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Preparation of Functional Silane-Stabilized Gold Colloids in the (Sub)nanometer Size Range

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A synthesis method is introduced for very small uniform gold particles (diameter less than 5 nm), based on the reduction of hydrogen tetrachloroaurate(III) in ethanol in the presence of (γ-mercaptopropyl)-trimethoxysilane (MPS). The surface layer of MPS molecules gives the gold particles a high colloidal stability and allows in principle further reaction with any silane coupling agent. Decrease of the HAuCl₄: MPS ratio allows a controlled reduction of gold particle size, resulting in remarkably uniform gold clusters of (sub)nanometer size, observed with high-angle-annular-dark-field scanning transmission electron microscopy. After attachment of (γ-aminopropyl)triethoxysilane (APS) to the MPS surface layer, other molecules may be covalently bound to the gold colloid via the amine group of APS. As an illustrative example we prepared in this manner gold particles labeled with a fluorescent dye. The chemical structure of the surface silanes was studied with Fourier transform infrared spectroscopy.

1. Introduction

Colloidal gold particles with a diameter of a few nanometers or less have many (possible) applications. For example, gold particles coupled to immunoreagents are used for detecting proteins, lipids, RNA and DNA in cell-biological electron-microscopy studies.[1] In addition, (sub)-nanometer-sized gold particles may be useful because of their optoelectronic properties. When the gold particles are surrounded by ligand shells of dielectric material (for example silica), they behave as quantum dots which could be employed in nano-electronic switches.[2]

Numerous preparation methods have been developed to grow and stabilize colloidal gold particles with diameters ranging from 0.8 to 60 nm (see for a review Handley[3]). Generally, colloidal gold sol preparation comprises the reduction of a molecular gold species in solution. In addition to ionic gold(III) species like $AuCl_4^-$, gold(I) complexes with (organic) ligand molecules are frequently used as reagents. After reduction of the gold(I) complex, the resulting gold particles are stabilized by ligands attached to their surface. In this way extremely small gold clusters can be formed, containing only a few tens of gold atoms. Examples are the $Au_{55}[P(phenyl)_3]_{12}Cl_6$ two-shell cluster with a core diameter of about 1.4 nm[2] and the undecagold cluster $Au_{11}[P(aryl)_3]_7(CN)_3$ with a core diameter of 0.8 nm,[4] both stabilized by triphenylphosphine groups.

Giersig and Mulvaney[5] showed that alkanethiols can be utilized to form stabilizing monolayers on already-prepared gold colloids. Brust et al.[6] then demonstrated that one can employ this ability of alkanethiols to form self-assembled monolayers[7−9] on gold for the preparation of gold nanoparticles. In their method, $AuCl_4^-$ was reduced in the presence of dodecanethiol to produce a stable colloid of thiol-capped gold nanoparticles of decreasing diameter with decreasing $AuCl_4^-$-to-thiol ratio. The role of the alkanethiol can be regarded as analogous to the one of the surfactant in stabilizing water-in-oil microemulsions.[10] By using the bifunctional stabilizer *p*-mercaptophenol, gold particles were provided with functional phenolic hydroxyl groups.[11]

In this communication we introduce an analogous preparation method for gold particles specifically designed for reactions with functional silanes. The method employs a mercaptosilane compound, which not only ensures colloidal stability of the gold particles but also provides them with alkoxysilane surface groups. The silane coupling agent (γ-mercaptopropyl)trimethoxysilane (MPS) was selected because its thiol group has a high affinity for gold, leading to a stabilizing MPS monolayer on the gold surface. The importance of this monolayer is its potentiality to react with the wide variety of (commercially available) organosilanes,[12] to produce hybrid colloids with various properties. The (hydrolyzable) methoxysilane groups of MPS point outward and easily react via siloxane binding[12] with the alkoxysilane groups of another silane compound, such as (γ-aminopropyl)triethoxysilane (APS) in this study. Through cross-linking, the surface silanes may form a cagelike structure which wraps up the gold core (see Figure 1, illustrating monolayer coverage of both MPS and APS). This cross-linked silane coat may prevent the MPS molecules from being liberated from the gold core by, for example, strongly reducing reagents applied during processing of the gold particles. The amine groups of the APS molecules at the particle periphery can serve

