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Novel Method for the Preparation of Polymeric Hollow Nanospheres Containing Silver Cores with Different Sizes

Daming Cheng, Xuedong Zhou, Haibing Xia, and
Hardy Sze On Chan*

Department of Chemistry, National University of Singapore,
3 Science Drive 3, Singapore, 117 543

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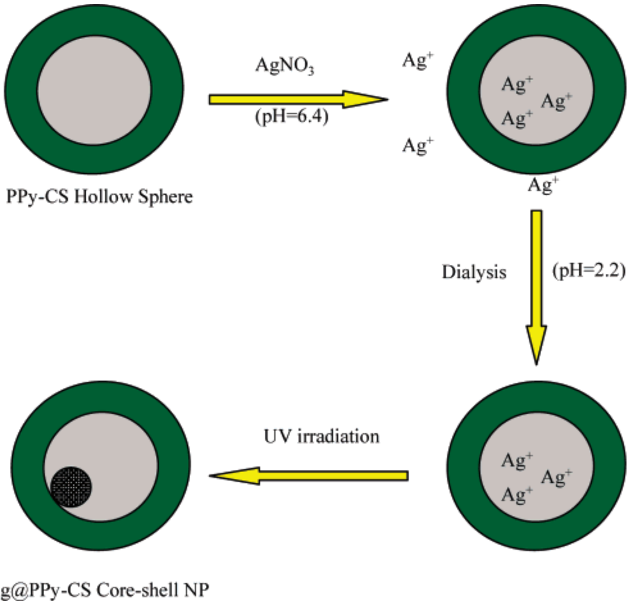
Recently, polymeric hollow nanospheres have attracted considerable research attention due to their large variety of applications in chemistry, biotechnology, and materials science.[1] The advantages of polymeric hollow nanosphere include its encapsulation property, controllable permeability, and surface functionality.[2] Many methods[3] have been developed to prepare these hollow nanostructures.

An important aspect about hollow nanospheres is that their functionalization could be achieved by encapsulating guest species, which would endow them with diverse properties. Hollow nanospheres functionalized with movable inorganic nanoparticle cores have been explored as novel nanostructures by several groups.[4] Nanoparticles such as tin, gold, or silica could be incorporated into the interior of hollow nanospheres. Novel properties can be introduced to the hollow nanospheres by this method. Lee et al.[4a] prepared Tin-encapsulated hollow carbon spheres as an anode material in lithium secondary batteries. The encapsulation of Sn nanoparticles with hollow carbon spheres improved the cycle performance of metal Sn as an anode material. Kamata et al.[4b] reported that the incorporation of Au nanoparticle as a movable core into a polymeric hollow sphere could provide an optical probe for monitoring the diffusion of chemical reagent into and out of the shell. Skirtach et al.[5] showed that, under laser illumination, the capsules containing Ag nanoparticles could be deformed or cut, thus providing a venue for remote release of encapsulated materials.

Scheme 1. Schematic Procedure for the Preparation of PPy-CS Hollow Nanospheres Containing Movable Ag Cores (Ag@PPy-CS)



The usual method for the preparation of hollow nanospheres with movable cores is based on a template-assisted approach.[4b,4c] First, the core (e.g., Au nanoparticle) particle is prepared and then it is coated with a polymeric shell. The shell is further functionalized with certain reactive groups to grow another polymer layer. With removal of the middle polymer layer using a solvent or calcination, hollow spheres with movable cores are formed. This method often needs a complicated organic synthetic technique to grow another polymer layer. It is also not convenient to control the size of the core nanoparticle.

In this communication, we describe an easy photoreduction method for producing a novel core−shell nanostructure: polypyrrole-chitosan (PPy-CS) hollow nanospheres containing movable Ag nanoparticles (Ag@PPy-CS). Compared with the usual approach, this method does not require the preparation of two polymer layers. In this method, hollow nanospheres were prepared first before the introduction of the core material. The formation of Ag core is achieved by an ultraviolet irradiation technique. No reduction reagent is needed because chitosan (one component of the PPy-CS hollow sphere) acts as the reducing reagent. The size of the Ag nanoparticles can be controlled easily by varying the concentration of AgNO$_3$. Thus, it can easily tune the optical property (surface plasmon resonance) of the core−shell nanostructure. This method affords a convenient platform for building novel core−shell nanostructures with controllable properties.

