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# Assembly of Silver Nanoparticles into Hollow Spheres Using Eu(III) Compound based on Trifluorothenoyl-Acetone

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**Abstract** The preparation of luminescent silver hollow spheres using Eu(III) compound based on trifluorothenoyl-acetone is described. The structure and size of silver hollow spheres were determined by TEM images. The result shows the formation of hollow structure and average size of the silver hollow spheres (0.9 μm). The silver hollow spheres were further characterized by UV absorption spectrum, SNOM and SEM images, suggesting them to be formed by self-assemble of some isolated silver nanoparticles. The luminescent properties of them were also investigated and they are shown to be high emission strength; moreover, they offer the distinct advantage of a lower packing density compared with other commercial luminescent products.

**Keywords** Assemble · Silver nanoparticles · Hollow · Luminescence

## Introduction

Inorganic hollow spheres of nanometer to micrometer dimensions represent an important class of materials, and are attended for wide potential applications [1], such as catalysts, fillers, coatings, and lightweight structural materials owing to their low density, large specific area, and surface permeability [2–5]. Especially, noble metal hollow spheres have attracted lots of attention for their remarkable optical properties [6, 7]. However, there are few works to report preparation of noble metal hollow spheres. Only, previous efforts to prepare noble metal hollow spheres have been focused on polymer-surfactant compels micelles [8] and using template methods [9]. The nanometer silver hollow spheres are difficult to be obtained and should be removed of the core, resulting in breaking of shell by these methods. Moreover, the functional metal hollow spheres cannot be obtained. In the design of multicompositional materials with spatially defined arrangements of the different components, block copolypeptides may be highly useful as structure-directing agents for nanoparticle assembly [10]. It is well-known that noble metals like gold and silver are capable of existing in the unoxidized state at the nanoscale and offer a unique surface chemistry that allows them to be used as platforms for self-assembly layers of organic molecules [11–14]. So, it is expected to prepare the nanometer noble metal hollow spheres by crystal self-assemble method under functional organic molecules assistant, which is easy to prepare and control. Furthermore, the hollow spheres containing functional molecules are expected to be functional properties.

So, here, a new route of synthesis silver hollow spheres is developed. The silver hollow spheres are formed by the self-assemble of silver nanoparticles assisted functional molecules of $Eu(TTA)_3 \cdot 2H_2O$. The Eu(III) organometallic compounds of $Eu(TTA)_3 \cdot 2H_2O$ as the dispersion and bridge of silver nanoparticle results in the self-assemble of them, along a certain axis in the *xy*-plane and the curl and extension of Eu(III) organometallic in a mixed

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solvent microenvironments for confining the 3D growth of silver hollow spheres. In other way, the fluorescence of silver hollow spheres is further observed, which is expected to apply in optical materials.

## Experiment Sections

### Synthesis of Rare-earth Complexes

$Eu(TTA)_3 \cdot 2H_2O$ (HTTA: trifluorothenoyl-acetone) were synthesized according to the literature [15] and the structure is shown in Scheme 1 and is confirmed by IR analysis, such as the C=O group at 1,614.5 $cm^{-1}$, $CF_3$ group at 1,357.4 $cm^{-1}$, C=C group at 1,541.8 $cm^{-1}$, and the Eu–O at 638.9 and 579.8 $cm^{-1}$. The result is consistent with previous work [15].

