Supplementary Information

Rhodium Doping Augments Photocatalytic Activity of Barium Titanate: Effect of Electronic Structure Engineering

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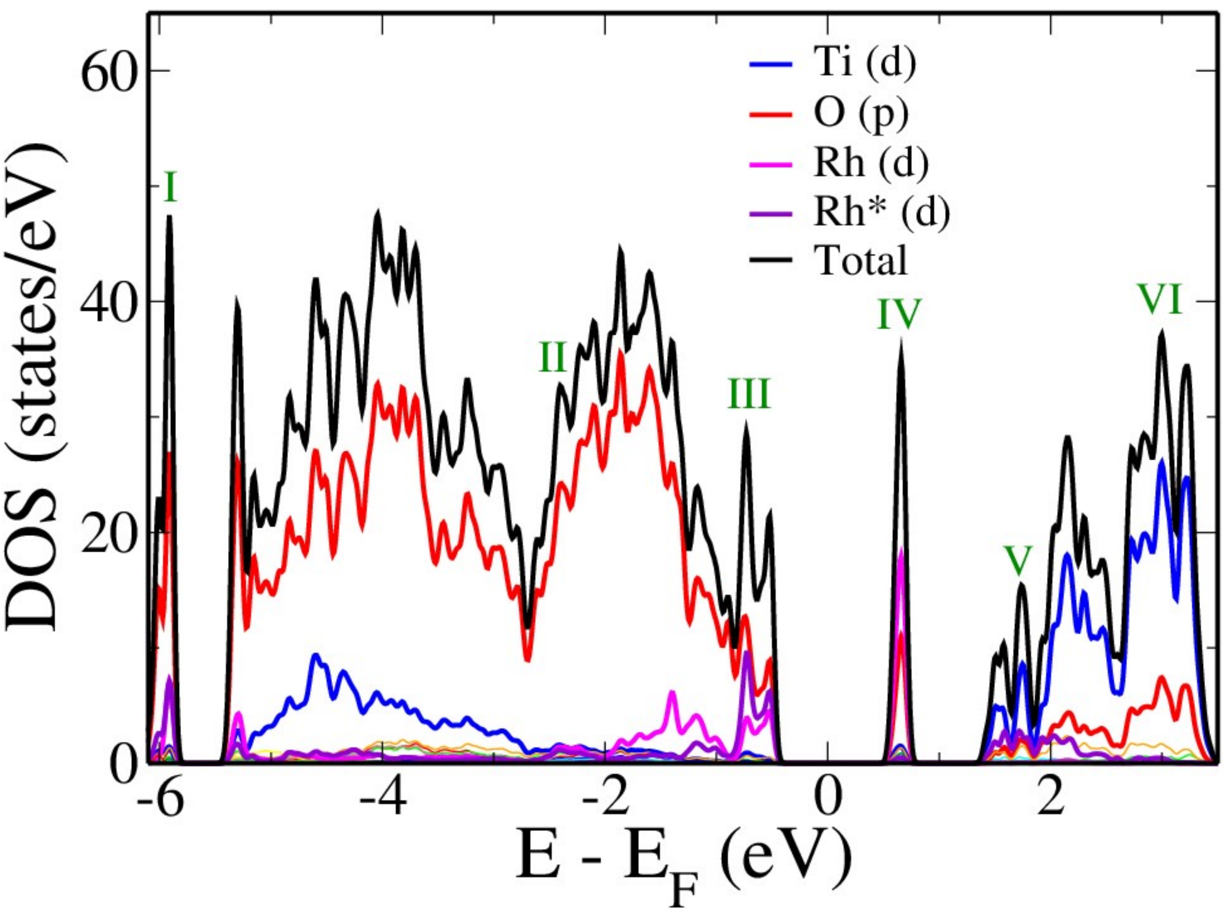

Figure S1. pdos of 2 x 2 x 2 supercell of *Rh* doped $BaTiO_3$ (case A) with one *Rh* in *Ti* site (lavender) indicated as *Rh** and another *Rh* in *Ba* site (pink).