The schematic procedure to produce Ag@PPy-CS nanostructure contains three main steps which are illustrated in Scheme 1. Our approach starts from polypyrrole-chitosan

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* Corresponding author: Prof. Hardy Sze On, Chan, Telephone: (65) 6874 2833.Fax: (65) 6779 1691. E-mail: chmcsoh@nus.edu.sg.

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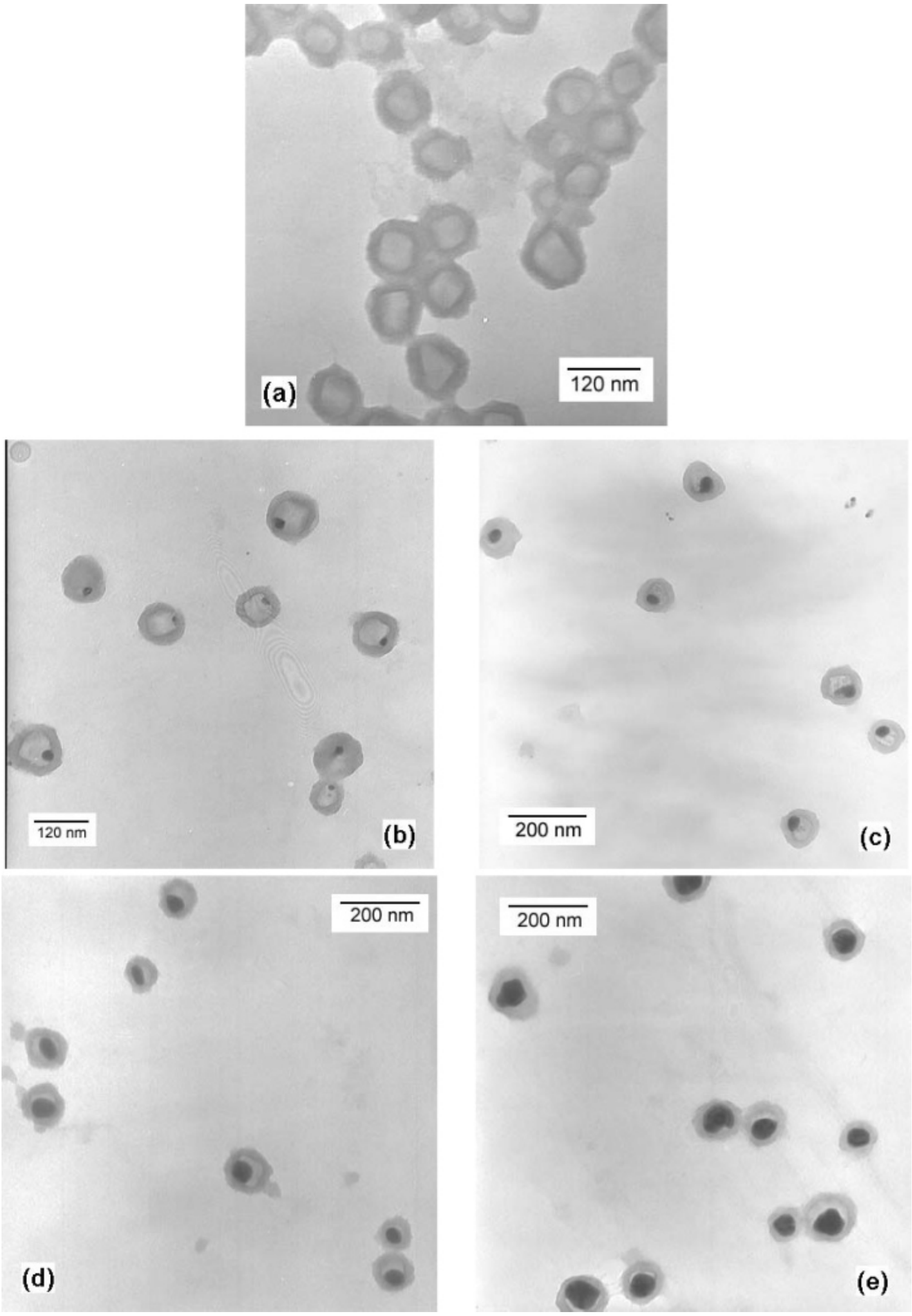

