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Luminescence from Surfactant-Free ZnO Quantum Dots Prepared by Laser Ablation in Liquid

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Highly transparent, luminescent and biocompatible ZnO quantum dots were prepared in water, methanol, and ethanol using liquid-phase pulsed laser ablation technique without using any surfactant. Transmission electron microscopy analysis confirmed the formation of good crystalline ZnO quantum dots with a uniform size distribution of 7 nm. The emission wavelength could be varied by varying the native defect chemistry of ZnO quantum dots and the laser fluence. Highly luminescent nontoxic ZnO quantum dots have exciting application potential as florescent probes in biomedical applications.
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Synthesis of nanoparticles has been the focus of an ever-increasing number of researchers worldwide, mainly due to their unique optical and electronic properties,[1-5] which make them ideal for a wide spectrum of applications ranging from displays[6] and lasers[7,8] to in vivo biological imaging and therapeutic agents.[9] A large number of preparation methods are reported to produce nanoparticles, such as magnetic liquids,[10] metal-polymer nanocomposites,[11] semiconductors,[12] and colloidal systems.[13] Over the past decade a technique known as liquid-phase pulsed laser ablation (LP-PLA) has aroused immense interest.[14,15] It involves the firing of laser pulses through liquids transparent to that wavelength on to the target surface. The ablation plume interacts with the surrounding liquid particles, creating cavitation bubbles which, upon their collapse, give rise to extremely high pressures and temperatures. These conditions are, however, localized and exist across the nanometer scale. LP-PLA has proven to be an effective method for preparation of many nanostructured materials, including nanocrystalline diamond,[16] cubic boron nitride,[17] and nanometer-sized particles of Ti,[18] Ag,[19] Au,[20] and TiC.[21] Wurtzite ZnO with a wide bandgap and excitonic energy of 60 meV has many important applications in UV light-emitting diodes, diode lasers, sensors, etc. Because zinc is a important trace element of humans,[22] ZnO is environmentally friendly and suitable for in vivo bioimaging and cancer detection. There have been recent reports on the synthesis of ZnO nanoparticles using LP-PLA from Zn target in an aqueous solution containing different surfactants.[23,24] Zeng et al.[24] used 1064 nm for ablation, which had greater penetration into the target, ablating more particulates.

Furthermore, without any surfactant these particles do not stand isolated. The use of metallic Zn target along with surfactants like sodium dodecyl sulfate gives rise to the formation of several by-products like $Zn(OH)_2$, and the quantum dots (QDs) were Zn/ZnO core shell structure. The present investigation is on surfactant-free pure ZnO QDs without any by-products using LP-PLA. To the best of our knowledge, LP-PLA has not been used for the synthesis of pure ZnO QDs without the use of surfactants. The literature survey shows that not much work has been done on the synthesis of ZnO QDs using methods without any surfactants. Recently we reported[25] the growth of luminescent, biocompatible ZnO QDs using the wet-chemical method without any surfactant. The preparation of high-quality ZnO QDs with specific interest in their luminescence properties and surface functionality with the aim of biological applications has not been studied widely.

In this work, we report the preparation of highly luminescent (visible to the naked eye on UV illumination), transparent, chemically pure, and crystalline ZnO QDs using LP-PLA without the aid of any surfactant. Clear, deep yellow, and bluish-violet emitting ZnO QDs fully dispersed in water, ethanol, and methanol were prepared directly from the ZnO targets by this technique without any by-product. Thus obtained biofriendly ZnO QDs can be used as fluorescent probes in various biomedical applications by easily attaching biomolecules to the bare surface of these ZnO QDs.

Experimental

A sintered ZnO (99.99%) mosaic target was used for the fabrication of ZnO QDs. ZnO target immersed in 20 mL of different liquid media like deionized water, methanol, and ethanol was ablated at room temperature by the third harmonic of a Nd:yittrium aluminum garnet laser (355 nm, repetition frequency of 10 Hz, pulse duration 9 ns). The spot size of the laser beam was 2 mm after focusing using a lens, and the ablation was done at laser fluences of 25, 35, and 45 mJ/pulse. The duration of laser ablation was 1 h in all the liquids. In water, ablation was also carried out for different durations of 1, 2, and 3 h by keeping the laser fluence at 45 mJ/pulse. This simple room-temperature technique produced highly transparent ZnO QDs well dispersed in respective liquid media. Formation of nanoparticles of ZnO was confirmed by transmission electron microscopy (TEM, JEOL) operating at an accelerating voltage of 200 kV. A small droplet of the liquid obtained after ablation was deposited onto a copper grid with carbon film for TEM analysis. Photoluminescence emission (PL) and excitation spectra were recorded using Jobin Yvon Fluoromax-3 spectrometer equipped with 150 W xenon lamp.

