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Research Article

Mesoporous Silica Coated CeF_3:Tb^{3+} Particles for Drug Release

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CeF_3:Tb^{3+} nanoparticles were successfully prepared by a polyol process using diethylene glycol (DEG) as solvent. After being coated with dense silica, these CeF_3:Tb^{3+} nanoparticles can be coated with mesoporous silica using nonionic triblock copolymer $EO_{20}PO_{70}EO_{20}$ (P 123) as structure-directing agent. The composite can load ibuprofen and release the drug in the PBS. The composite was characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), nitrogen absorption/desorption isotherms, fluorescence spectra, and UV/Vis absorption spectra, respectively. The composite particles have considerable large pore volume and large surface area. In addition, the composite still emits strong green fluorescence (Tb^{3+}) and can be used as fluorescent probes in drug delivery system.

1. INTRODUCTION

Currently, nanomaterials have been applied in many medical and biological fields, such as clinical diagnosis, drug delivery, fluorescent markers in vitro and in vivo [1–7], and so forth. Among these applications, drug delivery technology can bring both commercial and therapeutic values to health care products [8]. At the same time, mesoporous silica materials have been interesting in the use as controlled drug delivery matrixes to meet the need for prolonged and better controlled drug administration [9], due to their nontoxic and highly biocompatible nature, a highly regular pore structures, high specific pore volumes [9–13], and very high specific surface area with abundant Si−OH groups on the pore surface, which can react with appropriate drug functional groups and is suitable for loading and releasing drug in a more reproducible and predicable manner [14–24].

Several research groups have investigated the conventional mesoporous silica materials (such as M41S and SBA-n) used as drug delivery systems [14–21]. These systems exhibit sustained release properties [8, 17, 24, 25]. However, the use of bulk mesoporous silica materials in many applications suffers from some limitations, especially in targeted drug delivery mechanisms as the carrier and drug kinetics marker in the pharmacological research [9]. Recently, the composites of the nanoparticles and mesoporous silica have obtained more and more interest [26–28], especially the magnetic mesoporous silica materials which have been investigated for separation and delivery systems [3, 9, 27, 28]. However, the fluorescent mesoporous silica materials, as the delivery systems, were reported rarely. If one could combine the advantages of mesoporous silica and fluorescent particles to fabricate a composite, the composite can also be potential in the fields of drug delivery, disease diagnosis, and therapy. This is because the composite material not only has high pore volume for the storage and delivery of drugs, but also possesses fluorescence properties by which can be used to track and evaluate the efficiency of the drug release. The composite may target the path of delivery, furthermore supply the information about the mechanism of drugs delivery, and can be employed for qualitative and quantitative detection of disease position and drug release efficiency. Therefore, the design of mesoporous composite materials with fluorescence property and drug storage capability plays the key role in achieving this application.

In this paper, we choose the CeF_3:Tb^{3+} nanoparticles as the fluorescent labels and ibuprofen as the drug model. CeF_3 is a luminescent material with 100% activator concentration

[29, 30]. Doping Tb^{3+} in CeF_3 resulted in a strong green emission from Tb^{3+} due to an efficient energy transfer from Ce^{3+} to Tb^{3+} [31–34]. CeF_3:Tb^{3+} nanoparticles have potential application as fluorescent labels for biological molecules [34]. On the other hand, ibuprofen was used as a model drug due to its good pharmacological activity and the suitable molecule size of about 1.0×0.6 nm as well, which ensures its easy diffusion into or out of the mesoporous channels of as-prepared mesoporous silica [35–37]. Furthermore, ibuprofen is a nonsteroidal drug. Herein, we report the template-assisted scheme to fabricate uniform fluorescent nanoparticles with a fluorescent core/mesoporous silica shell structure. Then its drug storage and in vitro release property are demonstrated.

2. EXPERIMENTAL SECTION

2.1. Materials

$Tb(NO_3)_3$, $Ce(NO_3)_3 \cdot 6H_2O$ (99.99%, Shanghai Yuelong New Materials Co., Ltd., Shanghai, China), NH_4F (96%, Beijing Beihua Fine Chemical products Co., Ltd., Beijing, China) were used as starting materials and diethylene glycol (DEG) (analytical reagent, A. R. Beijing Yili Fine Chemicals Co., Ltd., Beijing, China) as the solvent for the preparation of CeF_3:Tb^{3+} nanoparticles, respectively. $Tb(NO_3)_3$ was prepared by dissolving Tb_4O_7 (99.99%, Shanghai Yuelong New Materials Co., Ltd.,) in dilute nitric acid.

