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# Fabrication of $Fe_3O_4$/ZnO magnetite core shell and its application in photocatalysis using sunlight

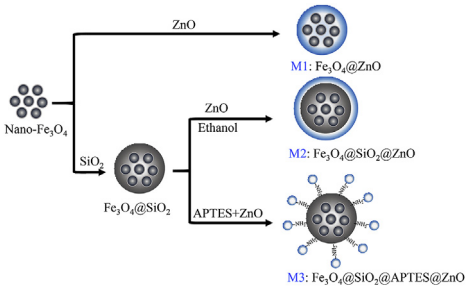
Shashi B. Atla[a], Wun-Rong Lin[b], Ting-Che Chien[a], Min-Jen Tseng[c], Jwu-Ching Shu[e], Chien-Cheng Chen[d], Chien-Yen Chen[a,f,*]

[a] Department of Earth and Environmental Sciences, National Chung Cheng University, 168, University Rd., Min-Hsiung, Chia-Yi, 62102, Taiwan, ROC
[b] Departments of Urology, Mackay Memorial Hospital, 92, Section 2 Chung San North Rd., Taipei 10449, Taiwan, ROC
[c] Department of Life Science, National Chung Cheng University, 168 University Road, Minhsiung, Chia-Yi 62102, Taiwan, ROC
[d] Department of Biotechnology, National Kaohsiung Normal University, No.62, Shenjhong Rd., Yanchao Township, Kaohsiung County, 82444, Taiwan, ROC
[e] Department of Medical Biotechnology and Laboratory Science, Chang Gung University, No.259, Wenhua 1st Rd., Guishan Dist., Taoyuan City, 33302, Taiwan, ROC
[f] Center for Innovative Research on Aging Society, National Chung Cheng University, 168, University Rd., Min-Hsiung, Chiayi 62102, Taiwan, ROC

## HIGHLIGHTS

- Magnetically separable ZnO nanomaterials were grown on iron oxide using silicon and APTES.
- The growth temperature was at room temperature in any step of the synthesis.
- The photocatalytic were studied upon sunlight irradiation.
- ZnO nanoparticles show superior photocatalytic activity.
- We report an easily recovered photocatalysis by magnetic separation.

## GRAPHICAL ABSTRACT

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## ABSTRACT

Three chore-shell magnetite ZnO catalysts ($Fe_3O_4$/ZnO: M1, $Fe_3O_4$/$SiO_2$/ZnO: M2, $Fe_3O_4$/$SiO_2$-APTS/ZnO: M3) were prepared, characterized and tested for their photocatalysis in the degradation of methylene blue (MB) dye under sunlight irradiation. M2 and M3 catalysts exhibited better kinetics and higher activity. The silica coating of $Fe_3O_4$ in M2 and M3 catalysts enhanced efficient transport of MB dye to the ZnO site and thus enhanced photocatalysis. Photocatalytic reactivity was also related to the defects present in the samples under the synthesized conditions. Photoluminescence studies indicated the order of the defects in ZnO catalyst as M2 > M3 > M1. The presence of ZnO defects in the samples (M2 & M3) slowed electron recombination time, enhanced hydroxyl radical formation and hence performed faster degradation of MB. The significant enhancement in photoactivity could be attributed to the synergistic effect of adsorption by silica and ZnO catalysis. The recycle experiments using external magnetic showed the remained activity which demonstrated the stable and efficient magnetic separable catalysts.

## 1. Introduction

Industry and households discharge several toxic organic compounds which are polluting water resources. The treatment of water is an important global issue. $TiO_2$ is a widely studied semiconductor photocatalyst for the destruction of organic pollutants due to its

* Corresponding author. Department of Earth and Environmental Sciences, National Chung Cheng University, 168, University Rd., Min-Hsiung, Chia-Yi, 62102, Taiwan, ROC.
*E-mail addresses:* chien-yen.chen@oriel.oxon.org, yen@eq.ccu.edu.tw (C.-Y. Chen).

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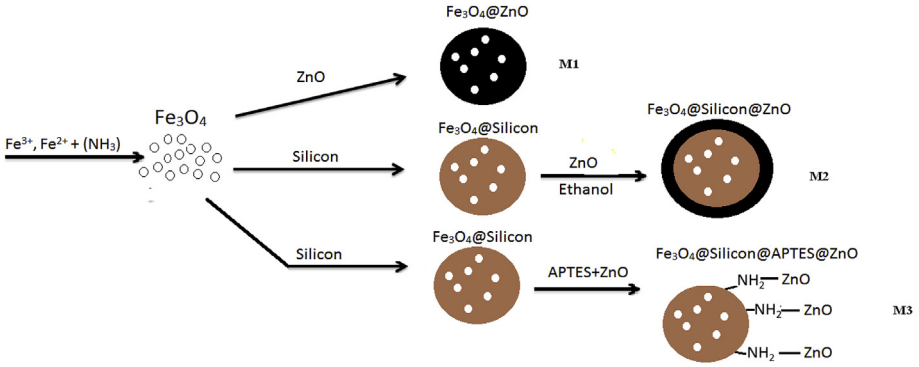


**Fig. 1.** Schematic diagram of the synthesis of catalysts M1, M2 and M3.

characteristics of high photosensitivity and nontoxic nature [1]. However another suitable alternative is low cost ZnO which possess similar band gap energy (3.2 eV) and same photodegradation mechanism with the advantageous position for large scale industrial use [2]. More researches have been recently developing the visible-light or sunlight responsive photocatalysts for environmental remediation. This is because photocatalysts can be carried out under ambient conditions and leads to complete mineralization of organic compounds. Another important factor for an efficient catalyst is the separation and recycle to avoid catalyst loss. It will be encouraging to fabricate a photocatalyst with a magnetic component. The magnetic separation technologies are more effective and more convenient than the traditional separation methods [3]. This unique properties could be achieved when semiconductor photocatalyst combines with different materials. Bi-functional materials that exhibits both magnetic and photocatalytic activity are smart materials for the development of environmentally benign catalytic process.

