CdSe quantum dots synthesized by laser ablation in water and their photovoltaic applications

Sabit Horoz, Liyou Lu, Qilin Dai, Jiajun Chen, Baichhabi Yakami, J. M. Pikal, Wenying Wang, and Jinke Tang

Citation: [Applied Physics Letters](#) **101**, 223902 (2012); doi: 10.1063/1.4768706

View online: <http://dx.doi.org/10.1063/1.4768706>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/apl/101/22?ver=pdfcov>

Published by the [AIP Publishing](#)

Articles you may be interested in

[Blue and green electroluminescence from CdSe nanocrystal quantum-dot-quantum-wells](#)

Appl. Phys. Lett. **105**, 203101 (2014); 10.1063/1.4902109

[Pulsed laser deposition of Mn doped CdSe quantum dots for improved solar cell performance](#)

Appl. Phys. Lett. **104**, 183901 (2014); 10.1063/1.4875107

[Optimization of growth conditions of type-II Zn\(Cd\)Te/ZnCdSe submonolayer quantum dot superlattices for intermediate band solar cells](#)

J. Vac. Sci. Technol. B **31**, 03C119 (2013); 10.1116/1.4797486

[Effect of metal oxide morphology on electron injection from CdSe quantum dots to ZnO](#)

Appl. Phys. Lett. **102**, 163119 (2013); 10.1063/1.4803173

[Insertion of CdSe quantum dots in ZnSe nanowires: Correlation of structural and chemical characterization with photoluminescence](#)

J. Appl. Phys. **110**, 034318 (2011); 10.1063/1.3618685

CdSe quantum dots synthesized by laser ablation in water and their photovoltaic applications

Sabit Horoz,¹ Liyou Lu,¹ Qilin Dai,¹ Jiajun Chen,¹ Baichhabi Yakami,² J. M. Pikal,² Wenyong Wang,¹ and Jinke Tang^{1,a)}

¹Department of Physics and Astronomy, University of Wyoming, Laramie, Wyoming 82071, USA

²Department of Electrical Engineering, University of Wyoming, Laramie, Wyoming 82071, USA

(Received 6 October 2012; accepted 8 November 2012; published online 27 November 2012)

CdSe quantum dots (QDs) have been prepared by a facile and clean synthesis method—laser ablation in water. The structural and luminescent properties of the CdSe QDs have been investigated. The CdSe QDs of wurtzite crystal structure have an average particle size of about 5 nm. The QDs can be attached to ZnO nanowires making them ideal for applications in QD-sensitized nanowire solar cells. A uniqueness of the QDs attached to the ZnO nanowires by this laser ablation method is that they do not contain ligands, and the preparation avoids the complicated process of ligand exchange. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4768706>]

Quantum dots (QDs) have great potential for applications in electronics and optoelectronics.^{1,2} They show special physical and chemical characteristics when their size is close to or smaller than the exciton Bohr radius, and this quantum confinement effect leads to tunable photoluminescence (PL) properties.^{2,3} In particular, their PL can be tuned by the size of the QDs, which gives them functionalities as sensitizers in photovoltaic solar cells.^{4,5}

There are different ways to synthesize QDs, for example, solution-based methods for colloidal QDs^{6–9} and deposition-based methods such as successive ionic layer adsorption and reaction (SILAR), chemical bath deposition (CBD), and atomic layer deposition (ALD).^{10–15} In our previous work, we have deposited CdSe QDs directly on Zn₂SnO₄ nanowires using pulsed laser deposition (PLD) in vacuum.¹⁶ PLD is a facile and clean physical vapor deposition method for QDs due to reduced formation of the by-products in the process. It is a method that can be applied at ambient temperature. In addition, it is an effective method to fabricate QDs without ligands. Ligands are unavoidable in the synthesis of colloidal QDs and are known to be a barrier for electron transfer from the QDs to the photoanode in QD-sensitized solar cells.^{15,16} It is desirable to develop QD-sensitized solar cells without ligands to achieve efficient electron transfer from the QDs to photoanode and improve the efficiency. Another attractive method to make QDs that retains the benefits of PLD is laser ablation of solid targets in a liquid environment.^{17–20} The major difference between laser ablation in a gaseous environment and in liquid is the stronger confinement and more rapid cooling of the expanding plasma plume in the latter case,¹⁹ which results in different products, for example, nanoparticles of smaller sizes. Laser ablation in liquid may also favor materials which can only be synthesized at relatively high pressure.¹⁷ It is an even simpler method than PLD as one does not need a vacuum chamber for laser ablation in liquid. During the past decade, preparation of nanoparticles, mostly metals, using laser ablation in liquid has been explored (see