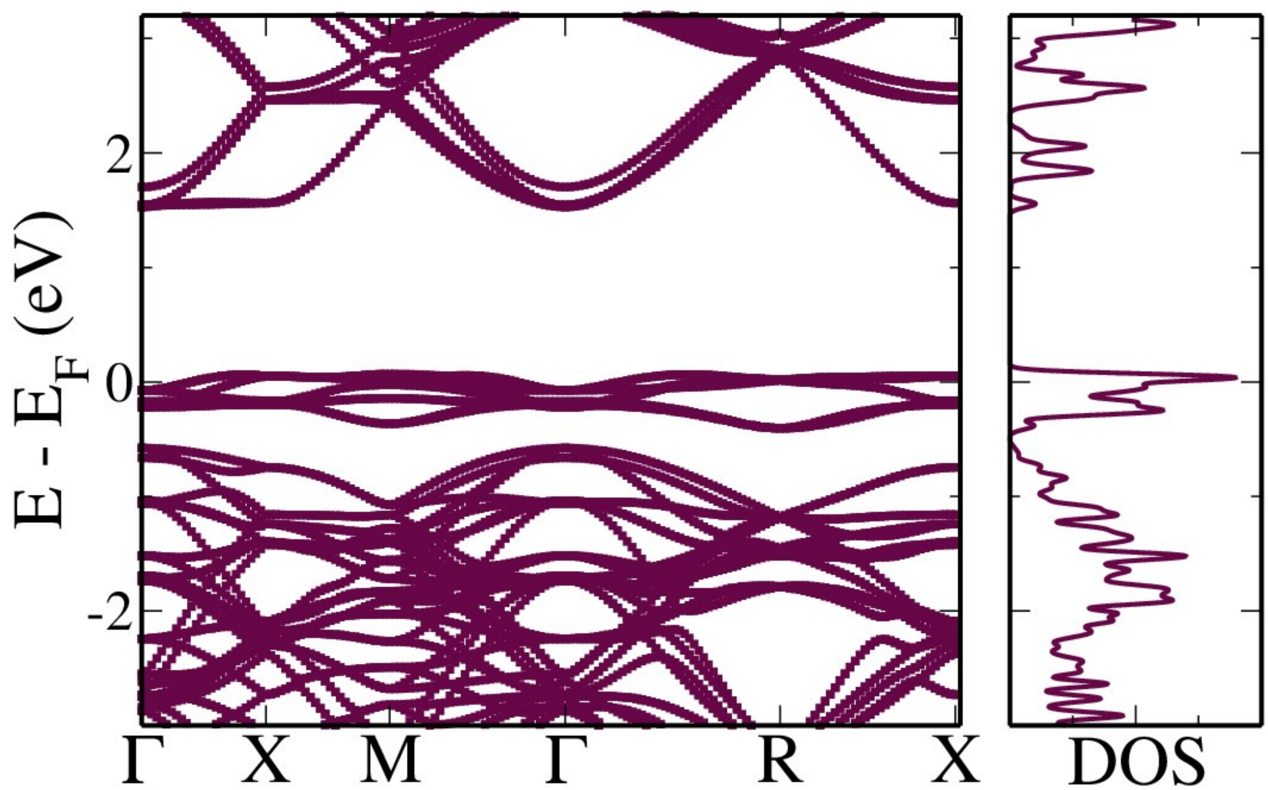

Figure S2. Electronic structure and DOS of 2 x 2 x 2 supercell of *Rh* doped $BaTiO_3$ with two *Rh* in *Ba* sites.

