Electronic Supplementary Information

Synthesis of silane surface modified ZnO quantum dots with ultrastable, strong and tunable luminescence

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Experimental Section

0.002 mol of $Zn(CH_3COO)_2{\cdot}2H_2O$ was dissolved in 20 mL of absolute ethanol and the solution was refluxed at 80℃ for 2 h under continuous stirring at atmospheric pressure. To synthesize silane surface modified ZnO QDs, the as-obtained solution was cooled to 0℃ in an ice water bath, and KH-560 was added to the solution and intensely stirred for 20 minutes to ensure adequate dispersion. Thereafter, Zn(Ⅱ) precursor was obtained. Meanwhile, a given amount of $LiOH{\cdot}H_2O$ was dissolved in ethanol by ultrasonic technique and then cooled down to 0℃. The Zn(Ⅱ) precursor and LiOH ethanol solution were mixed at a temperature of around 0℃, followed by extensive stirring for 30 minutes to obtain a transparent colorless solution containing ZnO QDs. Four different sizes of ZnO QDs (denoted by A, B, C and D) were realized under the molar ratio of $LiOH/Zn^{2+}$ with a value of 2.5, 1.9, 1.4 and 1.0 at the mixing temperature of 0℃, respectively. In addition, to obtain silane surface modified ZnO QDs with longer wavelength (sample E), 100 mL of the Zn(Ⅱ) precursor was reacted with 1 ml of 10 M NaOH aqueous solution at 80℃ under vigorous stirring for 30 minutes.

Control experiment was carried out in the absence of KH-560. Corresponding unmodified ZnO samples were denoted by A_0-E_0.

Silane surface modified ZnO samples (B, D, and E) were incorporated into polyvinyl alcohol (PVA) matrix, respectively. The as-prepared films were denoted by film-B, film-D, and film-E. These composite films were employed for anti-counterfeit applications in expensive high-end liquors.

The luminescent spectra were measured using a fluorescent photometer (Hitachi F-4600). Transmission electron microscope (TEM) images were taken on a JEM-2100F instrument (operated at 200 kV). Fourier transform infrared (FTIR) spectra were obtained with a Varian 3100 FTIR spectrometer by the KBr method. To evaluate the quantum yields of the ZnO QDs, quinine sulfate in 0.5 M sulfuric acid was used as a reference for samples emitting blue light while rhodamine 6G in ethanol was employed as a reference for samples with green and yellow emission according to the literature.[1,2]

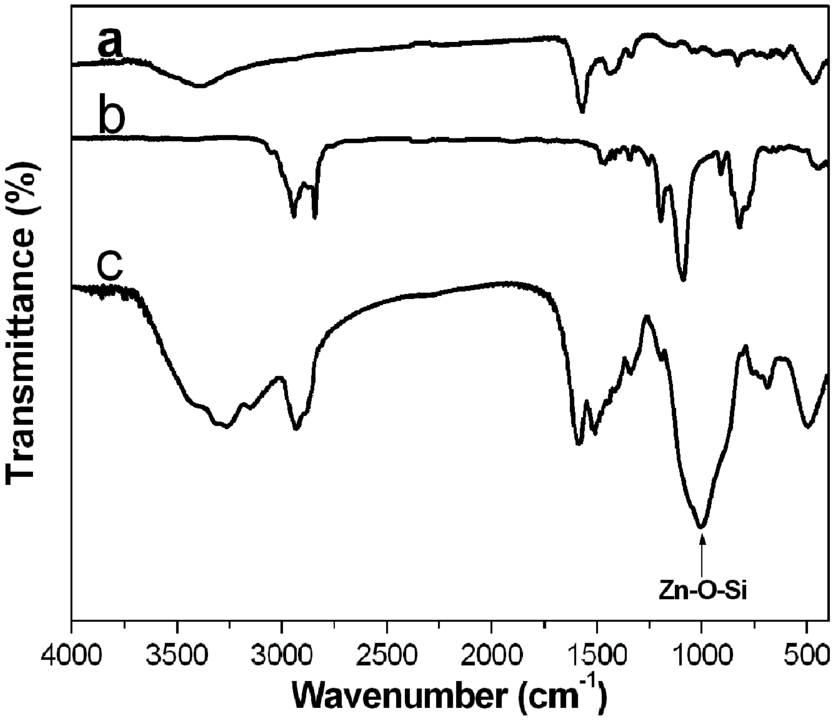

Figure S1. FTIR spectra of (a) unmodified ZnO QDs, (b) KH-560 and (c) silane surface modified ZnO QDs.

