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Martin Schulz-Dobrick, K. Vijaya Sarathy, and Martin Jansen

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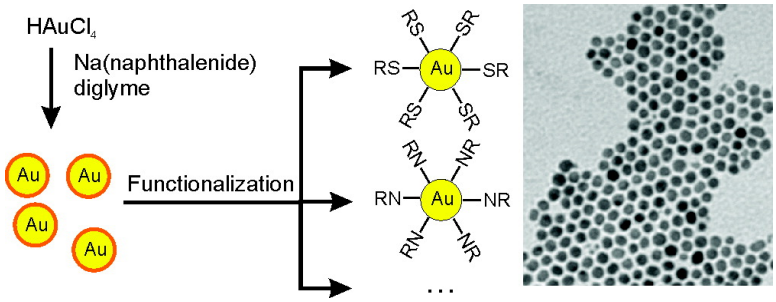

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Surfactant-Free Synthesis and Functionalization of Gold Nanoparticles

Martin Schulz-Dobrick, K. Vijaya Sarathy, and Martin Jansen*

Max Planck Institute for Solid State Research, Heisenbergstr. 1, 70569 Stuttgart, Germany

Received July 15, 2005; E-mail: M.Jansen@fkf.mpg.de

Although enjoying a history dating back to the days of Faraday's pioneering work,[1] gold nanoparticles are still intensively studied in current research.[2,3] This is mainly due to their applications in catalysis,[4,5] chemical sensing,[6,7] biolabeling,[8,9] and photonics.[10,11] Additionally, gold nanoparticles have served as building blocks for self-assembled two- and three-dimensional superlattices.[12−14] For most applications, control of the core size, shape, and dispersity and the nature of the ligand shell is desirable, along with a simple and widely applicable preparation method.

Two principal concepts can be distinguished in the solution synthesis of gold nanoparticles. The first, and older one, involves the reduction of tetrachloroaurate ions in aqueous media, employing reducing agents such as sodium citrate[15] or sodium borohydride. This step can be performed in the presence or absence of additional ligands, as the nanoparticles in the resulting hydrosols are stabilized electrostatically. Functionalization of the nanoparticles can easily be achieved, but is restricted to water-soluble ligands. However, the control over particle size and monodispersity in a particular synthetic protocol is rather poor. The second concept involves the synthesis in organic solvents. The most popular method is the two-phase synthesis reported by Brust et al.,[16] which involves the transfer of tetrachloroaurate ions into toluene with the use of tetraalkylammonium bromide and subsequent reduction with sodium borohydride in the presence of thiols. Depending on the reaction conditions, core sizes ranging from 1 to 4 nm can be achieved. Several simpler single-phase syntheses have been presented recently.[17−19] They employ the reduction with borohydrides that are soluble in the organic solvent in the presence of a capping ligand. If unpolar solvents (e.g., toluene) are used, additional surfactants have to be added to render the gold salt soluble. The advantages of all of these methods are (i) good control over the particle size and dispersity by tuning the gold salt-to-ligand ratio and reaction conditions,[20] (ii) the possibility of introducing a variety of functionalized ligands, and (iii) simple isolation, cleaning, and redispersion of the particles in different solvents. Disadvantages are the impurities that are introduced by the use of surfactants and the restriction of carrying out the reduction in the presence of the capping ligand. The latter can be partially circumvented if functional ligands are introduced by ligand exchange reactions on stable nanoparticles.[21−23] However, this approach is generally more elaborate and still suffers some limitations, especially the problem of getting a complete ligand exchange.

In this study, a new method of producing gold nanoparticles is presented that combines, in a way, the advantages of both concepts, which are a simple, surfactant-free synthesis, high variability in the introduction of functionalized ligands, and good control over the particle size. It was found that a solution of hydrogen tetrachloroaurate in diethylene glycol dimethyl ether (diglyme) can be reduced by a solution of sodium naphthalenide in diglyme to form gold nanoparticles. In this reaction, no further stabilizing surfactant is necessary, although sodium naphthalenide can be considered a rather harsh reducing agent. The resulting, weakly protected nanoparticles can straightforwardly be stabilized and functionalized by the addition of a variety of ligands. A detailed description of the synthesis and characterization techniques is given in the Supporting Information.

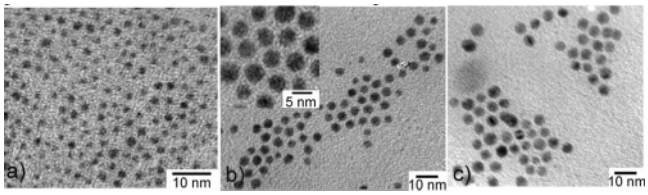

Figure 1. TEM images of different samples of dodecanethiol-capped gold nanoparticles with varying sizes: (a) 1.9 ± 0.4 nm, (b) 3.9 ± 0.7 nm, and (c) 5.2 ± 0.7 nm.

Upon dropwise addition of the sodium naphthalenide solution to the yellow aurate solution, the latter turns slightly green followed by a deep brown color, indicating the formation of gold nanoparticles. On further addition of the reducing agent, a dark purple color is arising, which can be attributed to the surface plasmon resonance, suggesting an increase in particle size above 2 nm.[24] The nanoparticle growth is slow in diglyme, but, on standing, they tend to agglomerate and form a loose purple precipitate within the course of several hours to 1 day. Attempts were made to isolate and clean the nanoparticles by a standard centrifugation and redispersion procedure, but the diglyme-protected nanoparticles coalesce irreversibly by applying this process and were not found to be redispersible.

