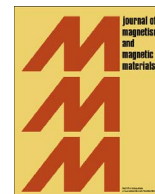




Contents lists available at ScienceDirect

Journal of Magnetism and Magnetic Materials

journal homepage: www.elsevier.com/locate/jmmmColloidal titania-silica-iron oxide nanocomposites and the effect from silica thickness on the photocatalytic and bactericidal activities[☆]Padtaraporn Chanhom^a, Nisanart Charoenlap^b, Boosayarat Tomapatanaget^a, Numpon Insin^{a,*}^a Department of Chemistry, Faculty of Science, Chulalongkorn University, Bangkok 10330, Thailand^b Laboratory of Biotechnology, Chulabhorn Research Institute, Bangkok 10210, Thailand

ARTICLE INFO

Keywords:

Photocatalyst
Nanocomposite
Superparamagnetic
Titania

ABSTRACT

New types of colloidal multifunctional nanocomposites that combine superparamagnetic character and high photocatalytic activity were synthesized and investigated. The superparamagnetic nanocomposites composed of anatase titania, silica, and iron oxide nanoparticles (TSI) were synthesized using thermal decomposition method followed by microemulsion method, without calcination at high temperature. Different techniques including X-ray diffraction (XRD) and transmission electron microscope (TEM) were used to characterize and confirm the structure of the nanocomposites. These nanocomposites showed high photocatalytic activity when used in the photodegradation of methylene blue under irradiation with a black light lamp. Moreover, the nanocomposites exhibited high antibacterial properties. From our study, the nanocomposites can be useful in various applications such as removal of pollutants with readily separation from the environment using an external magnetic field. These composites could effectively photo-degrade the dye at least three cycles without regeneration. The effects of silica shell thickness on the photocatalytic activity was investigated, and the thickness of 6 nm of the silica interlayer is enough for the inhibition of electron translocation between titania and iron oxide nanoparticles and maintaining the efficiency of photocatalytic activity of titania nanoparticles.

1. Introduction

Titania or titanium oxide (TiO₂) has become an attractive material for applications in different fields ranging from photocatalysis to medicine. The photocatalytic process has been reported to be more effective in the degradation of organic pollutants than other processes [1], and titania nanoparticles are one of the most interesting photocatalysts. The important advantages of titania are as follows [2,3]. First, titania is an excellent photocatalyst because it shows high photocatalytic activity in various reactions. Also, titania has physical and chemical stability; accordingly, it can destroy a variety of organic pollutants in different solutions without reduction in the catalytic activity and can be reused for many cycles. Moreover, titania is inexpensive, and non-toxic material that can transform a variety of toxic pollutants into harmless products. However, the post-treatment separation in titania slurry system after photocatalytic oxidation reaction has a serious limitation as it is difficult to separate and recover titania nanoparticles from the liquid phase. In order to solve this problem, one of the alternative approaches is coating titania particles on the surface of magnetic particles to equip them with magnetic responses for magnetic separation.

The two-component model, in which titania particles were directly coated onto the magnetic particles to form the magnetic particles/titania particles core/shell structures, has been reported [4]. Maghemite and magnetite particles were commonly used as the magnetic components due to their stability toward oxidation and low toxicity. However, low photocatalytic activity was observed because a direct contact of the magnetic core and titania shell could increase to the recombination of photogenerated electron-hole pairs [4,5]. The drawback could be overcome by inserting an interlayer comprising materials with large band gap to inhibit the recombination of electron-hole pairs for improving the photocatalytic activity. For this purpose, silica has been reported to be used as interlayer because other than its large band gap, silica exhibits high thermal and chemical stability and low toxicity [6].

The three-component structures of the magnetic core/insulator interlayer/photocatalyst shell composites composed of iron oxides/silica/titania have been reported to obtain a photocatalyst with high photocatalytic activity in combination with strong magnetic responses [6,7]. However, in these previous studies the three-component composites were in the size range of 300–550 nm or larger in diameters, at which the composites were likely to aggregate readily due to the

[☆]The star sign does not show up in the proof. In remembrance of His Majesty King Bhumibol Adulyadej (1927–2016), for his life-time dedication to Thailand.

