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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 $500\,^\circ C$ 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.

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.
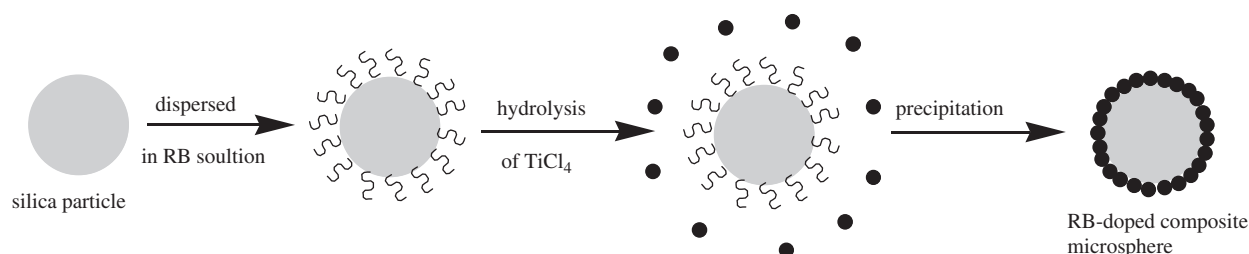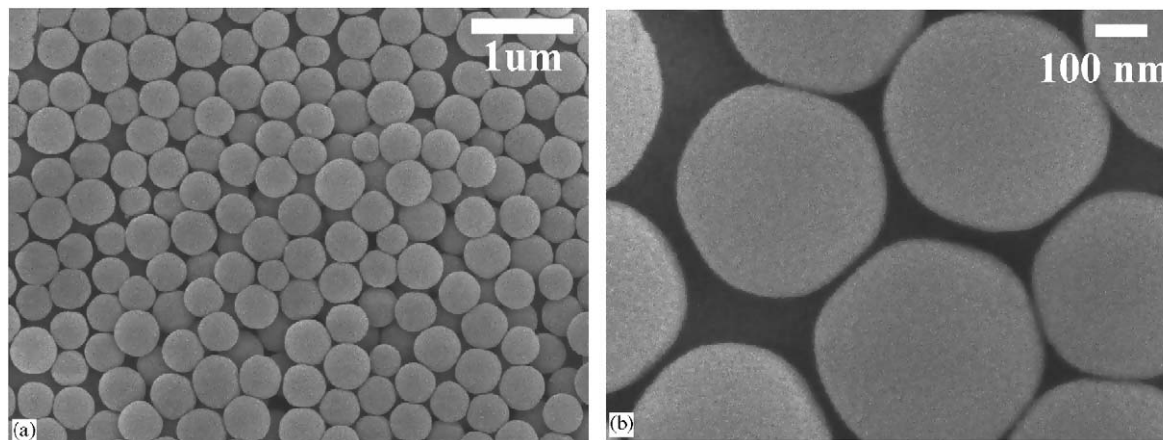
2.6. Characterization

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

Scheme 1. Formation mechanism of RB-doped SiO_2/TiO_2 composite microspheres.

Fig. 1. SEM images of SiO_2 particles.

groups of RB molecular chains to form hydrogen binding [20,21]. Since the RB molecular chains first contacted with the silica cores, then the other segments of molecular chains could absorb TiO_2 colloid particles in the solution by hydrogen binding. The TiO_2 particles deposited on the surface of the silica cores, resulting in the formation of uniform TiO_2 coatings. We found that the composite microspheres prepared without RB solution were not uniform and had many TiO_2 aggregates. This phenomenon can be explained as follows: RB molecules act as a bond between the SiO_2 and TiO_2 particles. RB molecules absorbed on the silica cores make the TiO_2 colloid particles easily deposited on the surface of the silica cores by hydrogen binding. However, in the absence of RB solution, there is no coalescent force between SiO_2 and TiO_2 particles. The TiO_2 colloid particles cannot aggregate on the surface of SiO_2 cores completely and they are easy to form TiO_2 aggregated particles. HCl and water bath also are in favor of the uniform precipitation of TiO_2 particles. HCl restrains the hydrolysis of $TiCl_4$ and makes the formation rate of TiO_2 particles slow, which can prevent the aggregation of TiO_2 particles. The water bath makes that the solution can be heated homogeneously, which is of benefit to that TiO_2 particles deposited on the surface of silica particles uniformly. As a result, uniform TiO_2 coatings on the silica cores were obtained.