The methods for the incorporation of magnetic component can be done by the addition of metal oxides (FeO, $Fe_2O_3$, $Fe_3O_4$), and ferrites of the spinel type with the general formula $MFe_2O_4$ (M = Co, Mn, Ni) [4]. Ferrites are the most widely used and studied magnetic materials in heterogeneous catalysis. Shahid et al. reported magnetically separable $MgFe_2O_4$ for photocatalytic degradation of methylene blue under visible light irradiation [5]. Wilson et al. reported the reusable Co-$Fe_2O_4$–ZnO nanospheres of core-shell that showed high UV photocatalytic activity for the degradation of methylene blue in water [6]. Shao et al. reported $ZnFe_2O_4$@ZnO for the degradation of methylene blue under UV irradiation [7]. Yan et al. reported alpha-$Fe_2O_3$/ZnO of core-shell structure with the degradation of methyl orange solution under UV irradiation [8]. Fu et al. reported magnetically separable $ZnFe_2O_4$-graphene nanocomposite photocatalyst for the degradation of methylene blue under visible light irradiation [9]. In their study the charge recombination has been minimized in the presence of graphene which enhanced the photocatalytic activity. The adsorption of MB was also enhanced in the presence of graphene.

The use of $Fe_3O_4$/silica/ZnO core shell have not been sufficiently investigated although ZnO has been used as catalyst. The adsorption of organic pollutant on the photocatalyst molecules is also a crucial factor for the significant enhancement in photocatalytic activity. Silica-gel is the most prominent material for coating with the advantages of easy surface modification. In this work, we highlight the comparative study of three different magnetically separable zinc oxide catalysts and their photocatalytic activities. A highly efficient sunlight photocatalyst of ZnO that can be magnetically separable was achieved with the use of simple silica gel and surface modification.

## 2. Experimental section

### 2.1. Materials and characterizations

Zinc Nitrate, $Zn(NO_3)_2$-$6H_2O$ (J. T. Baker, 99.4%), $C_2H_5OH$ (Panreac, 99.8%), Glycerol (Choneye, 99.9%), TMAH (Fluka, 25%), Methylene Blue (Fluka, 96%), Ammonia (Panreac, 25%), $FeCl_3$-$6H_2O$ (Riedel-de Haen, 99%), $FeCl_2$-$4H_2O$ (Alfa Aesar, 98%), Sodium silicate (Panreac), HCl (Sigma-aldrich, 37%), (3-aminopropyl) triethoxysilane (APTS) (Sigma-Aldrich, 99%), Methanol (Mallinckrodt, 99.9%), Acetone (Choneye 99.8%), Milli-Q water were used in this study.

Powder X-ray diffraction (XRD) patterns were recorded on a Shimadzu X-ray diffractometer (model LabX XRD-6000) equipped with Ni-filtered CuKα (λ = 0.1541 nm, 4 kVA, 30 mA) radiation and a graphite crystal monochromator. SEM measurements were carried out on a TOPCON ABT-150S scanning electron microscope (SEM). FTIR spectra of the samples were recorded on a Jasco FTIR-460 Plus spectrometer under ambient conditions using thin circular disks made by pressing a mixture of the sample and KBr. Absorption spectra were recorded using a Hewlett Packard scanning spectrophotometer. Photoluminescence spectra were recorded at room temperature on a Jobín Yvon/Labrà HR PL spectrometer (excitation wavelength of 325 nm).

### 2.2. Synthesis of magnetically separable ZnO

$Fe_3O_4$, $Fe_3O_4/SiO_2$ and $Fe_3O_4/SiO_2$-APTS involve multi-steps synthesis and were prepared according to the previously reported method [10,11]. ZnO particles were deposited on these magnetic particles using TMAH as the precipitating agent [12]. The schematic of the synthesis of magnetic catalysts is shown in Fig. 1. Initially magnetite ($Fe_3O_4$) was synthesized and used as a core for all the catalysts. These naked magnetic particles when coated with ZnO gave M1. Coating of magnetic core with silica followed by ZnO deposition resulted M2. Coating of magnetic core with silica followed by functionalization with APTS and ZnO deposition gave M3. In a typical synthesis the respective magnetic materials (0.5 g) were taken in absolute alcohol (60 ml) and $Zn(NO_3)_2.6H_2O$ (1.2 g) were added to the suspensions under stirring at room temperature. The mixtures were allowed to stir for 1 h. TMAH was added dropwise to the solutions until the pH was in the range of 12–13. The precipitation mixture was thoroughly mixed and allowed to stir for 15 min. The precipitates with solution were taken in an autoclave and heated at 100 °C for 5 h. The precipitated products were collected by centrifugation, washed with ethanol and dried in an oven at 50 °C.

### 2.3. Photocatalytic activity measurement

In a typical experiment, 30 ml MB solution (5 ppm) was placed in a glass cylindrical reactor (of 100-ml capacity) and the required amount of the desired catalyst was added. The resulting reaction mixture was