Figure 1. TEM images of (a) PPy-CS hollow nanospheres; (b) Ag@PPy-CS core−shell nanoparticles (size of Ag: 20 ± 4 nm); (c) Ag@PPy-CS core−shell nanoparticles (size of Ag: 36 ± 4 nm; (d) Ag@PPy-CS core−shell nanoparticles (size of Ag: 50 ± 6 nm); (e) Ag@PPy-CS core−shell nanoparticles (size of Ag: 60 ± 7 nm). From (b) to (e), the concentration of $AgNO_3$ solutions are 3.8×10^{-3} M, 5.7×10^{-3} M, 7.6×10^{-3} M, and 9.5×10^{-3} M, respectively.

(PPy-CS) hollow nanosphere, which is prepared according to a method reported by our group elsewhere.[6] In the first step, PPy-CS hollow nanospheres was dispersed in $AgNO_3$ solution for some time to allow Ag^+ ions to come into the interior of the hollow nanosphere. The pH of the dispersion is maintained at 6.4, at which the PPy-CS shell shows the best permeability for ions (see Supporting Information). The second step involves the removal of the unwanted Ag^+ ions outside the hollow spheres by dialysis using a membrane bag (Mw cut off: 3500). The pH of the dispersion is lowered to 2.2 before dialysis. At this pH, the PPy-CS shell shows the least permeability. The last step is the formation of Ag nanoparticle inside the PPy-CS hollow nanosphere by ultraviolet irradiation using a low-pressure mercury lamp ($\lambda = 365$ nm). Ag^+ ions are reduced to metallic Ag by the hydroxymethyl radicals generated by the photolysis of chitosan.[7]

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(6) Cheng, D.; Xia, H.; Chan, H. S. O. *Langmuir* **2004,** *20,* 9909. AgBr is used as a template to prepare PPy-CS hollow spheres. In fact, we have tried to produce Ag nanoparticles directly from the reduction of AgBr by $NaBH_4$ but it was unsuccessful as most of the Ag nanoparticles formed out of the hollow spheres. Moreover, direct conversion of AgBr nanoparticles to Ag nanoparticles by UV irradiation was attempted but it did not work.

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Figure 1 shows the TEM images of PPy-CS hollow spheres and Ag@PPy-CS core−shell nanoparticles. Figure 1a is a typical TEM image of PPy-CS hollow nanospheres. The image shows strong contrast between the dark ring and the pale center of the spherical particles, which indicates the formation of hollow structures. Most of them are spherical shape while some are less regular. The difference between the shapes of hollow nanospheres does not affect the photoreduction process. The outer diameter of the hollow nanosphere is 100 ± 15 nm while the inner diameter is about 62 ± 8 nm. Figure 1b is a TEM image of Ag@PPy-CS core−shell nanoparticles synthesized using the above approach ($AgNO_3$ concentration: 3.8×10^{-3} M). It can be seen that each Ag nanoparticle is located in the interior of each PPy-CS hollow sphere. Only a very small amount of Ag nanoparticles are observed out of the PPy-CS hollow nanospheres (less than 5%). The size of the Ag nanoparticles is about 20 ± 4 nm. The spherical shape of the hollow nanosphere is maintained after the incorporation of Ag nanoparticle. It is observed that most of the Ag nanoparticles are not located in the center of these hollow nanospheres. The Ag core tends to stick to the wall as a result of the attractive force between their surfaces. Similar phenomena have been reported by other groups.[4b,4d]