Results and Discussion

TEM analysis revealed that the resulting product after laser ablation with an energy of 25 mJ/pulse in water consisted of particles in the nanoregime, as shown in Fig. 1a. Statistical size analysis (Fig. 1b) shows almost uniform particle-size distribution with a particle size of 7 nm. The selective area electron diffraction (SAED) (Fig. 1c) exhibits a well-distinguishable concentric ring pattern representing the (100), (002), (102), (110), and (103) planes of hexagonal ZnO. This clearly shows the growth of crystalline ZnO QDs with random orientation. ZnO QDs were arranged in hexagonal shape as observed from a high-resolution TEM (HRTEM) image (Fig. 1d). The stacking of about 85 hexagonal unit cells makes a 7 nm sized hexagonal-shaped QD. The inset of Fig. 1d shows the arrangement of individual unit cells, which again demonstrates the crystalline quality of ZnO QDs. The Zn/ZnO composite nanoparticles grown by Zeng et al.[24] have an average particle size of 18 nm and are colored due to turbidity. An atomic-scale image shows the parallel lines of ions at intervals of 0.26 (Fig. 1e) and 0.28 nm (Fig. 1f) which correspond to (002) and (100) planes of ZnO, respectively. From TEM analysis, the formation of other molecules like $Zn(OH)_2$ or ZnO/Zn core shell formation is not found. Because the ejected molten material from the target normally reacts with medium only at

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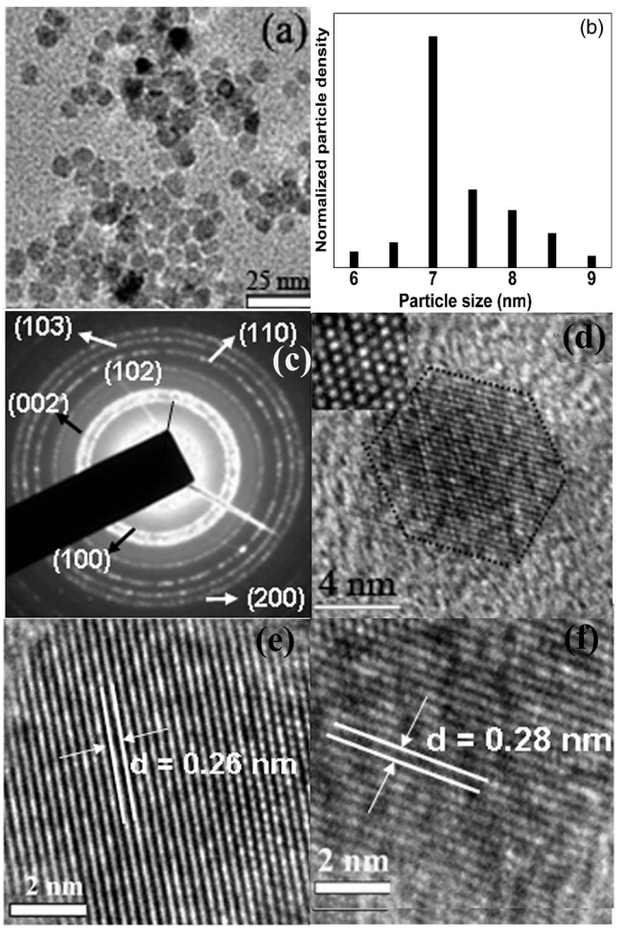

Figure 1. (a) TEM image, (b) particle-size distribution, and (c) SAED pattern of ZnO QDs obtained by laser ablation with a fluence of 25 mJ/pulse in water. (d) HRTEM image for a single QD and (inset) arrangement in the hexagonal close-packed mode. (e and f) HRTEM showing (002) and (100) planes, respectively.

