

# Lanthanum-doped ZnO quantum dots with greatly enhanced fluorescent quantum yield

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## Measurement of quantum yields.

The fluorescence quantum yield (QY) is an important parameter to evaluate the efficiency of the emission process in luminescent materials, which is defined as the ratio of the number of emitted photons to the number of absorbed photons per time unit.<sup>1</sup>

$$\Phi = \frac{\text{number of emitted photons}}{\text{number of absorbed photons}} \quad (1)$$

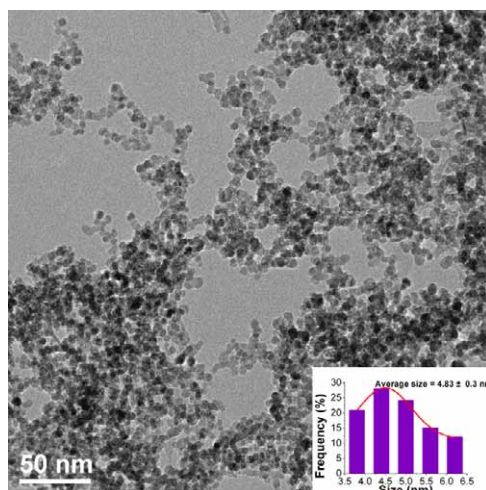
Usually, the relative quantum yield of the unknown is compared with that of a reference sample:

$$\Phi_X = \left( \frac{A_R}{A_X} \right) \left( \frac{F_R}{F_X} \right) \left( \frac{n_R}{n_X} \right)^2 \Phi_R \quad (2)$$

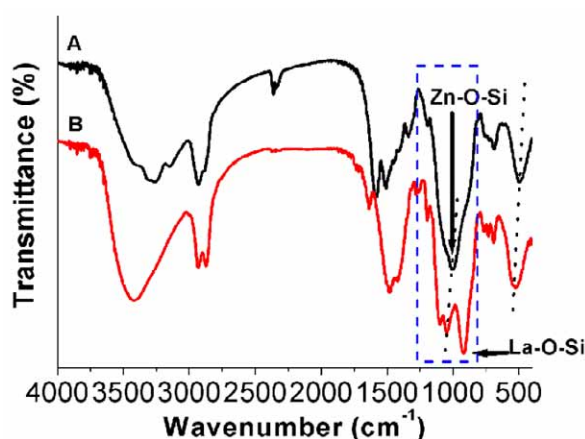
where  $\Phi$  is the luminescence quantum yield,  $A$  the absorbance at the excitation wavelength,  $F$  the integrated fluorescence intensity (that is, the area of the fluorescence spectrum), and  $n$  the refractive index of the solvents used. The subscripts  $R$  and  $X$  refer to the reference and the unknown, respectively. When the same solvent is used for both the reference and the unknown, the factor  $(n_X/n_R)^2$  will be equal to unity.

To minimize the errors, Rhodamine 6G in ethanol was selected as the standard, a well-accepted reference for green emission<sup>2</sup> and the same parameters were used for measuring the absorption and photoluminescence spectra of the standard materials and the tested samples. To overcome the errors caused by single-point measurement, we make the absorbance of both Rhodamine 6G and quantum dot ethanol solutions between 0.04 and

0.05<sup>3</sup> by tuning six different concentrations for each sample. Then, the QY of the test samples is calculated by equation (2).



