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In Situ Synthesis of Gold Nanoparticles Using Molecular Gels and Liquid Crystals from Vitamin-C Amphiphiles

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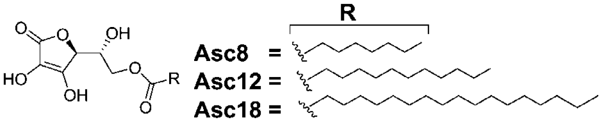
Vitamin-C (ascorbic acid, **AscA**) is a powerful antioxidant that inhibits free-radical-initiated lipid peroxidation, a process presumably implicated in a variety of chronic health problems such as aging, cancer, and cardiovascular diseases.[1] Literature study indicates that antioxidant activity of **AscA** and its hydrophobic derivatives is comparable, which is making them important in food-industry-related applications.[2−4] **AscA** is also known for the reduction of metal salts such as chloroauric acid to generate gold nanoparticles (GNPs) in the solution phase.[5] Upon self-assembly, **AscA**-based amphiphiles are known to form nanotubes and other structures.[6] The challenge is whether we can combine these two properties together. Hence, can we generate in situ synthezised GNPs embedded in organic self-assembled soft materials such as gels and liquid crystals? If so, do such nanostructures stabilize the GNPs? To understand and answer the above queries, we designed the **AscA** derivatives **Asc8**, **Asc12**, and **Asc18** (Scheme 1). In this communication, we successfully demonstrate the in situ synthesis and stabilization of GNPs in molecular gels and liquid crystals using self-assembling systems of **AscA**-based amphiphiles without using any external reducing/capping agents. We also discuss the self-assembling properties of amphiphilic **AscA** derivatives in the preparation of GNPs containing hydro/organogels and liquid crystals.

AscA amphiphiles (**Asc8**, **Asc12**, and **Asc18**) have been prepared using enzyme catalysis.[7] Biocatalysis is becoming a popular path for generating value-added products and chemicals because of the following advantages: enzymatic reactions minimize the formation of byproducts because of its extreme selectivity and often use less energy while producing high yields.[8] **AscA** contains one primary hydroxyl group, which selectively undergoes transesterification in the presence of a suitable acyl donor (vinyl esters were used as acyl donors) in the presence of *Candida antarctica* Lipase B (CALB) in excellent yields; a detailed synthetic scheme, procedure, and characterization have been given in the Supporting Information. **AscA**-based amphiphiles encompass the structural features required for the self-assembly; e.g., a polyhydroxyl sugar headgroup for the formation of a hydrogen-bonding network and a polymethylene hydrocarbon chain for van der Waals interactions. These groups synergistically act to form strong intermolecular interactions that lead to the gelation in various solvents. Typically, gelator (2−10 mg, 2−5% w/v) in required solvent (0.1−1 mL) was heated until the solid was completely dissolved and slowly cooled to room temperature. Qualitative information of the gel formation was obtained by observing the macroscopic behavior such as no gravitational flow in an inverted tube. All the obtained gels were found to be thermally reversible.

Scheme 1. Structure of Ascorbic Acid-Based Amphiphiles.



Amphiphiles **Asc8**−**Asc18** showed excellent gelation abilities in a broad range of solvents at low concentrations with noticeable thermal and temporal stabilities. Detailed gelation behavior and minimum gelation concentrations (MGC) are shown in Table S1 of the Supporting Information.

The gelation ability and gel stabilities are highly influenced by the length of hydrocarbon chain, for example, **Asc18** and **Asc12** formed stable hydrogels at room temperature with MGC values of 2 and 3.1% (w/v), respectively, whereas the MGC of **Asc8** was 4.3% and formed a hydrogel at 4 °C. Ambidextrous gelation (gelling in polar water and nonpolar organic solvents) behavior of these amphiphiles can be utilized to develop hybrid materials in a variety of solvents, including water.

