

---

# **Molecular Self-Assembly of Aliphatic Thiols on Gold Colloids**

---

**Carl S. Weisbecker, Margaret V. Merritt, and George M. Whitesides**

Harvard University, Chemistry Department, 12 Oxford Street,  
Cambridge, Massachusetts 02138

***Langmuir***<sup>®</sup>  
The ACS Journal of Surfaces and Colloids

Reprinted from  
Volume 12, Number 16, Pages 3763–3772

# Molecular Self-Assembly of Aliphatic Thiols on Gold Colloids

Carl S. Weisbecker, Margaret V. Merritt,<sup>†</sup> and George M. Whitesides\*

Harvard University, Chemistry Department, 12 Oxford Street,  
Cambridge, Massachusetts 02138

Received September 18, 1995\*

Self-assembled monolayers (SAMs) were formed on gold colloids in 50% aqueous ethanol in the presence of alkanethiols,  $\text{HS}(\text{CH}_2)_n\text{R}$ , where R represents a series of neutral and acidic functional groups. Chemisorption of alkanethiols onto the gold colloids significantly changed the rates of flocculation of the gold dispersions; the magnitudes of these pH-dependent changes were a function of chain length,  $n$ , and the terminal functionality, R, in a manner consistent with formation of SAMs on the colloid surface. The reduced rate of dissolution of alkanethiol-treated colloids by wet chemical etchants, transmission electron microscopy, and X-ray photoelectron spectroscopy data further support the formation of SAMs.

## Introduction

This paper describes the preparation and characterization of self-assembled monolayers (SAMs) of alkanethiols via adsorption of alkanethiols onto the surfaces of gold colloids in aqueous dispersions. The precursors of these SAMs are aliphatic thiols with the structure  $\text{HS}(\text{CH}_2)_n\text{R}$ , in which the functional group (R) stands for a variety of neutral and acidic functionalities. Changes in the optical spectra of flocculating colloids were used to infer the state of aggregation of the colloids and to characterize the resultant SAMs. We further characterized the alkanethiol-treated colloids by transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), and their dissolution rates in *aqua regia* and cyanide/ $\text{O}_2$  solutions.

The alkanethiolate-gold colloids prepared here via chemisorption of alkanethiols onto gold colloids are similar to alkanethiol-stabilized gold nanoparticles resulting from reduction of tetrachloroaurate in the presence of alkanethiols.<sup>1,2</sup> The diameter of the colloidal products is that of the gold colloid precursor (40 nm in the present study); the diameter of the nanoparticles, which varies from 1.5 to 20 nm, is determined by the ratio of tetrachloroaurate-to-thiol in the reaction.<sup>3</sup> The products formed via simultaneous Au(III) reduction and alkanethiol adsorption—using the same gold-to-thiol ratio and, hence, of the same approximate size—have been referred to by a variety of names: functionalized gold nanoparticles,<sup>2</sup> gold nanocrystals,<sup>3</sup> alkanethiol-stabilized gold clusters,<sup>4</sup> and alkanethiol-capped gold colloids.<sup>5</sup> The term “alkanethiol-stabilized gold clusters” will be used here to emphasize their stability<sup>4,6</sup> and to distinguish between these materials and those formed, in this study, by chemisorption of alkanethiols to extant gold colloids.

Of the gold clusters reported, those formed from the neutral alkanethiols  $[\text{CH}_3(\text{CH}_2)_n\text{SH}]$  have been most extensively characterized.<sup>2,4–6</sup> To date, there are no reports comparing the properties of alkanethiolate–gold colloids or cluster compounds formed from alkanethiols of differing functionality. The large differences in solubility of the cluster compounds make such comparative studies difficult. For example, the hydrophilic normal alkanethiol-stabilized gold clusters are soluble in most organic solvents, but that from a hydroxyalkane thiol precursor,  $\text{HO}(\text{CH}_2)_{16}\text{SH}$ , is not.<sup>6</sup> The present study, in which we directly monitor the optical properties of a gold colloid in the presence of a series of alkanethiols differing both in terminal functionality and in chain length, permits comparison of the resultant monolayers. The data reported here indicate that the properties of the alkanethiolate monolayers on gold colloids are similar to those of monolayers formed on planar surfaces and depend on the alkanethiol precursor.

There are a number of interesting applications of functionalized gold colloids that might benefit from the ability to tailor their surface properties using SAMs. The sol particle immunoassay (SPIA) exploits the color change (a shift from red to violet or blue) of aggregating colloids to test for an interaction between an antibody or antigen attached to the surface of the colloid and its binding partner in solution.<sup>7</sup> Self-assembly of colloidal gold or silver particles onto polymer substrates have produced reproducible surfaces of high activity for surface-enhanced Raman scattering (SERS).<sup>8,9</sup> Similar methods has been used to prepare Au colloid-modified electrodes.<sup>10</sup> Gold colloids are highly polarizable at optical frequencies, and there is evidence that their inherent third-order nonlinear susceptibility can be affected by aggregation or enhanced

\* On sabbatical leave, 1995–96, from the Department of Chemistry, Wellesley College, Wellesley, MA 02181.

