

Synthesis of europium-doped silica microspheres using the sol–gel microencapsulation method

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Abstract This paper demonstrates the preparation of europium (Eu^{3+}) doped silica microspheres using the W/O microencapsulation method. The water phase (W phase) solution is composed of partially hydrolyzed tetraethyl orthosilicate and acetylsalicylic acid acting as hydrophilic active agents. The $\text{Eu}(\text{NO}_3)_3 \cdot \text{H}_2\text{O}$ was added into the W phase solution before mixing with the oil phase solution. Under a controlled stirring treatment, the W/O emulsion is obtained by dispersing the W phase solution in cyclohexane containing Span60 as the surfactant. 3-aminopropyltriethoxysilane (APTES) is used as a gelling agent to encapsulate the micelles and Eu^{3+} doped silica microspheres with a mean size of around 2 μm can be obtained. The experimental parameters, such as the W/O ratio, stirring condition, the amount of APTES added and the temperature, are modified and their effects on the morphology and homogeneity of the resulting Eu^{3+} doped silica microspheres are systematically studied. The Eu^{3+} ions are successfully confined inside the silica microcapsules, exhibiting an optimal red emission with a doping concentration of 3 mol%.

Keywords Microencapsulation · W/O microemulsion · Sol–gel process · Europium · Fluorescence

1 Introduction

Silica-based glasses exhibit good chemical durability, high optical transparency in wide range and low thermal

coefficients, thus have received great interest in various optical applications. Recently, silica-based fluorescent particles have been investigated for their use in biological [1–3] and display and lightening applications [4, 5]. Among all types of phosphors, rare earth (RE) ions are considered as excellent candidates that provide definite fluorescent emission signals and good photochemical stability. For the past decade, synthesizing size- and shape-controllable particles has become an important target in materials research. Monodispersed and spherical particles offer the possibility of fabricating ordered arrays due to their natural self-assembly behavior in colloidal states. In addition, these phosphors exhibiting monodispersed and spherical morphology allows to provide good brightness, high resolution and low light scattering, which are ideal for newly developed display technologies [4, 5]. The Stöber method is used to synthesize size-defined and monodispersed silica spheres [6]; however, it uses a base-catalyzed hydrolysis reaction, which occurs at an extremely high pH environment in highly concentrated ammonia aqueous solutions. The addition of inorganic metallic salt, which are often the sources of RE ions, usually generates a rapid precipitation due to the violent reactions between salt and ammonia, leading to a disturbance in the formation of silica particles in spherical morphology. As such, the Stöber method is rarely used in the doping of prepared silica particles with other metallic ions. Other methods have been proposed in preparing spherical RE-doped silica particles by adding RE salts in the TEOS precursor solutions [7, 8]. However, the obtained silica spheres are either polydispersed or only a small fraction of the RE ions are introduced into the silica spheres. Alternatively, experiments have been performed in the synthesis of RE-doped silica microspheres using the core–shell technique by coating the RE containing layers onto the surface of the pure silica

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spheres [5, 9–11]. Nonetheless, a compromise between the doping concentration and the fluorescent intensities by controlling the thickness of the activated shell layers remains a challenge for many researchers. The W/O microemulsion method has been adopted to synthesize the silica nanospheres and microspheres [12–14], wherein water containing the base catalysts is dispersed in a hydrophobic solvent to form a stable W/O microemulsion. Then, the TEOS is added into the solution to produce hydrolysis and condensation on the surface of the water droplets to form silica spheres. Since this method requires a base-catalyzed reaction to TEOS, the RE salts are expected to be inconsistent in the formation of silica particles. Meanwhile, the microencapsulation method has been proposed to prepare the pure silica microspheres [15]. In this method, a partially hydrolyzed TEOS is modified using hydrophilic-active compounds to form a homogenous water phase solution, which is then mixed with an oil-phase solvent to obtain a W/O microemulsion. This method is successful in obtaining homogeneous silica microspheres. Since most of the RE salts exhibit good solubility in hydrophilic media, this method should be adapted for the present purpose. In the current work, trivalent europium (Eu^{3+}) is chosen as the fluorescent active ions due to their outstanding red emission signals. The preparation parameters on the morphological properties of Eu^{3+} doped silica microspheres, such as the W/O ratio of the microemulsion solution, the effect of the APTES on the microencapsulation process, the working temperature and the influences of the Eu^{3+} doping concentrations, are discussed. The photoluminescent performances of the prepared products are also investigated.

2 Experimental

The synthesis for the preparation of the pure silica microspheres is similar to that proposed by Ahn et al. [15]. Tetraethyl orthosilicate ($\text{Si}(\text{OC}_2\text{H}_5)_4$, TEOS), hydrochloric acid (HCl), cyclohexane (C_6H_{12}), sorbitan monostearate ($\text{C}_{24}\text{H}_{46}\text{O}_6$, Span60), (3-aminopropyl)-triethoxysilane ($\text{H}_2\text{N}(\text{CH}_2)_3\text{Si}(\text{OC}_2\text{H}_5)_3$, APTES), acetylsalicylic acid ($\text{C}_9\text{H}_8\text{O}_4$, ASA), and $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ were used as the starting materials. These materials were used without further purification. The experimental flowchart is summarized in Fig. 1.

