

Supporting Information

White and Tunable Emission from and Rhodamine B Detection by Modified Zinc Oxide Nanowalls

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1. Experimental Section

1.1. Synthesis of ZnO:Tb(III) Nanowalls. Zinc nitrate hexahydrate ($\geq 98\%$), potassium chloride ($\geq 99.0\%$), terbium nitrate pentahydrate (99.9%) were purchased from Sigma-Aldrich and used without further purification. Pristine and Tb-doped ZnO nanowalls were synthesized using a method described in detail elsewhere.¹ In a three-electrode electrochemical cell, potentiostatic amperometry at -1.4 V vs Ag/AgCl was used to deposit the undoped and Tb-doped ZnO nanowalls on ITO-glass used as the working electrode, in an aqueous solution of 0.1 M $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 0.1 M KCl mixed with 1 mM to 10 mM terbium nitrate pentahydrate. Deposition was maintained at a constant temperature of 80°C by using a water bath.

1.2. Surface Modification. Pt NPs (~ 3 nm dia.) dispersed in water, and Au NPs (~ 5 nm dia.) stabilized by 0.1 mM phosphate buffered solution (PBS) were purchased from Sigma-Aldrich. Ag NPs (~ 4.5 nm dia.) dispersed in cyclohexane were synthesized from a mixture of silver nitrate, hydrazine and 2-ethylhexyl hydrogen 2-ethylhexyl phosphonate (used as a stabilizer) according to a previous method.² The final concentration of the dispersed NPs was adjusted to be $25\ \mu\text{M}$ by diluting with an appropriate solvent: cyclohexane for Ag NPs, and water for Pt and Au NPs. The NPs were then deposited by immersing the ZnO nanowall samples in the NP-dispersed solution for 10 s. After drying in air, the dip-casting treatment of the nanowalls with the diluted NP-dispersed solution could be repeated as required.

A 10 mM solution of rhodamine B (RhB, Sigma-Aldrich, $\geq 95\%$ purity) was prepared by using CH_2Cl_2 (Sigma-Aldrich, 99.9% purity) for surface functionalization of ZnO:Tb(III). A small drop of the RhB solution was applied to the ZnO:Tb(III) nanowalls on ITO-glass, followed by drying in air. After each PL measurement, additional application of RhB drops was made, as required.

1.3. Characterization. The morphology and crystallography of Tb-doped ZnO nanowalls were examined by field-emission scanning electron microscopy (SEM) in a Zeiss Merlin microscope and by transmission electron microscopy (TEM) in a Zeiss Libra 200MC microscope, respectively. Chemical-state composition analysis of the sample was performed by X-ray photoelectron spectroscopy (XPS) in a Thermo-VG Scientific ESCALab 250 microprobe. Scanning Auger microscopy (SAM) was conducted in a Thermo-VG Scientific Microlab 350 microprobe to provide surface elemental composition analysis.

PL spectra were measured at 90° with an ARC 0.5 m Czerny–Turner monochromator equipped with a cooled Hamamatsu R-933-14 photomultiplier tube, using a 325 nm He-Cd laser as the excitation source. For low-temperature excitation spectral measurement, the sample was placed on the cold finger of a closed-cycle liquid helium refrigerator. To obtain the excitation spectrum, the sample was irradiated with the light from an Oriel 1000 W Xe lamp (with a working power of 600 W) passing through an Oriel MS257 monochromator.

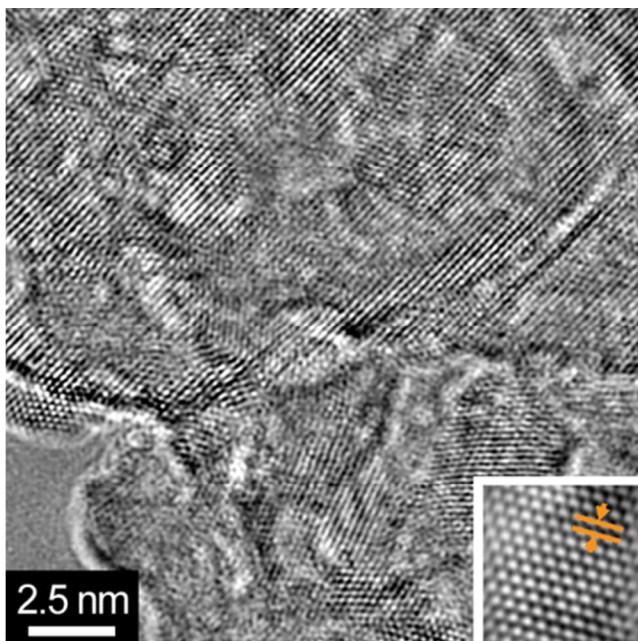


Figure S1. TEM and HRTEM (inset) images of Tb-doped ZnO nanowalls obtained with a Tb(III) concentration of 10 mM.

