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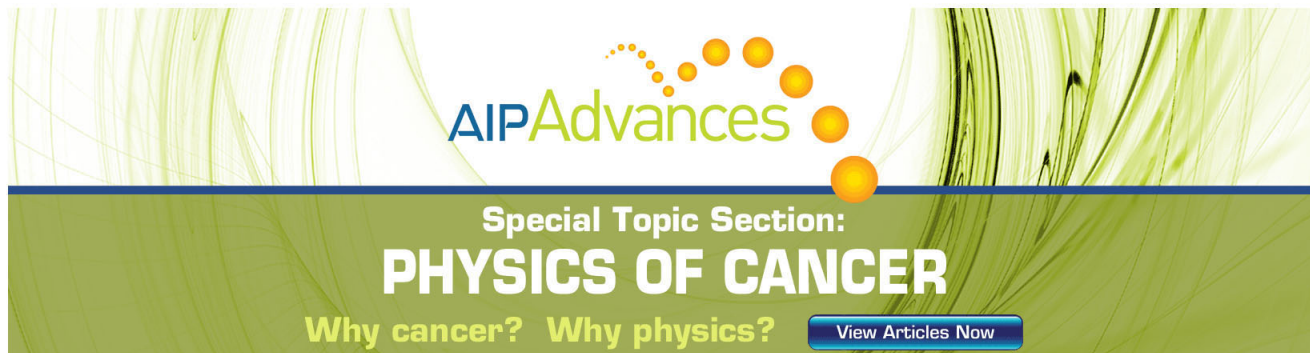
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Water soluble CdS nanoparticles with controllable size prepared via femtosecond laser ablation

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Small water soluble CdS nanocrystals (NCs) with excellent colloidal stability were prepared by femtosecond laser ablation of a bulk CdS target without using any surfactant. CdS NCs of different sizes ranging from 2.0 to 8.6 nm can be produced by simply adjusting the laser fluence at low values, which are just above the ablation threshold. The obtained CdS NCs show a relatively narrow size distribution, which gradually narrows as the laser fluence decreases, as can be seen in the transmission electronic microscopic images. UV-vis optical absorption, photoluminescence, and fluorescence lifetime were also used to characterize the NCs. These as-prepared small crystals show excellent water solubility and have good colloidal stability. Their size is easily controlled as well. Together, the above-mentioned properties make these NCs of interest for luminescence labeling and sensing applications. © 2007 American Institute of Physics. [DOI: [10.1063/1.2781382](https://doi.org/10.1063/1.2781382)]

I. INTRODUCTION

Semiconductor nanocrystals (NCs) are of great interest for both fundamental research and technical applications due to their strong size and morphology dependent properties as well as their excellent chemical processability.^{1,2} The ability to synthesize high quality semiconductor NCs in a controllable fashion has played a critical role in this very active field. Small, stable, water soluble NCs with high efficiency photoluminescence have been very attractive for biomedical labeling in recent years.^{3,4}

Many synthetic methods and materials such as diblock copolymers,⁵ metal-polymer nanocomposites,⁶ organometallic synthesis,⁷ reverse micelles,⁸ and vesicles⁹ have been used for the chemical preparation of nanoparticles of various semiconductor materials. Alternatively, a laser ablation technique has been developed and used as a successful physical method for nanofabrication in recent years.^{10–14} Using this method, certain size control can be easily achieved by varying the radiation parameters. Experimental difficulties which can arise, such as crystalline phase transformations^{15,16} and contamination byproducts, which are usually observed for chemically reactive materials, can be avoided using this method. However, recent reports indicate that rather large (20–300 nm) and strong dispersion (50–300 nm) nanoparticles are inevitably produced during laser ablation in pure water.^{17–23} Several attempts have been made recently to con-

trol the size of the particles produced such as substituting the nanosecond laser with a femtosecond laser so as to avoid target Joule heating during laser ablation, and using surfactants such as sodium dodecyl sulfate and cyclodextrins^{10,14,16,24,25} to effectively stabilize and reduce the size of nanoparticles. However, in most cases, nanoparticles covered with surfactants could be problematic for further applications.⁹ It is known that semiconductor NCs “capped” with long chain organic surfactants often have some non-band-edge luminescence, which is not favorable for the potential use in biological labeling.^{26–28}