In the first step, the TEOS was dissolved in water and was catalyzed using HCl under a fixed molar ratio of TEOS: H_2O :HCl at 1:1.6:1.8 $\times 10^{-4}$. The mixture was continuously stirred at room temperature for 12 h to undergo a partial hydrolysis reaction. The partially hydrolyzed TEOS was heated up to 55 °C, after which ASA was added as a hydrophilic active compound to increase its hydrophilic property. Various ratios of $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (from 0.5 to

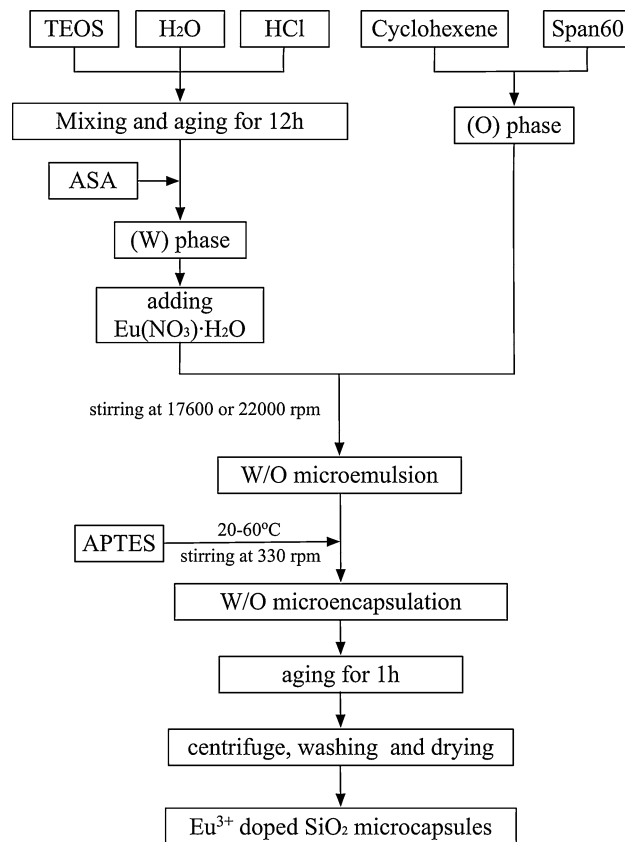


Fig. 1 Experimental flowchart

6 mol%) were added to form a transparent water phase (W phase) solution. Cyclohexene was used as the continuous oil phase (O phase) due to its immiscibility with TEOS and water. Besides, $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ is also insoluble in cyclohexene so that the Eu^{3+} ions can be perfectly confined in the W phase without leaking into the O phase. The Span60 was dissolved in cyclohexene at a fixed concentration of 10 wt% relative to the W phase solution. The W phase solution was immediately mixed into the cyclohexene with a dissolved Span60 in W/O ratio from 0.08 to 0.16 under rigorous stirring at 17,600 or 22,000 rpm for 1–2 min to form a stable and transparent W/O microemulsion. The APTES with a molar ratio from 1.5 to 3 % relative to TEOS was used as a gelling agent to encapsulate the W phase micelles. While the APTES was added, the working temperature was varied from 20 to 60 °C in order to investigate the effects of temperature on the encapsulation process. In addition, an agitation treatment at 330 rpm was applied for 1 or 30 min to disperse the APTES in the microemulsion solution homogeneously. The resulting mixture was then aged for 1 h without stirring to carry out the complete encapsulation. At this stage, the W/O microemulsion solution generated microcapsules that were initially transparent and then gradually turned to opaque and finally to milky white.