reviews in Refs. 17–20). However, the formation of semiconductor QDs with this method has been studied to a much lesser extent.^{21–23} Semaltianos *et al.* synthesized CdSe QDs by laser ablation in methanol using a femtosecond laser.²² On the other hand, CdSe QDs prepared using a nanosecond Nd:YAG laser failed to exhibit photoluminescence.²³ While it is believed there is a major difference in the particle formation mechanism between nanosecond and femtosecond lasers (in the former case the particles are formed from nucleation out of the vapor phase, while in the latter case the particles can be directly ejected from the target surface due to rapid energy transfer¹⁸), it does not appear to be the reason for the different results obtained in Refs. 22 and 23. These previous studies suggested water is not a good medium for laser ablation in liquid. QDs of CdS, CdSe, and CdTe fell out of the water suspension within hours.^{21,23} It should be mentioned here that preparation of QDs in water suspension is desirable for their incorporation into solar cells as it avoids complicated process of ligand exchange.

In this letter, we report synthesis of CdSe QDs by laser ablation of a bulk target in water using a nanosecond pulsed laser. The as-prepared CdSe QDs were subsequently used to make ligand-free QD-sensitized ZnO nanowire solar cells. The preparation, photoluminescent properties and device performance of the QDs and cells were investigated and analyzed. The performance of the cells suggests promising potential of this liquid based synthesis method for QD-sensitized photovoltaic solar cells.

Figure 1 shows the schematic diagram of a simple set up for laser ablation in liquid. The laser used in this experiment was a frequency quadrupled Nd:YAG laser LS-2147 ($\lambda = 266$ nm). The laser beam was focused by a lens onto a CdSe target (purchased from Alfa Aesar), which was submerged in deionized water inside of a fused quartz bowl as shown in Fig. 1. The lens of a focal length $f = 5$ cm was placed immediately in front of the quartz bowl. The locations of the lens and the CdSe target in the quartz bowl were adjusted such that the incident laser beam focuses on the surface of the target. The pumping energy of the laser varied between 37 and 40 J, which corresponds to a roughly estimated laser fluence of

^{a)} Author to whom correspondence should be addressed. Electronic mail: jtang2@uwyo.edu.

FIG. 1. The schematic diagram of a simple set up for laser ablation in water. Lower left inset: picture of a fused quartz bowl containing the CdSe QDs in water suspension.

1 J/cm^2 on the CdSe target surface. A repetition rate of 10 Hz was used for the 10 ns laser pulses. To collect sufficient amount of sample, the laser ablation was carried out for several hours. The formation of CdSe QDs in the water suspension was indicated by the change of color of the suspension during the laser ablation. The water suspension of CdSe was stable for 2 weeks in ambient atmosphere.

After the laser ablation, samples of CdSe QDs were prepared by placing droplets of the water suspension onto a clean silicon substrate and then drying at room temperature. The samples were examined by x-ray diffraction (XRD) afterward. Transmission electron microscopy (TEM) images of the CdSe QDs were obtained by drying out droplets of the suspension on carbon-coated copper grids. Photoluminescence spectra were measured for the QDs at room temperature. A tunable femtosecond laser was used as the excitation source and the PL was collected through a 1/2 m scanning monochromator using a high gain Si detector and lock-in amplifier locked to the laser repetition rate.

The CdSe QDs prepared with laser ablation in water were integrated with ZnO nanowires to make QD-sensitized solar cells. ZnO nanowires were first grown by a chemical vapor deposition (CVD) method on a FTO substrate.²⁴ Before adding the QDs, the ZnO nanowires were annealed under proper growth conditions to eliminate surface contaminations. The ZnO photo anode was then soaked in the as-prepared CdSe QDs in water for 4 h. Another FTO substrate was coated with 25-nm Pt and bonded together with the nanowire/FTO substrate through a hot-melt spacer (Bynel, Dupont, $75 \mu\text{m}$). A drop of electrolyte [0.5 M LiI (Aldrich), 50 mM I_2 (Alfa Aesar), and 0.5 M 4-tertbutylpyridine (Aldrich) in 3-methoxypropionitrile (Aldrich)] was infiltrated into the space between the two electrodes through the pre-drilled holes. The hot-melt glue was used to fill the holes and seal the cell well. The fabricated cells were tested under a simulated sunlight of 100 mW/cm^2 from a xenon lamp that was calibrated by a power meter.

The TEM images and particle size distribution of CdSe QDs synthesized by laser ablation in water are shown in Figs. 2(a) and 2(b). The images show well-crystallized and mostly separated QDs. The lattice fringes of a single crystal QD can be seen in the image shown in the inset of Fig. 2(a). The fringes correspond to the (002) planes of wurtzite CdSe. The size distribution of the QDs is relative broad, which is advantageous for sensitizing purpose. The average particle

size determined from the histogram of particle size distribution is about 5.1 nm.

