Monolayers of Thiol-Terminated Dendrimers on the Surface of Planar and Colloidal Gold

Victor Chechik and Richard M. Crooks*

Department of Chemistry, Texas A&M University, P.O. Box 30012,
College Station, Texas 77842-3012

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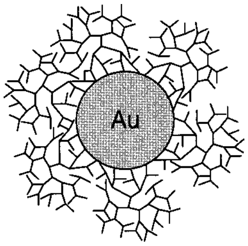
The synthesis of fourth-generation poly(amido−amine) (PAMAM) dendrimers having terminal groups partially or fully functionalized with thiol groups is described. These thiolated dendrimers form stable monolayers on planar Au substrates. X-ray photoelectron spectroscopy studies reveal that most of the thiol groups on dendrimers having 20% of their terminal primary amine groups functionalized can directly interact with the Au surface. This suggests that the dendrimer molecules are flexible and arrange themselves so as to maximize the number of Au/thiol interactions. Reduction of tetrachloroauric acid in the presence of thiol-modified dendrimers results in formation of water-soluble, dendrimer-stabilized nanoparticles. The particles are 1.5−2.1 nm in diameter depending on the Au/dendrimer ratio used. Stable nanoparticles can be obtained at Au/dendrimer ratios as large as 120:1.

Introduction

Here, we report the synthesis of poly(amido−amine) (PAMAM) dendrimers possessing terminal thiol groups. These materials adsorb strongly to Au and, therefore, can be used to prepare dendritic monolayers on planar Au substrates and dendrimer-stabilized Au nanoparticles (Chart 1). Such nanocomposite materials are of special interest,[1−3] as they have applications to sensor devices,[4,5] catalysis,[6,7] and nanoelectronics.[8−10]

Chart 1



Dendrimers are monodisperse, hyperbranched polymers possessing a well-defined structure.[11] We showed previously that amine-terminated PAMAM dendrimers assemble onto planar Au surfaces to form nearly close-packed monolayers.[12] Because of the low mass density within the dendrimer interior, however, such monolayers are highly permeable to small molecules.[13] PAMAM dendrimers also stabilize and assemble onto Au colloids.[14] In this configuration the dendrimer serves as a "nanofilter" that passes small or suitably charged molecular species but prevents other molecules from interacting with the colloid. Thus, both planar and colloidal Au coated with dendrimers have unique properties that make them well-suited for some specific applications of chemical sensors and catalysis that require a metal to be coated with a permselective organic shell.[7,13] It is the combination of well-defined structure and controlled permeability that makes dendrimers more attractive for preparing monolayers on gold for some applications than the thiol-modified linear polymers described earlier.[15]

The synthesis of Au colloids coated with commercially available dendrimers having terminal amine groups has recently been described by us and Esumi et al.[14,16] Similar studies have been reported by Murphy et al. for CdS.[17] The affinity of the terminal amine groups for Au is low,[18] however, and we found that such dendrimer-protected nanoparticles are only stable in solution and in the presence of a significant excess of the free dendrimer. Dendrons possessing a single thiol group at the focal point have been reported to form self-assembled monolayers on Au.[19] The presence of only one attachment point in these films, however, reduces packing efficiency.[19] In contrast,

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* To whom correspondence should be addressed. E-mail: crooks@tamu.edu. Voice: (409) 845-5629. Fax: (409) 845-1399.

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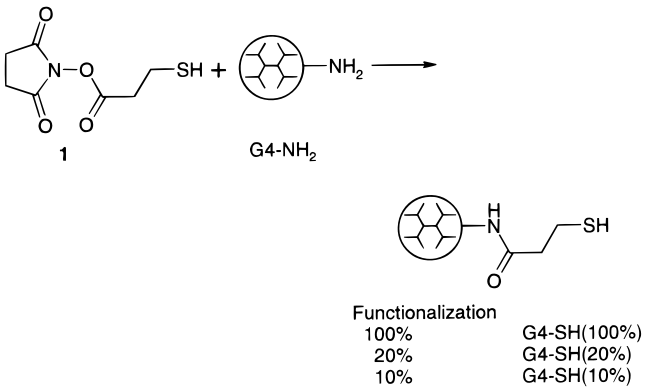
Scheme 1



polypodal interactions between Au and the thiol-modified dendrimers described here (Scheme 1) result in materials that are both tractable and stable.

