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Electronic Supplementary Information

Controlled photostability of luminescent nanocrystalline ZnO solution for selective detection of aldehydes

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Experimental

Materials and Reagents. All the chemicals were purchased from commercial sources (Sigma-Aldrich, Lancaster, Alfa Aesar and Gelest), and used without further purification, unless otherwise noted.

Synthesis of Silane-Functionalized ZnO Nanocrystals. The ZnO nanocrystals were synthesized similar to the procedures reported.[1] Zinc acetate (220 mg) was dissolved in ethanol (20 mL) in an Erlenmeyer flask, and oleic acid (70 μL) was added. In a separate flask, TMAH (360 mg) was dissolved in ethanol (5 mL). Both solutions were heated to boiling and mixed together quickly as a clear solution. The reaction mixture was kept boiling for exactly 2 min, and was stopped with the addition of 50 mL of ethanol. The reaction mixture was then cooled immediately in an ice bath at 0ºC. ZnO precipitates were centrifuged, collected, and redissolved in toluene (10 mL). The two-stage silanization was illustrated using N-(2-aminoethyl)aminopropyltrimethoxysilane (AEAPS) as an example. 0.1 M AEAPS solution in toluene (1 mL) and 0.1 M TMAH solution (1 mL) were added to the ZnO solution in toluene. The reaction mixture was stirred and heated to 85ºC for 15 min. It was centrifuged and washed three times with toluene to remove excess oleic acid. The precipitates were redispersed in toluene. 0.1 M TMAH solution (1 mL) was then added. The reaction mixture was heated to 85ºC for 30 min. The functionalized ZnO nanocrystals were then centrifuged, collected, and dried in vacuum oven overnight. The nanocrystals (~ 30 mg) were dissolved in 10 mL of deionized water. If necessary, formic acid (1 M) was added dropwise to increase the solubility of the nanocrystals. The stock solution was then filtered

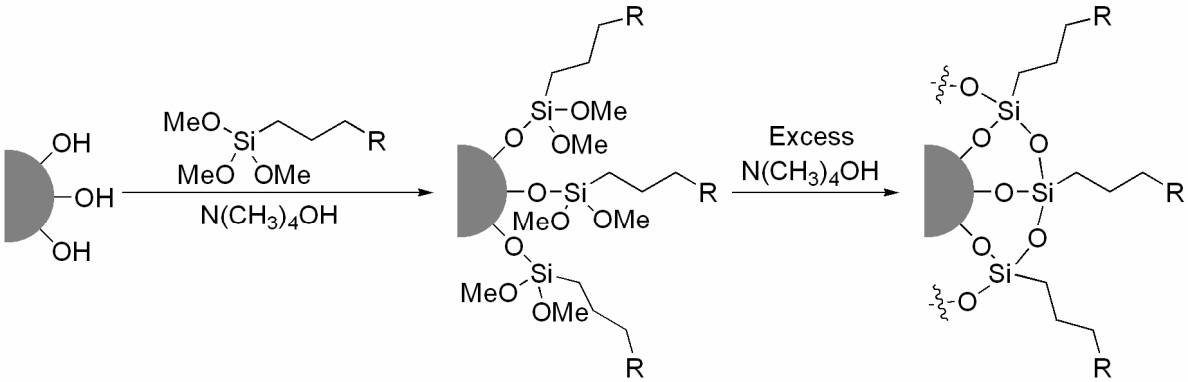
(1) Jana, N. R.; Chen, Y.; Peng, X. *Chem. Mater.* **2004**, *16*, 3931.

with a 0.2-μm membrane syringe filter prior to use. The concentration of nanocrystalline NH_2-ZnO solution was quantified by UV-visible spectrometry at a wavelength of 330 nm. The NH_2-ZnO solution should be diluted to the desired concentration right before the experiment since it was most stable at ~ 3 mg/mL.

Optical Property Measurement. Absorption spectra of samples were measured at room temperature on an Agilent 8453 UV-visible spectrometer. Luminescence spectra were measured at room temperature on a Jobin Yvon Horiba Fluorolog spectrometer.

High-Throughput Screening. Sample compounds were dissolved in DMSO, and 75 μL of the sample solution were mixed with an aqueous solution of NH_2-ZnO nanocrystals (5 μg/mL, 75 μL) in a 96-well plate. The plate was then exposed to UV light (λ_{max} = 365 nm, 50 W) from a flat-panel transilluminator (Wealtec) for 2 min. The luminescence intensity at 545 nm (excited at 345 nm) was recorded by a microplate reader (Tecan).

Scheme S1. Two-stage silanization of ZnO nanocrystals



R = NH_2, $NHCH_2CH_2NH_2$, PO_3CH_3, NMe_2, PO_3^-

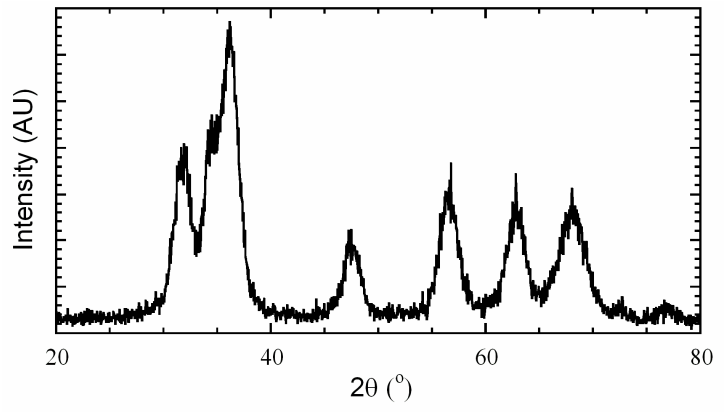


Figure S1. XRD pattern of AEAPS-functionalized ZnO nanocrystals.

