Communication

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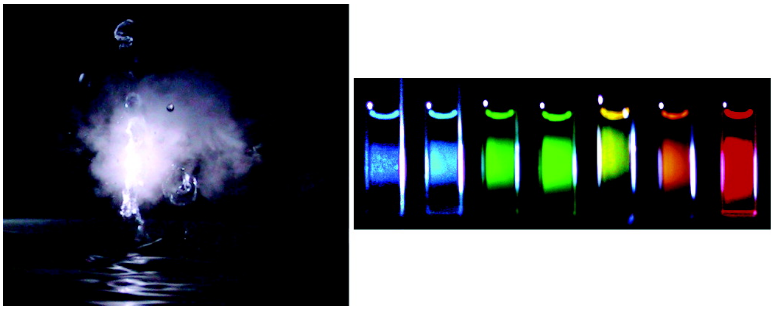

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Chemical Aerosol Flow Synthesis of Semiconductor Nanoparticles

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Various techniques have been used for the synthesis of semiconductor nanocrystals (i.e., quantum dots): arrested precipitation in solutions, synthesis in structured media, high-temperature pyrolysis, sonochemical, and radiolytic methods among others; each of these approaches, however, has significant limitations.[1] The synthesis and properties of cadmium selenide quantum dots are arguably the best studied of all nanomaterials (due to its tunable visible fluorescence and potential electronic and biomedical applications). Despite the elegant synthetic work of Bawendi,[2] Alivisatos,[3] and Peng[4] and their co-workers, the development of new synthetic methods that are able to produce well-defined materials of nanometer size (especially in a continuous scalable process) remains a serious challenge. We report here a continuous chemical aerosol flow synthesis (CAFS) for the production of semiconductor nanocrystals. A dense mist is created by ultrasonic nebulization of solutions of high boiling point liquids containing appropriate precursors. The mist is carried by an Ar gas stream into a heated tube furnace, and the synthesis proceeds in isolated microscale liquid-phase reactors (i.e., submicron droplets).

The conventional synthesis of quantum dots uses large volumes of high-boiling organic solvents at high temperatures into which aggressive and toxic chemicals must be injected quickly and reproducibly. Peng and co-workers[4] have explored the effects of precursor choice, Se/Cd ratio, as well as the length of reaction time in the traditional solution pyrolysis method demonstrated by Bawendi and co-workers.[2] Alivisatos and co-workers have very recently developed novel morphologies, including rods, arrows, tetrapods, and teardrops.[3] In addition, the synthesis of highly luminescent quantum dots from water solutions has been recently reported.[5]

Large-scale production of quantum dots is particularly difficult because temperature control and homogeneous mixing are difficult for fast reactions in large volumes, but critical for particle size uniformity. A microflow reactor can provide better temperature control by using capillary tubing,[6] but is likely to prove difficult to scale-up for large volume processing.

Aerosol-assisted methods have been used for the synthesis of a variety of inorganic and organic materials,[7] but nearly always these result in *gas*−*solid* aerosols, which have substantial disadvantages both in reaction dynamics and in particle homogeneity. For example, in prior reports on semiconductor preparation, particle sizes obtained by spray pyrolysis or other aerosol methods are relatively large, in the micron size region (~0.2−2 μm).[8] In these previous studies, the decomposition of precursors occurs in the gas phase, and a single large solid particle is formed from each initially dispersed droplet. This makes it difficult to prepare nanometer-sized particles, especially with well-defined size distributions.

To overcome the limitations of prior methodology, we have developed a continuous chemical aerosol flow synthesis (CAFS) for the production of nanomaterials. Solutions of high boiling point liquids containing appropriate precursors are diluted with a low boiling point solvent (toluene). An aerosol is created using an ultrasonic transducer working at 1.7 MHz taken from a home humidifier (cf. Supporting Information), and the dense mist so produced is carried by an Ar gas stream through a tube furnace, whose temperature is controllable from 180 to 400 °C. As the temperature of the droplets entering the furnace tube exceed the boiling point of toluene, the toluene evaporates, leaving submicron droplets of a concentrated solution of reactants in the high boiling point solvent. As the temperature inside the *liquid* droplets increases, the mixture inside reacts, forming surfactant-coated nanoparticles. These nanoparticles then exit the tube furnace and are rapidly cooled and collected in a solvent-filled bubbler. By nebulizing high boiling point liquids, we are able to generate many nanoparticles by chemical reactions *in the liquid phase of each droplet*, which results in narrow size distributions.

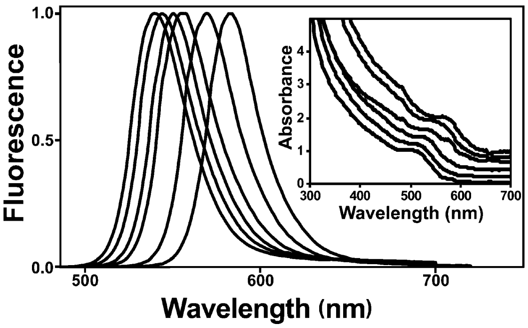

Figure 1. Band edge fluorescence and absorbance (inset) spectra of CdSe/stearic acid nanoparticles prepared by chemical aerosol flow synthesis at temperatures of 240, 260, 280, 300, 320, and 340 °C (from left to right) in toluene solution.

