Experimental and computational studies on doped-Ag_2O photocatalysts

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by

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CHAPTER 7: Summary and conclusions

7.1 Summary

This final chapter gives an overview of the thesis work. It is based on the crucial results found from the different investigations. The single-phase photocatalysts suffer from several limitations during a photocatalytic reaction. Therefore, doping strategies have been adopted to solve those issues. The incorporation of cation (Zn, Ni, and Cd) and an anion (sulfur) dopant in the Ag_2O lattice change its photocatalytic performance.

The first investigation introduces Zn in Ag_2O nanoparticles through a hydrothermal precipitation protocol. The experimental and parallel computational studies prove that Zn occupies an interstitial position in the Ag_2O lattice. Zn doping widens the bandgap of Ag_2O and increases charge carriers' separation in the material, improving its photocatalytic activity towards MO and RhB degradation. Better photocatalytic activity is reflected in the photocatalyst's TOF values (as shown in Chapter 3). Table 7.1 compares this work with the TOF values of other doped systems previously reported in the literature. It is appropriate to highlight the use of low energy consuming 14W cool LED light source in all photocatalytic investigations of this thesis. Thus, the synthesized Zn doped Ag_2O is a promising photocatalyst for MO degradation.

Table 7.1 Comparison of TOF values of differently doped photocatalysts (reported in the literature) with Zn-doped Ag_2O on MO degradation.

Photocatalysts	TOF (mol $g^{-1}min^{-1}$)	Light source	Reference
Eu doped SnO_2	1.75×10^{-7}	200W Philips HPL-N	(Bhosale et al., 2019)
Al doped ZnO	3.25×10^{-7}	20W UV lamp	(Xiaoliang et al.,

			2013)
Na doped ZnO	1.83×10^{-7}	20W UV lamp	(Xiaoliang et al., 2013)
Fe doped TiO_2	1.11×10^{-8}	200W Hg lamp	(X. H. Wang et al., 2006)
Sr doped Ag_2O	2.16×10^{-7}	Sunlight	(Kiani et al., 2019)
Zn doped Ag_2O (Chapter 3)	2.72×10^{-5}	14W cool white LED	**Our work (A3)**

Doping also changes the photocatalytic behavior of Ag_2O towards CIP degradation. The CIP degradations are performed with our prepared photocatalysts in Chapters 4 (Ni doping) and 6 (Cd doping). Both the types of cation doping shift the Ag_2O VB edge to a more positive potential value. But comparatively, Cd doping shifted the VB edge significantly, and because of this, superoxide radical generation was not possible for D1. It is also reflected in the lower TOF value (see Table 7.2) of the Cd doped Ag_2O system (D1) and its poor recyclability. Both the TOF value and recyclability increased for the D1/10V heterostructure (for TOF values, see Table 7.2). It is mainly due to a proper charge separation by the Z scheme mechanism. Overall, Ni-doped and Cd-doped $Ag_2O/BiVO_4$ photocatalysts are good for CIP degradation and comparable to the literature reported (see Table 7.2).

Table 7.2 Comparison of CIP degradation TOF values of doped photocatalysts (reported) with those prepared in this thesis.

Photocatalysts	TOF (mol $g^{-1}min^{-1}$)	Light source	Reference
B doped TiO_2	2.74×10^{-7}	Sunlight	(Manasa et al., 2021)
Ce doped TiO_2	1.37×10^{-7}	Sunlight	(Manasa et al., 2021)
Fe doped ZnO	5.7×10^{-7}	Sunlight	(Das et al., 2018)
Zn doped BiOCl	3.33×10^{-6}	300W Xenon lamp	(D. Xu et al., 2020)
Zn doped Cu_2O	3.57×10^{-7}	500W metal halide lamp	(X. Yu et al., 2019)
Ni-doped Ag_2O (Chapter 4)	6.55×10^{-6}	14W cool white LED	**Our work (N2)**
BiOCl/Cu doped Bi_2S_3	4.42×10^{-6}	300W Xe lamp	(Du et al., 2022)
g-C_3N_4/Ti_3C_2	1.81×10^{-6}	500W Xe lamp	(N. Liu et al., 2019)
Bi_2WO_6/Ta_3N_5	7.35×10^{-7}	300W Xe lamp	(S. Li et al., 2020)
Fe_2O_3/Bi_2WO_6	2.21×10^{-7}	300W Xe lamp	(S. Y. Song et al., 2020)
Cd doped Ag_2O (Chapter 6)	2.25×10^{-6}	14W LED lamp	**Our work (D1)**
Cd-doped Ag_2O/$BiVO_4$ (Chapter 6)	2.97×10^{-6}	14W LED lamp	**Our work (D1/10V)**

Photocatalytic RhB degradation is executed on Zn doped (Chapter 3) and sulfur (S) doped (Chapter 5) systems. The cation (Zn^{2+}) and anion (S^{2-}) doping cause a significant change in the Ag_2O lattice. The former is expanding, and the latter is contracting the native Ag_2O lattice structure. Even their photocatalytic mechanisms are different for the RhB degradation. The TOF values are represented in Table 7.3. Higher TOF of the Zn doped Ag_2O (A3) indicates it is better than S doped Ag_2O nanomaterial (B2) for RhB degradation. However, a comparison with the existing literature gives proper feedback on the activities of these two doped Ag_2O photocatalysts (see Table 7.3).

Table 7.3 Compares TOF of differently doped photocatalysts (reported in literature) for RhB degradation with the Zn-doped and S-doped Ag_2O photocatalysts prepared in this thesis.

Photocatalysts	**TOF (mol $g^{-1}min^{-1}$)**	**Light source**	**Reference**
Zn doped CdS	3.58×10^{-8}	Sunlight	(Singh et al., 2022)
B doped TiO_2	2.9×10^{-7}	500W Xe lamp	(Niu et al., 2020)
Ba doped ZnO	3.46×10^{-7}	500W UV-A lamp	(Shirdel & Behnajady, 2020)
Y doped CeO_2	1.67×10^{-7}	250W halogen lamp	(Akbari-Fakhrabadi et al., 2015)

Sr doped Ag_2O	3.46×10^{-7}	Sunlight	(Kiani et al., 2019)
S doped Ag_2O (Chapter 5)	1.18×10^{-5}	14W cool white LED	**Our work (B2)**
Zn doped Ag_2O (Chapter 3)	1.99×10^{-5}	14W cool white LED	**Our work (A3)**

7.2 Future scope of the thesis work

In conclusion, this thesis demonstrates that doping could be an efficient technique to tune a small bandgap semiconductor's electronic structure and thereby its photocatalytic performance. It will also be possible to prepare heterostructure with a doped photocatalyst. Therefore, the future scope of this work points out the following aspects.

- The photocatalytic properties of other small bandgap semiconductor materials such as cuprous oxide (Cu_2O), cupric oxide (CuO), α-MnO_2, etc., can be improved via doping by different metals and nonmetal ions.
- The prepared doped semiconductors can be components of different heterostructures for diverse photocatalytic applications.