U.G.C. MAJOR RESEARCH PROJECT

FINAL REPORT

(F. No: 43-222/2014(SR) dated 18.08.2015)

ज्ञान-विज्ञान विमुक्तये

Development of Visible Light Driven $TiO_2/ZnFe_2O_4$ Nanocomposites for Effective Environmental Remediation

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UNIVERSITY GRANTS COMMISSION
BAHADUR SHAH ZAFAR MARG
NEW DELHI – 110 002

PROFORMA FOR SUBMISSION OF INFORMATION AT THE TIME OF SENDING THE FINAL REPORT OF THE WORK DONE ON THE PROJECT

1.	Title of the Project	:	**Development of visible light driven $TiO_2/ZnFe_2O_4$ nanocomposites for effective environmental remediation**
2.	Name and Address of the Principal Investigator	:	**Dr. I. MUTHUVEL** 21/A/1, INIYAGAM Balaji Nagar Kuttalam – 609 801.
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4.	UGC Approval Letter No. and Date	:	F.No-43-222/2014(SR); dated 18.08.2015
5.	Date of Implementation	:	01.07.2015
6.	Tenure of the Project	:	3 years from 01.07.2015 to 30.06.2018
7.	Total Grant Allocated	:	Total Allocation (Rs.): **11,79,600/-**
8.	Total Grant Received	:	1st Installment (Rs.): 7,31,600/- 2nd Installment (Rs.): 2,68,281/-
9.	Final Expenditure	:	**Rs. 9,92,576/-**

10. Objectives of the project

a) To prepare the $ZnFe_2O_4$, $TiO_2/ZnFe_2O_4$, Ag-$TiO_2/ZnFe_2O_4$, Au-$TiO_2/ZnFe_2O_4$, Pd-$TiO_2/ZnFe_2O_4$, Ag/SO_4^{2-}-$TiO_2/ZnFe_2O_4$, GO/rGO, $ZnFe_2O_4$/GO, NrGO-$TiO_2/ZnFe_2O_4$, SrGO-$TiO_2/ZnFe_2O_4$ and BrGO-$TiO_2/ZnFe_2O_4$.

b) To characterize the synthesized nanocomposites by using XRD, FT-IR, SEM-EDX coupled with colour mapping, HR-TEM, UV-DRS and PL spectra studies.

c) To know the photodecolourization and photodegradation of pollutants against prepared nanocomposites.

d) To check the degradation of the dye by UV light and solar light irradiation.

e) To achieve effective mineralization of Reactive yellow 86 (RY 86), 2,4-dinitrophenol and Ciprofloxacin by using the prepared nanocomposites.

11. Whether objectives were achieved: Yes

12. Achievements from the project

We had prepared more than hundred photocatalysts and tested for their efficiency toward various pollutant degradation, among them, 11 photocatalysts were found to be efficient; hence, these 11 catalysts have been characterized. Most of these catalysts are nano-sized and both solar and UV active material. All catalysts had been tested for dye, phenol, drug degradation with UV and solar light.

13. Summary of the findings

The research work involves the degradation and mineralization of synthetic dye, phenol and drug present in industrial effluents by heterogeneous photocatalysis. Photodegradation of various pollutants like Reactive Yellow 86 (RY 86), 2,4-Dinitrophenol (2,4-DNP), Ciprofloxacin (Cip.) and real effluent collected from some nearby textile mill were performed using different photocatalysts under UV/solar light irradiation.

- TiO_2 is the well known efficient photocatalyst which has been extensively used for environmental protection, and it is still the most promising photocatalyst because of its exceptional properties such as low cost, non toxic, inertness, high efficiently and photostability. However, its large band gap (E_g = 3.2 eV) requires near UV light and it absorbs only the very small ultra violet part of solar light therefore hampers the applicability of photocatalysts in the large scale. However its unique properties can be harnessed by doping/modification to design new materials ($ZnFe_2O_4$, Ag, Au, Pd, GO, NrGO, SrGO and BrGO) photosensitive to visible light.

- The development of visible light photocatalysts has become one of the most important topics in photocatalysis research today. Hence we have developed suitably modified photocatalysts whose band gap energy will lie in such a region where it can be excited by solar radiation. These photocatalysts will be utilized effectively for the treatment of wastewaters containing organic contaminants present in the wastewater using solar light.

