

Supporting Information

Effective photocatalytic degradation of Rhodamine-B over Zn-doped BaO₂ and SrO₂ composites under UV and Sunlight Irradiation

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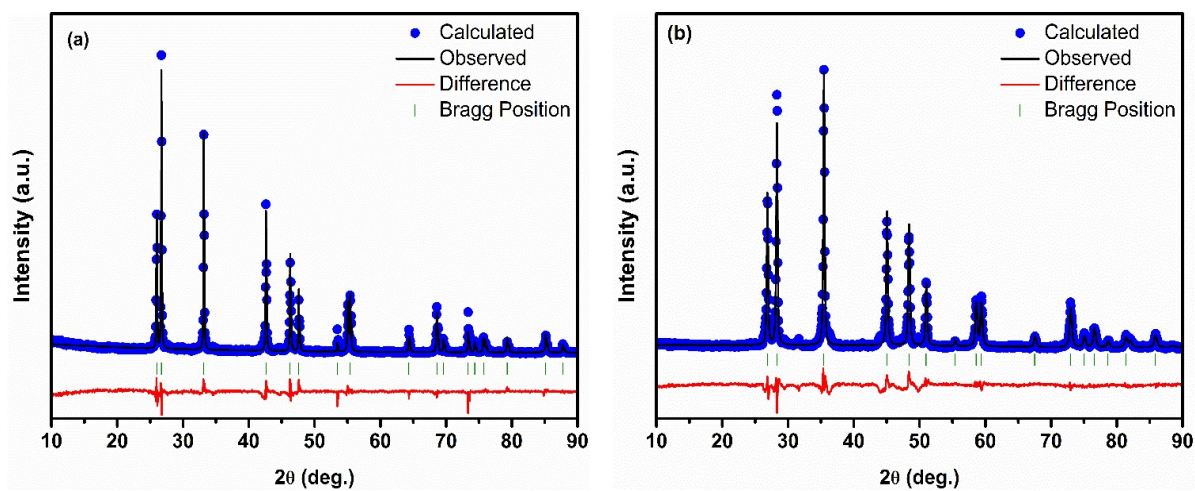


Fig. S1. Rietveld refinement results of (a) BaO₂ and (b) SrO₂ nanoparticles.

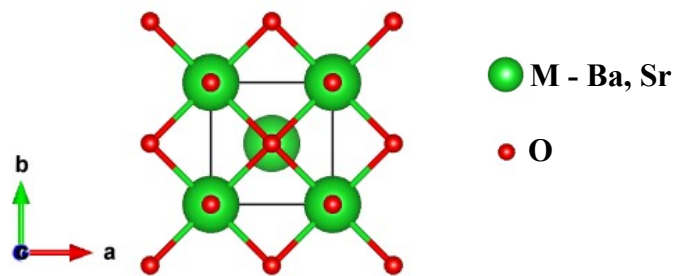


Fig. S2. Crystal structure of BaO₂ and SrO₂ nanoparticles.