The FTIR spectra of unmodified ZnO QDs, KH-560 and silane surface modified ZnO QDs are exhibited in Figure S1. As shown in spectrum C, the formation of a covalent Zn-O-Si bond is evident by the broad band centered at approximately 1000 cm^{-1}, indicating that silane has been successfully coated onto the surface of ZnO core for the surface modified ZnO QDs. This result agrees with the relevant reports.[3,4]

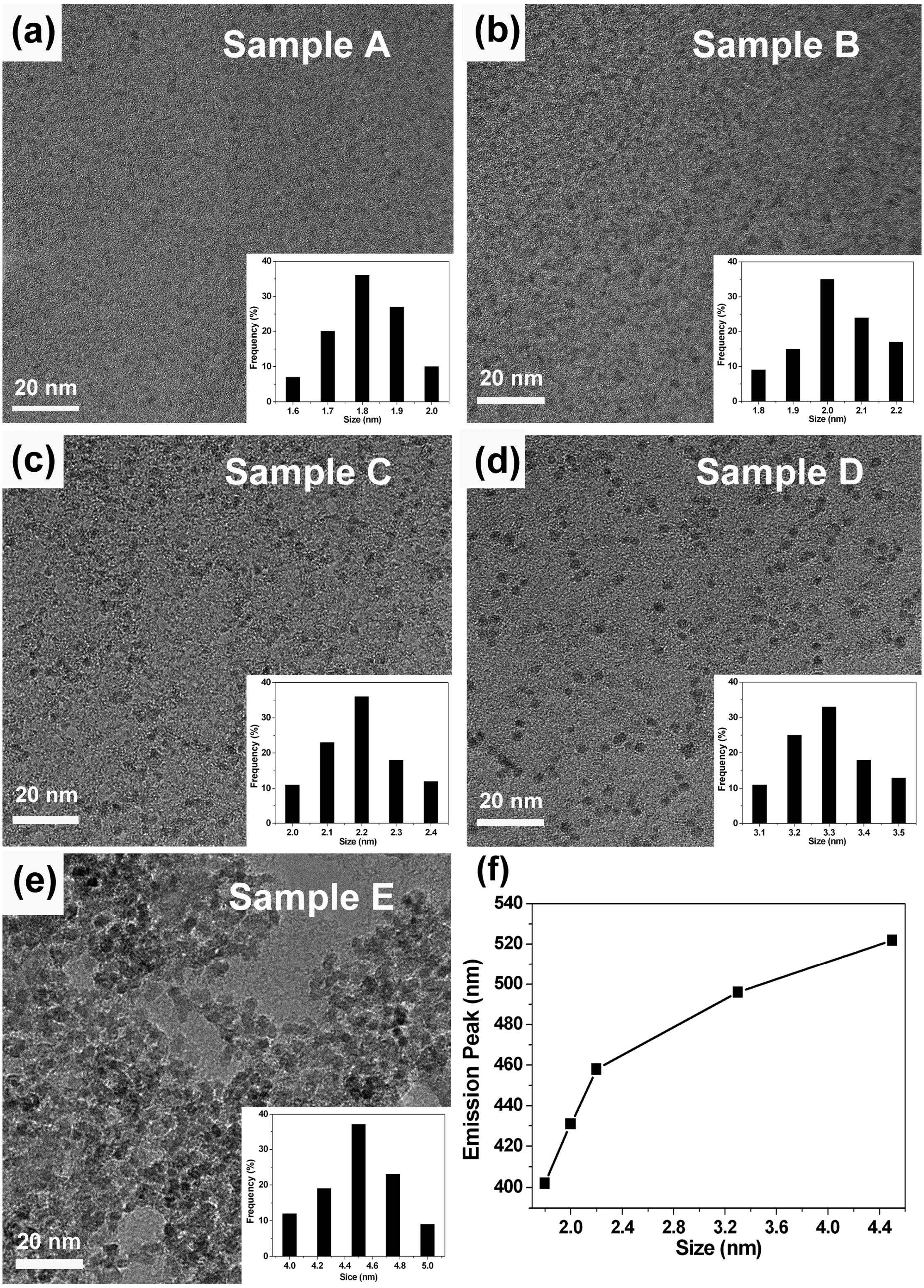

Figure S2. TEM images (a-e) and emission peak versus particle size (f) of silane surface modified ZnO QDs. The inset shows the histogram of ZnO size distribution. The average particle diameter is 1.8±0.2, 2.0±0.2, 2.2±0.2, 3.3±0.2, and 4.5±0.5 for Samples A-E, respectively.

