Electronic Supplementary Information

Enhanced Visible Photoluminescence in ZnO Quantum Dots by Promotion of Oxygen Vacancy Formation†

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EXPERIMENTAL PROCEDURES

1. Synthesis of multicolour emitting ZnO quantum dots

The starting precursors Zn(OAc)_2 (Sigma Aldrich, 99.99 %, metal basis) and LiOH (Sigma Aldrich, ≥ 98%, reagent grade) were used as received without further purification. The solvent used for synthesis was absolute ethanol (Analytical Reagent, China, Assay: 99.99 %). In a typical synthesis 0.549 g of (0.05M) Zn(OAc)_2 was dissolved in 50 ml of absolute ethanol by ultrasonic mixing followed by refluxing at 78º C under N₂ atmosphere to obtain a clear solution. Different molar concentrations of LiOH were prepared by ultrasonic mixing of LiOH powder in absolute ethanol by a degassing ultrasonic bath for 30 minutes. The above procedure removed small suspended gas bubbles present in the precursor solution to create an oxygen deficient environment during reaction. Reaction was initiated by the addition of LiOH solution into Zn(OAc)_2 solution at room temperature (RT), in a biphasic gas–liquid batch reactor, which could maintain inert environment for the synthesis. The schematic of a biphasic gas–liquid batch reactor operating at RT is given in Fig. S1. During reaction, volume ratio of gas to liquid was
maintained at 8.33 along with magnetic stirring for maintaining an oxygen free environment during synthesis.

![Biphasic gas–liquid batch reactor for defect rich ZnO QDs synthesis.](image)

**Fig. S1** Biphasic gas–liquid batch reactor for defect rich ZnO QDs synthesis.

In order to control the particle size, [Zn]/[LiOH] ratio was varied. The ZnO QDs (that precipitated at different [Zn]/[LiOH] ratio) were centrifuged in a cooling centrifuge at 0° C to prevent growth during separation and the precipitate obtained was washed with absolute ethanol to remove unreacted precursors. Characterization was carried out on purified QDs. Control experiments were performed under normal atmospheric conditions without ultrasonic degassing of the precursor solution for all molar ratio of [Zn]/[LiOH].

2. **Characterization**

X-ray powder diffraction (XRD) data were collected using Philips (PANalytical) powder diffractometer PW3040/60 X'pert Pro with Cu Kα radiation. The electron diffraction and
micrographs were recorded using JEOL JEM-2100F high-resolution transmission electron microscope (HRTEM). UV-Vis absorption spectra were acquired using JASCO V-570 UV-Vis Spectrophotometer (400-250nm) and the photoluminescence spectra were acquired using Perkin Elmer LS 55 model (Quinine sulfate and Rhodamine 6G were used as references for quantum yield (QY) calculation). Paramagnetic centres associated with single charged oxygen vacancy were studied using Varian E-112 EPR spectrometer.

![XRD pattern of samples synthesised with different [Zn]/[LiOH] ratio under inert environment.](image)

**Fig. S2** XRD pattern of samples synthesised with different [Zn]/[LiOH] ratio under inert environment.

The crystallite size is estimated from the X-ray line broadening using Scherrer formula.

\[ D = \frac{0.9\lambda}{B \cos \theta_B} \]  

Where \( \lambda \) is the X-ray wavelength (Cu K\(_\alpha\), \( \lambda = 0.15418 \) nm), \( \theta_B \) is the Bragg diffraction angle, and \( B \) is the full width at half-maximum. According to the diffraction peak positions and the width at half-maximum, the mean size of ZnO QDs was calculated, and the results are given in main text.
Surface atomic defect structures of the ZnO QDs is acquired by taking HRTEM images at different focal planes above and below the surface of each sample. These images were compared to obtain the focus value that gives us the most precise image of the surface. The defects observed in the image can be assigned to oxygen vacancy due to following two reasons,

1) Oxygen has the highest crystal diameter (0.248 nm) in Wurtzite ZnO, this is within the resolution limit (0.19 nm for JEOL JEM-2100F, operating voltage of the microscope was 200
keV) of TEM used in this study. In the case of Zinc, crystal diameter is 0.148 nm in Wurtzite ZnO; this is below the resolution limit of TEM (JEOL JEM-2100F).

