Iron oxide based p-n heterojunction photocatalysts

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Doctor of Philosophy

By

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CHAPTER 7

Overview

7.1 Overview

The chapter compares the photocatalytic properties of different heterostructures prepared as a part of this doctoral thesis. It helps shed light on additional perspectives, mechanisms, and inferences to the problems addressed herein. As mentioned earlier, most research reports published earlier in the literature have not given TOF values. Therefore, these values have been calculated using the information provided in the respective publication in literature in such cases. The thesis concludes with a short discussion on the future scope of this work.

7.2 Photocatalytic production of H_2O_2 by starch functionalized $Fe_3O_4/Ag/Ag_2O$ nanostructures

As discussed earlier, H_2O_2 is a potent, green oxidizing agent with only water and oxygen as its byproducts. It has various applications as a bleaching agent in the pulp/paper/textile industry, as an oxidizing agent in wastewater treatment, as a reagent for manufacturing many inorganic and organic compounds, as a hydrogen storage medium, and energy storage chemical for hydrogen fuel cell and as a mild disinfectant. Therefore, its production becomes more important. Table 7.1 compares the H_2O_2 production rate catalyzed by starch functionalized $Fe_3O_4/Ag/Ag_2O$ nanostructures with other photocatalysts reported earlier in the literature. This table also includes the experimental conditions of photocatalytic H_2O_2 production. The starch functionalized $Fe_3O_4/Ag/Ag_2O$ nanocomposite shows a better H_2O_2 production rate under relatively mild conditions. Sample C1 exhibits higher H_2O_2 production than C2. C1 has more percentage of Ag Component than the C2. H_2O_2 production increases with the metallic Ag ratio, reinforcing the suggestion that oxygen reduction occurs on the Ag part of the nanocomposite. Thus, fine Ag nanostructures on the SM could be acting as co-catalysts to reduce oxygen by the two-electron pathway through the plasmonic hot-electron formation. On the other hand, the LSPR of the Ag component could be making the re-emission of visible light possible, resulting in better photo-efficiency.

Table 7.1 Comparison of photocatalytic H_2O_2 generation result of various heterostructure photocatalyst studied earlier in literature with the one investigated in this work.

Material	Experimental Condition	H_2O_2 production rate	Reference
C1 (Chapter 3)	Water under visible light (($\lambda > 420$ nm)	2160 μmol (1 h)	This work
C2 (Chapter3)	Water under visible light (($\lambda > 420$ nm)	1830 μmol (1 h)	This work
$Au/SnO_2/TiO_2$	Water (O_2), EtOH, and NaF mixture solution under UV irradiation.	3040 μmol (25 h)	Zuo et al. (2019)
TiO_2/WO_3/rGO	Water with molecular oxygen (O_2) under visible light	270 μM (1h)	Zeng et al. (2017)
CdS	Water with molecular oxygen (O_2) under sunlight	1.35 μmol (12 h)	Thakur et al. (2017)
CdS/rGO		6.4 μmol (12 h)	
SN-GQD/TiO_2	Water with molecular oxygen (O_2) and propan-2-ol mixture solution under visible light ($\lambda > 420$ nm)	22.55 μmol (1 h)	Zheng et al. (2018)
QD/TiO_2	Water with molecular oxygen (O_2), EtOH mixture solution under visible light($\lambda > 420$ nm)	205.3 μmol (3 h)	Ma et al. (2018)
TiO_2@C (NA)	Water with molecular oxygen (O_2), proapn-2-ol mixture solution under UV light($\lambda > 320$ nm)	122 μM (4h)	Lee et al. (2019)
TiO_2@C (BA)		96 μM (4h)	

7.3 Photo-Fenton degradation of PNP

PNP is known for its deleterious effect and is considered a priority pollutant because of its stability. Thus its removal from the environment becomes more critical.

This thesis presents effective photo-Fenton methods for PNP degradation. Table 7.2 shows the comparison of TOF values for photo-Fenton degradation of PNP using different heterostructures.

Table 7.2 Comparison of TOF values using the different catalyst for photo-Fenton PNP degradation

Catalyst	**Light Source**	**TOF (moles gram^{-1} min^{-1}**	**Reference**
CF (Chapter 4)	Cool white LED (0.1470 W/cm^2, visible range light source)	1.17 x 10^{-5}	This work
S1 (Chapter 5)	Cool white LED (0.1470 W/cm^2, visible range light source)	5.04 x 10^{-6}	This work
S2 (Chapter 5)	Cool white LED (0.1470 W/cm^2, visible range light source)	8.36 x 10^{-6}	This work
CSP (Chapter 6)	Cool white LED (0.1470 W/cm^2, visible range light source)	2.01 x 10^{-5}	This work
FeVO4@BiOCl	UV (shortwave, 254 nm, 8 W)	9 x 10^{-6}	Eshaq *et al.* (2020)
Cu/Fe-AO-PAN fiber	500 W Xenon lamp	2.03 x10^{-7}	Wang *et al.* (2019)
Fe_3O_4@SiO_2@ZnO	300 W high-pressure Hg lamp	2.09 x 10^{-6}	Qin *et al.* (2017)
SiO_2/Fe_3O_4/C@TiO_2	UV light from a Xenon lamp (CHFXQ 500 W)	5.65 x 10^{-6}	Hou *et al.* (2016)
CuO/Al_2O_3	Microwave irradiation of 100 W power	8.2 x10^{-7}	Pan *et al.* (2015)
GO-Fe_2O_3	300W Dy Lamp (420nm visible light source)	2.5 x 10^{-6}	Guo *et al.* (2013)
kaolinite supported ferric oxalate	UV lamp	4.6 x 10^{-9}	Ayodele *et al.* (2013)
Fe-TiO_2	UV lamp	1.23 x 10^{-5}	Zhao *et al.* (2010)