Tetraethoxysilane (TEOS) (A. R. Beijing Beihua Fine Chemical products Co., Ltd.) and ammonia solution (25%) (NH_4OH) (A. R. Beijing Beihua Fine Chemical products Co., Ltd.) were used as the materials for thin silica layers deposition on the surfaces of CeF_3:Tb^{3+} nanoparticles with isopropyl alcohol (A. R. Beijing Beihua Fine Chemical products Co., Ltd.) as the solvent. Amphiphilic triblock copolymer $EO_{20}PO_{70}EO_{20}$ (poly (ethylene oxide)-block-poly (propylene oxide)-block-poly (ethylene oxide), with trade name Pluronic 123) (Aldrich Chemical Inc., Wis, USA) was used as the template source, deionized water and hydrochloric acid (HCl) (A. R. Beijing Beihua Fine Chemical products Co., Ltd.) as solvent and ethanol (A. R. Beijing Beihua Fine Chemical products Co., Ltd.) as the solvent for extracting the surfactant P123.

Ibuprofen (IBU) (Nanjing Chemical Reagent Co., Ltd., Nanjing, China) was used as model drug and phosphate buffer solution (PBS, pH = 7.4) consisting of 8.00 g dm^{-3} NaCl, 0.20 g dm^{-3} KCl, 1.44 g dm^{-3} Na_2HPO_4, and 0.24 g dm^{-3} KH_2PO_4 as solvent.

2.2. Synthesis of CeF_3:Tb^{3+} nanoparticles

The doping concentration of Tb^{3+} in CeF_3 host was 15 mol% of Ce^{3+} in CeF_3 host, which had been optimized previously [34]. Typically, 18 mmol NH_4F was dissolved in 50 mL DEG in an oil bath at 70°C to form a clear solution. At the same time, 50 mL DEG containing 5.1 mmol of $Ce(NO_3)_3 \cdot 6H_2O$ and 0.9 mmol of $Tb(NO_3)_3$ in 250 mL round-bottomed flask was stirred and heated until 100°C in the oil bath in an Ar atmosphere. When $Ce(NO_3)_3 \cdot 6H_2O$ and $Tb(NO_3)_3$ were dissolved completely, the temperature was increased to 200°C. Then, the solution of NH_4F was injected into it and the mixture was kept stirring for 1 hour at 200°C. The obtained suspension was cooled to room temperature and diluted with 100 mL ethanol. The CeF_3:Tb^{3+} nanoparticles were obtained by centrifugation at a speed of 4500 rpm. Then they were redispersed in ethanol and centrifuged several times to remove any extraneous material. Finally, the obtained CeF_3:Tb^{3+} nanoparticles were dried at 70°C in air.

2.3. Thin layers silica deposition on CeF_3:Tb^{3+} nanoparticles

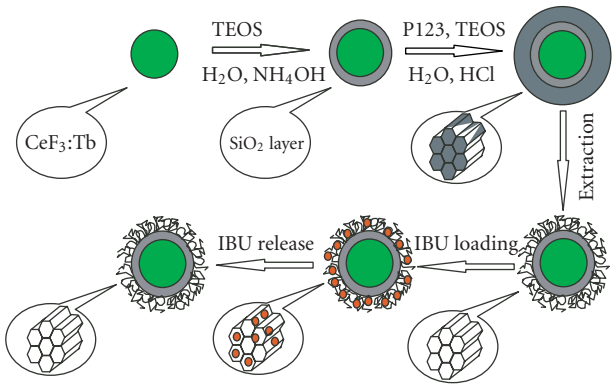
In a typical procedure [38–40], 0.1715 g CeF_3:Tb^{3+} nanoparticles were added into 200 mL isopropyl alcohol solution containing 0.45 mol dm^{-3} of NH_4OH and 3.05 mol dm^{-3} of H_2O, then the suspension was stirred 40°C for 30 minutes. Then, 0.8 mmol TEOS was added into the suspension and the mixture was stirred for 2 hours at 40°C. The product was obtained by the procedure of centrifugation and dispersion the same as the above part. In this way, silica coating CeF_3:Tb^{3+} nanoparticles were obtained.