Here we use X-ray photoelectron spectroscopy (XPS) and reflection infrared spectroscopy to confirm monolayer formation of thiolated and partially thiolated dendrimers on planar Au substrates. We have also prepared Au colloids using partially thiolated dendrimers as the stabilizing ligands, isolated them in pure form, and characterized them by transmission electron microscopy (TEM), UV−vis spectroscopy, and elemental analysis.

Experimental Section

Substrate Preparation. Substrates were prepared by electron-beam deposition of 10 nm of Ti followed by 200 nm of Au onto Si(100) wafers. Before use all substrates were cleaned in an ozone cleaner for 10 min (Boekel Industries, Inc., model 135500, Feasterville, PA). Monolayers were prepared by dipping the precleaned substrates into 1 mM solutions of the dendrimers in the appropriate solvent for 16 h, followed by thorough rinsing with the same solvent and blow-drying with nitrogen.

Spectroscopic Analysis. Fourier transform infrared-external reflectance spectroscopy (FTIR-ERS) measurements were made using a Bio-Rad FTS-40 spectrometer (Cambridge, MA) equipped with a Harrick Scientific Seagull reflection accessory (Ossining, NY) and a liquid-N_2-cooled MCT detector. Spectra were obtained using *p*-polarized light at an 85° angle of incidence with respect to substrate normal. Spectra were measured at 4 cm^{-1} resolution using between 100 and 300 scans. X-ray photoelectron spectra were acquired using a Perkin-Elmer (PHI) model 5500 spectrometer (Norwalk, CT). XPS data acquisition employed a pass energy of 29.35 eV, a step increment of 0.125 eV, and a Mg anode power of 400 W. UV−vis spectra were recorded on a Hewlett-Packard model HP-8453 spectrometer. NMR spectra were obtained using an XL-200E spectrometer. Ellipsometric measurements were performed using a Gaertner L2W26D ellipsometer (Chicago, IL) employing a 633.8 nm He/Ne laser and a 70.00 $\pm$ 0.02° angle of incidence relative to the substrate normal. Film thicknesses were calculated by assuming a standard homogeneous film model using Gaertner software. The refractive index of all dendrimer films was assumed to be 1.46.

Chemicals. Fourth-generation, amine-terminated PAMAM dendrimers (G4-NH_2) were generously provided by Dendritech, Inc. (Midland, MI). Deionized water (18 MΩ·cm Milli-Q, Millipore) and high-purity ethanol (EquiStar, Cincinnati, OH) were used for all monolayer manipulations. Other reagents were purchased from Aldrich Chemical Co. (Milwaukee, WI) and used as received. Solvents were of reagent grade or better.

***N*-Hydroxysuccinimidyl 3-mercaptopropanoate (1).** Thiol **1** was prepared by Zn/acetic acid reduction of the corresponding disulfide. The bis(*N*-hydroxysuccinimide ester) of 3,3′-dithiodipropionic acid[20] (2 g) was refluxed in THF (40 mL). Acetic acid (13 mL) was added followed by Zn (2 g), and the mixture was refluxed for 3 min. The progress of the reaction was monitored by TLC. Excessive reaction times lead to decomposition of the target thiol. The reaction mixture was then diluted with DCM (100 mL) and washed with water. The organic layer was dried with $MgSO_4$ and evaporated. The crude product was purified by flash chromatography with a 20/1 dichloromethane/ethyl acetate mixture (R_f 0.5) and stored in the freezer. Yield: 1.4 g (70%). ^1H NMR ($CDCl_3$) (δ, ppm): 3.02−2.82 m (8H, CH_2), 1.83 t (1H, SH). Anal. Found: C, 41.22; H, 4.57; N, 6.59. Calcd ($C_7H_9NO_4S$): C, 41.37; H, 4.46; N, 6.89.