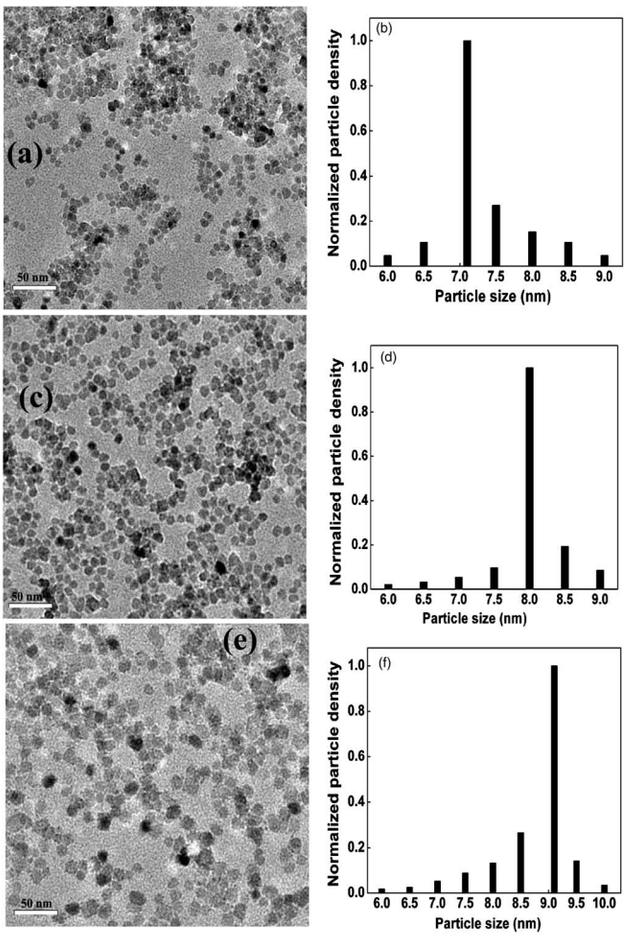

Figure 2. (a, c, and e) TEM and (b, d, and f) particle-size distribution of ZnO QDs dispersed in methanol prepared at laser fluences of 25, 35, and 45 mJ/pulse, respectively.

the outer surface,[26] the ejected plasma readily cools, thereby reforming ZnO itself. Because there are many surface defects, mainly due to surface oxygen deficiency (discussed later), these nanoparticles are charged. This surface charge provides a shield, preventing further agglomeration and thereby forming self-stabilized particles even in the absence of surfactant.

Figures 2a, c, and e show the TEM images, and b, d, and f represents the particle-size distribution pattern of the ZnO QDs prepared in methanol at laser fluences of 25, 35, and 45 mJ/pulse, respectively. It explicitly demonstrates the increase of both particle size and particle density with laser fluence. Particle sizes as observed from the size distribution (Fig. 2b, d, and f) are 7.1, 8, and 9.1 nm for ZnO QDs prepared at laser fluence of 25, 35, and 45 mJ/pulse, respectively. TEM shows a similar size distribution for those prepared in ethanol, whereas the QDs prepared in water by LP-PLA of ZnO do not show any variation in size when varying the fluence from 25 to 45 mJ/pulse. The thermodynamic conditions created by the laser-ablation plume in the liquid are localized to a nanometer scale which varies with laser fluence. This is the reason for the variation of particle size of ZnO QDs with laser fluence.

Figure 3 shows the absorption spectra of ZnO QDs (of sizes 7, 8.1, and 9 nm) dispersed in methanol prepared at a laser energy of 25, 35, and 45 mJ/pulse. The increase in laser energy (increase in particle size) resulted in red shift of the excitonic peak from 3.67 to 3.57 eV and a slightly broadened peak due to quantum size effects.[27]

PL measurement was performed on the QDs dispersed in water, ethanol, and methanol at an excitation wavelength of 345 nm. Deep-yellow luminescence was observed from the ZnO QDs dispersed in water. Figure 3a shows the photograph of highly transparent ZnO QDs (left) dispersed in water and their yellow emission under UV excitation. This yellow luminescence originates from the native oxygen defects of the prepared ZnO QDs (discussed later). Figures 4b-d show the PL spectra of ZnO QDs dispersed in water, ethanol, and methanol, respectively. Pure water, ethanol, and methanol do not show any emission under UV excitation. Each figure depicts the variation of PL intensity with the laser fluence at which these QDs were prepared in the liquid. A considerable increase in PL intensity with laser fluence is observed for all the samples. The increase in PL intensity with laser fluence cannot be attributed to an increase in particle density alone. There is a possibility of formation of more defect states at higher fluence which is not clear in the present investigation.