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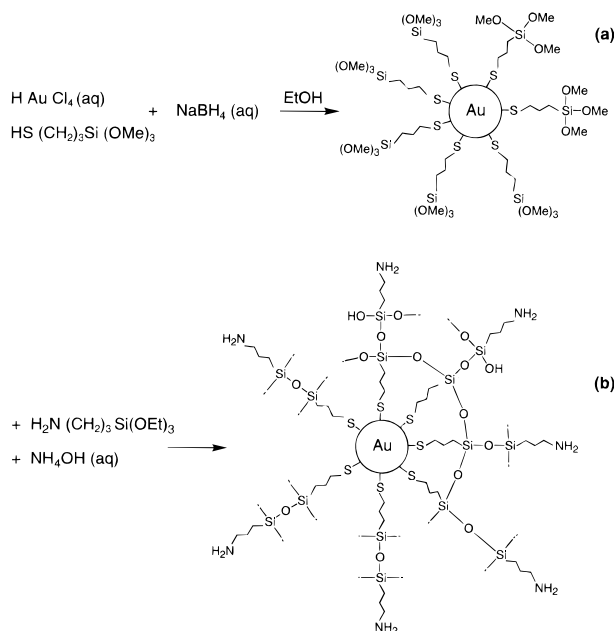
Figure 1. Schematic illustration of the reaction sequence: (a) Formation of MPS-stabilized gold nanoparticles by reduction with aqueous $NaBH_4$ of a $HAuCl_4$–MPS mixture in ethanol; (b) Basic idea of the coupling of APS to the MPS-stabilized gold particles. A cagelike silane structure is formed around the gold particle and (functional) amine groups are put at the particle periphery. (Additional products are left out of the reactions.)

as the substrate for further *covalent* reaction. An example in the present study is the attachment of fluoresceine isothiocyanate, which results in a fluorescent gold colloid.

Gold particles were characterized using transmission electron microscopy, high-angle annular dark-field scanning-transmission electron microscopy, and UV–vis absorption spectroscopy. The binding capacity of APS on the gold surface to the dye fluorescein isothiocyanate was investigated. To examine the chemical structure of the surface silanes on the gold particles, Fourier-transform infrared spectra were recorded.

2. Experimental Section

Materials. Absolute ethanol (Nedalco), ammonia (Merck, p.a. 25%), (γ-mercaptopropyl)trimethoxysilane (MPS, Fluka, >97% purity), (γ-aminopropyl)triethoxysilane (APS, Janssen, 99% purity), and fluorescein isothiocyanate (FITC, Sigma) were used as received. The concentration of the aqueous stock solution of hydrogen tetrachloroaurate(III), prepared with the strongly hygroscopic $HAuCl_4 \cdot (H_2O)_x$ (Janssen, 49 wt % Au), was determined by measuring the absorption peak of $AuCl_4^-$ at about 320 nm wavelength. The aqueous $HAuCl_4$ stock solution remained (visibly) unchanged upon storage at room temperature during several months. Gold sols prepared with a 3 month old $HAuCl_4$ stock solution did not show any difference in comparison to sols prepared with a fresh solution with respect to sol color, absorption spectra, and electron micrographs.

Because $NaBH_4$ slowly oxidizes in water, a fresh aqueous sodium borohydride solution (Janssen) was prepared before every series of experiments. Double-distilled water was used throughout the experiments. For gel filtration, a Sephadex LH-20 (Pharmacia Biotech) column was used with ethanol as the eluent. Sephadex LH-20 in ethanol shows a void volume percentage of 32% and, for polyethylene glycol, an exclusion limit at a molecular weight of about 4000 g/mol.

Preparation of Mercaptosilane-Stabilized Gold Particles. The gold sols were prepared in ethanol at room temperature by the reduction of $HAuCl_4$ with $NaBH_4$ in the presence of MPS as a particle stabilizer (see Figure 1a). To 10.0 mL of ethanol were successively added 1.00 mL of a x g/L MPS solution in ethanol and 200 μL of 13.5 mM aqueous $HAuCl_4$ solution. To change the $HAuCl_4$:MPS molar ratio (hereafter denoted as the

A:M ratio), the concentration of the MPS solution was varied between $x = 80$ mg/L (0.41 mM) and $x = 10.0$ g/L (50.9 mM). To the fresh $HAuCl_4$–MPS mixture, 200 μL of a 100 mM $NaBH_4$ aqueous solution was added in one portion under vigorous stirring. A $NaBH_4$:$HAuCl_4$ molar ratio beyond 7 ensured complete and fast reduction. Immediately, a coloring appeared which depended on the A:M ratio. This ratio is incorporated between brackets in the sol codes AuMps(6.62) to AuMps(0.053).

Gel filtration over a Sephadex LH-20 column was performed to remove free MPS and salts from the sols. The AuMps(0.529) sol migrated as a narrow brown band of constant width. The relative elution volume of ethanol needed for the particles to migrate through the column was roughly in the order of 30% of total column volume, implying that the MPS-stabilized gold particles elude at void volume.