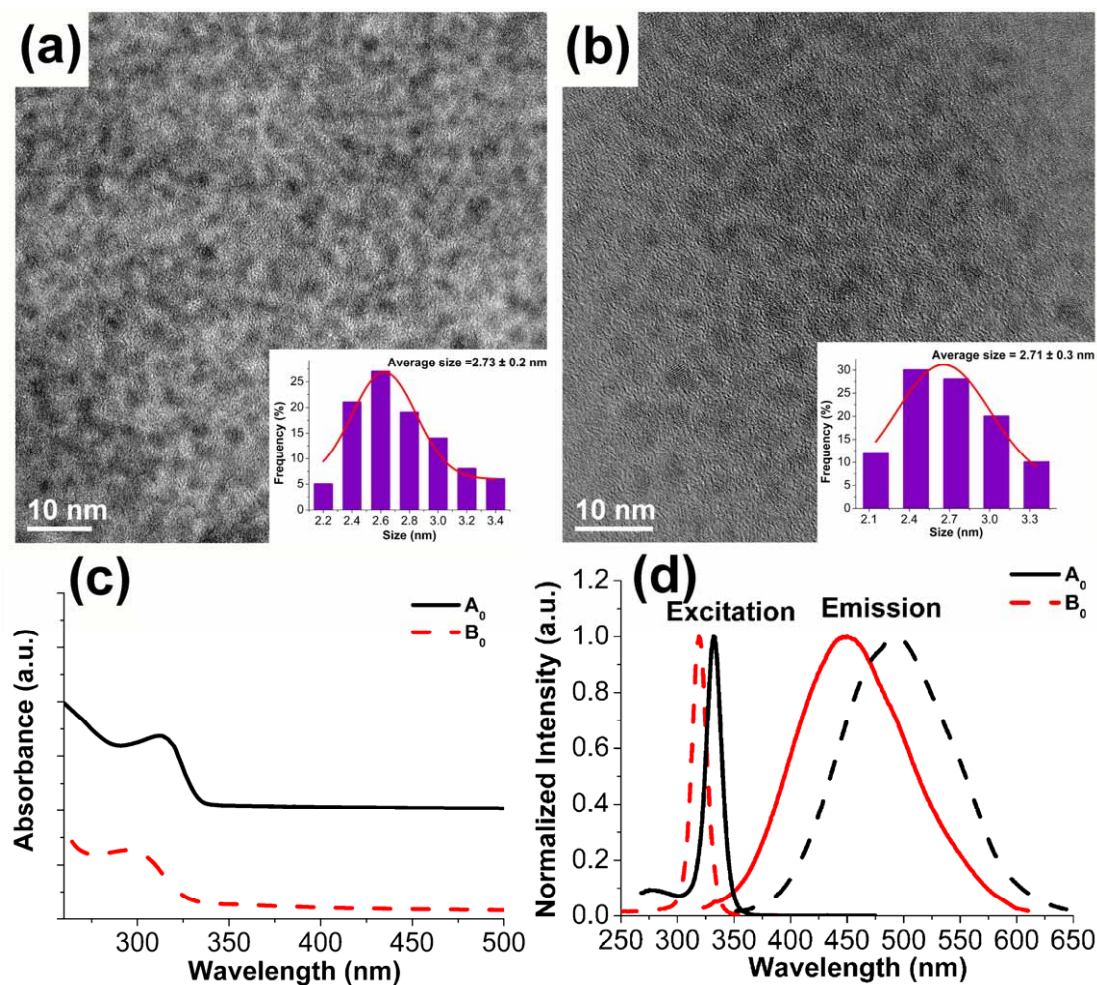
**Figure S1.** TEM images of un-doped ZnO QDs without surface-modification. The insets show the corresponding size distribution histogram.



**Figure S2.** FTIR spectra of (A) un-doped ZnO QDs with surface-modification and (B) 10 mol% La-doped ZnO QDs with surface-modification.

As shown in Figure S2, 930 cm<sup>-1</sup>~1110 cm<sup>-1</sup> is ascribed to M-O-Si (M=Si, Zn, La) vibrations. 1110 cm<sup>-1</sup> is assigned to Si-O-Si vibration,<sup>4</sup> La-O-Si (930 cm<sup>-1</sup>) peak appears at a position of 200 cm<sup>-1</sup> lower than Si-O-Si because La is heavier than Si.<sup>5</sup> The vibration of 1000 cm<sup>-1</sup> indicates the formation of Zn-O-Si bond,<sup>6</sup> and the vibration shifts to lower frequency at 1060 cm<sup>-1</sup> after incorporation of La<sup>3+</sup> ions. In addition, the Zn-O vibration is located at 489 cm<sup>-1</sup>, and it shifts to lower frequency at 540 cm<sup>-1</sup> which is ascribed to