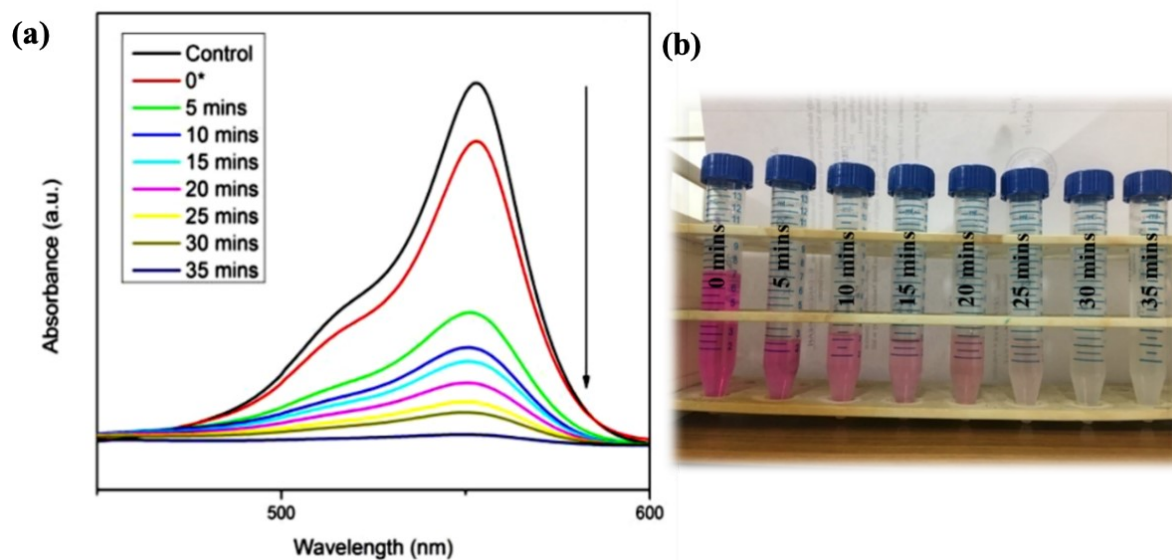


Fig. S3. (a) photocatalytic degradation of RhB and (b) photographs of RhB photodegradation at different times using BaO₂ photocatalysts under UV-light irradiation.

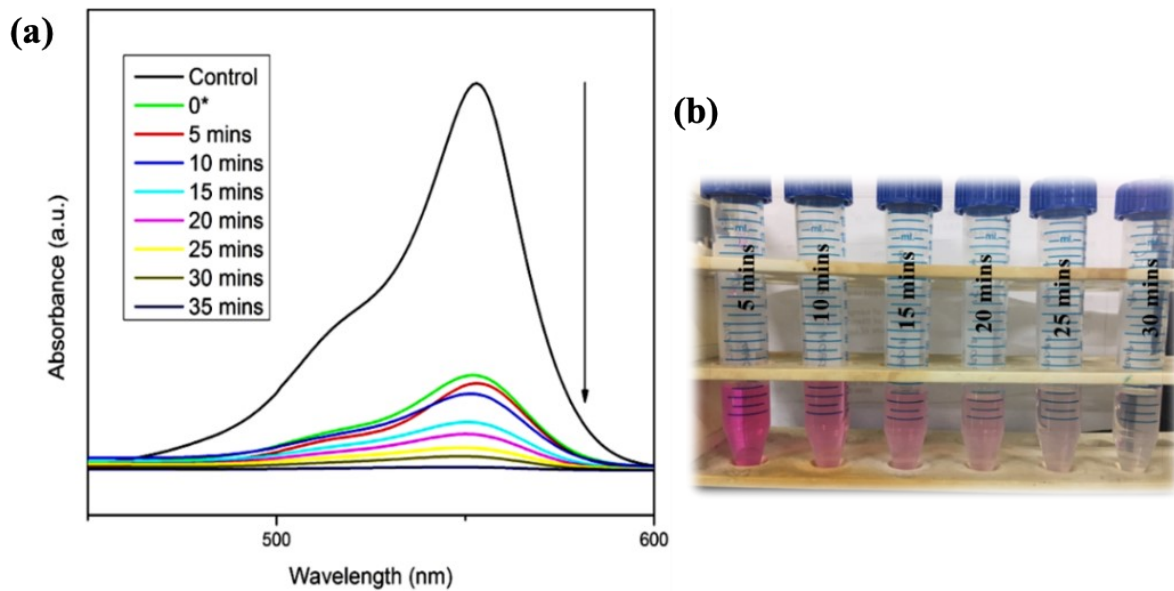


Fig. S4. (a) photocatalytic degradation of RhB and (b) photographs of RhB photodegradation at different times using SrO_2 photocatalysts under UV-light irradiation.

