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Thesis Outline

CHAPTER 1 introduces the current states of some of the related study and presents the corelated background with which builds this study in solving those found problems and fulfilling the future needs for further improvement methods to achieve better photocatalyst performance. More specifically special attention was identified related to the specified six important factors that influence the overall pollutant removal performance through photocatalytic reaction those are: (1) photon absorption, (2) exciton separation, (3) carrier diffusion, (4) carrier transfer, (5) mass transfer, and (6) separability. As illustrated in Figure 1, these six factors are depicted as pillars that would act to support the main objective of this study that is improving the photocatalytic performance of semiconductor based photocatalyst through modification and functionalization methods in order to address environmental problem in general and wastewater treatment in particular.

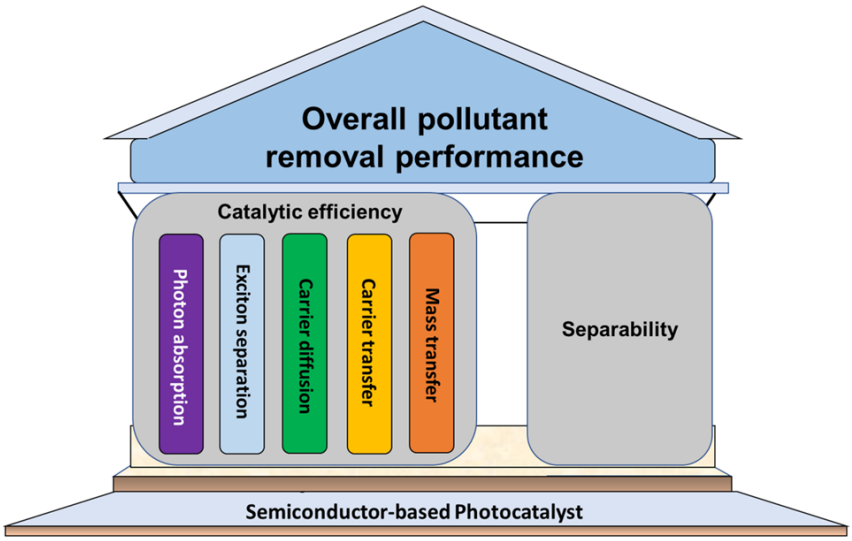

Figure 1. Pillars of identified factors that is essential in order to support and to contribute in an increase overall pollutant removal performance through photocatalytic reaction.

CHAPTER 2 highlights the modification of band-gap modification of TiO_2 semiconductor materials which is well-proven for its high photocatalytic activity and good thermal and chemical stability. However, the wide bandgap of TiO_2 means only UV light can produce the photogenerated charge carrier of electron and holes. Whereas only 3-4% of solar irradiation contains UV spectrum, while most of it, more than 42% are presents