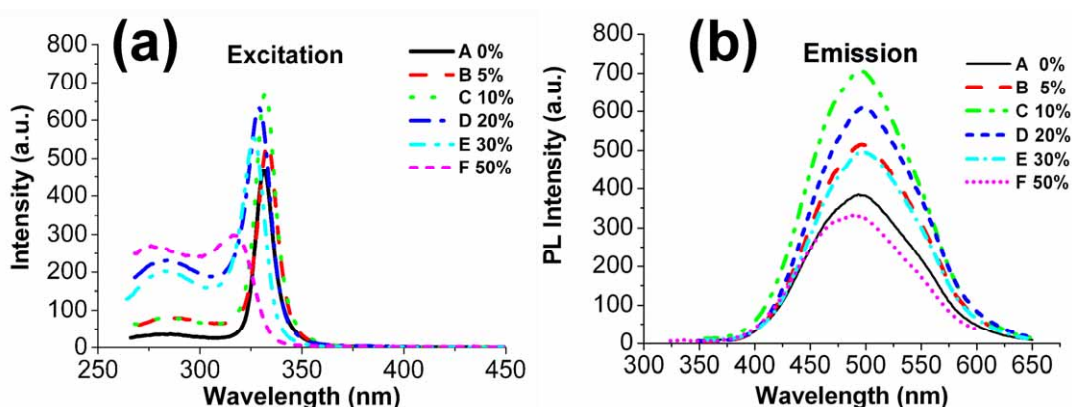
doping with  $\text{La}^{3+}$  ions,<sup>7</sup> because La atom is more active and easier to lose outer electrons than Zn atom. Thus, La serves as an electron donating group to ZnO, and makes Zn-O vibration shift to lower frequency in IR spectra. The above information indicates the formation of La–O–Zn bond. It can thus be deduced that at least a part of  $\text{La}^{3+}$  ions have been incorporated into the ZnO lattice by substituting  $\text{Zn}^{2+}$  ions similar to the report for Mg-doped ZnO QDs.<sup>7</sup>



**Figure S3.** TEM images of (a) the un-doped ZnO QDs (sample A<sub>0</sub>) and (b) the 10 mol% La-doped ZnO QDs (sample B<sub>0</sub>), and their corresponding (c) UV-Vis absorption and (d) normalized PL spectra. The insets in (a)-(b) show the corresponding size distributions.

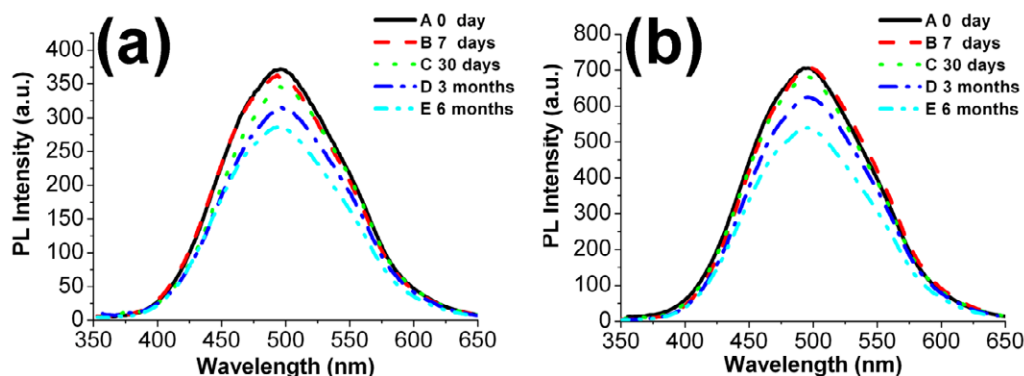
It can be seen from the above images (Figure S3a-b) that the size of the un-doped ZnO QDs (A<sub>0</sub>) and the 10 mol% La-doped ZnO QDs (B<sub>0</sub>) are almost the same (~ 2.7 nm). The band gap ( $E_g$ ) of the samples A<sub>0</sub> and B<sub>0</sub>, obtained according to the equation