We find CAFS to be a versatile and robust synthetic methodology. Different combinations of Cd and Se precursors, solvents, and surface stabilizers give high quality fluorescent CdSe nanoparticles with controllable sizes. Cd sources include CdO, $CdCO_3$, Cd naphthenate, and $Cd(CH_3CO_2)_2$. Trioctylphosphine selenide (TOPSe), formed from elemental Se dissolved in trioctylphosphine (TOP), works well as the Se source. The surfactant/solvent systems that have been explored include trioctylphosphine/trioctylphosphine oxide (TOP/TOPO) with or without dioctylamine, stearic acid (SA), hexadecylamine (HDA), or oleic acid (OLA). Similar procedures work with S and Te precursors (e.g., thiourea, TOPTe) to produce CdS and CdTe quantum dots, respectively.

For example, CdSe nanoparticles obtained by CAFS from TOP/TOPO/SA/HDA dissolved in toluene and nebulized through the tube furnace at 300 °C are highly fluorescent (quantum yield (QY) ≈ 25%, determined by comparison with the emission from rhodamine-6G) and with narrow band emission (full width at half-maximum (fwhm) ≈ 30 nm). Alternatively, CAFS of Cd acetate and TOPSe in stearic acid (SA) is simpler and works equally well (see Supporting Information), as illustrated by the absorbance and fluorescence spectra of nanoparticles so obtained (Figure 1). This approach is versatile and allows for the production of quantum dots emitting over a broad spectral region by simply changing the

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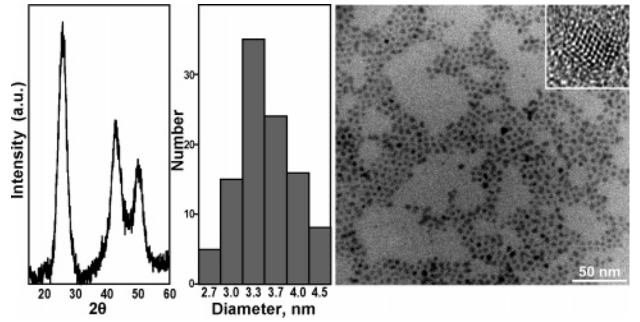

Figure 2. XRD (left), size distribution (center), and TEM (right) of CdSe/SA nanoparticles obtained by chemical aerosol flow synthesis at 340 °C. Inset (6 × 6 nm) shows HRTEM of one of these particles.

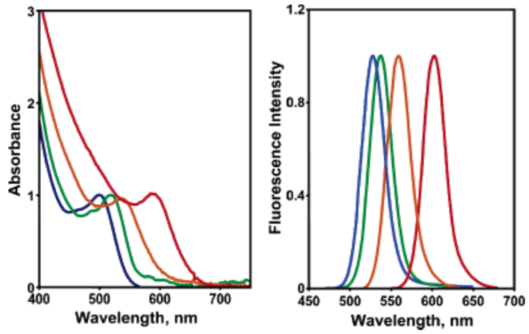

Figure 3. Absorbance (left) and fluorescence (right) of CdTe nanoparticles obtained at 300 °C. Cadmium concentration in the precursor solution increased from left to right (50−250 mM).

temperature of the tube furnace. Similar results were obtained by replacing SA with oleic acid (OLA) or hexadecylamine (HDA).

The size of obtained CdSe quantum dots can be estimated from literature data on the wavelength dependence of absorbance and fluorescence bands versus size.[4a,9] From these data, the size of our CdSe nanoparticles is tunable from 2 to 4 nm using the tube furnace temperature. For example, the size of CdSe quantum dots obtained from this mixture at 340°C is 3.5 nm according to the sizing curve.[9b] This was confirmed by our TEM (3.5 ± 0.4 nm) and XRD data (average from three peaks size is ~3.2 nm, from the Scherrer equation) (Figure 2).

As a further demonstration of the generality of the CAFS method, we have also examined the preparation of CdTe nanoparticles. CdTe nanostructured materials are of active interest as thin-film technology for solar cell application, in part, because band gap energy of CdTe (1.5 eV) matches well the solar spectrum.[10] We have successfully synthesized highly fluorescent CdTe quantum dots from CAFS of a mixture of CdO, octadecylphosphonic acid, octadecene, and toluene. Quantum yield of fluorescence of these nanoparticles is ~40% with fwhm ≈ 30 nm (Figure 3). Obtained in the gas phase, these high quality CdTe nanoparticles can be directly deposited on various substrates to fabricate CdTe solar cells, LED, or other quantum dots composites.

The nebulization rate of our very inexpensive system is ~1 mL/min (with yields of CdSe and CdTe nanoparticles up to ~100 mg/h depending on the nature of precursors, the gas flow, and the temperature of the furnace tube); the use of laboratory ultrasonic horn atomizers can give a liquid flow rate of up to 10 L/h (e.g., Sono-Tek Corp., www.sono-tek.com). Other designs of nebulizers can be used for large-scale production and are already commercially available for production of commodity powders from sprays.[7]

In conclusion, we have reported here a chemical aerosol flow synthesis as a new approach for the continuous production of high quality fluorescent CdS, CdSe, and CdTe nanoparticles. Chemical reactions proceed inside submicron liquid droplets of a high boiling point solvent in a heated inert gas stream; each liquid droplet is an individual phase-separated reactor. CAFS offers significant advantages over previous methods of nanoparticles synthesis: (1) the synthesis proceeds in isolated microscale reactors (i.e., micron or submicron liquid droplets); (2) the reaction zone is separated from the initial solution, which is kept at a much lower temperature (room or even cryogenic); (3) nanocrystals can be obtained in significant amounts with high quality and reproducibility; and (4) the nanoparticles are thermally quenched rapidly and can be easily deposited directly on surfaces or collected at low temperatures in any liquid. From ongoing studies, the extension of this methodology to the synthesis of nanostructured metals, oxides, polymers, and other materials appears to be general.

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Supporting Information Available: Experimental setup and Methods. This material is available free of charge via the Internet at http://pubs.acs.org.

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