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RESEARCH ARTICLE

"WORM-LIKE" SILICA SYNTHESIS AND ITS SHAPE CONTROL

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ABSTRACT

The research on synthesis of hollow silica structures in the nanoscale has flourished in recent years because of their importance in the development of catalysis1 and biomedical applications2. In this work, a novel "worm-like" silica nanostructure holding Ag particle and nanocavities in the same shell was first reported. Studies on this interesting structure discovered a facile one-pot method to construct cavities-containing silica nanostructure using Ag+ salt and ligand 11-MUA. Variation of the key reaction factors such as metal salt, thiol ligand, water concentration and TEOS hydrolysis rate, along with the characterization experiments on the initial Ag+/11-MUA composite implied that a metal ion/thiol ligand coordination polymer had formed under the experimental condition. Furthermore, the unstable coordination polymer could possibly act as the template for silica coating/growth. This new method is significant as it does not require any complicated pre-synthesis or post-treatment procedures. Beside the potential applications of the cavity structure, combination with Ag NP in the "worm-like" nanocomposite may provide new opportunity for hybrid nanostructure development.

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INTRODUCTION

The synthesis of hollow nanostructures has been of great interest in the field of chemistry and biomedical research. These hollow nanostructures have large surface area which can be further modified by attaching fluorescent labels or selective ligands. This property is especially valuable for their potential applications in optical imaging (Chen *et al.,* 2005), catalysis (Tanev *et al.,* 1994), and selective separation (Darbandi *et al.,* 2007). The nano-sized cavity and shell permeability also make them promising candidates for use in drug delivery and controlled release (Yang *et al.,* 2008). Among the various materials for construction of hollow nanostructures, silica has attracted extensive attention due to its high biocompatibility, ease of colloidal formation and surface functionalization ability. The most widely employed approach to synthesize hollow silica nanostructures typically involves the use of a template, which acts as a structure-directing agent for silica growth, and is usually removed by post-treatment (Yang *et al.,* 2011). For example, Mulvaney and co-workers have observed hollow silica sphere by oxidation of gold in Au@SiO_2 particle by cyanide ion (Giersig *et al.,* 1997).

Haam *et al.* have prepared silica-coated magnetic assemblies made from Fe_3O_4 and surfactant, and then treatment with hydrochloric acid and calcinations at 300°C can remove the template and result in hollow silica nanocontainers (Yang *et al.,* 2008). Organic polymers have also been exploited as templating agent. One such case was reported by Wu's group using pre-made polystyrene. Interestingly, the polystyrene core can be dissolved away by increasing the amount of ammonia during tetraethoxysilane (TEOS) hydrolysis, thus the formation of silica shell and the elimination of template can progress simultaneously (Chen *et al.,* 2006). Moreover, silica nanotubes can be made from different types of templates, and even transcribed from biological molecules like DNA (Okamoto *et al.,* 2004) and tobacco mosaic virus (TMV) (Royston *et al.,* 2006). However, the synthetic strategies mentioned above generally requires multi-steps, including preparation and functionalizing of template materials, deposition of silica to form core-shell structure, and removing of the template. The post-treatment process could also be inconvenient and time-consuming, which normally needs control of pH value, delicate choice of selective solvent or calcinations at high temperature.

Here, a "worm-like" structure which contains one silver nanoparticle and near-linear arranged cavities was first obtained. Further investigation revealed a facile route to synthesize silica nanostructure with cavities in a one-pot manner utilizing silver salts and 11-mercaptoundenoic acid (11-MUA) as shown in scheme 1.

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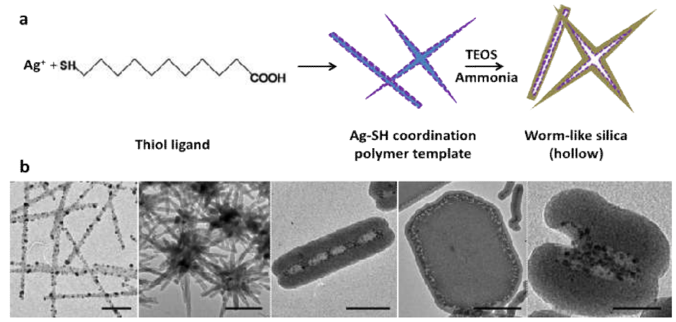

Figure 1.a) Schematics showing the mechanism of worm-like silica nanocavity formation by using coordination polymer as a template, b) TEM images of silica nanoscvities synthesized by using Ag-SH coordination polymer (left TEM image of b) as template. Scale bar: 200 nm

Moreover, this method can also be applied to other silver group metal salts and thiol-containing ligands. The possible mechanism is discussed and a metal-ion/thiol ligand coordination polymer template-assisted cavity formation mechanism is suggested.