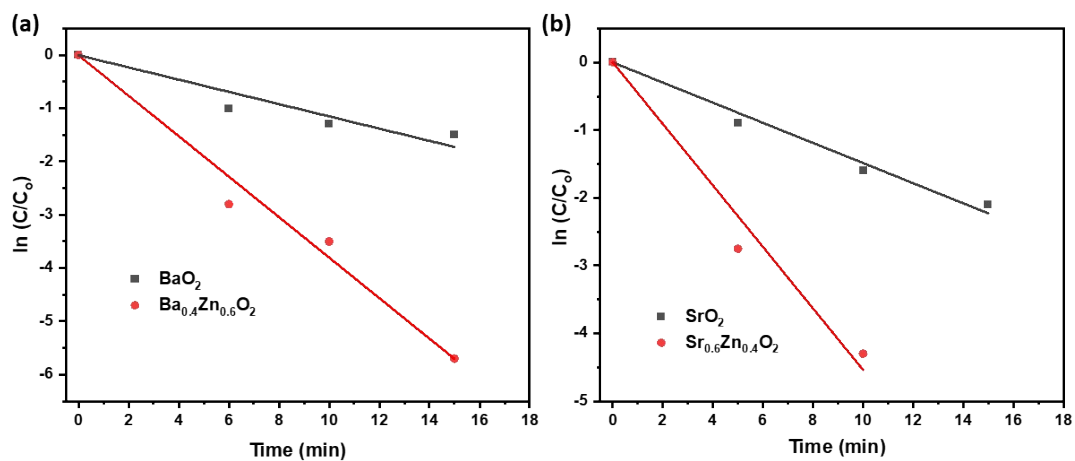


Fig. S5. First-order kinetic plots of RhB photodegradation using (a) BaO_2 and $\text{Ba}_{0.4}\text{Zn}_{0.6}\text{O}_2$ (b) SrO_2 and $\text{Sr}_{0.6}\text{Zn}_{0.4}\text{O}_2$ photocatalysts under UV-light illumination.

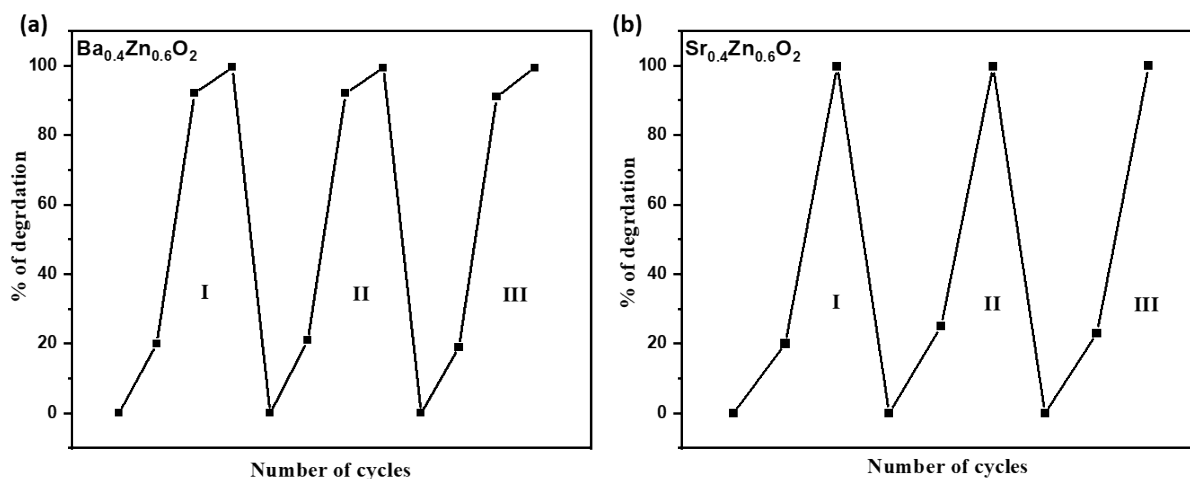


Fig. S6. Reusability of $\text{Ba}_{0.4}\text{Zn}_{0.6}\text{O}_2$ (a) and $\text{Sr}_{0.6}\text{Zn}_{0.4}\text{O}_2$ (b) for dye degradation under UV irradiation

Table S1. Rietveld refinement results for BaO₂ and SrO₂

Chemical formula		BaO ₂		SrO ₂			
Crystal system		Tetragonal		Tetragonal			
Space group		I4/mmm		I4/mmm			
a, Å		3.81(4)		3.57(3)			
c, Å		6.85(2)		6.62(4)			
V, Å ³		99.82(4)		84.82(2)			
Z		2		2			
Radiation		Cu Kα ₁		Cu Kα ₁			
Wavelength, Å		1.5406		1.5406			
2θ range, °		10-90		10-70			
R _{wp} , %		15.31		12.61			
R _{bragg} , %		11.83		9.62			
Compositi on	χ ²	Ba (wt%)		Sr (wt%)		Zn (wt%)	
		Theoreti cal	Experime ntal	Theoreti cal	Experime ntal	Theoreti cal	Experime ntal
Ba _{0.4} Zn _{0.6} O ₂		43.5	43.2			31.1	30.8
Sr _{0.6} Zn _{0.4} O 2				47.5	47.2	23.6	23.2