2.4. Synthesis of mesoporous silica encapsulation CeF_3:Tb^{3+} nanoparticles

In a typical synthesis [12], 1 g P123 was completely dissolved in 7.5 mL H_2O and 29 mL of 2.0 M HCl solution, then 0.7550 g CeF_3:Tb^{3+} nanoparticles with thin layers of silica were added and stirred at room temperature for 1 hour. The suspension was stirred at 40°C for 30 minutes. Then 1.2 mL TEOS was added into the suspension and the mixture was stirred for 15 minutes and then aged for 30 minutes at 40°C. The solid sample was washed and separated by centrifugation-dispersion cycles with ethanol, then dried for 3 hours at 100°C in air. Finally, the surfactant was removed by stirring the as-synthesized product in 100 mL ethanol and 2 g of dilute HCl solution at 80°C for 10 hours. After this treatment, the product was recovered by filtration, and washed with water and ethanol, and finally dried at 70°C in air.

2.5. Drug loading procedure and in vitro release study

To load IBU into mesoporous silica coating CeF_3:Tb^{3+} nanoparticles, 0.1585 g of the composite powder sample was added to 10 mL of ibuprofen ethanol solution (2.3 mg/mL) and soaked for 3 days under stirring. Then the powders were separated and thoroughly washed with ethanol, dried at 70°C in air. Filtrate was collected and properly diluted to determine the drug-loading amount by spectrophotometer. In order to evaluate the release profile of the material, the drug-loaded samples were compressed into tablet form (9 mm $\times$ 0.5 mm) by pressure (4 MPa). 0.0952 g of the tablet was soaked in 25 mL preheated PBS under mild stirring and the temperature was kept at 37 $\pm$ 1°C. Samples of 4 mL were withdrawn at a predetermined time, replaced by fresh preheated PBS, and spectrophotometrically analyzed for IBU at 222 nm. Calibration curve of IBU was determined by



Scheme 1: The diagram shows the whole formation processes for the mesoporous silica coating CeF_3:Tb^{3+} nanoparticles and IBU loading and release processes.

taking absorbance versus IBU concentration between 0 and 22.4 μg/mL as parameters.

The whole formation processes for the mesoporous silica coating CeF_3:Tb^{3+} nanoparticles and the subsequent IBU loading and release processes are shown in Scheme 1.

2.6. Characterization

X-ray diffraction (XRD) was carried out on a Rigaku-Dmax 2500 diffractometer with Cu Kα radiation ($\lambda = 0.15405$ nm). The accelerating voltage and emission current were 40 kV and 200 mA, respectively. TEM images were obtained using a JEOL 2010 transmission electron microscope operating at 200 kV. Samples for TEM were prepared by depositing a drop of ethanol suspension of the powder sample onto a copper grid and dried in air. The excitation and emission spectra were taken on an F-4500 spectrophotometer equipped with a 150 W xenon lamp as the excitation source. The UV/Vis absorption spectra were measured on a TU-1901 spectrophotometer. All the measurements were performed at room temperature. Nitrogen adsorption and desorption isotherms were carried out on a Nova 1000 analyzer at 77 K under a continuous adsorption condition, and the samples were degassed at 100°C overnight before measurement. Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) analyses were used to determine the surface area, pore size, and pore volume.

3. RESULTS AND DISCUSSION

3.1. Structure and morphological properties of the mesoporous silica coating CeF_3:Tb^{3+} nanocrystals

XRD, TEM, and nitrogen adsorption/desorption isotherms were employed to characterize the structure and morphological properties of the mesoporous silica coating CeF_3:Tb^{3+} nanocrystals. Figure 1 shows XRD patterns of the core material of mesoporous silica coating CeF_3:Tb^{3+} sample with the standard data for bulk CeF_3 as a reference and (a) the low-angle portion in the shell material (b). The results of XRD

