

## A General Template for Synthesis of Hollow Microsphere with Well-Defined Structure

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**ABSTRACT:** Using chitooligosaccharides (COS) as the backbones and polycaprolactones (PCL) as the branches, a novel type of amphiphilic graft copolymers with a large amount of free —OH and —NH<sub>2</sub> groups remained on the COS backbones was synthesized. The obtained Chitooligosaccharide-graft-poly( $\epsilon$ -caprolactone)(COS-g-PCL) was self-assembled into giant vesicles which served as templates for the preparation of hollow spheres of a series of metals(Au, Ag, Cu, Pt, and Pd). The method involved the initial mixing of COS-g-PCL and metal-containing groups or metal ions to generate corresponding complex, followed by adding the selective solvent of water to induce the self-assembly of the graft copolymers into giant vesicles; Metal ions were reduced and crosslinked by a subsequent calcination procedure to form metal hollow spheres. In addition, hybrid hollow spheres with fluorescent quantum dots and silica hollow spheres were also prepared by slightly modified procedures. A preliminary study on the trinitrotoluene sensor of CdS/vesicle hybrid hollow spheres revealed a considerable sensitivity, which exemplifies the distinct properties imparted by the hybrid hollow structure. All of the results demonstrate that the giant vesicles self-assembled from COS-g-PCL could be utilized as effective templates for the synthesis of various hollow spheres. Using Chitooligosaccharide-graft-poly( $\epsilon$ -caprolactone) vesicles as general templates, the hollow spheres of a series of metals such as Au, Ag, Cu, and Pt were produced. The method involved the initial absorption of metal ions from solution into the functional surface layer of the graft copolymer giant vesicles. Metal ions were reduced and crosslinked by a subsequent calcination procedure to form metal hollow spheres. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

**KEYWORDS:** polysaccharides; self-assembly; copolymers; membranes; grafting

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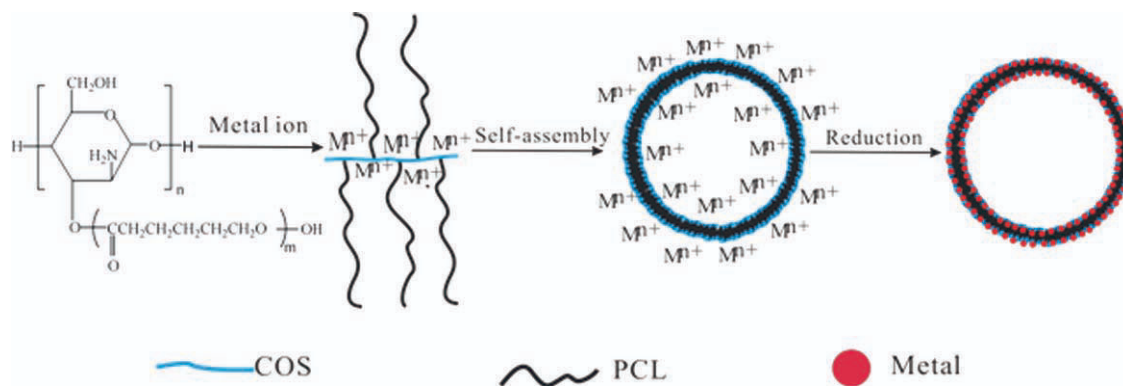
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### INTRODUCTION

The creation of hollow spheres with micrometer size and sub-micrometer size has been attracting much attention in recent years owing to their low density and large specific area. They have wide potential applications, for example, the controlled release capsules of drugs, catalysts, fillers, coatings, and lightweight structural materials.<sup>1–7</sup> Various methodologies have been developed to achieve this special structure. Template synthesis, for example, is a typical and effective route, and hard or soft templates, such as polymeric core supports, silica spheres, and liquid droplets, have been applied.<sup>8–19</sup> However, most of these template methods are based on outward growth from the surface of the template and the template cores have to be removed by diffusion through the shell of hollow spheres during the synthesis. The osmotic pressure associated with molecular diffusion may cause apertures or fragmentation on the shell. An alternative method of grow materials inwards, inside or onto the inte-

rior surface of a hollow sphere template was proposed.<sup>20</sup> In this case, it is crucial that the precursors diffuse inwards and grow onto the interior surface. For this goal, much effort has been devoted to the study and preparation of vesicles from amphiphiles. The bilayer structures of vesicles separated an aqueous interior from an aqueous exterior. The interface between the amphiphile groups and the solution presents a specific site for the growth of materials from solution. Crystal growth and solidification at the interface lead to transcriptive imprinting of the template morphology and the formation of hollow structured materials.<sup>21–23</sup>

So far, some vesicles such as dioctadecyldimethylammonium bromide,<sup>24</sup> poly(diallyldimethylammonium) chloride,<sup>25–27</sup> and mixtures of dodecyltrimethylammonium bromide and sodium dodecylbenzenesulfonate,<sup>28,29</sup> were successfully used to synthesize inorganic hollow spheres. For these vesicles self-assembled from small amphiphiles; however, the stability is still needed to



**Figure 1.** The structure of COS-g-PCL graft copolymers and the fabrication process of hybrid giant vesicles with metals. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

improve for synthesis of hollow spheres with well-defined structure.<sup>30</sup> Compared to vesicles self-assembled from small amphiphiles, vesicles from amphiphilic copolymers possessed unique properties such as good stability and broader range of accessible solvents.<sup>4</sup> This type of vesicles could be the promising candidate for synthesis of hollow spheres.

Using chitooligosaccharides (COS) as the backbones and polycaprolactones (PCL) as the branches, we recently succeeded in producing a novel type of amphiphilic graft copolymers with a large amount of free  $-\text{OH}$  and  $-\text{NH}_2$  groups remained on the COS backbones.<sup>31</sup> Self-assembly of these graft copolymers (COS-g-PCL) in 1,4-dioxane/water mixture solvent gave rise to giant vesicles with tunable size.<sup>32</sup> In these giant vesicles, every COS-g-PCL molecule is separated into a hydrophobic PCL core and a hydrophilic corona carrying  $-\text{OH}$  and  $-\text{NH}_2$  groups. These graft copolymer giant vesicles have integral and uniform surface functional layers, which made them perfect soft templates for synthesis of hollow spheres.