Dendrimer G4-SH(100%). Thiol **1** (500 mg) was dissolved in THF (1 mL) and diluted with absolute ethanol (7 mL). The reaction mixture was placed in a centrifuge tube and flashed with nitrogen followed by addition of a 10% methanol solution of G4-NH_2 (2.73 g). The mixture was left overnight under nitrogen. The oil that separated was centrifuged and washed with ethanol, and the still-wet oil was dissolved in a small amount of dichloromethane, precipitated with ethanol, and centrifuged again. Finally, the wet product was dissolved in a 1/10 ethanol/chloroform mixture. Use of dry solvents and inert atmosphere in all these procedures is essential for preparation of soluble material. These solutions are prone to gelation upon prolonged storage. This could be due to either slow air oxidation of the dendrimer thiol groups to the disulfides, thus cross-linking the molecules, or to a slow rearrangement of the dendrimer to a thermodynamically more stable, insoluble conformation. Solvent removal also renders the dendrimer insoluble in organic solvents. Dendrimer G4-SH(100%) is soluble in aqueous 0.1 M NaOH. NMR spectra showed no peaks due to unreacted amine groups of the dendrimer, which suggests near-complete functionalization. IR (thin film) (ν, cm^{-1}): 3280, 3074 (NH), 2544 (SH), 1650 (amide I), 1546 (amide II). ^1H NMR (NaOH/D_2O) (δ, ppm): 3.31 br s (376H, CONHCH_2), 2.87−2.32 m (876H, CH_2CO + CH_2S + $N(CH_2)_3$). ^{13}C NMR (NaOH/D_2O) (δ, ppm): 51.3 ($CONHCH_2CH_2N(CH_2)_3$), 49.2 ($N(CH_2)_3$), 42.0 (CH_2CH_2S), 38.7 ($CONHCH_2CH_2NHCO$), 36.9 ($CONHCH_2CH_2N(CH_2)_3$), 32.9 (NCH_2CH_2CO), 21.0 (CH_2S).

Dendrimers G4-SH(20%) and G4-SH(10%). Thiol **1** (40 and 20 mg for the synthesis of compounds G4-SH(20%) and G4-SH(10%), respectively) was dissolved in THF (1 mL) and diluted with ethanol (1 mL). A 24.8% methanol solution (883 mg) of G4-NH_2 was added, and the mixture was set aside overnight. It was then used for preparation of Au nanoparticles without further purification. The byproduct of the reaction, *N*-hydroxysuccinimide, was not removed from the partially functionalized dendrimers as it did not interfere with the monolayer/nanoparticles formation. TLC analysis confirmed complete transformation of thiol **1**. The average percentages of the thiol groups in the dendrimers (10 and 20%) were thus calculated from reaction stoichiometry.

Preparation of Au Nanoparticles. Solutions of dendrimers G4-SH(10%) and G4-SH(20%) resulting from the above synthesis (2 mL) were diluted with water (20 mL). A desired amount of tetrachloroauric acid ($HAuCl_4$) in water was added to the reaction mixture, and a 50× molar excess of $NaBH_4$ was added with vigorous stirring. The mixture was filtered the following day through a 0.65 μm nylon filter and rotor-evaporated at room temperature. The nanoparticles obtained were dissolved in 0.1 M NaCl and twice subjected to gel filtration through a 30-cm column packed with Sephadex G-150 gel (eluent, 0.1 M NaCl). All but the smallest nanoparticles eluted with the dead volume of the column, whereas excess dendrimer was retained. The elution of the retained dendrimer was monitored by UV spectroscopy at 245 nm. The purified nanoparticles were dialyzed with a cellulose membrane (Sigma Chemical Co., St. Louis, MO; molecular weight cutoff 12 000) to remove NaCl. Elemental analysis data for the product are given in Table 2.

