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ORIGINAL RESEARCH PAPER

Fabrication $Fe_3O_4/SiO_2/TiO_2$ Nanocomposites and Degradation of Rhodamine B Dyes under UV Light Irradiation

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ABSTRACT

Recycling and reusing of catalyst is an important factor to produce capable and low cast catalysts. Silica coated magnetic nanoparticles (Fe_3O_4/SiO_2) were synthesized via a simple sol-gel method with the aid of sonication. Fe_3O_4 nanoparticles. After that a layer of TiO_2 was constricted by hydrolyze and condensation of Teteranormalbuthyltitanate to produce $Fe_3O_4/SiO_2/TiO_2$ nanocompsite. As-synthesized nanparticles were characterized with X-Ray powder Diffraction, Fourier-Transform-Infrarotspektrometer, Transition Electron Microscopy and Scanning Electron Microscopy. In this study, a new kind of $Fe_3O_4/SiO_2/TiO_2$ photocatalyst was prepared with the purpose of using light and inhibiting the recombination of electrons and holes. In situ treatment of Rhdamine B in water was performed using this $Fe_3O_4/SiO_2/TiO_2$ photocatalyst. The purpose of this research was to provide a new method and the basic data for the removal of organic pollutants in water. $Fe_3O_4/SiO_2/TiO_2$ nanocomposite showed enhanced photocatalytic properties as evidenced by the enhanced photodegradation of Rhodamine B under ultra violet light irradiation.

INTRODUCTION

Magnetic nanoparticles are currently being investigated because of their numerous applications in several fields such as, medicine, magnetic resonance imaging, data storage, , and water remediation . It is often necessary to coat their surface with an organic or inorganic shell, in order to protect them from chemical degradation or agglomeration according to the environments in which they will be used.

The coating can also be performed in order to add new functionalities to the magnetic core, such as biological stealth, optical properties, catalytic or adsorbing capacity.

Over the past decades, titanium dioxide (TiO_2) nanoparticles have gained much attention as a photocatalyst and catalyst support [1]. TiO_2 nanoparticles have many advantages as compared to other photocatalysts, which include excellent high stability against chemical and photonic corrosion and high photocatalytic activity [2].

TiO_2 nanoparticles of small mean particle sizes possess high surface area and photocatalytic activity. However, TiO_2 nanoparticles of high surface area are thermally unstable and lose their surface area readily . Therefore, much effort has been focused on coating of TiO_2 on high surface area supports such as silica or alumina in order to stabilize TiO2 nanoparticles. TiO_2 nanoparticles could be difficult to recover and lost readily upon being dispersed into wastewater. One of the ways to overcome this problem is to coat TiO_2 onto magnetite (Fe_3O_4) cores and the resulting Fe_3O_4/TiO_2 Nanocomposite nanoparticles can be recovered easily through manipulation by external magnetic field. However, it was difficult to achieve complete coating

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of Fe_3O_4 nanoparticles with TiO_2 at nanometer scale using the sol-gel method [2]. Besides, TiO_2 would oxidize Fe_3O_4 nanoparticles and lead to a reduction of magnetic moment. Some researchers had attempted to coat a thin layer of SiO_2 between Fe_3O_4 nanoparticles and TiO_2 shell. The presence of a SiO_2 layer between TiO_2 shell and Fe_3O_4 nanoparticles could increase the lifetime of photogenerated holes which in turn, resulted in increased photoreactivity [3] . This is attributed to the SiO_2 layer which serves as an insulating layer between Fe_3O_4 nanoparticles (hole-electron trap center) and the TiO_2 shell. Herein, we have reported a facile and efficient synthesis approach for the fabrication of $Fe_3O_4/SiO_2/TiO_2$ discrete Nanocomposite nanoparticles by the sol-gel method with the aid of sonication [4]. Fe_3O_4 nanoparticles were being encapsulated inside discrete SiO_2 nanospheres within 90 minutes, and a TiO_2 layer was then coated directly onto each SiO_2 nanosphere via the sol-gel method. The photocatalyst properties of as-synthesized $Fe_3O_4/SiO_2/TiO_2$ Nanocomposite were evaluated by the photodegradation of Rhodamine B with or without UV light irradiation [5,6].

MATERIALS AND METHODS

Reactions of catalyst preparing were rune under an inert argon or nitrogen atmosphere. Polyethylene glycol 400 (PEG 400), hydrochloric acid, ammonium hydroxide 30%, , 2-propanol, iron(II) chloride hydrate, iron(III) chloride hydrate, tetraethyl orthosilicate (TEOS), tetranormalbuthyltitanate (TNBT),acetylacetone,ethanol and methanol were purchased from Merck company and all of them used without further purification. During all steps when water was needed, deionized water was used throughout.