In this article, using the COS-g-PCL vesicles as general templates, the hollow spheres of a series of metals such as Au, Ag, Cu, and Pt were produced. By the modified procedure, the COS-g-PCL vesicles were also adopted to prepare other materials such as silica hollow spheres and quantum dot hybrids. All

of the results demonstrate that the giant vesicles self-assembled from COS-g-PCL could be used as effective general templates to synthesize various hollow spheres, as well as quantum dot hybrids materials.

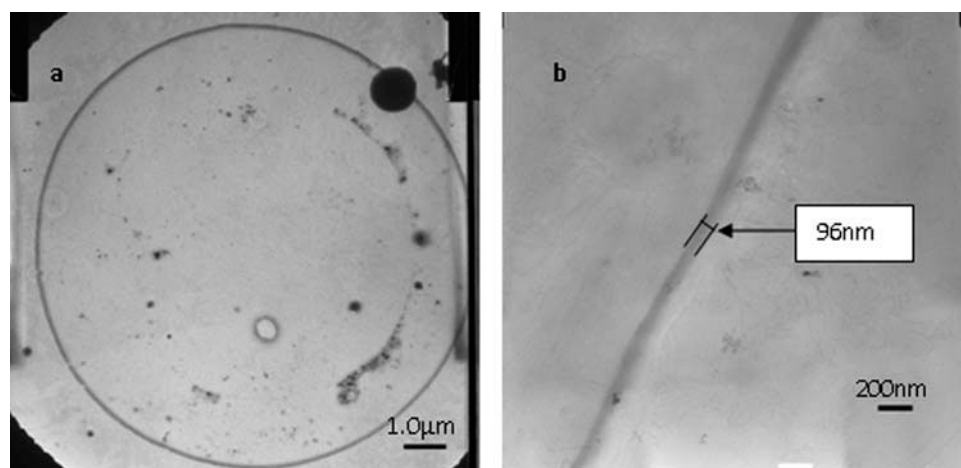
## EXPERIMENTAL

### Materials

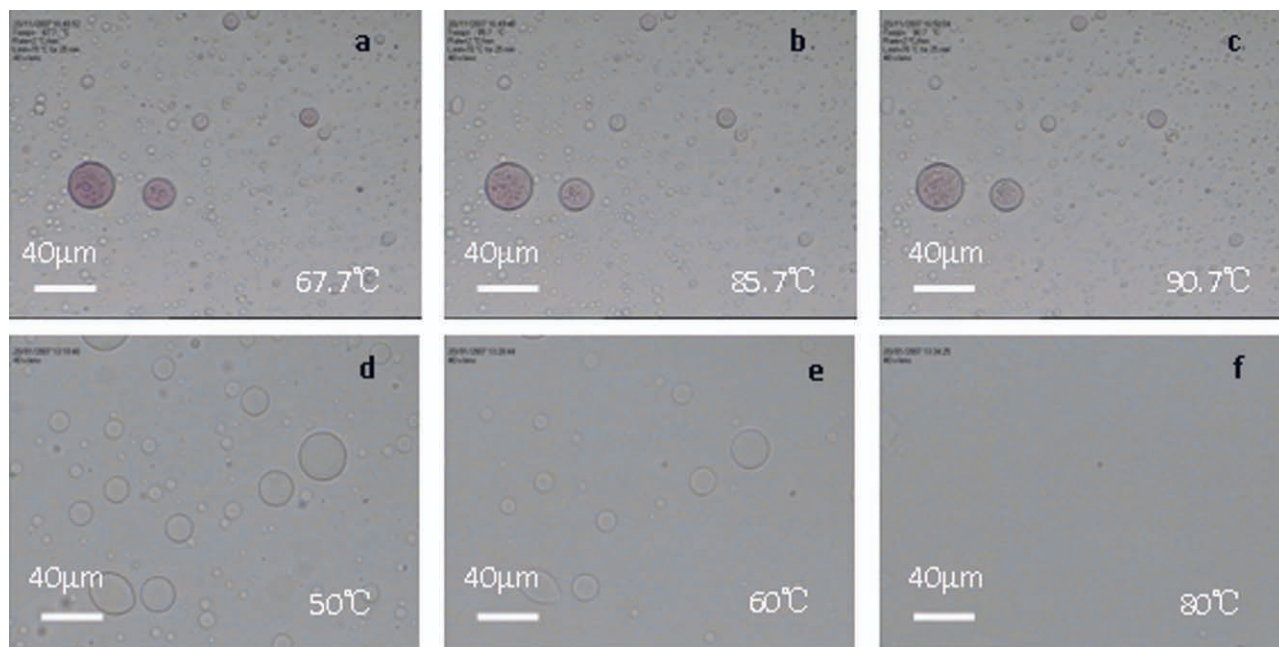
1,4-dioxane was purchased from Shanghai Guoyao Group (China).  $\text{HAuCl}_4$ ,  $\text{K}_2\text{PtCl}_6$ ,  $\text{AgNO}_3$ ,  $\text{PdCl}_4$ ,  $\text{Cu}(\text{acetate})_2$ ,  $\text{CdSO}_4$ ,  $\text{Na}_2\text{S}$ , and other reagents were used as received without further purification. Chitooligosaccharide-graft-poly( $\epsilon$ -caprolactone) (COS-g-PCL) were synthesized according to the previous literatures.<sup>31,32</sup> The number average weight of COS-g-PCL was  $1.4 \times 10^4$  g/mol determined by gel permeation chromatography (GPC). The average number of PCL chains per COS unit was 1.0. The average degree of polymerization of PCL branches grafted onto COS chain was 61 confirmed by  $^1\text{H}$  NMR.