Results and Discussion

Synthesis of Thiol-Modified Dendrimers. Thiol-terminated PAMAM dendrimers have previously been

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Table 1. Ellipsometric Thickness, Contact-Angle, and XPS Data for Monolayers Prepared from G4-NH$_2$, G4-SH(100%), G4-SH(20%), and G4-SH(10%)

			XPS elemental composition (atom %)[b]							
			found				calcd			
monolayer	thickness (nm)	contact angle (deg)[a]	C	N	O	S	C	N	O	S
G4-NH$_2$[c]	1.9	32								
G4-SH(100%)[d]	2.4	55	68	12	16	4.0	62	19	14	4.9
G4-SH(100%)[e]	1.1	26								
G4-SH(20%)	1.8	25	68	16	14	1.1	62	24	13	1.2
G4-SH(10%)	1.7	25								

[a] Advancing angle with water. [b] Excluding hydrogen. [c] Data from ref 12. [d] Deposited from 10% v/v $CHCl_3$/EtOH solution. [e] Deposited from aqueous 0.1 M NaOH.

Table 2. Average Diameter and Elemental Composition of Dendrimer-Coated Au Nanoparticles

				elemental anal. data			
				found (%)			
dendrimer	Au atoms/ dendrimer[a]	av particle diameter (nm)	std dev (nm)	C	H	N	Au atoms/ dendrimer[b]
G4-SH(10%)	3.2	1.6	0.7	36.8	7.1	15.7	30
G4-SH(10%)	40	1.5	0.5	26.6	4.7	10.2	80
G4-SH(10%)	120	2.1	1.0				
G4-SH(20%)	120	1.8	1.1	17.0	3.1	6.4	150

[a] In solution prior to reduction. [b] In purified nanoparticles calculated from elemental composition.

reported by Singh,[21] but the synthetic procedure involved several steps and resulted in only partial functionalization. We used a more straightforward one-step method: aminolysis of *N*-hydroxysuccinimidyl 3-mercaptopropanoate (**1**) converts the terminal amine groups of fourth-generation PAMAM dendrimers (G4-NH$_2$) to thiols (Scheme 1). Thiolated dendrimer G4-SH(100%) was isolated from the reaction mixture and characterized by FT-IR and NMR spectroscopy.[22] The appearance of peaks at 42.0 and 21.0 ppm in the ^{13}C NMR spectra, which are characteristic of RNHCO*C*H$_2$*C*H$_2$SH,[23,24] and the disappearance of peaks at 39.8 and 41.7 ppm, arising from the terminal RCONH*C*H$_2$*C*H$_2$NH$_2$ branches of unmodified dendrimer G4-NH$_2$,[11] confirm nearly complete (within experimental error, ca. 5%) functionalization of G4-NH$_2$.

G4-SH(100%) is only soluble and stable in strongly alkaline media in the absence of oxygen (conditions that ensure ionization of the terminal thiol groups). G4-SH(100%) can also be dissolved in ethanol/chloroform mixed solvent, but as discussed in the Experimental Section, these solutions are not stable. Partially thiolated dendrimers, however, are more tractable. Accordingly, we prepared dendrimers having only 10% and 20% of their primary amine groups converted to thiols. Dendrimers G4-SH(10%) and G4-SH(20%) are readily soluble in water and thus can be used to modify Au surfaces.

Thiolated-Dendrimer Monolayers on Planar Au Surfaces. Monolayers of G4-SH(100%) were prepared from aqueous 0.1 M NaOH solutions or 10% v/v chloroform/ethanol solutions, and monolayers of partially thiolated dendrimers were prepared from aqueous solutions. The concentration of dendrimers in the deposition solutions was 16 μM. The SAMs were characterized by ellipsometry, contact-angle measurements, and FTIR-ERS. The results indicate that monolayers of dendrimers G4-SH(20%) and G4-SH(10%) and monolayers prepared from mixed chloroform/ethanol solutions of G4-SH(100%) are comparable in coverage with those of unmodified dendrimer G4-NH$_2$, which we have previously shown to be nearly close-packed.[12] For example, Figure 1 compares FTIR-ERS spectra of dendrimer SAMs. The heights of the amide I and II peaks, present at 1665 and 1555 cm^{-1}, respectively, are characteristic of the number of dendrimers on the surface. These data indicate that the amide intensities, and thus the dendrimer coverages, for G4-NH$_2$ (prepared from ethanolic solution) and G4-SH(100%) (prepared in the mixed organic solvent) are roughly equivalent.[25] The spectra of G4-SH(20%) and G4-SH(10%) SAMs are likewise virtually indistinguishable from that of G4-NH$_2$. However, when the G4-SH(100%) monolayer is prepared from a 0.1 M NaOH solution (part c of Figure 1), FTIR-ERS spectra reveal a significant decrease in amide intensity. This is probably due to reduced surface coverage, which is likely a consequence of electrostatic repulsion between the highly charged, polyanionic dendrimers.