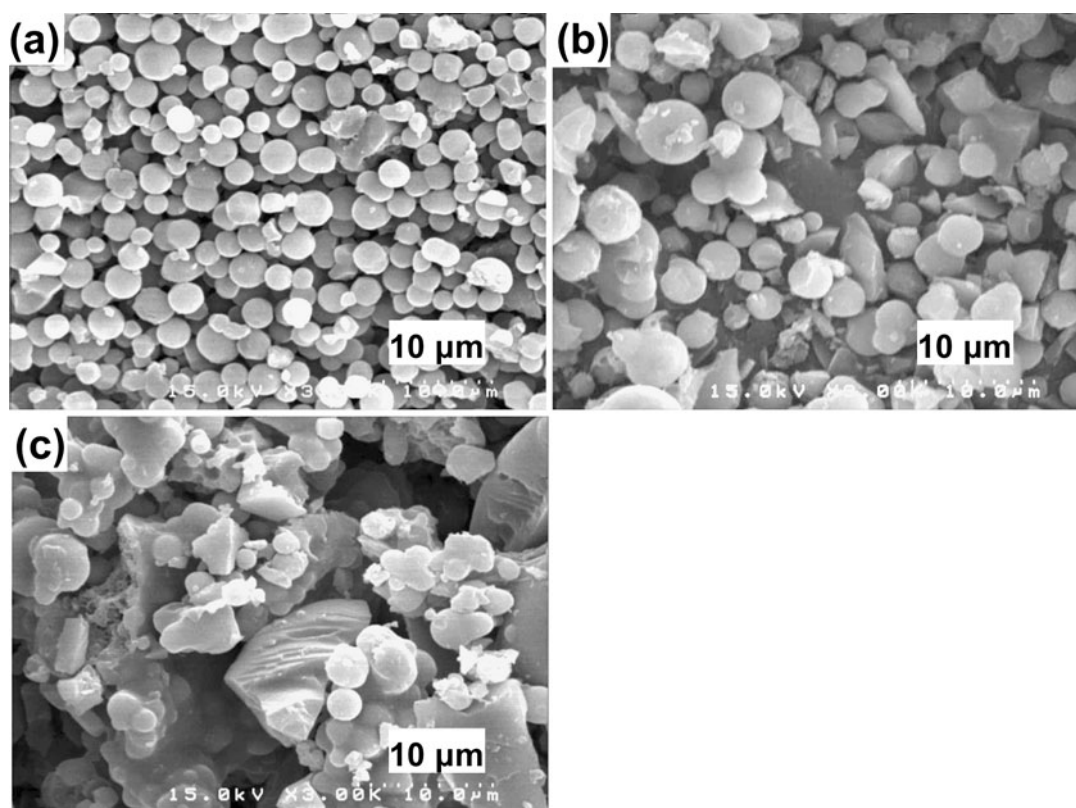


Fig. 2 SEM images of the microspheres obtained at the W/O ratio at **a** 0.08, **b** 0.12 and **c** 0.16

The precipitate was collected using the centrifugation technique and then washed with acetone three times to remove the surfactant and non-reacted substances. The obtained powders were dried in an oven at 80 °C for 3 h and then heat-treated at 1,000 °C for 2 h to remove the residual hydroxyl groups, known to be notorious quenching centers for the fluorescence of RE ions. The morphological observation was carried out using a Scanning Electron Microscope (SEM, Hitachi 4100), while the photoluminescent properties were characterized using fluorescence spectroscopy (Hitachi F-4500).

3 Results and discussion

Results show that the morphology of the obtained Eu^{3+} -doped silica spheres strongly depend on several experimental parameters at the same time. In the following discussions, the spheres were all prepared at optimal conditions with only one parameter modified. The details of the parameters are described in the conclusion.

3.1 W/O ratio

Figure 2 shows the SEM photographs of the Eu^{3+} -doped silica microspheres prepared in different W/O volume

ratios. As can be seen in Fig. 2a, the obtained products prepared at a W/O volume ratio of 0.08 are homogeneous and spherical with a mean size of around 2 μm . In addition, a portion of the large spheres over 5 μm appears, and some irregularly shaped fragments are detected when the W/O ratio increases to 0.12, as shown in Fig. 2b. The number of irregular fragments increases, and the spherical particles decreases when the W/O ratio further increases to 0.16, as shown in Fig. 2c. Since the amount of Span60 increases along with an increase in W/O ratio (fixed Span60/W phase at 10 wt%), the microcapsules become stable when the W/O ratio is as low as 0.08. This suggests that the probability of the collisions between the microcapsules increases at high W/O ratios, resulting in partially larger microcapsules as two or more microcapsules merges. During collision, the microcapsules become too large, eventually losing their stability, after which irregular fragments begin to appear. This is in accordance with SEM observations reported in Fig. 2, which shows that the spherical particle size increases with increasing W/O ratios, before eventually losing their spherical morphology.

3.2 Agitation treatments

In order to obtain a stable microemulsion, an appropriate agitation treatment is necessary to homogeneously disperse