### Preparation of Metal Hollow Spheres

Au hollow spheres were prepared as follows: 3 mL of COS-g-PCL solution in 1,4-dioxane (0.5 wt %) was mixed with 0.5 mL  $\text{HAuCl}_4$  aqueous solution (10 mM) and stirred for 30 min to obtain a mixture. 0.2 mL deionized water was added into the mixture to induce the self-assembly of COS-g-PCL into giant



**Figure 2.** a) The TEM image of vesicle containing  $\text{HAuCl}_4$ . b) The membrane of vesicle containing  $\text{HAuCl}_4$  at larger magnification.



**Figure 3.** The shapes of HAuCl<sub>4</sub>-containing vesicles (a, b, c) and pure COS-g-PCL vesicles (d, e, f) at different temperature. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

vesicles. 50 µL of the freshly KBH<sub>4</sub> aqueous solution(100 mM) was dropped into the giant vesicle suspension to reduce HAuCl<sub>4</sub> to Au atom. Finally, the Au hybrid giant vesicles were sintered at 400°C for 3 h under N<sub>2</sub> in a quartz tube for removing the COS-g-PCL to achieve Au hollow spheres.

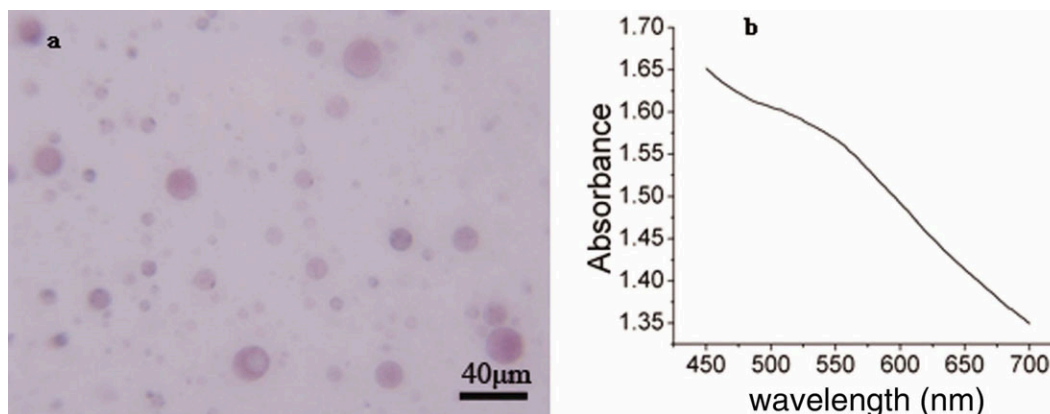
**Preparation of Silica Hollow Spheres**

For silica hollow sphere formation, 3 mL of COS-g-PCL solution in 1, 4-dioxane (0.5 wt %) was mixed with 0.5 mL HCl aqueous solution (10 mM) and dried with vortary evaporation to get thin film. The vesicles were prepared by sonication of thin films in water, which was a prerequisite for the fabrication of the silica hollow spheres. Tetraethyl orthosilicate (Merck) was then added by dropwise to the giant vesicle suspension under stirring. The amount of tetraethyl orthosilicate was adjusted to the molar ratio of 10 : 1 silica

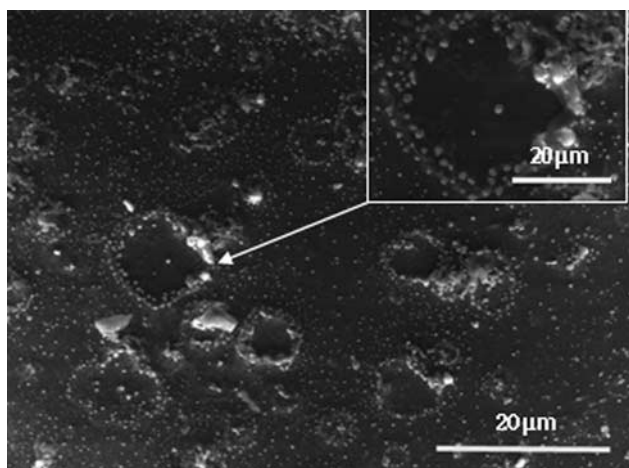
precursor to pyranose units in COS. The polycondensation reactions were stopped after 24 h at room temperature. Finally, the samples were dried by air. To remove the templates, the dried powders were calcined at 400°C in an electrically heated furnace.

**Preparation of Semiconductor/Vesicle Hybrid Hollow Spheres**

The typical CdS/vesicle hybrid hollow spheres were prepared as follows: 3 mL of COS-g-PCL solution in 1, 4-dioxane (0.5 wt %) was mixed with 0.5 mL CdSO<sub>4</sub> aqueous solution (10 mM) and stirred for 30 min to obtain a mixture. 0.2 mL deionized water was added into the mixture to induce the self-assembly of COS-g-PCL into giant vesicles. 50 µL of Na<sub>2</sub>S aqueous solution(100 mM) was dropped into the giant vesicle suspension to prepare the hybrid vesicles.



**Figure 4.** (a) The optical micrograph of Au hybrid giant vesicles appearing purple, suggesting Au colloids was originated. (b) The surface plasma of Au particle, confirming that the existence of Au colloids. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



**Figure 5.** The SEM of the fragment of Au hollow spheres after calcinations at 400°C. The inset shows the fragment at larger magnification.