### Preparation of Silver Hollow Spheres

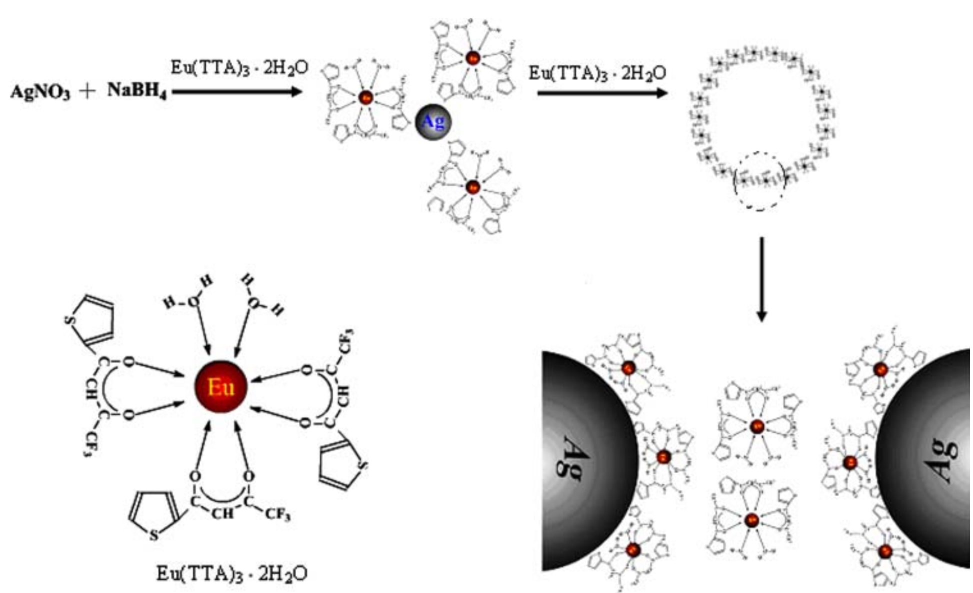
Silver hollow spheres were prepared according to the process as shown in Scheme 1. The first step is to synthesize the Ag colloidal solution in the presence of $Eu(TTA)_3 \cdot 2H_2O$ complex according to the literature [16]. The morphology and size of silver nanoparticles and the surface plasma on resonant absorption peak are determined to be sphere with an average size of 21.5 and 425.2 nm by transmission electron microscope (TEM) and UV–Vis absorption spectrum, respectively. In the second step, the silver colloidal TFH solution with a concentration of $6.34 \times 10^{-4}$ M was obtain and added to be 1 mmol free $Eu(TTA)_3 \cdot 2H_2O$ complex. After this, centrifuging (3,000 rpm) gave a brown acetone/water precipitate, and supernatant solution containing excess $Eu(TTA)_3 \cdot 2H_2O$ was extracted. The precipitates were again dissolved to acetone. The purification procedure was repeated for three times. Morphology and size of the sample was obtained by using TEM, scanning electron microscopy (SEM), and scanning near-field optical microscopy (SNOM). The samples were also characterized by UV–Vis spectroscopy and fluorescence spectroscopy.

## Results and Discussions

The silver/$Eu(TTA)_3 \cdot 2H_2O$ composite nanoparticles were prepared by the interaction between Ag nanoparticles and thiophene chromophores group of $Eu(TTA)_3 \cdot 2H_2O$, and the $CF_3$ groups of $Eu(TTA)_3 \cdot 2H_2O$ extend away from the Ag nanoparticle to provide solubility of the nanoparticles, which has been discussed in previous work [16]. So it is not discussed in detail here. It is further found that if the concentration of silver/$Eu(TTA)_3 \cdot 2H_2O$ composite nanoparticles is kept at more than $6.34 \times 10^{-4}$ M and 1 mmol free $Eu(TTA)_3 \cdot 2H_2O$ is present in the solution, silver hollow spheres are formed by self-assemble of silver/$Eu(TTA)_3 \cdot 2H_2O$ composite nanoparticles as shown in Scheme 1. Free $Eu(TTA)_3 \cdot 2H_2O$ is as bridge of silver/$Eu(TTA)_3 \cdot 2H_2O$ composite nanoparticles by the interaction between Ag nanoparticles and thiophene chromophores, too.

The formation of silver hollow spheres is determined by the TEM images as shown in Fig. 1. These spherical particles as shown in Fig. 1a have pale regions in the central parts in contrast to darks, indicating them to be hollow structure. Figure 1a further shows the size range from 0.6 to 1.5 μm and the average size is 0.9 μm. Compared with the silver hollow spheres previously