* Corresponding author.

E-mail address: Numpon.I@chula.ac.th (N. Insin).

<http://dx.doi.org/10.1016/j.jmmm.2016.10.123>

Received 26 June 2016; Received in revised form 19 October 2016; Accepted 23 October 2016

Available online xxxx

0304-8853/ © 2016 Elsevier B.V. All rights reserved.

magnetic dipole interaction of each particle and low colloidal stability for the particles of large sizes. In order to reduce the aggregation and increase the surface area and photocatalytic activity of the composites, the sizes of the composites should be smaller with the iron oxides components are in their superparamagnetic state where the magnetic attraction between particles is not observed. It has been reported that the magnetite and maghemite nanoparticles with the size ranging from 4 to 50 nm in diameter exhibit superparamagnetic character [8–13] and the magnetic photocatalyst should incorporate the iron oxides nanoparticles of these sizes to become colloidally stable.

In this work we have synthesized superparamagnetic iron oxide/silica/titania nanocomposites that were colloidally stable in order to diminish particle agglomeration using a combination of thermal decomposition and reverse microemulsion methods. Superparamagnetic iron oxide nanoparticles, prepared by thermal decomposition of iron-oleate complex, were encapsulated inside discrete silica nanospheres, and titania was coated onto surface of silica using the reverse microemulsion method. Under mild conditions, titania was transformed from amorphous phase to anatase, resulting in the titania-silica-iron oxide nanocomposites (TSI) with low aggregation, high colloidal stability and low energy consumption in the preparation. The photocatalytic properties of as-synthesized core-shell nanocomposites were evaluated by the degradation of methylene blue under UV irradiation. Also, titania has been reported to kill bacteria because of their photocatalytic activity [14]; therefore, the bactericidal activity of the new magnetic titania nanocomposites was investigated using a Gram-positive *Staphylococcus aureus* as a model. *S. aureus* is a human pathogenic bacterium, which is defined as one of the major causes of healthcare-associated Infections (HAI) by Center of Control Diseases (CDC) [15]. *S. aureus* causes many diseases, including bacteremia [16], pneumonia [17], and endocarditis [18], especially in immunocompromised or immunosuppressed patients who are hospitalized for a long period of time. Moreover, *S. aureus* has ability to acquire antibiotic resistances from other organisms, resulting in high number of resistant *S. aureus* strains that is more difficult to cure with antibiotic. This life-threatening infection is currently of a major concern worldwide. Thus, other than searching for new antibiotics, a novel strategy for treatment of *S. aureus* infection should be considered.

2. Experimental section

2.1. Materials

Iron (III) chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), 1-octadecene, Igepal CO-520, Tetrabutyl orthotitanate (TBOT) were purchased from Aldrich. Tetraethyl orthosilicate (TEOS) and Cetyltrimethylammonium bromide ($\text{C}_{19}\text{H}_{42}\text{BrN}$, CTAB) were purchased from Fluka. All chemical reagents were of analytical grade and used without further purification.

2.1.1. Syntheses of nanocomposites

The synthesis of monodisperse iron oxide nanoparticles (I) was performed using a method reported earlier with some modification [8,9]. 8 mmol of iron (III) chloride was dissolved in de-ionized water (10 mL). 24 mmol of sodium oleate was transferred into the iron (III) chloride solution. Then, 56 mL mixture of ethanol, de-ionized water, and hexane (the volume ratio of ethanol:water:hexane=1.33:1:2.33) were added to the above solution, and the mixture was refluxed at 70 °C for 4 h. After being washed in de-ionized water for three times, the resulting iron-oleate complex was collected using centrifugation. Then, hexane was removed by evaporation under reduced pressure. The sticky iron-oleate complex precursor was dispersed in a mixed solvent comprising oleic acid and 1-octadecene with the weight ratio of oleic acid:iron-oleate complex:1-octadecene of 1:6.3:35. The mixture solution was slowly heated to 320 °C and maintained at that temperature for 30 min under nitrogen gas. Iron oxide nanoparticles were

precipitated and collected by centrifugation.