Synthesis and mechanism study

Thiol (-SH) and carboxylic acid (–COOH) terminated ligands (e.g. 11-MUA) are commonly used for surface functionalization in silica coating of noble metal nanoparticles. This type of ligand usually has strong specific interaction with the metal surface via the thiol terminal, so it can be adsorbed on the metal substrate[13]. In addition, its carboxylic acid group can render the surface vitreophilic and assist silica deposition (Ung *et al.,* 1998; Bain *et al.,* 1998). For example, in silica encapsulation of Au NPs modified from Stöber's method (Song *et al.,* 2015), the Au surface can be functionalized by mixing Au NPs with 11-MUA, and the subsequent TEOS hydrolysis in presence of ammonia catalyst will yield homogeneous Au@SiO_2 nanoparticles with average shell thickness of around 20nm (Fig. S1).

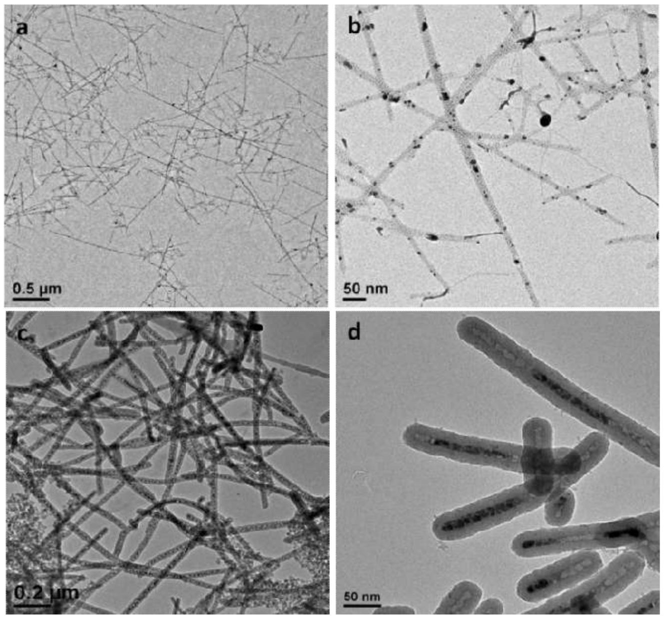

Figure 2. TEM images of coordination polymer and silica nanocavities: a) coordination polymer at lower magnification and b) higher magnification; c) silica nanocavities at lower magnification and d) higher magnification. $AgNO_3$ and thiol ligand 11-MUA were used in synthesis

However, when the same method was applied to Ag NPs with similar size, an unexpected "worm-like" structure which contains one silver particle and several nanocavities was discovered (Fig. S2). Although the incorporation of Ag NP is consistent with the case of Au NP, the creation of "holes" inside the same silica shell is quite interesting. After careful inspection of all the chemical components present in this system, it was realized that the major difference between this one and the Au@SiO_2 system is the etching of silver by ammonia. The chemical reaction of Ag etching is given in Equation 1.

$$4Ag + 8NH_3 + 2H_2O + O_2 \rightarrow 4Ag(NH_3)_2{}^+ + 4OH^-$$
(Equation 1)

In this reaction, silver ion with oxidation state of +1 is produced. In order to verify the crucial role of the generated silver ion in the formation of "worm-like" structure, another experiment using silver salt $AgClO_4$ instead of silver particle was conducted under the same condition. The amount of $AgClO_4$ added was calculated based on the concentration of $AgClO_4$ used during Ag NP synthesis and the assumption that all the Ag was converted to Ag^+ for estimation. The detailed calculation process is shown as follows:

(I) Ag concentration in Ag colloid solution:

$$\frac{[AgClO_4] * V_{AgClO_4}}{V_{total}} = \frac{10mM * 1mL}{100mL} = 0.1mM$$

(ii) Amount of Ag^+ in experimental solution:

$$[Ag] * V_{Ag} = 0.1mM * 1.5mL = 1.5 * 10^{-4}mmol$$

(iii) Amount of $AgClO_4$ added:

$$\frac{M_{Ag^+}}{[AgClO_4]_{stock}} = \frac{1.5 * 10^{-4}mmol}{10mM} = 1.5 * 10^{-5}L = 15\mu L$$

The TEM results of $AgNO_3$ product clearly show that a similar "headless-worm" shaped silica structure with nanocavities was successfully fabricated (Fig. 2 and Fig. S3). This method for generating nano-sized cavities inside silica needs neither complicated pre-synthesis of template, nor tedious post-treatment procedures (Wang *et al.,* 2016; Yu *et al.,* 2017). Besides, the whole process does not require solvent exchange and can be done in a one-pot manner under mild conditions. Thus this novel route is exceptionally valuable and may provide new insight in hollow silica structure construction.