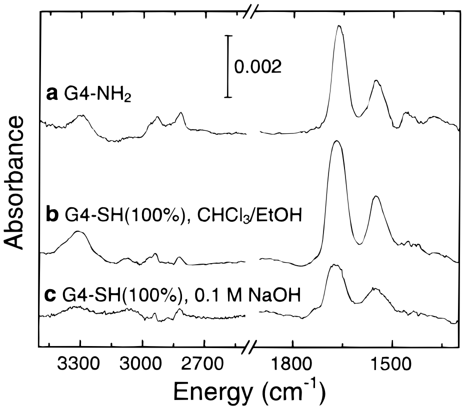

Figure 1. FTIR-ERS spectra of dendrimer SAMs: (a) G4-NH$_2$; (b) G4-SH(100%) prepared from 10% v/v $CHCl_3$/EtOH; (c) G4-SH(100%) prepared in 0.1 M aqueous NaOH.

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(22) Structural formula of dendrimer G4-NH$_2$ is $(CH_2N(RN(RN(RN(RN(RNH_2)_2)_2)_2)_2)_2$, where R = $CH_2CH_2CONHCH_2CH_2$.

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(25) The increased number of amide bonds in G4-SH(100%) compared to G4-NH2 (188 vs 124) is almost quantitatively compensated for by the increased size of the molecule (ca. 5.5-6.0 nm vs 4.5 nm). Thus, the intensity of the amide peaks should be similar for these monolayers (provided the fractional surface coverage is the same for both). A similar argument applies to G4-SH(20%) and G4−SH(10%).

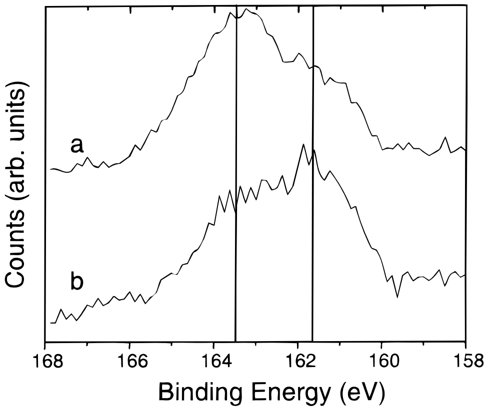

Figure 2. High-resolution XPS spectra of monolayers of (a) G4-SH(100%) prepared in 10% v/v $CHCl_3$/EtOH and (b) G4-SH(20%) in the S 2p region. The vertical scale of a and b are different.

Ellipsometric thickness measurements (Table 1) are in accord with the spectroscopic data. Dendrimer monolayers having their surface dominated by amine groups (G4-NH_2, G4-SH(20%), and G4-SH(10%)) have low contact angles with water, while monolayers of G4-SH(100%) deposited from the chloroform/ethanol mixture are more hydrophobic. In contrast, G4-SH(100%) monolayers prepared in aqueous alkaline solutions have significantly lower contact angles (26° vs 55°), which is consistent with formation of a charged surface.