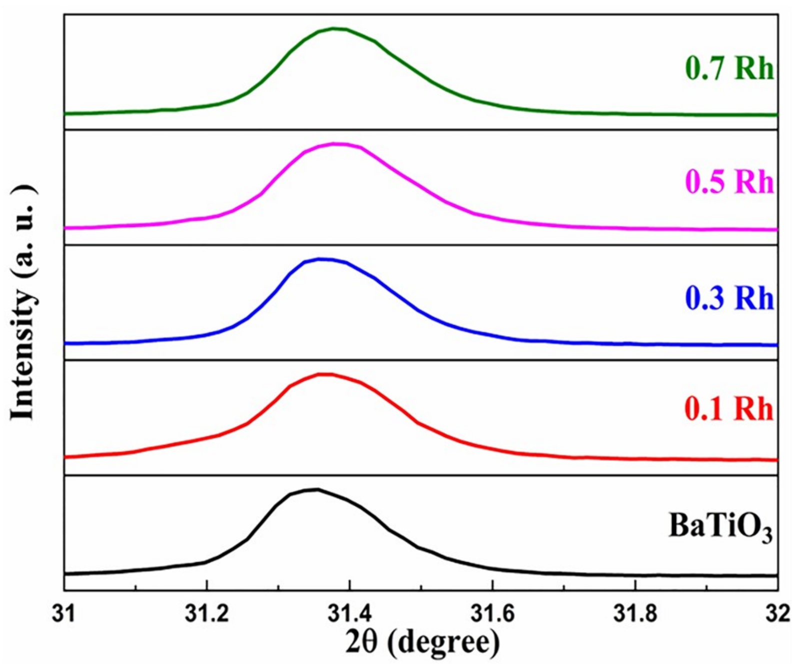

Figure S3. XRD patterns of synthesized samples showing (110) peak shift to higher θ values.

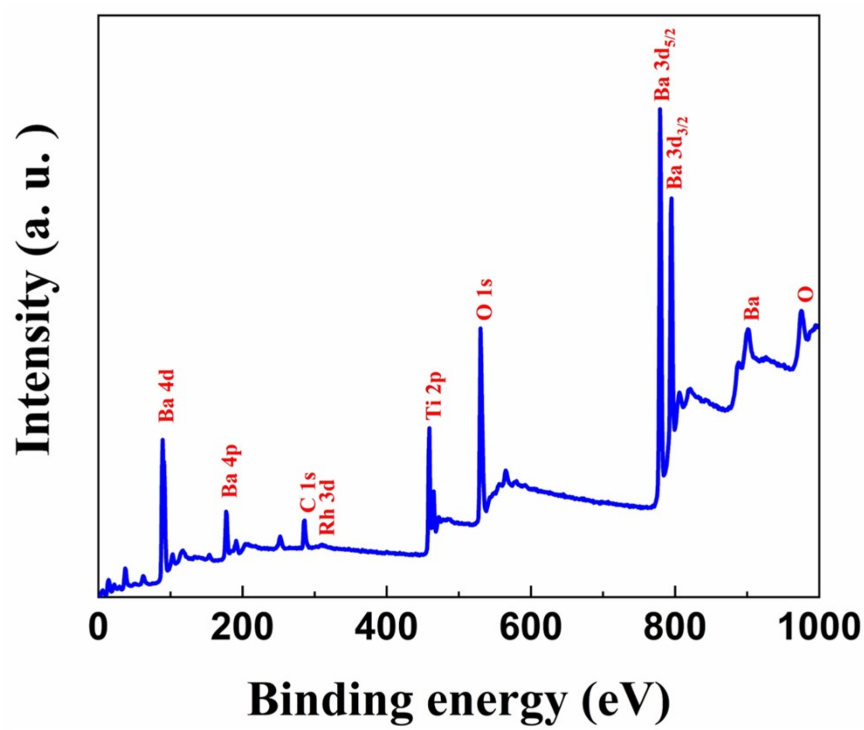

Figure S4. XPS survey spectrum of 0.5 Rh.