FT Infrared (FT-IR) spectra were obtained as potassium bromide pellets in the range of 400–4000 cm^{-1} with a 6300 JASCO Perkin Elmer spectrophotometer. XRD patterns were recorded by a Bruker D8 Advanced, X-ray diffractometer using Ni-filtered Cu Ká radiation. SEM images were obtained using an VEGA-II TESCAN . TEM images were obtained using an CM120 . The UV-vis spectra of the samples were taken on a UV-vis spectrophotometer (Shimadzu, UV-2550, Japan) + visible sources of 400 W Osram lamps.

Synthesis of the catalyst support (Fe_3O_4@SiO_2 nanoparticles)

The catalyst support comprised of silica-coated magnetic NPs was synthesized by a co-precipitation method.These nanoparticles were prepared by chemical co-precipitation of Fe^{3+} and Fe^{2+} ions with a molar ratio of 2:1. Typically, $FeCl_3.6H_2O$ (5.838 g) and $FeCl_2.4H_2O$ (2.147 g) were dissolved in 38 mL degased HCl 0.4 molar. Then, this solution was added to 300 mL of degased 25% NH_4OH quickly in one portion while stirring in ultrasound bath. The addition of the base to the Fe^{2+}/Fe^{3+} salt solution resulted in the formation of the black precipitate of MNPs immediately. Stirring in ultrasound bath continued for another 90 min. Black solid collected by magnet and washed with ethanol and distilled water three times. Then the sediment dispersed in 150 ml distilled water.

Since Fe_3O_4 nanoparticles are delicate to heat and oxidation miliues, to protect their surfase and to preventing oxidation to Fe_2O_3, surface of magnetic nanoparticles coated by athinlyer of SiO_2.The SiO_2shell can effectively prevent chemical degradation andphotodissolution property of Fe_3O_4 particles making the photocatalyst recycleable after multiple reaction cycles, and promote the photocatalytic activity of TiO_2 by decreasing the adverse influence of magnetic core.At the second step for synthesis of silica-coated Fe_3O_4 nanoparticles, 50 mL of previous suspension added to a solution of 250 mL 2-Propanol that contained ammonium hydroxide (4.5 mL). This dispersion was homogenized by ultrasonic vibration. Then, 6 mL tetraethoxysilane (TEOS) was slowly added. Finally, silica was formed on the surface of magnetite nanoparticles through hydrolysis and condensation process. The resulting silica-coated Fe_3O_4 nanoparticles were thoroughly washed with deionized water and collected by magnetic separation, followed by drying at 45 °C under vacuum for 12 h

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Synthesis of Fe_3O_4@SiO_2@TiO_2 nanocomposite

Specifically, 0.7g of Fe_3O_4@SiO_2nanoparticles were dispersed in 150 ml of merck ethanol and sonicated for 20 minutes. After that 5 ml PEG 400 was added to the mixture. In second vessel, 8 ml Tetranormalbuthyltitanate was added to 20 ml of Merck ethanol and 1 ml acetylacetone and stirred on magnetic stirrer for 10 minutes. Second vessel was added slowly to above mixturewhile gentlyshaking by mechanical stirrer. After 20 minutes, 3 ml deionized water was added and final mixture stirred at 70 °C for 12 hours.The obtained gray products were separated by an external magnet and washedthoroughly with ethanol and

deionized water before drying at 60 °C.Subsequently, the powder was calcined at 400°C in air for 2 h to improve the crystallinity of the obtained $Fe_3O_4@SiO_2@TiO_2$ nanoparticles.

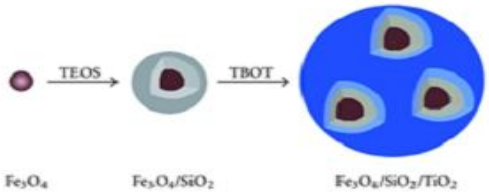

Fig. 1. Procedure for the synthesis of $Fe_3O_4@SiO_2@TiO_2$

RESULTS AND DISCUSSION

The morphology of $Fe_3O_4@SiO_2@TiO_2$ samplespowder were evaluated by scanning electron microscopy (SEM) illustrated in (Fig. 2). Images reveals that for $Fe_3O_4@SiO_2@TiO_2$ synthesized by co-precipitation method that has been calcinatedin 400 °C, particles almost are monosize with mediocre size about 30 nm.