2) When considering the different scattering powers of electron by heavy atom Zn and light atom O, the bright contrast in TEM micrograph is a result of O, while the dark contrast is from heavy Zn atom.

Fig. S4 (a) UV-visible absorption spectra of ZnO QDs suspended in ethanol. (b) $(\alpha h\nu)^2$ versus $h\nu$ plot obtained from absorption curve.
The particle size of QDs can be obtained from UV-Vis absorption spectroscopy. For direct band gap semiconductors the relationship between the absorption coefficient near the absorption edge and the excitation energy \( (hv) \) obeys the following relation.

\[
(\alpha hv)^2 = A(hv - E_{g(bulk)})
\]

…..(2)

Where \( A \) is a parameter that relates to the effective mass associated with valence and conduction bands, and \( E_{g(bulk)} \) is the bulk band gap. From this relationship, we can obtain the band gap values of ZnO QDs with different absorption edges.

Fig. S4b shows the absorbance spectra for ZnO QDs replotted according to eq 2. Extrapolating the linear part until it intersects with the \( hv \) axis, the intercept is the band gap value for each sample. The band gap values \( (E_g) \) obtained was inserted into to an approximation (eq 3) reported by Schoenhalz et al. to obtain corresponding diameter ‘\( d \)’ of the nanocrystal and the results are shown in main text (table 1).

\[
E_g = 3.41 + 3.87 \times d^{1.83}
\]

…..(3)

**Fig. S5** Variation of (a) bandgap and (b) visible emission maxima (converted to eV from the data of Fig. 3a) with diameter of ZnO QDs.
Fig. S6 PL intensity comparison (by fixing the optical density of samples at an absorbance of 0.08 at 340 nm) of different colour emitting ZnO QDs synthesized by varying molar ratio of [Zn]/[LiOH] in oxygen deficient and oxygen rich environment. a) [Zn]/[LiOH] = 0.25 b) [Zn]/[LiOH] = 0.33 c) [Zn]/[LiOH] = 0.67 d) [Zn]/[LiOH] = 1 and e) [Zn]/[LiOH] = 2. Integrated PL intensity of $\lambda_{\text{max}}$ were taken for comparison.
**Fig. S7** Quantum yield comparison of different colour emitting ZnO QDs synthesized under oxygen deficient milieu and control with standard dyes (Quinine sulfate and Rhodamine 6G). a) [Zn]/[LiOH] = 0.25 b) [Zn]/[LiOH] = 0.33 c) [Zn]/[LiOH] = 0.67 d) [Zn]/[LiOH] = 1 and e) [Zn]/[LiOH] = 2.
In Quantum yield (QY) estimation\(^4\), typically ZnO QDs and the standards (Quinine sulfate in 0.1 N H\(_2\)SO\(_4\) and Rhodamine 6G) are irradiated by the same excitation light. The quantum yields of ZnO QDs were calculated using equation 4.

\[
\Phi = \Phi_s \left[\left(I \cdot A_s \cdot n^2\right)/\left(I_s \cdot A_s \cdot n_s^2\right)\right]
\]  

…..(4)

where \(\Phi\) is the quantum yield, \(I\) is the integrated intensity, \(A\) is the optical density and \(n\) is the refractive index of the solvent. The subscript \(S\) refers to the standard reference of known quantum yield. The excitation wavelength of both the sample and the standard should have similar optical density. Here we fixed the optical density of sample and standard at an absorbance of 0.08 at 340 nm. Then the integrated emissions of both PL spectra were compared to calculate the QY of the sample, taking into account the QY value of the standard as 0.55 for Quinine sulfate and 0.95 for Rhodamine 6G. The refractive indexes of water and ethanol are 1.333 and 1.3614 respectively.

References