Decomposition of Monolayer Coverage on Gold Nanoparticles by UV/ozone Treatment

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Au nanoparticles, covered with cationic dichain surfactant on the whole surface, were treated with UV/ozone. FT-IR spectra of the Au nanoparticles with bottom-, upper-, and fully covered surfactant monolayers revealed a variable decomposition rate. The sum frequency generation spectra of the treated nanoparticles showed that the surface coverage of gold nanoparticles lose the centrosymmetric structure, implying asymmetric distribution of the protected surfactant molecules. The UV–vis electronic absorption spectra suggested stable nanoparticle monolayer film structure after UV/ozone irradiation.

The synthesis of nanoparticles consisting of metallic nanocrystal cores and organic monolayer shells is the goal of active research by various groups, owing to their potentially interesting technological applications.[1] Monolayer coverage of nanoparticles for appropriate functionalization, which can drastically change the physical and chemical properties of the nanoparticles, is a key factor in the application of these materials.[2,3] For example, the capping ligands on the surfaces of nanoparticles usually play a critical role in shape-control processes.[4] Therefore, various methods to "engineer" such materials with controlled precision have long been sought.

Recently, the introduction of two or more covered-organic compounds has become a major challenge for certain assembly requirements. Although molecular exchange methods[5] have been used to accomplish this, the random distributions of the substituent have limited further quantitative modification with desired organic compounds for special assembly, which prevent the path for the construction of elaborate nanosized devices. In a previous paper,[6] Au nanoparticles, half-covered with cationic amphiphile molecules, have been prepared at the air–water interface, but the preparation time was longer than 24 h.

If we are able to easily remove quantitatively organic compounds from desired regions on a nanoparticle surface and then coat other compounds at these vacant regions without deformation of the nanoparticle, we could construct target structures of nanoparticles for special applications by the use of the modified particles. The UV/ozone method has been demonstrated to be effective for cleaning the surfaces of metal planar plates.[7] The UV/ozone irradiation changes organic compounds into volatile species. Spherical gold nanoparticles have a unique centrosymmetric property and are easy to aggregate, and thus the elimination of surface compositions by the UV/ozone treatment should be a special technique to make nanoparticles with a part shell. In this study, we have used the UV/ozone cleaning method to eliminate a predetermined fraction of capping molecules on the Au nanoparticles. The process of decomposition of the capping agent from the particles was monitored using FT-IR and sum frequency generation (SFG) spectroscopies. To our knowledge, this is the first report of UV/ozone treatment of spherical metal nanoparticles for subsequent elaborate assembly.

Au nanoparticles were prepared by the standard technique of citrate reduction of $HAuCl_4$.[8] 100 mL of aqueous solution of Au nanoparticles was mixed with 50 mL of toluene solution of 0.1 mg/mL dioctadecyldimethylammonium chloride (DODAC). In order to transfer Au nanoparticles to the toluene phase, the mixed solution was vigorously shaken for a few minutes, and was then permitted to stand for 24 h. Free DODAC molecules were removed through toluene washing by centrifugation for 5 times. TEM measurement shows the monodispersed nanoaprticles with the size of ca. 15 nm. The DODAC-covered Au nanoparticles (the molecular length of DODAC is ca. 25 Å) were subjected to spreading onto the air–water interface for preparation of Langmuir–Blodgett (LB) films of the particle monolayer (Figure 1a). Monolayers of half DODAC-covered nanoparticles (Figure 1b and c) was also prepared at air–liquid interface by the previous method,[6] where DODAC was used as spreading compound and Au solution was subphase. Sum frequency spectra were recorded in the methyl/methylene C–H stretching region with a picosecond laser spectrometer (Tokyo Instruments, Inc). The UV/ozone treatment was performed using an 11-W panel low-pressure Hg lamp (Ushio) under O_2 atmosphere. FT-IR transmission spectra were recorded with a Nicolet 510 M instrument.

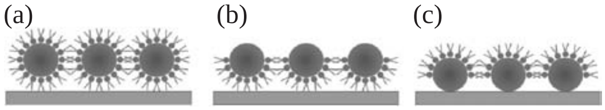

Figure 1. Schematic illustration of (a) fully-covered, (b) bottom-capped and, (c) upper-capped Au nanoparticle monolayer.