Chemical compositions calculated from the intensities of peaks in X-ray photoelectron spectroscopy (XPS) survey spectra are in a good agreement with the theoretical values (Table 1). High-resolution XPS data in the S 2p region provide key information about how the thiolated dendrimers bind to the Au surface. The XPS spectrum of the G4-SH(100%) monolayer (prepared in the mixed organic solvent) reveals a broad peak at 163.5 eV with a shoulder at 161.7 eV (part a of Figure 2). The latter results from the poorly resolved $2p_{3/2}$ and $2p_{1/2}$ peaks of the S atom of RS^- groups attached to the Au surface.[26,27] The large unresolved peak at 163.5 eV is due to the sulfur $2p_{1/2}$ and $2p_{3/2}$ orbitals of the SH groups not interacting with Au (that is, those on the upper periphery of the dendrimers). The position of this peak is in excellent agreement with that reported for the free thiol groups in SAMs prepared from α,ω-dithiols.[28-30] This result suggests that the majority (about 70%) of the G4-SH(100%) thiol groups do not interact strongly with the Au surface. This conclusion is consistent with our previously reported model of surface-confined dendrimers being adsorbed to surfaces as oblate spheriods.[12,31]

Monolayers prepared from G4-SH(20%) are different from those prepared from the fully thiolated dendrimers. The XPS spectrum (part b of Figure 2) reveals a broad unresolved peak centered at 161.7 eV (RS^- species), but there is little free thiol signal in the 164-eV region. This implies that most of the thiol groups of G4-SH(20%) are directly attached to the Au surface. This important observation bears upon the flexibility of the terminal groups in PAMAM dendrimers. The fact that most of the thiol groups, which must be randomly distributed around the dendrimer exterior, can directly interact with the Au surface during monolayer formation suggests that the dendrimers can readily change their conformation to maximize the number of Au/thiol links. That is, the dendrimers, which are inherently flexible materials, must distort in such a way that most of the thiol terminal groups accumulate on one side of the dendrimer molecules.

Dendrimer-Coated Au Nanoclusters (Au/G4-SH). We recently reported the preparation of Au nanoclusters stabilized with G4-NH_2 (Au/G4-NH_2).[14] We found, however, that while Au/G4-NH_2 nanocomposites are stable indefinitely in solutions containing an excess of free dendrimer, their stability decreases sharply when either the solvent or the excess free dendrimer is eliminated. For example, complete removal of water from dendrimer solutions by rotorary evaporation at 40 °C or by high-speed centrifugation (40 000 rpm, 1 h, 25 °C) gives rise to black powders that are insoluble in any solvent.[14] Gel filtration (see Experimental Section) permits separation of the nanoclusters from the excess dendrimer, but agglomeration occurs upon concentration by solvent evaporation.

Additional evidence for lability of G4-NH_2 on colloidal Au comes from the following ligand-exchange experiment. When an aqueous solution of Au/G4-NH_2 nanoclusters is exposed to a stoichiometric amount of *n*-octanethiol (with respect to the dendrimer) in ethanol, formation of a mixed *n*-octanethiol/G4-NH_2 monolayer results.[32] These mixed-monolayer-protected nanoclusters precipitate from solution after 3 days of exposure to the thiol. After being rinsed with ethanol to remove unbound thiol and dendrimer, the precipitate was analyzed by transmission FT-IR, which confirmed the presence of both G4-NH_2 and *n*-octanethiol adsorbed to the Au surface. Mixed-monolayer-coated nanoclusters were then dissolved in chloroform and extracted with water. Importantly, no dendrimer was found (FT-IR) in the chloroform solution after extraction, whereas *n*-octanethiol (and nanoparticles) remained. We infer that the dendrimer desorbed from the surface of nanoparticles and was extracted into water. This experiment indicates that dendrimers bind only reversibly to the surface of the Au particles, which may well be responsible for the poor stability of the nanoclusters in the absence of excess dendrimer.