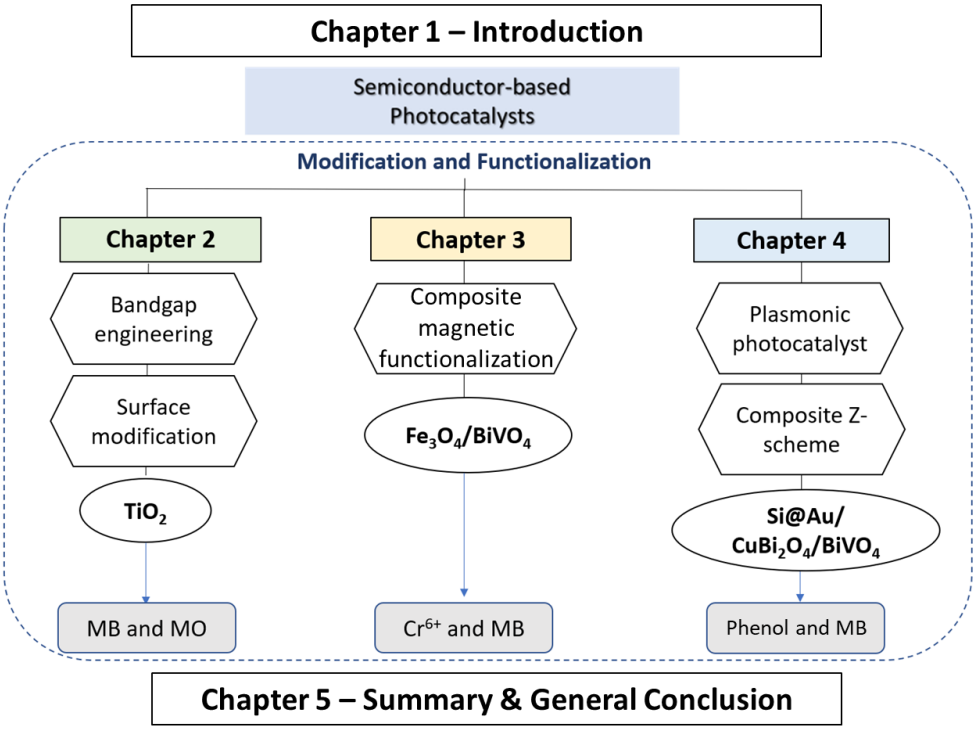

Figure 2. General outlines of the thesis which consist of 5 main chapters covering the introduction and study background section, introduced modification and functionalization for given semiconductor-based photocatalysts and their application in wastewater treatment, and summary of the research findings.

in the form of visible light. As a result, this chapter would like to address the main issue of photon absorption in TiO_2 by the approach of facile one-step solvothermal process in order to introduce nitrogen as non-metal doping and at the same time produces surface modification through CTAB templating method that result in high specific surface area through the presence of porous structure that contributes to improvement of mass transfer property. In addition to optimization on synthesis parameter, characterization method also performed to support the explanation of modified photocatalyst such as specific surface area, reduction in bandgap and doping amount/elemental composition. Novel facile one-step solvothermal process has been successfully developed to introduce both N-doping as well as mesoporous structure for surface modified TiO2. The as-synthesized N-doped TiO2 has relatively large surface area of 148 m^2/g even though the particle size is relatively large (~3µm) due to the presence of mesoporous structure. In addition, N-doping has been confirmed by XPS characterization (2.29 at%), with N act as impurity sensitization for adsorbed nitrogen species (399.7 eV). Under visible light, the synthesized NTi1 photocatalyst could degrade 92% of initial methyl orange (MO)

concentration inside 3 hours and 95% of initial methylene blue (MB) concentration. The achieved result of visible light photocatalytic activity in MB and MO degradation is highly improved as compared with the performance of commercial photocatalyst such as that showed by Degussa P25 and Wako anatase. To avoid the possibility of decolorization in MB the performed COD test also showed low COD number which proved that the MB has been degraded into shorter chain through photocatalytic treatment. Furthermore, the reusability also been confirmed up until 4th usage cycle, displaying that synthesized NTi1 still that maintain high level of more than 99% MB degradation as compared to the initial level of photocatalytic performance.

CHAPTER 3 demonstrates the solution of instantaneous separation brought by $Fe_3O_4/BiVO_4$ as composite material. Even though the modification performed in previous chapter manage to address the photon absorption issues and mass transfer limitation resulting in the enhancement of N-doped mesoporous TiO_2 performance under visible light irradiation, issues of separability still persist as notified by the relatively long settling time, of minimum 4 hours, for the modified NTi1 photocatalyst. Keeping with this matter, there is a need for better separation method which could shorten the retrieval process and improve the recovery of catalyst. Fe_3O_4 as could bring the induced magnetization due to its known ferrimagnetic property. However due to the p-type conductivity of Fe_3O_4, single might not result in satisfying pollutant degradation performance, where photooxidation is expected to be the dominant route. For this reason, $BiVO_4$ which has the potential deep anodic band-level will be utilized as tandem to p-type Fe_3O_4 semiconductor. In this chapter, $Fe_3O_4/BiVO_4$ has been successfully synthesized both through facile hydrothermal and co-precipitation method to make magnetically separable catalyst. The introduction of Fe_3O_4 would not only solve heterogeneous catalyst separation problem with instantaneous induced magnetization but also added the ability of the composite catalyst as toxic Cr (VI) heavy metal cation treatment in addition of methylene blue degradation in wastewater. Under the optimum Fe:Bi ratio of 1:4, both the MB degradation and Cr (VI) could proceed best, as compared with the $BiVO_4$ or Fe_3O_4 photocatalyst, with Cr (VI) photoreduction rate of 98% and MB degradation of 82%, due to sensitization effect of Fe_3O_4 thus reducing $BiVO_4$ main bottleneck of high surface recombination. At higher Fe ratio, there was a tendency for $Fe_3O_4/BiVO_4$ composite which form into p-n heterojunction to undergo direct charge transfer mechanism, resulting in low photooxidation and photooxidation potential.