Binding of Aminosilane to MPS-Stabilized Gold Particles. Compared to other organosilane coupling agents, aminosilanes show a higher binding reactivity toward silica surfaces owing to the γ-amine group, which catalyzes the formation of siloxane bonds.[12] For this reaction, sufficient water needs to be present to protonate the amine and hydrolyze the alkoxy groups. Excess water, however, stimulates the formation of APS multilayers. Since we aimed at binding a monolayer of APS to the silane groups of MPS on the gold particle surface, the reaction was performed in the presence of about 6 vol % of water. Also, ammonia was added (1 M) as a catalyst for siloxane-bond formation[13] to stimulate cross-linking between neighboring silanes on the particle surface.

A purified APS-modified gold sol was prepared as follows. One milliliter of sol AuMps(0.529) was immediately after its preparation purified by gel filtration over a Sephadex LH-20 column with ethanol as eluent. About 3 mL sol was collected. To this were added 100 μL of a 10.0 g/L APS solution in ethanol and 250 μL of ammonia (25% NH_3). This was stirred at room temperature for 15 min. Then again, 1 mL of this sol was purified from ammonia and excess APS over the column in ethanol (final code AuMps(0.529)Aps).

Binding of Aminosilane-Bound FITC to MPS-Stabilized Gold Particles. For the preparation of FITC-covered gold particles, the FITC was first coupled to the APS (FITC forms an isothiourea linkage with the APS amine) by bringing 50 mM of each in ethanol and stirring for 2 h (APS-FITC). To 11.4 mL of the unpurified sol AuMps(0.529) were added 100 μL of the 50 mM APS-FITC solution and 500 μL of ammonia (25% NH_3). This mixture was heated at 60 °C for 4 h. Then, this sol was transferred to water and purified from ammonia and excess APS-FITC by dialysis in a cellulose tube against demineralized water for 1 week until no FITC could be visually observed in the supernatant (final code AuMps(0.529)Fitc).

Characterization Techniques. Bright-field images were made with a Philips EM-420 transmission electron microscope (TEM) operated at 80 kV. High-angle-annular-dark-field images were made with a Philips CM-200 scanning-transmission electron microscope (HAADF-STEM) equipped with a field emission gun and operated at 200 kV. Sample preparation for TEM and STEM was performed by dipping a carbon-supported 400-mesh copper electron-microscopy grid in the alcosol, draining the excess alcosol from the grid, and drying in the air. Near-ultraviolet–visible absorption spectra were recorded for wavelengths between 290 and 700 nm with a Spectronic 200 UV spectrophotometer. Fourier-transform infrared (FT-IR) spectroscopy was performed on a Perkin–Elmer System 2000 FT-IR spectrometer with an attenuated total reflection unit equipped with a ZnSe crystal (SpectraTech). The sample solution was deposited on the crystal and dried by evaporating its solvent in the air at room temperature. The MPS and APS samples were applied as 10 g/L solutions in ethanol.

3. Results and Discussion

Mercaptosilane-Stabilized Gold Sols. Influence of $HAuCl_4$-to-MPS Ratio. In Table 1 the results are shown of the reduction by $NaBH_4$ of a series of $HAuCl_4$–MPS mixtures with varying A:M ratio. Upon addition of

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Table 1. Alcosols of MPS-Stabilized Gold Particles[a]

sample code[b]	appearance	D_{TEM} (nm)
AuMps(6.62)	black sediment	aggregated
AuMps(5.29)	wine-red sol	3–5
AuMps(1.70)	orange sol	2–3
AuMps(0.529)	light brown sol	1.0–1.5
AuMps(0.106)	yellow-brown sol	≤1.0
AuMps(0.053)	light yellow solution	?

[a] Appearances of the sols and the estimated sizes of their particles. In all sols [Au] = 1.75×10^{-4} M. [b] The HAuCl$_4$:MPS molar ratio is shown in parentheses.

a little MPS, corresponding to a A:M ratio higher than about 6, all the gold immediately flocculated and formed a (purple-)black sediment. Upon adding more MPS, stable sols were formed which showed a trend in their color from wine-red for sol AuMps(5.29) to yellow-brown for sol AuMps(0.106).

For the preparation of sol AuMps(0.106), the NaBH$_4$ was not added immediately after mixing the MPS and HAuCl$_4$. A stable gold sol was only obtained after the HAuCl$_4$–MPS mixture first had been stirred for about 10 min until it had changed from yellow to colorless. This color change also took place for the other A:M ratios and took more time for increasing A:M ratio. The absorption spectrum was recorded in time for a HAuCl$_4$–MPS mixture of A:M ratio 0.529. After the 1.00 mL of 1.0 g/L MPS and 200 μL of 13.5 mM HAuCl$_4$ were mixed in 10 mL of ethanol, the absorption band at 320 nm, being characteristic for AuCl$_4^-$, gradually decreased in intensity (without shifting its position) until it completely disappeared after a hundred minutes. The solution then was colorless. Apparently, the AuCl$_4^-$ complex gradually changed into a MPS–gold complex. It may be possible that the thiol group of MPS, by oxidizing to a disufide, reduces the Au-(III) from the tetrachloroaurate to Au(I) which complexes with MPS. The addition of NaBH$_4$ then further reduces this Au(I) complex to form MPS-capped gold particles.