Tetraethyl orthosilicate (TEOS) was used as silicon source for the preparation of silica-coated iron oxide nanoparticle (SI) using the reverse microemulsion method similar to previous reports [19,20]. Typically, 9.88g of Igepal CO-520 was dispersed in cyclohexane by sonication. Then, 90 mg of iron oxide nanoparticles were added to solution under continuous stirring. Afterward, 700 μL of 25% ammonium hydroxide solution and 600 μL of TEOS were added to the above mixture solution. The reaction was continually stirred for 16 h at room temperature. Finally, the silica-coated iron oxide nanoparticles were precipitated in ethanol using centrifugation.

In the preparation of silica-coated iron oxide nanoparticles, the effect of the amount of TEOS on the thickness of silica shell was investigated. The process of silica thickness variation was done following the method above but varied amounts of TEOS were added in the mixture solution. Three different volumes of TEOS (150, 600 and 2400 μL) were used in preparation of silica layer. The SI nanocomposites of different silica thickness were further coated with titania.

The reverse microemulsion method for coating titania nanoparticle on the silica-iron oxide surface to obtain titania-silica-iron oxide nanocomposites (TSI) was modified from previous research [21]. Firstly, 7.3 mL of 1-hexanol was used as solvent for dispersing as-synthesized silica-coated iron oxide (SI) nanoparticles. 3g of cetyltrimethylammonium bromide (CTAB) was added to the silica-coated iron oxide solution. Secondly, the mixed solution was continuously stirred at room temperature for 1 h. Afterward, 50 μL of tetrabutyl orthotitanate (TBOT) and 1 mL of de-ionized water were added into the mixture. The reaction mixture was refluxed at 80 °C for 24 h under vigorous stirring. Finally, the sample was centrifuged and washed with ethanol and de-ionized water, and the final product was re-dispersed in PBS buffer (pH 7.4) for bactericidal activity. For comparison, titania-coated iron oxide nanoparticles (TI) and pure titania photocatalyst (T) were prepared in the same method mentioned above.

2.2. Characterization methods

2.2.1. X-ray Electron Diffraction (XRD)

The crystalline phases of iron oxides and titania nanoparticles were characterized using a D/MAX 2200 X-ray diffractometer (Rigaku, Japan) with Cu-K α radiation at an accelerating voltage of 40 kV and an applied current of 30 mA. The XRD patterns of composites, iron oxides and titania nanoparticles were recorded at 2θ in a range of 20–80°.

2.2.2. Transmission electron microscopy (TEM)

TEM images were taken using a JEOL 2100 microscope (Japan) at an accelerating voltage of 120 kV. One drop of the colloidal solutions, prepared by dispersing a small amount of nanoparticles in ethanol using an ultrasonic treatment for at least 2 min, was placed onto a formvar-coated copper grid and dried at room temperature for TEM measurement. The images were used to study the sizes and morphology of particles and the thickness of the coating of the layers.

2.3. Measurement of photocatalytic activity

The photocatalytic activity of the as-prepared nanocomposite was investigated by measuring the degradation of methylene blue solution upon UV irradiation and comparing with the titania-coated iron oxide nanoparticles and iron oxide nanoparticles. A 36 W black light blue UV lamp was used as the irradiation light source. For each photocatalytic experiment, photocatalyst nanocomposites with 45 mg of iron oxide nanoparticles were dispersed in a 30 mL aqueous solution of 12 ppm methylene blue. The suspension was kept in dark to obtain an adsorption-desorption equilibrium for the catalyst, water and dye before irradiation. At given intervals of UV irradiation for 0–5 h, sample was collected, and the catalyst was separated from the solution

Download English Version:

<https://daneshyari.com/en/article/5491155>

Download Persian Version:

<https://daneshyari.com/article/5491155>

[Daneshyari.com](https://daneshyari.com)