

UV-Assisted in Situ Synthesis of Silver Nanostructures in a Metallogel Network

Nguyen Ngoc Thang^{1,*}, Liu Jui Hsiang²

¹Hanoi University of Science and Technology – No. 1, Dai Co Viet Str., Hai Ba Trung, Ha Noi, Viet Nam

²National Cheng Kung University - No. 1, Daxue Road, East District, Tainan, Taiwan

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Abstract

In this paper, we represent the green synthesis of silver nanostructures using a metallogel of silver ions incorporated with Cholesteryl Pyridine Carbamate (CPC) gelator as a soft template and the UV-induced reduction of silver ions to silver nanoparticles (AgNPs). The metallogel and AgNPs were characterized by UV-Vis spectroscopy, scanning electron microscopy (SEM) coupled with an energy dispersive spectrometer (EDS), and transmission electron microscopy (TEM). The results from UV-Vis analysis confirmed a 1/2 ratio of silver ion to the CPC ligand in the complex, and the stability constant of the complex (K_c) was about $1.03 \times 10^{15} M^2$, indicative of very stable coordination of the complex in ethanol. Morphological measurements revealed the highly fibrous network structure observed in both the neat CPC gel and the metallogel. Furthermore, the formation of "hairy stem-like" hollow fibers containing AgNPs were observed in the metallogel after UV irradiation, which is a rare observation in other metallogels.

Keywords: Cholesteryl Pyridine Carbamate, Metallogel, Silver nanoparticles, UV-assisted synthesis.

1. Introduction

Designing supramolecular gelators with novel functions which self-assemble to generate nanoscale materials is an exciting area of current research interest [1, 2]. Within this field, metallogels are a relatively new kind of molecular gel in which metallic elements actively participate in gel formation. To fabricate the metallogels, low molecular metal complexes have been used for gelation through H-bonding, π - π stacking, van der Waals forces, and metal-ligand coordination [3]. Clearly, the incorporation of metal ions into the supramolecular gels could not only subtly tune the gelation ability by metal-ligand interactions but also endow with the outstanding redox, catalytic, and optical properties associated with the metal centers, which are not accessible to supramolecular gels [4]. So far, a variety of metallogels formed from various transition-metal complexes, including silver, gold, copper and iron complexes have been reported [3-5]. Some of them were found to be responsive to different external stimuli such as light, redox, and chemicals [5]. In addition, metallogels have recently been utilized for the in situ synthesis of metal nanoparticles [6, 7].

In our earlier study, a chiral molecule cholesteryl pyridine carbamate (CPC) containing cholesteryl, pyridine and urethane groups had been

synthesized [8]. The CPC molecule and its metallic complex exhibited gelation ability the mixture solvent of water and anisole to form tubular structures in the 3D gel networks. These organized nanotubes acted as a structure-directing template for the in situ construction of AgNPs linear arrays and ultralong silver nanowires via the classic silver mirror reaction. In continuation to our previous efforts, present interest is to perform in situ synthesis of AgNPs in the metallogel using the UV-induced reduction method, without adding external reducing or capping agents.

2. Experimental section

2.1 General methods

Cholesteryl pyridine carbamate (Fig. 1a) was synthesized according to the method reported in our previous work [8]. All analytical grade chemicals and solvents were purchased from commercial suppliers and used as received without further purification. Deionized (DI) water was obtained using a Millipore-Q system.

To measure the stability constant of the Ag^+ /CPC complex (Fig.1b), an appropriate amount of $AgNO_3$ in ethanol was gradually added to a very dilute solution of CPC in ethanol. After sonication and standing for 10 min in ambient conditions, the sample was subjected to the UV/Vis absorption measurement. The reason that ethanol was used instead of water, is to promote the complex formation

* Corresponding author: (+84) 904 309930
Email: thang.nguyennhoc@hust.edu.vn

of the silver ion and CPC ligand, giving a more accurate UV/Vis analysis.

