Nonaqueous Synthesis of Colloidal $ZnGa_2O_4$ Nanocrystals and Their Photoluminescence Properties

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Fluorescent semiconductor nanocrystals have attracted intensive interest during the past decade because of their promising applications in various fields, especially those in biological labels and biomedicine.[1] Chalcogenide nanocrystals, which are one of the best-studied semiconductor quantum dot systems, contribute to significant advances not only in fundamental research and technical applications but also in the synthesis of semiconductor nanocrystals because of their strong size-dependent photoluminescence and high quantum yields.[2] As the well developed method for these high-quality nanocrystals, the rapid injection of organic precursors into a mixture of coordinating solvents and ligands at elevated temperature could result in semiconducting nanocrystals not only with nearly monodisperse size and shape but also with high quantum yields. However, some factors considered, such as safety, stability, environment problems, and complex of synthesis procedures, their potential technical applications may be seriously limited although these materials show high performance as fluorescence materials. Therefore, much work focused on the search for environmentally more benign nanomaterials with fluorescent performance satisfying application requirements. For example, ZnO quantum dots with quantum yields of 30–80% have been prepared.[3] Haase et al. recently reported rare earth phosphate nanocrystals with 70% photoluminescence quantum yield,[4] and also quantum-sized carbon dots have been prepared for bright and colorful photoluminescence.[5]

$ZnGa_2O_4$ has received attention because of its important applications in vacuum fluorescent displays and field emission displays as a low-voltage cathode-luminescence blue phosphor.[6] Its excellent chemical stability offers advantages over sulfur-based phosphors. With a band gap of 4.4–4.7 eV, $ZnGa_2O_4$ is also potentially useful as a transparent conducting oxide with transparency through the violet to near UV region.[7] Although there has been some reports in the literature about photoluminescence (PL) of $ZnGa_2O_4$ nanomaterials, almost all of these studies have been performed on dried powders or films,[8] and PL quantum yields of these nanomaterials have never been addressed in the literature probably because of their low emission efficiency. However, it is generally accepted that the quantum yields of many materials can be markedly improved by preparing them as colloidal solutions, for which the sulfur-based phosphors are an outstanding example.[2] With respect to the use of these nanocrystals for biological applications, stable colloidal solutions are indispensable. Therefore, it is not only necessary to develop suitable methods for synthesizing ternary metal oxides like $ZnGa_2O_4$ nanocrystals but also to find ways to disperse them in water or organic solvents. To achieve these goals two pivotal problems need to be solved. One is the design of the synthesis route to $ZnGa_2O_4$ nanocrystals, and the other one is the surface modification of the nanocrystals.

Herein, we present a facile synthesis of highly luminescent $ZnGa_2O_4$ nanocrystals using the nonaqueous sol–gel method in the absence of surfactants or ligands. Nonaqueous sol–gel processes in organic solvents have recently attracted considerable interest for synthesis of nanomaterials because they are able to overcome many of the specific problems typical for aqueous systems.[9–15] In this approach, $ZnGa_2O_4$ nanocrystals with some functional chemical groups on their sufaces are obtained directly by solvothermally reacting metal acetylacetonates with benzylamine (experimental details are

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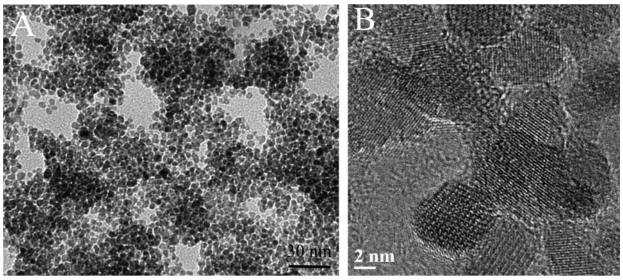

Figure 1. (A) Overview TEM and (B) HRTEM image of $ZnGa_2O_4$ nanocrystals.

given in Supporting Information). The metal acetylacetonates and benzylamine not only act as reactant and solvent but also act as stabilizing agent. The resulting nanocrystals without further surface modification can be readily dispersed in chloroform to form a fully transparent colloidal solution. The colloidal solution shows a strong blue-light emission at about 427 nm, and their PL quantum yield for the bare particles already reaches 6.8%.