Table S2. Composition by ICP - OES

Table S3. Amount of H₂O₂ released in aqueous suspension

x	H ₂ O ₂ amount (±2 ppm)	
	Ba _{1-x} Zn _x O ₂	Sr _{1-x} Zn _x O ₂
0	10	9
0.2	15	15
0.4	19	28
0.6	25	22
0.8	20	18

Table S4 Comparison results of photocatalytic degradation of RhB with different photocatalysts under UV light irradiation (N.S Not studied).

Compound	Catalyst quantity (mg)	RhB concentration (ppm)	Degradation efficiency (%)	Rate constant k (min ⁻¹)	Time (min)	References
Zn ₂ SnO ₄	40	5	99.0	0.0124	90	1
Pt/TiO ₂	100	10	97.5	0.0172	120	2
Pt-TiO ₂	300	10	63.0	0.0053	180	3
Ag-ZnO	25	5	99.0	N.S	60	4
CeO ₂ -Y ₂ O ₃	40	10	99.0	N.S	120	5
Zn doped CdS	20	5	85.0	N.S	135	6
SnO ₂ /TiO ₂	100	10	92.0	0.0084	180	7
Ba_{0.4}Zn_{0.6}O₂	25	10	99.90	0.344	15	Present work
Sr_{0.6}Zn_{0.4}O₂	25	10	99.80	0.394	10	Present work

Table S5 Comparison studies of the photodegradation of RhB using various photocatalysts under direct sunlight illumination (N.S: not studied).

Compound	Catalyst quantity (mg)	RhB dye (ppm)	Degradation efficiency (%)	Rate constant k (min ⁻¹)	Time (min)	References
MoF	20	2	96.7	N.S	30	8
Zn doped CdS	20	5	65.0	N.S	135	6
S-TiO ₂	50	10	97.0	0.280	120	9
Au-ZnO	100	10	85.0	0.291	90	10
BiVO ₄	100	5	97.0	N.S	600	11
RGO/BiVO ₄	100	5	98.50	N.S	600	12
AgI/ZnO	15	5	98.50	N.S	150	13
H ₃ PW ₁₂ O ₄₀ /TiO ₂	4.5	12	89.80	0.180	240	14

MWCNT/WO ₃	50	10	92.0	0.230	150	15
Ba_{0.4}Zn_{0.6}O₂	25	10	99.80	2.480	90	Present work
Sr_{0.6}Zn_{0.4}O₂	25	10	99.50	2.340	90	Present work

REFERENCES

- [1] Rovisco, A.; Branquinho, R.; Deuermeier, J.; Freire, T.; Fortunato, E.; Martins, R.; Barquinha, P. Shape Effect of Zinc-Tin Oxide Nanostructures on Photodegradation of Methylene Blue and Rhodamine B under UV and Visible Light. *ACS Appl. Nano Mater.*, **2021**, *4* (2), 1149–1161.
- [2] Mai H.; Abdel-Khalek, M.A.; Ahmed. M.F.; Abdel-Messih, Fathy, E.S. Synthesis of Mesoporous Pt/TiO₂ Nanoparticles by Incipient Wetness Route for Photocatalytic Degradation of Rhodamine B and Methyl Orange Dyes under UV and Sunlight Radiations. *Mater. Sci. Technol.*, DOI: <https://doi.org/10.1016/j.mset.2022.08.001>
- [3] Pol, R.; Guerrero, M.; García-Lecina, E.; Altube, A.; Rossinyol, E.; Garroni, S.; Baró, M. D.; Pons, J.; Sort, J.; Pellicer, E. Ni-, Pt- and (Ni/Pt)-Doped TiO₂ Nanophotocatalysts: A Smart Approach for Sustainable Degradation of Rhodamine B Dye. *Appl. Catal. B: Environ.*, **2016**, *181*, 270–278.
- [4] Rokesh, K.; Mohan, S. C.; Karuppuchamy, S.; Jothivenkatachalam, K. Photo-Assisted Advanced Oxidation Processes for Rhodamine B Degradation Using ZnO-Ag Nanocomposite Materials. *J. Environ. Chem. Eng.*, **2018**, *6* (3), 3610–3620.
- [5] Magdalane, C. M.; Kaviyarasu, K.; Vijaya, J. J.; Siddhardha, B.; Jeyaraj, B.; Kennedy, J.; Maaza, M. Evaluation on the Heterostructured CeO₂/Y₂O₃ Binary Metal Oxide Nanocomposites for UV/Vis Light Induced Photocatalytic