3.2. Scanning electron microscopy measurement

Fig. 1 shows the SEM images of silica particles that were used as the core particles in the synthesis of composite microspheres. It clearly reveals that the silica particles exhibit regular spherical shape and uniform size. The mean diameter of particles is about 400 nm. From the high-magnification image (Fig. 1b), it can be seen that the surface of silica particles is smooth. Fig. 2 shows the SEM images of RB-doped SiO_2/TiO_2 composite particles. The low-magnification SEM image shown in Fig. 2a exhibits that composite particles all maintain the regular spherical shape and narrow size distribution. It indicates that TiO_2 prepared by this method can precipitate on the surface of silica homogeneously. The size of the particles is similar to that of the silica particles. This is due to that TiO_2 layer precipitated on the silica particles is thin. Compared with silica particles, the surface of composite microspheres is rough, which can be confirmed from Fig. 2b. This is the result of that TiO_2 gained from the hydrolysis of $TiCl_4$ deposited on the surface of silica in the form of nanoparticles. The SEM images of the RB-doped SiO_2/TiO_2 particles calcined at 800 °C are shown in Fig. 3. The shape of composite particles is still spherical and the particles have also a narrow size distribution. No fractured composite microsphere was found, which demonstrated
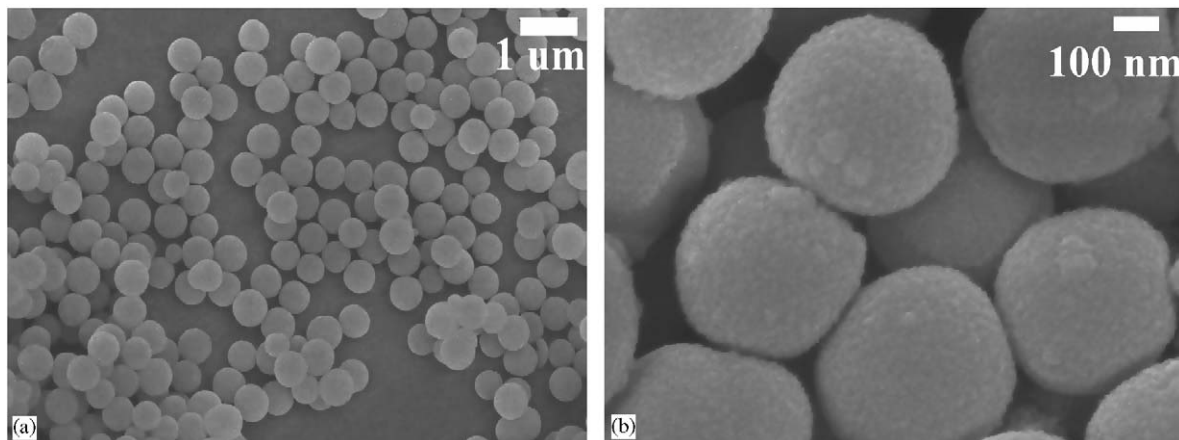
Fig. 2. SEM images of RB-doped SiO$_2$/TiO$_2$ particles.
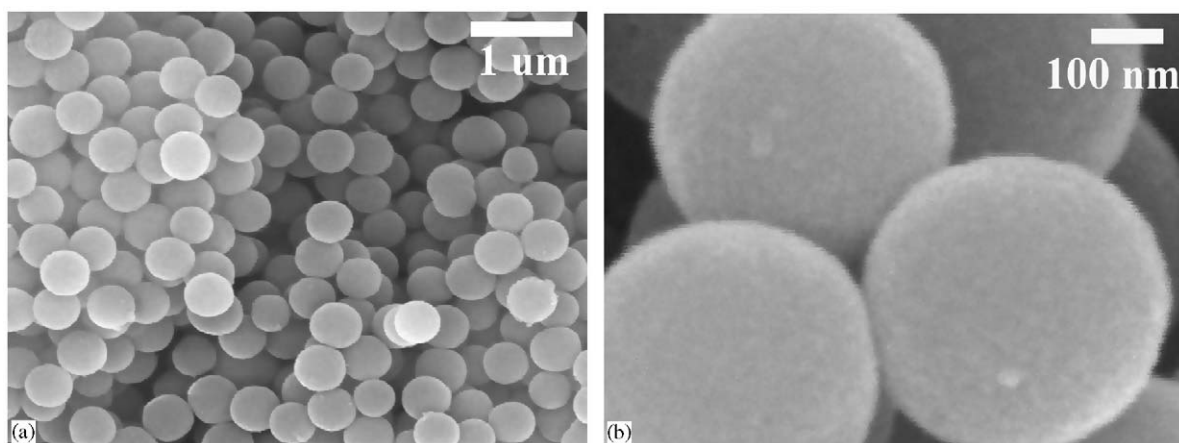

