High Stable Exciton Emission from SnO_2 Quantum Dots Grown via a Facile "Top-down" Strategy

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Abstract— SnO_2 is a promising wide band gap semiconductor for next generation ultraviolet (UV) non-polar optoelectronic devices applications. The development of SnO_2-based optoelectronic devices is obsessed by its low exciton emission efficiency. In this study, quantum confined SnO_2 nanocrystals have been facilely fabricated via pulsed laser ablation in liquid. The intensity of exciton emission from SnO_2 quantum dots (QDs) was stable for at least two years. The SnO_2 QDs possess high thermal stable exciton emission at 300 nm in water. Therefore, we have shown that SnO_2 QDs can be a potential luminescent material suitable for the realization of ultraviolet B non-polar light emitting devices and lasing devices.

The research on ultraviolet (UV) light emitting devices is enormously stimulated by the demand of full solid state lightning, integrated photonics, environmental circulation and biomedical diagnostics, and et al. [1]. Tin oxide (SnO_2) is an IV-VI semiconductors with wide direct band gap of 3.6 eV (3.2 eV for ZnO), high exciton binding energy of 130 meV (60 meV or ZnO), and exotic electrical characteristics (e.g., electron mobility: $\sim$250 cm^2/Vs, concentration: $\sim10^{19}/cm^3$), supreme chemical and physical stability [2, 3]. Moreover, SnO_2 and other IV-VI semiconductors have weak ionicity of chemical bond, and the p-type doping, which have greatly obsess the progress of ZnO-based light emitting devices, can be more facilely realized.

The SnO_2-based light emitting devices with different structures have been demonstrated [1, 4–6]. The main difficulty that cumbers the development of SnO_2-based light emitting devices is its weak exciton emission efficiency. Most of the UV luminescence from SnO_2 nanowires, films, or single crystal is believed to originate from the defects or unidentified impurities rather than the free exciton emission [7–10]. The valence band and the conduction band of the SnO_2 have same parity symmetry, and the dipole transition probability between the conduction and valence band is quite low [11]. As a result, the exciton or band-to-band emission can hardly be obtained in SnO_2 films or bulk. For quantum materials, the band structures of semiconductors will be modified due to the quantum confinement effect, and exciton emission is anticipated to be realized in quantum confined SnO_2 nanocrystals. At the same time, the intensity of exciton emission will dramatically increase with size decreasing according to the theoretical calculation [12]. In this study, we report on the thermal stability of exciton emission from high quality SnO_2 QDs grown by PLAL technique, a "top-down" strategy. The resultant SnO_2 QDs exhibit extra-high performance exciton emission properties at $\sim$300 nm, which may be applied for UV-B QDs light emitting devices.

Figure 1(b) indicates the typical photoluminescence (PL) spectra and the thermal stability of SnO_2 QDs in water in the wavelength range of 275 nm$\sim$460 nm. There are two emission peaks observed from the PL spectrum of the SnO_2 QDs: the dominant exciton emission peak at wavelength of $\sim$300 nm and weak defects-related emission peak at $\sim$404 nm. The detailed fabrication process can be found in our previous investigation [13]. The origination of the above two peaks has been demonstrated in our previous report [13]. It should be noted that the room temperature exciton emission intensity increases with storage time interval increasing at ambient temperature or high temperature at 90°C in a sealed bottle, as shown in Figure 1(b). There are some defects existed on the surface of as-prepared SnO_2 QDs, the crystal quality may be enhanced for long time storage, and defects will decrease after storage. This is consistent with the PL spectrum results, i.e., the ratio of exciton-to-defects intensity gradually increased with storage time. At the same time, the exciton emission peak slightly red shift with storage time increasing, which may be due to the SnO_2 QDs particle size grows up during storage. It should be pointed out that the exciton

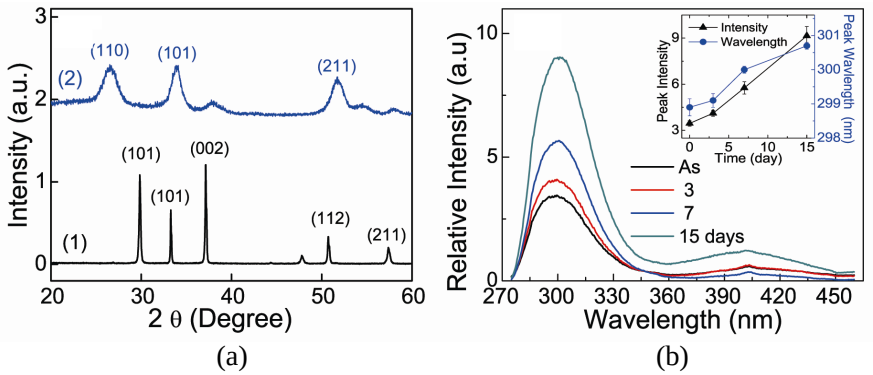

Figure 1: (a) X-ray diffraction (XRD) of (1) SnO starting material and (2) as-prepared SnO_2 nanoparticles by ns pulsed laser ablation. (b) PL Stability of SnO_2 QDs after different storage time interval at 90°C.

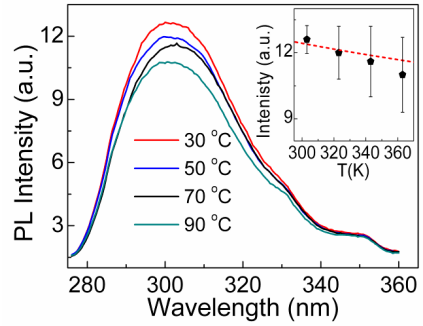

Figure 2: Thermal stability of exciton emission from SnO_2 QDs. inset, variation of peak intensity with temperature, redline: fitting curve, error bar: standard deviation.

emission intensity of SnO_2 QDs did not show any decrease even storage in ambient temperature for more than 24 months.

SnO_2 has supreme physical and chemical stability, which has been applied for chemical sensors, photocatalysis and solar cells. The SnO_2 nanocrystals exhibit high stable photoluminescence properties in several solvents, such as ethanol, acetone, and toluene [1]. For actual light emitting devices applications, the SnO_2 QDs need suffer from the increased temperature due to device resistance-induced heat. In order to understand the thermal stability of exciton emission, the PL spectrum of SnO_2 QDs in water at different temperature (30°C to 90 °C) was *in situ* investigated, as shown in Figure 2. The exciton emission of SnO_2 QDs exhibits high thermal stability; and the intensity only slightly decreases (∼9%) with temperature increasing from room temperature to 90°C.

In the intermediate temperature range, the variation in PL intensity mainly can be attributed to partial thermal dissociation of excitons. The temperature dependence of the exciton intensity can therefore be modeled by [14],

$$I_{FX}(T) = \frac{A}{1 + Be^{-\frac{E_b}{k_B T}}} \tag{1}$$

where E_g is the exciton binding energy, k_B is the Boltzmann constant. The temperature dependence of the exciton peak intensity is plotted in inset in Fig. 2. The results can be well described by the Eq. (1), and the fitted value of E_b is 140.9 meV, which is well consistent with the SnO_2 QDs exciton binding energy of 147 meV deduced from the optical absorption spectra [13].

In summary, the quantum confined SnO_2 nanocrystals have been facilely fabricated by nanosecond laser ablation of SnO in liquid. The SnO_2 QDs exhibit high performance exciton emission at 300 nm. The exciton emission manifests high thermal and time stability. The resultant SnO_2 QDs has strong enough exciton emission efficiency and thermal stability for development of ultraviolet-B band light emitting devices and laser devices.

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