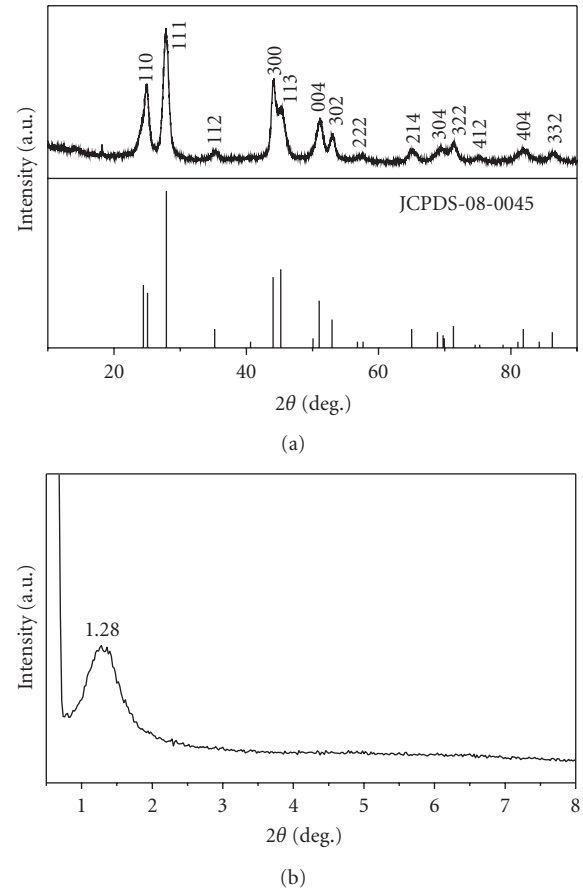


Figure 1: XRD patterns of the mesoporous silica coating CeF_3:Tb^{3+} sample with the core material with the standard data for bulk CeF_3 as a reference (a) and the low-angle portion in the shell material (b).

(in Figure 1(a)) indicate that the core material is crystallized well and all the peaks are in good agreement with hexagonal phase structure known from bulk CeF_3 phase (JCPDS card no. 08-0045). The diffraction peaks for CeF_3:Tb^{3+} core material are broadened due to the smaller crystallite size. The low-angle XRD pattern of the composite (in Figure 1(b)) shows a unique intense maximum at $2\theta = 1.28°$. This pattern indicates that mesoscopic order is preserved in the outer layer of silica.

Figure 2 shows the TEM micrographs of the mesoporous silica coating CeF_3:Tb^{3+} sample (a) with high-resolution micrographs of the outer layer (b) and the core part (c). TEM micrograph in Figure 2(a) shows that the composite sample was aggregated to some extent and the size of the composite particles is between 50 nm and 100 nm. The size is very suitable to drug delivery, because a particle size range between 50 and 300 nm is strictly demanded for drug delivery, and above 300 nm, a significant proportion of particles will be trapped in the lungs and liver, while too small particles will not carry large quantity of drug. TEM micrograph in Figure 2(b) shows that the mesoporous silica possesses ordered hexagonal pore systems, which confirmed the result of the low-angle part of XRD and was further confirmed by the nitrogen

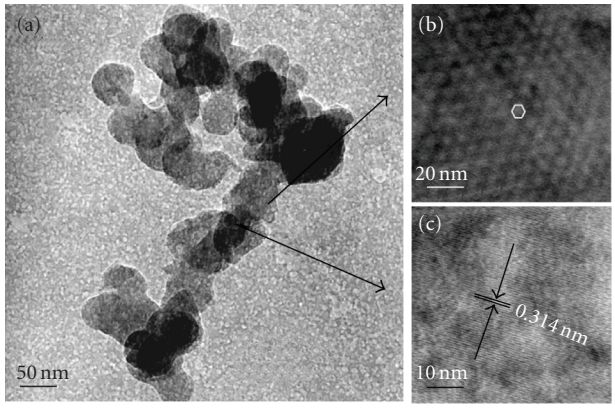


FIGURE 2: TEM micrographs of the mesoporous silica coating CeF_3:Tb^{3+} sample (a) with high-resolution micrographs of the outer layer (b) and the core part (c).

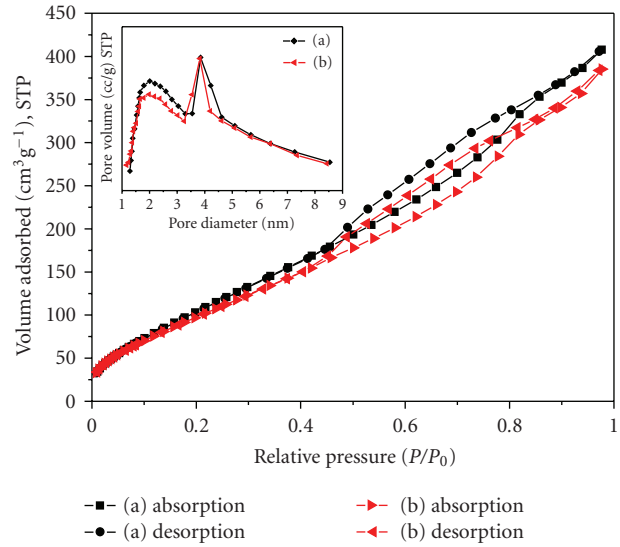


FIGURE 3: The nitrogen adsorption/desorption isotherms of the mesoporous silica coating CeF_3:Tb^{3+} particles and IBU-loading composite and their pore size distributions in the inset pattern.

adsorption/desorption isotherms. The high-resolution TEM micrograph of the core material (Figure 2(c)) clearly displays the resolved lattice fringes with a constant spacing of 0.314 nm ascribed to the (111) plane of CeF_3, which is indicative of the high crystallinity of these CeF_3:Tb^{3+} nanoparticles. The purpose of this thin dense silica layer is to protect the fluorescent core from leaching into the mother system and the resultant silica surface also facilitates the assembly of structure-directing agent (P 123).