Fe_3O_4 nanoparticles were being encapsulated within the SiO_2 shells upon the hydrolysis and condensation of TEOS as new bonds of Fe–O–Si were formed between the interface of Fe_3O_4 and TEOS. Ultrasonication was used to accelerate the hydrolysis of TEOS. This was followed by lateral polymerization, and the formation of a threedimensional network via siloxane formation (Si–O–Si), to produce a homogenous SiO_2 coating.

(SiO_2) between TiO_2 coating and magnetic material was proposed for better coating of TiO_2 layer and to avoid photodissolution of iron.

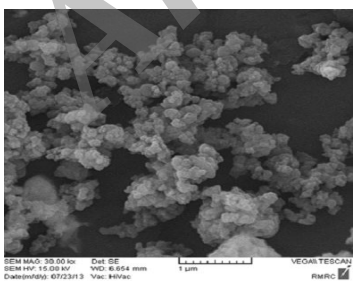

Fig. 2. SEM image of Fe_3O_4/SiO_2 c: $Fe_3O_4/SiO_2/TiO_2$ magnetic nanoparticle.

The synthesized nanocomposite was characterized using FT-IR (Fig. 3). The background corrected FT-IR spectra of MNPs are shown in (Fig. 3. a).The broad band around 3400 cm^{-1} can be assigned to O-H stretching vibration which is assigned to the surface OH groups of Fe_3O_4 NPs. The absorption bands around 580-610 cm^{-1} is attributed to the vibration of Fe-O bond in Fe_3O_4. In the FT-IR spectrum of $Fe_3O_4@SiO_2$ and $Fe_3O_4@SiO_2/TiO_2$ .the band at about 1100 cm^{-1} is assigned to stretch of Si-O bond and the SiO-H/TiO-H groups are appeared by the very broad IR absorption band in the 2800-3700 cm^{-1} region. In the(Fig. 3c), the ratio of 580-610 cm^{-1} to the 1100 cm^{-1} show that the coating of TiO_2 is not core-shell nanoparticle. The structure was synthesized as nanocomposite format ($Fe_3O_4@SiO_2/TiO_2$) [7].

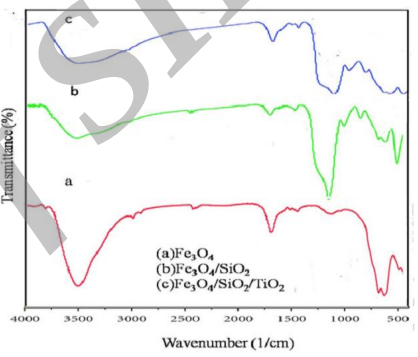

Fig. 3. FT-IR a) Fe_3O_4 nanoparticles b) Fe_3O4/SiO_2 c) $Fe_3O_4/SiO_2/TiO_2$

The XRD patterns of photocatalysts are compared in Fig. 4. Only the diffraction peaks of typical anatase TiO_2 were observed with 2θ at 25.3°, 37.9°, 48.2°, 54.0°, 55.1°, 62.6°. Diffraction peaks of titanate and Fe_3O_4 crystal didn't appear. This indicates that the Fe_3O_4 is well encapsulated by SiO_2, and no interaction between Fe_3O_4 and TiO_2 occurs [8,9].

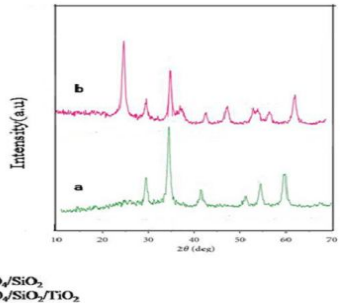

Fig. 4. XRD pattern of Fe_3O_4/SiO_2 (a) and $Fe_3O_4/SiO_2/TiO_2$ (b)

Fig. 5 shows Transmission electron microscopy (TEM)image of $Fe_3O_4/SiO_2/TiO_2$ nanoparticles. Based on TEM image, the ultrafine particle diameter size of the synthesized Fe3O4 is about 20-40 nm.