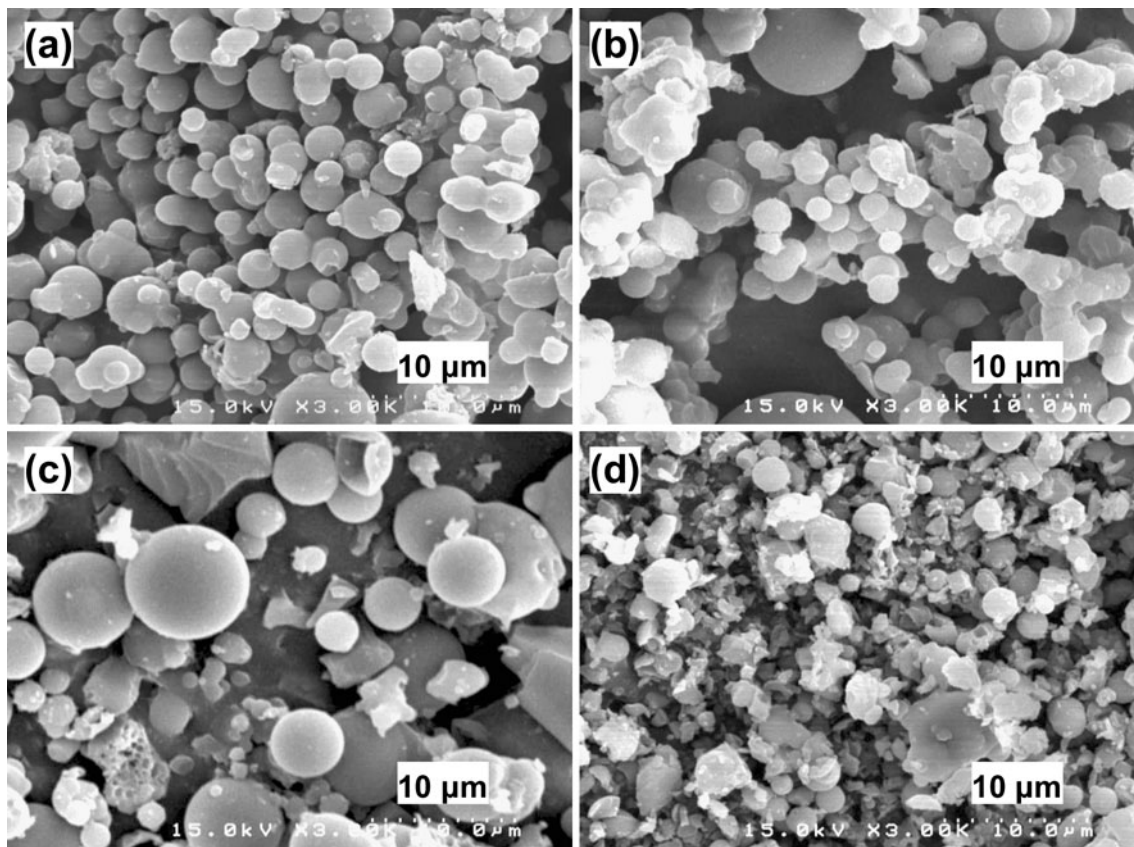


Fig. 3 SEM images of the microspheres obtained under an agitation treatment at **a** 17,600 rpm/1 min, **b** 17,600 rpm/2 min; **c** 22,000 rpm/1 min and **d** 22,000 rpm/2 min

the W phase in the O phase solution. In this section, several different agitation treatments were applied to explore the suitable impeller speed and application period for the formation of the microemulsion. The Eu^{3+} doped silica microspheres obtained from the microemulsion solution prepared with an agitation treatment at 17,600 rpm for 1 and 2 min are shown in Fig. 3a, b, respectively. As can be seen in the figures, the microspheres are relatively homogeneous when agitated for 1 min, after which aggregates of small spheres and some large spheres begin to emerge when the agitation extends to 2 min. As the impeller speed increases to 22,000 rpm, the inhomogeneous spheres with some irregular fragments begin to appear when agitated for 1 min, as shown in Fig. 3c. The spherical morphology is totally destroyed upon performing the agitation treatment at 22,000 rpm for 2 min, as shown in Fig. 3d. Results show that the increase of the impeller speed and application period is detrimental to the stability of the microcapsules. It has been reported in some literatures that the average particle sizes decreases with increasing the impeller speed due to the increase of interfacial tension to break down the droplets into several droplets of smaller size [16, 17]. However, this trend is occurred only at a moderate agitation speed ranging from 750 to 1,500 rpm. In parallel,

some proposed that the increase of collision rate enhances the coalescence of droplets and thus induces particle growth [18–20]. In the present case, we suggest that the W phase droplets have been cut to their limit small size due to the strong interfacial tension at an agitation speed as high as 17,600 rpm. A longer or a more vigorous agitation under such high agitation speed may increase the probability of collisions among micelles, eventually provoking a coagulation of micelles, which leads to the creation of larger microspheres. As the coagulations become too evident, the micelles become too large to retain their stabilities, before finally breaking into small and shapeless fragments due to the violent agitations.

3.3 Addition of APTES

In the microencapsulation method, the APTES was used as a gelling agent which is a crucial factor in ensuring the morphological properties of the obtained products. The APTES exhibits a chemical structure similar to that of TEOS, wherein one of the ethoxy ligands is replaced by a reactive terminal $-\text{NH}_2$ group; it is also widely used as a coupling agent to enhance the adhesion between organic and inorganic materials [21–23]. The active $-\text{NH}_2$ terminal