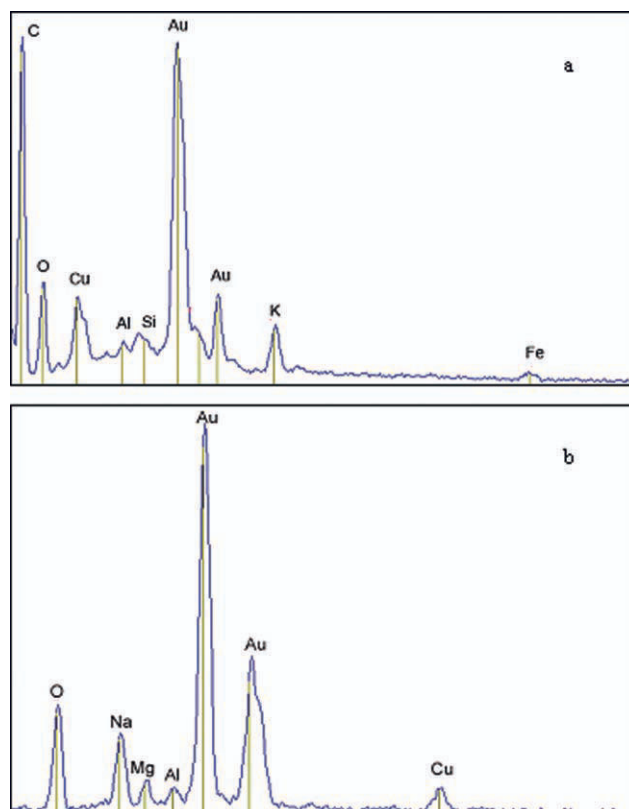
### Characterization

The scanning electron microscope (SEM) images were recorded with model XL30 ESEM FEG from Micro FEI Philips at room temperature. Transferring electron microscopy (TEM) was performed on a JEOL JEM-1200 electron microscope at an acceleration voltage of 120KV. Fluorescence images were recorded using the microscopy (Olympus BX 51, Olympus Optical, Tokyo, Japan) with 330–380 nm excitation wavelength. Images were recorded with a digital CCD camera interfaced to a computer, and operated by the software provided by the camera manufacturer. Fluorescence spectra were collected on a Perkin Elmer instrument (LS-55) using 260 nm excitation. UV-vis absorption spectra were recorded on a Lambda 35 UV-vis spectrophotometer by scanning the solution in a 1 cm quartz cell.

## RESULTS AND DISCUSSION

### Preparation of Metal Hollow Spheres

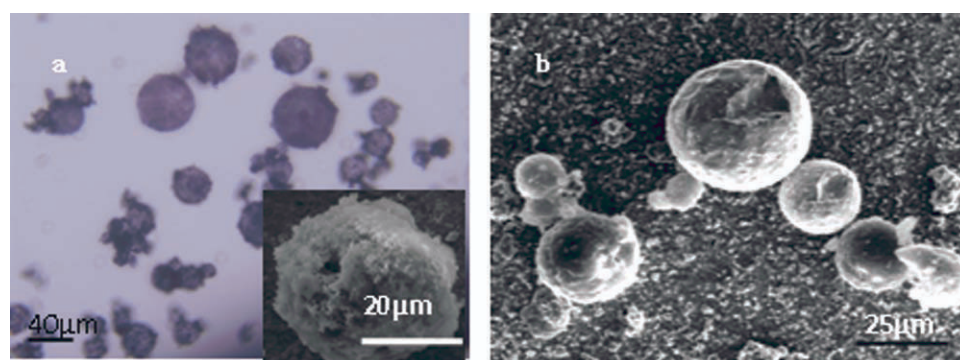
It is known that COS possessing —OH and —NH<sub>2</sub> groups has a strong affinity to metal cations through coordination or electrostatic interaction. Taking this in mind, the graft copolymer was firstly mixed with metal-containing groups or metal cations to generate corresponding complex, followed by adding the selective solvent of water to induce the self-assembly of the graft



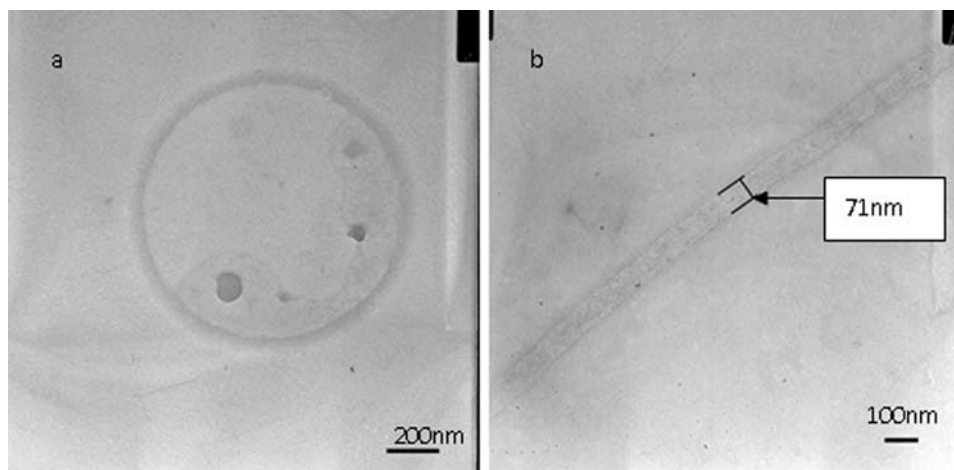
**Figure 7.** Electron dispersion spectroscopy of Au hybrid vesicle (a) and Au hollow sphere (b). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

copolymers into giant vesicles. After the formation of giant vesicles containing metal ion, the freshly prepared KBH<sub>4</sub> aqueous solution was added into the giant vesicle suspension. The metal ions located on the exterior and interior surface of giant vesicles were reduced simultaneously to obtain metal hybrid giant vesicles. The mentioned procedure was illustrated in Figure 1. To achieve metal hollow spheres, the obtained hybrid giant vesicles were required to be sintered at 400°C for 3 h under N<sub>2</sub> in a quartz tube to remove the templates of vesicles.

When COS-g-PCL mixed with HAuCl<sub>4</sub>, the HAuCl<sub>4</sub>-containing vesicles were obtained. In the presence of Au element, the



**Figure 6.** (a) The optical micrograph of Au hybrid vesicles prepared with a large excess of HAuCl<sub>4</sub>. The inset is the SEM image of Au hybrid vesicle. (b) The Au hollow spheres obtained at sinter of 400°C. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 8.** (a) The TEM image of vesicle containing copper ions. (b) The membrane of vesicle containing copper ions at larger magnification.