In this article, we report the synthesis and the determination of the optical properties of CdS formed by femtosecond laser ablation in a surfactant-free environment. It should be noted that relatively small sizes (<9 nm) and narrow distributions [<5 nm at full width at half maximum (FWHM)] of NCs can be produced by optimizing the laser parameters and focusing conditions during the preparation without using any surfactant. The obtained water soluble NCs showed exceptional colloidal stability. And as the laser fluence was decreased, the particle size and size distribution also decreased. The possible explanation for this has been explored from the aspect of laser-matter interaction mechanics.

II. EXPERIMENT

The typical experiment was carried out with a Ti/sapphire laser, which provided 100 fs FWHM pulses (wavelength 800 nm, maximum energy 1 mJ/pulse, repetition rate

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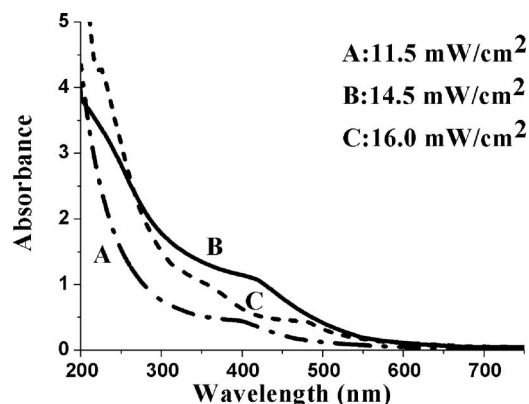


FIG. 1. UV-vis optical absorption spectra of CdS NCs ablated at various laser fluences for Sample A: 11.5 mW/cm², Sample B: 14.5 mW/cm², and Sample C: 16.0 mW/cm².

1 kHz). The ablation was performed at different laser fluences, which were adjusted carefully to minimize the influence of the instability of radiation energy. The laser irradiates vertically to a pure CdS plate, which was surface polished and fixed in the bottom of a cuvette filled with de-ionized water. The cuvette was placed on a three-dimensional optical adjusting rack, which repetitively moved horizontally at a constant speed of 0.1 mm/s. For all samples, the ablation was performed during 5 min at low fluences (≤ 20 mW/cm²).

Absorption spectra were recorded on a UV-3101PC UV-Vis-NIR scanning spectrophotometer (Shimadzu). Room-temperature emission spectra were measured using a Hitachi F-4500 spectrophotometer equipped with a 150 W Xe-arc lamp. Fluorescent dynamics were performed on an FL920-

Fluorescence Lifetime spectrometer (Edinburgh Instruments) with MCP-PMT, in which the excitation light source was an NF 900 ns flash lamp with 1 ns pulse duration. Transmission electronic microscopic (TEM) imaging of the sample was conducted on a JEM-2010 transmission electronic microscope (JEOL Co., Japan) by placing a drop of the as-sampled solution on a carbon-coated copper grid immediately after the synthesis of samples.

III. RESULTS AND DISCUSSION

As shown in Fig. 1, the obtained CdS NCs ablated at 16.0 mW/cm² (Sample C) exhibited a well-resolved 1Se-1Sh transition²⁹ at ~ 480 nm, which is considerably blue-shifted relative to the absorption onset of bulk CdS (515 nm), indicating quantum confinement. With decreasing the laser fluence from 16.0 to 11.5 mW/cm², the absorption edges of the CdS NCs were shifted gradually from 480 to 396 nm, suggesting that smaller CdS clusters were produced at lower laser fluence. The band gaps obtained from the excitonic peak of the absorption spectra are approximately 3.12, 2.98, and 2.58 eV for Samples A, B, and C, respectively. Furthermore, the sizes of the three samples observed from the TEM images (Fig. 2) are 2.0, 2.5, and 8.6 nm, correspondingly. It is reported that the calculations based on the tight-binding scheme yield band gaps of approximately 3.4 and 3.1 eV for the 2.0 and 2.5 nm NCs, respectively,³⁰ which agree reasonably well with the experimental results in the present study. On the other hand, the calculated results, based on the effective mass approximation by Brus³¹ and others, suggest a band gap of 2.6 eV for NC size of 8.6 nm.