The XRD pattern of the CdSe QDs is shown in Fig. 3. The pattern shows clear diffraction peaks that can be identified as from CdSe of wurtzite hexagonal crystal structure.²⁵ The standard XRD peak positions of wurtzite CdSe are shown as vertical bars beneath the experimental data. The two extra peaks at 30.3° and 34.5° are from SiO_2 (Ref. 26) and Si substrate,²⁷ respectively. We have used very slow

FIG. 2. (a) TEM images of CdSe QDs synthesized by laser ablation in water, and inset is a magnified image showing the lattice fringes of a single crystal QD; (b) histogram of particle size distribution.

FIG. 3. XRD pattern of CdSe QDs synthesized by laser ablation in water. The standard XRD peak positions of wurtzite CdSe are shown as vertical bars underneath the experimental data.

scan in order to get enough diffraction intensities from the QDs, which picked up signals from the oxide on the surface of the Si substrate.

The peak widths of the relatively strong (100), (101), and (110) diffractions were used to estimate the particle size of CdSe QDs using Scherrer formula as given in Eq. (1)

$$t = 0.9\lambda / (\beta \cos \theta), \quad (1)$$

where t is the mean size of the QDs, λ is the wavelength of x-ray, β is the broadening measured as the full width at half maximum (FWHM) in radians, and θ is Bragg's diffraction angle. The size of the CdSe QDs found from the XRD peak width is about 5.0 nm, in good agreement with the TEM images.

The PL spectrum of the CdSe QDs prepared by laser ablation is shown in Fig. 4. The spectrum was obtained for the CdSe QDs prepared in methanol as it was difficult to get accurate PL signals in water suspension. An excitation wavelength $\lambda_{\text{ex}} = 370$ nm was used. The PL peak of the QDs is located around $\lambda_{\text{peak}} = 553$ nm indicating the quantum

FIG. 4. Photoluminescence spectrum showing CdSe QD emission at $\lambda = 553$ nm, corresponding to an average particle size of 5.4 nm.

FIG. 5. SEM image of CdSe QD sensitized ZnO nanowires.

confinement effect. The band gap of bulk CdSe is $E_g = 1.739$ eV ($\lambda \approx 713$ nm).²² From the blue shift of the peak position, the size of the CdSe QDs was estimated to be about 5.4 nm using the formula given in Ref. 28, which was close to the values obtained from the TEM and XRD data.

QD-sensitized solar cells have been fabricated using the laser ablation synthesized CdSe QDs. Figure 5 shows a scanning electron microscopy (SEM) image of ZnO nanowires after soaking in CdSe QD water suspension. Figure 6 shows the current density versus voltage (J-V) of the solar cell tested under 100 mW/cm^2 light intensity. The open circuit voltage is about 0.48 V, which shows the promising application potential of this liquid based method to grow CdSe QDs. Although the overall conversion efficiency is not high due to the low short circuit current density (0.43 mA/cm^2) and low fill factor, the open circuit voltage is comparable to similar solar cells using CdSe QDs made with solution based methods.⁸ One possible reason for the low current density is the inadequate amount of QDs attached to the ZnO nanowires,

FIG. 6. J-V plots of a sensitized solar cell using QDs prepared with laser ablation in water.

which can be improved by adjusting the soaking time of nanowires in the QD suspension or the QD density in water.

In summary, we have presented an alternative approach to make QDs by the method of laser ablation in water, which is a facile, clean, and effective synthesis method for QDs for solar cell applications due to the reduced formation of by-products in the process. This method can also be used with organic solvents when needed. We have evaluated the structural properties of the CdSe QDs by TEM and XRD. We have also investigated the photoluminescent properties of the CdSe QDs. The size distribution of the QDs was relatively broad with an average particle size of 5.1 nm as determined by TEM analysis. This is compared with the sizes of 5.0 nm from the XRD peak widths and 5.4 nm from the PL spectrum. The as-prepared QDs are ligand-free, which eliminates or reduces the barrier to extracting and transferring the electrons from the QDs to the nanowires, thus, can potentially improve the efficiency of QD-sensitized solar cells. The QDs in water suspension makes it possible to directly place them on the nanowire photoanode without complicated process of ligand exchange. The cell performance, with the short circuit current density of 0.43 mA/cm² and open circuit voltage of 0.48 V, suggests great potential of such-prepared QDs in photovoltaic applications.

This work was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering under Award DE-FG02-10ER46728.

¹A. P. Alivisatos, *Science* **271**, 933 (1996).

