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Size-Tunable Phosphorescence in Colloidal Metastable γ-Ga_2O_3 Nanocrystals

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Abstract: We report a colloidal synthesis of gallium oxide (Ga_2O_3) nanocrystals having metastable cubic crystal structure (γ phase) and uniform size distribution. Using the synthesized nanocrystal size series we demonstrate for the first time a size-tunable photoluminescence in Ga_2O_3 from ultraviolet to blue, with the emission shifting to lower energies with increasing nanocrystal size. The observed photoluminescence is dominated by defect-based donor−acceptor pair recombination and has a lifetime of several milliseconds. Importantly, the decay of this phosphorescence is also size dependent. The phosphorescence energy and the decay rate increase with decreasing nanocrystal size, owing to a reduced donor−acceptor separation. These results allow for a rational and predictable tuning of the optical properties of this technologically important material and demonstrate the possibility of manipulating the localized defect interactions via nanocrystal size. Furthermore, the same defect states, particularly donors, are also implicated in electrical conductivity rendering monodispersed Ga_2O_3 nanocrystals a promising material for multifunctional optoelectronic structures and devices.

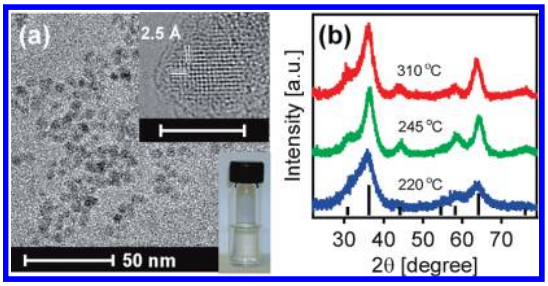

Figure 1. (a) TEM image of 6.0 ± 1.1 nm Ga_2O_3 NCs synthesized at 310 °C. Insets: (Top) High resolution TEM image of a single NC (scale bar, 5 nm). Lattice spacings match (311) *d*-spacing of cubic Ga_2O_3. (Bottom) Photograph of a NC colloidal suspension. (b) XRD patterns of Ga_2O_3 NCs prepared at different temperatures. Black lines: XRD of bulk cubic Ga_2O_3.

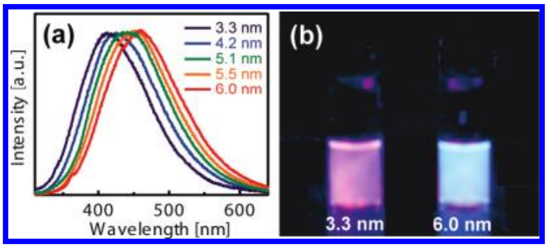

Figure 2. (a) 300 K PL spectra of γ-Ga_2O_3 NCs ranging from 3.3 to 6.0 nm excited with $\lambda = 250$ nm. (b) Photograph of colloidal 3.3 and 6.0 nm γ-Ga_2O_3 NCs illuminated with 250 nm UV light.

Transparent conducting oxide (TCO) nanostructures have recently attracted much scientific and practical interest because of their transparency as well as a range of crystal lattice structures and technologically relevant properties.[1,2] Among TCOs gallium oxide (Ga_2O_3) is considered to be the widest band gap semiconductor ($E_g \approx 4.9$ eV) and has been long known to exhibit both high conductivity[3] and visible photoluminescence (PL).[4,5] Owing to its properties Ga_2O_3 can be used in optoelectronics, including the development of inexpensive light-emitting devices (LEDs) and displays,[6] as well as for sensors[7] and in photocatalysis.[8] Furthermore, this combination of properties allows for the design of novel multifunctional devices.

Structural defects such as oxygen vacancies play a crucial role in defining the properties of TCOs.[9] The conductivity of Ga_2O_3 prepared under reducing conditions originates from the presence of oxygen vacancies, which act as shallow donors with the activation energy of ca. 0.02−0.03 eV.[3,10] PL properties of Ga_2O_3 have also been associated with internal defects.[5,10] Although the emission intensity of monoclinic (β phase) Ga_2O_3 has been shown to be sensitive to the preparation method,[5] the systematic and reproducible tuning of the luminescence energy has not yet been demonstrated. Other high-energy phases of Ga_2O_3 have been much less studied and understood, due in part to the difficulties in their controlled synthesis and isolation.[11,12] PL has been reported, however, for powders of metastable γ-Ga_2O_3 with cubic crystal structure.[11] In this work we report the synthesis of truly colloidal γ-Ga_2O_3 nanocrystals (NCs) and, for the first time, demonstrate size-tunable PL in Ga_2O_3. The observed PL is dominated by associated donor−acceptor pair recombination and has a lifetime of several milliseconds. This electron−hole recombination between charged defect sites acting as donors and acceptors is strongly influenced by Coulombic interactions and, as such, is dependent on their separation. These results allow for predictable tuning of the optical properties of Ga_2O_3 and demonstrate the possibility of manipulating the localized defect interactions through NC size.

