

## A Spray-Based Method for the Production of Semiconductor Nanocrystals

Lilac Amirav,<sup>†</sup> Aviv Amirav,<sup>‡</sup> and Efrat Lifshitz<sup>\*,†</sup>

*Department of Chemistry, Solid State Institute and Russell Berrie Nanotechnology Institute, Technion, Haifa 32000, Israel, and School of Chemistry, Sackler Faculty of Exact Sciences, Tel Aviv University, Tel Aviv 69978, Israel*

*Received: March 15, 2005; In Final Form: April 18, 2005*

We present a spray based-method for the formation and production of semiconductor nanocrystals that provides an attractive alternative to the commonly used epitaxial and colloidal procedures. According to this spray-based method, mainly thermospray, solutions of semiconductor salts are first sprayed into monodispersed droplets, which subsequently become solid nanocrystals by solvent evaporation. A semiconductor nanocrystal is produced from a single spray droplet upon the full vaporization of the solvent. The average diameter and size distribution of the final nanocrystals are controlled and determined by the solute concentration of the sprayed solution and by the droplet size, hence by the spray production parameters. The spray-produced nanocrystals are collected on any selected solid support. Representative results, shown in this letter, reveal the formation of CdS nanocrystals in the size range of 3 to 6 nanometers and with a size distribution of as low as five percent. A further structural analysis of these nanocrystals showed that they were formed in the zinc blende phase with a high degree of crystallinity.

### Introduction

In the past two decades, significant attention has been devoted to the physics of low dimensional semiconductor structures. Among those, semiconductor nanoparticles are of particular interest, due to the pronounced influence of the three-dimensional size confinement on their electronic and optical properties.<sup>1–6</sup> Extensive effort has been devoted to the production of high quality semiconductor nanoparticles, motivated by their potential use in new and emerging technologies. Currently, there are two main methods for the fabrication of semiconductor nanoparticles, namely epitaxial growth<sup>7</sup> and colloidal chemistry techniques.<sup>8–11</sup> Epitaxial growth of nanoparticles produces relatively large dots, with weak quantum confinement.<sup>12</sup> The liberty to choose the substrate is limited, and the nanoparticles cannot be assembled in a closed pack array. Furthermore, this method requires ultrahigh vacuum equipment as well as other complex and expensive equipment. The colloidal method requires inert and elevated temperature conditions, enabling reproducible formation of nanoparticles, with a variety of sizes and shapes, with initial size distributions of about 10% in diameter, and with some control of surface properties. However, doping of colloidal nanoparticles is inhibited due to the large diffusivity of the dopant to the nanocrystalline surfaces at the elevated temperatures required. Furthermore, the organic capping plays a key-role in any self-assembly created by these nanoparticles, preventing the formation of highly packed structures. Such closely packed arrays of nanoparticles have potential uses in any future application where good conductivity properties are required.

We present a novel spray-based technique for the formation and production of high quality semiconductor nanocrystals that offers an attractive alternative to the conventional production methods. According to this spray-based method, mainly thermospray, aqueous or organic solutions of semiconductor salts are first sprayed into monodispersed droplets, which subsequently become solid nanocrystals by solvent evaporation. The semiconductor nanocrystals are produced, each from a single spray droplet, upon the full vaporization of the solvent. The average diameter and size distribution of the final nanocrystals can be controlled and determined by the solute concentration of the sprayed solution and by the droplet size, hence by the spray production parameters. The spray-produced nanocrystals are then collected on any selected solid support.

The present method uniquely enables the production of free, uncoated semiconductor nanocrystals, in contrast to the colloidal method. As a result, arrays prepared by this method have the potential of creating the densest possible structures due to the absence of organic capping. Electron transport properties as well as energy transfer mechanisms, which strongly depend on the nanocrystals' packing, could be measured within a new and more interesting range of interparticle distances.