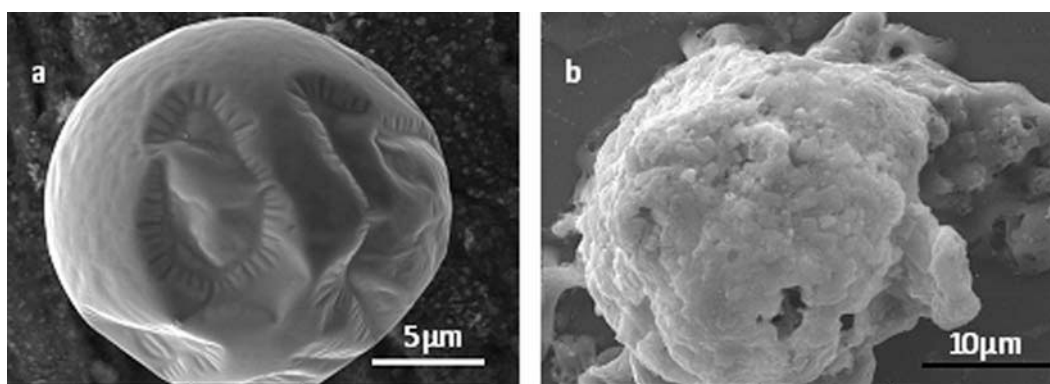
scanning electron microscope (SEM) pictures of vesicles were taken without other staining reagents. The dark parts in the scanning electron microscope (SEM) pictures are Au element-containing section of vesicles. As shown in Figure 2, Au element was distributed evenly across the membrane of vesicle. Compared to the vesicles without  $\text{HAuCl}_4$ , the membrane thickness of vesicle was increased from 23 nm to 96 nm<sup>32</sup> [Figure 2(b)]. This indicated that the membranes of vesicles had transformed from bilayer structure to four-layer structure.<sup>32</sup> As a result, the stability of COS-g-PCL vesicles was enhanced greatly. As shown in Figure 3, the shapes of  $\text{HAuCl}_4$ -containing vesicles keep intact at higher temperature while the pure COS-g-PCL vesicles gradually dissolve in 1, 4-dioxane/water mixtures at temperature above 60°C. With the stable giant vesicles, Au particles can be easily prepared *in situ* on the membranes of vesicles without fragmentation. Figure 4(a) showed that the optical micrograph of Au hybrid giant vesicles which was obtained by adding  $\text{KBH}_4$  aqueous solution. The Au hybrid giant vesicles appear purple, suggesting Au particles were originated. Figure 4(b) demonstrated the surface plasma of Au particles with absorption peak at 540 nm was existed.

In the experiments, when the relative lower content of  $\text{HAuCl}_4$  was presented in the vesicle suspension, the obtained Au particles packed loosely in the bilayer of vesicles. They would collapse during the course of calcination. Figure 5 exhibited the

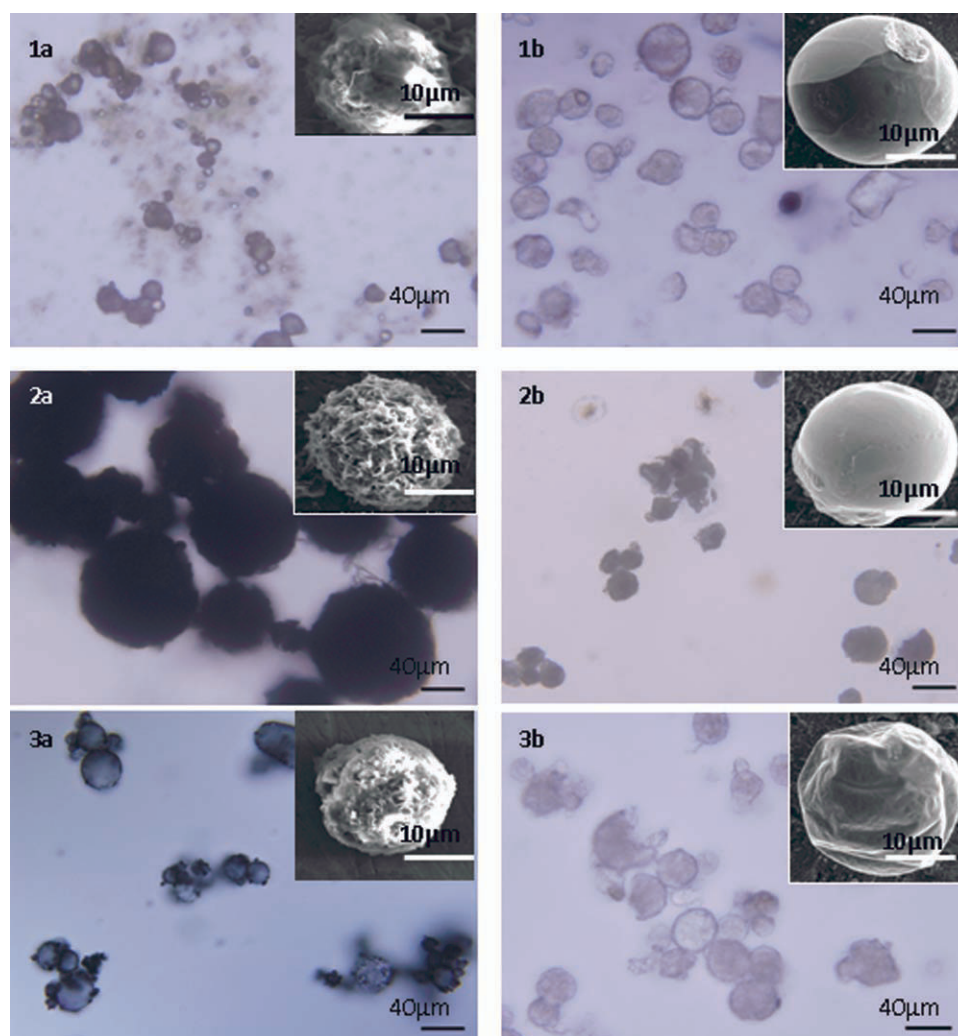
scanning electron microscope (SEM) of fragment of Au hollow spheres after calcinations. It was found that the Au particles are located evenly on the interior and exterior surface of spheres, suggesting that  $\text{KBH}_4$  could penetrate the vesicle membranes and reacted with  $\text{HAuCl}_4$  which was anchored on the membrane interior of vesicles.

