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# UV luminescent organic-capped ZnO quantum dots synthesized by alkoxide hydrolysis with dilute water

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ABSTRACT

A novel synthesis route to organic-capped and colloidal ZnO quantum dots (QDs) has been developed. Specifically, zinc-di-*t*-butoxide and zinc-di-*n*-butoxide are hydrolyzed by very dilute water (400–600 mass ppm) in hydrophilic benzylamine and polymerized to ZnO by dehydration and/or a butanol elimination reaction. Growth of the ZnO QDs and exchange of the surface capping ligand from the hydroxyl groups and/or benzylamine to the oleylamine occur by heating the colloidal solution after addition of the oleylamine at 100–180 °C. The final ZnO QDs with diameters in the range of 3–7 nm are highly dispersible in various organic solvents. The ZnO QDs exhibit the quantum size effect upon UV emission; it was controlled between 3.39 and 3.54 eV in the present study. The defect-related Vis emission decreased and the UV emission becomes dominant when zinc-di-*n*-butoxide with a 99.99% zinc purity is used as the starting material. The intensity of the photoluminescence UV emission is 1.5 times higher than that of the Vis emission.



## 1. Introduction

Zinc oxide (ZnO) has attracted considerable interest as a material for light-emitting devices that emit in the ultraviolet (UV) region because of its wide band gap (3.37 eV) and high exciton binding energy (60 meV) [1]. In addition, its low toxicity and high natural abundance make it a potential rival to nitride semiconductors. The energy band gap of ZnO is generally adjusted by alloying with MgO [1]. However, it is difficult to increase the UV emission energy in light-emitting devices because the alloying range of rock-salt MgO with wurtzite ZnO is very limited [2]. In ZnO nanoparticles that are a few nanometers in diameter, i.e., quantum dots (QDs), the optical band gap and the UV emission energy both increase with their decreasing size without alloying due to the quantum size effect [3]. Consequently, ZnO QDs are promising for realizing advanced UV-emitting devices that have adjustable emission energies. Colloidal QDs, whose surfaces are capped by organic surfactant molecules, are very suitable for fabricating thin film devices due to their high affinity for organic polymers. Several thin film light-emitting devices have been fabricated utilizing colloidal QDs [4–6]. Over the past two decades, several methods for synthesizing colloidal ZnO QDs have been developed, such as the ester elimination reaction between zinc acetate and lower alcohols, the oxidation of metallic nanoparticles, the thermolysis of zinc organometallics and the amide elimination reaction [7–13]. However, these synthesis methods have a serious disadvantage such that the resulting ZnO QDs exhibit an intense defect-related emission in the visible (Vis) region. In the worst cases, no UV emission is observed, especially for QDs with diameters below 5 nm. It is strongly desired to develop a method that is capable of synthesizing high-quality ZnO QDs that emit intense UV light without any defect-related Vis emission. Based on previous studies on bulk ZnO, the Vis emission from ZnO QDs is assumed to be related to defects such as oxygen vacancies and metallic impurities, e.g., copper and alkaline metals [1]. Thus, to suppress the Vis emission, it is necessary to synthesize ZnO QDs with fewer oxygen vacancies and a higher metallic purity. In order to decrease the oxygen vacancies, polymerization of a zinc monomer accompanying the formation of –Zn–O–Zn– linkages, such as the successive dehydration of the hydroxyl group after the ester elimination reaction [7], is a suitable reaction. On the other hand, using a high purity zinc source should increase the metallic purity of the resulting ZnO QDs.

The alkoxide hydrolysis is a well-known synthesis route to oxides, and it is a candidate reaction for the above mentioned purpose. For example, synthesis of well crystallized $TiO_2$ nanocrystals with several nm in diameter by the titanium butoxide hydrolysis was reported [14]. Formation of zinc oxide with ~10 μm from the alkoxide was also reported [15]. However, the alkoxide hydrolysis results the particles, whose surfaces should be covered

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with hydroxyl- and alkoxy-groups. Because one of our goal is to synthesize organic-capped ZnO QDs that are colloidally dispersible in organic solvent, the alkoxide hydrolysis is not adequate on its own.

In the present study, we have studied the synthesis of organic-capped and colloidal ZnO QDs for which the UV emission is both dominant and adjustable by using zinc alkoxides as the starting materials. As a result, a novel synthesis route has been developed; it consists of alkoxide hydrolysis with very dilute water and exchange of the surface capping ligand from the hydroxyl and alkoxy group and/or benzylamine to the oleylamine. The final QD size is highly controllable by the synthesis temperature and time; the energy of the UV emission was controlled in the range from 3.39 to 3.54 eV in the present study. A 1.5 times higher UV photoluminescence intensity than the Vis emission has been successfully achieved for ZnO QDs synthesized from an alkoxide with the high zinc purity of 99.99%.