Fig. 3. SEM images of RB-doped SiO$_2$/TiO$_2$ particles calcined at 800 °C.

that the spherical shape of composite particles is steady. From Fig. 3b, we also can find that the surface of the composite particles after calcination became smooth again. This is due to that TiO$_2$ particles on the surface of silica particles underwent the transformation from amorphous state to rutile and the TiO$_2$ nanosized crystals were arrayed regularly.

3.3. X-ray powder diffraction patterns

Fig. 4 is the XRD patterns of the product that was calcined at different temperatures for 3 h. Below 500 °C, there are no diffraction peaks and the TiO$_2$ shells appear in an amorphous state. The particles calcined above 500 °C display clear crystalline reflection peaks that are characteristic to the rutile TiO$_2$. The diffraction peaks with 2θ at 27.42°, 36.1° and 54.36° can be readily indexed as (110), (101) and (201) diffraction of the rutile structures of TiO$_2$, respectively. It can be seen that the intensity of the diffraction peaks is not very strong owing to the effect of amorphous silica in the composite particles. The average

crystallite size of TiO$_2$ component is about 4 nm using Scherer's equation estimation from rutile characteristic diffraction peak. This result suggests that the TiO$_2$ shell is composed of nanosized crystals. It is further confirmed that TiO$_2$ particles deposited on the surface of silica in the form of nanoparticles. We also can find that no anatase appeared at different temperatures, which informs that this method avoids anatase–rutile TiO$_2$ phase transformation. The similar result has been obtained in our previous work [22]. It is related to the nature and structure of the starting materials and the preparation methods [23]. Rutile is an abundant polymorph and thermodynamically stable phase. Its high refractive index and chemical inert, even in strongly acidic or basic environments, make rutile an ideal white pigment and excellent photocatalyst [23,24].

3.4. The photocatalytic experiment

In order to examine the catalytic property of composite microspheres, the photocatalytic degradation of K$_2$Cr$_2$O$_7$ in microspheres suspension was investigated. Fig. 5 is the
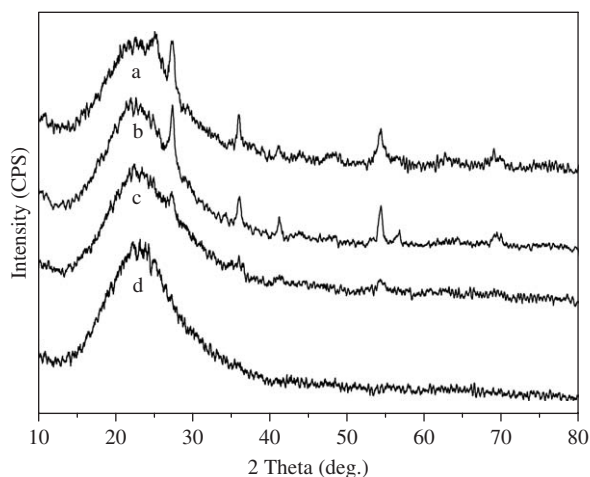
Fig. 4. XRD patterns of the composite microspheres calcined at (a) 800 °C; (b) 600 °C; (c) 500 °C; (d) 400 °C.
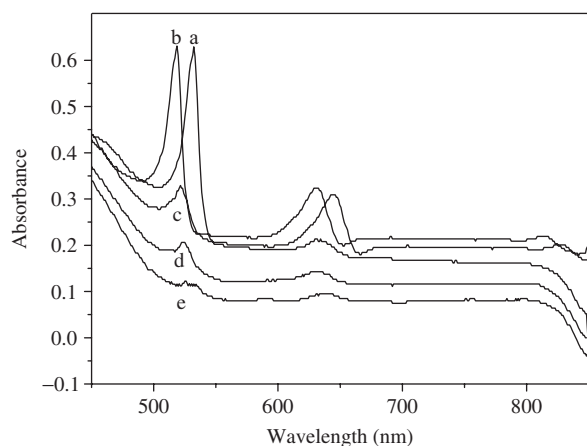

Fig. 5. UV-Vis spectra of $K_2Cr_2O_7$ solution after UV irradiation for different times: (a) blank test of silica particles; composite particles as catalyst (b) 0 h, (c) 1 h, (d) 2 h, (e) 3 h.