One advantage of our method is that the size of the core nanoparticles could be easily controlled. By increasing the concentration of $AgNO_3$, we can increase the size of Ag nanoparticles (Figure 1b−1e). Figure 1c shows the TEM image of Ag@PPy-CS core−shell nanoparticles with Ag size of about 36 ± 4 nm. For Figure 1d, the size of Ag nanoparticle has increased to 50 ± 6 nm. Nearly half of the interior of the hollow nanosphere is occupied by Ag nanoparticle. Further increasing the size of Ag nanoparticle (60 ± 7 nm) caused filling of nearly 90% of the interior of the hollow nanosphere.

The proposed formation mechanism of Ag nanoparticles within the hollow nanospheres can be best explained in terms of a photoreduction process.[8] The Ag^+ ions are reduced to metallic Ag by the hydroxymethyl radicals generated by the photolysis of chitosan.[7] Here chitosan acts as the reducing agent. The primary hydroxyl function of chitosan is oxidized to the carboxylate group. Primarily, the nuclei are formed with a homogeneous distribution throughout the solution. They tend to aggregate to form bigger particles and/or the remaining ions in the bulk get absorbed on the surface of already formed particles where successive reduction takes place.

Due to the interaction with the external electromagnetic field induced by light, nanometer-sized metal nanoparticles usually exhibit strong surface plasmon resonances.[9] For Ag nanoparticles, there is a surface plasmon absorption at about 400−450 nm, the position of which is dependent on factors such as particle size, shape, and dielectric properties of the surrounding media.[9b] Figure 2 shows the UV−vis absorption spectra of PPy-CS hollow nanosphere and Ag@PPy-CS core−shell nanoparticles with different sizes of Ag. Figure 2a is the UV−vis absorption spectrum of PPy-CS nanosphere. A broad band centered at 440 nm together with a high-intensity broad band in the range of 600−1100 nm confirms the presence of polypyrrole, which is in agreement with the previous report.[6] The spectra from Figure 2b to Figure 2e show the UV−vis absorption spectra of Ag@PPy-CS core−shell nanoparticles with increased size of Ag. A strong surface plasmon absorption located in the range of 400−460 nm appears at all of the spectra. As the size of Ag nanoparticle increases, the position of the plasmon absorption of Ag could shift from 399.5 to 455 nm (Figure 2b−2e). This observation is consistent with the predictions based on the Mie scattering theory.[9b,10] Due to the strong plasmon absorption of Ag nanoparticles, the absorption peaks arising from the PPy-CS polymer shell are not observed in the absorption spectra of Ag@PPy-CS core−shell nanoparticles.

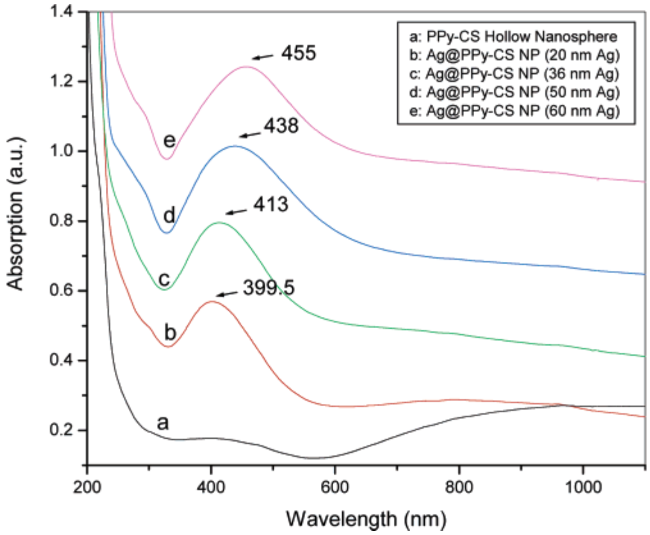

Figure 2. UV−vis absorption spectra of (a) PPy-CS hollow nanospheres; (b) Ag@PPy-CS core−shell nanoparticles (size of Ag: 20 ± 4 nm); (c) Ag@PPy-CS core−shell nanoparticles (size of Ag: 36 ± 4 nm; (d) Ag@PPy-CS core−shell nanoparticles (size of Ag: 50 ± 6 nm); (e) Ag@PPy-CS core−shell nanoparticles (size of Ag: 60 ± 7 nm).