A blue shift in PL maximum was observed with a decrease of laser fluence in the case of QDs grown in methanol (from 2.41 eV at 45 mJ/pulse to 2.6 eV at 25 mJ/pulse) and ethanol (from 2.27 eV at 45 mJ/pulse to 2.35 eV at 25 mJ/pulse). However, the PL peak position remains unchanged for QDs grown in water.

The origin of yellow luminescence due to oxygen vacancy was further supported by the experiment done with oxygen bubbled into

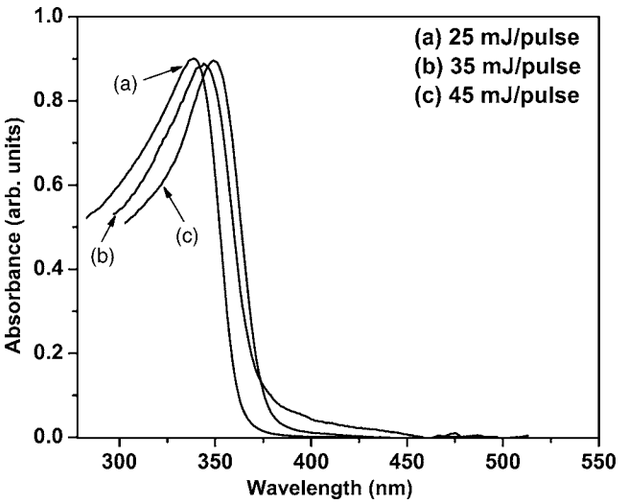

Figure 3. Absorption spectra of ZnO QDs in methanol prepared at (a) 25, (b) 35, and (c) 45 mJ/pulse.

the water during laser ablation of ZnO targets. Interestingly, PL spectrum shows an emission peaking at 408 and 427 nm in the violet blue region, suppressing the yellow emission (Fig. 5a) when oxygen was bubbled through liquid during the ablation. This emergence of deep bluish-violet emission opens the possibility of tuning emission color for different biomedical applications. The inset of Fig. 5a shows the photograph of deep bluish-violet emission. During bubbling the oxygen-defect density was considerably reduced, tending toward more stoichiometric ZnO QDs. This further supports that yellow luminescence originates from oxygen vacancies. Emission at 408 nm is due to the transition of electrons from shallow donor levels to the valance band.[28] According to Lin et al.,[29] the energy gap between the valance band and energy level of interstitial zinc is

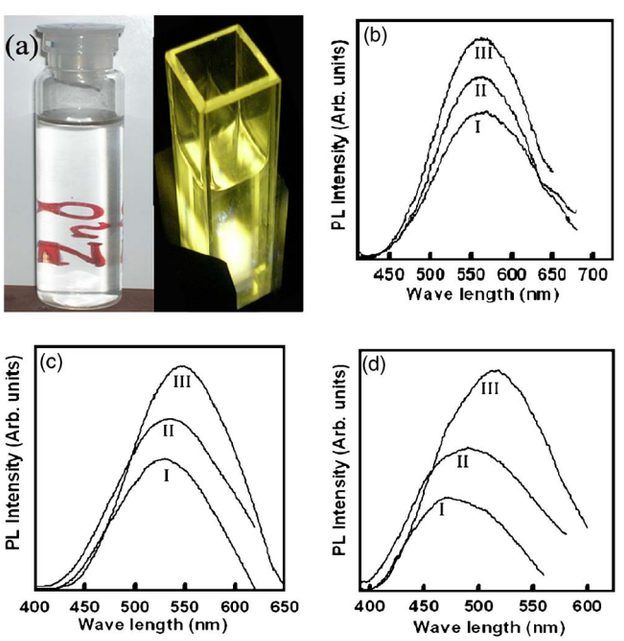

Figure 4. (Color online) (a) Photograph of transparent ZnO QDs obtained by laser ablation in water with a fluence of 25 mJ/pulse (left) and its yellow emission (right). (b) PL spectra of ZnO QDs in water, (c) ethanol, and (d) methanol. In each figure, curve I (25 mJ/pulse), curve II (35 mJ/pulse), and curve III (45 mJ/pulse) represents the laser fluence.