Control experiments and Mechanism study

To test the influence of anion ion, different silver salts with the same concentration as $AgClO_4$ were employed in these experiments. The outcome demonstrated that although different counter-ion was present in the solution, silica structure with nanocavities could still be obtained (Fig. 3) which shows the generality of the method. As illustrated above, the Ag^+ ion plays a key role in the cavity building, while the anion is less important. To examine whether other metal ions have the similar ability, two types of salts were utilized in these experiments. The first type contains the metal ions in the same chemical group of silver, such as Au^+ and Cu^{2+}, and the other one has a distinct cation Na^+ (see supporting information Fig. S4). From the TEM results of the Ag group cations (Fig. 3), it could be noticed that even though the shape of the nanostructure were different from that attained from the Ag^+ experiments, holes could still be created within the silica shell. In the case of Au^+, due to the low solubility of the salt AuCl in this system (Figure S4), a saturated solution of Au^+ was added; hence the effective concentration of Au^+ is actually smaller than the concentration of Ag^+ used in the original.

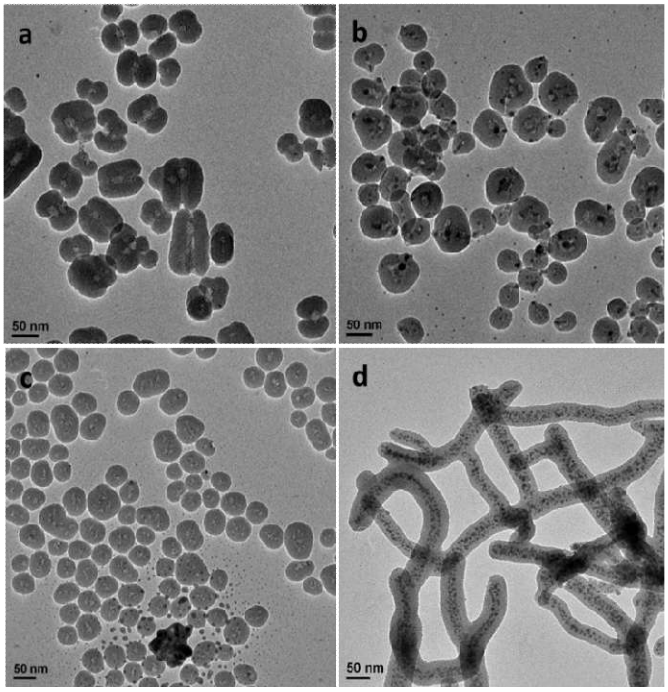

Figure 3. TEM images of silica nanoscvities formed at the present of different kinds of thiol Ag salts: a) $AgClO_4$ higher concentration, b) $AgClO_4$ lower concentration, c) CF_3COOAg, and d) higher concentration of $AgNO_3$. The thiol ligand 11-MUA was used in all these synthesis

As seen from the result, the ligand 11-MUA is necessary for cavity generation. To investigate whether this property is unique for 11-MUA, three control experiments with similar organic thiol ligands with (i) longer carbon chain length (16-MHA), (ii) shorter carbon chain length (3-MPA), and (iii) a benzene ring (4-MPAA) were conducted. The structures of the four thiol ligands are given in Figure 4 and Figure S6. The experimental results are displayed in supporting information. When the ligand with shorter chain length or a benzene ring was used, the holes became smaller (around 8nm) and some dark residue appeared nearby. Nevertheless, the indication of cavity formation can be clearly seen. Coordination polymers (CP) consist of metal ions connected with organic ligands through coordination interactions and further extend into network structures (Battern and Robson, 1998; Gianneschi *et al.,* 2005). Among the different metal ions, the study of Ag^+ CP has attracted much attention because silver ion has flexible coordination modes (Hu *et al.,* 2010), and the argentophilic interactions between Ag^+ also open up new opportunities for design of novel crystal structures (Phillips *et al.,* 2005). In previous research, strong Ag-S bonds were found in the AgSR coordination polymers, and the compounds usually had a layered crystal structure (Fig. S7). Those AgSR CPs are generally obtained via self-assembly from silver salts and thiolate ligands (Dance *et al.,* 1991; Fijolek *et al.,* 1997). In our system, the presence of Ag^+ ion and thiol group terminated ligand provided with the strong interaction between these two components could probably lead to the formation of a coordination polymer as well.