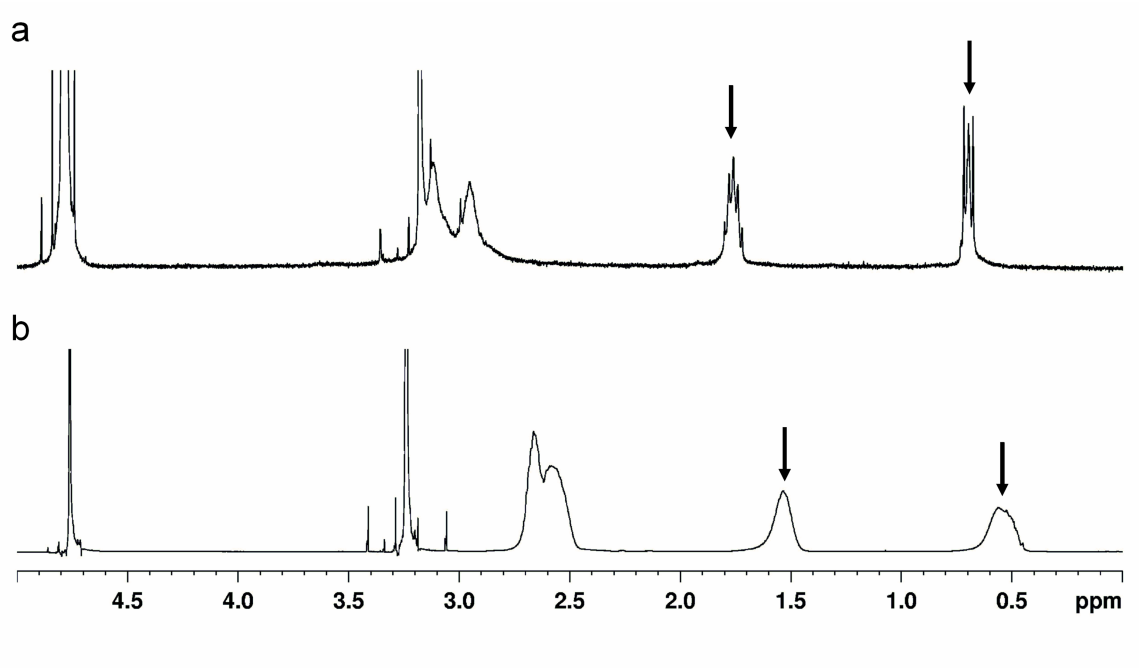


Figure S2. NMR spectra of (a) AEAPS-functionalized ZnO nanocrystals, and (b) AEAPS in D_2O containing 0.16% formic acid. The NMR signals marked with an arrow are attributed to the first two Si-adjacent CH_2 species of the -Si-CH_2-CH_2-CH_2- linker chain.

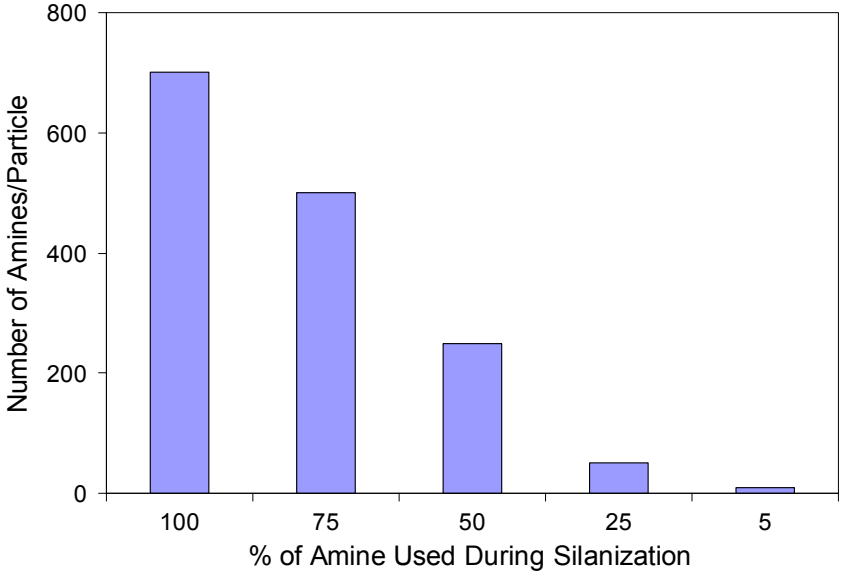


Figure S3. Estimated number of primary amines per ZnO particle with mixed surface functional groups. ZnO nanoparticles were silanized with a mixture of AEAPS (primary amine) and dimethylaminopropyltrimethoxysilane. The number of primary amines was estimated by fluorescamine titration.