The addition of NaBH$_4$ to a HAuCl$_4$–MPS mixture (immediately after mixing) of a very low A:M ratio of 0.053, yielded a light yellow solution (sol AuMps(0.053)). In the transmission electron microscope, no particulate gold was observed in bright field. We do not have a clear understanding of the gold species in this solution. Possibly some kind of gold–MPS–chloride complex is present.

Electron Microscopy. The particle size determinations by electron microscopy (see Table 1) reveal that a decrease of the A:M ratio causes a decrease of the particle diameter from about 3–5 nm for sol AuMps(5.29) to about 1 nm or even smaller for sol AuMps(0.106). The gold particles of sol AuMps(5.29), visualized by TEM (Figure 2a), are quite nonisometric and nonuniform in size. The aggregates of these particles on the micrograph are due to drying effects on the EM grid. The TEM micrograph of AuMps(0.529) (Figure 2b) shows nanometer-sized gold particles in an aggregate structure in which the individual particles cannot be identified anymore. With HAADF-STEM on the same sample grid, the individual AuMps-(0.529) particles can be visualized (Figure 2c). Due to the lack of a clear correlation between the dark-field representation of the particles and their actual size, the particle size can only be estimated to be in the range of 1.0–1.5 nm. Figure 2c illustrates that the gold particles, whatever their precise diameters, have quite uniform dimensions. The micrograph also suggests that the particles have an isometric shape. The particles of AuMps(0.106) show a dark-field intensity which is less bright than that of the AuMps(0.529) particles. Therefore, they are probably even smaller than those of AuMps(0.529), and of subnanometer size.
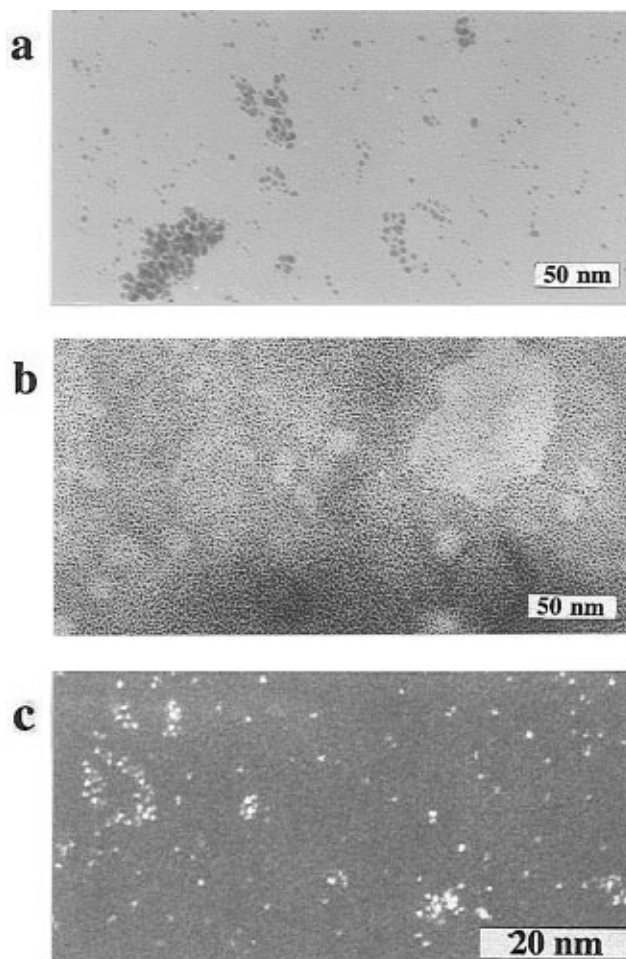
Figure 2. Electron micrographs of MPS-stabilized gold particles: (a) TEM image of sol AuMps(5.29); (b) TEM image of sol AuMps(0.529); (c) HAADF-STEM image of sol AuMps-(0.529).
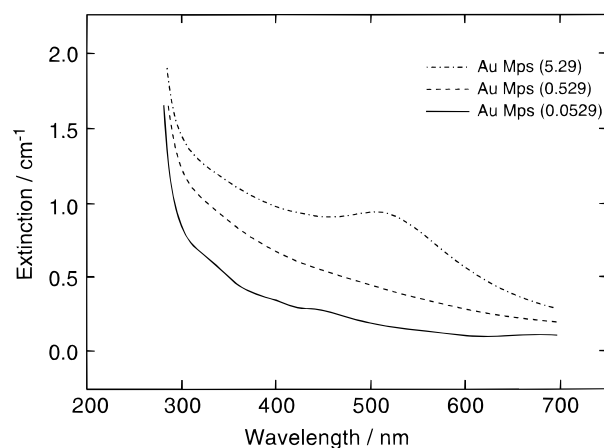
Figure 3. UV–visible absorption spectra of MPS-stabilized gold sols AuMps(5.29), AuMps(0.529), and AuMps(0.053).

