

Facile fabrication of porous hollow upconversion capsules using hydrothermal treatment



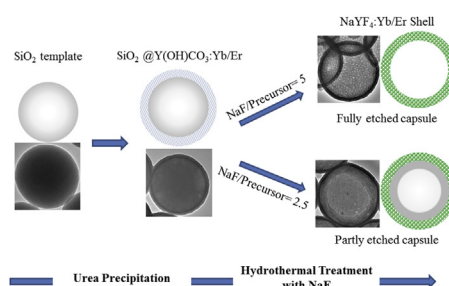
Syed Mujtaba ul Hassan, Yoshitaka Kitamoto*

Department of Innovative and Engineered Materials, Tokyo Institute of Technology, 4259 Nagatsuta-cho, Midori-ku, Yokohama, Kanagawa, 226-850, Japan

HIGHLIGHTS

- The upconversion capsules were fabricated using silica particles as a sacrificial template from a facile hydrothermal route.
- The etching of the silica template and formation of upconversion shell were achieved in a single step.
- The NaF amount plays a critical part in etching yielding partly and fully etched upconversion capsules.
- The fabrication method is versatile and tunable in terms of phase and size.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 13 April 2015

Received in revised form

15 August 2015

Accepted 4 October 2015

Available online 24 October 2015

Keywords:

Chemical synthesis

Etching

Luminescence

Inorganic compounds

ABSTRACT

Water dispersible $\text{SiO}_2@\text{NaYF}_4:\text{Yb/Er}$ double-shell (referred as partly etched; upconversion exterior shell with underneath silica interior shell) capsules and $\text{NaYF}_4:\text{Yb/Er}$ (referred as fully etched) capsules with well-defined morphology are fabricated through a facile hydrothermal process. These capsules are envisioned for biomedical applications such as photoluminescence imaging and drug delivery. Sacrificial silica template particles are first coated with a $\text{Y}(\text{OH})\text{CO}_3:\text{Yb/Er}$ shell using an urea precipitation method and resulting composites are converted to capsular structure by incubating with sodium fluoride (NaF). A possible mechanism of the porous shell formation of $\text{NaYF}_4:\text{Yb/Er}$ and simultaneous etching of silica template is explained in terms of ion-exchange reaction and surface protected etching. It is found that the ratio of NaF to initial rare-earth-precursor plays a critical role to obtain the partly etched and fully etched capsules. These capsules exhibit luminescence properties as evaluated by upconversion (UC) characterization, which is of prime importance for biomedical imaging, making them suitable for theranostic applications.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Hollow capsular structures with porous shells of functional materials have been considered ideal for biomedical applications such as drug delivery and imaging due to their high drug loading space and high specific surface [1–8]. There have been many functional materials used for hollow porous structures, and among these, upconversion (UC) nanostructures have recently evoked

* Corresponding author. Department of Innovative and Engineered Materials, Interdisciplinary Graduate School of Science and Engineering, Tokyo Institute of Technology, 4259 Nagatsuta-cho, Midori-ku, Yokohama, Kanagawa, 226-8502, Japan.

E-mail addresses: hassan.s.aa@m.titech.ac.jp (S.M. Hassan), kitamoto.y.aa@m.titech.ac.jp (Y. Kitamoto).

special interest due to their unique properties [9–16]. UC nanostructures can be excited by infrared (IR) light rather than high energy visible or ultraviolet (UV) light which is required for excitation of quantum dots and dyes [17–21]. In human body, the absorption coefficient in visible to UV region is high due to hemoglobin and that in far-IR region is also high due to water [22]. The emission and excitation bands of UC materials lie in near-IR region, known as biological window, which is considered ideal for biomedical applications [23]. The UC material includes rare-earth elements which are used as a host, emitter, and activator. The UC efficiency depends upon the phonon energy of the host material. Among the host materials, fluoride based inorganic hosts doped with rare-earth elements are considered to be the most efficient due to their low phonon energy, high stability, and little photo-damage [24–28]. Porous hollow UC capsules of a few hundred nanometer in size, which are made of rare-earth doped fluorides, combine drug loading with photoluminescence imaging, offering an attractive multifunctional platform [8–11,14,29,30].

A fabrication method assisted by a hard sacrificial template is one of the common ways to synthesize hollow capsular structures having many advantages such as well-defined shapes and good dispersibility. Many types of hard template such as polymers (polystyrene, melamine formaldehyde (MF)), metallic particles (Au), and inorganic materials (SiO_2 , CaCO_3) have been reported to synthesize a capsular structure [31–34]. In particular, silica particles are very attractive because of their cost effectiveness, monodispersibility, and size tunability [35,36]. There have been few reports using silica as a hard template to synthesize UC capsular structures. J. Park et al. prepared $\text{SiO}_2@\text{Re}_2\text{O}_3$ ($\text{Re}=\text{Gd}, \text{Eu}, \text{Y}$) beads using silica particles; the capsular structure was obtained after hydrogen fluoride (HF) treatment [37]. For oxide-host based UC capsules, the size was in micrometer range ($\sim 1 \mu\text{m}$), and the oxide host has higher phonon energy ($\sim 600 \text{ cm}^{-1}$) as compared with fluoride-based hosts ($\sim 350 \text{ cm}^{-1}$) [38,39]. S. Tan et al. successfully synthesized a core-shell structure with an UC shell on silica templates using oleic acid as a capping agent [40]. However, the shell was not porous, and the resulting core-shell did not have capsular structure in addition to the lack of water dispersibility. X. Zhu et al. used $\text{Fe}_3\text{O}_4@\text{SiO}_2$ composites as a template to coat with an UC shell and obtained the rattle type structure after HF treatment [30]. The rattle structure possessed the excellent magnetic and UC properties but the synthesis process utilized HF, which is hazardous. H. Liu et al. also used $\text{Fe}_3\text{O}_4@\text{SiO}_2$ composites to fabricate the rattle type structure with UC and magnetic properties; instead of fluoride-based UC shell, oxide-based UC shell was chosen in this rattle structure [9]. In the most cases using silica templates, materials of UC capsular structures were oxide-host based. In case of fluoride-based UC capsules using silica templates, HF is generally used as a fluoride source and an etching agent. Regarding the size of capsules, intravenous biomedical applications require the size less than 400 nm [41,42]. Thus, there are problems to develop a simple and relatively safe chemical synthesis method to fabricate fluoride-based UC capsules using hard templates with the size of less than 400 nm.