UV-Vis spectra of $K_2Cr_2O_7$ solution after UV irradiation for different times. It can be seen that the absorption peaks of $K_2Cr_2O_7$ solution using silica particles suspension as the blank are not changed along with the reaction time. It reveals that pure silica particles have no photocatalytic property. $K_2Cr_2O_7$ solution using composite particles as catalyst before degradation also has strong absorption peaks. Comparing with the blank test, a blue shift from 532 to 520 nm for the characteristic absorption peaks of $K_2Cr_2O_7$ solution can be observed. This is due to that surface-induced states of the TiO_2 shell consisting of nanosized crystals lead to the blue shift of spectra. The reaction of $K_2Cr_2O_7$ solution using composite particles as catalyst was carried out, the absorption peaks decreased. After 3 h, the absorption peaks were very weak. It indicates that the TiO_2 shells of composite microspheres exhibit well photocatalytic property.

3.5. Dye-leakage test

Dye-doped fluorescent particles often suffer from a serious dye leakage from the matrix after dispersion of the fluorescent particles in an aqueous solution, which may limit the potential applications of fluorescent particles. A leakage test of the RB-doped composite particles was carried out in order to examine the stability of dye molecules in the matrix. The comparison of fluorescence intensity of the samples (dye molecules after coating with TiO_2 and that of before coating with TiO_2) immersed in water for different times is shown in Fig. 6. We can find that silica particles without coating with TiO_2 also have some fluorescence intensity. This indicates that the RB molecules have been absorbed on the surface of silica particles. The fluorescence intensity of RB-doped SiO_2/TiO_2 particles before immersing in water is much higher than that without coating with TiO_2. It reveals that TiO_2 layer kept the dye molecules absorbed on the silica particles from being washed off by water in the separation process and also TiO_2 layer entrapped many dye molecules. It can be seen that the fluorescence intensity is still very high when composite particles were immersed in water for 96 h, whereas the fluorescence intensity of the particles without coating with TiO_2 is very low when they were immersed in water only for 24 h. It can indicate that RB molecules were doped inside the composite particles very well and were very stable in the matrix. Because there was an electrostatic attraction between the silica core and the dye molecule, the dye could remain in the matrix well. And also the layer of TiO_2 could restrict the leakage of dye molecules from the matrix efficiently. The photostability of fluorescence dyes is environmentally sensitive, and singlet state oxygen molecules play the main role of photobleaching of the fluorescence dye molecules in the excited state [25]. Here, the layer of TiO_2 also can keep dye molecules from contacting with oxygen molecules, and prevent the decomposition. From Fig. 6, we also find that the fluorescence intensity of composite particles immersed in water for 24 h
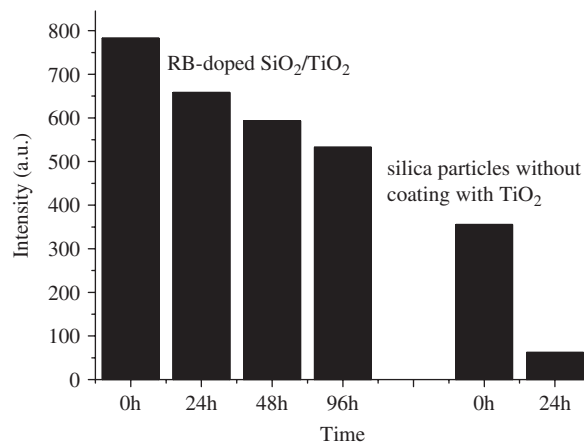

Fig. 6. Dye-leakage testing of composite particles.

decreased more than that of other samples. This can be explained as follows: Some RB molecules absorbed on the surface of particles when the composite particles were prepared in the solution, and then these RB molecules first diffused into the solution when the particles were immersed in aqueous solution.