UV–vis Absorption Spectra. As shown by the absorption spectra (Figure 3), the wine-red color of sol AuMps(5.29) is connected to the presence of the broad rudimentary plasmon absorption band at 520 nm wavelength. This band, being typical for particulate gold sols, is absent in the spectrum of the light-brown sol AuMps-(0.529). The disappearance of the plasmon band from the spectrum can be attributed to quantum-size effects accompanying the reduction of the gold particle dimensions. Duff et al.[14] found the plasmon band present for

a scarlet sol of 4.3-nm gold particles, and its near absence (shoulder) for an orange-brown sol of 1.4-nm gold particles. In view of the color and spectrum of sol AuMps(0.529), our particle size estimation of 1.0−1.5 nm seems to be plausible.

Particle Growth. The uniformity in the nanometer-sized gold particles of AuMps(0.529) is quite remarkable. It should be noted that a homogeneous gold nucleation inevitably produces a fairly broad distribution of particles because of the statistical fluctuations underlying the nucleation process. The distribution may then narrow in time during further particle growth. The uniform size of the AuMps(0.529) particles indicates that the MPS molecules control the nucleation of the gold.

It had no effect on the particle size or sol stability whether the NaBH$_4$ reductor solution was added to the HAuCl$_4$−MPS mixture at once or in a sequence of smaller portions. After every portion added, a certain corresponding amount of gold particles was formed, expressed by an increasing intensity of the sol color. The UV−vis absorption spectrum preserved its trend, and the gold particles were as uniform as in the case that all NaBH$_4$ was added at once. In fact, only the initial A:M ratio determined the particle size and uniformity. To obtain a sol that retains its stability in time, however, it is essential that the total molar amount of added NaBH$_4$ is about 7 times the amount of HAuCl$_4$.

So the MPS seems to stabilize the lyophobic gold nuclei in ethanol in a manner which resembles the role of the surfactant in the spontaneous formation of a water-in-oil microemulsion. This should be distinguished from the situation in which gold colloids first homogeneously nucleate (and grow) and only afterward are covered by stabilizing MPS molecules.

Our preparation method apparently does not allow for stable sols with particle diameters above 5 nm. This is probably due to stronger van der Waals attractions between larger gold particles and the fact that MPS groups do not contribute to a stabilizing surface charge. (As will be discussed later in this section, the methoxysilane groups of MPS indeed are hardly hydrolyzed in ethanol.)

For the 3-to-5-nm particles of sol AuMps(5.29), the A:M ratio indicates that about 0.3 MPS molecule is present per surface gold atom. It has been shown that 3-nm gold particles covered by self-assembled monolayers of dodecanethiol contain about 0.5 alkanethiol per surface gold atom.[10] So it can be assumed that practically all added MPS molecules are present on the surface of the AuMps-(5.29) gold particles. That MPS forms a less dense monolayer compared to dodecanethiol may be caused by the bulky trimethoxysilane endgroup of MPS. On the nanometer-sized AuMps(0.529) particles roughly six MPS molecules are available per surface gold atom, and on the (sub)nanometer-sized AuMps(0.106) particles even about 30. Obviously, to stabilize increasingly small gold clusters, an increasing excess amount of MPS is necessary.

Modification of Mercaptosilane−Gold with Aminosilane. Amine Functionality. Investigation of the (purified) light-brown alcosol AuMps(0.529)Aps by STEM (Figure 4) showed that the gold cores still had the same degree of homogeneity as before the modification with APS. Obviously, the modification had not led to aggregation of the particles; particle doublets and triplets probably were formed during the drying of the sol on the EM grid. The alcosol AuMps(0.529)Aps could be transformed to an aquasol by dialysis against demineralized water while retaining its colloidal stability.
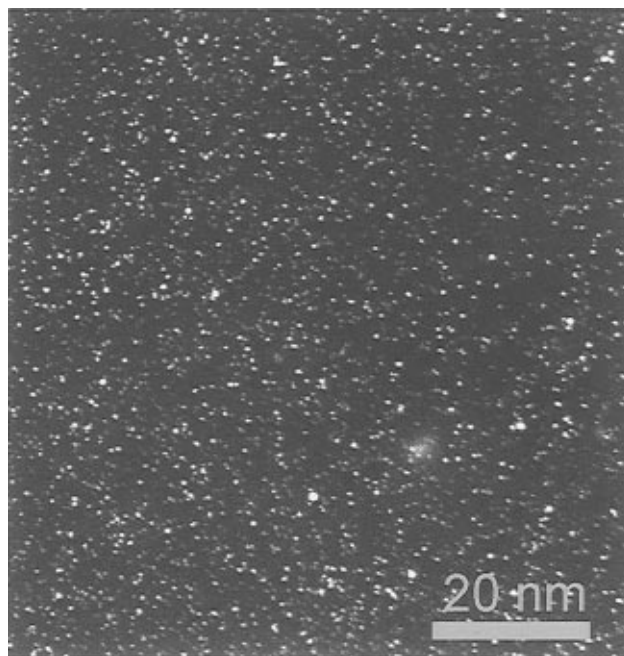
Figure 4. High-resolution HAADF-STEM image of sol AuMps-(0.529)Aps.