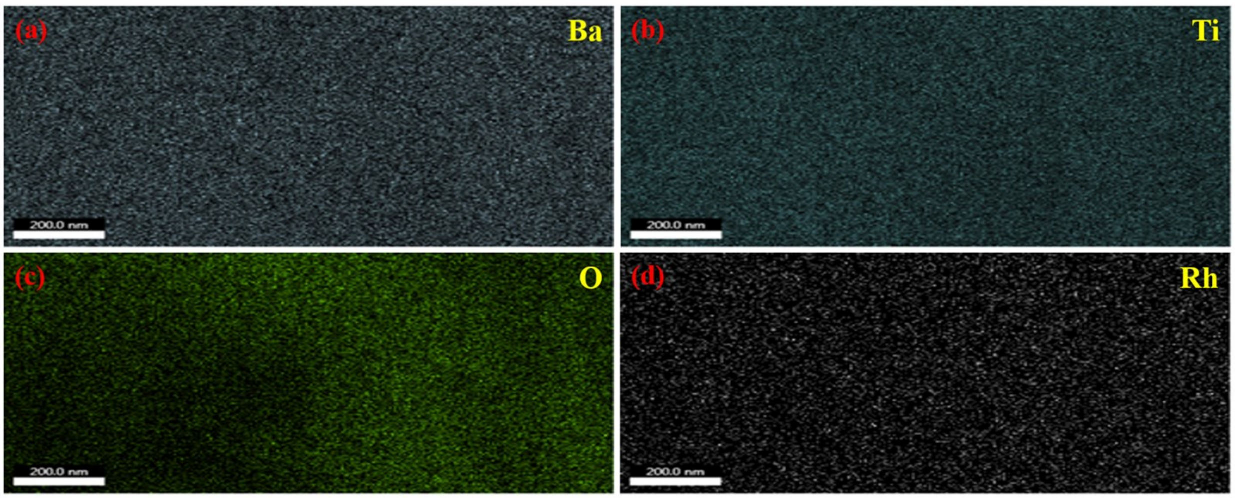

Figure S5. Spot EDX of a) *Ba*, b) *Ti*, c) *O* and d) *Rh* in 0.5 Rh.

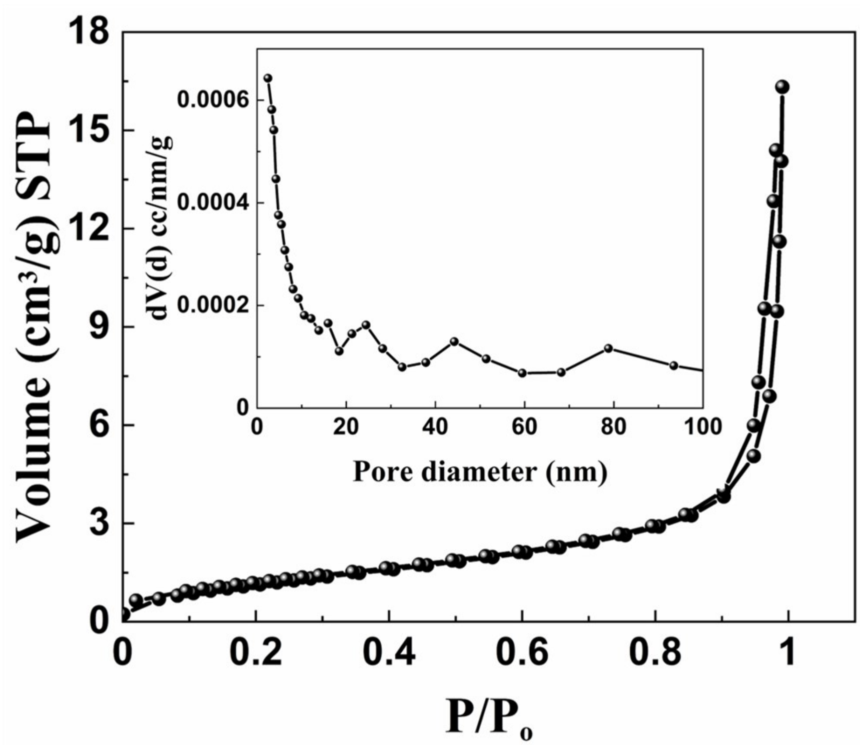

Figure S6. BET surface area analysis of $BaTiO_3$ (inset shows pore size distribution).