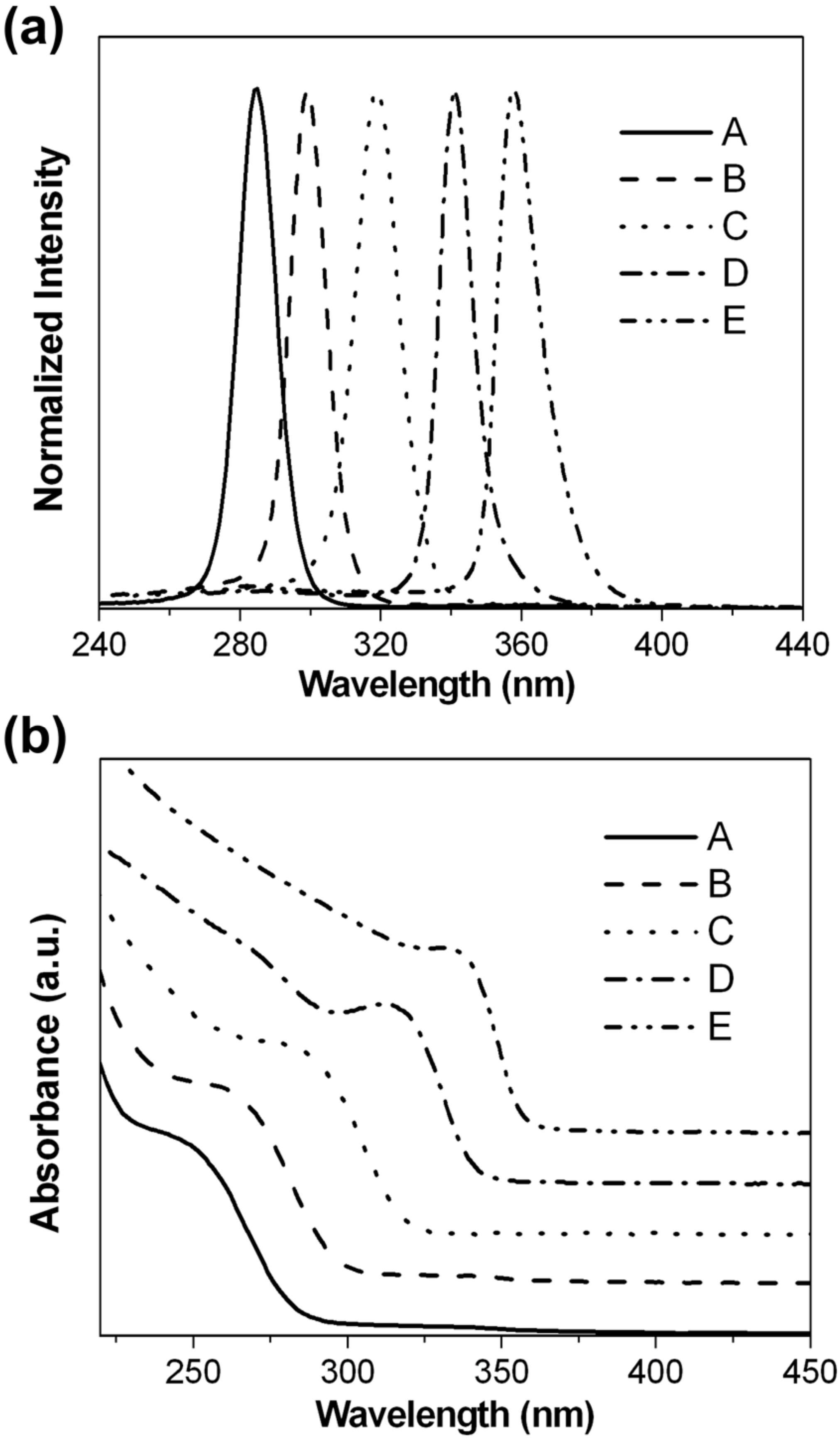

Figure S3. (a) Excitation and (b) absorption spectra of samples A-E.