Logical design and development of organic−inorganic hybrid materials have been gaining enormous attention in recent years.[9] Among them, in situ NPs preparation methods are rather uncommon.[9a] **AscA** is known to reduce Au(III) to Au(0) to form gold nanoparticles (GNPs).[5] Thus, we wanted

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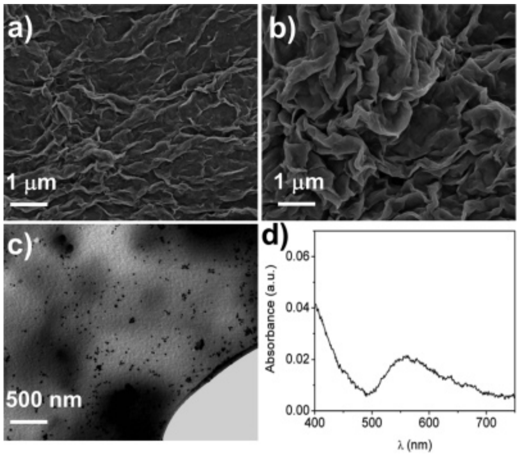

Figure 1. SEM images of **Asc18** hydrogels (a) without and (b) with GNPs; (c) TEM image of GNP-containing **Asc18** hydrogel; (d) absorption spectra of GNPs prepared in **Asc18** hydrogel.

to explore the possibility of using self-assembled **AscA**-based amphiphiles as reducing agents for $HAuCl_4$ to subsequently stabilize the GNPs. To test this hypothesis, we added 3 mg of **Asc18** to a 5 mol % $HAuCl_4$ solution in water and heated it at 40−50 °C to become a homogeneous solution; upon heating, the initially yellow colored solution became colorless and turned pink, which suggests the formation of GNPs. At room temperature, a GNP-embedded pink gel was formed (see Figure S1 of the Supporting Information). This process has been confirmed by using a UV−visible spectrophotometer, with the appearance of surface plasmon band at longer wavelength (∼555 nm) suggesting the presence of GNPs.

Characterization of GNP-embedded gels was carried out using scanning (SEM) and transmission (TEM) electron microscopy (Figure 1). Examination of the xerogels of hydrogels under SEM shows the existence of wrinkled soft sheet-like morphologies (Figure 1a). Importantly, the presence of GNPs within the hydrogel did not change the basic morphology of the gel (Figure 1b). On the contrary, Bhattacharya et al. recently showed that external doping of GNPs in hydrogels resulted in drastic changes in the basic morphology of gel architecture.[10] We believe, in this instance, that the reason for retention of the native morphology of the gel could be due to the in situ preparation methods, where NP and gel formation occurs simultaneously, and the gelator itself acts as a reducing and stabilizing agent. TEM analysis showed the presence of well-dispersed GNPs that were distributed throughout the gel (Figure 1c). GNP-embedded gels were stable for many months. TEM images showed that resulting GNPs were spherical and in the size range of 11−18 nm (Figure 1c). GNP-embedded gels were dried and dissolved in acetone and subjected to UV−vis spectroscopy. As shown in Figure 1d, this sample showed a characteristic plasmon resonance band at 555 nm, indicating the existence of gold particles in nanoscale dimensions.

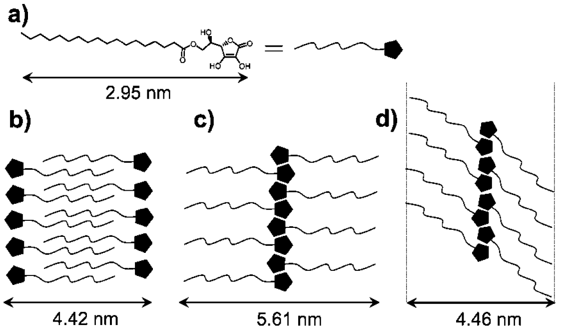

Figure 2. Cartoonic representation of (a) **Asc18** amphiphile. Proposed mode of self-assembly in (b) hydrogel and (c, d) organogel.