CHAPTER 4 emphasizes the development of novel plasmonic material in the form of Si@Au (core@shell) nanostructure. The performed modification highlighted in Chapter 3 managed to improve the separability factor and tackle the exciton separation factor due to efficient charge separation through different photooxidation and photoreduction sites. However, the direct electron charge transfer mode was found to be responsible in reducing the potential overdrive of respective photocatalytic reaction. Through comprehensive analysis both in terms of experimental fabrication and numerical simulation, Si@Au nanostructure is expected to address the limitation of previous chapter. Fabrication of Si@Au (core@shell) nanostructures was successfully carried out from the corresponding constituent of Au NPs and Si NPs through solution reduction method. The synthesized Si@Au (25@5 nm) has complementary UV-vis absorption spectrum to the FDTD numerical simulation result, that also picked up the electric field enhancement up to more than 5 times within the vicinity of material's surface. Moreover, SAED of the HR-TEM characterization also observed combined Si rings and Au spots for crystalline Au structures. Lastly, the Si@Au nanostructures exhibited low photorecombination as reflected by minimum photoluminescence (PL), in contrary to the bare Si NPs which emitted PL spectrum at $\lambda = 520$ nm. With the features of increased electric field intensity and effective electron transport thus low charge recombination, the Si@Au nanoshell structures is potential to be further used as plasmonic photocatalyst. This indicated by the integration on $CuBi_2O_4/BiVO_4$ (CBO/BVO) semiconductor in an attempt for all solid-state Z-scheme plasmonic photocatalyst. which was able to give improvement on photocatalytic degradation of phenol, with more than 95% phenol degradation achieved inside 3 hours. The presence of Si@Au was believed could serve as effective solid-state mediator that drive forward the Z-scheme charge transfer for high photooxidation and photoreduction potential.

CHAPTER 5 outlines the general conclusions of the research, the application of research findings, including also future recommendation on ways to further improve current research results and prospective of this research area. We have introduced several different modification and functionalization method for photocatalyst material for the degradation of various organic pollutants, heavy metal ions, and volatile organic compound. The developed semiconductor-based successfully modified and functionalized under facile method and displayed significant photocatalytic efficiency improvement by overcome limiting factors and issues

concerning each chapter. Although appropriate modification/functionalization has been introduced to, we will be able to produce an ideal photocatalyst in the future, i.e. one that have superior characteristics out of the six supporting pillars, by combining findings of the performed modification and functionalization that were obtained throughout this doctoral course research. With appropriate reactor development and scale up process we believe these prepared modifications and functionalized photocatalysts could offer sustainable solution to wastewater treatment in particular, as well as for gas phase pollutant, microbial/virus inactivation, and renewable energies in its extended application.

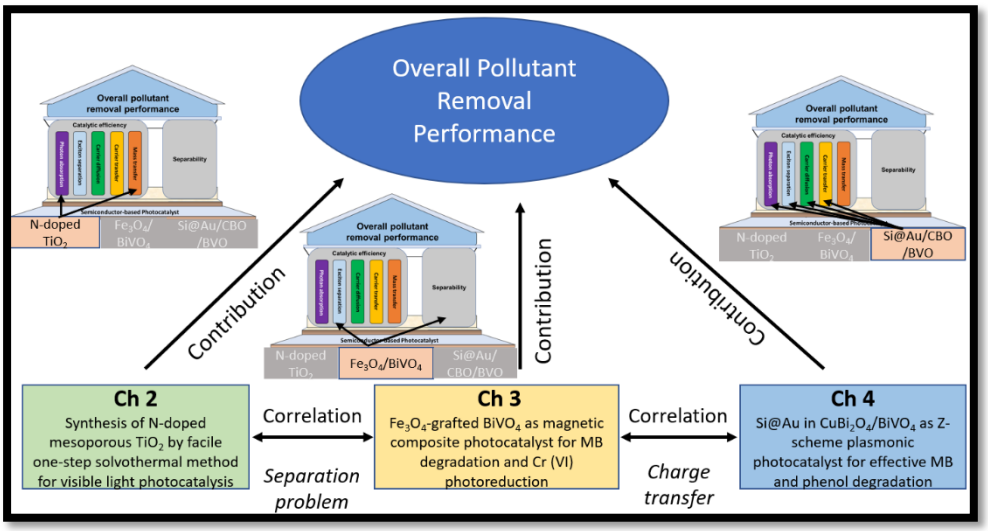

Figure 3. Summary on the contribution of each of the performed modification and functionalization methods on acting pillars that support overall pollutant removal performance.