²B. O. Dabbousi, J. Rodriguez-Viejo, F. V. Mikulec, J. R. Heine, H. Mat-toussi, R. Ober, K. F. Jensen, and M. G. Bawendi, *J. Phys. Chem. B* **101**, 9463 (1997).

³S. Neeleswar, C. L. Chen, C. B. Tsai, and Y. Y. Chen, *Phys. Rev. B* **71**, 201307 (2005).

⁴J. B. Sambur, T. Novet, and B. A. Parkinson, *Science* **330**, 63 (2010).

⁵S. Ruhle, M. Shalom, and A. Zaban, *Chem. Phys. Chem.* **11**, 2290 (2010).

⁶R. Vogel, K. Pohl, and H. Weller, *Chem. Phys. Lett.* **174**, 241 (1990).

⁷L. Li, X. Yang, J. Gao, H. Tian, J. Zhao, A. Hagfeldt, and L. Sun, *J. Am. Chem. Soc.* **133**, 8458 (2011).

⁸K. S. Leschkes, R. Divakar, J. Basu, E. Enache-Pommer, J. E. Boercker, C. B. Carter, U. R. Kortshagen, D. J. Norris, and E. S. Aydil, *Nano Lett.* **7**, 1793 (2007).

⁹I. J. Kramer and E. H. Sargent, *ACS Nano* **5**, 8506 (2011).

¹⁰B. R. Sankapal, S. D. Sartale, C. D. Lokhande, and A. Ennaoui, *Sol. Energy Mater. Sol. Cells* **83**, 447 (2004).

¹¹Q. Shen, J. Kobayashi, L. J. Diguna, and T. Toyoda, *J. Appl. Phys.* **103**, 084304 (2008).

¹²I. Mora-Sero and J. J. Bisquert, *Phys. Chem. Lett.* **1**, 3046 (2010).

¹³Y. Tak, S. J. Hong, J. S. Lee, and K. Yong, *Cryst. Growth Des.* **9**, 2627 (2009).

¹⁴D. R. Baker and P. V. Kamat, *Adv. Funct. Mater.* **19**, 805 (2009).

¹⁵N. P. Dasgupta, H. J. Jung, O. Trejo, M. T. McDowell, A. Hryciw, M. Brongersma, R. Sinclair, and F. B. Prinz, *Nano Lett.* **11**, 934 (2011).

¹⁶Q. Dai, J. Chen, L. Lu, J. Tang, and W. Wang, *Nano Lett.* **12**, 4187 (2012).

¹⁷H. Zeng, X. W. Du, S. C. Singh, S. A. Kulinich, S. Yang, J. He, and W. Cai, *Adv. Funct. Mater.* **22**, 1333 (2012).

¹⁸N. G. Semaltianos, *Crit. Rev. Solid State Mater. Sci.* **35**, 105 (2010).

¹⁹Z. Yan and D. B. Chrisey, *J. Photochem. Photobiol. C: Photochem. Rev.* **13**, 204 (2012).

²⁰A. V. Simakin, V. V. Voronov, N. A. Kirichenko, and G. A. Shafeev, *Appl. Phys. A* **79**, 1127 (2004).

²¹K. V. Anikin, N. N. Melnik, A. V. Simakin, G. A. Shafeev, V. V. Voronov, and A. G. Vitukhnovsky, *Chem. Phys. Lett.* **366**, 357 (2002).

²²N. G. Semaltianos, S. Logothetidis, W. Perrie, S. Romani, R. J. Potter, M. Sharp, P. French, G. Dearden, and K. G. Watkins, *Europhys. Lett.* **84**, 47001 (2008).

²³A. A. Ruth and J. A. Young, *Colloids Surf. A: Physicochem. Eng. Aspects* **279**, 121 (2006).

²⁴L. Lu, J. Chen, L. Li, and W. Wang, *Nanoscale Res. Lett.* **7**, 293 (2012).

²⁵G. Ramalingam and J. Madhavan, *Arch. Appl. Sci. Res.* **3**, 217 (2011), available at: <http://scholarsresearchlibrary.com/aasr-vol3-iss3/AASR-2011-3-3-217-224.html>.

²⁶N. L. Ross, J. F. Shu, R. M. Hazen, and T. Gasparik, *Am. Mineral.* **75**, 739 (1990).

²⁷M. C. Morris, H. F. McMurdie, E. H. Evans, B. Paretkin, J. H. de Groot, C. R. Hubbard, and S. J. Carnel, *Natl. Bur. Stand. (U.S.) Monogr.* **25**, 13 (1976).

²⁸L. Brus, *J. Phys. Chem.* **90**, 2555 (1986).