In order to obtain perfect Au hollow spheres, it is needed to increase the content of  $\text{HAuCl}_4$ . At higher content of  $\text{HAuCl}_4$  in vesicle suspension, it was found that most of the  $\text{HAuCl}_4$  could also be reduced by  $\text{KBH}_4$  to Au particles on the membranes of vesicles, only accompanied by a small amount of Au particles in suspension. This indicated that excess of  $\text{HAuCl}_4$  can be reduced and grow on the membranes of vesicles with the initially formed Au nanoparticles as seed. The images of the Au metal hybrid vesicle in suspension with higher content of  $\text{HAuCl}_4$  and the sintered Au metal hollow spheres at 400°C were given in Figure 6. Electron dispersion spectroscopy was used to ascertain the chemical identity of the corresponding vesicles (Figure 7). It was found that C atoms were almost removed by sinter at 400°C, suggesting that the templates of COS-g-PCL vesicles were removed and Au hollow spheres were obtained.

With the same method, copper acetate solution was introduced instead of  $\text{HAuCl}_4$ . The SEM pictures of copper ion-containing vesicles were shown in Figure 8. Unlike  $\text{HAuCl}_4$ -containing



**Figure 9.** The SEM images of hollow spheres made from Cu metal (a) and Au metal (b)



**Figure 10.** Representative optical micrograph of various metal hybrid vesicles and their corresponding metal hollow spheres. (1 a, 1 b) Ag hybrid vesicles and Ag hollow spheres; (2 a, 2 b) Pd hybrid vesicles and Pd hollow spheres; (3 a, 3 b) Pt hybrid vesicles and Pt hollow spheres. The insets in all pictures show the corresponding images of scanning electron microscope (SEM). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

vesicles, the membrane thickness of vesicle was increased from 23 nm<sup>32</sup> to 71 nm [Figure 8(b)], suggesting vesicles were changed from bilayer structure<sup>32</sup> to three-layer structure. Furthermore, the obtained Cu metal hollow spheres were different from the Au metal spheres. The Cu metal hollow spheres were made of smooth film [Figure 9(a)], while the Au metal spheres were made of Au particles [Figure 9(b)].

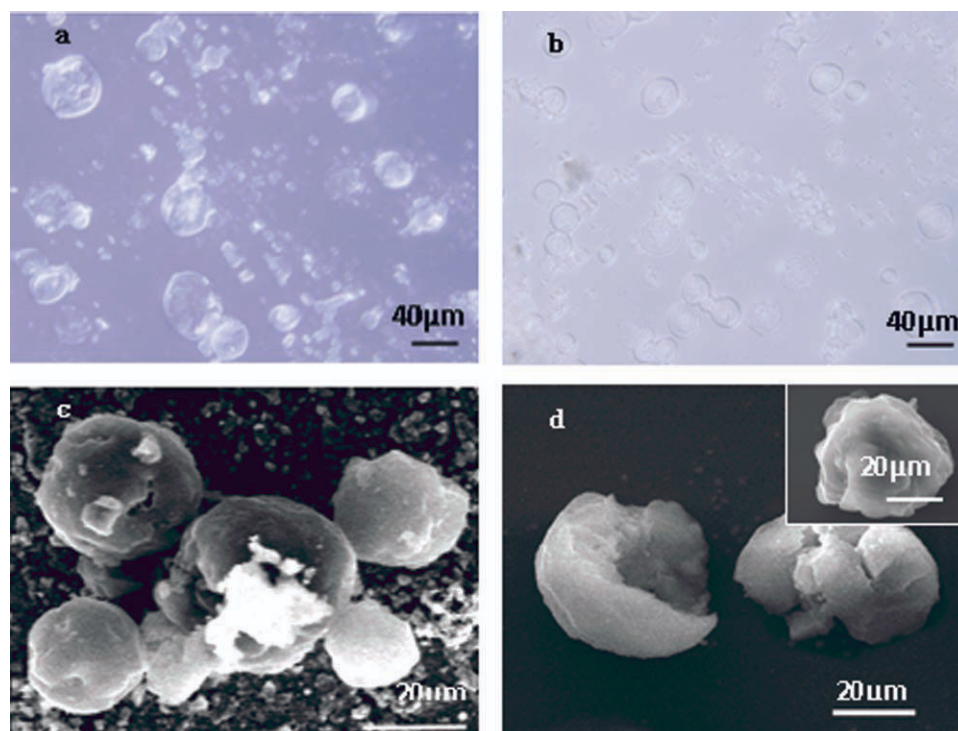
Accordingly, various metal hybrid vesicles could be prepared easily using the different metal-containing reagents such as silver nitrate, palladium chloride, potassium chloroplatinate. Figure 10 show the optical micrograph of these metal hybrid vesicles obtained by addition of KBH<sub>4</sub> aqueous solution and metal hollow spheres obtained by sinter, with the inset of scanning electron microscope (SEM) pictures. The differences among these metal spheres are under investigation and would be reported later.

#### Preparation of Silica Hollow Spheres

Recently, it was demonstrated that synthetic and biological polymers that contain secondary and tertiary amino groups

within the chain, or primary amino functions on the side groups, are capable of catalyzing the formation of silica spheres with diameters ranging from 50 to 400 nm.<sup>33–36</sup> There are many of —NH<sub>2</sub> groups on the membrane of COS-g-PCL vesicles. These groups could be utilized to catalyze the hydrolysis of tetraethyl orthosilicate to obtain silica. So, the COS-g-PCL vesicles can be used as templates for silica hollow spheres. Figure 11 showed the optical micrograph and scanning electron microscope (SEM) images of silica spheres in the presence of COS-g-PCL vesicles and silica spheres after sintered at 400°C. The silica spheres exhibited diameter from 20–60 μm. The fragment of silica spheres shows that they have a hollow core [Figure 11(d)]. It therefore confirmed that COS-g-PCL vesicles were acting as templates for the formation of silica spheres.

