

Supporting Information

Photocatalysis with Pt-Au-ZnO and Au-ZnO Hybrids: Effect of Charge Accumulation and Discharge Properties of Metal Nanoparticles

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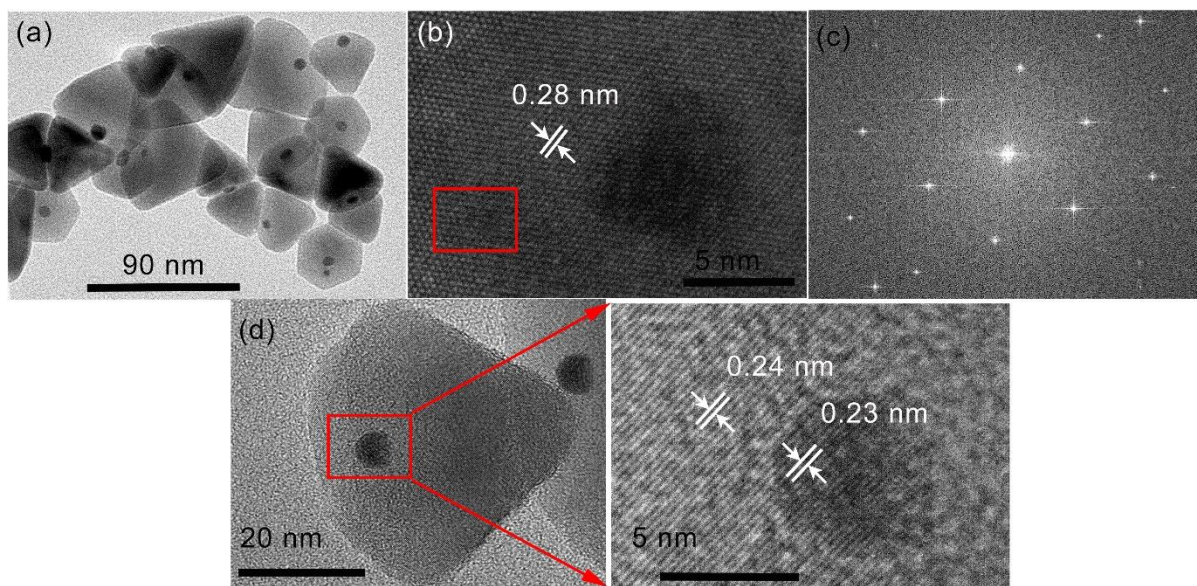


Figure S1: (a) TEM image of Au-ZnO hybrid nanoparticles. (b) High resolution TEM image of the basal facet of Au-ZnO hybrid acquired along [0001] zone axis. (c) FFT pattern obtained from the marked region in (b). (d) High resolution TEM image showing the epitaxial relationship at the Au-ZnO interface.

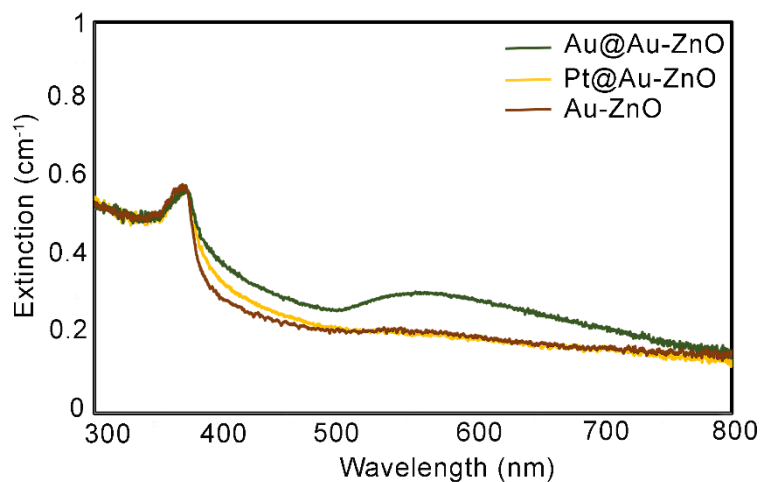


Figure S2: UV-Visible extinction spectra obtained prior to photocatalysis experiments (to confirm that all catalysts were at the same concentration).