The UV/Vis absorption spectra were obtained from a Jasco V-550 spectrophotometer. Morphology of metallogel and AgNPs were asserted by a JEOL JEM-1200CX II Transmission Electron Microscope (TEM) and a JEOL HR-FESEM JSM-6700F Scanning Electron Microscope (SEM) coupled with an energy dispersive spectrometer (EDS).

2.2 Preparation of silver nanoparticles

Silver nitrate (AgNO_3 , 0.5 mol equiv.) dissolved in water (1.0 mL) was slowly added into a solution of CPC in ethanol (10 mL, 10 g/L) and subsequently agitated to ensure even mixing. The mixture was then cooled to room temperature to form stable metallogels. The resulting metallogel was exposed to 365 nm UV light (1000W) for given times from a distance of 5 cm, at room temperature. The opaque metallogel turned to a yellow hybrid material, indicating the formation of AgNPs (Fig. 1c). The reaction was typically stopped by the adsorption of the sample on a TEM grid or SEM substrate.

3. Results and discussion

3.1 Formation of the complex gel

According to our previous report, the synthesis of a chiral gelator, cholesteryl pyridine carbamate (CPC) and the preparation of the CPC nanofibers in various solvents were provided in detail [8]. It also suggested that this nanofiber may be utilized as an active template for the fabrication of inorganic/hybrid materials by transcription.

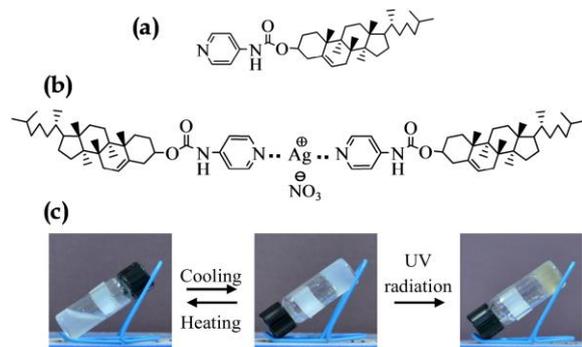


Fig. 1. Chemical structures of (a) cholesteryl pyridine carbamate (CPC) and (b) its silver coordinated complex; Photographs of (c) thermoreversible sol-gel transition of CPC/Ethanol and the in situ preparation of AgNPs via CPC gel template.

Our idea was to use the CPC nanofibers as the scaffold, reducing and stabilizing agents to direct the nucleation, deposition, and growth of AgNPs via the coordination between silver ion and the pyridine and

the urethane groups of the CPC molecules, followed by the UV-induced reduction of the silver ion into metallic silver. However, the gel templates may lose their structural characteristics in the presence of ionic precursors in some cases. The reason is that the added ionic precursors may change the system conditions, such as ionic strength, and interfere with the self-assembled structures. Herein, when an amount aqueous solution of AgNO_3 is introduced into a solution of CPC/ethanol at the critical gelation concentration (10 g/L), (Ag@CPC sol), the mixed solution immediately turned opaque, indicating the coordinate formation of silver ions with the CPC molecules. Besides, the mixture quickly formed a gel (Ag@CPC gel) upon being placed in a refrigerator for several minutes (Fig. 1c).

3.2 Characterization of coordination

To shed light on the interaction between the CPC molecules and silver ions, UV/Vis absorption spectra were employed to determine the effect of the stoichiometry between the CPC molecules and silver ions on the formation of the complex gel. The concentration of CPC was fixed at 3.7×10^{-6} M, and considerable hypsochromic (blue) shifts of the UV absorption were observed by altering the added amount of silver ion to 7.0×10^{-6} M, indicating the formation of the silver complex (Fig. 2).