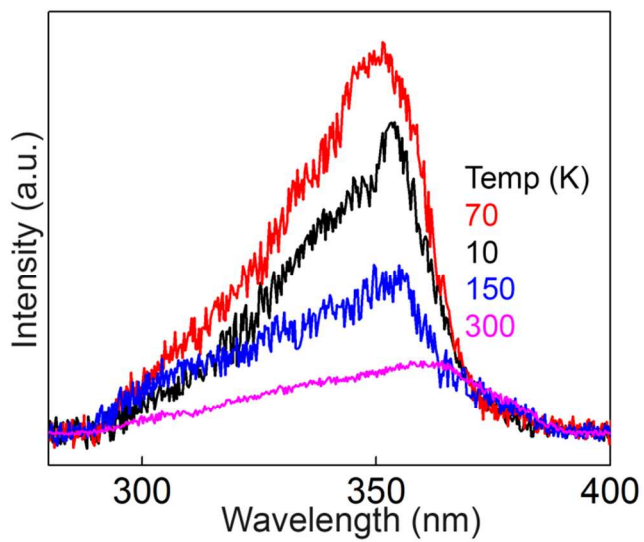


Figure S2. Excitation spectra ($\lambda_{\text{em}} = 545 \text{ nm}$) of the Tb-doped ZnO nanowalls obtained with a 10 mM Tb(III) concentration measured at 10, 70, 150 and 300 K.

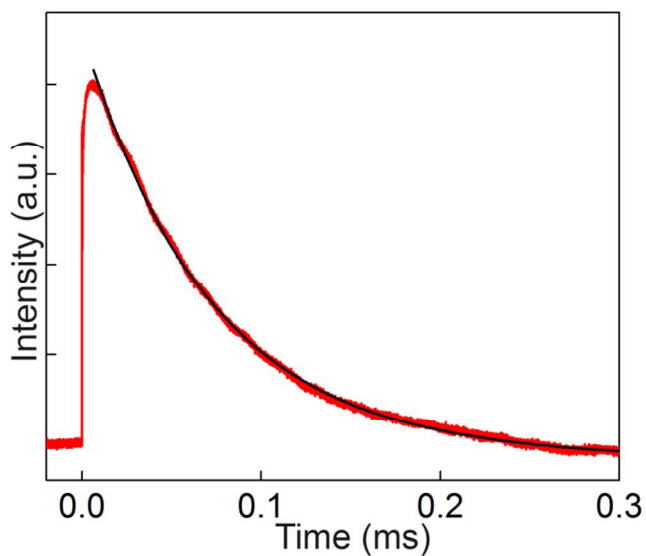


Figure S3. Curve-fitting of the time profile of the visible emission ($\lambda_{\text{ex}} = 337.1 \text{ nm}$) at 545 nm from Tb-doped ZnO nanowalls obtained with a 10 mM Tb(III) concentration.

Table S1. The CIE x,y color coordinates and emission color of undoped ZnO, ZnO:Tb(III) and RhB/ZnO:Tb(III).

	Color coordinate (x,y)	Color
Undoped ZnO	(0.4190, 0.4989)	Yellow
1mM Tb(III)	(0.4201, 0.4950)	Yellow
5mM Tb(III)	(0.3820, 0.4477)	Yellowish green
10mM Tb(III)	(0.3489, 0.3881)	White
10mM Tb(III)/Ag NP	(0.4181, 0.4976)	Yellow
10mM Tb(III)/Au NP	(0.4226, 0.4992)	Yellow
10mM Tb(III)/Pt NP	(0.4082, 0.5001)	Yellow
RhB/ZnO:Tb(III) (1 drop)	(0.4724, 0.4183)	Orange
RhB/ZnO:Tb(III) (3 drops)	(0.5772, 0.3820)	Red