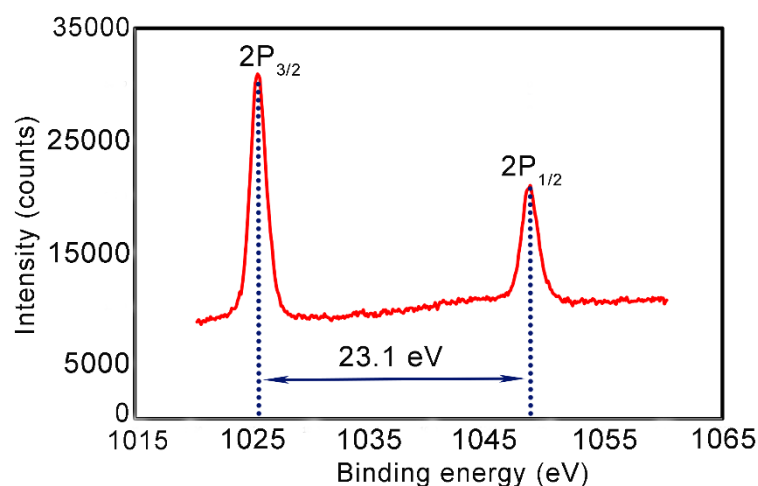


Figure S3: High resolution XPS spectrum of Zn 2p doublet.

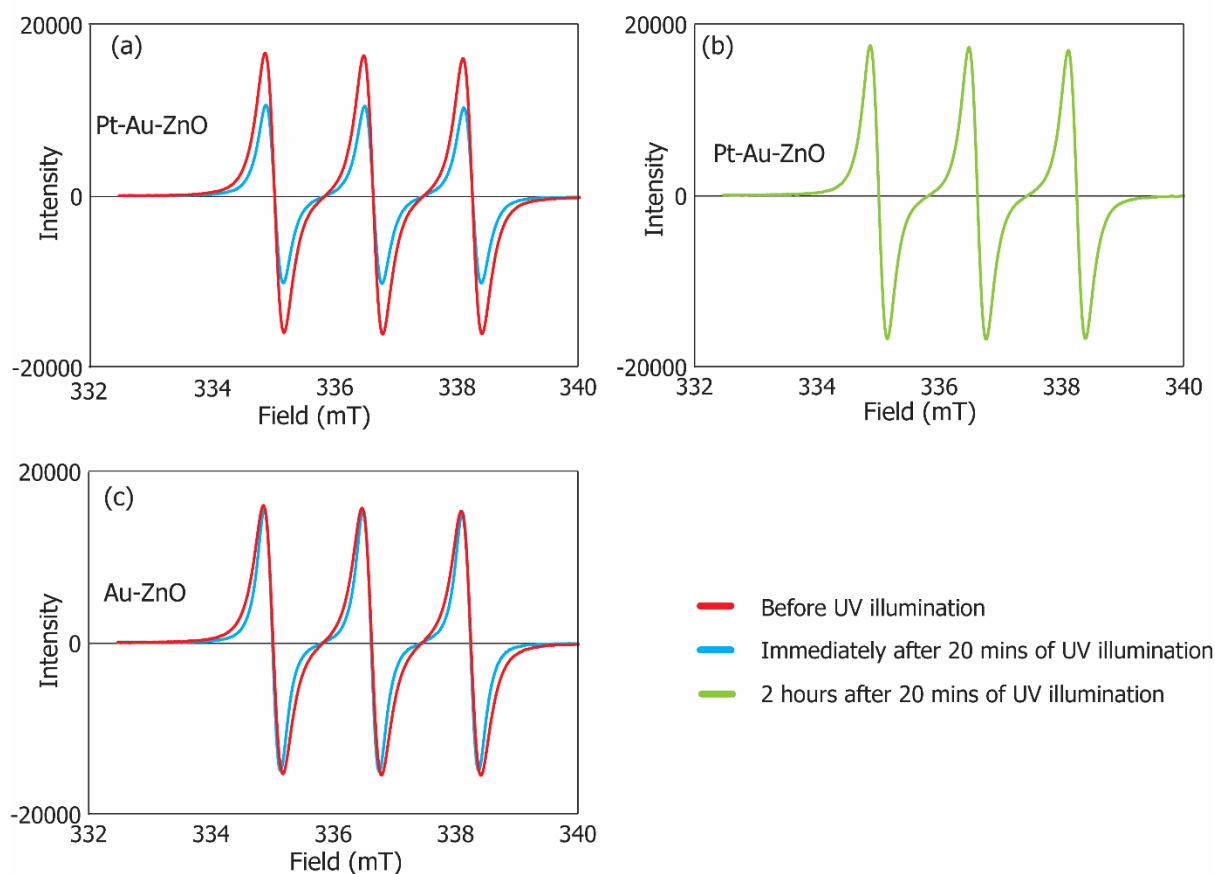


Figure S4. (a) ESR spectra of TEMPO collected before and after the photocatalytic reaction when Pt-Au-ZnO was used as the catalyst. (b) ESR spectrum of TEMPO after standing the reaction system in (a) for 2 hours after turning off the UV light and (c) ESR spectra of TEMPO collected before and after the photocatalytic reaction when Au-ZnO was used as the catalyst.

