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An Optical Absorption Investigation of Cross-Linking of Gold Colloidal Particles with a Small Dithiol Molecule

K. Subramanya Mayya, Vijaya Patil, and Murali Sastry*

Materials Chemistry Division, National Chemical Laboratory, Pune 411008, India

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The controlled aggregation of colloidal metal particles is a problem of technological importance in the generation of, for example, quantum wires. In this communication, we present results of an optical absorption spectroscopy investigation of the flocculation of gold colloidal particles capped with a small bifunctional molecule (1,3-propanedithiol). The self-assembly of the dithiol molecule on the gold surface leads to thiol surface functionalization of the colloidal particles, which may thereafter be used to chemically cross-link the gold clusters. Optical absorption measurements performed immediately after capping the gold colloidal particle surface with the dithiol molecules clearly show the growth of a long-wavelength component, indicating that the clusters aggregate in open string-like structures. Increasing the surface coverage of the dithiol molecules on the clusters leads to a greater flocculation rate, but prevents the formation of large gold clusters in direct contact, as indicated by X-ray diffraction measurements of the aggregates. This approach of controlled cross-linking of colloidal particles may have important applications in the generation of metal cluster networks.

There is much current interest in the synthesis of ligand[1,2] and surfactant[3—7] stabilized colloidal nanoparticles. The excellent control over particle size and monodispersity that can be exercised and the fact that particles of many different compositions can be easily grown by the colloidal route has made this an important starting point for generating nanostructures.[8,9] Capping of the colloidal particles by the self-assembly of suitable surfactants introduces an additional degree of freedom which can be used for stabilization of the particles in solution and/or modification of the colloidal particle surface by a judicious choice of the surfactant terminal functionality.[5,10—15] Derivatization of colloidal particles enables tailoring of the physicochemical properties of the clusters,[5,16] in addition to the possibility of forming nanoparticle films by self-assembly.[10,12,17—20] From a fundamental point of view, capping of clusters represents a three-dimensional analogue of self-assembled monolayers on planar surfaces with some important differences being identified and understood.[5,6,16,21,22]

One exciting application of colloidal metal particles is in the generation of quantum wires,[2,23—25] and superclusters of varying geometries[11,26,27] made up of chains of metal cluster aggregates. An important problem in this application is the controlled organization of such structures in a colloidal solution and the ability to tailor the separation between metal particles and, consequently, electron transport in the structures.[11,26,27] A possible route for organizing such structures in colloidal solution is through capping of the metal particles with surfactants which can chemically cross-link clusters, as has been demonstrated for gold clusters using alkanedithiols.[11,27] In this communication, we present details of an optical absorption spectroscopy investigation of the flocculation of colloidal gold particles capped with a small dithiol molecule, $SH(CH_2)_3SH$ (1,3-propanedithiol, PDT). This bifunctional molecule was chosen since the size of the molecule would ensure adequate coupling between the gold colloidal particles as well as prevent the attachment of the two thiol groups to the same gold particle.[26] Gold is known to form a strong thiolate bond, leading to self-assembled monolayers of the dithiol molecule on the cluster (Fig. 1).[5,13] The terminal thiol group could then chemisorb on another cluster, thereby leading to cross-linking of the colloidal particles (Fig. 1, B), which can be easily followed using optical absorption spectroscopy. The changes in the optical properties as a function of cluster surface coverage with the dithiol have been quantified in terms of a semi-empirical flocculation parameter (FP) introduced by Whitesides et al.[5] and subsequently modified by us.[15] The nature of the flocs was determined from X-ray diffraction studies of the precipitate

