

## Supplementary Information

# 3d and 4d Transition Metal Doped ZnO Nanoparticles Anchored on CdZnS for Photodegradation of Rhodamine B

*Ann Wangari Mureithi,<sup>1</sup> Chen Song,<sup>1</sup> Kim Tran Tran,<sup>1</sup> Hawi N. Nyiera,<sup>1</sup> Xueni Huang,<sup>1</sup> Tejas S. Bhosale,<sup>1</sup> Abiodun Daniel Aderibigbe,<sup>1,2</sup> Ranjana Burma,<sup>1</sup> Steven L. Suib,<sup>1,2</sup> Jing Zhao<sup>1,2\*</sup>*

<sup>1</sup> Department of Chemistry, University of Connecticut, 55 North Eagleville Rd, Storrs Mansfield, Connecticut 06269-3060, United States

<sup>2</sup> Institute of Materials Science, University of Connecticut, 97 North Eagleville Rd, Storrs Mansfield, Connecticut 06269-3137, United States

Table S1. Calculated crystallite sizes of ZnO and Ag, Mn, and Co-doped ZnO nanoparticle

| Sample | 2 $\theta$ | Diameter (nm) |
|--------|------------|---------------|
| ZnO    | 36.22      | 7.30          |
| AgZnO  | 36.22      | 3.41          |
| CoZnO  | 36.27      | 5.58          |
| MnZnO  | 36.25      | 5.07          |

The crystallite sizes were calculated using Scherrer's equation below from the XRD data.

$$D = k\lambda / \beta \cos\theta$$

where D, k,  $\beta$ , and  $\theta$  represent the crystallite size, shape factor (0.95), half-width of the diffraction band, and Braggs diffraction angle (peak position in radians).

The band gap was determined using the Kubelka Munk Function. Graphs of  $(F(R)h\nu)^n$  vs  $h\nu$  were plotted, where  $h\nu$  is the energy term and  $F(R)$  is the K-M function =  $k/s$ .  $k$  is the molar absorption coefficient  $k = (1-R)^2$  and  $s$  is the scatter factor.  $R$  is reflectance obtained using DRS data in Figure S1.  $n$  is 0.5 for indirect semiconductors. Optical band gaps of doped and undoped ZnO nanoparticles were determined using the Kubelka-Munk function and are shown in Figures S1(b) to (e). Obtained values reveal a slight narrowing of the band gap for doped ZnO from 3.2 eV for ZnO nanoparticles to 2.9, 2.9, and 3.1 eV for AgZnO, CoZnO, and MnZnO respectively. Previous reports have suggested that introducing dopant ions into semiconductors creates dopant states that

could be above the VB or below the CB, hence narrowing the band gap of the semiconductor and increasing the absorption of visible light [59,60].