To investigate if the APS modification had provided the gold particles with functional amine groups that are able to bind foreign species, the following procedure was followed. An excess amount of FITC in ethanol was added to the AuMps(0.529)Aps alcosol and purified after 2 h over the Sephadex LH-20 column. The collected gold fraction did not show any visibly detectable FITC coloring, and also with UV−vis absorption spectroscopy the characteristic 500-nm band of FITC could not be detected.

Infrared Spectroscopy. To understand the apparent lack of functional amine groups on the gold particle surface (is there any APS present on the surface?), FT-IR measurements have been performed on MPS, APS, and sol AuMps(0.529)Aps (Figure 5). The band assignments from literature[15−21] are shown in Table 2.

The spectrum of MPS shows the domination of bands that are typical for methoxysilane groups (2959, 2840, and 1191 cm^{-1}). The only indication of the hydrolysis of these groups is a weak band of Si−OH at 954 cm^{-1}. Bands typical of Si−O−Si bonds are absent. On the other hand, the spectrum of APS shows a Si−OH (silanol) band (961 cm^{-1}) that is considerably stronger than that of MPS. Moreover, APS shows explicit Si−O−Si (siloxane) bands (1114 and ∼1003 cm^{-1}). So during room-temperature drying for preparation, MPS preserves most of its methoxysilane groups, while in APS the ethoxysilane groups are considerably hydrolyzed by atmospheric water to silanols, which in turn are condensed to cross-linking siloxane bonds. This is no surprising result, because, as

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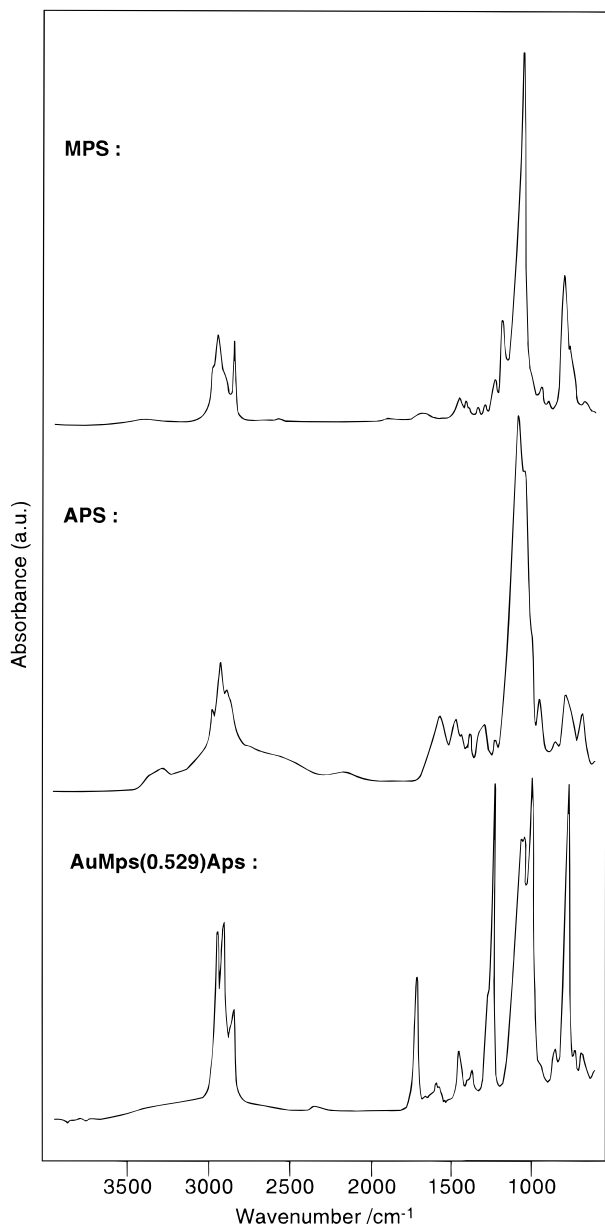
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Figure 5. FT-IR spectra of (γ-mercaptopropyl)trimethoxysilane (MPS), (γ-aminopropyl)triethoxysilane (APS), and gold sol AuMps(0.529)Aps.

pointed out in section 2, the γ-amine group of APS catalyzes the formation of siloxane bonds.