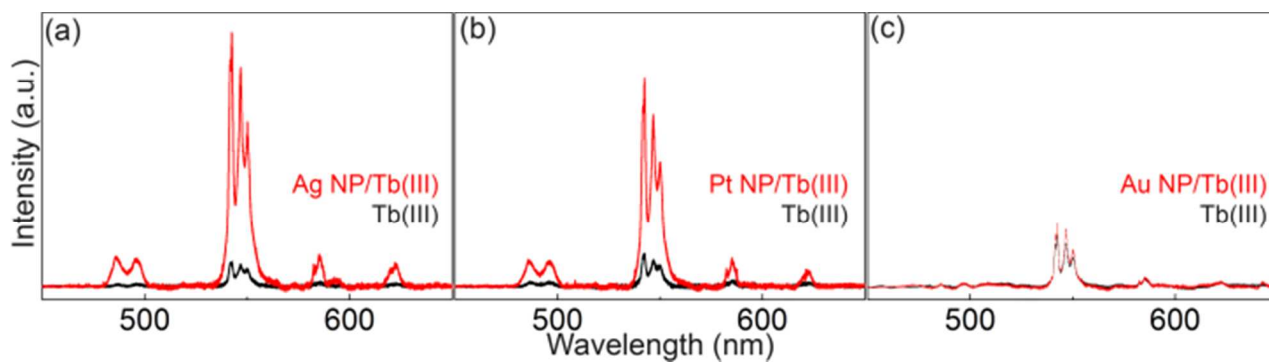


Figure S4. Comparison of the relative intensities of Tb emission features ($\lambda_{\text{ex}} = 325$ nm) from pristine ZnO:Tb(III) nanowalls and those decorated with optimized amounts of (a) Ag, (b) Pt, and (c) Au NPs providing the LSPR effect.

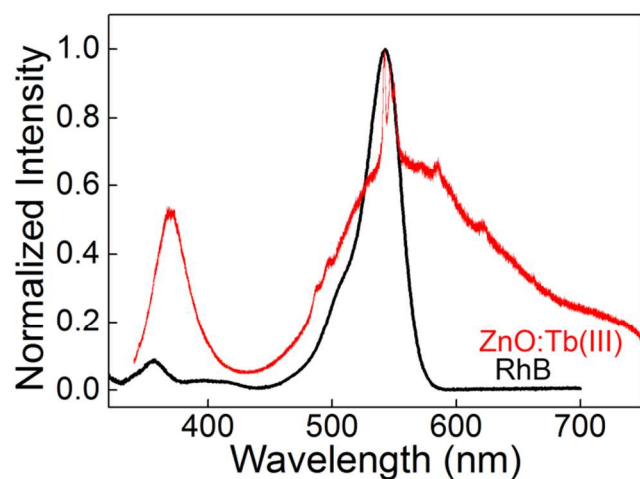


Figure S5. Absorption spectrum of RhB dissolved in water and PL spectrum ($\lambda_{\text{ex}} = 325$ nm) of ZnO:Tb(III) nanowalls.

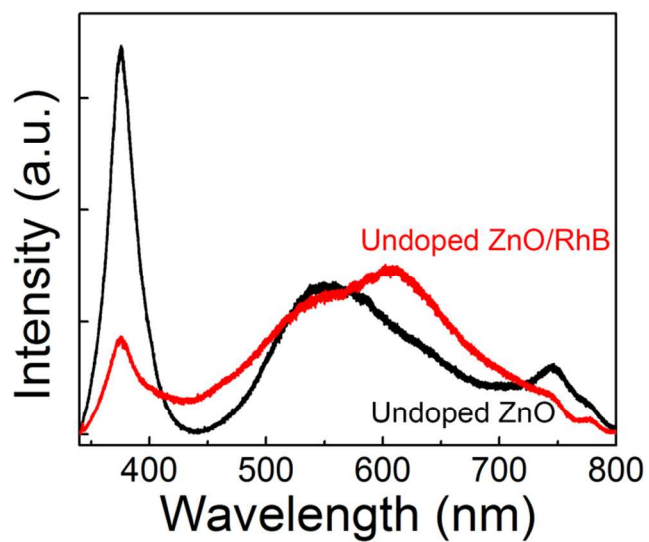


Figure S6. PL emission spectra ($\lambda_{\text{ex}} = 325 \text{ nm}$) of undoped ZnO and RhB functionalized undoped ZnO.

2. References

- (1) Kang, J.-S.; Jeong, Y.-K.; Kang, J.-G.; Zhao, L.; Sohn, Y.; Pradhan, D.; Leung, K. T. *J. Phys. Chem. C* **2015**, *119*, 2142–2147.
- (2) Kim, J.; Jeong, Y.; Sohn, Y.; Kang, J. *Langmuir* **2012**, *28*, 9842–9848.