From the X-ray diffraction (XRD) patterns (see Figure S2 of the Supporting Information) of the gels of **Asc18** prepared from water and toluene, we calculated the long spacings (d) and discussed these values to postulate the possible mode of self-assembly in the gel state. Possibly, lamellar structures were formed by these amphiphiles in gels. In XRD experiments, the hydrogel of **Asc18** showed a long distance spacing of 4.42 nm, which is higher than the molecular length of **Asc18** (2.95 nm from the optimized geometry calculations, see the Supporting Information) and much lower than double the extended molecular length. Thus, it can be predicted that highly interdigitated bilayer-like structures are present at the molecular level (Figure 2b). Interestingly, organogel of **Asc18** showed two equally populated major long distance spacings of 5.61 and 4.46 nm (see Figure S2 of the Supporting Information). Thus, in the case of $d = 5.61$ nm, head-to-head arrangement would be possible, which is closer to double the molecular length (Figure 2c). On the other hand, in the case of $d = 4.46$ nm, there could be two possible ways to explain how these molecules could self-assemble, which is shown in parts b and d of Figure 2. The first is similar to the self-assembly in hydrogel and the second is head-to-head packing while alkyl chains are tilting with respect to normal to the layer plane (Figure 2d). However, in the organogel, it is unlikely that hydrophobic parts are facing inside the assembly, and hydrophilic headgroups are exposed to the outer polar solvent; hence, we believe that in organogels, there exist two types of head-to-head packing modes, as shown in parts c and d of Figure 2. XRD traces of GNP-embedded gels showed patterns similar to those of gels without GNPs, which indicates that the presence of GNPs did not alter the self-assembly mode of these amphiphiles.

Another form of self-assembled organic materials is liquid crystals (LCs), which have a direct function in display applications, ferroelectric materials, photonics, etc., and could be tailored two- or three-dimensional structures easily using external stimuli such as light and electric or magnetic fields.[11] Literature study reveals that attempts have been made to assemble NPs in LCs.[12] However, in those instances, external doping of NPs has been carried out. There are no reports on demostrating in situ synthesis of NPs using LC-forming mesogens. This study presents the preparation of stable LC−GNP conjugates by in situ synthesis of GNPs using liquid crystalline **Asc18**. Previously, Taubert et al. reported the preparation of CuCl nanoplatelets from the ionic liquid-crystal precursor bis(dodecylpyridinium) tetrachlorocuprate

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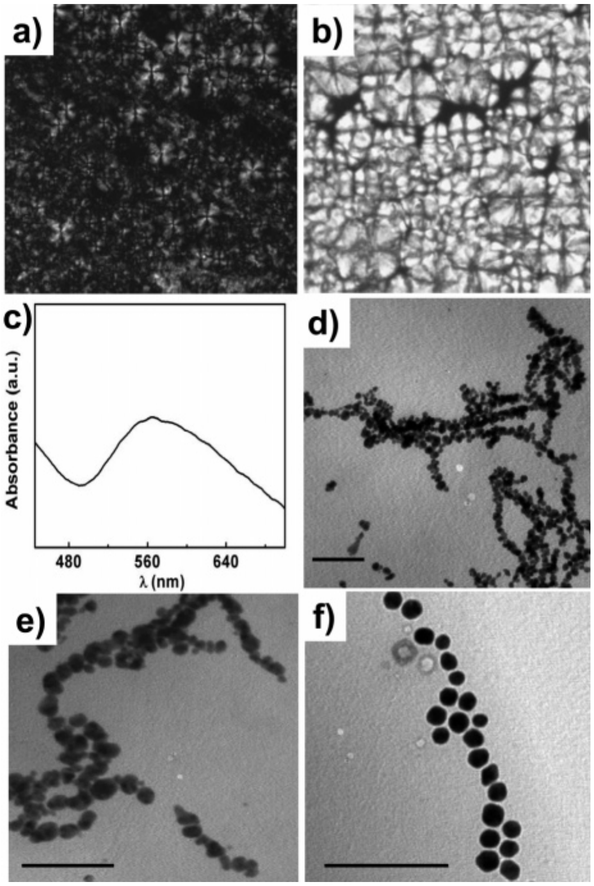