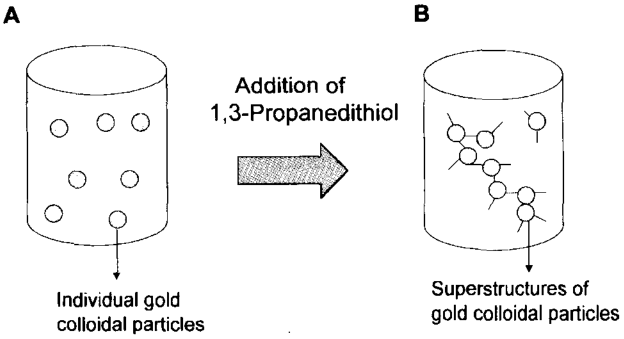

Fig. 1. Schematic illustrating the capping and cross-linking of colloidal gold particles with a small dithiol molecule, 1,3-propanedithiol. A—dispersed colloidal gold particles in the as-prepared solution and B—gold particles cross-linked with PDT molecules.

which formed after aging the solutions for ca. 2 d. Presented below are details of the investigation.

Experimental

The gold colloidal particles were prepared using a procedure outlined by Lee and Meisel,[28] and described in detail elsewhere.[18] In brief, after 240 mg of $HAuCl_4$ was dissolved in 500 ml of water, the solution was brought to boiling. A solution of 1% sodium citrate (50 ml) was added and the boiling continued. The thus-formed gold hydrosol had a pH of 3 and was purple in color with the cluster size distribution exceptionally stable over a period of months, as determined by optical absorption spectroscopy. The particle size was determined from a transmission electron microscopy investigation of the colloidal solution to be 130±25 Å.[18] After cooling, the gold clusters were capped with the dithiol molecule, PDT, by mixing to 9 ml of the cooled gold hydrosol 1 ml of the dithiol in absolute ethanol. The concentration of the dithiol in ethanol was adjusted to yield overall concentrations of the surfactant in the hydrosol-ethanol mixture of 10^{-4}, 10^{-5}, and 10^{-6} M (M = mol dm^{-3}). Upon addition of the surfactant, the colloidal solution slowly changed color from purple to a deeper shade of the color. Optical absorption measurements on the colloidal solutions were performed as a function of time using a UV-vis Hewlett–Packard 8452 diode array spectrophotometer at 2 nm spectral resolution. During the measurement period, the colloidal solution was clear with no evidence for precipitate formation, and therefore effects due to the scattering of light may be ruled out. Upon further aging for a period of 2 d, a black precipitate formed which was collected by filtration, washed thoroughly with ethanol and water and analyzed by X-ray diffraction on a Philips PW 1830 X-ray diffractometer using Cu $K\alpha$ radiation.

Results and Discussion

The formation of networks of colloidal gold particles initiated through the cross-linking molecule, PDT, is illustrated in Fig. 1. The optical absorption spectra, recorded as a function of time for the gold colloidal particles capped with 10^{-4} M of PDT together with the uncapped hydrosol, are shown in Fig. 2. The time was measured from the instant of mixing the ethanolic solution of the dithiol molecules to the gold hydrosol, as described earlier. It is clear that in addition to the primary peak (indicated by a dashed line), a component at higher wavelengths develops, which shifts to the red with time (indicated by arrows in Fig. 2). The growth of a longer-wavelength component in the UV-vis spectra of the colloidal solution indicates flocculation of the particles.[29,30] The formation of aggregated structures lifts the 3-fold degeneracy of the dipole plasma vibration modes, resulting in two plasmon vibration modes.[29,30] The higher wavelength component is the longitudinal resonance, and is known to shift to higher wavelengths as the aspect ratio of the aggregate increases, as would occur during the formation of open, string-like structures.[29,30] The growth of a long-wavelength component and its shift to higher wavelengths with time is observed for the 10^{-4} M dithiol capped gold particles (Fig. 2); the nature of the aggregates formed may be explained as above. The formation of aggregates in open string-like structures is characteristic of diffusion-limited colloid aggregation (DLCA) where there is no repulsive interaction between the particles,[31] which was the case in this study. Reaction-limited colloid aggregation (RLCA), which occurs in systems with large repulsive forces between colloidal particles,[31] leads to more close-packed structures, and thus a smaller shift in the longitudinal plasma vibration mode, contrary to our observation. Obtaining such structures is important, as mentioned earlier, for the generation of quantum wires.