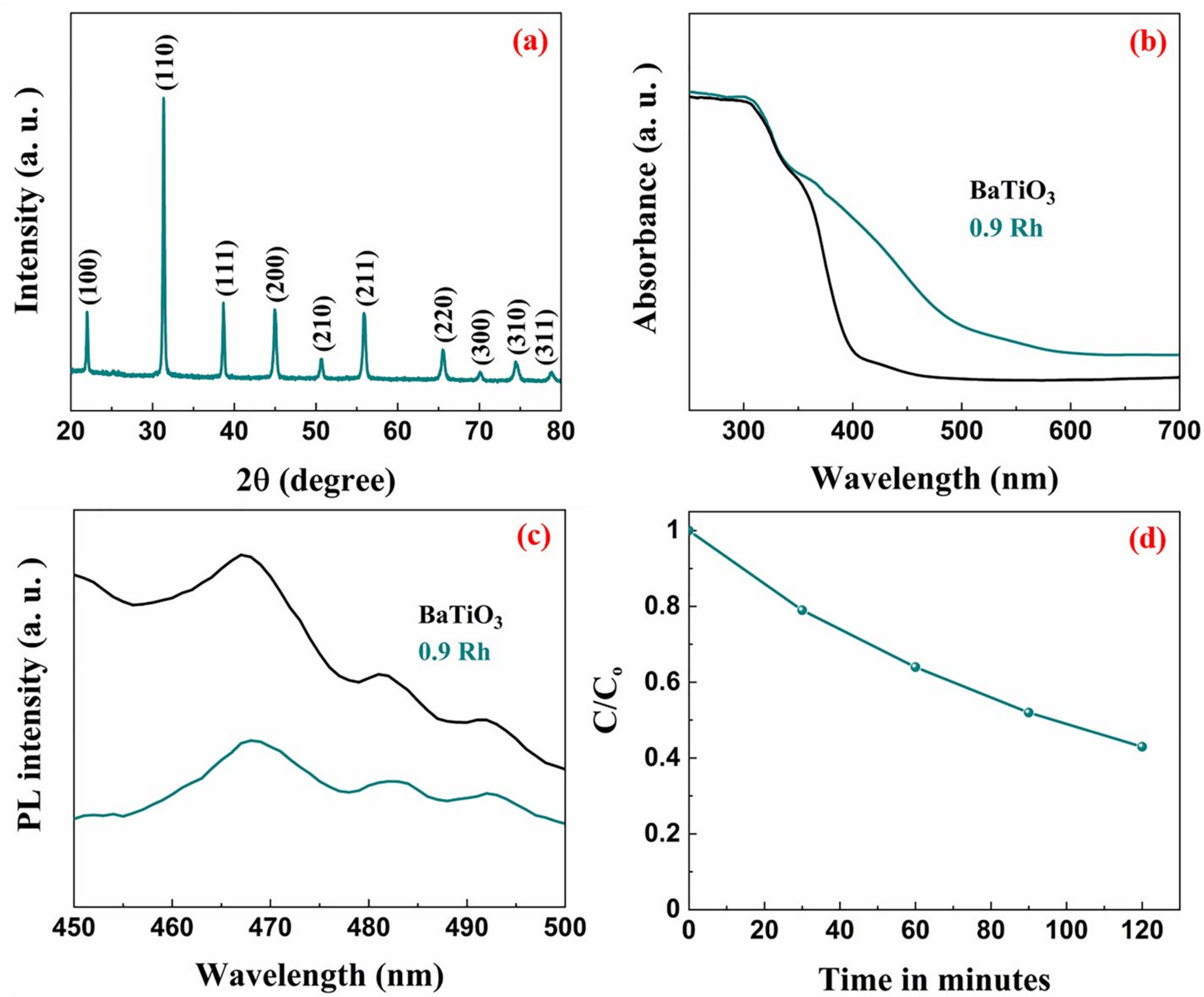

Figure S7. a) XRD of 0.9 Rh, b) UV and c) PL spectra of $BaTiO_3$ and 0.9 Rh and d) photocatalytic degradation of MB using 0.9 Rh.

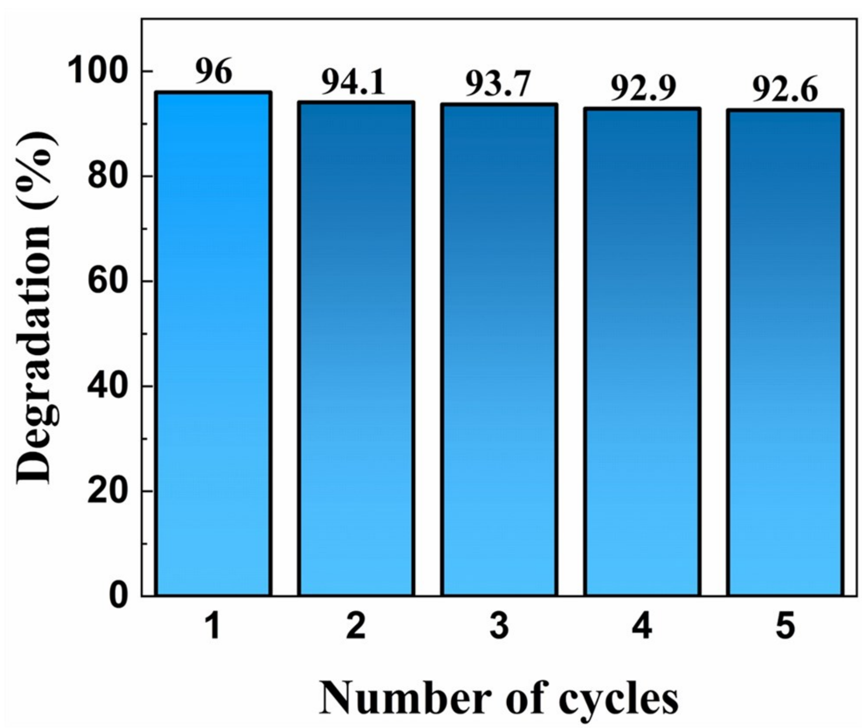

Figure S8. Cyclic stability test of 0.5 Rh.