- $ZnFe_2O_4$ nanomaterial, nanocomposites like $TiO_2/ZnFe_2O_4$, Ag-$TiO_2/ZnFe_2O_4$, Au-$TiO_2/ZnFe_2O_4$, Pd-$TiO_2/ZnFe_2O_4$, Ag/SO_4^{2-}-$TiO_2/ZnFe_2O_4$, $ZnFe_2O_4$/GO, ternary nanostructured photocatalysts like NrGO-$TiO_2/ZnFe_2O_4$, SrGO-$TiO_2/ZnFe_2O_4$ and BrGO-$TiO_2/ZnFe_2O_4$ were synthesized by facile hydrothermal method. The prepared photocatalytic materials were characterized with X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), scanning electron microscopy (SEM), high resolution transmission electron microscopy (HR-TEM), UV-vis diffuse reflectance spectroscopy (UV-vis-DRS) and photoluminescence spectroscopy (PL). The photocatalytic activity was evaluated using dye, pollutant and drug as a model organic compound. The reaction pathway and mechanism of free radical induced mineralization of pollutants in presence of artificial UV light, natural sunlight and photocatalyst was evaluated by monitoring the temporal evolution of intermediates in the solution.

The outcomes of the present study are

- Photocatalytic degradation of all pollutants (RY 86, 2,4-DNP and Cip.) was facilitated by the presence of catalyst. Experimental results showed that initial rate of photomineralization of each pollutant increased with enhance in catalyst load up to an optimum loading. Further increased catalysts load showed no effect.

- The degradation rate for all the pollutants was found to be pseudo-first order with respect to their concentration within the experimental range.

- The increased photocatalytic activity of noble metal loaded M-TiO_2/$ZnFe_2O_4$ (M = Ag, Au, Pd) due to the illumination with UV /solar light, the photogenerated electron experiences a vectorial transfer from CB of TiO_2 to CB of $ZnFe_2O_4$ as CB of $ZnFe_2O_4$ has a higher positive potential. This transfer increases the charge separation efficiency. Further the nobel metal like Ag, Au, Pd can trap the electron photogenerated electron from both TiO_2 and $ZnFe_2O_4$ and reduces the recombination of electron-hole pair. By these two processes the lifetimes of electron and hole increase, leading enhanced photocatalytic activity. M-TiO_2/$ZnFe_2O_4$ was found to stable and reusable up to five runs.

- The enhanced photocatalytic activity of non-metal loaded XrGO-TiO_2/$ZnFe_2O_4$ (X = N, S, B) due to the excited electrons on irradiation migrate to the conduction band of $ZnFe_2O_4$; from there, the electrons get transferred through XrGO (X = N, S, B) medium toward reaction site and form superoxide radical anion with dissolved oxygen. This helps to reduce the electron hole recombination. Hydroxyl radicals produced after holes reacting with water. The hydroxyl radical and superoxide radical anion degrade the pollutants into products such as CO_2, H_2O, and mineral acids.

- $ZnFe_2O_4$ nanomaterial was synthesised and used as Fenton like photocatalyst for the mineralization of the pollutants quickly by using H_2O_2 as oxidant to degrade the pollutants. Fe^{3+} on the surface of $ZnFe_2O_4$ can be photoreduced to Fe^{2+} and simultaneously initiate the reaction to produce $^{\bullet}OH$ in the presence of H_2O_2. $^{\bullet}OH$ radicals can oxidize the pollutant molecules. This cycle is continued throughout the period that the H_2O_2 is present. Finally, the pollutant molecule can be mineralized into CO_2 and H_2O.

- GO-$ZnFe_2O_4$ nanocomposite was synthesised and used as heterogeneous Fenton like photocatalytic degradation of pollutants quickly by using H_2O_2 as oxidant. The enhanced efficiency of the GO-$ZnFe_2O_4$ composite in the degradation of pollutants presumably results from the following reasons. Firstly, graphene oxide (GO) improves the adsorption of dye and H_2O_2 due to its large surface area and the presence of oxygen-containing functionalities on the surface of the catalyst. Secondly, H_2O_2 can act as an efficient electron scavenger to form $^{\bullet}OH$ on the surface of the graphene oxides, which not only enhances oxidation ability but also fleetingly reduces electronic accumulation on the surface of graphene oxides. Generally, in heterogeneous Fenton-like catalysts, a Lewis acid, which is associated with iron could facilitate the reduction of the ferric ion by H_2O_2 attracting the electron density from the iron center. This facilitation will accelerate the whole Fenton-like reaction as the reduction of ferric ion is the dominant rate-determining step of the Fenton-like reaction.

14. Contribution to the society

The project finds high significance relevant to the wastewater treatment as the results can make revolutionary changes in the concept of wastewater treatment. Utilization of solar energy is a cost effective method for wastewater treatment. This study will provide the data on various semiconductor nanocomposites and their efficiencies in the detoxification of organic pollutants wastewater. Central Pollution Control Board, State Pollution Control Board and various research organizations that are engaged in this field can make use of the results of these studies. Study on pilot scale treatment can be used by the industries to design their effluent treatment plants.

15. Whether any Ph.D. Enrolled/Produced out of the project

Yes. The project fellow Mr. P. Suppuraj, Registered Ph.D. in Department of Chemistry, Annamalai University.

