

Supporting information

for

Visible light induced enhanced photocatalytic degradation of organic pollutants in aqueous media using Ag doped hollow TiO₂ nanospheres

Siddhartha Sankar Boxi, Santanu Paria*

Interfaces and Nanomaterials Laboratory, Department of Chemical Engineering, National Institute of Technology, Rourkela 769008, Orissa, India.

The distribution of particle size of AgBr, TiO₂, AgBr/TiO₂ and Ag-h-TiO₂ nanoparticles were measured in dynamic light scattering (DLS) instrument. The DLS data in Figure 1 shows that the average particle size was 16.89, 41.52, 20.81 and 20.79 nm for AgBr, TiO₂, AgBr/TiO₂ core/shell and Ag-h-TiO₂ nanoparticles, respectively.

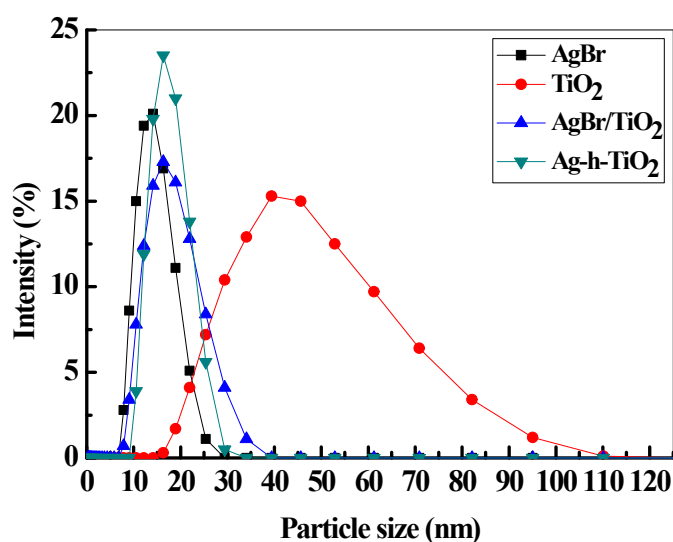


Figure S1. Particle size distribution of AgBr, TiO₂, AgBr/TiO₂ and Ag-h-TiO₂ nanoparticles measured by dynamic light scattering (DLS).

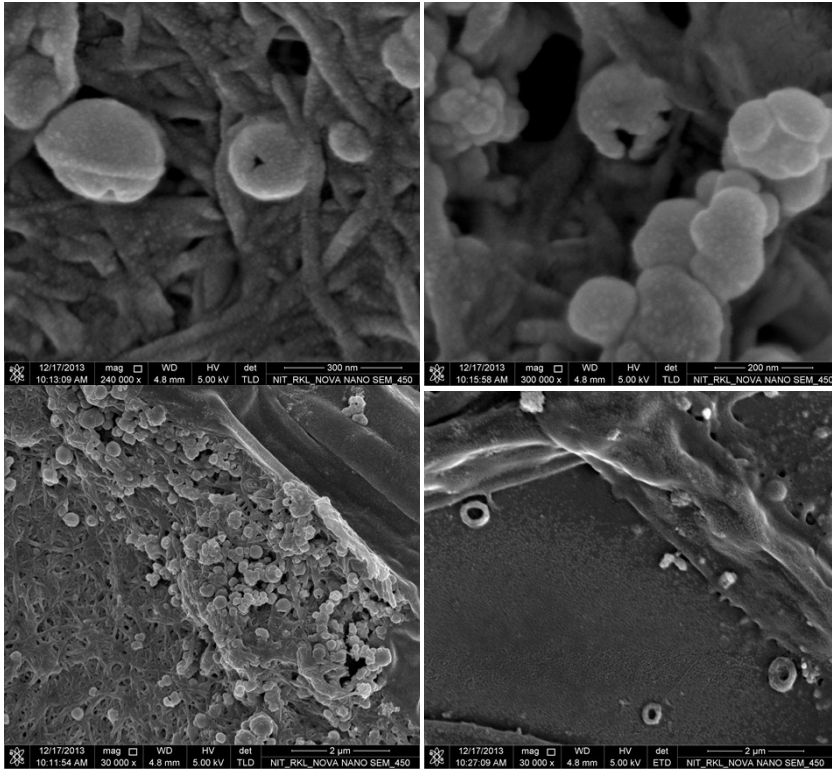


Figure S2: FE-SEM images of Ag-h-TiO₂ nanoparticles with some broken hollow structure.