Table S1. Comparison of photocatalytic activity of 0.5 Rh sample with reported literatures.

Photocatalysts	**Light source**	**Pollutant used**	**Degradation extent and Time**	**Reference**
Rh doped $BaTiO_3$	Visible light source (High pressure 250 W Hg vapor lamp)	Methylene Blue	96 %, 120 min	Present work
N doped $BaTiO_3$	Visible light source (300 W Xe lamp, UV cutoff filter)	Rhodamine B	50 %, 240 min	Cao et al. 2014 [1]
$BaTiO_3$@g-C_3N_4 composite	Solar simulator (200 W Xe lamp)	Methyl orange	76 %, 360 min	Xian et al. 2015 [2]
$BaTiO_3$@graphene nanocomposite	Visible light source (500 W Xe lamp, UV cutoff filter)	Methylene blue	69.5 %, 480 min	Wang et al. 2015 [3]
Mn doped $BaTiO_3$	Visible light source (300 W Tungsten lamp)	Methylene blue	97.04 %, 360 min	Nageri and Kumar 2018 [4]
$Au_x/BaTiO_3$ heterostructure	All spectrum light source (300 W Xe lamp, cutoff filter)	Methyl orange	80 %, 75 min 97 %, 75 min	Xu et al. 2019 [5]
W doped $BaTiO_3$	18 UV lamps as UV light source and 2 metal halide lamps as visible light source	Tetracycline	UV-A light: 77 % Visible light: 80 % in 180 min	Demircivi and Simsek 2019 [6]
Fe-Cr co-doped $BaTiO_3$	Solar simulator (Xe lamp)	Methyl orange	94 %, 90 min	Amaechi et al. 2019 [7]
Ce doped $BaTiO_3$	UV light source (254 nm) and visible light source (400−750 nm, 300 W tungsten-halogen lamp)	Methylene blue Methyl violet Congo red	90.2 %, 120 min 82.4 %, 120 min 78.5 %, 120 min	Senthilkumar et al. 2019 [8]
Cr^{3+} doped $BaTiO_3$	Solar simulator (150 W Xe lamp)	Methyl orange	87 %, 90 min	Amaechi et al. 2019 [9]
Ag doped $BaTiO_3$ composite	UV-vis light source (300 W Xe lamp)	Rhodamine B	61 %, 75 min 83 %, 75 min	Xu et al. 2019 [10]
$BaTiO_3$@graphene oxide composite	UV-vis light source (Xe lamp)	Methylene blue	95 %, 180 min	Mengting et al. 2019 [11]
Fe doped $BaTiO_3$	Solar simulator (150 W Xe lamp)	Methyl orange	75 %, 90 min	Amaechi et al. 2019 [12]
$BaTiO_3$@carbon	18 UV lamps as	Tetracycline	UV-A light: 96	Demircivi et

fiber catalyst	UV-A light source and 2 metal halide lamps as visible light source		% Visible light: 92 % in 180 min	al. 2020 [13]
N-Ni co-doped $(Na_{0.5}Bi_{0.5})TiO_3$-$BaTiO_3$	300 W Xe lamp (PLS-SXE300+/UV)	Rhodamine B Dibenzothiophene	92.4 %, 80 min 90.37 %, 150 min	Xiao et al. 2020 [14]