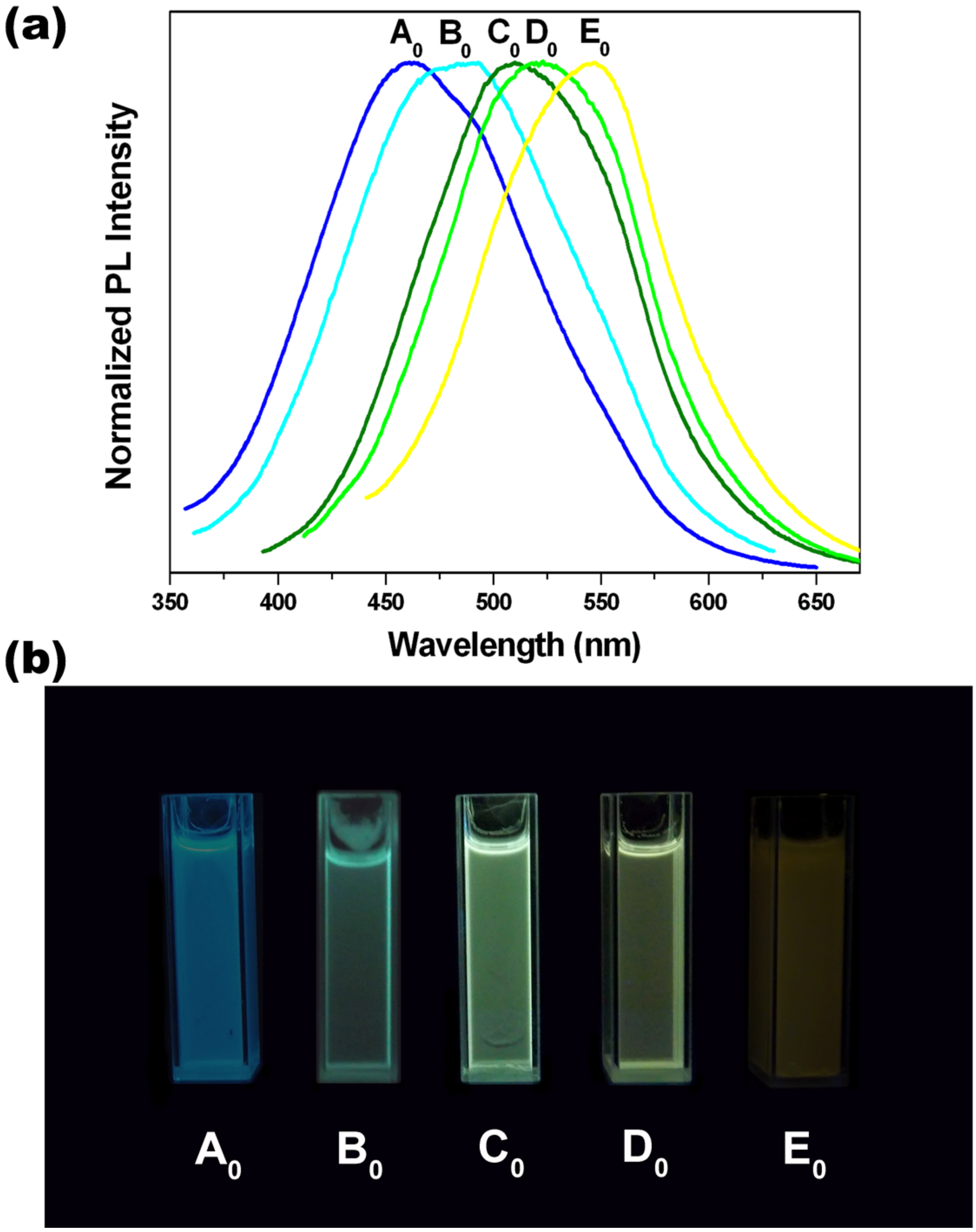

Figure S4. (a) PL spectra and (b) digital photograph of unmodified ZnO samples (A_0-E_0) under 302 nm UV light irradiation.