Figure 1A shows a transmission electron microscopy (TEM) image of the as-synthesized $ZnGa_2O_4$ nanocrystals. The sizes and shapes of these nanocrystals are rather uniform, and there are almost no large agglomerates existing in the sample, even though no additional stabilizing agent was added and no size selection was used. The high-resolution transmission electron microscopy (HRTEM) image of the $ZnGa_2O_4$ nanocrystals is presented in Figure 1B. The well-developed lattice fringes are randomly oriented, which on the one hand confirm the high crystallinity of the sample and on the other hand prove that the particles are not coalesced. The absence of grain boundaries is clearly observed on the HRTEM image, evidencing a crystallite size predominantly in the range from 6 to 8 nm, and each particle is a single crystal. The X-ray powder diffraction (XRD) pattern of a dried sample is displayed in Figure 2. It confirms the highly crystalline cubic structure of the $ZnGa_2O_4$ nanocrystals.

The resulting transparent colloidal solution in chloroform (Figure 3A) shows an intense blue emission under a UV lamp (Figure 3B), which is not found for the corresponding powders and films.

Room-temperature absorption and PL spectra (excitation and emission) of this colloidal solution are shown in Figure 4. The excitation spectrum (Figure 4B, red curve) shows that $ZnGa_2O_4$ colloids exhibit the strongest peak at 330 nm monitored at an excitation wavelength of 427 nm, which is in good agreement with the result from the UV–vis absorption spectrum (Figure 4A). The emission spectrum (Figure 4, black curve) shows a peak position at 427 nm with excitation at 330 nm, a blue shift from the previous reports in which the peaks were generally centered at 450–470 nm.[8] This distinct blue shift is probably due to the reduced particle size and the corresponding quantum size effect, because it is well-known that in semiconductor nanocrystals the absorbance onset and emission maximum shift to higher energy with decreasing size.[12] The observed brightness of PL is reflected in the high emission quantum yield. The quantum yield was calculated to be 6.8%, excited at 347 nm. It has been demonstrated that the blue emission of $ZnGa_2O_4$ phosphors originated from the self-activation center of the octahedral Ga-–O group in the spinel lattices and the Ga^{3+} ions combine with UV-generated free electrons produced in oxygen vacancies.[6,8]

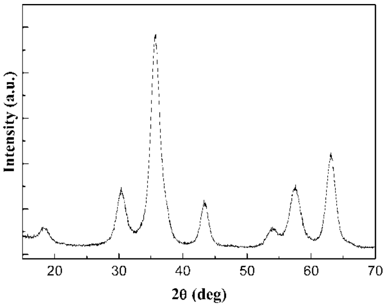

Figure 2. XRD powder pattern of $ZnGa_2O_4$.

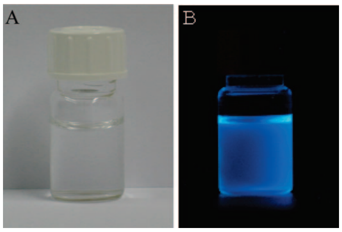

Figure 3. Photographs of the $ZnGa_2O_4$ colloidal solution (A) in sunlight and (B) under a 365 nm UV lamp.

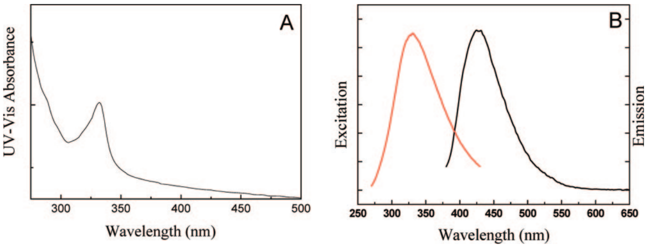

Figure 4. (A) UV–vis absorption. (B) Excitation spectrum (red) and room temperature PL spectrum of the $ZnGa_2O_4$ colloids (black).

Without any doubt, the surface properties of nanocrystals are the key for their use in many fields, especially in biological applications. The strong tendency of nanocrystals to aggregate and to grow spontaneously, as a result of their high surface areas, leads to reduced luminescence efficiency and photochemical degradation. Therefore, the modification of the nanocrystal surface usually represents a crucial and difficult task. By appropriate surface modification, the excitation can efficiently be confined to the nanocrystal core;

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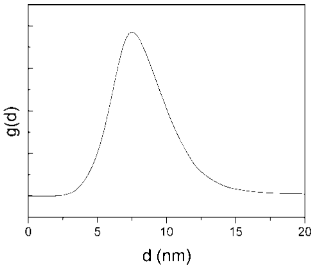

