Reduced Reactivity of Aged Au Nanoparticles in Ligand Exchange Reactions

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Here, we report a dramatically reduced reactivity of aged Au nanoparticles in a place exchange reaction. The ligand exchange reaction is an extremely versatile tool for the preparation of functionalized metal nanoparticles.[1] This method is fast and simple to use; it allows one to introduce functional groups that are incompatible with other methods for nanoparticle synthesis. The importance of ligand exchange reaction made it a subject of several mechanistic studies; many aspects of this process are, however, still unclear.[1] In particular, a recent report by the R. W. Murray group suggests a new role of oxygen in mediating the exchange reaction.[2]

We have recently reported that disulfides, usually assumed to be inactive in the exchange reaction, undergo partial exchange with Au nanoparticles protected by phosphines or short-chain thiols (Scheme 1).[3]

Scheme 1. Place-Exchange Reaction of Nanoparticles I with Disulfide II
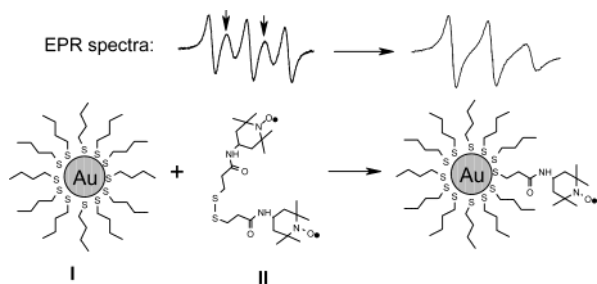
This reaction can be conveniently monitored by EPR spectroscopy, provided the disulfide is functionalized with a spin label, e.g., disulfide **II**. The kinetics of the reaction can be followed by the disappearance of the second or fourth peak in the EPR spectra (shown with arrows in Scheme 1). These peaks originate from the spin–spin interactions between the adjacent spin labels in unbound disulfide **II**; as the S–S bond is broken during the exchange reaction, these peaks gradually disappear from the spectra.[3]

We were interested in studying the kinetics of the exchange reaction between *n*-butanethiol-protected Au nanoparticles **I** and disulfide **II** (Scheme 1). We found, however, that kinetic runs showed poor reproducibility. To test if this poor reproducibility was due to the presence of oxygen, we carried out reactions in inert atmosphere. However, a reaction carried out under argon showed the same kinetics as the parent reaction performed in air.

Importantly, we found that aging of the Au nanoparticles in solution strongly affects the rate of the ligand exchange reaction. A freshly prepared solution of Au nanoparticles **I** in chlorobenzene reacted with disulfide **II** at a much faster rate than the solution which had been left to age for several hours. The poor reproducibility of the exchange kinetics was thus due to different times which the Au nanoparticles had been aged for during their synthesis and sample preparation. Nanoparticles with the same aging history showed good reproducibility of kinetics of the ligand exchange.
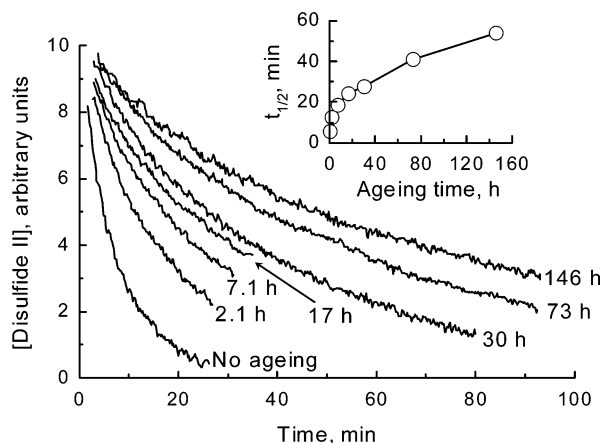

Figure 1. Kinetic profiles of the exchange reaction of nanoparticles **I** with ligand **II**. The nanoparticles were aged in a chlorobenzene solution prior to reaction for variable periods of time (as labeled on the graph). The inset shows the half-reaction time of the exchange reaction as a function of the aging time.

Figure 1 shows kinetic profiles of the exchange reaction of nanoparticles **I** (0.05 mM) with disulfide **II** (0.025 mM) in chlorobenzene at room temperature. Nanoparticles were synthesized by a literature procedure[4] that was modified to minimize reaction and workup time (to reduce aging during preparation). The 0.1 mM Au nanoparticle solution in chlorobenzene was then aged at room temperature for different periods of time prior to the exchange reaction. One can see (Figure 1) that aging has a very profound impact on the reactivity of nanoparticles: freshly prepared solutions react up to 10 times faster than the solutions aged for 1 week.

The core of the Au nanoparticles used in this study has ca. 500 gold atoms and is coated with ca. 150 ligands. Exchange reaction with excess disulfide, however, would only replace a maximum of ca. 3–5 ligands per particle. (the exact number of exchangeable ligands is batch-dependent). As reactions in Figure 1 were carried out at 1:2 ligand to nanoparticle stoichiometry, nearly complete exchange was observed at longer times. Aging, however, appears to have no impact on the maximum number of exchangeable ligands.