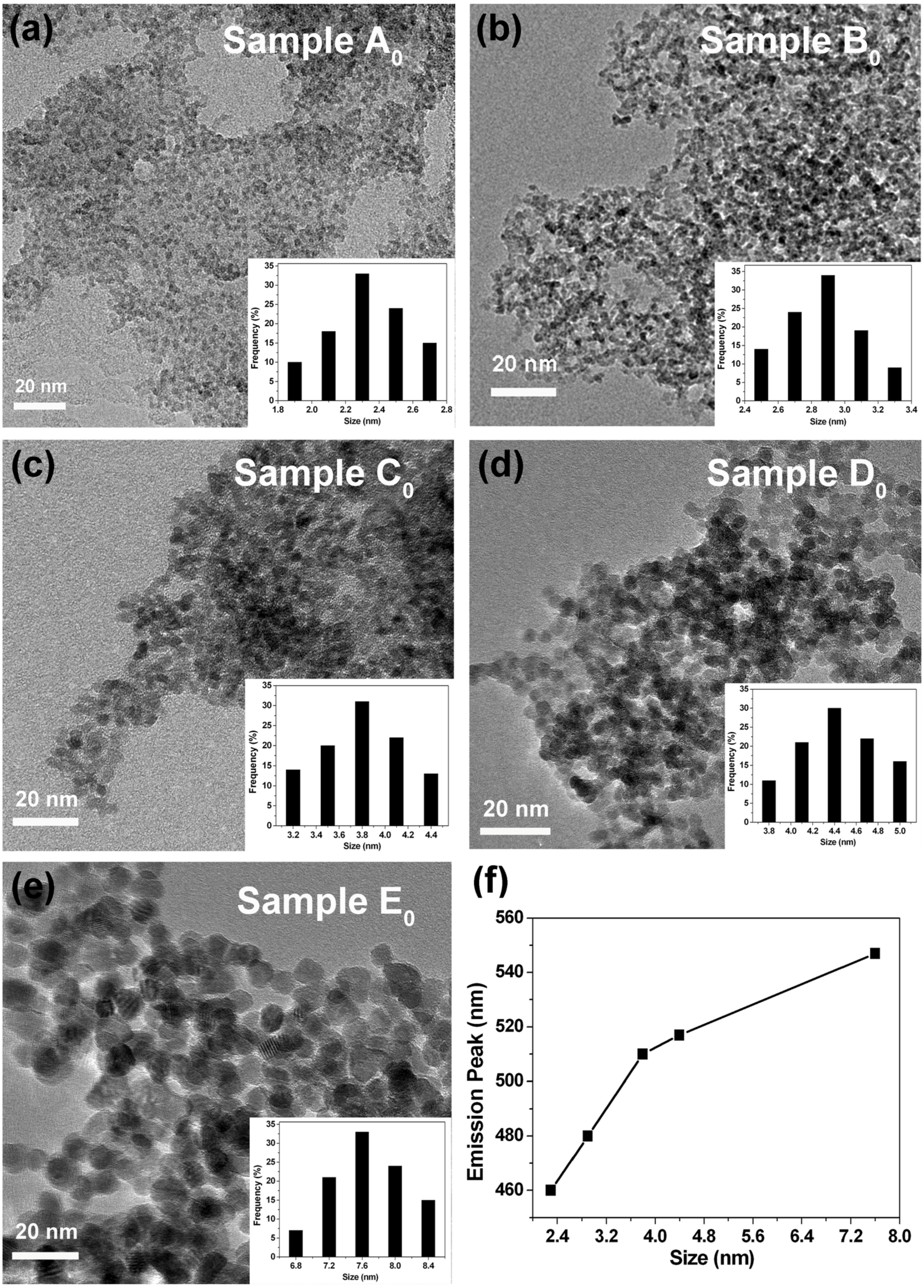

Figure S5. TEM images (a-e) and emission peak versus particle size (f) of unmodified ZnO QDs. The inset shows the histogram of ZnO size distribution. The average particle diameter is 2.3±0.4, 2.9±0.4, 3.8±0.6, 4.4±0.6, and 7.6±0.8 for Sample A_0-E_0, respectively.