The nitrogen adsorption/desorption isotherms of mesoporous silica coating CeF_3:Tb^{3+} particles in Figure 3(a) indicate a linear increase in the amount of adsorbed nitrogen at a low relative pressure ($P/P_0 = 0.45$). According to the IUPAC, it can be classified as a type of H2 hysteresis. The steep increase in nitrogen at relative pressures in the range between $P/P_0 = 0.45$ and 0.85 reflects a type of IV isotherm characteristic of mesoporous materials. A large hysteresis between the adsorption and desorption branches, which is characteristic of highly porous materials, confirms the formation of mesopores on the fluorescent particles. From the inset curve (a), the porous silica shell of the composite consists of two kinds of pores, a part of micropores and the other part of mesopores. Calculated from the nitrogen isotherm with the BJH method, an average pore diameter is determined to be 5.9 nm. The BET surface area and the BJH pore volume are 428 m^2/g and 0.63 cm^3/g, respectively, which is considerably large since all the cores have been included in the calculations. Compared with that in Figure 3(a), the isotherms of IBU-loading composite (in Figure 3(b)) have changed, so do the pore distribution in the inset curve (b). From these results, we can draw a conclusion that the drug was successfully loaded into the pores of the composite.

3.2. Photoluminescent properties

Figure 4 gives the excitation (a) and emission spectra (b) of the mesoporous silica coating CeF_3:Tb^{3+} particles and the inserted photograph of the IBU-loading composite in the release process under irradiation of a 254 nm UV lamp. Monitored with the 543 nm emission ($^5D_4$–$^7F_5$) of Tb^{3+}, the excitation spectrum (in Figure 4(a)) consists of a broad and strong band with a maximum of 252 nm, which corresponds to the transitions from the ground state $^2F_{5/2}$ of Ce^{3+} to the excited Ce^{3+} 5d states [41]. Under the excitation of 252 nm UV lamp, the emission spectrum (in Figure 4b) consists of two parts: the broad band emission in the region of 300–450 nm (peaking at 336 nm) and the sharp peaks between 450 and 650 nm (peaking at 489, 543, 584, 618 nm). The former is due to 5d–4f transition of Ce^{3+} ion, and the latter due to $^5D_4$–^7F_J ($J = 6, 5, 4, 3$) transitions of Tb^{3+} ion with $^5D_4$–$^7F_5$ (543 nm) being the most prominent group, respectively [34]. In the inserted photograph, the IBU-loading composite

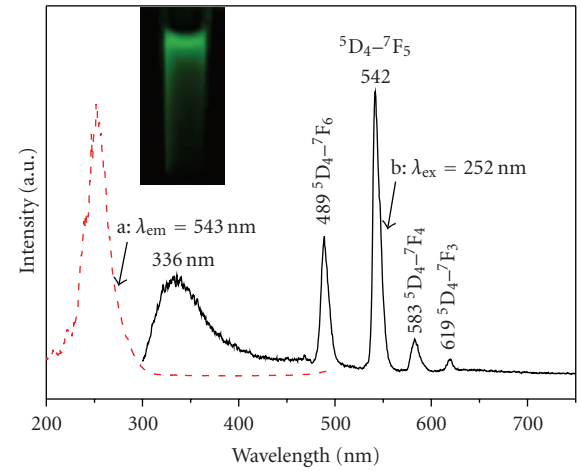


FIGURE 4: The excitation (a) and emission spectra (b) of the mesoporous silica coating CeF_3:Tb^{3+} particles and the inserted photograph of the IBU-loading composite in the release process under irradiation of a 254 nm UV lamp.