As mentioned earlier, G4-NH_2 monolayers are quite stable on planar Au.[12] In contrast, *n*-alkylamines bind only weakly and reversibly to such substrates.[18] The reduced stability of the *n*-alkylamines compared to the dendrimers is a consequence of the monopodal nature of the Au/*n*-alkylamine interaction compared to the more stable polypodal Au/dendrimer interaction. A similar effect is likely responsible for destabilization of amine-terminated dendrimers on Au colloids. That is, because the dendrimers are spherical in shape and generally somewhat larger than the Au colloids, only a fraction of the terminal amine groups of each dendrimer are able to interact directly with the colloidal Au surface (Chart 1). This reduction in the number of Au/amine interactions destabilizes the composite.

Au nanoclusters coated with partially thiolated dendrimers G4-SH(20%) and G4-SH(10%) can be prepared

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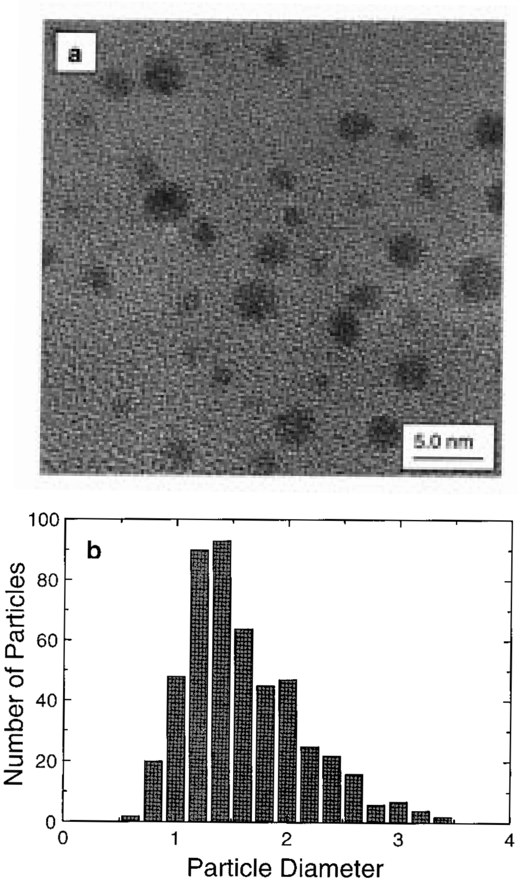

Figure 3. (a) Typical transmission electron micrograph and (b) particle-size distribution of Au nanoparticles coated with G4-SH(10%) (Au:dendrimer molar ratio prior to reduction 40:1).

using our previously described approach for preparing Au/G4-NH_2 composites,[14] which involves reduction of aqueous $HAuCl_4$ with $NaBH_4$ in the presence of dendrimers. The resulting materials can be isolated in pure form using gel filtration in a NaCl buffer followed by desalting (dialysis). Purification by centrifugation is also possible but requires very long spinning times (>5 h at 60 000 rpm) due to the small size of the Au particles (vide infra). Evaporation at 25 °C results in materials that are completely soluble in water. However, evaporation at elevated temperature (>40 °C) or prolonged storage (several days) reduces solubility.

Enhanced stability of the thiolated dendrimers, compared to the amine-stabilized materials, is also signaled by the low concentration of dendrimer required to prepare nanocrystals. For example, we have prepared stable nanocomposites from solutions containing as little as 1 dendrimer molecule/120 Au atoms. To our knowledge, this is the highest Au/stabilizer-ligand ratio reported for nanoparticle preparation and stabilization. Apparently, polypodal chelation of Au clusters by thiols provides very fast and efficient stabilization of the incipient particles.

We examined the size distribution of nanoparticles prepared using G4-SH(20%) and G4-SH(10%) at different Au/dendrimer ratios. A typical TEM image and a histogram of size distribution are shown in Figure 3, and the average size of the nanoparticles as a function of the Au/dendrimer ratio used to prepare them are given in Table 2. The thiolated dendrimers yield Au colloids that are substantially smaller than those protected by G4-NH_2 dendrimers (2.5−3.0 nm).[14] This is probably due to the strong Au−thiol interactions, which control particle growth. The average particle size is the same for Au:G4-SH(10%) molar ratios of 3.2:1 and 40:1. Use of a higher Au/dendrimer ratio (120:1) leads to an increase in the average colloid size. We believe this is a consequence of the limited number of dendrimer molecules available to interact with the growing particles. Indeed, elemental analysis (Table 2) indicates that at an Au/dendrimer ratio of 120:1 almost all dendrimer in the solution becomes incorporated into the nanocomposites. This follows from the fact that the Au/dendrimer ratio in the pure composite obtained by gel filtration/dialysis is almost the same as that in the reaction mixture prior to reduction (Table 2).[33]