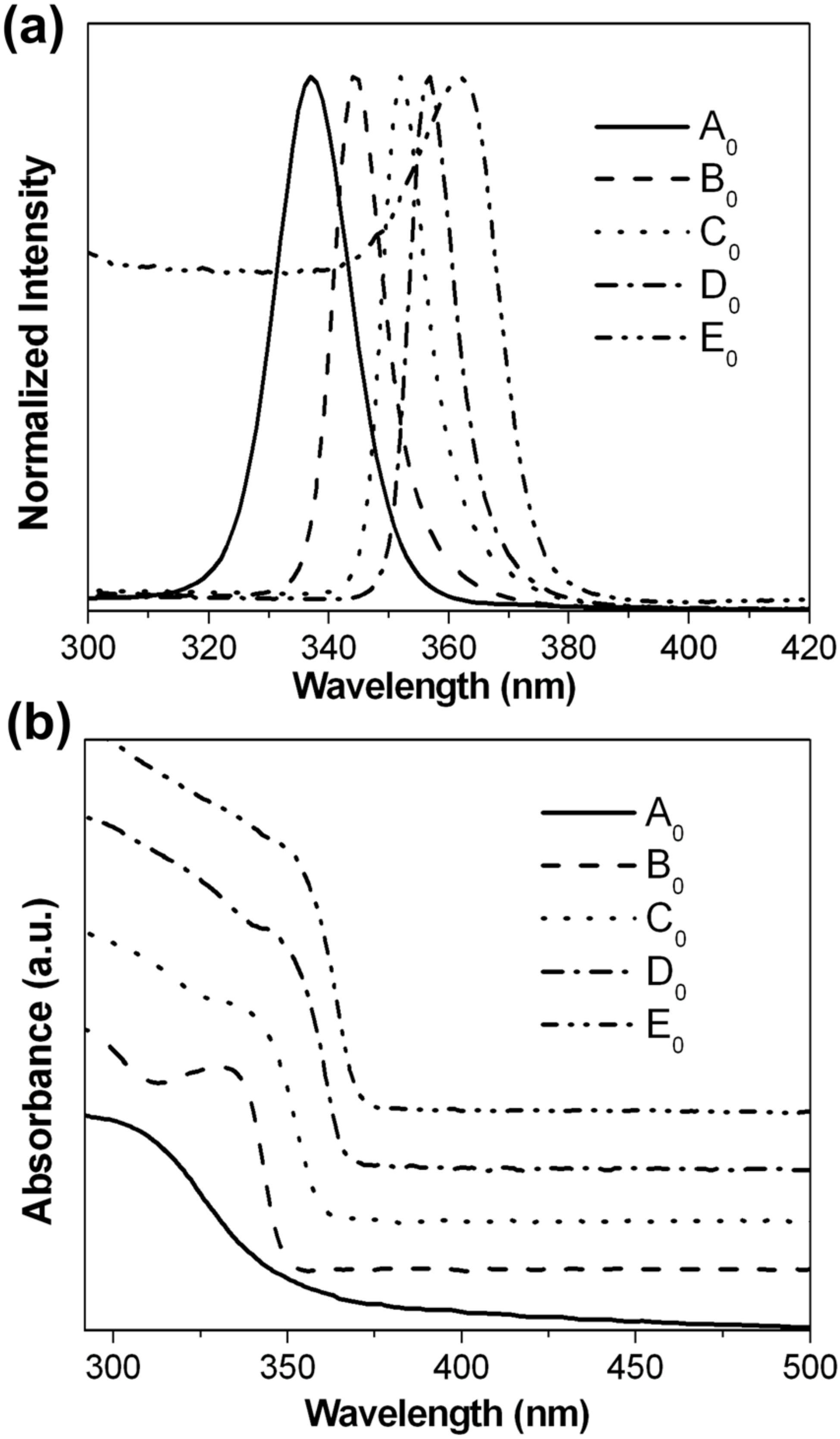

Figure S6. (a) Excitation and (2) absorption spectra of samples A_0-E_0. The left part of the excitation spectrum of sample E_0 is different from other samples possibly due to their different reaction conditions.[2,5]