16. List of publications

1. P. Suppuraj, G. Thirunarayanan, M. Swaminathan and **I. Muthuvel**, Facile synthesis of spinel nanocrystalline $ZnFe_2O_4$: Enhanced photocatalytic and microbial applications, *Materials Science and Applied Chemistry*, 34 (2017) 5-11.

2. P. Suppuraj, K. Thirumalai, S. Parthiban, M. Swaminathan and **I. Muthuvel**, Novel Ag-TiO_2/$ZnFe_2O_4$ nanocomposites for effective photocatalytic, electrocatalytic and cytotoxicity applications, *Journal of Nanoscience and Nanotechnology*, 19 (2019) 1–10.

3. P. Suppuraj, S. Parthiban, M. Swaminathan and **I. Muthuvel**, Hydrothermal fabrication of ternary NrGO-TiO_2/$ZnFe_2O_4$ nanocomposites for effective photocatalytic and fuel cell applications, *Materials Today Proceedings*, 2019 (Accepted). doi:10.1016/j.matpr.2019.04.104

4. **I. Muthuvel**, G. Thirunarayanan, S. Dineshkumar, Effect of substituents on 4-(substituted phenyl sulfonamide)benzoic acids by IR and NMR spectra, *World Scientific News*, 128 (2019) 216-233.

5. S. Rajasri, B. Krishnakumar, Abilio J.F.N. Sobral, S. Balachandran, M. Swaminathan and **I. Muthuvel**, Development of $Cd_3(PO_4)_2$/rGO coupled semiconductor system for effective mineralization of Basic Violet 10 (BV 10) under UV-A light, *Materials Today Proceedings,* 2019 (Accepted). doi:10.1016/j.matpr.2019.04.109

6. K. Gowthami, B. Krishnakumar, Abilio J.F.N. Sobral, G. Thirunarayanan, M. Swaminathan, T. Rajachandrasekar and **I. Muthuvel**, Fabrication of hybrid $Fe_2V_4O_{13}$/ZnO heterostructure for effective mineralization of aqueous methyl orange solution, *Journal of Nanoscience and Nanotechnology,* 2019 (Accepted).

7. K. Gowthami, P. Suppuraj, G. Thirunarayanan, B. Krishnakumar, A.J.F.N. Sobral, M. Swaminathan and **I. Muthuvel**, $Fe_2V_4O_{13}$ assisted hetero-Fenton mineralization of methyl orange under UV-A light irradiation, *Iranian Chemical Communication,* 6 (2018) 97-108.

8. **I. Muthuvel**, K. Gowthami, G. Thirunarayanan, P. Suppuraj, B. Krishnakumar, A.J.F.N. Sobral and M. Swaminathan, Graphene oxide – $Fe_2V_4O_{13}$ hybrid material as highly efficient hetero-Fenton catalyst for degradation of Methyl Orange, *International Journal of Industrial Chemistry,* (2019). doi: 10.1007/s40090-019-0173-8

9. S. Rajasri, S. Balachandran, B. Krishnakumar, A.J.F.N. Sobral, M. Swaminathan, G. Thirunarayanan, N. Pasupathy and **I. Muthuvel,** Solar light driven $Zn_3(PO_4)_2$/ZnO heterostructure: enhanced photocatalytic mineralization of Basic Violet 10, *International Journal of Current Advanced Research*, 7 (2018) 11297-11301.

10. S. Rajasri, B. Krishnakumar, A.J.F.N. Sobral, S. Balachandran, M. Swaminathan, N. Pasupathy and **I. Muthuvel**, Development of $Zn_3(PO_4)_2$/ZnO-coupled semiconductor system for effective mineralization of Basic Violet 10 (BV 10) under UV-A light, *International Journal of Recent Scientific Research,* 8 (2017) 20688-20695.

11. V. Ananthi, K. Rajalakshmi, **I. Muthuvel** and G. Thirunarayanan, Solid acidic $FeCl_3$/Bentonite catalyzed solvent-free condensation: Synthesis, spectral studies and antimicrobial activities of some aryl hydrazine Schiff's bases, *Annales Universitatis Mariae Curie-Sklodowska, sectio AA–Chemia*, 71 (2017) 127.

12. S.J. Joseph, K. Ranganathan, R. Suresh, R. Arulkumaran, R. Sundararajan, D. Kamalakkannan, S.P. Sakthinathan, G. Vanangamudi, S. Dineshkumar, K. Thirumurthy, **I. Muthuvel**, G. Thirunarayanan and K. Viveksarathi, Synthesis, characterization and synthetic applications of fly-ash: H_3PO_4 nanocatalyst, *Materials Science and Applied Chemistry*, 34 (2017) 12-20

13. **I. Muthuvel**, S. Dineshkumar, K. Thirumurthy, S. Rajasri and G. Thirunarayanan, A new solid acid catalysedbenotonite/$FeCl_3$ for aldol condensation under solvent free condition, *Indian Journal of Chemistry*, 55B (2016) 252-260.