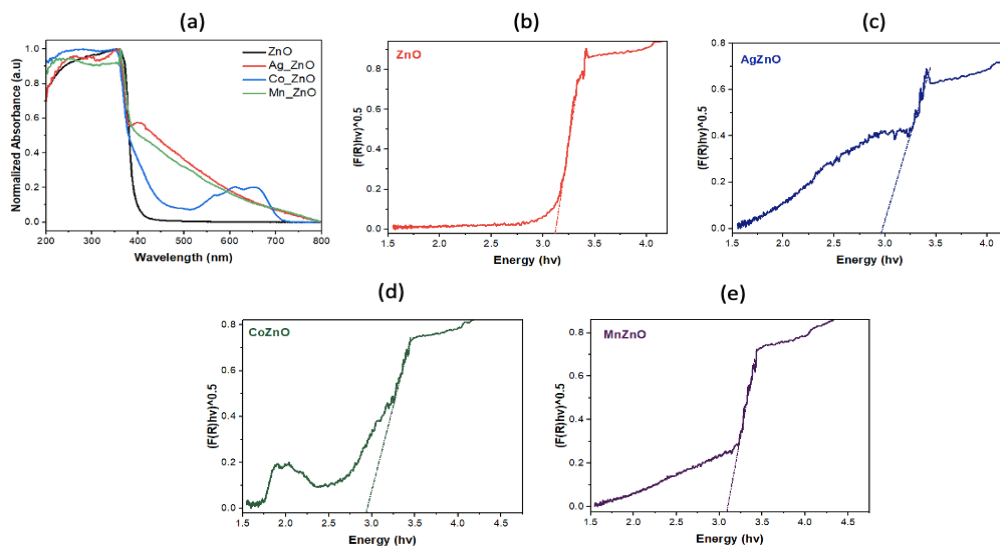


Figure S1. (a) Diffuse reflectance UV-vis spectra of ZnO and Ag, Co and Mn doped ZnO nanoparticles. (b) to (e) are the band gap determination plot of  $(F(R)hv)^n$  vs  $hv$  obtained from diffuse reflectance data.

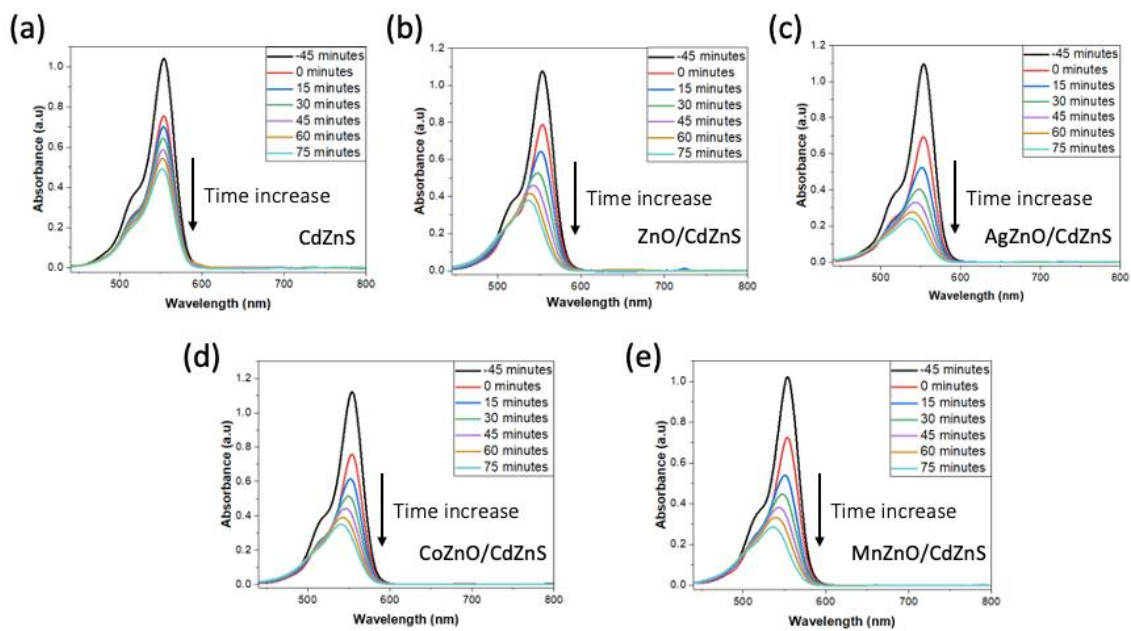


Figure S2. (a-e) UV-vis spectra for the degradation of Rhodamine B using different photocatalysts.