Quantum yield calculation

Quantum yield was calculated using the equation (1), where phenol was taken as the reference. The refractive index and quantum yield of phenol were taken 1.5425 and 0.14 respectively.

$$Q.Y_S = Q.Y_R \left(\frac{\text{Grad}_S}{\text{Grad}_R} \right) \times \left(\frac{\eta_S}{\eta_R} \right)^2 \text{-----(1)}$$

Where, Q.Y_S – Quantum yield of the sample

Q.Y_R – Quantum yield of the reference (Phenol)

Grad_S – Slope of the Integrate intensity vs. absorbance line for sample

Grad_R – Slope of the Integrate intensity vs. absorbance line for reference (Phenol)

η_S – Refractive index of the sample

η_R – Refractive index of the reference (Phenol)

Table S1. Comparison of the present work of nitrobenzene degradation with the published literature

Catalyst	catalyst dose	Initial NB conc	Light source	Time	parameters	% deg.	Ref.
N-Ce-TiO ₂	1 g/L	50 mg/L	visible lamp, 300 W	4 hrs	30°C	53	1
TiO ₂	0.2 g/L	50.1 mg/L	14 W UV lamp, 254 nm	3 hrs	air feeding of 150 mL/min	90	2
Nano crystalline TiO ₂	0.2 g/L	49.94 mg/L	mercury vapour lamp	8 hrs	air purging	98%	3
Ce-TiO ₂	0.1 g/L	25 mg/L	Visible lamp 500 W	7 hrs	pH 9	100	4
Pt/Cd ₂ Sb ₂ O _{6,8}	2.5 g/L	100.047 mg/L	Xenon lamp	3 hrs	CH ₃ OH	~100	5
TSA-MIP-TiO ₂	0.1 g/L	6.153 mg/L	9 W UV lamp, 253.7 nm	90 min	-	>95	6

Degradation of metronidazole (MTZ) antibiotic has been studied by different technologies such as ultraviolet (UV) irradiation, ⁷ Oxidation processes using UV, UV/H₂O₂, H₂O₂/Fe²⁺, and UV/H₂O₂/Fe²⁺, ⁸ etc. In general these processes are expensive and complicated. ⁹ Use of Closed Bottle Test (CBT) for MTZ degradation is also not effective because of its low degradation efficiency (25.6%) even after 28 days of incubation time.¹⁰ Apart from these conventional method, use of photocatalyst were also studied as listed in Table S2. It shows lower degradation rate in visible light irradiation, 100% degradation was only achieved in UV-light irradiation and in high catalyst dose. In this approach our synthesized photocatalyst degraded 94.77% MTZ in visible light irradiation, 30 mg/L initial MTZ concentration, 0.5 g/L catalyst dose, and irradiation time of 120min.

Table S2. Comparison of the present work of metronidazole degradation with the published literature

Catalyst	catalyst dose	Initial NB conc	Light source	Time	parameters	% deg.	Ref.
ZnSnO ₃ /RGO nanocomposites	1 g/L	5 mg/L	500 W, visible lamp	180 min		72.5	11
Zn ₂ GeO ₄	1 g/L	10 mg/L	UV light lamp ($\lambda = 253.7$ nm)	80 min	-	~100	12
nZVM	0.1 g/L	100 mg/L	-	-	251°C, pH dependent, O ₂ flow	84	13