$(\alpha h\nu)^2 = A(h\nu - E_g)$ , are 3.735 eV and 3.746 eV, respectively. In Figure S3c-d, the UV-Vis absorption and photoluminescence properties of the La-doped ZnO QDs are compared with those of the un-doped ZnO QDs with the same size, which excludes the influence due to size changing. The results show that the La incorporation affects the band gap and photoluminescence properties of ZnO QDs. This gives an experimental evidence for the theoretical studies on the broadening band gap and blue shift of the optical absorption by La-doping reported previously by Liu et al.<sup>9</sup>



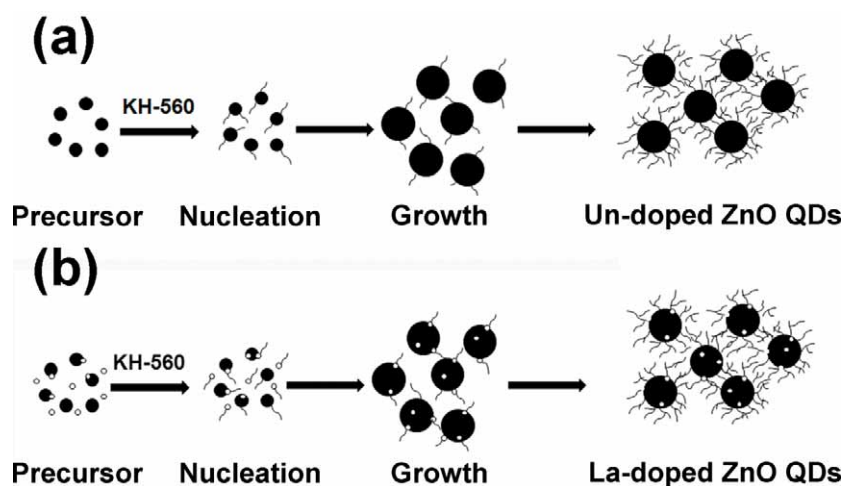
**Figure S4.** (a) PL excitation spectra and (b) PL emission spectra of the samples A-F. The percentage of La-A: 0 mol%, B: 5 mol%, C: 10 mol %, D: 20 mol %, E: 30 mol %, F: 50 mol %.

For ZnO QDs, the optimal emission cannot be excited at the excitonic peak from the absorption spectrum. There are different optimal excitation wavelengths for ZnO QDs with different sizes and doped-La<sup>3+</sup> loadings.<sup>7</sup> The optimal excitation wavelengths are obtained in terms of the following three steps: first, the absorption edge of the UV-Vis absorption (Figure 5a) is used as a primary excitation wavelength, a corresponding emission spectrum is then got; second, from this emission spectrum an excitation spectrum as shown in Figure S4a is obtained by setting the emission wavelength at the emission peak; finally, the excitation peak from the excitation spectrum is chosen as the optimal excitation wavelength, and the final emission spectrum as shown in Figure 4b is got under this optimal excitation wavelength.



**Figure S5.** PL stability of (a) un-doped ZnO QDs with surface-modification and (b) La-doped ZnO QDs with surface-modification.

The PL spectra of the un-doped ZnO QDs and La-doped ZnO QDs were recorded via a fluorescent spectroscopy (Hitachi F-4600) at different times, comprising 0 days, 7 days, 30 days, 3 months and 6 months. The high stability of the surface modified ZnO QDs has been achieved as shown in Figure S5 not like unmodified ZnO QDs with a poor stability.<sup>8</sup> The spectra shows the similar PL stability of both the La-doped ZnO QDs and un-doped ZnO QDs with surface-modification, indicating that the high PL stability of ZnO QDs with KH 560 surface modification<sup>8</sup> is not destroyed after introducing La to the quantum dots.



**Figure S6.** Schematic diagram for probable growth process of (a) un-doped ZnO QDs with surface-modification and (b,c) La-doped ZnO QDs with surface-modification. In the above schematic diagram, the black ball, white ball and curve represent ZnO, La<sup>3+</sup> ions, KH-560, respectively.



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