

Supporting Information

Photoluminescent ZnO nanoparticles synthesized at the interface between air and triethylene glycol

Huan-Ming Xiong,* Ri-Zhao Ma, Su-Feng Wang and Yong-Yao Xia

Department of Chemistry and Shanghai Key Laboratory of Molecular Catalysis and Innovative
Materials, Fudan University, Shanghai 200433, P.R. China

E-mail: hmxiong@fudan.edu.cn

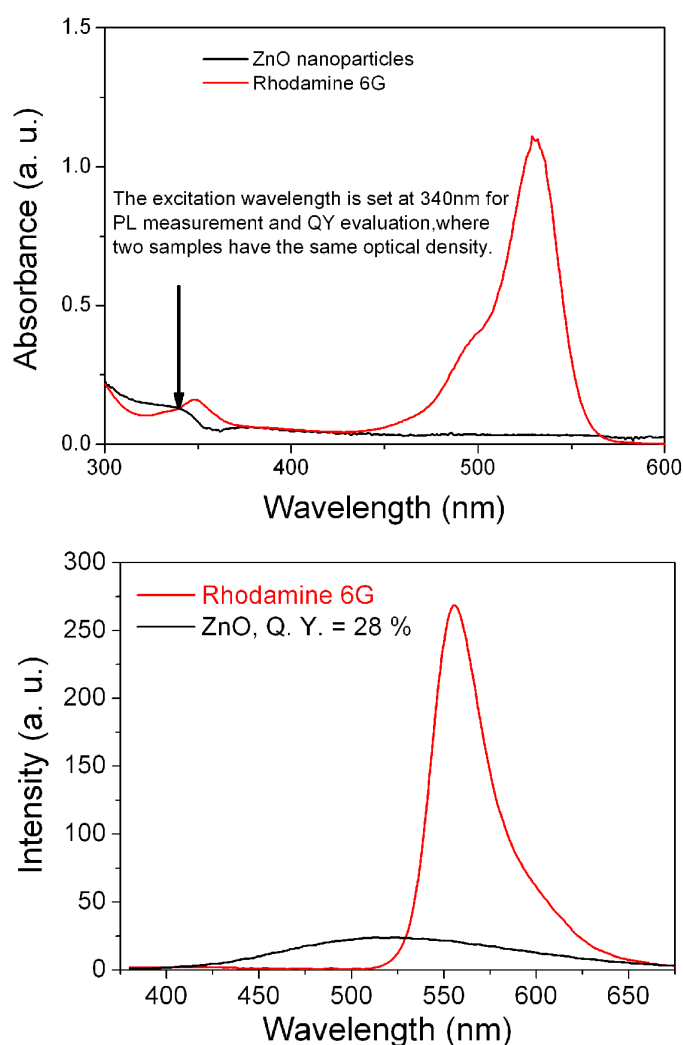


Figure S1. In a typical procedure of QY estimation, the sample (ZnO) and the standard (R6G) should be irradiated by the same excitation light, and at the light wavelength both the sample and the standard should have similar optical density. Then the integrated emissions of both PL spectra are compared to calculate the QY of the sample, taking into account the QY value of the standard. (See *J. Am. Chem. Soc.*, 2002, **124**, 2049.) For R6G in ethanol, the standard QY is 95 %. After comparing the emission areas of both ethanol solutions, the QY of ZnO nanoparticles is figured out to be 28 %.

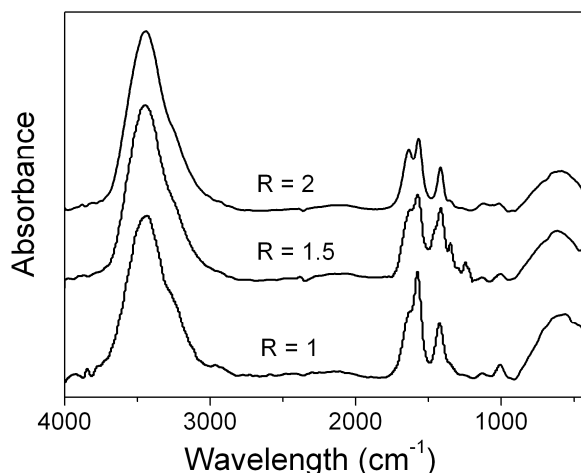


Figure S2. In a control experiment, ZnO nanoparticles are prepared in TEG under the protection of nitrogen gas. After nonsolvent precipitation and washing, the ZnO samples are dried in a vacuum oven. The IR spectra of three samples only show very weak absorbance at 1100 cm⁻¹ where is the typical band for C-O-C of TEG, indicating that only a tiny amount of TEG are adsorbed on ZnO nanoparticles. Hence, this control experiment proves that TEG cannot be oxidized without air and thus it will not be modified onto ZnO through chemical bonds. The IR bands at about 1600 and 1400 cm⁻¹ are ascribed to coordination between acetate groups and Zn ions on ZnO surface, which has been reported in Ref. 25 and 29.

