$CuWO_4$-based composite photocatalysts for the degradation of organic pollutants

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By

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Chapter 7

This final chapter summarizes the thesis work. The present research work aims to fabricate photocatalysts for the degradation of organic pollutants such as CIP, MO, RhB, TET, etc. During a photocatalytic reaction, single-phase photocatalysts have numerous constraints that lower their photocatalytic performance. As a result, strategies for fabricating direct dual semiconductor-based heterostructures have been introduced to solve these challenges. The Ag-based semiconductors and $CuWO_4$ have suitable band edge positions and fulfill other requirements for fabricating dual semiconductor-based heterostructures leading to Z-scheme photocatalysts. For the said purpose, this thesis investigates the fabrication of Z-scheme photocatalysts $AgI/CuWO_4$, $Ag_3PO_4/CuWO_4$, $Ag_3VO_4/CuWO_4$, and $Ag_2MoO_4/CuWO_4$ for improving the photocatalytic performance. Nanocomposites were synthesized using a two-step chemical method. Different characterization techniques like XRD, TEM, HRTEM, XPS, PL, UV-DRS, etc. have been utilized for the characterization of as-prepared nanocomposites. Under light irradiation, pure nanoparticles $CuWO_4$ and Ag-based semiconductors (AgI, Ag_3PO_4, Ag_3VO_4, and Ag_2MoO_4) show little or no photocatalytic activity for organic pollutants degradation compared to corresponding nanocomposites $AgI/CuWO_4$, $Ag_3PO_4/CuWO_4$, $Ag_3VO_4/CuWO_4$, and $Ag_2MoO_4/CuWO_4$, respectively. Furthermore, the recyclability of photocatalysts without a substantial change in photocatalytic activity suggested the catalysts' great stability and reproducibility. In addition, scavenger experiments were used to determine active species responsible for the degradation of organic pollutants.

The first and second investigation is on the development and photocatalytic capabilities of the $AgI/CuWO_4$, and $Ag_3PO_4/CuWO_4$ nanocomposite system for the degradation of Ciprofloxacin (CIP). On the surface of $CuWO_4$ nanoparticles, different weight % (10, 20, and 30) of AgI and Ag_3PO_4 were deposited. The Z-scheme photocatalysts $AgI/CuWO_4$ and $Ag_3PO_4/CuWO_4$ as investigated by XPS studies demonstrated strong photocatalytic activity as measured by a high TOF value for aerobic CIP degradation. TOF values of CIP degradation catalyzed by different nanoparticles/composites are shown in Table 7.1 and compared with 2 A/C (20 wt% $AgI/CuWO_4$) and 20% AW (20 wt% $Ag_3PO_4/CuWO_4$) nanocomposites. Among $AgI/CuWO_4$ and $Ag_3PO_4/CuWO_4$, $Ag_3PO_4/CuWO_4$ is most effective for CIP degradation and found to be better or equivalent to those reported in the literature. The photoexcited holes and superoxide radicals are the dominant active species responsible for the degradation of CIP with these photocatalysts.

Table 7.1: Comparison of CIP degradation turnover frequency (TOF) values over different photocatalysts

Photocatalysts	Light source	Turn over frequency ($mol.g^{-1}.min^{-1}$)	References
$Bi_2S_3/BiOBr$	300W Xe lamp	2.6×10^{-4}	(Y. Hong et al., 2017)
$AgI/BiOBr$	300W Xe lamp	9×10^{-4}	(Yu et al., 2018)
$WO_3/BiOBr$	300W Xe lamp	4.7×10^{-4}	(Ling & Dai, 2020)
Ag_3PO_4/WO_3	300W Xe lamp	3.3×10^{-3}	(T. Wang et al., 2016)
$Ag_3PO_4/BiPO_4$	500W Xe lamp	1×10^{-3}	(Zhu et al., 2022)
$AgI/CuWO_4$	Cool white LED (1070 W/m^2)	0.5×10^{-3}	Chapter 3
$Ag_3PO_4/CuWO_4$	Cool white LED (1070 W/m^2)	1.6×10^{-3}	Chapter 4

In addition, $Ag_3PO_4/CuWO_4$ is further employed for visible light photocatalytic degradation of tetracycline (TET). TOF values of TET degradation catalyzed by different nanoparticles/composites reported previously were compared with 20% AW (20 wt% $Ag_3PO_4/CuWO_4$) and have been displayed in Table 4.4 (see Chapter 4). It shows that 20% AW nanocomposite is also effective for TET degradation and found to be better than those reported in the literature. In the case of TET degradation, photoexcited holes are the dominant active species responsible for degradation followed by superoxide radicals.