Figure 5. Particle size distribution obtained by AUC analysis of the as-synthesized $ZnGa_2O_4$ nanocrystals. *d* is the diameter of the particles, and *g*(*d*) is the differential distribution. Note that the curve is not desmeared for diffusional broadening.

nonradiative relaxation pathways are avoided, and photochemical degradation is prevented. In our case, the significant improvement of PL efficiency for $ZnGa_2O_4$ nanocrystals may be attributed to its excellent surface properties, which seems to be defect-poor even without further inorganic coating. The size distribution was investigated by analytical ultracentrifugation (AUC), which has proven to be a versatile tool for the measurement of the particle size distribution of colloidal samples. In contrast to TEM, AUC detects all particles of a colloidal sample without sampling preselection with a resolution of the particle size distribution in the Angstrom range.[16] As shown in Figure 5, the particle size distribution ranges from about 5 to 12 nm, with a peak maximum at 7.5 nm, which is in good agreement with the particle sizes measured by TEM and which also confirms again the absence of any large agglomerates. It is important to point out that the $ZnGa_2O_4$ nanocrystals can directly be redispersed in chloroform without the use of any additional surface modifying agents.

The good dispersibility of the $ZnGa_2O_4$ nanocrystals in chloroform is closely related to their surface properties that are a direct consequence of the nonaqueous sol–gel procedure. In contrast to our previous work on crystalline titania nanoparticle sols where the particle surface has to be functionalized with enediol ligands to provide good dispersibility,[17] the wet $ZnGa_2O_4$ precipitate prepared from the corresponding metal acetylacetonates and benzylamine can directly be redispersed in chloroform, yielding a completely transparent and colorless dispersion. Similarly good dispersibility was only observed in the case of tin oxide nanoparticles prepared from tin tetrachloride and benzyl alcohol.[18] In the latter example the stabilization was attributed to the formation of hydrochloric acid as a side product. Because $ZnGa_2O_4$ was synthesized without any metal halide precursors, it must be presence of organic ligands that has a positive influence on the particle size and redispersibility. The formation mechanism of metal oxide nanocrystals based on the reaction of metal acetylacetonates and benzylamine was previously described,[19] and a detailed formation mechanism encompassing solvolysis of the acetylacetonate ligand, involving C–C cleavage as well as ketimine and aldol-like condensation steps, was proposed, in which *N*-isopropylidenebenzylamine, 4-benzylamino-3-penten-2-one, and *N*-benzylacetamide were the main species found in the final mixture. These organic ligands and the solvent itself can adsorb on the surface of the nanocrystals, as it can be proven by Fourier transform infrared (FT-IR) also for the present case. Figure 6 shows, in addition to vibrational bands belonging to Zn–O–Ga and adsorbed water at 750 and 3300 cm^{-1}, other vibrational bands that are difficult to assign unambiguously but are clearly attributed to organic compounds. The bands at 2963 and 3033 cm^{-1} are characteristic of the C–H vibration of benzene rings, and the bands at 1563 and 1495 cm^{-1} are typical C=O and C–O vibrations when carbonyl groups coordinate with metal atoms in a bridging manner. The band at 1563 cm^{-1} is also possibly ascribed to a C=N vibration. Therefore, it is evident that a shell of organic molecules is attached to the surface of the nanoparticles.

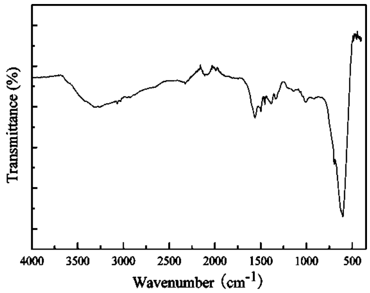

Figure 6. FT-IR spectrum of the dried and washed $ZnGa_2O_4$ nanopowder.

According to the adsorption spectrum in Figure 3A, these organic molecules have no fluorescence and they act only as stabilizing agents. It is straightforward to use them also as a potential source for appropriate organic derivatization, but they can also be substituted by other organic ligands, for example, to prove water dispersability.

In conclusion, we have presented the nonaqueous synthesis of crystalline $ZnGa_2O_4$ nanocrystals with a mean size of about 7 nm and with a narrow particle size distribution. The nanocrystals can easily be dispersed in chloroform to form stable colloids without the use of any additional stabilizers. Strong blue fluorescence was observed from the clear colloidal solution of the nanocrystals under UV light. These observations point to a potential use of the particles as a new class of fluorescent biomarkers which are more stable and more biologically benign than the currently employed Cd derivatives.

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Supporting Information Available: Experimental procedures (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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