The crystalline structures of the PPy-CS hollow nanosphere and Ag@PPy-CS core−shell nanosphere are analyzed using X-ray diffraction (XRD) (Figure 3). The XRD pattern of the PPy-CS hollow nanosphere (spectrum a) shows that there is a broad band centered at $2\theta = 26.5°$, which is consistent with the amorphous structure of PPy-CS.[6] The XRD spectrum of Ag@PPy-CS core−shell nanoparticle (size of Ag: 20 ± 4 nm) (spectrum b) shows several sharp diffraction peaks in addition to the broad peak related to PPy-CS. The sharp peaks located at $2\theta = 38.2°$, 44.3°, 64.5°, and 77.4° are assigned to (111), (200), (220), and (311) planes of the cubic structure of metallic Ag. These data are in excellent agreement with the JPCDS data (File No.: PDF# 00-001-1164). No diffraction peaks that correspond to silver halide or silver oxide are observed, which confirms that component of the core is metallic Ag.

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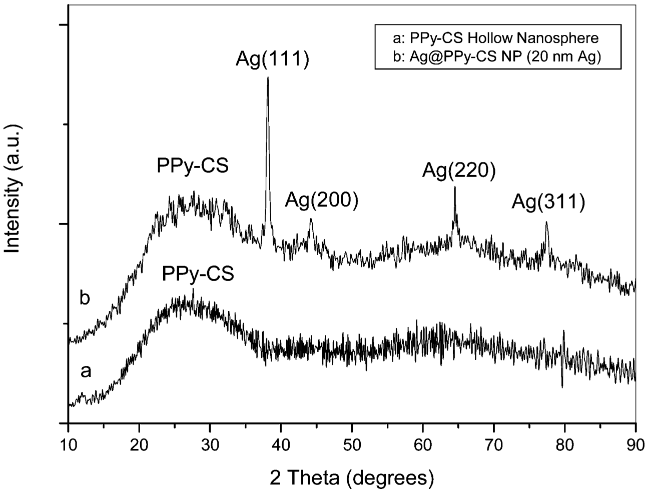

Figure 3. XRD patterns (a) PPy-CS hollow nanospheres; (b) Ag@PPy-CS core−shell nanoparticles (size of Ag: 20 ± 4 nm).

In conclusion, we present a simple but efficient photoreduction method for the synthesis of a novel nanostructure: Ag@PPy-CS core−shell nanoparticle with movable Ag core. This method has the following two characteristics: (i) core nanoparticles are formed only after the formation of the hollow spheres and (ii) formation of Ag nanoparticles is a simple one-stop photoreduction process. No additional reduction reagent is needed. Although only silver is demonstrated in this work, other light-sensitive inorganic materials (e.g., Au, CdS, or TiO_2) can also be incorporated into the interior of the hollow nanospheres. The surface plasmon absorption of Ag@PPy-CS core−shell nanoparticle could be tuned in the range of 399.5−455 nm by simply changing the size of Ag nanoparticles. This novel core−shell nanostructure may find application as a new drug delivery system. We are currently developing smart laser-responsive carrier systems[11] based on this novel core−shell nanostructure.

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Supporting Information Available: Preparation and characterization of the PPy-CS hollow nanospheres and Ag@PPy-CS core-shell nanoparticles and measurement of the permeability of the PPy-CS shell (PDF). This material is available free of charge via the Internet at http:// pubs.acs.org.

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