## 2. Materials and methods

### 2.1. Materials

Zinc di-*t*-butoxide ($Zn(O\text{-}t\text{-}Bu)_2$, Alfa Aesar, 99.5%), zinc di-*n*-butoxide ($Zn(O\text{-}n\text{-}Bu)_2$, Kojundo Chemical Laboratory, 99.99%), oleylamine (OLA, Aldrich, 70%), benzylamine (BZA, 99%, Kishida Chemicals), ethanol (Sigma–Aldrich, Japan, $\geqslant$99.5%), methanol (Sigma–Aldrich, Japan, 99.8%), hexane (Sigma–Aldrich, $\geqslant$99%), acetone (Kishida Chemicals, $\geqslant$99.5%) and chloroform (Sigma–Aldrich, Japan, $\geqslant$99.8%) are commercially available. BZA and OLA were distilled before use. All other chemicals were used without further purification.

### 2.2. Synthesis of colloidal ZnO QDs

The zinc alkoxide (0.1 mmol) and 3 mL of BZA were loaded into a glass vial (12 mL capacity). The solution in the vial was heated at 60 °C for 60–120 min using a reciprocal shaker. The insoluble residue was then centrifugally separated from the solution. Three milliliters of OLA was added and mixed, and the mixture in the glass vial was placed in an oil bath maintained at 100–180 °C for a predetermined time. All the above procedures were conducted in an Ar atmosphere.

### 2.3. Characterization

The powdered samples were extracted from the colloidal solution by adding ethanol or methanol, and the precipitate was washed in hexane and ethanol and dried under vacuum at room temperature. The obtained crystalline phase was identified using powder X-ray diffraction (XRD) (Rigaku, RINT2500, Cu K$\alpha$ radiation using a curved graphite receiving monochromator). The average grain size was evaluated from the full-width at half-maximum of the XRD peaks using the following Scherrer equation:

$$d = \frac{1.2\lambda}{\beta \cos\theta}, \tag{1}$$

where $\lambda$ is the X-ray wavelength, $\beta$ is the line broadening at half the maximum intensity; 1.2 is employed as the shape factor assuming spherical shape [16].

The UV–Vis absorption spectra were recorded by a Hitachi U4000 spectrophotometer. Photoluminescence (PL) and photoluminescence excitation (PLE) spectra were acquired using a JASCO FP6500 spectrometer with a monochromated xenon discharge lamp at a wavelength of 325 nm as the excitation source. Standard fluorometer cells made of $SiO_2$ glass, whose optical path length was 10 mm, were used for both the optical absorption and PL spectroscopies. Powdered ZnO QDs extracted from the product solution were redispersed in chloroform until the absorbance of the solution became 0.1 at a 300 nm wavelength, and then subjected to the optical measurements. The PL intensity detected with the spectrometer was calibrated, i.e., radiation intensity of the excitation light and the sensitivity of both the monochromator and detector were calibrated using a calibrated tungsten halogen light and the luminescence of the dye, Rhodamine B. The photoluminescence quantum yield (PLQY) was evaluated using the following equation:

$$Q_x = Q_{std}(F_x/F_{std})(A_{std}/A_x)\left(n_x^2/n_{std}^2\right), \tag{2}$$

where $Q$, $F$, $A$ and $n$ denote PLQY, the integral PL intensity, and the optical density and reflective index of the solvent, respectively. The subscripts x and std indicate the parameters for the specimen and standard sample, respectively. PBD (EXCITON, Inc.) was used as the standard sample, and its PLQY, $Q_{std}$, was 83% for the 313 nm excitation wavelength. For both the specimen and standard, the optical densities at the excitation wavelength, i.e., 325 nm, adjusted to 0.08. $n_x^2/n_{std}^2$ was 1 in the present case because of the using the same solvent.

High-resolution transmission electron micrographs (HREM) were obtained by a JEOL JEM-2000EX with an accelerating voltage of 200 kV. To acquire the NMR spectra, 20 μL of the reaction mixture was added to 400 μL of a DMSO-$d_6$ solution. All NMR spectra were recorded at 27 °C by a Bruker ARX-500 NMR spectrometer. The two-dimensional totally correlated spectroscopy (TOCSY) experiments were performed using Bruker XWIN-NMR software. The chemical shifts were referenced to TMS as the internal standard.

## 3. Results and discussion

### 3.1. Synthesis of ZnO QDs and their optical properties

The solution after the reaction between $Zn(O\text{-}t\text{-}Bu)_2$ and BZA at 60 °C and after the centrifugally separation of the insoluble residue was transparent and colorless. When ethanol was added into the solution, the solution became translucent due to aggregation of the solid component. The XRD profile of the precipitate, which is

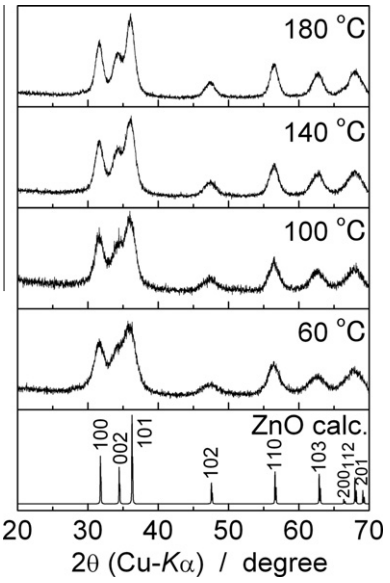


**Fig. 1.** XRD profiles of ZnO QDs synthesized at various temperatures. Heating above 100 °C was carried out for 10 min.