The size-controlled synthesis of colloidal γ-Ga_2O_3 NCs was performed in oleylamine (OA) as a coordinating solvent. In a 100 mL flask 0.5 g of gallium acetylacetonate ($Ga(acac)_3$) was mixed with 7.0 g of OA, and the temperature of the mixture was raised to 80 °C. After $Ga(acac)_3$ was fully dissolved, the solution was degassed and heated to 200−310 °C at the average rate of 3 °C/min while continuously stirring under a flow of argon. This reaction mixture was refluxed at the desired temperature for 7 h. The NCs were then precipitated with an equal volume of ethanol and centrifuged at 3000 rpm for 5 min. The obtained white powder was washed 3 times with ethanol followed by centrifugation. Finally, NCs were capped with tri-*n*-octylphosphine oxide (TOPO) and dispersed in hexane or toluene.[2] The average size can be tuned by growth temperature from 3.3 ± 0.5 nm (at 200 °C) to 6.0 ± 1.1 nm (at 310 °C).

A transmission electron microscopy (TEM) image of typical NCs synthesized at 310 °C is shown in Figure 1a. The NCs have quasi-spherical morphology with an average size of 6.0 ± 1.1 nm (Figures S1, 2), and form clear colorless suspensions in nonpolar organic

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solvents (Figure 1a, bottom inset). These NCs are highly crystalline and have a cubic crystal structure (γ-Ga_2O_3), as evident from the high resolution TEM image (Figure 1a, top inset) and X-ray diffraction (XRD) pattern (Figure 1b, red). The broadening of XRD peaks increases for NCs synthesized at lower reaction temperatures due to a decrease in average NC sizes (Figure 1b). We have recently shown that metastable phases of TCOs can be spontaneously stabilized with high selectivity in colloidal NCs by controlling their sizes and growth kinetics, owing to the surface energy and surface stress contributions.[2,13] The formation of γ-Ga_2O_3 NCs demonstrates the generality of that process and indicates that the size-structure correlation in colloidal syntheses leads to a high degree of structural selectivity and phase purity even for materials that exhibit several allotropic modifications.

The absorption spectra of the series of γ-Ga_2O_3 NCs are nearly identical (Figure S3) indicating the negligible effect of quantum confinement in the studied size range, contrary to some previous suggestions.[11] This is expected based on the large effective mass of electrons ($m_e \approx 0.34m_0$) and tight exciton binding in Ga_2O_3.[12] Figure 2a shows PL spectra of γ-Ga_2O_3 NCs ranging in diameters from 3.3 to 6.0 nm, excited in the conduction band. The syntheses resulted in NCs which are strongly emissive from near-UV to blue, with an average quantum yield of 23%. The observed PL is size-tunable, and the spectra exhibit a significant red shift with increasing NC size. The large Stokes shifts (Figure S4) indicate a localized nature of recombining electrons and holes. A photograph of 3.3 and 6.0 nm diameter NC samples (Figure 2b) qualitatively illustrates the intensity and size dependence of the emitted light. These data, together with the PL spectra of bulk β-Ga_2O_3 (Figure S5), indicate that both size and structure play a key role in defining the properties of Ga_2O_3.