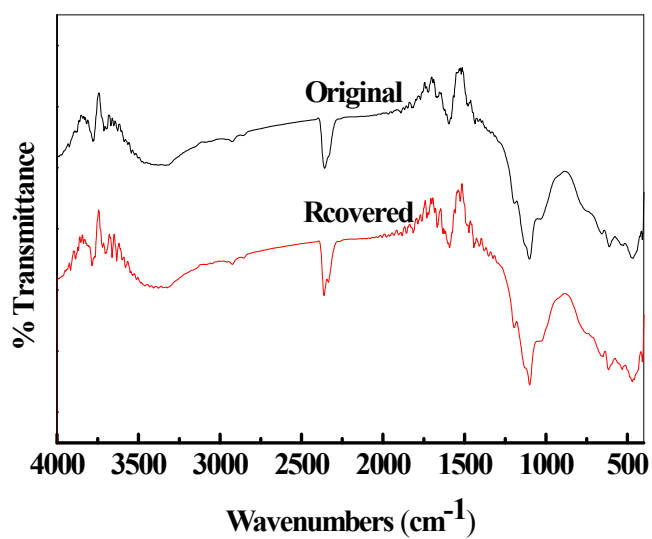


Figure S3. FT-IR spectra of Ag-h-TiO₂ before and after photocatalytic degradation of MTZ solution under visible light.