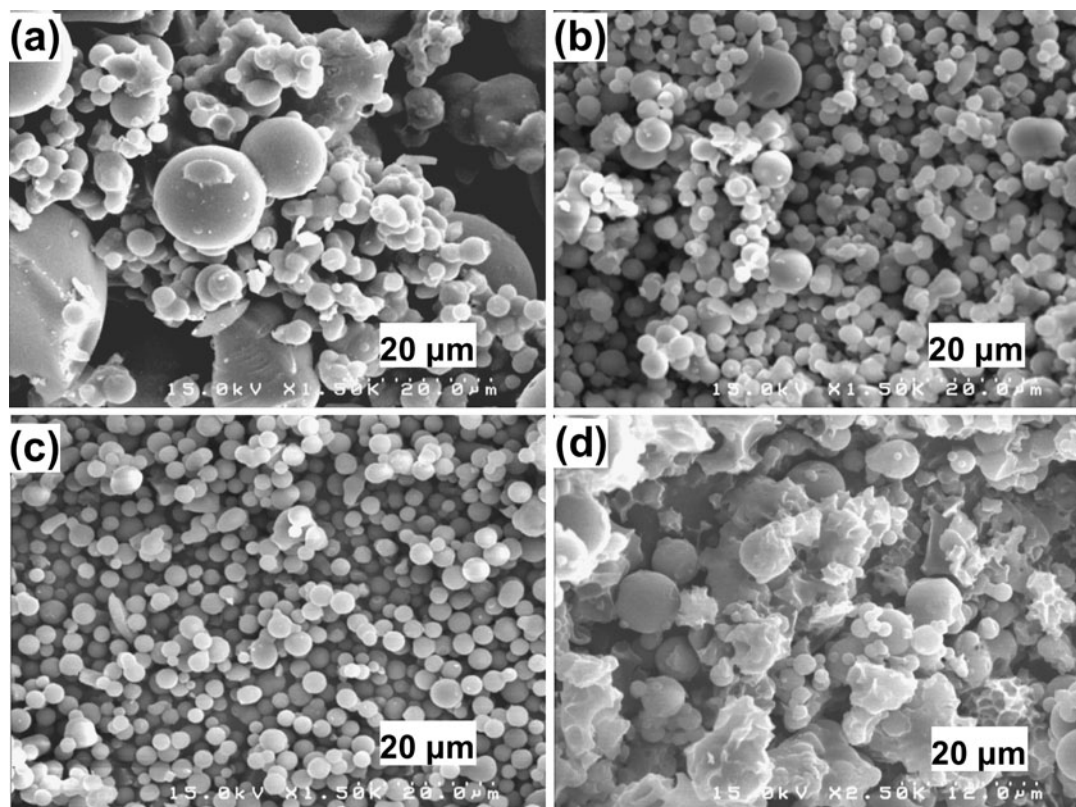


Fig. 4 SEM images of the microspheres obtained at the concentration of APTES of **a** 1.5, **b** 1.75, **c** 2 and **d** 3 mol% relative to the W phase solution

group can interact with hydroxyl groups and form a rigid aminopropyl silane (APS) polymerized network [22, 24–26]. Moreover, due to its base property, the APTES also allows the acceleration of the hydrolysis rate of TEOS [27]. Adding the APTES is necessary in carrying out the encapsulation process. In cases in which the APTES is not used, the microemulsion remains transparent and no solid precipitation is revealed even if the solution is aged for several days. In the current work, different amounts of APTES from 1.5 to 3 mol% relative to the W phase solution were added into the microemulsion solution at 50 °C. The resulting microspheres are shown in Fig. 4. As can be seen, the particle sizes are inhomogeneous and some extremely large particles can be observed when APTES is controlled at 1.5 mol%, as shown in Fig. 4a. Inhomogeneity improves by increasing the amount of APTES to 1.75 mol%, although partial agglomeration still remains, as shown in Fig. 4b. The homogeneous silica microspheres with a mean size of around 2 μm are obtained when the amount of APTES increases to 2 mol%, as shown in Fig. 4c. Nevertheless, large particles seem to reappear at an APTES adding ratio of 3 mol%, as shown in Fig. 4d. It is known that the hydrolysis rate of APTES is five times slower than that of TEOS [28]. In this case, APTES should not hydrolyze individually but only interact with hydroxyl

groups of the partially hydrolyzed TEOS or the very small amount of water from $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, which solely exists in the micelles, especially when the O phase is water free. When the quantity of APTES is sufficient to form a rigid APS layer cover the surface of all the micelles, stable microcapsules can be obtained. Otherwise, the micelles tend to coagulate in order to decrease the surface area. The amount of APTES has to be at least 2 mol% to encapsulate all micelles. If the system contains too much APTES, the excess are dissolved in the O phase; however, this might change the electrostatic state and the pH value of the microemulsion solution, resulting in the coagulation of the micelles. This phenomenon has also been observed by Bagwe et al. [29] who reported an agglomeration of APTES modified silica nanoparticles with increasing concentrations of APTES.