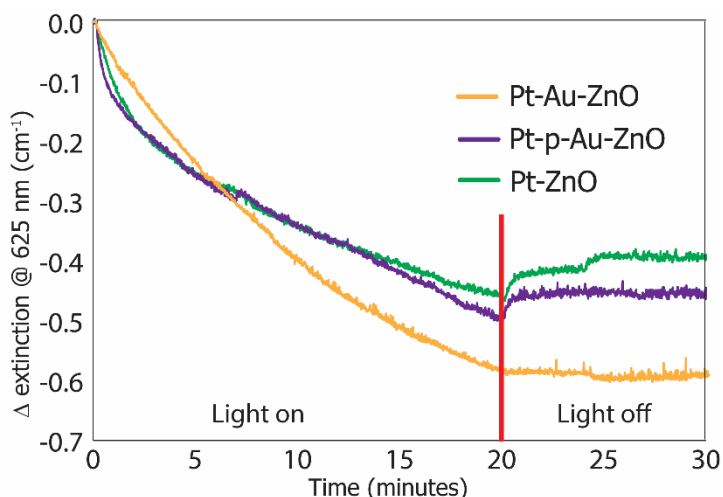


Figure S5: Time-resolved UV-Visible extinction spectra collected during photocatalytic reduction/degradation of toluidine blue for Pt-Au-ZnO, Pt-p-Au-ZnO and Pt-ZnO. It is interesting to note here that photocatalysis rate of Pt-p-Au-ZnO and Pt-ZnO during the first few seconds is greater compared to that of Pt-Au-ZnO. Although Pt metal exhibits fast electron discharge, the metal-semiconductor interface in these particles (Pt-p-Au-ZnO and Pt-ZnO) are non-epitaxial. The charge transfer via the non-epitaxial interface is expected to be inefficient compared to the epitaxial interface. Therefore, there might be some electron accumulation at ZnO and Au surfaces leading to the photoreduction of toluidine blue, albeit slower compared to photoreduction rates of Au-ZnO and Au@Au-ZnO hybrids discussed in the main article. In Pt-Au-ZnO, the metal-semiconductor interface is epitaxial, therefore, rapid electron discharge occurs via the Pt nanoparticle (lacks negative shift in Fermi level potential).

S6: Computational method

Quantum-chemical modeling was performed within the framework of density functional theory (DFT)^{1,2} using plane-wave basis set and the PAW method^{3,4} within local density approximation (LDA) as implemented in VASP.⁵⁻⁷ For the Brillouin zone sampling gamma-centered Monkhorst-Pack scheme⁸ with a $2 \times 2 \times 1$ k -point mesh was chosen. The plane wave basis cut-off energy $E_{\text{cutoff}} = 350$ eV was used. The vacuum spacing of 15 Å perpendicular to surface planes was incorporated within the simulation cell to avoid spurious interactions. All calculations were performed until the maximal force acting on any atom became less than 0.05 eV/Å. All structures were visualized in VESTA.⁹

S7: Calculation of absolute redox potential

Absolute redox potential was calculated according to Ref.¹⁰

The following relationship exists between the absolute potential scale (V) and physical scale (eV).

$$ABSOLUTE\ POTENTIAL\ SCALE = -(PHYSICAL\ SCALE) \quad (1)$$

The following relationship exists between the absolute potential ($E(abs)/V$) and the redox potential with respect to standard hydrogen electrode ($E(SHE)/V$).