Figure 2 shows the band intensities of CH_2 antisymmetric stretching mode in the monolayer of DODAC-covered Au particles as a function of UV/ozone exposure time. The upper-capped surfactants decomposed most rapidly, while the bottom-capped surfactants were minimally affected. This shows that the decomposition of the organic compound starts from the upper part of the nanoparticles, which is well suited to the photolysis mechanism. The mechanism of the UV cleaning procedure by using a low-pressure Hg lamp involves UV excitation of surface species by the 253.7-nm line and conversion of molecular oxygen to ozone and atomic oxygen by the 184.9-nm line. These strong oxidizers then decompose the UV excited organic contaminants to volatile groups.[11] When DODAC-covered nanoparticles were irradiated with a low-pressure Hg lamp, the bottom molecules would be minimally decomposed because only ≈20% UV light in the region from 200 to 300 nm is able to transmit through the Au nanoparticle core, which was confirmed by the UV–vis measurements of Au nanoparticle films. The upper molecules were thus easily removed, reflected by the rapid decomposition

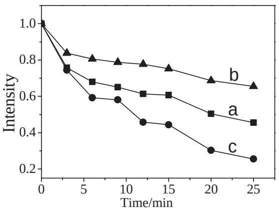

Figure 2. Normalized intensities of CH_2 antisymmetric stretching mode as a function of UV/ozone exposure time. (a) fully-covered, (b) bottom-capped, and (c) upper-capped.

rate in Figure 2. Comparison of the three curves in detail shows the different percentage of DODAC molecules remained, they are ca. 70, 50, and 30%, for bottom-capped, fully-covered, and upper-capped gold nanoparticles, respectively. This result should arise from the decomposition of some side molecules of gold nanoparticles. The other important finding from the FT-IR resluts is that the percentage of covered molecules can be controlled by manipulating the irradiation time, although this is not very accurate, to appropriately modify the gold nanoparticles for desired assembly.

SFG spectroscopy has recently been developed into a powerful tool to study monolayer adsorbed on dielectric and metal surfaces, and has a potential to clarify capping agents being in a symmetric (centrosymmetric) environment or not.[6,9] To gain further evidence for the fact that a part of DODAC molecules adsorbed onto the nanoparticles are removed by the UV/ozone treatment, we measured SFG spectra of the fully covered gold nanoparticle monolayers before and after the UV/ozone treatment. Plots (a) and (b) in Figure 3 show the SFG spectra for the half- and fully covered Au nanoparticles monolayer in the CH stretching region, respectively. The strong band at 2960 cm^{-1} arose from the terminal methyl groups of the alkyl chains of DODAC for the half-covered Au nanoparticles, while methylene stretching peaks at 2860 and 2910 cm^{-1} were weak. According to the previous report,[6] weak methylene modes are due to the all-trans conformation of the alkyl chains. Comparing curve (a) with curve (b) in Figure 3, it can be seen that the methyl band is not observed for the fully covered Au nanoparticles (Figure 3b). This agrees with the fact that the methyl groups of DODAC are in a locally centrosymmetric environment, since SF generation does not arise from molecules in centrosymmetric or isotropic environments.[10]

Curve (c) in Figure 3 shows SFG spectra for the fully covered gold nanoparticle monolayer film after the UV/ozone treatment. The CH_3 characteristic peak of the surfactant alkyl chain at 2960 cm^{-1} became detectable with exposure to UV/ozone. This indicates a lack of centrosymmetric structure of the DODAC coverage, i.e., an asymmetric distribution of DODAC on the surfaces of the particles due to the decomposition of a part of the DODAC molecules. The alkyl chains for the remaining DODAC on Au nanoparticles retain the initial conformation, that is, the all-trans conformation, as indicated by the absence of the methylene band at 2860 and 2910 cm^{-1} in curve (c) in Figure 3.

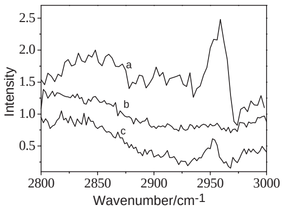

Figure 3. SFG spectra collected from the particles monolayer film in the methyl/methylene C–H stretching region (a) upper-capped, (b) fully covered gold nanoparticle, and (c) fully covered gold nanoparticle was treated with UV/ozone for 10 min.

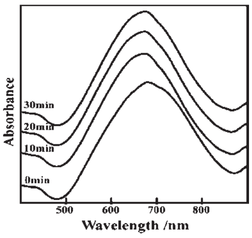

Figure 4. UV–vis spectra of whole DODAC-covered gold nanoparticles treated with UV/ozone for varying times.

It is well known that the peak position of the plasmon band of Au nanoparticles is a good monitor for the aggregation state of the Au nanoparticles. We therefore measured UV–vis spectra of the Au nanoparticle film to clarify the effect of the UV/ozone treatment on the state of the nanoparticles in the monolayer. From the UV–vis spectra shown in Figure 4, the absorption of the DODAC-covered gold nanoparticle film is located in ca. 650 nm, which suggests a smaller nanoparticle spacing than the average particle diameter,[11] and the peak position was unchanged after the UV/ozone treatment. This implies that the nanoparticles do not move or aggregate by the UV/ozone treatment in the monolayer films. The UV/ozone process only affects adsorbed surface species and not the inert substrate.

This letter reports the first study of the surface cleaning process for spherical gold nanoparticles and reveals the photolysis mechanism of surface species, which provides a possible way for quantitative surface modification of nanoparticles with additional compounds as the base for building blocks of elaborate nanosized architectures.

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