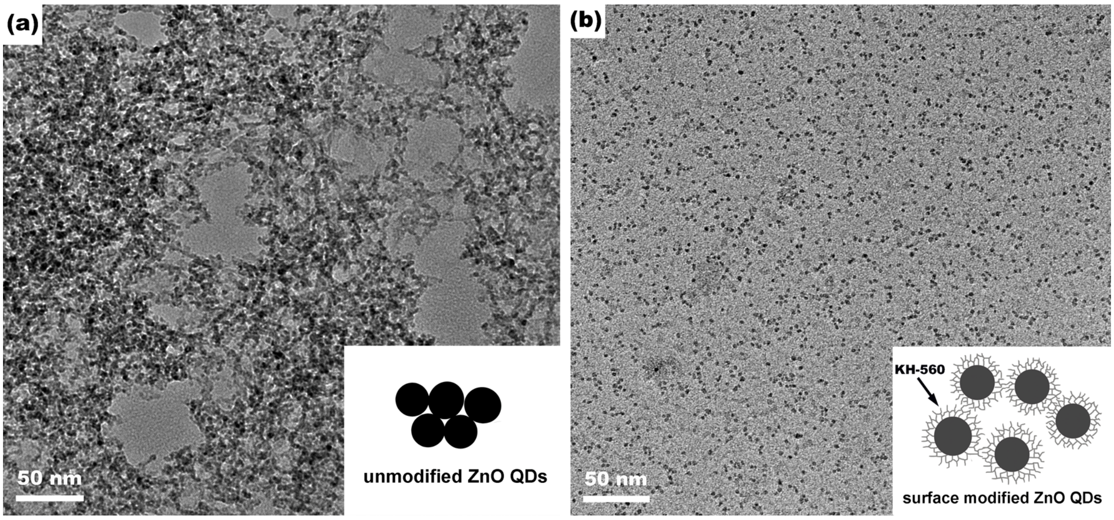

Figure S7. TEM images of (a) unmodified ZnO QDs and (b) silane surface modified ZnO QDs. The insets denote schematics for surface states of the unmodified and modified cases.

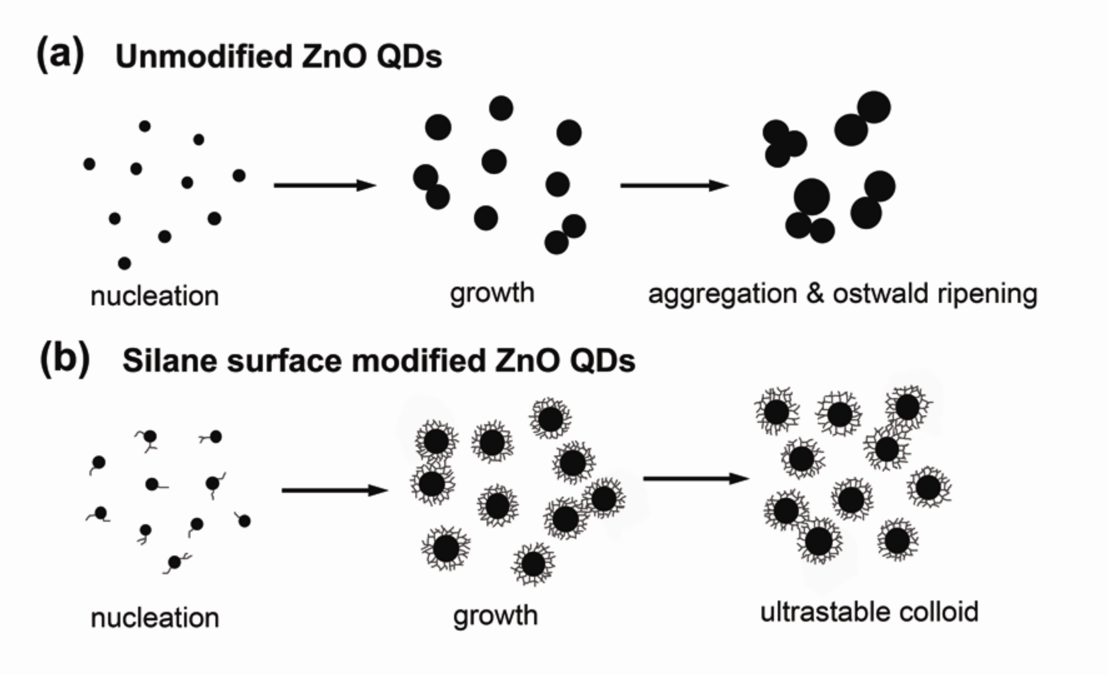

Figure S8. Schematic representation for the growth process of (a) unmodified ZnO QDs and (b) KH-560 surface modified ZnO QDs.