**Scheme 1** Illustration of formation of silver hollow spheres by the two-step route



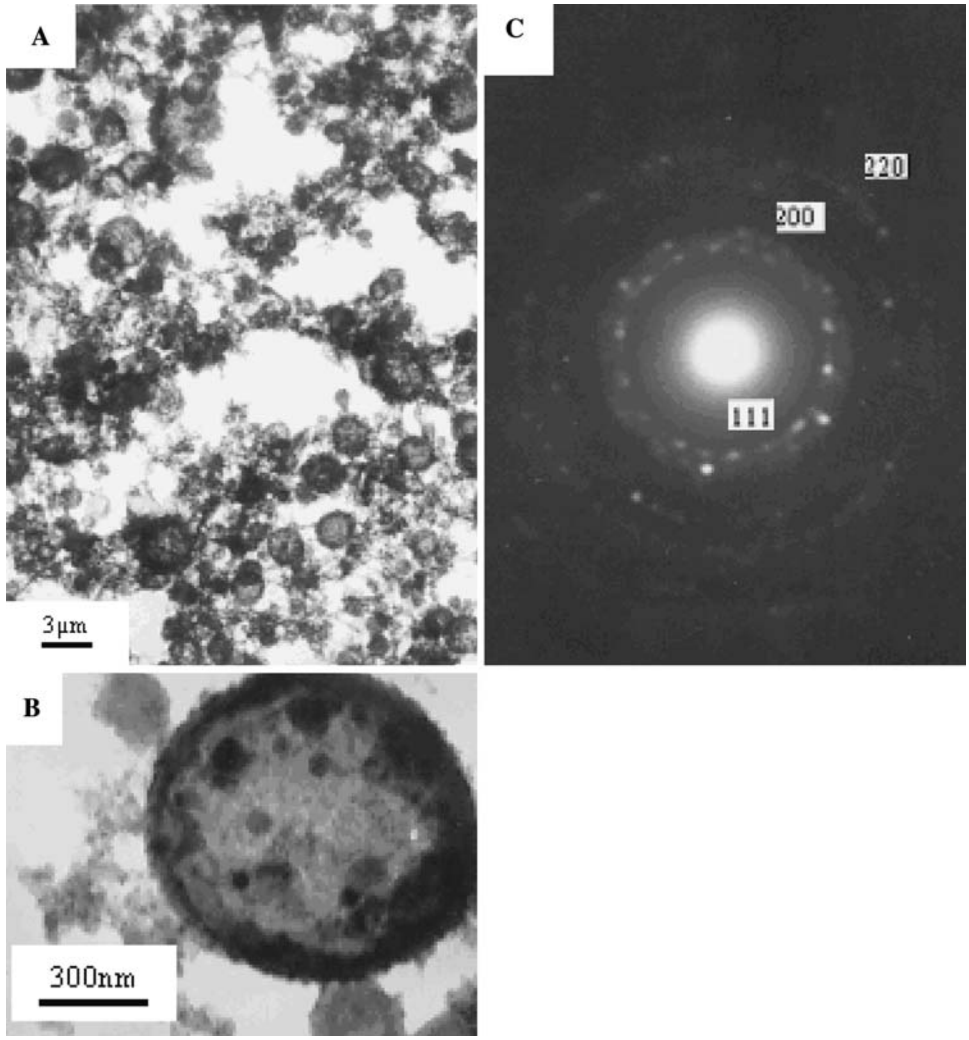



**Fig. 1** (**a**) TEM images of the silver hollow spheres, (**b**) HRTEM images of the silver hollow spheres, and (**c**) ED pattern of the silver hollow spheres

produced in template synthesis [17], the size is smaller. The shell of dark edges consists of the silver nanoparticles capped $Eu(TTA)_3 \cdot 2H_2O$ complex for assembling, and the pale regions exclude the possibility alone silver nanoparticles capped $Eu(TTA)_3 \cdot 2H_2O$ complex and free $Eu(TTA)_3 \cdot 2H_2O$ complex as shown in Fig. 1b. It also further clearly shows that uniformity shell structure of silver hollow spheres is with the shell thickness ranging from 40 to 100 nm. From the size of isolated silver nanoparticles (21.5 nm), we can determine that the shell is formed by 2–5 layers of silver nanoparticles aggregate. Typical electron diffraction pattern image of Ag nanoparticles is also shown in Fig. 1c, which shows growing parallel to (111), (200), and (220) planes of cubic silver, indicating the hollow spheres containing crystal Ag.

The UV–Vis absorption spectrum of the silver hollow spheres and pure $Eu(TTA)_3 \cdot 2H_2O$ in THF solution are compared in Fig. 2. As is well-known, the peak at 423.2 nm is the surface plasmon resonant absorption of silver nanoparticles as shown in curve B of Fig. 2, suggesting that the silver hollow spheres consisted of silver nanoparticles. The surface plasmon resonant absorption cannot be observed in previous work [17] because the silver hollow spheres are submicrometer and do not consist of silver nanoparticles. At the same time, an observation of the two curves A and B shows the almost same $\pi$–$\pi$* absorption peak (343.9 and 345.7 nm) of TTA, which is different from previous work [16, 18, 19]. The result is attributed that the additional free $Eu(TTA)_3 \cdot 2H_2O$ do not form J-aggregate and only acts as bridge between silver nanoparticles. The result further confirms that the formation of silver hollow spheres by self-assemble of Ag nanoparticles assisted with $Eu(TTA)_3 \cdot 2H_2O$.