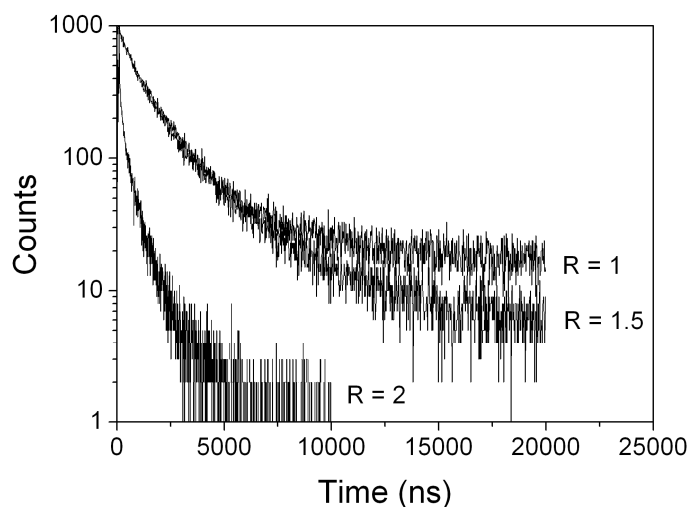


Figure S3. Decay curves of ZnO nanoparticles are recorded by an Edinburgh FLS 920 Spectrometer. The emission maxima are monitored at 530 nm (R = 1), 510 nm (R = 1.5) and 490 nm (R = 2) respectively. All three curves are fit into a two exponential formula, and the Chi-squared χ values are very close to 1. $F(t) = A + B_1 \exp(-t/\tau_1) + B_2 \exp(-t/\tau_2)$

For ZnO (R = 1), $\tau_1 = 3066$ ns (51.31 %), $\tau_2 = 1000$ ns (49.69 %), $B_1 = 220$, $B_2 = 640$, $\chi = 1.123$.

For ZnO (R = 1.5), $\tau_1 = 2750$ ns (50.08 %), $\tau_2 = 885$ ns (49.92 %), $B_1 = 225$, $B_2 = 697$, $\chi = 1.077$.

For ZnO (R = 2), $\tau_1 = 729$ ns (74.08 %), $\tau_2 = 109$ ns (25.92 %), $B_1 = 143$, $B_2 = 333$, $\chi = 1.001$.

The data of ZnO (R = 1) and ZnO (R = 1.5) are similar with the results reported in Ref. 18 and *Langmuir* 2003, **19**, 3006. Hence, the trap-state emission of both samples can be interpreted as recombination of shallowly trapped electrons and deeply trapped holes. However, the results like those of ZnO (R = 2) are not seen in literature.

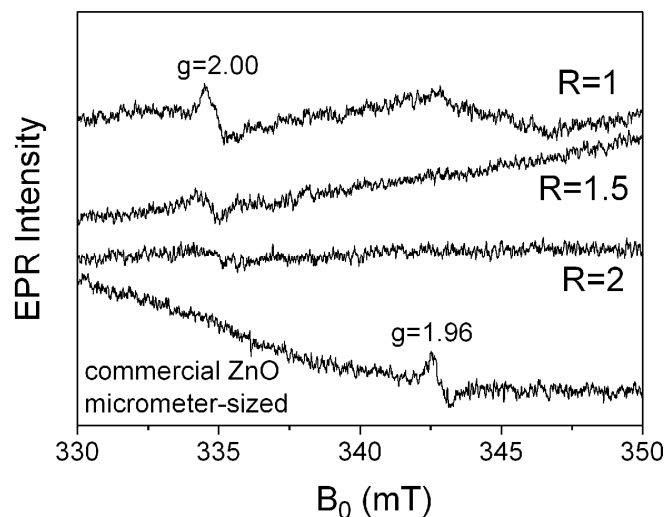


Figure S4. Electron paramagnetic resonance (EPR) data are obtained by a JEOL JES-FA200 spectrometer. Unfortunately, there are some faults with the spectrometer and thus the noise signals are rather strong. Nevertheless, the data clearly show the commercial micrometer-sized ZnO powder has signal at $g = 1.96$ representing bulk defects. For the ZnO nanoparticles of 3 ~ 4 nm, such bulk defects cannot be detected but another signal at $g = 2.00$ emerges which is attributed to surface defects. (See *Chem. Mater.* 2010, **22**, 2203.) Although these nanoparticles have similar particle size, their aggregation degrees are different for three samples so that the amounts of TEG ligands on ZnO surfaces are different (Fig. 7). The EPR signal at $g = 2.00$ decreases when R increases, indicating that the ZnO (R=2) is best protected and its surface defects are well passivated. It should be mentioned that the above results are qualitative and not accurate due to spectrometer errors.