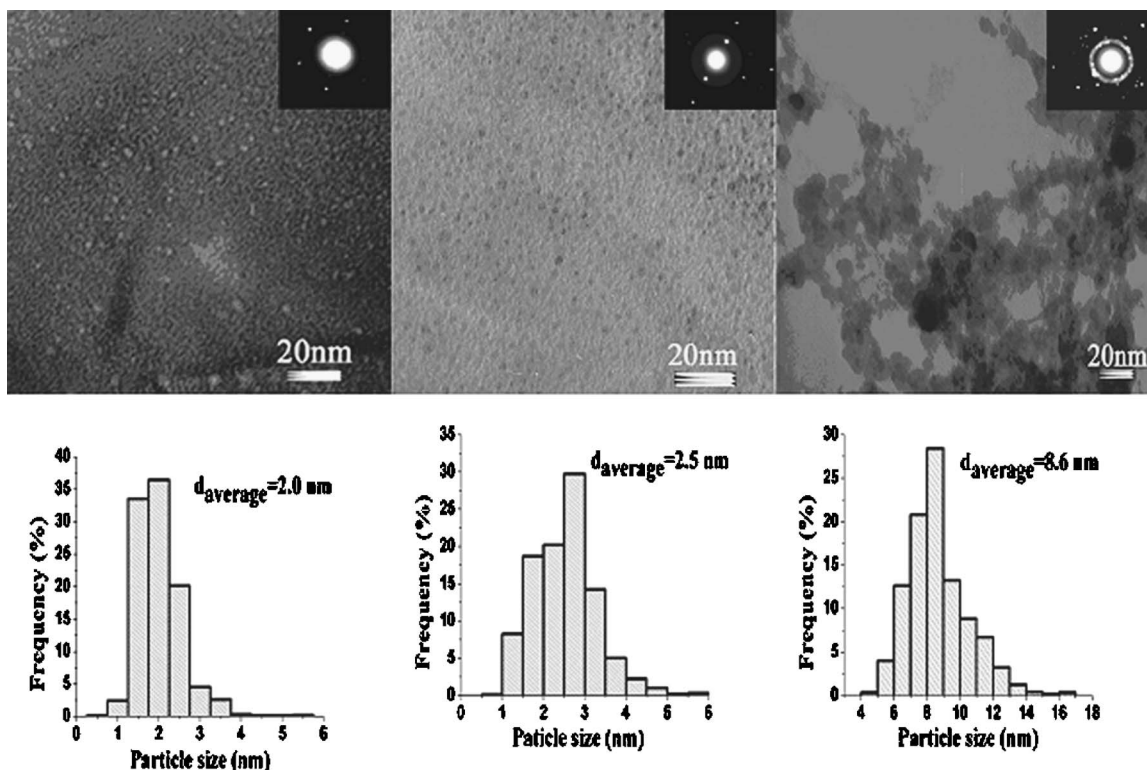


FIG. 2. TEM images of the as-prepared CdS NCs and corresponding size distribution produced at different laser fluences: 11.5 mW/cm² (left), 14.5 mW/cm² (middle), and 16.0 mW/cm² (right).