To further confirm the formation of silver hollow spheres, the typical surface morphology of SNOM is shown in Fig. 3. Figure 3a suggests that the silver hollow spheres are an average diameter of 0.9 μm, which is consistent with the result of TEM images. The typical transmission image of SNOM of the silver hollow spheres is further

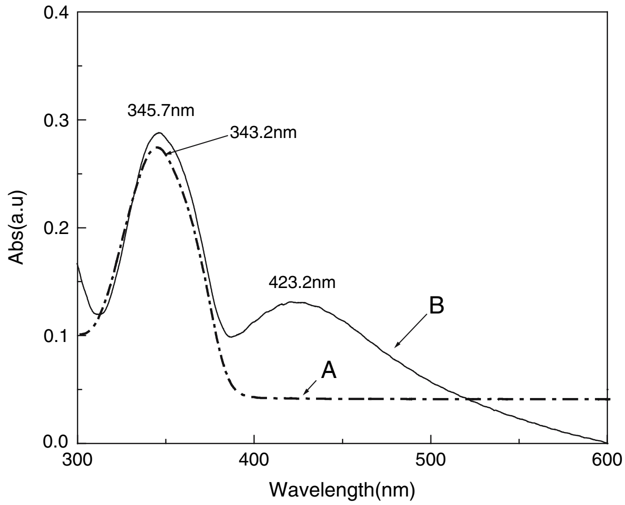



**Fig. 2** (**a**) The UV absorption of pure $Eu(TTA)_3 \cdot 2H_2O$ complexes and (**b**) silver hollow spheres in THF solution

characterized in Fig. 3b, indicating that the in-laser at 457 nm is almost absorbed for plasmon resonant absorption of silver nanoparticles. The result further confirms that the silver hollow spheres shown in Fig. 3a are attributed to the silver nanoparticles assembling.

The surface properties of silver hollow spheres are further shown in the SEM images (Fig. 4). It shows that the spheres are indeed hollow at magnification and suggests that the silver hollow spheres consist entirely of uniform silver nanoparticles in the diameter of 21.5 nm. Figure 4b also indicates that the outer surface of these silver hollow spheres is not perfectly smooth. From SEM observation the proportion of broken spheres appears to be $<1\%$ (Fig. 4a), the present silver hollow spheres are much more difficult to break, resulting from that the silver shells are much more robust compared with the metal hollow spheres produced previously in other synthesis routes [20–22].

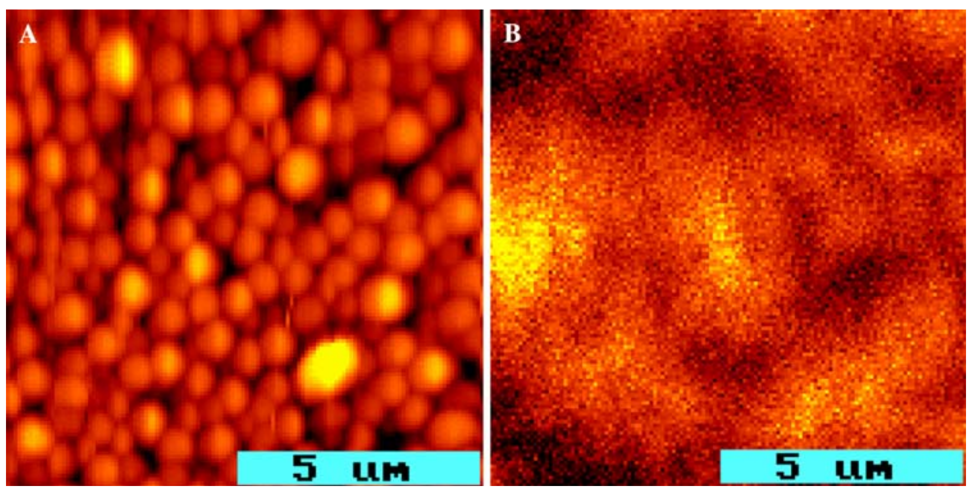



**Fig. 3** (**a**) The SNOM surface image of silver hollow spheres. (**b**) The SNOM transmittance image of silver hollow spheres