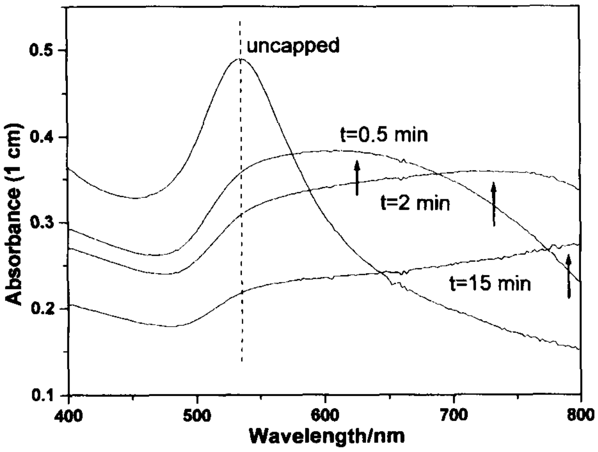

Fig. 2. Optical absorption spectra recorded at different times from capping the gold colloidal particle solution with 10^{-4} M dithiol molecule along with the uncapped gold sol spectrum. The dashed line indicates the position of the transverse plasmon mode while the arrows indicate the position of the longitudinal mode.

Figures 3 and 4 show the optical absorption spectra recorded as a function of time after capping the gold colloidal particles with 10^{-5} and 10^{-6} M concentration dithiol molecules, respectively. As for the 10^{-4} M capping case, the growth of a longer wavelength component which steadily red shifts with time is observed for the above-mentioned two

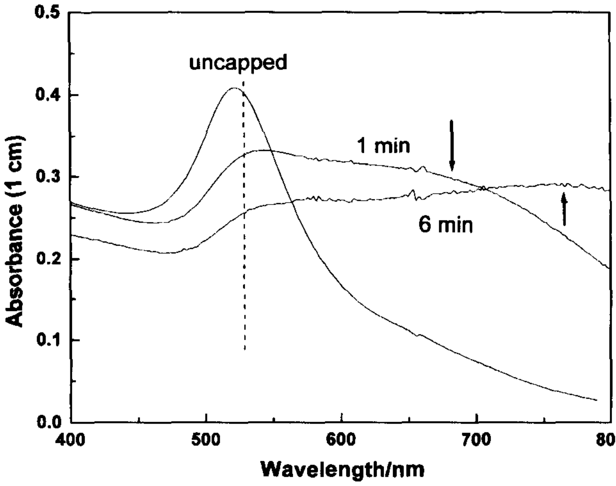

Fig. 3. Optical absorption spectra recorded at different times from capping the gold colloidal particle solution with 10^{-5} M dithiol molecule along with the uncapped gold sol spectrum. The dashed line indicates the position of the transverse plasmon mode while the arrows indicate the position of the longitudinal mode.

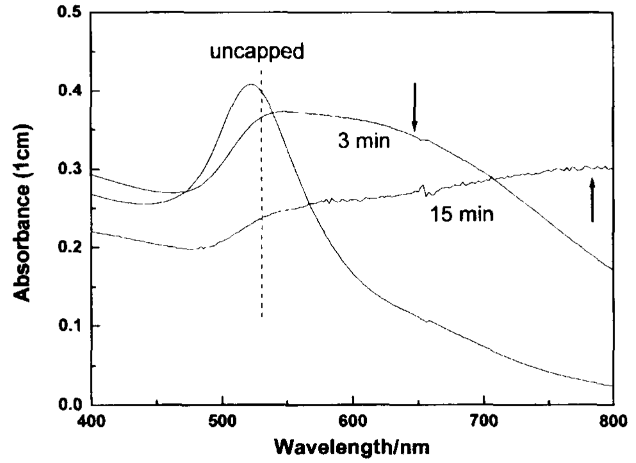

Fig. 4. Optical absorption spectra recorded at different times from capping of the gold solution with 10^{-6} M dithiol molecule along with the uncapped gold sol spectrum. The dashed line indicates the position of the transverse plasmon mode while the arrows indicate the position of the longitudinal mode.

concentrations as well, and is indicative of cross-linking of the gold particles into string-like structures.

