

Dissolution Kinetics of Zinc Oxide Nanoparticles: Real-time Monitoring by a Zn²⁺-specific Fluorescent Probe

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Supporting information

Synthesis of zinc oxide nanoparticles (ZnONPs) and zinc oxide nanorods (ZnONRs)

20 nm ZnONPs (20-ZnONPs) were synthesized using a wet chemical method.¹ Briefly, 1.98 g of zinc acetate dihydrate was added to 40 mL of methanol and the solution was refluxed for several minutes with vigorous stirring. 3 mL of water was added to the solution. 30 mL of methanol containing 0.72 g of sodium hydroxide was then added dropwise to the resulting solution for 30 min. White precipitate was collected by centrifugation, washed for 3 times by a mixture of acetone and ethanol (1:1) and oven dried at 70 °C for one day. Synthesis of the 70 nm ZnONPs (70-ZnONPs) followed the same method except for changing the content of added water from 3 mL to 15 mL.

For synthesizing the polyvinylpyrrolidone (PVP)-coated ZnONPs (PVP-ZnONPs), 0.88 g of zinc acetate dihydrate and 0.6668 g of PVP (55 000 average molecular weight) were dissolved in a 40 mL of boiling ethanol in a reflux.² To this solution, 0.288 g of sodium hydroxide dissolved in a 40 mL ethanol-water mixture (volume ratio of ethanol:water = 4:1) was added dropwise under vigorous stirring for 30 min. The solution was then removed from the heat source and cooled down to room temperature. After 7 days storage in 4 °C, white precipitate was collected by centrifugation and redispersed with 40 mL ultrapure water containing 10 mg of PVP by sonication.

ZnO nanorods (ZnONRs) were synthesized according to a reported method with a minor modification.³ 14.75 g of zinc acetate and 7.4 g of potassium hydroxide were dissolved with 60 and 32 mL of methanol, respectively. These two solutions were mixed and refluxed for 72 h. The resulting white precipitate was collected by centrifugation, washed several times with water and ethanol, and oven dried at 70 °C for one day.

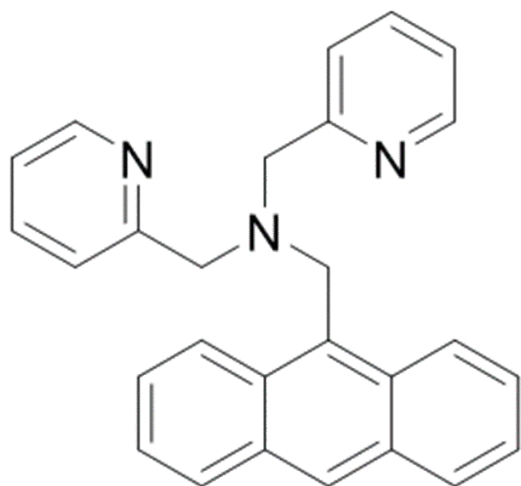


Fig S1. Chemical structure of (9-Anthrylmethyl)bis(2-pyridylmethyl)-amine (AMBPA).⁴