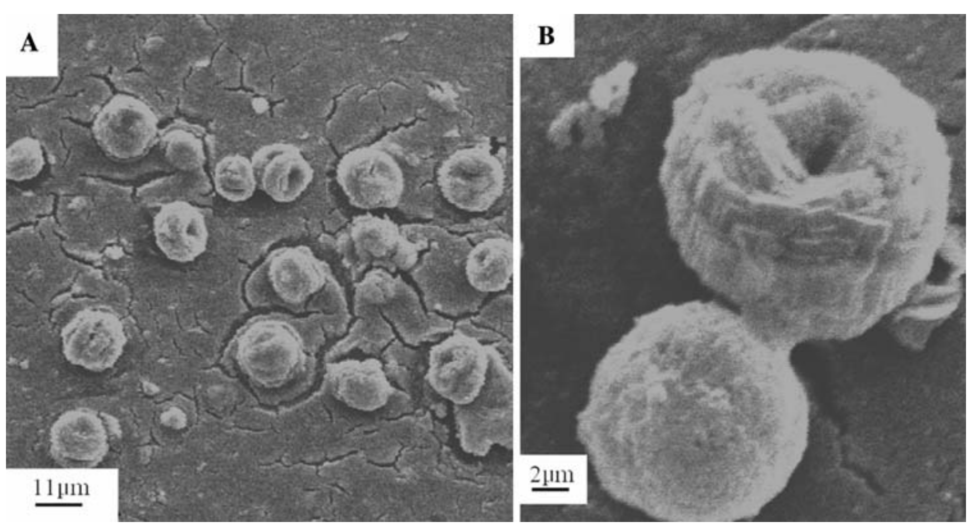



**Fig. 4** (**a**) SEM images of the silver hollow spheres and (**b**) HRFSEM images of the silver hollow spheres

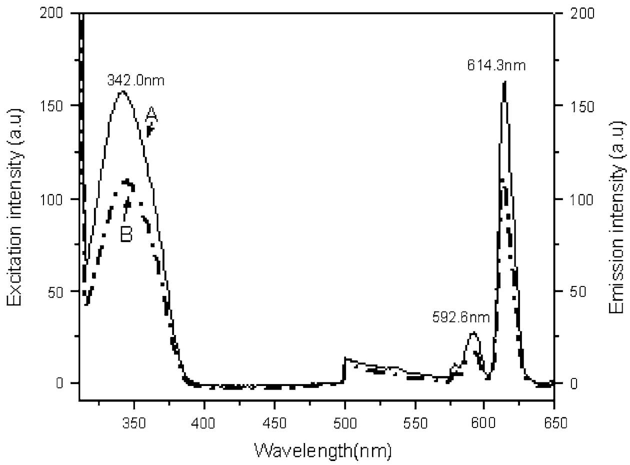



**Fig. 5** Fluorescent spectra of (**a**) pure $Eu(TTA)_3 \cdot 2H_2O$ complexes and (**b**) silver hollow spheres in THF solution

The fluorescent properties of silver hollow spheres are also investigated as shown in Fig. 5, along with pure $Eu(TTA)_3 \cdot 2H_2O$ complexes solution. The left curves show the similar excitation peak of 342.0 nm for silver hollow sphere and $Eu(TTA)_3 \cdot 2H_2O$ complex solution, which is consistent with previous work [16]. The emission spectra of silver hollow sphere and $Eu(TTA)_3 \cdot 2H_2O$ complex solution are shown in right curves of Fig. 5, too. The similar emission spectra provide the typical red luminescent peaks at 592.0 and 613.0 nm, which is attributed to $^5D_0$–$^7F_{0-1}$ transitions of Eu(III) ion, by excitation at 342.0 nm. However, the emission strength of silver hollow sphere solution is slightly lower than that of pure $Eu(TTA)_3 \cdot 2H_2O$ complexes solution. These fluorescent spectra provide value information about interactions of silver nanoparticles aggregate to silver hollow sphere. These results show that the silver hollow sphere is expected to be a new kind of fluorescent material.

## Conclusions

In conclusion, silver hollow spheres have been successfully synthesized using two-step approach. This radiation synthetic pathway provides an important example of well-ordered and functional silver hollow spheres with designed morphology. The unique silver shell structure obtained here may be promising candidates for both fundamental research and application, and it is believed that assembling synthesis based on functional molecules represents a novel route to prepare functional inorganic hollow sphere, which is a topic of intense interest. Moreover, the silver hollow spheres have high luminescent property at 614.3 nm, which is to be applied in optical materials.

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