- Degradation of Rhodamine - B Dye for Textile Engineering Application. *J. Alloys Compd.*, **2017**, 727, 1324–1337.
- [6] Singh, A.; Singh, D.; Ahmed, B. and Ojha, A.K. Sun/UV-Light Driven Photocatalytic Degradation of Rhodamine B Dye by Zn Doped CdS Nanostructures as Photocatalyst. *Mater. Chem. Phys.*, **2022**, 277, 125531.
- [7] Abdel-Messih, M. F.; Ahmed, M. A.; El-Sayed, A. S. Photocatalytic Decolorization of Rhodamine B Dye Using Novel Mesoporous SnO₂-TiO₂ Nano Mixed Oxides Prepared by Sol-Gel Method. *J. Photochem. Photobiol.*, **2013**, 260, 1–8.
- [8] Li, X.H.; Liu, Y.; Lin, H.Y.; Xu, N.; Zhang, Z.; Liu, G.C. and Wang. X.L., Solvent-Induced Two Co-Based 3D Metal–Organic Frameworks as Platforms for the High Degradation of Rhodamine B Under Sunlight. *Cryst. Growth Des.*, **2022**, 22, 3845–3852.
- [9] Zhu, M.; Zhai, C.; Qiu, L.; Lu, C.; Paton, A. S.; Du, Y.; Goh, M. C. New Method to Synthesize S-Doped TiO₂ with Stable and Highly Efficient Photocatalytic Performance under Indoor Sunlight Irradiation. *ACS Sustain. Chem. Eng.*, **2015**, 3 (12), 3123–3129.
- [10] Mondal, C.; Pal, J.; Ganguly, M.; Sinha, A. K.; Jana, J.; Pal, T. A One Pot Synthesis of Au-ZnO Nanocomposites for Plasmon-Enhanced Sunlight Driven Photocatalytic Activity. *New J. Chem.*, **2014**, 38 (7), 2999–3005.
- [11] Dong, S.; Feng, J.; Li, Y.; Hu, L.; Liu, M.; Wang, Y.; Pi, Y.; Sun, J.; Sun, J. Shape-Controlled Synthesis of BiVO₄ Hierarchical Structures with Unique Natural-Sunlight-Driven Photocatalytic Activity. *Appl. Catal. B: Environ.*, **2014**, 152-153 (1), 413–424.

- [12] Dong, S.; Cui, Y.; Wang, Y.; Li, Y.; Hu, L.; Sun, J.; Sun, J. Designing Three-Dimensional Acicular Sheaf Shaped BiVO₄/Reduced Graphene Oxide Composites for Efficient Sunlight-Driven Photocatalytic Degradation of Dye Wastewater. *Chem. Eng. J.*, **2014**, *249*, 102–110.
- [13] Wang, X.; Wan, X.; Xu, X.; Chen, X. Facile Fabrication of Highly Efficient AgI/ZnO Heterojunction and Its Application of Methylene Blue and Rhodamine B Solutions Degradation under Natural Sunlight. *Appl. Surf. Sci.*, **2014**, *321*, 10–18.
- [14] Lu, N.; Zhao, Y.; Liu, H.; Guo, Y.; Yuan, X.; Xu, H.; Peng, H.; Qin, H. Design of Polyoxometallate-Titania Composite Film (H₃PW₁₂O₄₀/TiO₂) for the Degradation of an Aqueous Dye Rhodamine B under the Simulated Sunlight Irradiation. *J. Hazard. Mater.*, **2012**, *199*, 1–8.
- [15] Saleh, T. A.; Gupta, V. K. Functionalization of Tungsten Oxide into MWCNT and Its Application for Sunlight-Induced Degradation of Rhodamine B. *J. Colloid Interface Sci.*, **2011**, *362* (2), 337–344.