The formation of Z-scheme photocatalysts also alters photocatalytic behavior towards MO degradation. MO degradation has been carried out in the third objective of this thesis (Chapter 5). The prepared 20 wt% $Ag_3VO_4/CuWO_4$ photocatalysts perform well for MO degradation and are equivalent to those described in the literature (see Table 5.2, chapter 5). The photoexcited holes are the dominant active species responsible for the degradation of MO.

For the degradation of Rhodamine (RhB), chapter 6 investigated the $Ag_2MoO_4/CuWO_4$ nanocomposites with different weight % of Ag_2MoO_4 (5, 10, and 15) on $CuWO_4$. 20% $AgI/CuWO_4$ has been also utilized for RhB degradation. The Z-scheme photocatalysts $AgI/CuWO_4$ and $Ag_2MoO_4/CuWO_4$ as revealed by XPS studies demonstrated strong photocatalytic activity as measured by a high TOF value for aerobic RhB degradation. TOF values of RhB degradation catalyzed by different nanoparticles/composites reported in the literature are compared with 2 A/C (20 wt% $AgI/CuWO_4$), and 10% MW (10 wt% $Ag_2MoO_4/CuWO_4$) nanocomposites has been shown in Table 7.2. The superoxide radicals are the dominant active species responsible for the degradation of RhB with both photocatalysts (2 AC and 10% MW).

Table 7.2: Comparison of RHB degradation turnover frequency (TOF) values over different photocatalysts

Photocatalysts	**Light source**	**Turnover frequency ($mol.g^{-1}.min^{-1}$)**	**References**
AgI/ZnO	300W Xe lamp	1.2×10^{-3}	(Shaker-Agjekandy & Habibi-Yangjeh, 2015)
g-C_3N_4/AgI	500W Xe lamp	2.5×10^{-3}	(Huang et al., 2021)
Ag_3PO_4/Ag_2MoO_4	300W Xe lamp	7.7×10^{-3}	(Cao et al., 2017)
AgI /$CuWO_4$	Cool white LED (1070 W/m^2)	4.3×10^{-3}	Chapter 1
Ag_2MoO_4/WO_3	300W Xe lamp	0.012×10^{-3}	(Wang et al., 2019)
β-Ag_2MoO_4/$BiVO_4$	300W Xe lamp	4.63×10^{-3}	(Chen et al., 2019)
Ag_3PO_4/Ag_2MoO_4	300W Xe lamp	7.7×10^{-3}	(Cao et al., 2017)
Ag_2MoO_4/$CuWO_4$	250W Hg lamp	3.5×10^{-3}	Chapter 6

Finally, this thesis work emphasizes that Ag-based semiconductors can be used as a semiconductor component with another as $CuWO_4$ for the fabrication of efficient Z-scheme photocatalysts. The fabrication of a Z-scheme photocatalyst by combining two semiconductor heterostructures into composites increases light absorption and plasmonic excitation. As a result, the photocatalytic efficacy of such nanocomposites improves significantly. As a result, the following aspects can be addressed for future research:

- The as prepared nanocomposites AgI/$CuWO_4$, Ag_3PO_4/$CuWO_4$, Ag_3VO_4/$CuWO_4$, and Ag_2MoO_4/$CuWO_4$ can be utilized for photoelectrochemical water splitting.

- The electrochemical properties of prepared nanocomposites AgI/$CuWO_4$, Ag_3PO_4/$CuWO_4$, Ag_3VO_4/$CuWO_4$, and Ag_2MoO_4/$CuWO_4$ can be explored in redox batteries.
- The as prepared nanocomposites AgI/$CuWO_4$, Ag_3PO_4/$CuWO_4$, Ag_3VO_4/$CuWO_4$, and Ag_2MoO_4/$CuWO_4$ can be explored for photocatlaytic organic transformations.
- The fabrication of Z-scheme ternary composite materials based on Ag-based semiconductors, Ag and $CuWO_4$ for various photocatalytic applications.
- It is also possible to investigate the influence of visible light intensity on the photocatalytic efficiency of these prepared nanocomposites.