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Preparation of uniform rhodamine B-doped SiO_2/TiO_2 composite microspheres

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Abstract

Uniform rhodamine B (RB)-doped SiO_2/TiO_2 composite microspheres with catalytic and fluorescent properties were prepared by an easy and economical method in this paper. The composite microspheres were built up with well-dispersed silica particles as the cores, RB as both the doped agent and stabilizer, and the TiO_2 shells were obtained through the hydrolysis of $TiCl_4$ in water bath. The morphology and structure of the particles were characterized by scanning electron microscopy (SEM) and X-ray powder diffraction (XRD). The characterization results indicate that composite particles are all in spherical shape and have a narrow size distribution. The composite particles calcined above 500 °C reveal clear crystalline reflection peaks of the rutile TiO_2 which exhibits well catalytic property. The photocatalytic experiment was carried out in order to examine the catalytic property of composite microspheres. The fluorescent property of particles was also investigated. Dye-leakage test indicates that RB molecules entrapped in the composite particles by this method are stable inside the particles.

Keywords: Uniform; Composite microspheres; Rhodamine B-doped; Multi-functional

1. Introduction

Functional composite microspheres often exhibit improved physical and chemical properties over their single-component counterparts and hence are very useful in catalysis [1,2], optical device [3], separation [4,5], artificial cells [6], chemical and biological sensing [7], etc. At present, kinds of functional composite microspheres have been prepared. More recently, with the development of the preparation of functional microspheres, increasing interest has been devoted to the exploration of multi-functional composite microspheres which exhibit more improved physical and chemical properties and can be used in extended fields. For example, Zhao et al. have prepared Ni/polystyrene/TiO_2 microspheres and SiO_2/Ni/TiO_2 microspheres that exhibit good responses to the external electric and magnetic fields [8,9]. Magnetic thermoresponsive microspheres that combine both superparamagnetic and thermoresponsive properties have been elaborated as reported by Shoukuan Fu [10].

TiO_2 is a material of important interest because of its scientific characteristics including a broad functionality, stability, long-term and no toxicity. TiO_2 coating on the supports has been studied for a wide variety of uses such as antifouling, deodorizing applications, because of their photocatalytic properties and photovoltaic effect [11,12]. And continuous thin shells of TiO_2 precipitated on the supports were achieved by the hydrolysis of organic titania precursors such as titanium butanol, titanium isopropoxide and titanium ethoxide [8,9,13–16]. However, the organic titania precursors are expensive, which may restrict the further potential applications. And so far as, little attention has been focused on preparation of well-dispersed TiO_2 coating on the supports from the hydrolysis of economical inorganic titania precursors. The rapid hydrolysis rate of inorganic titania precursors makes it difficult to coat TiO_2 on the supports homogeneously. Rhodamine dyes occupy an important position due to their useful photochemical and photophysical properties among different

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dyes. Rhodamine dyes have high fluorescence quantum yield, which makes them useful in applications like lasers, fluorescence labeling, etc. [17]. But organic dyes are not photostable and bleach out quickly. Attempts are being made to make composite particles such that dye molecules are entrapped in the matrix and organic or inorganic protective shell is built around them.

In this paper, we prepare the uniform rhodamine B (RB)-doped SiO_2/TiO_2 composite microspheres which exhibit well catalytic and fluorescent properties through a one-step and economical way firstly. In the RB solution, the well-dispersed silica particles are used as the template, and the hydrolysis of $TiCl_4$ leads to the formation of well-dispersed RB-doped SiO_2/TiO_2 composite microspheres. Here, RB is the doped agent and also a stabilizer. The surface activity of RB molecules is beneficial for the adherence between TiO_2 shell and SiO_2 core. It plays an important role in the process of the precipitation of TiO_2 particles on the surface of SiO_2 cores uniformly. One of the major problems with fluorescent particles is leakage of the dye molecules from the particles after dispersing in aqueous medium [18]. RB doped into the microspheres by this method is stable inside the microspheres. And the TiO_2 shell can prevent the photobleaching of RB molecules efficiently.

2. Experimental

2.1. Materials

Tetraethyl orthosilicate (TEOS, 98%) as a silica source, ammonium hydroxide as a catalyst, ethanol as a solvent, RB as the doped agent and stabilizer. All chemicals were used as received without further purification.

2.2. Preparation of silica particles

Silica particles were synthesized by base-catalyzed hydrolysis of TEOS, as described by stöber et al. [19]. Briefly, 12.22 mL of aqueous ammonia (25 wt%) was added into a solution containing 30 mL of ethanol and 2.22 mL of deionized water. Separately, 4.02 mL of TEOS was mixed with 25.4 mL of ethanol. The two solutions were rapidly mixed under vigorous stirring. The reaction mixture was kept stirring for 8 h to yield uniform silica particles. Then, the resulting silica particles were separated by centrifugation at 3000 rpm for 15 min and washed four times with water. Finally, the silica particles were dried at 50 °C for 24 h in vacuum oven.

2.3. Preparation of dye-doped SiO_2/TiO_2 particles

Typically, 0.5 g of silica particles was dispersed in 50 mL of ethanol containing 10^{-2} M of RB by sonication for 15 min. Then 30 mL of aqueous solution containing 6 M of HCl and 0.5 M of $TiCl_4$ was added into the above solution. The suspension was stirred for 4 h in a water bath at 80 °C. After centrifuged and washed by water several times, the composite particles were dried in vacuum at 50 °C for 24 h.

2.4. The photocatalytic experiment

0.2 g of composite particles calcined at 800 °C was added into 50 mL of 10^{-3} M $K_2Cr_2O_7$ aqueous solution. After sonication for 15 min, the above suspension was stirred vigorously under the irradiation of a 25-W ultraviolet (UV) lamp. After every hour for 3 h, 10 mL of above solution was taken out, respectively, and then centrifuged; the supernatant was characterized by UV-Vis spectra.

The blank test of silica particles was also carried out to compare the photocatalytic activity of composite particles.

2.5. Dye-leakage testing

The as-prepared dye-doped SiO_2/TiO_2 particles were divided into four parts. And then the four samples were immersed in water for 0, 24, 48 and 96 h, respectively. Before fluorescence measurement, each sample was washed and separated from the supernatant and then dried in vacuum at 50 °C for 24 h.

In order to contrast the dye leakage of dye molecules after coating with TiO_2 and that of before coating with TiO_2, the sample was prepared by the same method (experimental section 2.3) without the addition of $TiCl_4$/HCl solution. Then the dye-leakage testing was carried out in the above way.

2.6. Characterization

The sizes and morphologies of the product were examined by scanning electron microscopy (SEM; JEOL JEM 200CX). X-ray powder diffraction (XRD) patterns of the samples were carried out with Siemens D5005 X-ray diffractometer. The UV-Vis analysis was carried out on a 756MC UV-Vis spectrophotometer. Fluorescence spectra were measured with a Hitachi F-4500 fluorophotometer.

3. Results and discussion

3.1. The formation mechanism of composite microspheres

Scheme 1 shows the formation mechanism of RB-doped SiO_2/TiO_2 microspheres. The silica particles as cores were first dispersed in RB solution by sonication. Here, RB is both the doped agent and a stabilizer. It plays an important role in the formation of uniform TiO_2 coatings. RB molecule is a positive surfactant, and the surface of silica exhibits negative charge property. So the RB molecule can easily absorb on the surface of silica particles through electrostatic force. There are the oxide groups of titanium hydroxyl groups on the surface of TiO_2 colloid particles. And these oxide groups can connect with the hydrogen