To probe the origin of the aging behavior, we studied the properties of freshly made and aged nanoparticles using other analytical methods. Figure 2 shows TEM images of freshly made (a) and aged (b) nanoparticles **I**. The average particle size and the size distribution were 2.6 ± 1.0 nm and 2.7 ± 0.9 nm for nanoparticles freshly prepared and aged for 65 h, respectively. Clearly, there was no change in the particle size within the experimental error. Increase in particle size and partial aggregation was only observed at much longer aging times (>2 weeks). This is consistent with the literature observation that while particle size increases substantially with increased reaction time during nanoparticle synthesis, purified particles are stable in core size for weeks.[5] No aggregation is observed after the exchange reaction.
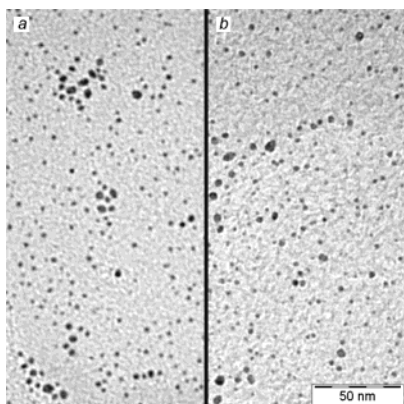
Figure 2. TEM images of freshly prepared (a) and aged (b) nanoparticles **I**. The aged sample was left for 65 h in a chlorobenzene solution. The scale bar is the same for both images.
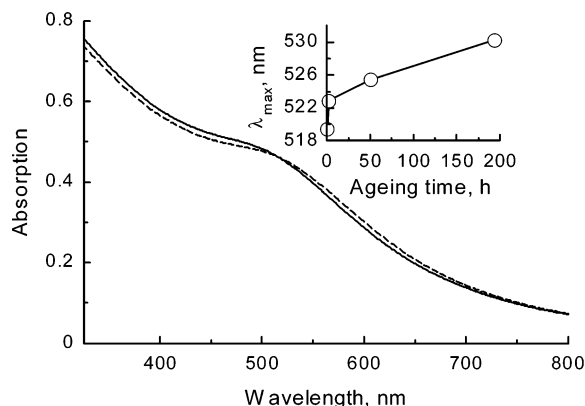

Figure 3. UV spectra of freshly prepared (solid line) and aged for 194 h (dashed line) 1 μM solution of nanoparticles **I** in chlorobenzene. The inset shows the λ_{max} for the surface plasmon peak as a function of aging time.

Figure 3 shows the UV spectra of nanoparticles **I** as a function of aging time. The important feature of the spectra is a surface plasmon peak (a shoulder at ca. 520 nm). Although all spectra have similar line shape, peak-fitting analysis revealed that λ_{max} for the plasmon peak contribution undergoes a substantial red-shift with increased aging time. The intensity of the plasmon peak was, however, nearly constant. This further confirms that the particle size is not affected by aging.[6]

The combination of TEM and UV data thus reveals that the particle size is not affected by aging within the time scale of our experiments. The shift in the position of the plasmon band (Figure 3) is therefore most likely caused by small changes in particle morphology upon aging. It is interesting to note that the time dependence of UV spectra and reaction kinetics (see insets in Figures 1 and 3) is quite similar. This time dependence cannot be fitted by a simple exponential model assuming first-order decay of exchangeable sites. Aging is therefore a complex reaction that involves several fast and slow processes.

We propose that the dramatic effect of aging on reactivity is due to reorganization of the nanoparticle surface. As the number of exchangeable sites per nanoparticle is very small (vide supra), they are likely to be defect sites rather than regular geometric features of a faceted nanoparticle (e.g., vertex or edge sites). The decreased reactivity of aged nanoparticles can thus be explained by annealing or stabilization of the high-energy defect sites on the nanoparticle surface.

A recent study[7] reported that aging of less stable, phosphine-protected Au nanoparticles leads to a rapid increase in particle size. Thiol-protected particles showed very slow change in particle size,
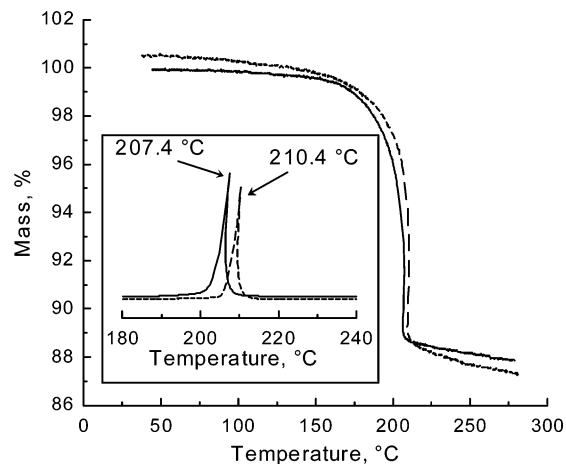

Figure 4. Thermal gravimetric analysis of freshly prepared (solid line) and aged for 63 h (dashed line) nanoparticles **I**. The inset shows the corresponding differential scanning calorimetry (DSC) traces. The numbers in the inset are the temperatures of the DSC maxima.

consistent with the results of our work. Subtle changes in nanoparticle behavior during aging was attributed to changes in the particle morphology.[7]

To get more insight into the processes taking place during aging, we performed thermal analysis of freshly made and aged nanoparticles **I**. The results are in Figure 4. Rapid mass loss is observed above 200 °C, consistent with desorption of the ligands from the Au surface.[8] The decomposition of the aged nanoparticles, however, occurs at a slightly higher temperature than the freshly prepared sample. This is further confirmed by the differential scanning calorimetry traces shown on the inset in Figure 4. The enhanced thermal stability of the aged nanoparticles is consistent with the proposed surface reorganization during aging. If such reorganization involved just 3−5 defect sites on the surface, one might expect to see no noticeable changes in the nanoparticle thermal properties; results in Figure 4 thus suggest that reorganization probably affects a substantial proportion of the surface atoms.

In conclusion, we have shown that the reactivity of Au nanoparticles in place-exchange with disulfides is greatly reduced by aging in solution at room temperature. The likely origin of this effect is a slow reorganization of the nanoparticle surface.

Supporting Information Available: Full details of Au nanoparticle synthesis and characterization and details of the kinetic study and the kinetic model (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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