The definite proof that APS is indeed bound to the AuMps(0.529)Aps particles is the presence in their spectrum of a strong C-N band at 1074 cm^{-1}. The spectrum of AuMps(0.529)Aps further shows a strong band of methoxysilane (2961 cm^{-1}) coming from MPS and strong bands of siloxane bonds (1094 and 1026 cm^{-1}). So although APS molecules are bound to the MPS molecules on the gold particle surface through siloxane bonds, a significant amount of unreacted methoxide groups of MPS are still present in the particle surface layer. The siloxane bands in the AuMps(0.529)Aps spectrum are also strongly present in the APS spectrum. Therefore, probably a large portion of the siloxane bonds measured in the AuMps-(0.529)Aps FT-IR sample have originated from APS−ethoxysilane condensation during sample drying.

In the AuMps(0.529)Aps spectrum, any bands of the SH and NH$_2$ groups of MPS and APS, respectively, are not visible. The already very weak band of the SH group of MPS has disappeared due to its chemisorption on the

gold particle. A more explicit disappearance of the S−H stretching mode on thiol-to-gold binding was formerly observed by Brust et al.[11] Probably it can be attributed to the removal of the thiol hydrogen. In the case of APS, we already know that the amine group is not available as a free group at the particle surface. Firstly, the aminopropyl of APS might be turned toward the gold surface, penetrating into the MPS monolayer. This penetration seems plausible as the methoxy groups of the MPS molecules on the gold surface show no signs of intensive hydrolysis and cross-linking. The situation may be thermodynamically favorable, the hydrophobic propyl groups of APS being lined up parallel to those of MPS. Sterically, however, it seems unfavorable, the triethoxysilane end groups of APS being quite bulky. Furthermore, it would mean that the amine groups of APS would be present on or near the surface of the gold core. Indeed, it has been found by Liz-Marzán et al.[22] that the primary γ-amine of APS shows a tendency to adsorb on the gold surface (by that creating the ability to grow a silica coat around gold particles).

A second possibility would be that the aminopropyl is indeed pointing outward from the gold particle surface but that the amine undergoes severe hydrogen binding to silanol groups at the surface. Boerio et al.[20] postulated that this hydrogen binding is so strong that the silanol proton can be considered as intermediate between the amine group and the silanolate ion.

A striking feature is that the 700−1260 cm^{-1} region of the AuMps(0.529)Aps spectrum shows much resemblance, in both band wavenumber and intensity, with the spectrum of poly(dimethylsiloxane)[23] (PDMS, "silicon oil"). The reference FT-IR spectrum of PDMS shows the band sequence [23]: 1261 cm^{-1} (strong), 1093 cm^{-1} (strong asymmetric Si−O−Si stretch), 1023 cm^{-1} (strong symmetric Si−O−Si stretch), 841 cm^{-1} (moderate), 800 cm^{-1} (strong Si−CH$_3$ stretch), 754 cm^{-1} (weak), 702 cm^{-1} (moderate). This might imply that the siloxane bonds on the particle surface are connected in a linear chain-like fashion. A more three-dimensional cross-linking would have caused the appearance of more bands and would have increased band broadening and shifting.

A peculiar band in the AuMps(0.529)Aps spectrum is that at 1730 cm^{-1}, which can only be assigned to a carbonyl stretching vibration of an ester compound. The band seems too strong to be imputed to a contamination. Curious in this context are the findings of Furukawa et al.[15] who studied the adsorption of APS on an aluminum oxide surface. They found IR-absorption bands typical of an aldehyde and postulated that the ethanol produced by hydrolysis of the adsorbed silane underwent oxidation to form acetaldehyde on the Al$_2$O$_3$ surface, which probably acted as a catalyst. In our case the gold surface (in cooperation with the amine group ?) may also have some catalyzing effect on the oxidation of alcohol to an ester.