3.4 Temperature effect of the encapsulation process

The working temperature for the encapsulation process is also an important factor. In the current experiment, the microemulsion solutions were heated at the respective temperatures of 20, 25, 50 and 60 °C, before adding the APTES. The spheres become quite large and polydispersed upon the application of tremendous agglomeration with the

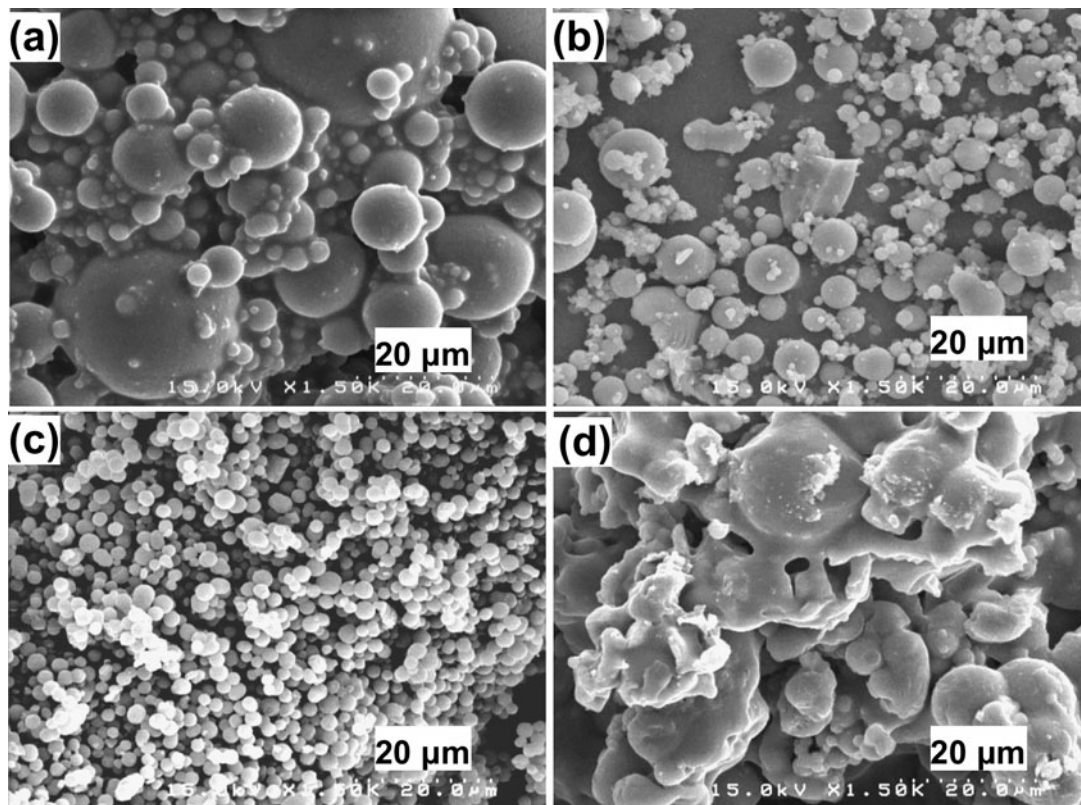


Fig. 5 SEM images of the microspheres obtained at **a** 20 °C, **b** 30 °C, **c** 50 °C and **d** 60 °C during the encapsulation process

temperature controlled at 20 °C, as shown in Fig. 5a. As the temperature increases to 30 °C, the agglomerations improve, but a fraction of the large particles still remain, as shown in Fig. 5b. The small particle sizes with a narrow size distribution are obtained at 50 °C, as shown in Fig. 5c. On the other hand, the silica microcapsules become unstable, and the spherical morphology becomes completely destroyed as the temperature further increases to 60 °C, as shown in Fig. 5d. It has been observed that the APTES forms a denser and more structured APS layer at 50 and 70 °C than that forms at room temperature [26, 30]. Besides, the hydrolysis and condensation reactions of TEOS can be also enhanced when the temperature is increased. Thus, the interaction rate between the APTES and TEOS also increases at a higher temperature. For the encapsulation carried out at 20 °C, the interaction between the APTES and TEOS is not fast enough or the as-formed APS layer is not rigid enough to immobilize the microcapsules, thus the coagulation occurs before the encapsulation is completed. The coagulation is effectively eliminated by increasing the interaction rate or by improving the structure of the APS layer at higher temperatures. Despite the good stability of the microcapsules in using the APTES at a higher temperature, the surfactant SPAN60 can still be damaged at a temperature of as high as 60 °C due to its low thermal resistance. The Span60 melts at 60 °C and the

microcapsules lose their stabilities, resulting in their complete destruction.

3.5 Stirring treatment during encapsulation process

In order to homogeneously disperse the APTES in the microemulsion solution, a stirring treatment was applied at a mild rotary speed of 330 rpm for 1 and 30 min and the SEM images of their resulting products are as illustrated in Fig. 6. It can be seen that the spheres are relatively small and monodispersed upon using the stirring treatment for only 1 min (Fig. 6a), but a great number of large spheres with sizes over 10 μm appear upon extending the stirring treatment to 30 min (Fig. 6b). This demonstrates that the stirring treatment increases the probability of the collisions between the micelles and induces an enlargement in the sphere sizes. Accordingly, the encapsulation process is better carried out at a static environment so as to obtain uniform microspheres.