References

1. Cao, J.; Ji, Y.; Tian, C.; Yi, Z. Synthesis and Enhancement of Visible Light Activities of Nitrogen-Doped $BaTiO_3$. *J. Alloys Compd.* 2014, 615, 243-248.
2. Xian, T.; Yang, H.; Di, L. J.; Dai, J. F. Enhanced Photocatalytic Activity of $BaTiO_3$@ g-C_3N_4 for the Degradation of Methyl Orange under Simulated Sunlight Irradiation. *J. Alloys Compd.* 2015, 622, 1098-1104.
3. Wang, R. X.; Zhu, Q.; Wang, W. S.; Fan, C. M.; Xu, A.W. $BaTiO_3$–Graphene Nanocomposites: Synthesis and Visible Light Photocatalytic Activity. *New J. Chem.* 2015, 39, 4407-4413.
4. Nageri, M.; Kumar, V. Manganese-Doped $BaTiO_3$ Nanotube Arrays for Enhanced Visible Light Photocatalytic Applications. *Mater. Chem. Phys.* 2018, 213, 400-405.
5. Xu, S.; Guo, L.; Sun, Q.; Wang, Z. L. Piezotronic Effect Enhanced Plasmonic Photocatalysis by AuNPs/$BaTiO_3$ Heterostructures. *Adv. Funct. Mater.* 2019, 29, 1808737.
6. Demircivi, P.; Simsek, E. B. Visible-Light-Enhanced Photoactivity of Perovskite-Type W-Doped $BaTiO_3$ Photocatalyst for Photodegradation of Tetracycline. *J. Alloys Compd.* 2019, 774, 795-802.
7. Amaechi, I. C.; Hadj Youssef, A.; Rawach, D.; Claverie, J. P.; Sun, S.; Ruediger, A. Ferroelectric Fe–Cr Codoped $BaTiO_3$ Nanoparticles for the Photocatalytic Oxidation of Azo Dyes. *ACS Appl. Nano Mater.* 2019, 2, 2890-2901.
8. Senthilkumar, P.; Jency, D. A.; Kavinkumar, T.; Dhayanithi, D.; Dhanuskodi, S.; Umadevi, M.; Manivannan, S.; Giridharan, N. V.; Thiagarajan, V.; Sriramkumar, M.; Jothivenkatachalam, K. Built-in Electric Field Assisted Photocatalytic Dye Degradation and Photoelectrochemical Water Splitting of Ferroelectric Ce Doped $BaTiO_3$ Nanoassemblies. *ACS Sustain. Chem. Eng.* 2019, 7, 12032-12043.
9. Amaechi, I. C.; Kolhatkar, G.; Youssef, A. H.; Rawach, D.; Sun, S.; Ruediger, A. B-Site Modified Photoferroic Cr^{3+}-Doped Barium Titanate Nanoparticles: Microwave-Assisted Hydrothermal Synthesis, Photocatalytic and Electrochemical Properties. *RSC Adv.* 2019, 9, 20806-20817.
10. Xu, S.; Liu, Z.; Zhang, M.; Guo, L. Piezotronics Enhanced Photocatalytic Activities of Ag-$BaTiO_3$ Plasmonic Photocatalysts. *J. Alloys Compd.* 2019, 801, 483-488.

11. Mengting, Z.; Kurniawan, T. A.; Fei, S.; Ouyang, T.; Othman, M. H. D.; Rezakazemi, M.; Shirazian, S. Applicability of $BaTiO_3$/Graphene Oxide (GO) Composite for Enhanced Photodegradation of Methylene Blue (MB) in Synthetic Wastewater under UV–Vis Irradiation. *Environ. Pollut.* 2019, 255, 113182.
12. Amaechi, I. C.; Youssef, A. H.; Kolhatkar, G.; Rawach, D.; Gomez-Yañez, C.; Claverie, J. P.; Sun, S.; Ruediger, A. Ultrafast Microwave-Assisted Hydrothermal Synthesis and Photocatalytic Behaviour of Ferroelectric Fe^{3+}-Doped $BaTiO_3$ Nanoparticles under Simulated Sunlight. *Catal. Today* 2019, DOI: https://doi.org/10.1016/j.cattod.2019.07.021.
13. Demircivi, P.; Gulen, B.; Simsek, E. B.; Berek, D. Enhanced Photocatalytic Degradation of Tetracycline using Hydrothermally Synthesized Carbon Fiber Decorated $BaTiO_3$. *Mater. Chem. Phys.* 2020, 241, 122236.
14. Xiao, H.; Luo, C.; Huangfu, G.; Guo, Y. Boosting the Photocatalytic Ability of Bandgap Engineered $(Na_{0.5}Bi_{0.5})TiO_3$-$BaTiO_3$ by N-Ni Co-doping. *J. Phys. Chem. C* 2020, 124, 11810-11818.