### Experimental Section

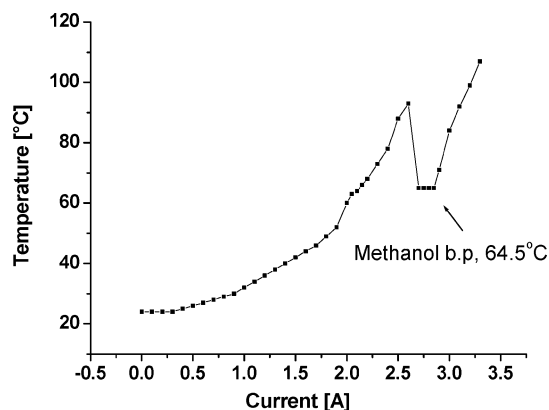
Cadmium sulfide nanocrystals have been intensively investigated in the past few years and thus serve as a good sample for demonstrating our spray-based method. Cadmium sulfide powder (Aldrich) was dissolved in HPLC-grade methanol and solubility was confirmed by absorption measurements according to the Beer–Lambert law. The semiconductor powder can be dissolved either in the form of an ionic salt or as an intact non-ionized compound in the solution. Droplets of the solution of cadmium sulfide were generated using pneumatically assisted

\* Corresponding author. Phone: 972-4-8293987, Fax: 972-4-8295703, E-mail: ssefrat@tx.technion.ac.il.

<sup>†</sup> Technion.

<sup>‡</sup> Tel Aviv University.





**Figure 2.** Plot measure of the solvent temperature versus the heating current provided to the solvent delivery capillary.

ment are given in Figure 2. Spray-produced particles were collected from different points of the plot for HRTEM analysis. Due to the high internal pressure in the capillary, the boiling point of the solvent is raised and the vaporization begins at relatively high temperatures. With the spray formation, a relief of the pressure is followed by a sharp decrease of the temperature. The temperature then remains nearly constant until the vaporization is complete since the heat flux is used to provide the latent heat to the solvent. At the point corresponding to complete vaporization the temperature again rises rapidly since only the heat capacity of the vapor is available to absorb the input energy.

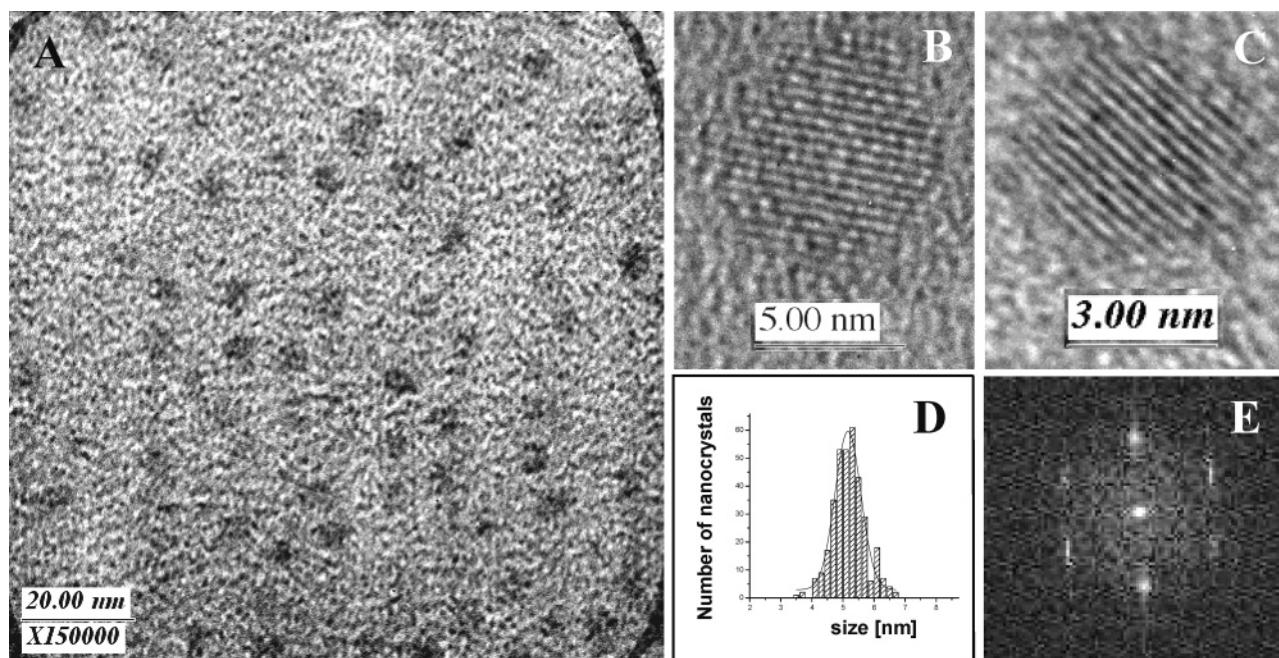
The vapor produced by the vaporization acts as an internal nebulizing 'gas' and aids the break-up of the liquid stream into droplets. Its high output pressure introduces a rise in the input HPLC pump pressure for a fixed flow rate. The length of the capillary from the end of the heating zone to the outlet and the capillary internal diameter were found to affect the amount by which the pressure increases.