Previous investigation on the catalytic role of macromolecules, such as poly(allylamine) or poly(lysine), showed that these polymers are cationically charged in aqueous systems at neutral pH.<sup>37</sup> In our case, this catalyzed template leads to multilayer silica structure at ambient conditions [the inset of Figure



**Figure 11.** The optical micrograph and SEM images of silica hybrid vesicles and silica hollow spheres. (a) the optical micrograph of silica hybrid vesicles; (b) the optical micrograph of silica hollow spheres; (c) SEM images of silica hollow spheres; (d) the fragment of silica hollow spheres. The inset in image d shows the multilayer structure of silica hollow spheres. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

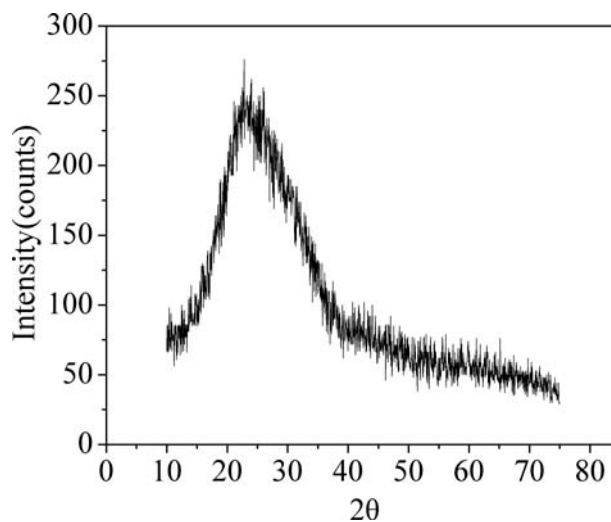
11(d)], avoiding either strong alkaline conditions or high temperature in common processing technology.<sup>38</sup> The observed layered structures of the spheres did not necessarily represent crystallinity of the silica, because the observed X-ray diffraction (XRD) patterns did not exhibit the strict peak one would expect for crystals (Figure 12). As for the multilayered structure, we could not give feasible mechanism.

#### Preparation of Semiconductor/Vesicle Hybrid Hollow Spheres

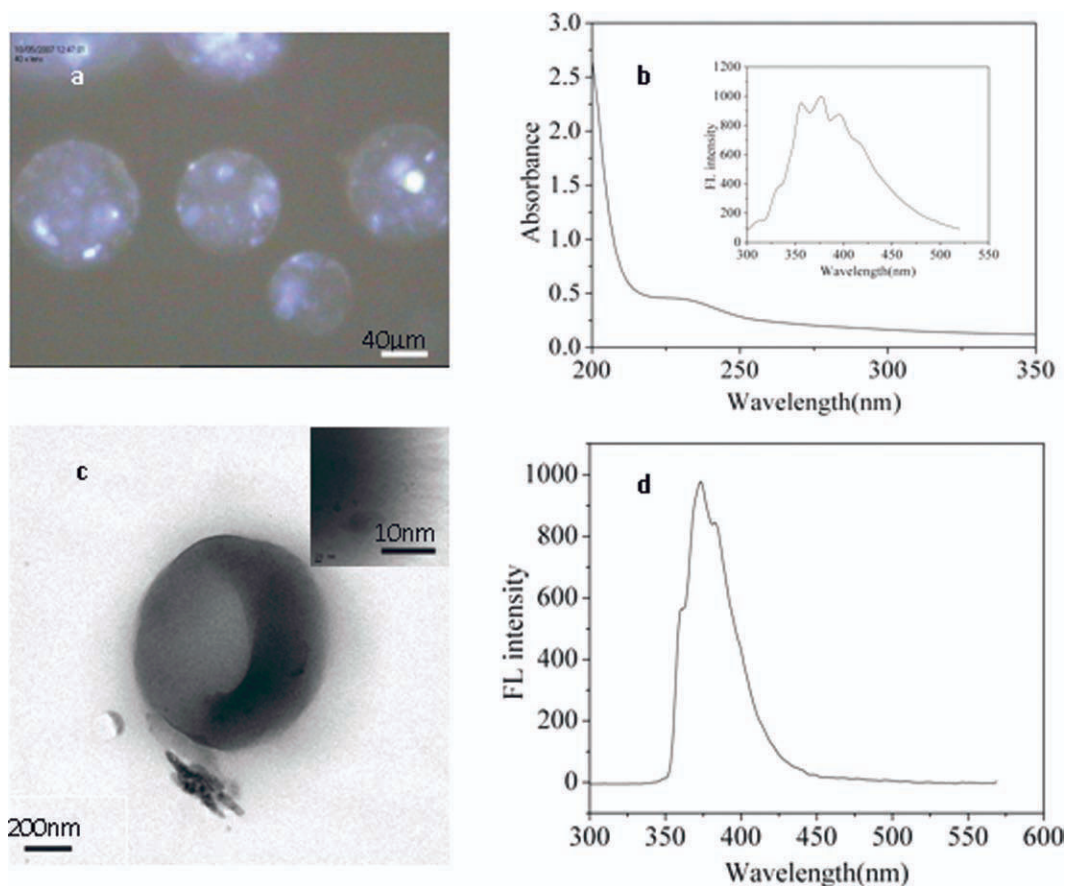
Semiconductor nanocrystals and quantum dots (QDs) have also attracted great interest from the biological and medical communities.<sup>39–45</sup> Compared with conventional organic fluorophores (e.g., typical organic chromophores), QDs have high luminescence, high resistance to photobleaching, narrow spectral line widths, and tunable emissions that can be excited using a single wavelength.<sup>46,47</sup>