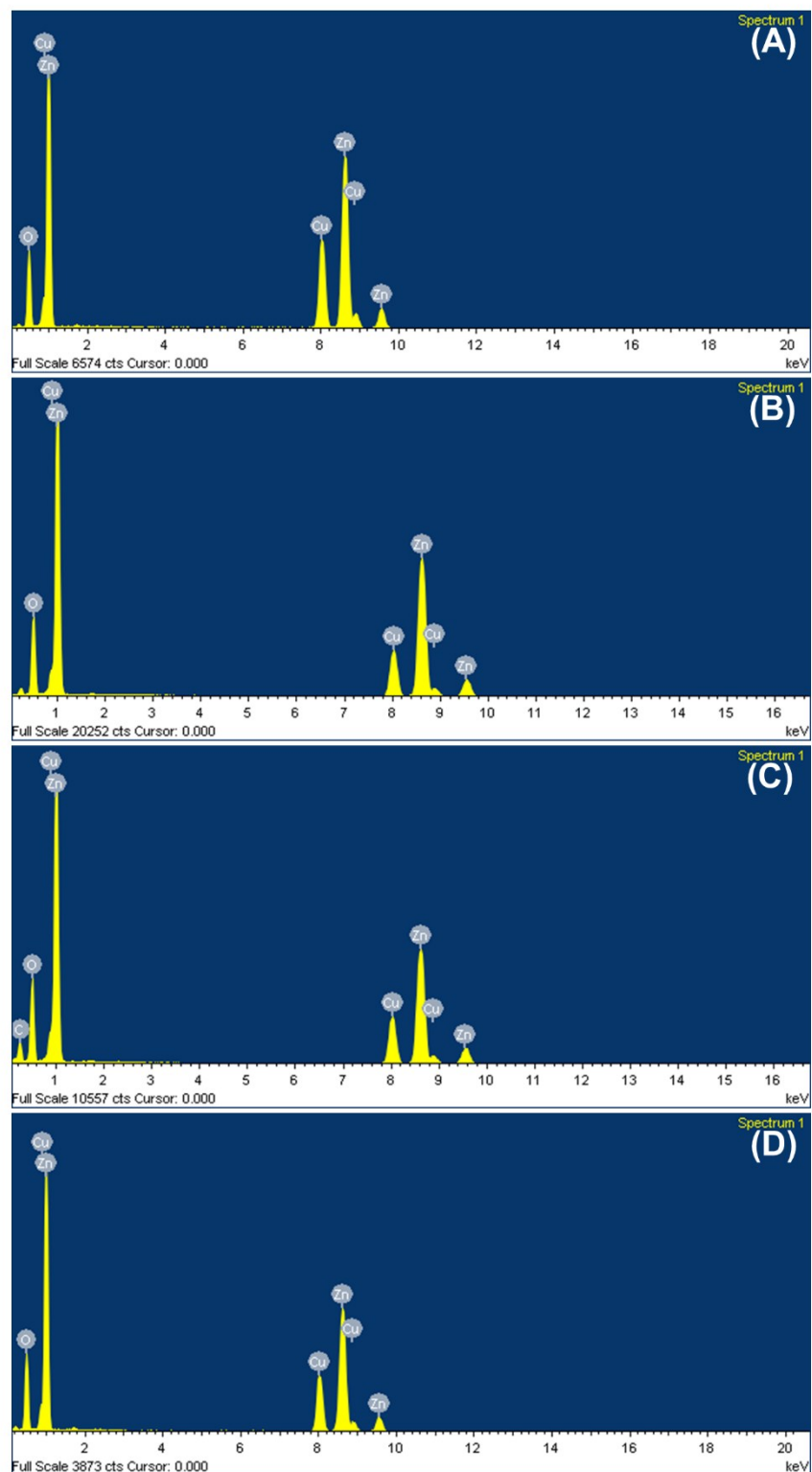


Fig. S2 Energy-dispersive X-ray spectroscopy (EDX) images of (A) 20-ZnONPs, (B) 70-ZnONPs, (C) PVP-ZnONPs and (D) ZnONRs.

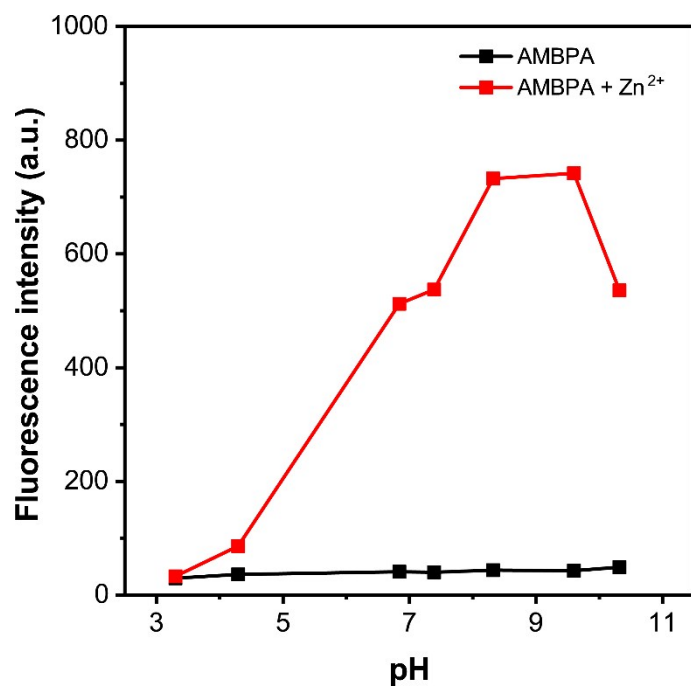


Fig. S3 Fluorescence emission of 10 μM AMBPA in SM7 medium with different pH in the presence and absence of 500 $\mu\text{g Zn L}^{-1}$ (from $\text{Zn}(\text{NO}_3)_2$) ($\lambda_{\text{ex}} = 373 \text{ nm}$; $\lambda_{\text{em}} = 423 \text{ nm}$).