The TOF value obtained for Photo-Fenton degradation of PNP on CSP was higher than those obtained over other catalysts. The formation of p-n-p heterojunction enhances the charge separation in CSP, resulting in increased photocatalytic activity.

7.4 Photo- Fenton degradation of MO

Table 7.3 presents the TOF values obtained for the different catalysts for the photo- Fenton degradation of MO. The MO degradation TOF value found over S2 was found to best among those reported to date in the literature. In the case of CSP, the deposition of Cu_2O on S2 reduces the photo-Fenton degradation of MO. As we discussed earlier, the primary criterion for a heterogeneous photo-Fenton reaction is the cleavage of H_2O_2 for $OH^{\cdot}$ radical formation. Hence, increased adsorption of MO on the catalytic surface may be hindering H_2O_2 cleavage to $OH^{\cdot}$ radical [Kuntail *et al.* (2020)].

Table 7.3 Comparison of TOF values using the different catalyst for photo-Fenton PNP degradation

Catalyst	Light Source	TOF (moles gram^{-1} min^{-1})	References
CF (Chapter 4)	Cool white LED (0.1470 W/cm^2, visible range light source)	2.66 x 10^{-5}	This work
S1 (Chapter 5)	Cool white LED (0.1470 W/cm^2, visible range light source)	3.56 x 10^{-5}	This work
S2 (Chapter5)	Cool white LED (0.1470 W/cm^2, visible range light source)	1.26 x 10^{-4}	This work
CSP (Chapter 6)	Cool white LED (0.1470 W/cm^2, visible range light source)	7.5 x 10^{-5}	This work
$CuCr_2O4/CeO_2$	50 W cool white LED	1.99 x 10^{-7}	Ghorai *et al.* (2021)
α-FeOOH QDS/g-C_3N_4	500 W Xe lamp with UV cutoff filter (> 420 nm)	5.09 x 10^{-5}	Qian *et al.* (2018)

$Fe_2O_3/Au/SiO_2$	300-W xenon lamp with a filter (λ>420 nm)	1.52×10^{-6}	Xiao *et al.* (2019)
ZnO/CuO nanocomposite	Cool white LED (0.980 W/cm^2, visible range light source)	1.44×10^{-6}	Nayak *et al.* (2019)
$Fe_2O_3/Au/SiO_2$	300-W xenon lamp with a filter (λ>420 nm)	1.52×10^{-6}	Xiao *et al.* (2019)
Fe_2O_3-SiO_2	1000 W tungsten-halide lamp (Philips) equipped with wavelength cutoff filters (λ> 420 nm)	1.97×10^{-6}	Zhou *et al.* (2018)
α-FeOOH QDS/g-C_3N_4	500 W Xe lamp with UV cutoff filter (> 420 nm)	5.09×10^{-5}	Qian *et al.* (2018)
α-Fe_2O_3/Bi_2WO_6	UV light (ca. 90 W/m^2)	2.03×10^{-6}	Jaramillo-Páez *et al.* (2017)
TiO_2/ β-FeOOH	Visible light(500 W xenon lamp and UV light (Hg Lamp)	8.76×10^{-6}(VL) 9.88×10^{-6} (UV)	Xu *et al.* (2013)

7.5 Future scope of this work

In conclusion, this thesis emphasizes that the iron oxide phases with proper alignment can be used to prepare p-n heterojunction photocatalysts by coupled with other semiconducting materials. Also, introducing a noble metal nanostructure in semiconductor material increases the light absorption through LSPR. Therefore, future studies should consider the following aspects.

- Synthesis of Fe_3O_4/β-FeOOH p-n heterojunction photocatalysts and the investigation of its photocatalytic properties
- Synthesis of Fe_3O_4/β-FeOOH/Ag p-n heterojunction photocatalysts and the investigation of its photocatalytic properties.
- Synthesis of α-FeOOH/Ag/Ag_2O p-n heterojunction photocatalysts and the investigation of its photocatalytic properties.
- Synthesis of α-FeOOH/ β-FeOOH /Ag p-n heterojunction photocatalysts and the

investigation of its photocatalytic properties.

- The effect of visible light intensity on these photocatalysts can also be studied.
- Effect of other support materials, such as other carbon derivatives in the stability and reusability of catalyst need to be investigated.