3.6 Eu³⁺ doping effect

Figure 7 shows the SEM images of silica microspheres for different Eu³⁺ concentrations. The sphere size distribution is not strongly affected by the Eu³⁺ doping concentrations, and the average sphere size is around 2 μm regardless of

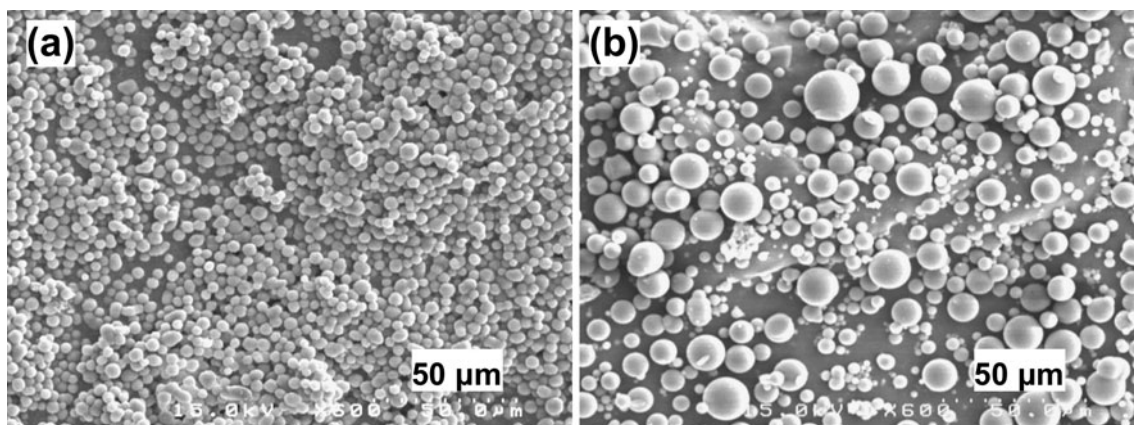


Fig. 6 SEM images of the microspheres treating with an agitation at 330 rpm for **a** 1 min and **b** 30 min when APTES was added

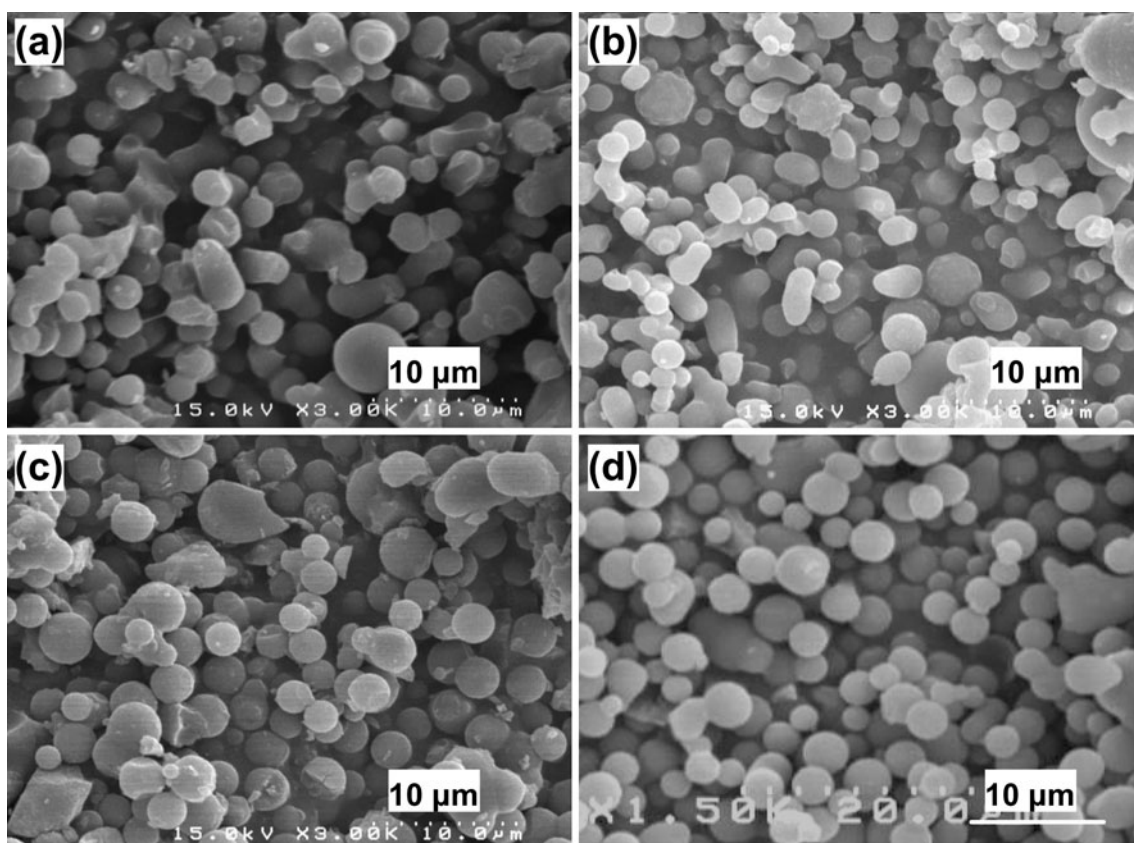


Fig. 7 SEM images of the microspheres doping with **a** 1, **b** 2, **c** 3 and **d** 6 mol% of Eu^{3+}