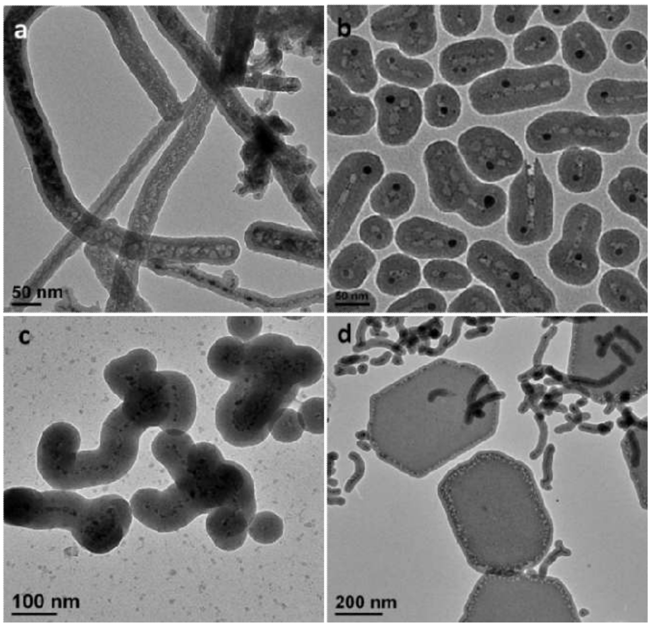

Figure 4. TEM images of silica nanoscvitiesformed at the present of different kinds of thiol ligands: a) 11-MUA, b) 16-MHA, c) 3-MPA, and d) 4-MPAA. $AgClO_4$ under the same concentration was used in synthesis

Furthermore, the *in situ* formed coordination polymer may serve as the template for the complex silica nanostructure construction as shown in Figure 1. In the attempt to prove the generation of the Ag (I) coordination polymer, a separate experiment without TEOS and ammonia was carried out (see supporting information Fig. S8). As can be seen from the TEM images, a network-like structure can be observed against the background (Fig. S8). By increasing the concentration of Ag^+ and 11-MUA to 20 times of that in the original solution, more intact structures with regular shape were attained (Fig. S9). Based on the outcome from controlled experiments and various characterizations, a template-assisted silica nanostructure formation mechanism is proposed (Scheme 1):

As shown in the TEM images from solution containing only Ag^+ salt and 11-MUA, an unstable network was already formed even before TEOS addition. Moreover, the UV-vis spectra and IR assignments (table 1 and supporting information) provided further evidence of the existence of the Ag^+/11-MUA coordination polymer. This new kind of coordination polymer might possess a structure similar to its AgSR analogues, which have a layered structure. The thiol-terminal could bind with Ag^+ through coordination interaction, and the carboxylic acid-terminal on the outer layer could serve as an anchor for silica deposition just as in the case of silica coating of metal nanoparticles. In order to rule out the other possibilities we did the following two control experiments: applying the TEOS hydrolysis and thiol ligand without the present of Ag ions to check the final product; and applying the Ag ions together with TEOS hydrolysis without the presence of thiol ligand in the solution to check the final product while keeping the other experimental condition the same as above standard experiments. According to the Figure 5a-5b it is clearly to see that there is no silica nanocavity formation in these two control experiments, which means that both the Ag ions and the thiol ligand are necessary for the warm-like structure formation. Based on the above control experiments as well as the IR spectra we could confirm the critical formation of coordination polymer template during the silica nanocavity formation process.