$$E(abs)/V = E(SHE)/V + 4.44 \quad (2)$$

Toluidine blue

Toluidine blue/leuco-toluidine blue (TB/TB²⁻), $E(SHE)/V = 0.034\text{ V}^{11}$

Therefore, from equation (2) above, $E(abs)/V$ (TB/TB²⁻) = 4.47 V

TEMPO

TEMPO/TEMPO⁺, $E(SHE)/V = 0.76\text{ V}^{12}$

Therefore, from equation (2) above, $E(abs)/V$ (TEMPO/TEMPO⁺) = ~5.2 V

ZnO

Valence band position of ZnO ~ - 7.4 eV¹³

Therefore, from equation (1) above, $E(abs)/V \sim 7.4\text{ V}$

S8: Calculation of initial photoreduction rate

The photoreduction rate expressed in this paper represents the net relative rate of change in color absorbing molecules in the solution, calculated by measuring the change in the absorbance over time. The initial photoreduction rate can be calculated by only using time resolved data from a sufficiently short time period at the start of photoreduction. During this short time period, the change in absorption changes linearly with time with the gradient equal to the initial photoreduction rate. The time period used for initial photoreduction rate calculations was the time required for the total photoreduction to reach 50% of the maximum photoreduction achieved.

S9: Photodegradation mechanism

Figure 1 below shows the IR spectrum obtained from a dried Au-ZnO hybrid sample. The broad peak centered at 3360 cm⁻¹ is attributed to surface bound hydroxyl (OH) species. Note

that Au-ZnO was used as the precursor to prepare Pt-Au-ZnO and Au@Au-ZnO hybrid nanoparticles.

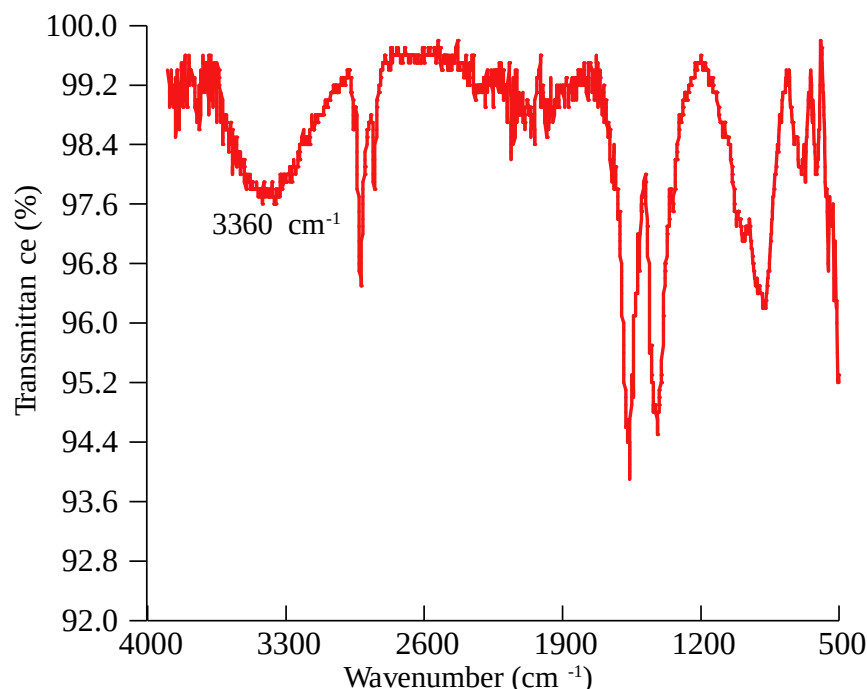
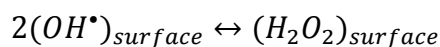
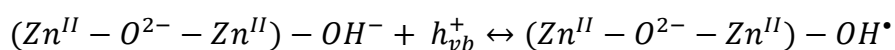


Figure S6: IR spectrum of Au-ZnO powder.

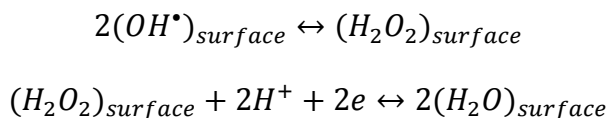
In semiconductors, such as ZnO and TiO₂, photogenerated hole trapping by surface-OH can generate hydroxyl radicals (OH[•]).^{14, 15} Surface OH[•] plays the key role in the photodegradation of organic dye molecules. Particularly, for the Pt-Au-ZnO system studied here, more OH[•] could be generated owing to efficient electro-hole separation, as discussed in the manuscript. Further, surface peroxo-species can also be formed by combination of OH[•] radicals:



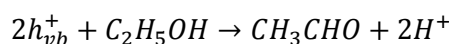
Degradation/mineralization pathways of thiazine type dye molecules to CO₂, NH₄⁺, NO₃⁻ and SO₄²⁻ in the presence OH[•] are well documented in the literature.¹⁶

The electron acceptor in the Pt-Au-ZnO system: The work function of Pt is ~5.64 V on the absolute potential scale. Due to absence of electron accumulation in the Pt-Au-ZnO photocatalyst, the redox potential of photogenerated electrons in Pt-Au-ZnO should be close to ~ 5.64 V. Therefore, the redox potential of the electron acceptor should be more positive compared to this value. Upon UV irradiation of the Pt-Au-ZnO system, a number of reactions can take place at the photocatalyst surface (Refer ref¹⁴ for reactions occurring at TiO₂ surface).