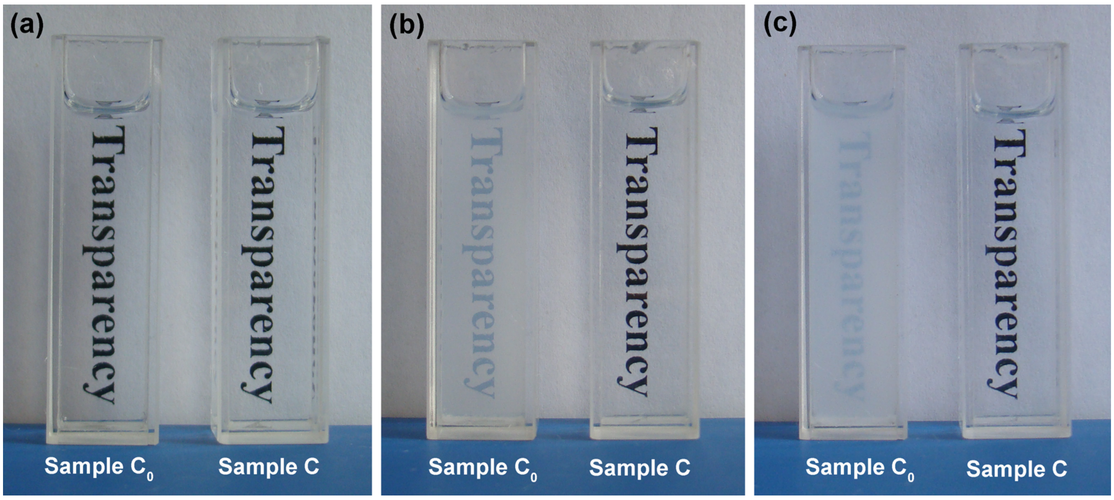

Figure S9. Photographs of unmodified ZnO QD colloids (sample C_0) and KH-560 surface modified ZnO QD colloids (sample C) after (a) 0 day, (b) 2 days, and (c) 9 weeks.

Figure S10. Digital photos of KH-560 modified ZnO QDs/PVA composite films for anti-counterfeit applications in expensive high-end liquors under (a) sunlight and (b) 302 nm UV light irradiation (from left to right: pure PVA film, film-B, film-D, and film-E). Obviously, the composite films emit visible lights with expected blue-yellow colors for anti-counterfeit purpose while the pure PVA film shows no emitting light under UV irradiation.

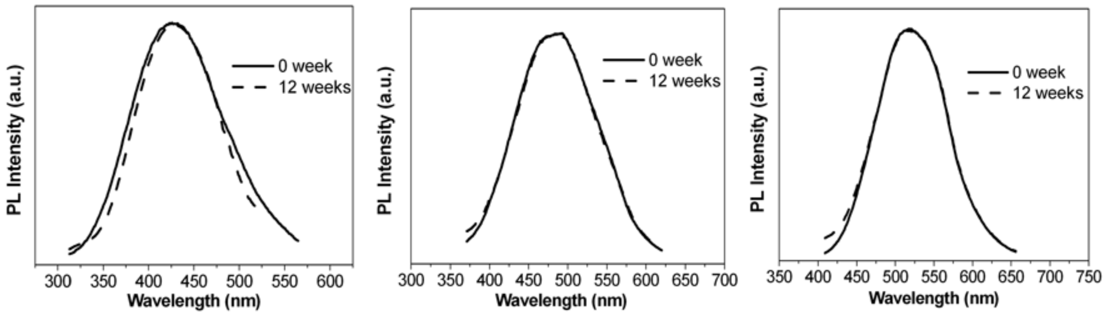

Figure S11. PL spectra of the ZnO QDs embedded composite films (film-B, film-D and film-E) recorded at zero and twelve weeks.

References

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