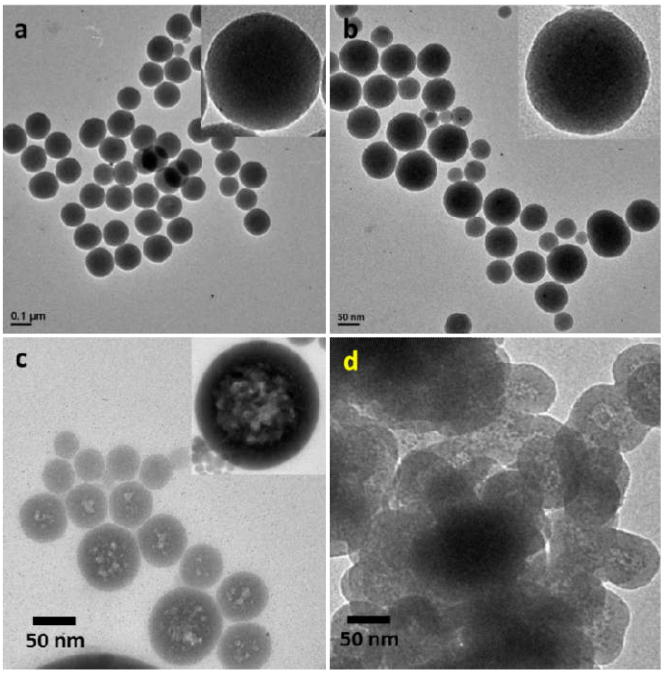

Figure 5(a-b). TEM images of silica nanoparticles formed at the present of different: a) 11-MUA without the present of Ag ions, and b) $AgClO_4$ without the present of thiol ligand while all the other reaction parameters are the same; and TEM images of silica nanocavity synthesized at the present of different metal ions, c) Co $^{2+}$ ($CoCl_2$ was used at the same concentration as silver salt), and d) Fe $^{3+}$ ($FeCl_3$ was used at the same concentration as silver salt)

Generality of the method

Similar coordination polymers may also have formed when Co^{2+}, Fe^{3+}, Au^{+} and Cu^{2+} were utilized (higher concentration), since they have similar chemical properties to silver and could interact with thiol group through "metal-S" bond formation (Bertilsson and Liedberg, 1993; Cobianco *et al.,* 2000) (Fig 5 and Fig S10, S16). The result from Na^{+} ion is consistent with this hypothesis as well, while it could not coordinate with thiol ligand, only silica spheres were observed. The different morphologies of the silica nanostructure obtained with various Ag group metal ions and thiol ligands could be caused by inherent different shapes of these coordination polymers generated under the experimental condition. The instability of the CP may account for the cavities found in these silica nanostructures. The images taken from the initial product before TEOS addition showed that holes were already present inside the whole structure, and this could be related to the solubility of the CP in the current solvent system. Analysis of the results from altered water concentration samples indicates that the CP may have lower solubility in water than in isopropanol (see supporting information Fig. S11). In consequence, when higher concentration of water was used, more CP would precipitate out and form more intact structure; while in solution with lower water content, more CP would dissolve. In the experimental solvent, partial dissolution of the CP may have occurred, and the subsequent silica coating led to cavity-containing structures. At the same time, It is known that the TEOS hydrolyses rate can be slowed down by reducing the amount of ammonia (Song and Ding, 2015). In a control experiment, half the amount of the ammonia (15µL) was added into the solution. Interestingly, some band-like structures were observed surrounded by incomplete silica hemispheres (Fig. S12). This result suggests that a template is probably formed before silica deposition.

Table 1. IR spectra peaks assignments of 11-MUA and $AgNO_3$/11-MUA coordination polymer

	Wavelength (nm)	Peak assignment
11-MUA	2668	SH stretching
	2918, 2849	CH stretching
	1699	C=O stretching
Ag^{+}/11-MUA	2914, 2845	CH stretching
	1692	C=O stretching

Table 1 IR spectra peaks assignments of 11-MUA and $AgNO_3$/11-MUA coordination polymer.

Conclusion

In summary, a facile one-step method to synthesize silica structure with nano-sized cavities was discovered in this work, which is inspired from investigations of an interesting "worm-like" hollow silica nanostructure. This method probably makes use of an Ag^{+}/11-MUA template and can be extend to other Ag-like metal ions and thiol ligands. Further characterization of the Ag^{+}/11-MUA product by TEM, UV-vis and IR measurement (Fig. S13-S14) helped to confirm the generation of the metal ion/organic ligand coordination polymer template. Moreover, the partial dissolution of the coordination polymer in the solvent system was proposed to be the main cause of the cavity formation. This method has been explored to other metal ions (such as Au, Cu, and Co) and we could get similar silica nanocavities. These nanocavities within the silica shell can potentially be functionalized for nanoparticles self-assembly, drug delivery, catalysts, or selective sensors.[26,27,28]

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