From Figs. 2, 3, and 4, it is clear that the capping of the clusters with the dithiol molecule initiates cross-linking of the gold particles, which are otherwise extremely stable at the pH of preparation. However, to effectively compare the rate at which aggregate formation occurs as a function of time for varying PDT capping concentrations, a method whereby the flocculation rate can be quantified would be useful. Therefore, we have calculated a semi-empirical "flocculation parameter" (FP) first introduced by Whitesides et al.[5] with some modification, as detailed in an earlier publication.[15] The FP was defined to be the integrated area between 600 and 800 nm in the optical-absorption spectrum of a gold colloidal solution.[5] Defined in this fashion, it is clear that the FP for the 15 min sol of Fig. 3 would be less than that for the 3 min sol, which is contrary to the physical mechanism. In order to account for such problems, we had suggested the following minor modification in the definition of the FP, which we reiterate here for completeness. In the first step, all of the spectra (including the uncapped sol spectrum) have been normalized to the intensity at the *transverse* surface plasmon resonance wavelength. This wavelength is 540 nm for the uncapped gold sol, while the transverse plasmon vibrations for the flocculated sols are indicated by the dashed lines in Figs. 2, 3, and 4. The areas of the various absorption spectra were then calculated between the wavelength limits, 600 and 800 nm, following which the area of the uncapped gold sol was subtracted to yield a modified FP. This would enable a comparison of the degree of flocculation as well as the rate of flocculation for the different capping concentrations of this study.

The FP was calculated for the optical absorption spectra recorded as a function of time for the different dithiol concentrations (some representative spectra of which have been shown in Figs. 2, 3, and 4), and are shown in Fig. 5. For all

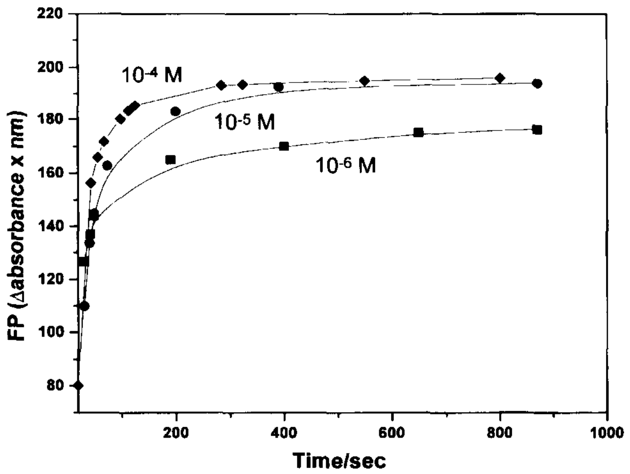

Fig. 5. The flocculation parameter (FP) as a function of time calculated for different capping concentrations of the dithiol molecule in the gold colloidal solution, representative spectra of which are shown in Figs. 2, 3, and 4.

capping concentrations, it is apparent that there is initially fast flocculation of the gold particles, followed by a slower rate of aggregation. The steady-state FP was highest for clusters capped with 10^{-4} M dithiol molecules; this value is marginally higher than that for the 10^{-5} M capping case. A larger FP is indicative of an increase in the aspect ratio of the string-like aggregates, or in other words, longer chains. An increase in the dithiol concentration would lead to a larger surface coverage of the gold clusters and, consequently, to an increase in the probability for linking with other clusters, as observed. As discussed earlier, it is known that flocculation in the absence of a repulsive barrier (DLCA) leads to the formation of open string-like structures.[31]