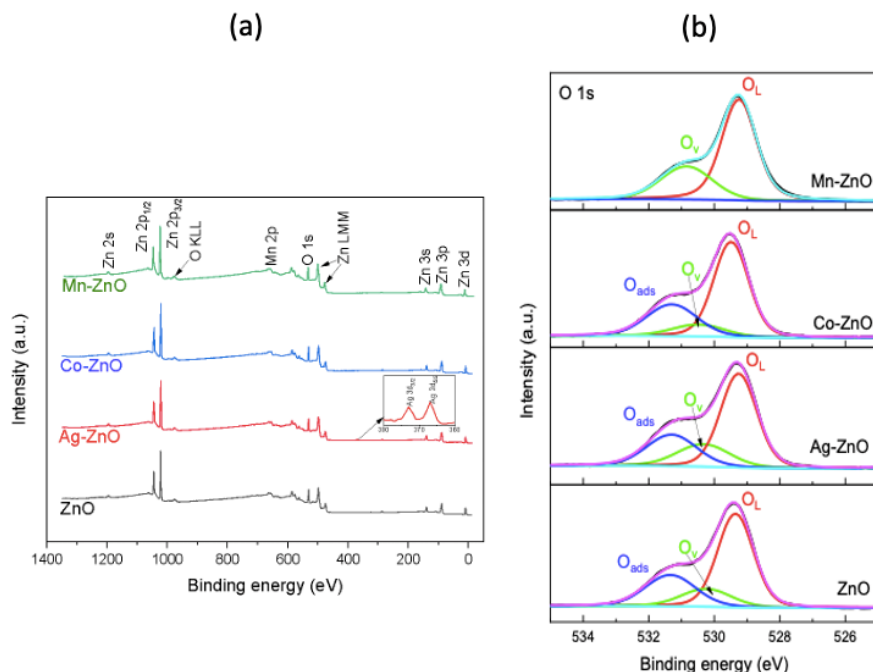


Figure S3. (a) XPS spectra for O 1s, Zn 2p, Mn 2p, Zn 3s and Zn 3d and Ag 3d. (b) Enlarged XPS spectra of O1s peaks and deconvolutions representing the binding energies of the lattice oxygen ( $O_L$ ), chemisorbed oxygen ( $O_{ads}$ ), and oxygen vacancies ( $O_v$ ).

The high-resolution XPS spectra for undoped and Ag, Co, and Mn-doped ZnO nanoparticles are shown in Figure S3a. Alongside the peaks assigned to O 1s, Zn 3s, Zn 3p, and Zn 3d of ZnO, peaks of Mn 2p and Ag 3d in MnZnO and AgZnO respectively were also observed. There were no Co-related peaks observed for CoZnO. The magnified region of the AgZnO spectrum represents two major peaks at ~374 and ~368 eV, corresponding to Ag 3d<sub>3/2</sub> and Ag 3d<sub>5/2</sub> binding energies, respectively, indicating the presence of metallic Ag [61]. As displayed in Figure 3Sb, upon deconvolution of the O 1s core spectrum by Gaussian functions, three peaks were obtained: a peak at ~529.3 eV corresponding to  $O^{2-}$  ion in the ZnO lattice, a peak at ~530.3 eV attributed to the oxygen vacancies, and a peak at ~531.3 eV of  $O^{2-}$  credited to adsorbed oxygen on the surface of the nanoparticles [19]. Oxygen vacancies are point defects that could act as electron traps in the

event of photoexcitation. The trapped electrons could then be released and used in the photocatalytic reaction [62]. Thus, oxygen vacancies are desired in photocatalysts to reduce fast exciton recombination [63]. The composition of each component listed in Table S2 reveals that the percentage of oxygen vacancies was in the order  $\text{MnZnO} > \text{AgZnO} > \text{ZnO} > \text{CoZnO}$ .

Table S2. Percent lattice composition, adsorbed, and defect oxygen for undoped and doped ZnO nanoparticles.

| Sample | Peak             | BE (eV) | FWHM (eV) | Composition (%) |
|--------|------------------|---------|-----------|-----------------|
| ZnO    | O <sub>L</sub>   | 529.4   | 1.29      | 57.6            |
|        | O <sub>V</sub>   | 530.3   | 1.80      | 15.4            |
|        | O <sub>ads</sub> | 531.3   | 1.80      | 27.0            |
| AgZnO  | O <sub>L</sub>   | 529.3   | 1.30      | 55.2            |
|        | O <sub>V</sub>   | 530.3   | 1.90      | 19.2            |
|        | O <sub>ads</sub> | 531.3   | 1.80      | 25.6            |
| CoZnO  | O <sub>L</sub>   | 529.5   | 1.25      | 60.1            |
|        | O <sub>V</sub>   | 530.5   | 1.90      | 11.2            |
|        | O <sub>ads</sub> | 531.3   | 1.80      | 28.7            |
| MnZnO  | O <sub>L</sub>   | 529.3   | 1.25      | 68.9            |
|        | O <sub>V</sub>   | 530.9   | 1.85      | 31.1            |