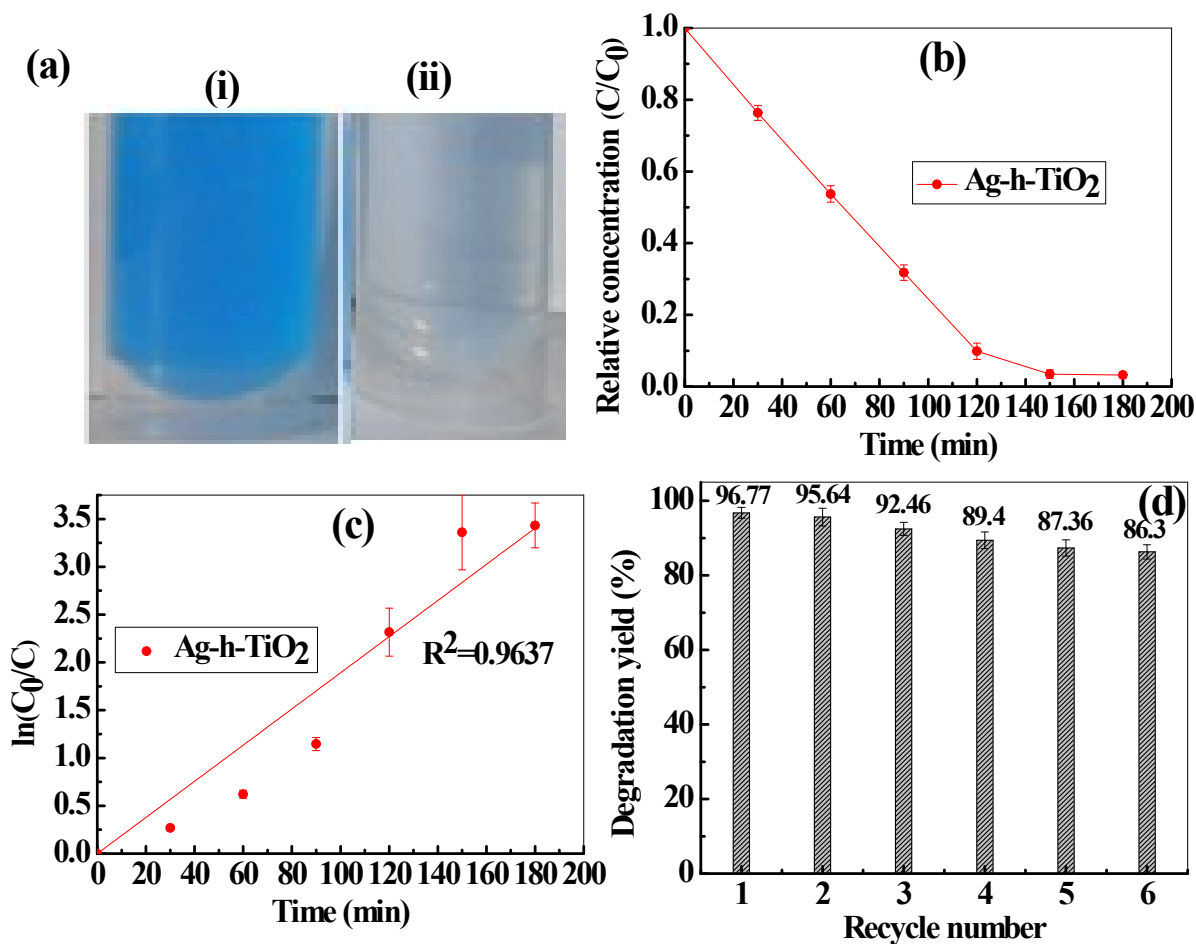


Figure S4. (a) The images of the methylene blue solution before (i) and after degradation under (ii: Ag-h-TiO₂). (b) Photocatalytic degradation and (c) Kinetic data for the degradation of MBD solution in high pressure mercury vapour lamp under Ag-h-TiO₂ NPs. (d) Recycling test of Ag-h-TiO₂ for the degradation of MBD solution under visible light.

References

- Shen, X. -Z.; Liu, Z. -C.; Xie, S. -M.; Guo, J. Degradation of nitrobenzene using titania photocatalyst co-doped with nitrogen and cerium under visible light illumination. *J. Hazard. Mater.* **2009**, *162*, 1193–1198.
- Wang, T. -J.; Hsieh, M. -T.; Shi, T. -E.; Kuei, C. -H. UV-Irradiated Photo catalytic Degradation of Nitrobenzene by Titania Binding on Quartz Tube. *Int. J. Photoenergy.* **2012**, 1-8, doi:10.1155/2012/681941.
- Tayade, R. J.; Kulkarni, R. G.; Jasra, R. V. Photocatalytic Degradation of Aqueous Nitrobenzene by Nanocrystalline TiO₂. *Ind. Eng. Chem. Res.* **2006**, *45*, 922-927.

4. Synthesis and Characterization of Cerium Doped Titanium Catalyst for the Degradation of Nitrobenzene Using Visible Light. *Int. J. Photoenergy*. **2014**, 1-9, doi:10.1155/2014/756408.
5. Baeissa, E. S. Pt/Cd₂Sb₂O_{6,8} Nanoparticles for efficient Visible Light Photocatalysis. *Ceram. Int.* **2014**, *40*, 7195-7201.
6. Shen, X.; Zhu, L.; Wang, N.; Zhang, T.; Tang, H. Selective photocatalytic degradation of nitrobenzene facilitated by molecular imprinting with a transition state analog. *Catal. Today* **2014**, *225*, 164–170.
7. Prados-Joya, G.; Sánchez-Polo, M.; Rivera-Utrilla, J.; Ferro-garcía, M. Photodegradation of the Antibiotics Nitroimidazoles in Aqueous Solution by Ultraviolet Radiation. *Water Res.* 2011, *45*, 393–403.
8. Shemer, H.; Kunukcu, Y. K.; Linden, K. G. Degradation of the Pharmaceutical Metronidazole via UV, Fenton and Photo-Fenton processes. *Chemosphere* 2006, *63*, 269–276.
9. Johnson, M. B.; Mehrvar, M. Aqueous Metronidazole Degradation by UV/H₂O₂ Process in Single-and Multi-Lamp Tubular Photoreactors: Kinetics and Reactor Design. *Ind. Eng. Chem. Res.* 2008, *47*, 6525–6537.
10. Alexy, R.; Kümpel, T.; Kümmerer, K. Assessment of Degradation of 18 Antibiotics in the Closed Bottle Test. *Chemosphere* 2004, *57*, 505–512.
11. Dong, S.; Sun, J.; Li, Y.; Yu, C.; Li, Y.; Sun, J. ZnSnO₃ Hollow Nanospheres/Reduced Graphene Oxide Nanocomposites as High-Performance Photocatalysts for Degradation of Metronidazole. *Applied Catalysis B: Environmental* 2014, *144*, 386–393.
12. Liu, J.; Zhang, G.; Jimmy C. Yu, J. C.; Guo, Y. In Situ Synthesis of Zn₂GeO₄ Hollow Spheres and their Enhanced Photocatalytic Activity for the Degradation of Antibiotic Metronidazole. *Dalton Trans.* 2013, *42*, 5092–5099.
13. Fang, Z.; Qiu, X.; Chen, J.; Qiu, X. Degradation of Metronidazole by Nanoscale Zero-Valent Metal Prepared from Steel Pickling Waste Liquor. *Applied Catalysis B: Environmental* 2010, *100*, 221–228.