Optical excitation of β-Ga_2O_3 through the band gap usually results in two different emission components, UV (high-energy) and blue (low-energy). UV emission has been attributed to the recombination of a self-trapped exciton, while the blue emission arises from the tunnel recombination of an electron on a donor with a hole on an acceptor, where the donor is an oxygen vacancy (V_O^x) and the acceptor could be either a gallium ion vacancy (V_{Ga}''') or a pair of charged vacancies ($(V_O,V_{Ga})'$).[10] The dominant blue emission has a much longer lifetime[4] and can be distinguished by delayed PL measurements. Figure 3a shows the PL spectra of γ-Ga_2O_3 NCs 2 ms after excitation. For delay times $t > 100$ μs after excitation, the high-energy component vanishes (the half-life has been suggested to be ca. 30 ns in β-Ga_2O_3),[4] and the low-energy component remains as phosphorescence. This afterglow persists for several milliseconds upon the initial excitation. The decay dynamics of this feature was studied for different NC sizes using time-resolved PL (Figure 3b). The decay curves cannot be fit accurately to either single or biexponential functions (Figure S6), suggesting that the decay dynamics is not driven by the transition probability of the recombination centers. Importantly, the decay rate is strongly size dependent and increases with decreasing NC size. The half-lives for 3.3, 4.2, and 6.0 nm NCs are determined to be 4.66, 4.90, and 5.67 μs, respectively. This phenomenon has not been previously reported due to the unavailability of colloidal NCs with controlled sizes and size distributions.

Both steady-state and time-resolved PL results can be considered in the context of the associated donor−acceptor pair (DAP) model.[14] According to this model an electron excited into the conduction band is trapped by a donor (in this case an oxygen vacancy). The first step in the relaxation process is a tunnel transfer of the electron from the donor to an acceptor to form a trapped exciton. This step is followed by recombination of the exciton at the acceptor site.

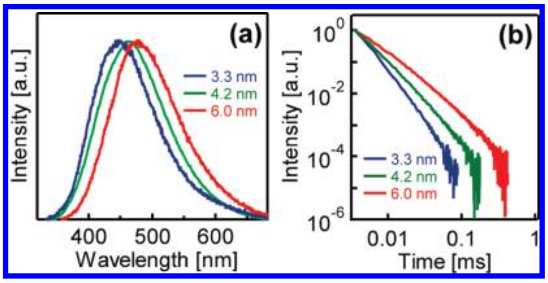

Figure 3. (a) Delayed PL spectra of γ-Ga_2O_3 NCs having different sizes, collected 2 ms after excitation into band gap. (b) Phosphorescence decay dynamics of γ-Ga_2O_3 NCs in (a). The samples were excited at 250 nm and measured at maximum of the phosphorescence peak.

The energy of emitted light is determined by the Coulombic interactions between ionized donors and acceptors and can be expressed as

$$E = E_g - (E_d + E_a) + E_C \pm nE_{\text{phonon}} \qquad (1)$$

where E_g is the band gap energy, E_d and E_a are the donor and acceptor binding energies, respectively, $E_C = e^2/4\pi\varepsilon r$ is the Coulombic interaction term, and E_{phonon} represents the energies of phonons involved in the radiative transitions. The average donor−acceptor separation (r) decreases with decreasing NC size leading to an increase in the emission energy. Assuming that E_d and E_a are size independent, r is estimated to be within an order of magnitude larger in 6.0 than in 3.3 nm NCs. The emission intensity arising from donor−acceptor recombination at time t depends on the concentration of the majority defects, in this case donors, and the recombination probability for a donor−acceptor pair with separation r (see also Supporting Information).[14]

Shortening of the phosphorescence lifetime with decreasing NC size is therefore also associated with reduced distances between donors and acceptors. The calculated phosphorescence decay curves using modified DAP model are in very good agreement with the experimental data for different NC sizes (Figure S7).[14] Taken together these data suggest that a decrease in r with decreasing NC size is a consequence of the higher concentration of point defects and smaller domain volumes. A higher defect concentration may be caused by a lower synthesis temperature and possibly a greater propensity for defect formation in NCs with higher surface areas.

In summary, in this work we reported the first size-controlled synthesis of colloidal γ-Ga_2O_3 NCs and demonstrated size tunable PL from UV to blue. The NCs exhibit long lifetime phosphorescence arising from donor−acceptor pair recombination. The size-controlled synthesis of colloidal γ-Ga_2O_3 NCs enables the manipulation of their optical properties by tuning the interactions of localized defects. These defects are also responsible for electrical conductivity, and the ability to tune their optical properties is very promising for application in multifunctional optoelectronic materials and devices.

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Supporting Information Available: Experimental details; NC size distributions; absorption/excitation and PL spectra; calculated emission decays. This material is available free of charge via the Internet at http://pubs.acs.org.

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