Modification with Aminosilane-Bound FITC. Although APS molecules can be attached to the particle surface, the amines lose their chemical functionality precluding conjugation to foreign (bio)molecules like FITC and immunoglobulins. However, this problem can be evaded by first binding the molecule to the amine of APS, after which the modified APS can be attached to the gold particle surface through siloxane binding. Sol AuMps-(0.529)Fitc was prepared this way and then transferred to water by dialysis (thus removing unbound FITC-APS). It showed a dominant yellow-green fluorescent coloring

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Table 2. Tentative Assignment of the FT-IR Absorption Bands (in cm⁻¹) of the Silane Coupling Agents MPS and APS and of the APS-Modified MPS-Stabilized Gold Sol AuMps(0.529)Aps[a]

MPS	APS	AuMps(0.529)Aps	assignment	ref(s)
	3280 (w)		$\nu(NH_2)$ sym	15, 16
	2973 (m)		$\nu(CH_3)$ asym of C_2H_5	17
2959 (sh)		2961 (s)	$\nu(CH_3)$ asym of Si−OCH₃	15, 18
2941 (s)	2927 (s)	2927 (s)	$\nu(CH_2)$ asym	16, 19
2882 (sh)	2886 (m)		?	
	2865 (sh)	2857 (m)	$\nu(CH_2)$ sym of C_2H_5	15
2840 (s)			$\nu(CH_3)$ sym of Si−O−CH₃	16, 19
2570 (w)			$\nu(S-H)$	17
		1730 (s)	$\nu(C=O)$ of $R_1-O-C(=O)-R_2$	17
	1573 (m)		$\delta(NH_2)$	15, 16, 19
	1482 (m)	1462 (m)	$\delta(CH_2)$ of propyl	19
1444 (w)	1443 (w)		$\delta(CH_2)$ of propyl	19
1412 (w)	1410 (w)	1405 (w)	$\delta(Si-CH_2)$	19
1392 (w)	1390 (w)	1380 (w)	$\delta(CH_2)$ of propyl	17
1300 (w)	1300 (m)		$\omega(CH_2)$ or $\tau(CH_2)$ of propyl (?)	20
		1267 (sh)	?	
1241 (m)			SiCH₂ (??)	17
1191 (m)			$\rho(Si-O-CH_3)$	19
	~1160 (sh)		Si−O−C₂H₅ (??)	17
	1114 (s)	1094 (s)	$\nu(Si-O-Si)$ asym	19, 20, 21
1084 (s)			$\nu(C-O)$ sym	19
	1073 (s)	1074 (s)	$\nu(C-N)$ sym	19
	~1003 (sh)	1026 (s)	$\nu(Si-O-Si)$ sym	16, 19, 20
954 (w)	961 (m)	963 (sh)	$\nu(Si-OH)$	19
	859 (w)	864 (w)	?	
814 (s)	793 (m)	800 (s)	$\nu(Si-CH_2)$ (?)	19, 21
768 (sh)		743 (w)	?	
688 (w)	697 (m)	705 (w)	?	

[a] The samples have been air-dried at room temperature. Key: s, strong; m, moderate; w, weak; sh, shoulder; ν, stretch; δ, deformation; ω, wagging; ρ, rocking; τ, twisting.

of the FITC. This demonstrated that FITC molecules were indeed present at the particle surface. The FITC emission signal had been quenched however, which may be caused by the following. First, the quenching may be the result of a high surface density of FITC molecules, and secondly, it may result from energy transfer to electronic levels in the gold particle. As we merely wanted to demonstrate the effectiveness of binding FITC to the gold particles as a model substance for other (bio)compounds, we have not further investigated this sol.

4. Conclusions

Gold particles of size between about 1 and 5 nm can be easily prepared by reduction of HAuCl₄ in the presence of the mercaptosilane MPS. The particle size is determined by the amount of gold surface formed by the self-assembling process of MPS at a certain gold-to-MPS ratio. The particle uniformity increases with decreasing particle size. The aminosilane APS can be attached through siloxane bonds to the MPS on the gold particle surface, but the APS is situated in such a manner that its amine group has lost its chemical functionality. The siloxane bonds between MPS and APS on the surface probably form a linear or cyclic chainlike structure, the details of which are yet unclear.

The coupling of foreign molecules onto the gold particles can be accomplished indirectly by first binding the molecule (as example we used FITC) to the γ-amine of APS, after which the ethoxysilanes of APS (probably partially hydrated) provide the coupling to the methoxy-silanes of MPS (hardly hydrated) on the gold particle. This procedure illustrates the potentiality for binding organic and inorganic functional species to the MPS-stabilized gold particles. Many more examples can be imagined, taking into account the large amount of (commercially) available organosilanes, which can be combined with the gold colloids to form hybrid organic−inorganic materials.[24]

With respect to application of our synthesis method we note the following. For cytochemical labeling, gold particles are at present generally noncovalently coupled to the biological probes.[25] Hainfeld and Furuya[26] showed that covalent coupling improves the efficiency of labeling. To couple our APS-modified gold particles to biomolecules, a way has to be found to keep the APS amines functional. Another option would be to use cross-linking reagents, bound to APS. For application in nanostructured materials, the MPS-APS silane coat (of controllable thickness) will keep the gold nanoparticles at a constant distance apart, which is essential for a controlled electron-hopping conductivity.[27]

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