Figure 3. POM images of (a) SmA* phase of **Asc18** at 132.7 °C and (b) SmA* phase of **Asc18-GNPs** at 120 °C. (c) Absorption spectra of GNPs embedded in LCs. (d−f) TEM images of GNPs in LCs at different magnification. All scale bars = 100 nm.

in the presence of 6-*O*-palmitoyl ascorbic acid.[13] Herein we examined the LC-forming properties of **Asc18** and in situ synthesis of GNPs using **Asc18** to generate LC−GNP conjugates using polarized optical microscope (POM), differential scanning calorimetric (DSC), and TEM studies (Figure 3). Amphiphile **Asc18** melts to a smecticA (SmA*) LC phase at 112.9 °C, which transformed into an isotropic phase at 147.1 °C. The SmA* phase was identified from the characterstic focal conic textures using POM (Figure 3a). In the cooling phase, SmA* was observed from 122.1 to 78.0 °C. DSC thermogram (Figure S3 of the Supporting Information) shows the endotherms observed at 112.9 and 147.1 °C that correspond to the Cr−SmA* and SmA*−isotropic phase transitions, respectively. In agreement with POM results, DSC results also evidenced that a SmA* phase exists between 122.1 and 78.0 °C. The DSC thermogram in the cooling cycle shows two more exotherms after the crystallization peak, which could be due to the crystal-to-crystal transitions. At these temperatures significant changes in the textures were not observed in POM.

Further, we explored the utility of the **Asc18**-based LC system in GNP synthesis by in situ reduction to develop GNP-embedded LCs as hybrid materials. GNP-containing LC films were prepared as follows. The amphiphile **Asc18** was dissolved in acetone (2 mL). To this, 5 mol % $HAuCl_4$ in acetone was added and the solution was drop-casted on a glass plate; the solvent was then evaporated. The film thus obtained was heated at 125 °C (SmA* phase) for 3 min and slowly cooled to room temperature. Upon heating, the color of the film changed to a pink, which suggested the formation of GNPs; it was earlier proposed that these changes were due to the reduction of Au(III) to Au(0).[9a] The UV−visible spectra of the LC film has showed a characteristic absorbance at 561 nm corresponding to the surface plasmon band of the GNPs (Figure 3c). Interestingly, the presence of in situ prepared GNPs did not affect the inherent phase formation of **Asc18**. GNP-embedded LC hybrid materials showed characterstic focal conic textures in POM (Figure 3b), which is an indication of the SmA* phase.

LC−GNP hybrids were studied under DSC (see Figure S3 of the Supporting Information). In the heating cycle, the SmA* phase was observed at 110.5 °C and isotropized at 144.51 °C. A slight decrease in the melting temperatures was seen for the GNP-containing **Asc18**. Optical properties of GNP−LCs did not change with the time, indicating that these LC−GNP conjugates are stable over a long period of time. To examine GNPs in the LC matrix, we carried out an akin experiment on a carbon-coated grid for TEM. The GNP-doped LC film contained spherical particles that are arranged in random threadlike structures (Figure 3d−f). This arrangement was seen throughout the grid. The size range of the GNPs was ~16−25 nm. We carried out further experiments to delineate the effect of $HAuCl_4$ concentration (1−7 mol %) on the size and shape of GNPs; we observed similar behavior with all concentrations of $HAuCl_4$. Importantly, these LC−GNP conjugates were stable for a few months.

In summary, we have demonstrated the in situ synthesis and stabilization of GNPs in various self-assembled systems such as low-molecular-weight gels and liquid crystals using amphiphilic **AscA** derivatives. In both instances, hybrid materials were well-characterized by using different techniques, and the materials were stable for several months. Demonstration of organic nanoaggregates as an excellent medium for stabilizing the NPs may become handy in developing organic−inorganic hybrid materials for various applications such as novel catalytic materials, sensors, and advanced displays. Detailed structural studies and further extension of the generation of different metal NPs using these systems are currently under investigation.

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Supporting Information Available: Synthesis and characterization of **AscA**-based amphiphiles, XRD, DSC graphs, gelation table, gel images, and details of ab initio calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

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