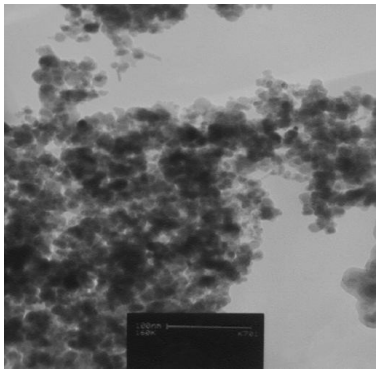

Fig4.TEM image of $Fe_3O_4/SiO_2/TiO_2$ magnetic nanoparticle

Photocatalyst degradation of Rhodamine B by $Fe_3O_4@SiO_2@TiO_2$ Agnanoparticle was performed under ultraviolet light irradiation. Changing in dye concentration was handled by UV absorption spectroscopy. Amount of the Rhodamine B degradation in time of t (DP(t)) was calculated as follows:

$$DP(t) = \frac{A_0 - A_t}{A_0} \times 100$$

Where A_0 and A_t are the absorbance value of the solution at 0 and t minute, respectively.

To aproving catalysts effect, the mixture stirred in dark miliue. No dye degradation after 40 minutes without using UV light irradiation or nanopowderphotocatalysts, so the contribution of self-degradation was insignificant. As time passed, dye decomposed and the color of the solution became brighteruntill at t = 40 min a rather transparent solution was obtained. Results for the changes in the concentration of dye after 40 min under UV irradiation.. After 40 minutes, the degradation percentage of $Fe_3O_4@SiO_2@TiO_2$ - obtained 64% (Fig. 6).

CONCLUSION

In this study, a simple and facile synthesis approach was developed for the preparation of a magnetically separable photocatalyst consisting of an Fe_3O_4 core, an SiO_2 intermediate layer, and a photocatalytically active TiO_2. This synthesis method was rapid and did not require the addition of any surfactant to direct the formation of SiO_2 or TiO_2 shells. The photocatalytic activity of TiO_2 surface shell was not affected by the intermediate SiO_2 layer and Fe_3O_4 core. The $Fe_3O_4/SiO_2/TiO_2$ nanoparticles possessed high specific surface area and exhibited a good photocatalytic activity for the photodegradation of Rhodamine B dye in aqueous solution

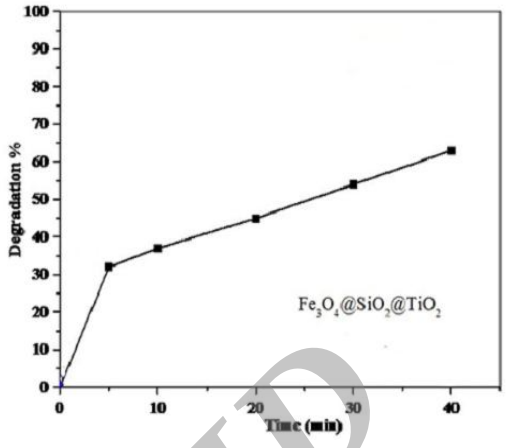

Fig. 6. Degradation of Rhodamine B dyes by $Fe_3O_4/SiO_2/TiO_2$ magnetic nanoparticle

CONFLICT OF INTEREST

The authors declare that there are no conflicts of interest regarding the publication of this manuscript.

REFERENCES

[1] E. Beyers, E. Biermans, S. Ribbens, K. De Witte, M. Mertens, V. Meynen, S. Bals, G. Van Tendeloo, E. F. Vansant, P. Cool, Applied Catalysis B: Environmental. 88 (2009), 515-524.
[2] S. C. Pang, S. Y. Kho, S. F. Chin, Journal of Nanomaterials. (2012).
[3] T. A. Gad-Allah, S. Kato, S. Satokawa, T. Kojima, Solid State Sciences. 9 (2007), 737-743.
[4] A.-L. Morel, S. I. Nikitenko, K. Gionnet, A. Wattiaux, J. Lai-Kee-Him, C. Labrugere, B. Chevalier, G. Deleris, C. Petibois, A. Brisson, M. Simonoff, ACS Nano. 2 (2008), 847-856.
[5] Osuna, K. M. Gregorio-Jauregui, J. G. Gaona-Lozano, I. M. d. l. Garza-Rodr, , guez, A. Ilyna, E. D, a. Barriga-Castro, H. Saade, Ra,. G. L, , pez, J. Nanomaterials. 2012 (2012), 103-103.
[6] S. C. Pang, S. Y. Kho, S. F. Chin, J. Nanomaterials. 2012 (2012), 125-125.
[7] L. E. Ahangar, K. Movassaghi, M. Emadi, F. Yaghoobi, Nano. Chem. Res. 1 (2016), 33-39.
[8] Z. Peng, H. Tang, Y. Tang, K. F. Yao, H. H. Shao, International Journal of Photoenergy. 2014 (2014), 8.

[9] Y. Kobayashi, S. Saeki, M. Yoshida, D. Nagao, M. Konno, Journal of Sol-Gel Science and Technology. 45 (2007), 35-41.

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