Figure 2 depicts the TEM pictures and corresponding size distribution of CdS NCs produced by laser ablation at different laser fluences. The mean sizes are about 2.0, 2.5, and 8.6 nm and correspond to 11.5, 14.5, and 16.0 mW/cm² laser fluence, respectively. The water soluble CdS nanoparticles were found to be well dispersed with a narrow size distribution and the colloid was exceptionally stable for at least 3 months without using any surfactant during the preparation. The lattice fringes of crystals indicate the formation of crystallized nanoparticles (see insets in Fig. 2 top).

In addition, the results also indicate that smaller size and narrower size distribution CdS NCs were obtained at lower laser fluence (see Fig. 2 bottom). For the laser fluences used in our range, the single-peak Gaussian extrapolation was adequate for all the three samples. When the laser fluence is set to 16.0, 14.5, and 11.5 mW/cm² the size distributions at FWHM are 1.8, 2.6, and 4.8 nm, respectively. The results are in good agreement with the recent experimental investigations on particle formation by laser ablation.^{10–15} Kabashin *et al.* used a femtosecond laser to ablate a gold target in de-ionized water to produce colloidal gold nanoparticles.¹³ They analyzed the scanning electron microscopy (SEM) pictures of the crater on the gold target surface and concluded that the possible reason for a wider distribution at higher laser fluence is related to the plasma-related heating. Actually, to a large extent, the size distribution is determined by the focusing conditions, such as the distance and the angle between the focal plane and the target surface. The laser pulse is incident vertically (in the *z* direction) to the target surface and taken to be time constant and Gaussian in shape. The pulse is modeled by a succession of planes, on which the spatial distribution of the energy fluence is described by

$$E(x,y) = \sqrt{\pi}\tau I_0 \exp[-(x^2 + y^2)/\rho^2], \quad (1)$$

where I_0 is the peak fluence at the center of the beam, and ρ and τ are the spatial radius and the temporal radius, respectively. The laser fluence distribution $F(x,y)$ is then given by

$$F(x,y) = F' \exp[-2(x^2 + y^2)/\omega^2], \quad (2)$$

where $F' = F(0,0) = 2P_0/\pi\omega^2$ represents the maximum of laser fluence, which is proportional to the total power of the beam P_0 .³² When the laser fluence $F(x,y)$ surpasses the ablation threshold F_{th} , CdS nanoparticles are produced, which are also accompanied by the presence of a plasma plume on the target surface. For example, if the focal plane is overlapped with the target surface, and $F' > F_{th}$, then the plane region comprised of the fluences ranging from F_{th} to F' will be ablated. Consider that the particle size is determined by the laser fluence, the greater the difference between F' and F_{th} , the larger the region that can be ablated, consequently the broader the distribution of nanoparticle sizes will be.

Room temperature photoluminescence (PL) spectra of the three samples are shown in Fig. 3. The PL spectra of the prepared CdS NCs upon excitation at 300 nm suggest that with increasing the laser fluence from 11.5 to 16.0 mW/cm², the PL band blue-shifts gradually from 405 to 487 nm accompanied by a gradual increase in the spectral width. A representative PL spectrum recorded from 2.5 nm diameter CdS nanoparticles shows a peak centered at 2.93

