^{3d,i} This mechanism implies that the growth rates of the rods are significantly faster than the adsorption of the amines on the rods. The difference in the binding energy of the amines to the different facets of the rod can result in exclusive adsorption of the amines on the metal end, which leads to anisotropic growth from the S or the Se terminal.⁶ The rods grow from nearly spherical to elongated nuclei (Supporting Information), and the fully grown rods may be attached together to form long wires probably via an oriented attachment mechanism similar to that proposed by Penn and Banfield.⁷

The wurtzite structures of all compositions are further supported by X-ray powder diffractions (XRD). Furthermore, small angle XRD spectra verify the assembly of the rods into ordered 2D supercrystals (Supporting Information).

Figure 2 displays the UV–vis and the PL spectra of the synthesized rods and wires dispersed in dichloromethane. The ZnS and ZnSe rods gave almost identical UV–vis spectra, indicating that the (narrow) width is the major controlling dimension, as expected.

The observed absorption thresholds at 300, 390, 485, and 572 nm with distinct peaks at 285, 301, 465, and 551 nm for ZnS, ZnSe,

CdS, and CdSe, respectively, are blue-shifted compared to reported bulk band gaps of ZnS (3.6 eV), ZnSe (2.6–2.8 eV), CdS (2.5 eV), and CdSe (1.84 eV), thus confirming the high degree of quantum confinement in the synthesized rods and wires. The observed spectral features for the rods and wires are significantly sharper and blue-shifted to a greater extent relative to the corresponding bulk semiconductor. These features are attributed to high uniformity and ultra narrow width of the rods and wires.

The room temperature PL spectra of all nanowires, as well as rods, show strong, narrow, and blue-shifted (compared to the bulk) main band gap emission at 300, 424, 487, and 580 nm for ZnS, ZnSe, CdS, and CdSe, respectively, which again confirms the high degrees of quantum confinement and uniformity of the rods and wires. For CdS, the peak at 530 nm is most probably due to the formation of trace amounts of large spherical particles. Other low-energy emission bands at 428 nm for ZnS; 486, 505, and 528 nm for ZnSe; and 586 nm for CdS are attributed to surface emissions and possible metal vacancies. Detailed PL characterizations are currently under investigation.

In conclusion, we 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. Moreover, the method is general, applies to a large variety of metal sulfides and selenides, and provides a scalable and flexible approach for device applications.

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Supporting Information Available: TEM of CdS nanorods, XEM of intermediate more spherical and elongated nuclei, XRD of all four compositions, and small angle XRD of ZnS nanorods. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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