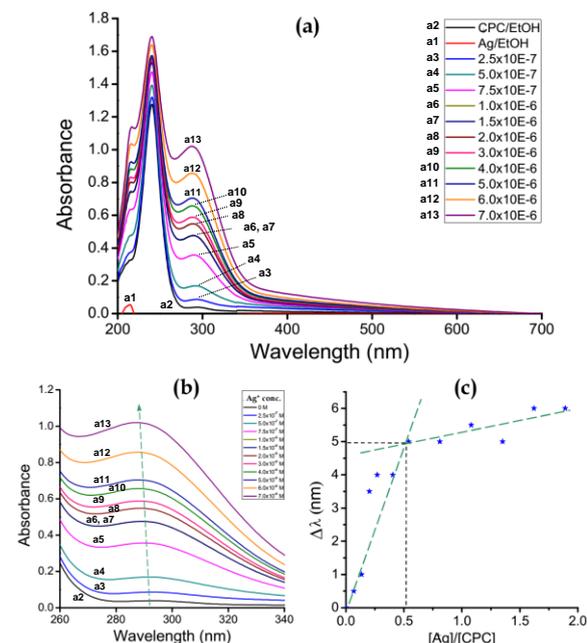
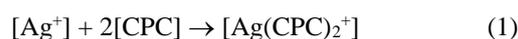


Fig. 2. (a, b) UV/Vis absorption spectra of the CPC/ethanol solution (fixed at 3.7×10^{-6} M) with different amounts of silver ions (0, 2.5×10^{-7} , 5.0×10^{-7} , 7.5×10^{-7} , 1.0×10^{-6} , 1.5×10^{-6} , 2.0×10^{-6} , 3.0×10^{-6} , 4.0×10^{-6} , 5.0×10^{-6} , 6.0×10^{-6} , and 7.0×10^{-6} M); (c) Band shift of the complex corresponding to neat CPC versus the concentration ratio of Ag^+/CPC .

Reaction equation:



The stability constant of the complex is obtained via the reaction equation (1):

$$K_c = \frac{[\text{Ag}(\text{CPC})_2^+]}{[\text{Ag}^+][\text{CPC}]^2} = \frac{[\text{Ag}(\text{CPC})_2^+]}{([\text{Ag}^+]_0 - [\text{Ag}(\text{CPC})_2^+])([\text{CPC}]_0 - 2[\text{Ag}(\text{CPC})_2^+])^2} \quad (2)$$

where:

$[\text{Ag}^+]$, $[\text{CPC}]$, and $[\text{Ag}(\text{CPC})_2^+]$ are the concentrations of silver ion, CPC, and complex at equilibrium, respectively.

$[\text{Ag}^+]_0$ and $[\text{CPC}]_0$ mean the general concentration of added silver ion and CPC, respectively.

When α is applied as the concentration ratio of silver ion to CPC in the complex solution, α can be calculated as follows:

$$\alpha = \frac{[\text{Ag}^+]_0}{[\text{CPC}]_0} \quad (3)$$

To obtain the ratio of coordinated CPC to the total CPC, β was defined:

$$\beta = \frac{[\text{CPC}]_0 - [\text{CPC}]}{[\text{CPC}]_0} = \frac{2[\text{Ag}(\text{CPC})_2^+]}{[\text{CPC}]_0} \quad (4)$$

By combining equations (2-4), K_c can be shown as:

$$K_c = \frac{\beta}{(2\alpha - \beta)(1 - \beta)^2 [\text{CPC}]_0^2} \quad (5)$$

The concentration ratio of bound CPC to the total CPC can also be expressed as:

$$\beta = \frac{\lambda_{cs} - \lambda_{CPC}}{\lambda_{opt} - \lambda_{CPC}} = \frac{\Delta\lambda_{cs}}{\Delta\lambda_{opt}} \quad (6)$$

where:

λ_{cs} is the wavelength of the absorption band of the complex solution.

λ_{CPC} is the wavelength of the absorption band of CPC.

λ_{opt} is the wavelength of the absorption band of the complex at which all CPC ligands coordinates with the silver ions.

$\Delta\lambda_{cs}$ denotes the band shift of the complex corresponding to CPC.

$\Delta\lambda_{opt}$ refers to the band shift of the complex corresponding to CPC at which all CPC ligands coordinates with the silver ions.