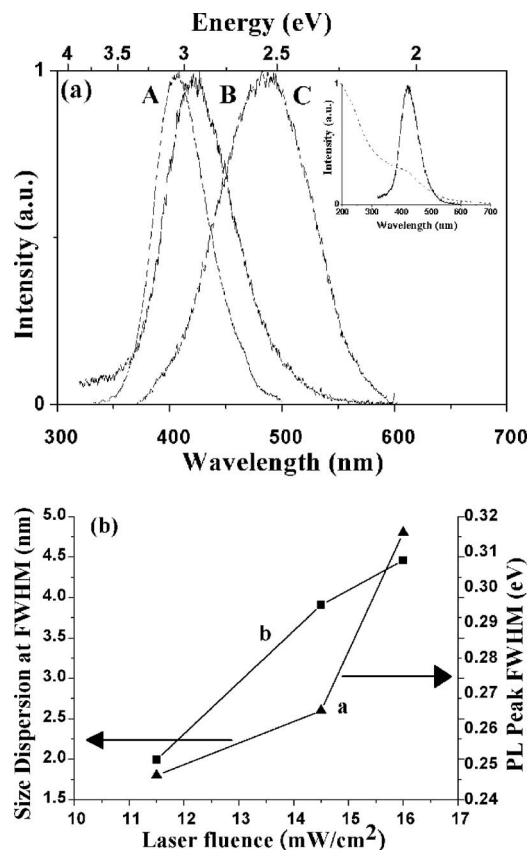


FIG. 3. (a) Normalized room temperature PL emissions of CdS nanoparticles (excitation at 300 nm). The inset presents the normalized absorption and PL spectra of Sample B. (b) Size distributions (triangles) and photoluminescence spectra (squares) at FWHM as a function of the laser fluence.

eV (422 nm) with a line width of 0.295 eV [see in Fig. 3(a) inset]. The observed broad PL peak is commonly attributed to that reported for the 1Se-1Sh excitonic transition. Comparatively, the photoluminescence spectra at FWHM are 0.251, 0.295, and 0.308 eV corresponding to Samples A, B, and C, respectively, which shows the same trend as the size distribution when the laser fluence increases [Fig. 3(b)]. The result suggests that the spectral width is related to the inhomogeneous distribution of the NCs, i.e., the broadening of the photoluminescence spectrum width is attributed to excitonic emission overlap for different sizes of CdS NCs.

The spectral characteristics of the CdS NCs in Sample B in water were further studied by the PL lifetime decay profiles as a function of emission wavelength. The obtained decay times are 3.7, 4.9, 5.4, 5.6, and 5.9 ns, respectively, when shifting the detection to the low-energy side of the emission. It is shown in the inset of Fig. 3(a) together with Fig. 4 that the decay times are sensitive to the monitoring wavelength and they are relatively longer at longer wavelengths. These observations might suggest two aspects: on the one hand, the slight difference in decay times indicates the same recombination kinetics, which are commonly in accordance with excitonic transitions of different size of CdS NCs; on the other hand, the smaller particles, with a larger surface area to volume, have more dangling and terminated bonds, as well as screw and other point defects. These surface states, acting as quenching centers in the luminescence, would increase the

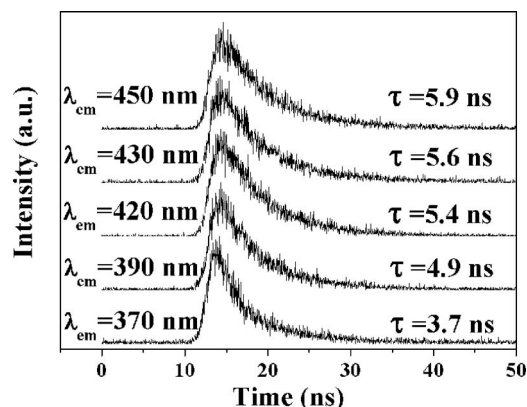


FIG. 4. Room temperature fluorescent decay curves of Sample B monitored at 370, 390, 420, 430, and 450 nm.

nonradiative tunneling rate, so a shorter lifetime would be obtained for the small nanoparticles.³³ Furthermore, a quantum size effect on the radiative recombination rate may be attributed to the decrease of the lifetime.³⁴

IV. CONCLUSIONS

Water soluble CdS NCs were produced by femtosecond laser ablation without using any surfactant. Three samples were synthesized with different mean particle sizes by simply controlling the laser fluence. The obtained particles were homogeneous in size and showed excellent stability. The influence of laser fluence on NC size distribution was investigated from both the aspect of the laser-matter interaction and the spectra characteristics. The results suggest that a broader size distribution of the particles would be present when the laser fluence is much larger than the ablation threshold. This study reveals that laser ablation of semiconductors in a liquid media is an effective method to synthesize nanoparticles with controlled size. The minimal size and dispersion of the produced particles make them very attractive for biosensing and other applications.

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