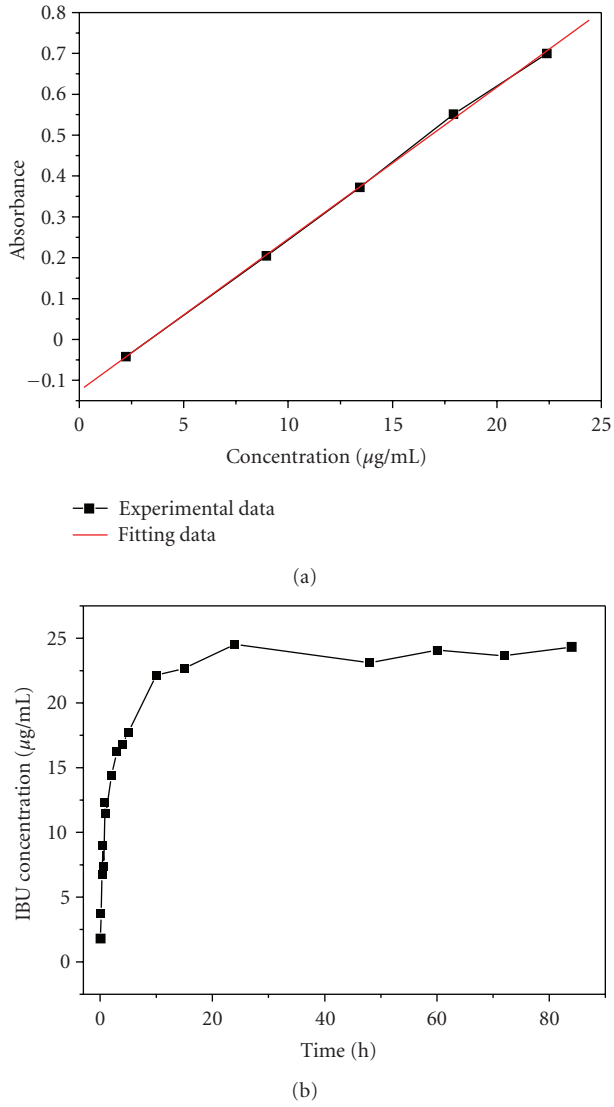


FIGURE 5: The calibration curve of IBU (a) and the release kinetics result of IBU as a function of time from the mesoporous silica coating CeF_3:Tb^{3+} particles (b).

in the release process shows strong green emission under the irradiation of a 254 nm UV lamp. The photograph indicates that the mesoporous silica coating CeF_3:Tb^{3+} nanoparticles can be used as a fluorescent label in the drug system.

3.3. *In vitro IBU release*

Figure 5 shows the calibration curve of IBU (a) and the release kinetics result of IBU as a function of time from the mesoporous silica coating CeF_3:Tb^{3+} nanoparticles (b). The calibration curve (in Figure 5(a)) fits the Lambert and Beers law

$$A = 0.03715 \times C - 0.12562, \quad (1)$$

where A is the absorbance and C is the concentration (μg/mL).

During the drug release study in vitro, calculation of the corrected concentration of released IBU is based on the following equation [21]:

$$C_{\text{tcorr}} = C_t + \frac{v}{V\sum_0^{t-1} C_t}, \quad (2)$$

where C_{tcorr} is the corrected concentration at time t, C_t is the apparent concentration at time t, v is the volume of sample taken and V is the total volume of dissolution medium. Small and large molecular drugs can be entrapped within the mesopores by an impregnation process and liberated via diffusion-controlled mechanism [8]. The silanol groups presented at the mesopores surface were selected as reaction sites to form hydrogen bonding with the carboxyl group of IBU, when IBU was impregnated into the pore channels. In the release process, the solvent entered the drug-matrix phase through pores. The drug was dissolved slowly into the fluid phase and diffused from the system along the solvent-filled capillary channels. The result (in Figure 5(b)) shows that the burst release of 50% of drug is in 2 hours followed by the slow release and 100% complete release reached in 24 hours. The initial burst release may be due to the excessive drugs which were weakly entrapped inside the mesopores or located at the outer surface of mesoporous silica coating nanoparticles, and the slow release of the rest of IBU is attributed to the strong interaction between IBU molecules and the mesopore surface.

4. CONCLUSIONS

In conclusion, the CeF_3:Tb^{3+} nanoparticles have been successfully coating by mesoporous silica using P123 as structure-directing agent. The mesoporous silica shell possesses a part of ordered hexagonal mesoporous system and a part of microporous structure. The composite retains the green fluorescent properties and possesses considerable large pore volume and large surface area. Ibuprofen can be loaded into the channels of the composite and the drug incorporated can be released in 24 hours. Therefore, this composite can be potentially used as fluorescent probes in the targeted drug delivery system.

ACKNOWLEDGMENTS

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