From the plot of Fig. 2, $\Delta\lambda_{opt}$ is calculated to be ca. 4.9 nm. If the stoichiometry of silver ion to CPC ligand (α) is 1/2, hence $\Delta\lambda_{cs}$ is interpolated from the plot to be ca. 4.7 nm. Being substituted into the equation (6), β is calculated to be ca. 0.959. Thus, the stability constant of the complex (K_c) is estimated to be about $1.03 \times 10^{15} \text{ M}^{-2}$, indicative of very stable coordination of the complex.

3.3 Morphologies of the gels

TEM and SEM measurements of the CPC/Ethanol and Ag@CPC xerogels were performed to obtain visual images of the self-assembled CPC molecules in absent and present of silver ions, Fig. 3. As revealed in the micrographs of samples, the self-assembled CPC molecules formed highly fibrous networks in both the neat CPC gel (Fig. 3a,c) and metallogel (Fig. 3b,d). Interestingly, closer observation of the TEM micrograph of the Ag@CPC metallogel (Fig. 3d) exposed the self-assembled nanostructures of both nanofibers and nanotubes. The nanotubes are hollow with inner diameters varying from several to a few tens of nanometers. The formation of the tubular fibers in the metallogel suggested that the silver ions caused some changes during self-assembly. We speculated that such tubes were made of a multi-bilayer of CPC interacting with silver ions by coordination forces.

3.4 UV-induced reduction of AgNPs embedded metallogel

During UV irradiation, the color of the prepared metallogel changed from colorless to yellow, indicating the formation of AgNPs in the Ag@CPC gel, Fig. 1c. To get more evidences of the formation of Ag-NPs in the gel, TEM, SEM and EDS measurements of small piece of hybrid gels had taken place after given time of UV exposure. As shown in Fig. 3e, f, the SEM and TEM images of the hybrid samples after 10 mins of UV treatment showed ultrafine AgNPs with average diameter of several nanometers embedded in the nanofibers. The EDS profile of the hybrid xerogel, Fig. 3g, exhibited Ag, C, O and N elemental compounds, in which the signals of C, O and N originate from the substrate. Interestingly, the TEM micrograph of the UV-exposed metallogel revealed "hairy stem-like" hollow fibers containing AgNPs, which is a rare observation in other gels.

It could be affirmed that metallic silver was formed instantaneously in the Ag@CPC nanotubes in the initial UV irradiation state. It was proven by the TEM images in Fig. 3e, in which the borders of the nanotubes could be observed because of increasing electron density. However, it was difficult to detect silver clusters inside the nanotubes' sheaths due to

extremely well dispersed silver clusters, presumably in the subnanometer size, on the inner surface of the tubules. We predicted that silver nuclei were formed at the binding sites between silver ions and CPC molecules on the nanotube's wall. Then, by gathering the surrounding silver atoms, the nuclei gradually grow into clusters that may act as the seeds for the growth of larger AgNPs. Nevertheless, UV radiation has been reported to exhibit a small penetration depth due to its low energy. After a certain time, the number of AgNPs on nanotubes' sheaths was much enough to inhibit the UV light penetrating into the nanotubes' wall. Hence, silver nanostructures were grown on the surface of the hollow nanofibers alike dense hairs on the stem.