the doping concentration. However, a slight agglomeration in the microspheres is observed when preparing them with 1 and 2 mol% of Eu^{3+} ions, as shown in Fig. 7a, b, respectively. The homogeneity gradually improves when the doping concentrations increases to 3 and 6 mol%, as shown in Fig. 7c, d, respectively. The NO_3^- usually acts as a catalyst for the hydrolysis and condensation of TEOS, and the water ratio is also a determinant factor in controlling the hydrolysis rate for the sol–gel transition. The

addition of $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ induces a rapid hydrolysis in TEOS because white precipitation occurs when the W phase solution did not mix immediately with the O phase. In the current study, the $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ can be considered as a hydrolysis accelerator to both TEOS and APTES. For the W phase containing a higher Eu^{3+} doping concentration, the encapsulation process can be performed within a shorter period of time to avoid the agglomeration between microcapsules.

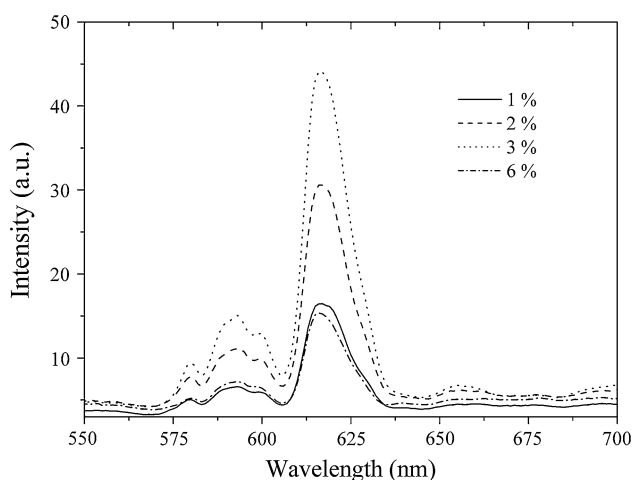


Fig. 8 Emission spectra of the microspheres doping with **a** 1, **b** 2, **c** 3 and **d** 6 mol% of Eu^{3+}

Figure 8 shows the emission spectra of Eu^{3+} doped silica microspheres for various Eu^{3+} concentrations under an excitation of 392 nm. A strong red emission is observed at 618 nm assigned to the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ transition of Eu^{3+} ions and at other weaker emission bands at 579, 586, and 655 nm relative to the other f–f transitions. As can be seen, the optical emission intensities increase when the doping concentration increases to 3 mol%. A concentration quenching occurs when the doping concentration further increases to 6 mol%. Accordingly, 3 mol% was assigned as the optimal doping concentration of Eu^{3+} in silica microspheres. Moreover, absorption and photoluminescent characterizations were performed to the filtrate in order to verify if the Eu^{3+} ions were completely captured inside the microcapsules. The results confirm that neither absorption nor no emission signals are detected from the filtrates.

4 Conclusion

Eu^{3+} -doped silica microspheres have been successfully prepared using the sol–gel microencapsulation method, through which sphere sizes with a homogeneous size distribution of around 2 μm have been obtained. The results show that several working parameters play important roles and must be carefully controlled for the morphological properties of the prepared microspheres. The collisions between the micelles have to be avoided by decreasing the W/O ratio to 0.08 in order to effectively obtain monodispersed silica microspheres. The high-speed agitation at 17,600 rpm for 1 min allows the formation of a homogeneous W/O microemulsion, whereas a higher impeller speed or a longer agitation period increases the probability of collisions. The encapsulation process, in which the amount of the APTES added and the working temperature

are the important factors, is also crucial. The quantity of the APTES is optimal at 2 mol% and is sufficient to cover the surfaces of all the micelles. A rapid interaction of the TEOS and the APTES, which can be achieved by increasing the working temperature to 50 °C and by adding a higher concentration of $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ in the W phase, has been proven to be beneficial in stabilizing the microcapsules. The Eu^{3+} ions have also been successfully encapsulated in the silica microspheres, and a strong red emission is obtained with an optimal doping concentration of 3 mol%. As can be seen in the synthesis of Eu^{3+} -doped silica microspheres, other types of inorganic salts can be incorporated in the silica microspheres using the sol–gel microencapsulation method.

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