CdS/vesicle hybrid was prepared by dropwise addition of  $S^{2+}$  [10 mM  $Na_2S$ ] to vesicle suspension containing  $Cd^{2+}$  cations. Figure 13 gave the results of CdS/vesicle hybrid obtained. In Figure 13(a), Blue images were observed by fluorescence microscopy. In Figure 13(b), the absorption and luminescence spectra were recorded for the CdS/vesicle hybrid at 25°C. A significant absorption of UV light at 230 nm was revealed with a 285 nm blue-shift when compared with the characteristic absorption of the corresponding band-gap of bulk CdS (515 nm), reflecting the quantum confinement effect of the CdS nanocrystal. As the size of the particles was directly related to the absorption wavelength due to the size quantization effect,<sup>48</sup> the diameter of the individual CdS particles was estimated to be about 0.7 nm

based on the effective-mass approximation. Upon excitation with light at a wavelength of 230 nm, the CdS/vesicle hybrid exhibited photoluminescence with a maximum emission at around 377 nm [Figure 13(b) inset]. This emission peak was assigned to the deep-trap combination in the CdS nanoparticles and was further indicative of the quantum size effect.<sup>49</sup> The small clusters was shifted so strongly to higher photon energies that the photoexcited electron was in a state close to the ionization threshold. In this size regime, the nature of the optical



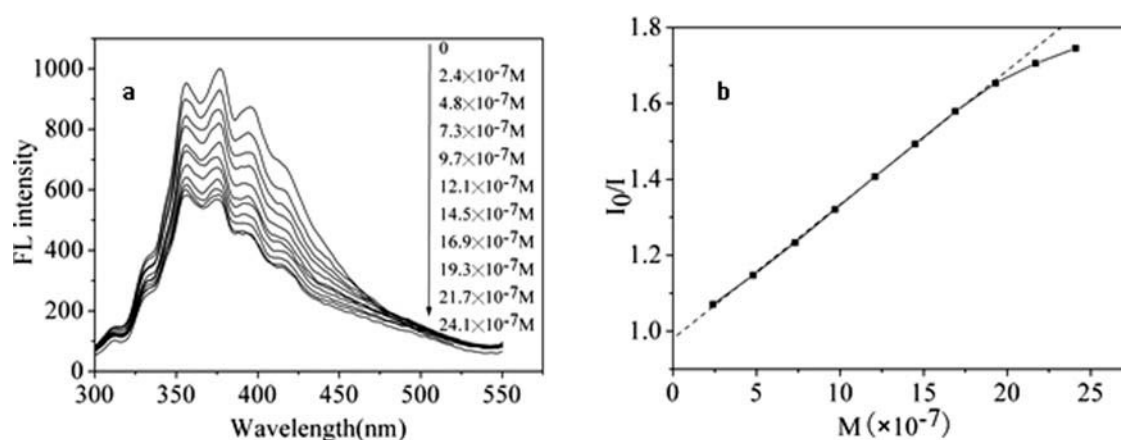
**Figure 12.** X-ray diffraction spectra of silica hollow spheres.



**Figure 13.** (a) Fluorescence images recorded by microscopy with 330–380 nm excitation wavelength; (b) UV absorbance spectra of CdS/vesicle hybrid. The inset shows the photoluminescence emission spectra which excited at 230 nm; (c) TEM image of CdS/vesicle hybrid. The inset shows the portion at larger magnification; (d) Fluorescence emission spectra of the destroyed CdS/vesicle in 1, 4-dioxane, which excited at 230 nm. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

transition should, gradually, change from excitonic excitations to charge-transfer transitions. Thus, a change of the chemical environment/solvent should strongly influence the spectral position of the absorption band, as it is known to occur in molecular photochemistry. In the vesicle, the interior of vesicle offered

a different environment from the exterior, resulting in the two dominate peaks of fluorescence emission spectra which were located at 362 nm and 375 nm, respectively. To verify this, CdS/vesicle suspension was dissolved in a great excess of 1, 4-dioxane and only one dominate peak (375 nm) was found because of



**Figure 14.** (a) The fluorescence intensity dependence of CdS/vesicle hybrid on the concentration of TNT; (b) Stern-volmer plot for the quenching by TNT of CdS/vesicle hybrid emitting at wavelength of 370 nm.



the destroying of different environment [Figure 13(d)]. These small clusters possessed too few atoms to define a core crystal structure the diffractograms of CdS/vesicle hybrid exhibit only very broad diffraction peaks from which a clear identification of the crystalline structure is, obviously, not possible and it is rather difficult for TEM to reliably determine the shape. [Figure 13(c)] But, from TEM pictures, it can be seen that the CdS clusters are distributed evenly on the shell of vesicles.

We examined the ability of the CdS/vesicle hybrid to detect soluble trinitrotoluene (TNT). With CdS/vesicle hybrid suspension as sensor in water, the fluorescence was monitored upon addition of TNT at increasing concentration. Figure 14(a) shows a typical experiment examining changes in the fluorescence intensity of 370 nm emitting clusters with increasing concentrations of added TNT. The data show a progressive concentration-dependent loss with increasing TNT concentration. The Stern-Volmer plots obtained for the quenching processes were linear within the range of TNT concentrations from  $2.5 \times 10^{-7}$  to  $2 \times 10^{-6}$ M, as shown in Figure 14(b). The results proved the ability of the designed CdS/vesicle hybrid to function as an effective sensor.

## CONCLUSIONS

In summary, a general method for the synthesis of hollow spheres has been developed using graft copolymer giant vesicles prepared from chito oligosaccharide-graft-poly( $\epsilon$ -caprolactone). Hollow spheres of a series of metals (Au, Cu, Ag, Pt, and Pd) were prepared in this way. The method involved the initial mixing of COS-g-PCL and metal-containing groups or metal cations to generate corresponding complex, followed by adding the selective solvent of water to induce the self-assembly of the graft copolymers into giant vesicles; these were then reduced and crosslinked in a subsequent calcination procedure to form metal hollow spheres. The type of graft copolymer giant vesicle used as templates had integral and uniform surface functional layers, which made surface modification unnecessary and ensured homogeneity of the membranes. In addition, fluorescent quantum dots hybrid giant vesicles and hollow spheres of silica were also prepared by slightly modified procedures. All of the results demonstrated that the giant vesicles with surface functional layers could be used as an effective template to synthesize various hollow microspheres. A preliminary study on the TNT sensor of CdS/vesicle hybrid hollow spheres revealed a considerable sensitivity, which exemplifies the distinct properties imparted by the hybrid hollow structure.

## ACKNOWLEDGMENTS

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