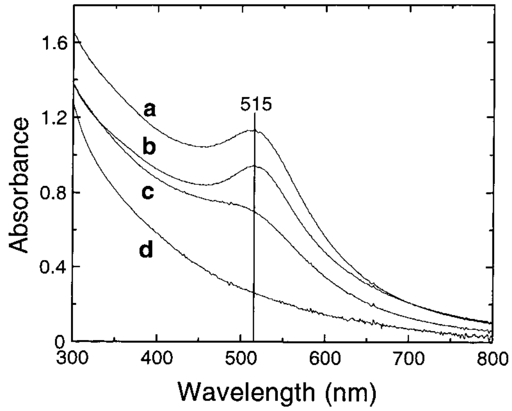

Figure 4. UV−vis spectra of Au nanoparticles coated with (a, c, d) G4-SH(10%) and (b) G4-SH(20%). Au:dendrimer molar ratios prior to reduction: (a, b) 120:1; (c) 40:1; (d) 3.2:1.

The magnitude of the particle size distribution (part b of Figure 3) is not too surprising, because there is also an unknown distribution in the number of thiol groups per dendrimer for G4-SH(20%) and G4-SH(10%). That is, while the *average* degree of functionalization of these dendrimers is 20% and 10%, respectively, the actual number of thiol groups on the termini of individual dendrimers varies. Assuming that the thiolation reaction proceeds on individual dendrimer branches without affecting the reactivity of nearby amines, we might expect a Gaussian distribution of thiolated dendrimers functionalized to different extents. If the number of thiols per dendrimer is strongly coupled to Au-particle growth, as seems likely, then the particle size distribution should be Gaussian and reflect the magnitude of the thiolation distribution.

UV−vis spectra of the thiolated Au/dendrimer nanocomposites are consistent with the TEM data. Particles obtained using a low Au/dendrimer ratio (part d of Figure 4) are too small to reveal the plasmon band typical of Au colloids. In contrast, particles prepared using higher Au/dendrimer ratios exhibit a characteristic adsorption at ca. 510−515 nm (parts a−c of Figure 4). The high intensity of this peak is probably due not so much to the increased average diameter of the particles but to the presence of a small number of strongly absorbing larger particles (4−5 nm in diameter).

Conclusion

We have prepared PAMAM dendrimers functionalized partially and nearly completely with thiol groups. The strong affinity of sulfur for Au results in stable monolayers

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(33) Elemental analysis showed that C/H/N ratios are correct within ca. 15% error, which points to the likely presence of some impurities in the samples. This error is passed on to the calculated values of the Au/dendrimer ratio. The error is, however, much smaller than the changes of Au/dendrimer ratio between the samples and, therefore, does not invalidate our conclusions.

of dendrimers on planar Au surfaces. XPS studies reveal that, in monolayers of partially functionalized dendrimers, most of the thiol groups directly interact with the Au surface. This implies that the dendrimer molecules are highly flexible and can readily undergo a conformational change to accumulate thiol terminal groups (once randomly distributed on the dendrimer periphery) primarily on just one side of the molecule.

Thiol-modified dendrimers also act as efficient stabilizers for Au nanoparticles. The particles obtained are small (1−2 nm) even when the reduction is carried out in the presence of an excess of the Au salt (up to 120 Au atoms/dendrimer). Such nanocomposites are stable and can be isolated in a pure form by gel filtration. The ease of preparation of these materials, coupled with the permeability of the dendrimer stabilizer, makes them attractive candidates for use in sensing devices and for catalysis. We are presently using these and related materials for these purposes.[6,7,34,35]

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