3.6. Effect of the concentration of reactant on the property and morphology of composite particles

In order to investigate the effect of reactant concentration on the property and morphology of composite particles, a series of samples were prepared using the same silica core particles and conditions described in the experimental section except for changing the concentration of RB and $TiCl_4$, separately. The effect of the concentrations of RB and $TiCl_4$ on the fluorescence intensity is shown in Figs. 7 and 8, respectively. As expected, with the higher concentration of RB or $TiCl_4$ in the reactant solution, the fluorescence intensity of composite particles all increased. It can be explained as follows: When the concentration of RB in solution is higher, there are more RB molecules that can absorb on the surface of silica particles, and also the TiO_2 layer can entrap more RB molecules in the shell; with the increasing concentration of $TiCl_4$, the shell of TiO_2 will be thicker, and then more RB molecules can be entrapped in the shell. Therefore, we can obtain composite particles with different fluorescence intensity through changing the reactant concentration. Additionally, in contrast with the sample of dye molecules before coating with TiO_2, a blue shift from 595 to 585 nm for the emission band can also be observed both in Figs. 7 and 8. This is also attributed to the existence of the TiO_2 nanosized crystals on the surface of composite particles.

Moreover, the effect of reactant concentration on the morphology and size distribution of composite particles was investigated. When the concentration of $TiCl_4$ was increased to 2 M, the prepared product appears polydisperse and there are many small particles among the composite particles. This is attributed to the fact that: At
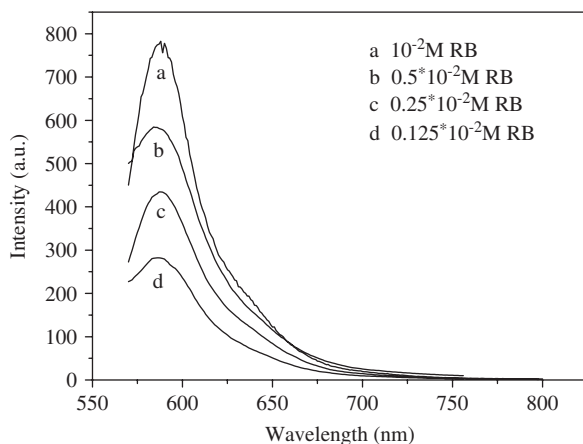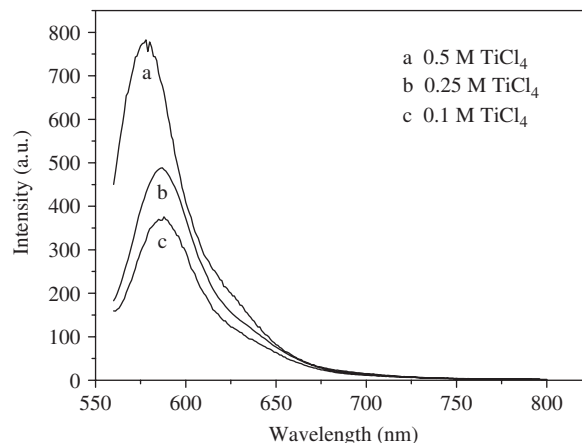

Fig. 8. Effect of the concentration of $TiCl_4$ on the fluorescence intensity.

a higher $TiCl_4$ concentration, the formation rate and amount of TiO_2 colloid particles increased, which caused many colloid particles to aggregate and to form TiO_2 aggregated particles. The similar result was also gained when the concentration of RB increased to 0.1 M. This is due to that a large amount of RB molecules were not only absorbed on the surface of silica particles but also assisted the aggregation of TiO_2 particles.

4. Conclusion

In summary, the uniform RB-doped SiO_2/TiO_2 composite microspheres are prepared by a novel method using the silica spheres as cores, and then introducing the RB and TiO_2 components to the silica cores by the hydrolysis of $TiCl_4$ in RB solution in water bath. The resulting composite particles are all in spherical shape and have a narrow size distribution. XRD spectra indicate that the composite particles calcined above 500 °C exhibit clear crystalline reflection peaks of the rutile TiO_2. The photocatalytic experiment shows that the composite particles present well catalytic property. Fluorescence spectra reveal that fluorescence intensity of the composite microspheres will increase with the increasing of reactant concentration. Dye-leakage test shows that RB molecules are entrapped in the particles well and the TiO_2 protective layer is built around them. The TiO_2 shell can restrict the leakage and photobleaching of dye efficiently. Because the composite microspheres exhibit well fluorescent and catalytic properties, they can be used in catalysis, fluorescent labeling and bioanalysis. Moreover, the easy and economical method can be extended to the preparation of other multifunctional composite microspheres.

Fig. 7. Effect of the concentration of RB on the fluorescence intensity.

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