After reduction, the nanoparticles are presumably stabilized only by solvent molecules, which should be easily replaced by ligands that offer stronger binding groups, such as thiols or amines, and an enduring stabilization of the nanoparticles. At first, 1-dodecanethiol was chosen as a capping ligand, which was added in excess to stirred solutions of the weakly protected nanoparticles. Ligand binding is fast, and the unpolar nanoparticles readily precipitated from the diglyme solution. They could be isolated by centrifugation, cleaned by washing with ethanol to remove diglyme, naphthalene, and excess unbound ligand, and were found to be redispersible in various unpolar solvents. To determine particle size and dispersity, the dodecanethiol-capped nanoparticles were investigated by TEM. Figure 1 shows TEM images of gold nanoparticles that were obtained by capping weakly stabilized nanoparticle solutions, which were prepared with different amounts of reduction solution. The average size of the nanoparticles increases with increasing amounts of reduction solution, which was already suggested by the evolution of the surface plasmon resonance. The size of the dodecanethiol-capped nanoparticles could be tuned within the range of 1.9 to 5.2 nm. Addition of a high excess of reduction solution did not result in larger particles. The achieved dispersities of 15−20% are narrow and comparable to the leading methods in the field, especially since no further treatments, such as size-selective precipitation or thermal annealing,[25,26] were applied.

To investigate the variability of the synthesis, different ligands with various functional groups were employed for long-term

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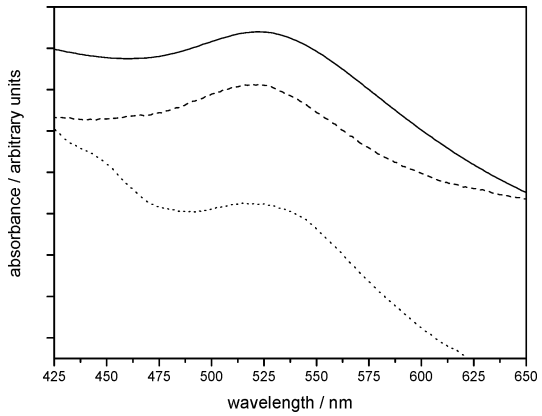

Figure 2. UV−vis absorption spectra of gold nanoparticles capped with different ligands. Solid line: dodecanethiol capped, avg. size = 4.7 nm, toluene solution. Dashed line: dodecylamine, 4.2 nm, toluene. Dotted line: 2-(dimethylamino)ethanethiol hydrochloride, 5.3 nm, water.

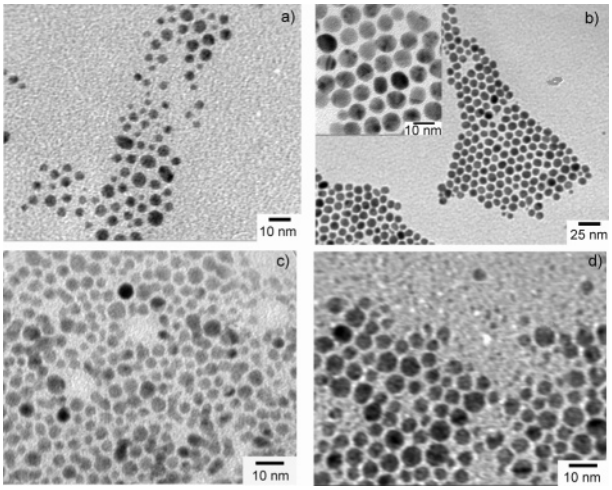

Figure 3. TEM images of different samples of dodecylamine-capped gold nanoparticles (a and b) and water-soluble 2-(dimethylamino)ethanethiol hydrochloride-capped gold nanoparticles (c and d). The average particle sizes of the corresponding samples are (a) 4.2 ± 1.1 nm, (b) 8.9 ± 1.3 nm, (c) 4.1 ± 1.2 nm, and (d) 5.3 ± 1.3 nm.

stabilization of the gold nanoparticles. Ligands with thiol or amine binding groups that lead to gold nanoparticles that are soluble in organic solvents were added as a solution in diglyme or toluene to the weakly stabilized nanoparticle solutions, and the ligand-capped nanoparticles were isolated and cleaned by standard precipitation and redispersion cycles. Water-soluble gold nanoparticles were obtained by the use of 2-(dimethylamino)ethanethiol hydrochloride as a ligand, which was added in CH_2Cl_2.

The nanoparticles were characterized by UV−vis spectroscopy and TEM microscopy. Figure 2 shows the characteristic surface plasmon resonance in the absorption spectra of gold nanoparticles capped with different types of ligands. In Figure 3, TEM images of nanoparticles exhibiting different size and ligand types are depicted. Notably, larger particles could be obtained with amine ligands than with thiol ligands. Figure 2b shows a TEM image of 8.9 nm dodecylamine-capped nanoparticles, which exhibit a narrow dispersity, as indicated by the formation of 2D hexagonal close-packed arrays. This implies a significant particle growth during the ligand-binding process of the weaker amine ligands as compared to the stronger thiol ligands.

In conclusion, a new, facile synthesis for gold nanoparticles is presented. It combines the advantages of a surfactant-free formation of a weakly stabilized nanoparticle solution with the control over particle size and narrow dispersity. Subsequent functionalization with a variety of capping ligands is straightforwardly accomplished. The strict separation of particle formation and functionalization is particularly useful for the preparation of gold nanoparticles capped by ligands carrying functional groups that are not stable against reducing agents. Additionally, this method is applicable for the fast synthesis of many, differently capped gold nanoparticles for screening purposes.

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Supporting Information Available: Details of synthesis and characterization techniques and FT-IR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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