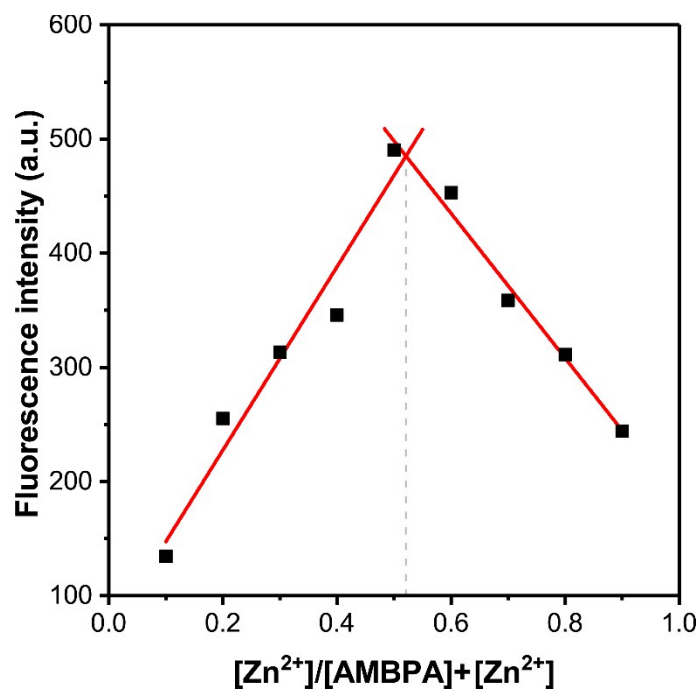


Fig. S4 Job's plot for determining the stoichiometry of AMBPA with Zn^{2+} ($\lambda_{ex} = 373$ nm). Fluorescence at 423 nm was plotted as a function of the molar ratio: $[Zn^{2+}]/[AMBPA] + [Zn^{2+}]$. $[AMBPA] + [Zn^{2+}]$ was kept constant at 10 μ M.

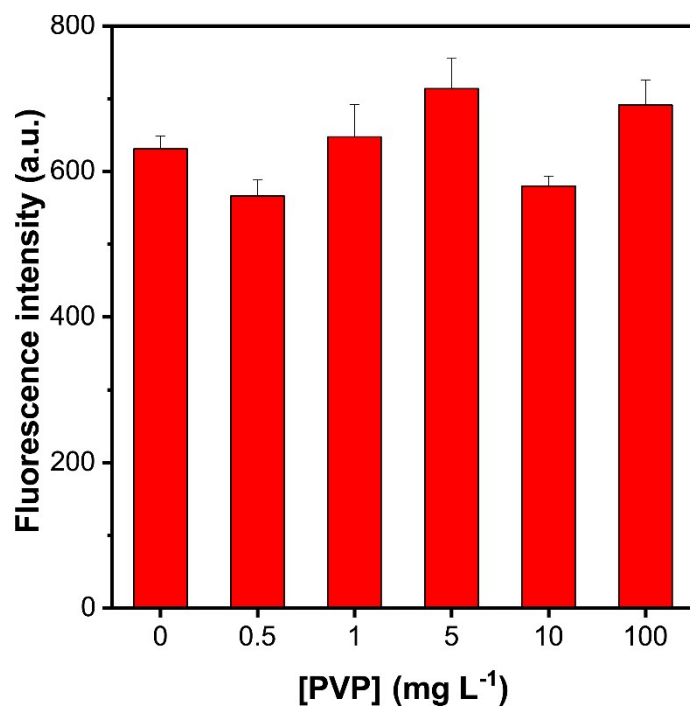


Fig. S5 Fluorescence emission of 10 μM AMBPA at 423 nm in the presence of 500 $\mu\text{g Zn L}^{-1}$ and different concentrations of polyvinylpyrrolidone (PVP) ($\lambda_{\text{ex}} = 373 \text{ nm}$).

Reference

1. C.-M. Wu, J. Baltrusaitis, E. G. Gillan and V. H. Grassian, Sulfur Dioxide Adsorption on ZnO Nanoparticles and Nanorods, *J. Phys. Chem. C*, 2011, **115**, 10164–10172.
2. C. Jiang, H. Hsu-Kim, Direct *in situ* measurement of dissolved zinc in the presence of zinc oxide nanoparticles using anodic stripping voltammetry. *Environ. Sci.: Processes Impacts*, 2014, **16**, 2536–2544.
3. Y. Yang and T. Liu, Fabrication and characterization of graphene oxide/zinc oxide nanorods hybrid, *Appl. Surf. Sci.*, 2011, **257**, 8950–8954.
4. K. Kubo and A. Mori, PET fluoroionophores for Zn^{2+} and Cu^{2+} : complexation and fluorescence behavior of anthracene derivatives having diethylamine, N-methylpiperazine and N,N-bis(2-picolyl)amine units, *J. Mater. Chem.*, 2005, **15**, 2902–2907.