Green Synthesis of CuO-ZnO Nanocomposite for Efficient Photodegradation of Methylene Blue and Reduction of 4-Nitrophenol

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Figure S1. Photographic image of Verbascum sinaiticum Benth plant.

The bandgap of the samples was obtained employing Tauc's formula¹ given by the equation $(\alpha h\nu)^n = C$ ($h\nu - E_g$), where α , h, v, E_g , n, and C were the absorption coefficient, Planck's constant, light frequency, bandgap energy, the power factor of the transition mode (2 for direct, 0.5 for indirect), and constant related to the material, respectively. The direct bandgap energy of the samples was obtained from the curves fitting of $(\alpha h\nu)^2 vs hv$ as depicted in Figure S2.^{2,3} The estimated bandgap from the fitted graph

was 3.01 for ZnO, 2.18 for CuO, and 2.74 eV for CuO-ZnO NCs. The result revealed that the bandgap of the CuO-ZnO NCs is lower than the ZnO NPs alone.



Figure S2: Tauc's plot of ZnO and CuO-ZnO samples using the corresponding absorbance (bandgap analysis).



Figure S3: (A and B) TEM, (C) HRTEM, and (D) Fast Fourier Transform (FFT) of CuO-ZnO NCs.



Figure S4: (A) Electron image, (B) EDS Layered mappings, EDS elemental mappings of zinc (Zn), copper (Cu), and oxygen (O), and (C) EDS spectrum of CuO-ZnO obtained using GH

In the process of reusing the catalysts, the used catalysts were separated by centrifugation, washed with water and ethanol three times each, dried at 60 °C overnight, and then reused in the next run.⁴ Stability is one of the important factors to consider when it comes to the reusability of the catalyst. To this end, the recyclability of the CuO-ZnO NCs was evaluated against the photocatalytic degradation of MB for up to four cycles. The degradation performance of each of the four reuse runs is shown in Figure S5. CuO-ZnO NCs revealed an 82 percent efficiency in the first, 79.5 percent in the second, 78 percent in the third, and 70 percent in the fourth run, suggesting fairly good stability (Figure S6A). In the fourth cycle, there was a relatively sudden drop in efficiency, which could be attributed to photocorrosion, or adsorption of dye molecules onto the catalyst surface, decreasing the active surface and light absorption.^{2,4,5} In this respect, CuO-ZnO NCs is a stable and recyclable photocatalyst for the degradation of MB under visible light illumination. In a similar manner, the catalyst recyclability against reduction of 4-NP was also evaluated using the same recovery procedure. The efficiency for each run was found to be 99% (1st), 98.4% (2nd), 97% (3rd), and 96.3% (4th) which indicates excellent recyclability of the material for reduction of 4-NP (Figure S6B). Accordingly, the little change in the efficiency of the catalyst after four cycles suggests CuO-ZnO NCs are promising catalysts for treating organic pollutants in water.



Figure S5: Comparison of the efficiencies for four successive cycles of (A) MB photodegradation, and (B) 4-NP reduction to 4-aminophenol.



Figure S6 Nitrogen adsorption-desorption isotherms and BJH pore size distributions of CuO-ZnO NCs samples (inset).

References

- Saravanakkumar, D.; Sivaranjani, S.; Kaviyarasu, K.; Ayeshamariam, A.; Ravikumar, B.;
 Pandiarajan, S.; Veeralakshmi, C.; Jayachandran, M.; Maaza, M. Synthesis and Characterization of ZnO-CuO Nanocomposites Powder by Modified Perfume Spray Pyrolysis Method and Its Antimicrobial Investigation. *J. Semicond.* 2018, *39* (3), 033001.
- Lei, X.; Cao, Y.; Chen, Q.; Ao, X.; Fang, Y.; Liu, B. ZIF-8 Derived Hollow CuO/ZnO Material for Study of Enhanced Photocatalytic Performance. *Colloids Surfaces A Physicochem. Eng. Asp.* 2019, *568*, 1–10.
- (3) Momeni, M. M. Fabrication of Copper Decorated Tungsten Oxide-Titanium Oxide Nanotubes by Photochemical Deposition Technique and Their Photocatalytic Application under Visible Light.

Appl. Surf. Sci. 2015, 357, 160-166.

- Mathalai Sundaram, C.; Kalpana, S.; Rafi Ahamed, S.; Sivaganesan, V.; Nandhakumar, E. Studies on the Catalytic Activity of CuO/TiO2/ZnO Ternary Nanocomposites Prepared via One Step Hydrothermal Green Approach. *Mater. Res. Express* 2019, 6 (12), 125043.
- (5) Thatikayala, D.; Min, B. Ginkgo Leaves Extract-Assisted Synthesis of ZnO/CuO Nanocrystals for Efficient UV-Induced Photodegradation of Organic Dyes and Antibacterial Activity. J. Mater. Sci. Mater. Electron. 2021, 32 (13), 17154–17169.