Aging of the three different gold colloidal solutions (capped with 10^{-4}, 10^{-5}, and 10^{-6} M dithiol) for 2 d resulted in the formation of a black precipitate. After thorough washing and drying of the precipitates, films of the precipitates were formed on Si (111) wafers and analyzed using XRD. The X-ray diffraction patterns obtained from films formed from the precipitates are shown for the three capping concentrations in Fig. 6. The capping concentrations are indicated next to the respective curves. The Bragg-peak assignments are also indicated in the figure. It is observed that the widths of the Bragg peaks decrease as the concentration of the dithiol surfactant molecule in the precipitate decreases. The cluster size in the flocs was determined from the Bragg widths using the Scherrer formula[32] for three surfactant concentrations of 10^{-4}, 10^{-5}, and 10^{-6} M to be 150, 200, and 270 Å, respectively. This indicates that the cluster size in the flocs increases with decreasing coverage of the clusters.

A comparison of the steady-state flocculation parameter values for the three PDT concentrations shown in Fig. 5 with the X-ray diffraction results of Fig. 6 indicates an apparent contradiction. While the FP for 10^{-6} M capping with PDT is slightly less than that for the other two concentrations (indicating smaller flocs), the size of the gold cluster aggre-

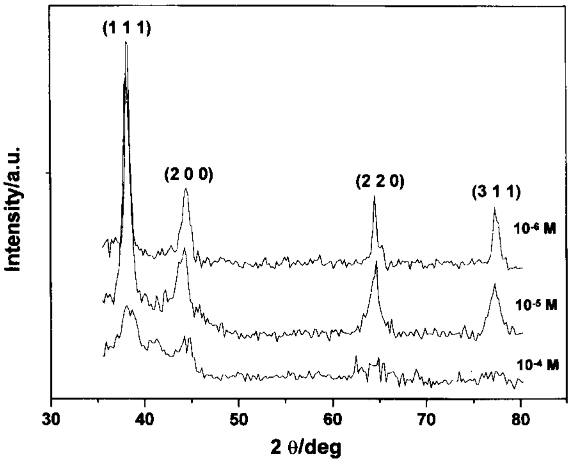

Fig. 6. X-Ray diffraction patterns of the precipitates of gold colloidal particles; the dithiol capping concentrations are indicated next to the corresponding curves.

gates, as indicated by XRD, is larger (270 Å compared to 200 and 150 Å for larger PDT concentrations). This contradiction may be resolved if one considers that the condition for the occurrence of the longitudinal plasma mode is dipole coupling between clusters separated by less than 2—3 diameters, i.e., the clusters need not be in *direct contact*. Thus, even though the cross-linked gold particle aggregates may be smaller in size, as indicated from the optical absorption spectra, this does not have any bearing on the dimensions of gold aggregates in direct contact, an aspect which is determined solely by the surface coverage of the surfactant on the clusters. Increasing the concentration of PDT molecules in solution leads to a larger surface coverage of the clusters, and consequently to less probability for sintering with neighboring gold particles, as is observed from the XRD measurements. A clear trend in the sintered particle size with PDT surface coverage is seen (Fig. 6), which may be satisfactorily understood along the above-mentioned lines. We would like to point out that the FP data calculated after 15 min of aggregation has been correlated with XRD particle-size data determined for the precipitates after ca. 2 d of aging the PDT capped gold sol. While we believe the trends in the XRD measurements are meaningful, the exact magnitude of the particle size may be quite different from the size of the gold particle aggregates in the gold hydrosol 15 min after aging the solution.

In conclusion, optical absorption spectroscopy measurements indicate that cross-linking of gold clusters capped with a small dithiol molecule (1,3-propanedithiol) occurs in open string-like structures, the degree of aggregation of which can be controlled by controlling the cluster surface coverage with the dithiol molecule. Increasing the dithiol surface coverage prevents direct contact between the clusters. This technique shows promise for the generation of ordered assemblies of colloidal particles in solution with tailorable optoelectronic properties.

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