For instance, $(\text{H}_2\text{O}_2)_{\text{surface}}$ can be formed as shown above; $(\text{H}_2\text{O}_2)_{\text{surface}}$ is a good electron acceptor ($E_{\text{abs}} = \sim 5.79 \text{ V}$ vs SHE at pH 7).



H^+ required for the above reaction can be formed by oxidation of ethanol.



$(\text{H}_2\text{O})_{\text{surface}}$ formed above would also take part in further chain reactions.

References

1. Hohenberg, P. & Kohn, W. Inhomogeneous Electron Gas. *Phys. Rev.* **136**, B864–B871 (1964).
2. Kohn, W. & Sham, L. J. Self-Consistent Equations Including Exchange and Correlation Effects. *Phys. Rev.* **140**, A1133–A1138 (1965).
3. Blöchl, P. E. Projector Augmented-Wave Method. *Phys. Rev. B* **50**, 17953–17979 (1994).
4. Kresse, G. & Joubert, D. From Ultrasoft Pseudopotentials to the Projector Augmented-Wave Method. *Phys. Rev. B* **59**, 1758–1775 (1999).
5. Kresse, G. & Hafner, J. *Ab initio* Molecular Dynamics for Liquid Metals. *Phys. Rev. B* **47**, 558–561 (1993).
6. Kresse, G. & Hafner, J. *Ab initio* Molecular-Dynamics Simulation of the Liquid-Metal–Amorphous-Semiconductor Transition in Germanium. *Phys. Rev. B* **49**, 14251–14269 (1994).
7. Kresse, G. & Furthmüller, J. Efficient Iterative Schemes for *ab initio* Total-Energy Calculations Using a Plane-Wave Basis Set. *Phys. Rev. B* **54**, 11169–11186 (1996).
8. Monkhorst, H. J. & Pack, J. D. Special Points for Brillouin-Zone Integrations. *Phys. Rev. B* **13**, 5188–5192 (1976).
9. Momma, K. & Izumi, F. VESTA 3 for Three-Dimensional Visualization of Crystal, Volumetric and Morphology data. *J. Appl. Crystallogr.* **44**, 1272–1276 (2011).

10. Trasatti, S. The Absolute Electrode Potential: An Explanatory Note (Recommendations 1986). *Pure Appl. Chem.* **1986**, 58, 955-966.
11. Clark, W. M. Oxidation-Reduction Potentials of Organic Systems; The Williams & Wilkins Co.: Baltimore, **1960**.
12. Hodgson, J. L.; Namazian, M.; Bottle, S. E.; Coote, M. L. One-Electron Oxidation and Reduction Potentials of Nitroxide Antioxidants: A Theoretical Study. *J. Phys. Chem. A* **2007**, 111, 13595-13605
13. Ravirajan, P.; Peiró, A. M.; Nazeeruddin, M. K.; Graetzel, M.; Bradley, D. D. C.; Durrant, J. R.; Nelson, J. Hybrid Polymer/Zinc Oxide Photovoltaic Devices with Vertically Oriented ZnO Nanorods and an Amphiphilic Molecular Interface Layer. *J. Phys. Chem. B* **2006**, 110, 7635-7639
14. Pelizzetti, E.; Minero, C. Mechanism of the Photo-Oxidative Degradation of Organic Pollutants over TiO₂ Particles. *Electrochim. Acta* **1993**, 38, 47-55.
15. Jing, L.; Xu, Z.; Sun, X.; Shang, J.; Cai, W. The Surface Properties and Photocatalytic Activities of ZnO Ultrafine Particles. *Appl. Surf. Sci.* **2001**, 180, 308-314.
16. Houas, A.; Lachheb, H.; Ksibi, M.; Elaloui, E.; Guillard, C.; Herrmann, J.-M. Photocatalytic Degradation Pathway of Methylene Blue in Water. *Appl. Catal., B* **2001**, 31, 145-157.