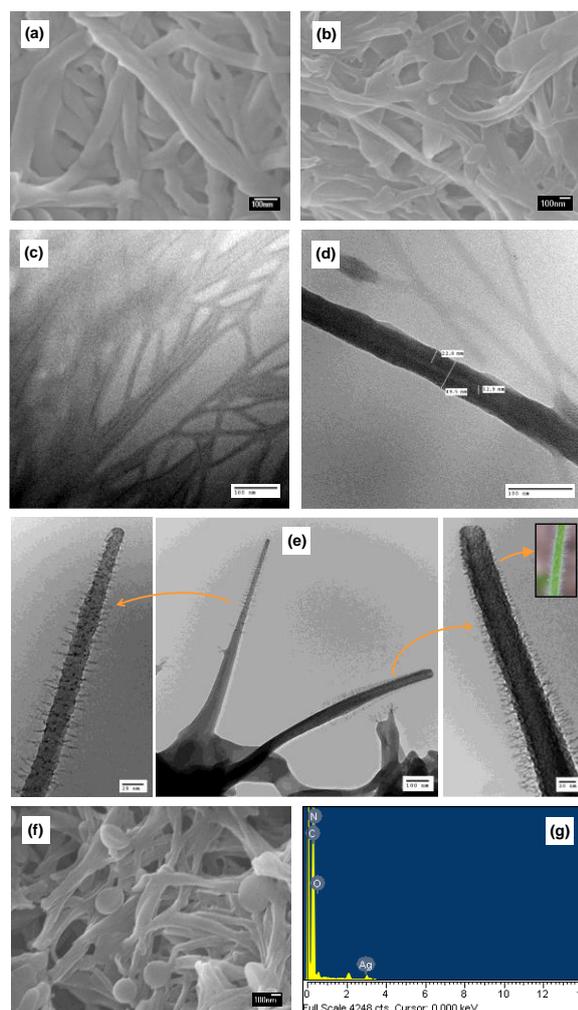


Fig. 3. SEM images of xerogels: (a) CPC/Ethanol, (b) Ag@CPC, and (f) AgNPs@CPC; TEM images of xerogel: (c) CPC/Ethanol, (d) Ag@CPC, and (e) AgNPs@CPC; (g) EDS of AgNPs in the hybrid gel.

4. Conclusion

Herein, the AgNPs were successfully fabricated via a metallo gel template-directed synthesis using the

UV irradiation as a green method without any external reductant. The CPC/Ethanol gel, Ag@CPC metallo gel and AgNPs were well characterized by UV-Vis, TEM, SEM and EDS analyses. The UV-Vis measurements confirmed the stoichiometry of the silver ion-CPC ligand complex was 1:2 in ethanol. The fibrous network structure had been observed in the TEM and SEM micrographs of the gels. Furthermore, the tubular nanofibers in the metallo gel and "hairy stem-like" hollow fibers in the UV-exposed gel found in the current work were a rare observation in previous reports.

Acknowledgments

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References

- [1] M. Lisar, C. Sanchez, Inorganic and Hybrid Nanofibrous Materials Templated with Organogelators. *Chemistry of Materials*, 20 (2008) 782-820.
- [2] T. Shimizu, M. Masuda, H. Minamikawa, Supramolecular Nanotube Architectures Based on Amphiphilic Molecules. *Chemical Reviews*, 105 (2005) 1401-1444.
- [3] Q. Liu, Y. Wang, W. Li, L. Wu, Structural Characterization and Chemical Response of a Ag-Coordinated Supramolecular Gel, *Langmuir*, 23 (2007) 8217-8223.
- [4] M. Kimura, T. Hatanaka, H. Nomoto, J. Takizawa, T. Fukawa, Y. Tatewaki, H. Shirai, Self-Assembled Helical Nanofibers Made of Achiral Molecular Disks Having Molecular Adapter, *Chemistry of Materials*, 22 (2010) 5732-5738.
- [5] S. Basak, J. Nanda, A. Banerjee, Multi-stimuli responsive self-healing metallo-hydrogels: tuning of the gel recovery property, *Chemical Communications*, 50 (2014) 2356-2359.
- [6] S. Ray, A.K. Das, A. Banerjee, Smart oligopeptide gels: in situ formation and stabilization of gold and silver nanoparticles within supramolecular organogel networks, *Chemical Communications*, (2006) 2816-2818.
- [7] M. Cametti, Z. Dzolic, New frontiers in hybrid materials: noble metal nanoparticles - supramolecular gel systems, *Chemical Communications*, 50 (2014) 8273-8286.
- [8] N. T. Nguyen, N. T., J. H. Liu, Wet chemical synthesis of silver nanowires based on a soft template of cholesteryl pyridine carbamate organogel. *Science of Advanced Materials*, 7(2015), 1282-1290.