The products of a spray obtained with a tube heating current of 2.0 A and a measured temperature of 64 °C were collected.

The resulted CdS nanoparticles obtained this way had an average size of  $5.6 \pm 0.9$  nm and a size distribution of about 16%. This relatively wide size distribution serves as an evidence for the instability of the thermospray at that point. The products of a second spray were obtained with a tube heating current of 2.6 A and with a measured temperature of 66 °C. The location of the point on the temperature versus current plot indicates that a stable spray was achieved. The resulting CdS nanoparticles were found to have an average size of  $5.1 \pm 0.5$  nm and a size distribution of less than 9%. The products of a third spray were obtained with a tube heating current of 2.7 A, with a measured temperature of 66 °C, and were collected near the end of the vaporization process (as indicated by the point location on the plot). The results showed CdS crystals in a size range of some tenth of microns. Under these conditions the CdS concentration in the solvent was close to saturation prior to exiting the tube. Thus, at a certain level of vaporization the CdS crystallizes prior to leaving the capillary and before the final spray formation. These conditions favor micron-sized particles as received by the aforementioned spray.

Other spray production parameters, such as the liquid flow rate, pneumatic assisting aspects such as nebulizing gas flow rate and temperature, and the quartz outlet shape and location relative to the capillary outlet, were optimized for the production of high quality CdS nanocrystals. The HRTEM analysis revealed spherical CdS nanocrystals, with average diameter that varied between 3.1 and 5.6 nanometers and a standard deviation of as little as five percent (representative size distribution histogram shown in Figure 3D). These results demonstrate the usefulness of this novel technique. The CdS nanocrystals, shown in Figure 3A–C, exhibit well resolved cubic lattice fringes. Selected area electron diffraction and fast Fourier transform of the pictures (shown in Figure 3E) confirm the formation of nanocrystals with a zinc blende cubic structure and a high degree of crystallinity.

Other spray-produced nanocrystals were collected for 1 h on a fused silica slide for optical measurements. A third harmonic



**Figure 3.** (A) HRTEM picture of CdS nanocrystals produced by pneumatically assisted thermospray with an average size of 5.1 nm and size distribution width of less than 10 percent. (B, C) Representative HRTEM pictures of two single CdS nanocrystals from samples with an average size of 5.6 and 3.1 nm, respectively. (D) Size distribution histogram associated with the sample presented in A. (E) Fast Fourier transform picture of a single nanocrystal, showing the zinc blende structure.