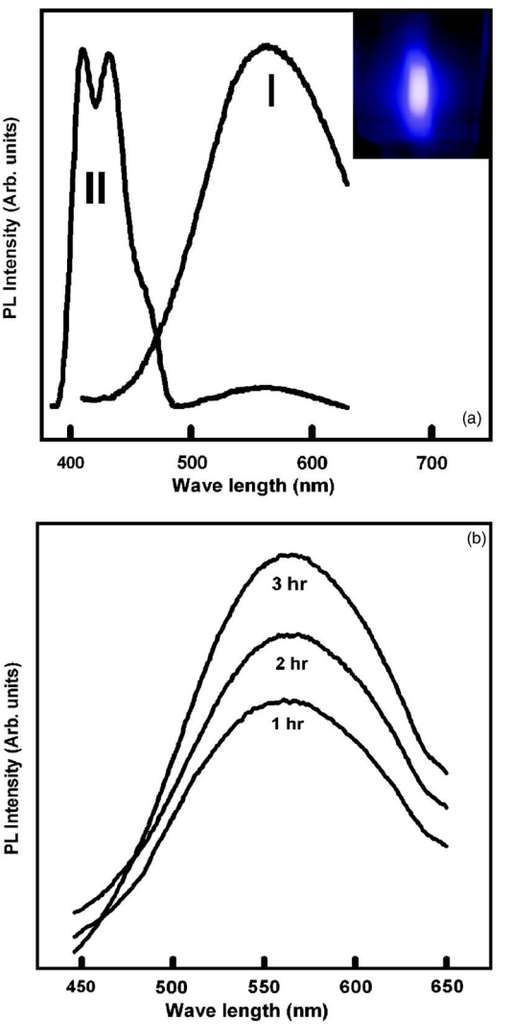

Figure 5. (Color online) (a) PL spectra of ZnO QDs prepared without (curve I) and with (curve II) oxygen atmosphere. (Inset) Photo of bluish-violet luminescence. (b) PL spectra of ZnO QDs in water for various durations of ablation.

2.9 eV. This is consistent with PL emission at 427 nm in the present study. Future application potential of ZnO QDs resides in the biomedical field, where growth of QDs in a biofriendly medium like water and its luminescent emission has been studied for various ablation times. Figure 5b shows the PL of QDs dispersed in water prepared at different ablation times, 1, 2, and 3 h, keeping the laser fluence at 45 mJ. It is found that PL intensity increases with duration of laser ablation without any shift in PL peak position. The increase in PL intensity is due to the increased density of QDs of the same size. The transparency of prepared ZnO QDs remained as such even though the duration of ablation was 3 h. The maximum concentration of ZnO QDs that was achieved while maintaining transparency was 17.5 μg/mL.

Semiconductor QDs have been covalently linked (in vivo) to biorecognition molecules such as peptides, antibodies, and nucleic acids for application as fluorescent probes.[30,31] The ZnO QDs prepared in the present study can be used in various biomedical applications by conjugating with ligands like poly(ethylene glycol) that are soluble in both mediums. Then they can be used as fluorescent probes in cancer targeting and imaging by attaching the corresponding antibodies to the bare surface of ZnO QDs.

Conclusion

In conclusion, highly transparent, deep-yellow and bluish-violet emitting, biocompatible 7 nm sized ZnO QDs were prepared in various liquid media using LP-PLA without using any surfactant. The emission wavelength was tuned by playing the defect chemistry and varying the laser fluence. The origin of yellow luminescence is due to oxygen vacancies. Highly luminescent biofriendly ZnO QDs can be used as fluorescent probes in cancer diagnosis and therapy.

Acknowledgments

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