In the present study, uniform silica particles of $\sim 100 \text{ nm}$ and $\sim 300 \text{ nm}$ in size are used to prepare core-shell $\text{SiO}_2@\text{Y}(\text{OH})\text{CO}_3:\text{Yb}/\text{Er}$ composites via a homogenous precipitation method using urea and rare-earth precursors followed by a hydrothermal process to convert $\text{SiO}_2@\text{Y}(\text{OH})\text{CO}_3:\text{Yb}/\text{Er}$ composite particles to $\text{NaYF}_4:\text{Yb}/\text{Er}$ UC capsules in one step. The hydrothermal process converted the $\text{Y}(\text{OH})\text{CO}_3:\text{Yb}/\text{Er}$ shell to the $\text{NaYF}_4:\text{Yb}/\text{Er}$ shell, and simultaneously dissolved the silica cores. The effect of the ratio of NaF to precursors on the etching mechanism of the silica cores in the hydrothermal process is discussed in detail. Moreover, the crystal phase and the size of the capsules have been easily tuned, revealing the versatility

of the synthesis process.

2. Experimental methods

2.1. Materials

$\text{YCl}_3 \cdot 6\text{H}_2\text{O}$ (Wako, 99.9%), $\text{YbCl}_3 \cdot 6\text{H}_2\text{O}$ (Wako, 99.9%), $\text{ErCl}_3 \cdot 6\text{H}_2\text{O}$ (Wako, 99.9%), $\text{GdCl}_3 \cdot 6\text{H}_2\text{O}$ (Wako, 99.9%), NaF (Sigma Aldrich, 99%) and urea (Wako, 99.9%) were purchased and used as starting materials without any purification.

2.2. Preparation of upconversion capsule

UC capsules were synthesized using silica particles in a typical sacrificial template method. The amorphous $\text{Y}(\text{OH})\text{CO}_3:\text{Yb}/\text{Er}$ shell was synthesized on the silica particles of 300 nm in diameter by a homogenous precipitation method [9]. In a typical method, 30 mg of silica particles were dispersed in 100 mL deionized water under agitation at 313 K for 45 min. Then 0.25 M urea was added followed by the addition of rare-earth precursors (with ratios Y:Yb:Er; 78:20:2) of 0.4 mmol under agitation. To tune the crystal phase, 0.4 mmol of $\text{GdCl}_3 \cdot 6\text{H}_2\text{O}$ aqueous solution was used as a precursor. Afterward, the mixture was transferred to a three-neck flask and heated under sealed environment for 2 h at 363 K with vigorous stirring. After heating, the flask was cooled rapidly. $\text{SiO}_2@\text{Y}(\text{OH})\text{CO}_3:\text{Yb}/\text{Er}$ composite particles were separated by centrifuging and washed with water and ethanol three times each. $\text{NaYF}_4:\text{Yb}/\text{Er}$ UC capsules were synthesized by a hydrothermal treatment of the $\text{SiO}_2@\text{Y}(\text{OH})\text{CO}_3:\text{Yb}/\text{Er}$ composite particles with NaF in deionized water of 32 mL using 50 mL autoclave at 473 K for 8 h. The molar ratio of NaF to rare-earth precursors was kept at 2.5 and 5 to synthesize partly etched and fully etched capsules, respectively. After the autoclave was naturally cooled to room temperature, the product was isolated by centrifuging and was washed with deionized water. To tune the size of the capsules, the same synthesis protocol was used for 100 nm silica template-particles with the ratio of NaF to rare-earth precursor of 5.

2.3. Characterization

The crystal structure of the capsules was investigated using powder X-ray diffractometry (Rigaku, RINT 2100 V). The morphology was observed using a transmission electron microscope (Hitachi, H-8100). The UC characterization was done using a laser diode (LD) module of 980 nm in wavelength as an excitation source with a fluorescence spectrophotometer (Hitachi F-7000). The chemical composition such as molar ratios of rare-earth elements was determined using inductively coupled plasma mass spectroscopy (Shimadzu-ICPS-8000).

3. Results and discussion

The synthesis scheme of the capsular structure is shown in Fig. 1. The amorphous $\text{SiO}_2@\text{Y}(\text{OH})\text{CO}_3:\text{Yb}/\text{Er}$ composite particles were synthesized via a homogeneous precipitation method with rare-earth precursors and urea using silica template particles shown in Fig. 2(a). The silica particles have a negative zeta potential ($\sim -45 \text{ mV}$) owing to many hydroxyl groups on their surface. The surface hydroxyl groups not only provide excellent dispersion of the silica particles but also work as nucleation sites for the $\text{Y}(\text{OH})\text{CO}_3:\text{Yb}/\text{Er}$ shell by forming a bond of Y–O–Si between rare-earth ions and silica, so that no additional surface modification is required [9]. The overall reaction can be given as;

Download English Version:

<https://daneshyari.com/en/article/1520974>

Download Persian Version:

<https://daneshyari.com/article/1520974>

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