Nd:YAG laser with a 355 nm wavelength was used as an excitation source. Our preliminary results (to be presented elsewhere) showed a strong luminescence with a peak at 437 nm (2.84 eV) corresponding to average nanocrystal size of 3.6 nm. Photoluminescence measurements conducted at various temperatures between 4 and 300 K showed temperature-independent behavior. This finding suggests that the light emission spectrum emerges from a single process, most likely an excitonic recombination in high quality, defect-free nanocrystals.

### Conclusions

A novel thermospray method was presented for the formation and production of semiconductor nanocrystals. This method involves a solution-based procedure that is simple, cheap, and requires only a small amount of starting materials. It further avoids prolonged handling of hazardous precursors as required in known colloidal procedures. High quality CdS nanocrystals were obtained using this method, within the size range of 3 to 6 nanometers. These nanocrystals exhibit high degree of crystallinity in the zinc blende phase and size distribution of as low as five percent. These results demonstrate the usefulness of our novel method. Furthermore, we claim that our method offers several new and unique features and advantages not exhibited by currently available methods. These features and their demonstration are currently being examined.

**Acknowledgment.** This project was supported by the Israel Science Foundation, project # 156/03-12.6 and by the James Franck Center for Laser Matter Interaction. The research was

carried out at the Russell Berrie Nanotechnology Institute at the Technion. The authors express their deep gratitude for the donation of Matilda and Gabriel Barnett.

### References and Notes

- (1) Brus, L. E. *J. Chem. Phys.* **1984**, *80*, 4403.
- (2) Brus, L. E. *J. Chem. Phys.* **1986**, *90*, 2555.
- (3) Wang, Y.; Herron, N. *J. Phys. Chem.* **1991**, *95*, 525.
- (4) Norris, D. J.; Efros, A. L.; Rosen, M.; Bawendi, M. *Phys. Rev. B* **1996**, *53*, 16347.
- (5) Alivisatos, A. P. *J. Phys. Chem.* **1996**, *100*, 13226.
- (6) Efros, A. L.; Rosen, M. *Annu. Rev. Mater. Sci.* **2000**, *30*, 475.
- (7) Stranski, N.; Krastanow, V. L. *Akad. Wiss. Lit. Mainz Math. — Natur. Kl. IIb* **1938**, *146*, 797.
- (8) Murray, C. B.; Kagan, C. R.; Bawendi, M. G. *Annu. Rev. Mater. Sci.* **2000**, *30*, 545.
- (9) Murray, C. B.; Norris, D. J.; Bawendi, M. G. *J. Am. Chem. Soc.* **1993**, *115*, 8706.
- (10) Manna, L.; Scher, E. C.; Alivisatos, A. P. *J. Cluster Sci.* **2002**, *13*(4), 521.
- (11) Peng, Z. A.; Peng, X. *J. Am. Chem. Soc.* **2001**, *123*, 1389.
- (12) Sakaki, H. *J. Cryst. Growth* **2003**, *251*, 9.
- (13) Willoughby, R. C.; Browner, R. F. *Anal. Chem.* **1984**, *56*, 2626.
- (14) Zhang, X.; Chen, D.; Marquardt, R.; Koropchak, J. A. *Microchem. J.* **2000**, *66*, 17.
- (15) Lenggorgo, W.; Okuyama, K.; de la Mora, J. F.; Tohge, N. *J. Aerosol Sci.* **2000**, *31*(1), 121.
- (16) Clifford, R. H.; Tan, H.; Liu, H.; Montaser, A.; Zarrin, F.; Keady, P. B. *Spectrochim. Acta B* **1993**, *48*, 1221.
- (17) Koropchak, J. A.; Veber, M. *Crit. Rev. Anal. Chem.* **1992**, *23*, 113.
- (18) Conner, T. S.; Yang, J.; Koropchak, J. A. *Spectrochim. Acta B* **1997**, *52*, 1087.
- (19) Mora, J.; Canals, A.; Hernandis, V. *Spectrochim. Acta B* **1996**, *51*, 1535.
- (20) Vestal, M. L.; Fergusson, G. J. *Anal. Chem.* **1985**, *57*, 2373.