† To whom correspondence should be addressed. Fax: 617-495-9857. Telephone: 617-495-9430. E-mail: gwhitesides@gmwgroup.harvard.edu.

© Abstract published in *Advance ACS Abstracts*, July 15, 1996.

(1) Brust, M.; Walker, M.; Bethell, D.; Schiffrin, D. J.; Whyman, R. *J. Chem. Soc., Chem. Commun.* **1994**, 801–802.

(2) Brust, M.; Fink, J.; Bethell, D.; Schiffrin, E. J.; Kiely, C. *J. Chem. Soc., Chem. Commun.* **1995**, 1655–1656.

(3) Leff, D. V.; Ohara, P. C.; Heath, J. R.; Gelbart, W. M. *J. Phys. Chem.* **1995**, 99, 7036–7041.

(4) Terrill, R. H.; Postlethwaite, T. A.; Chen, C.-H.; Poon, D. D.; Terzis, A.; Chen, A.; Hutchison, J. E.; Clark, M. R.; Wignall, G.; Londono, J. D.; Superfine, R.; Flavio, M.; Johnson, C. S., Jr.; Samulski, E. T.; Murray, R. W. *J. Am. Chem. Soc.* **1995**, 117, 12537–12548.

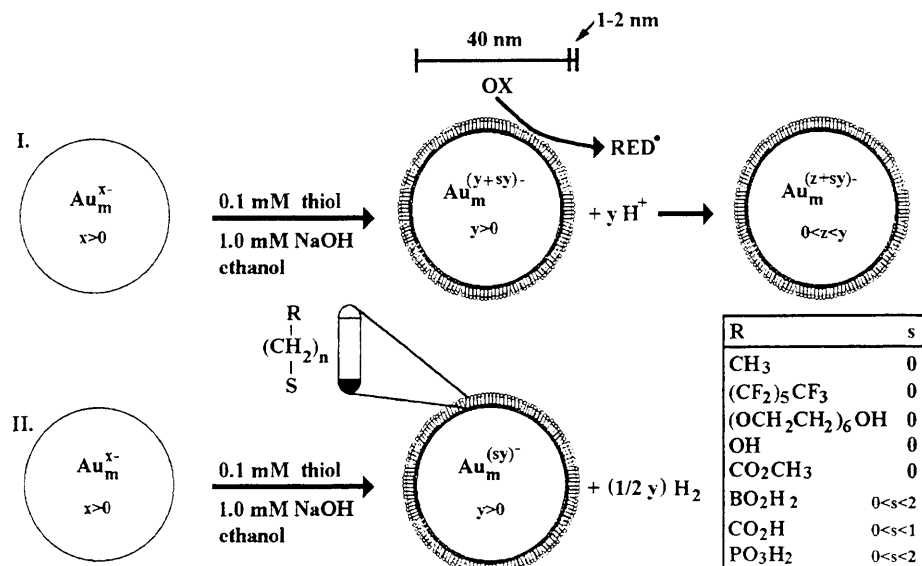
(5) Badia, A.; Gao, W.; Singh, S.; Memers, L.; Cuccia, L.; Reven, L. *Langmuir* **1996**, 12, 1262–1269.

(6) (a) Schmid, G. *Chem. Rev.* **1992**, 92, 1709–1727. (b) Schmid, G., Ed. *Clusters and Colloids, From Theory to Applications*; VCH: Weinheim, 1994.

(7) (a) Shigekawa, B. L.; Hsieh, Y.-A. Ligand Gold Bonding, US Patent #05294369, 1994. (b) Martin, J. M. C.; Paques, M.; Van der Velden-Groot, T. A. M.; Beuvery, E. C. *J. Immunoassay* **1990**, 11 (1), 31–47. (c) Van Erp, R.; Gribnau, T. C. J.; Van Sommeren, A. P. G.; Bloemers, H. P. J. *J. Immunoassay* **1991**, 12 (3), 425–443.

(8) (a) Freeman, G. G.; Grabar, K. C.; Allison, K. J.; Bright, R. M.; Davis, J. A.; Guthrie, A. P.; Mommer, M. B.; Jackson, M. A.; Smith, P. C.; Water, D. G.; Natan, M. J. *Science* **1995**, 267, 1629–1632. (b) Grabar, K. C.; Freeman, R. G.; Hommer, M. B.; Natan, M. J. *Anal. Chem.* **1995**, 67, 735–743. (c) Grabar, K. C.; Smith, P. C.; Musick, M. D.; Dabis, J. A.; Walter, D. G.; Jackson, M. A.; Guthrie, A. P.; Natan, M. J. *J. Am. Chem. Soc.* **1996**, 118, 1148–1153.

(9) Maeda, U.; Yamamoto, H.; Kitano, H. *J. Phys. Chem.* **1995**, 99, 4837–4841.



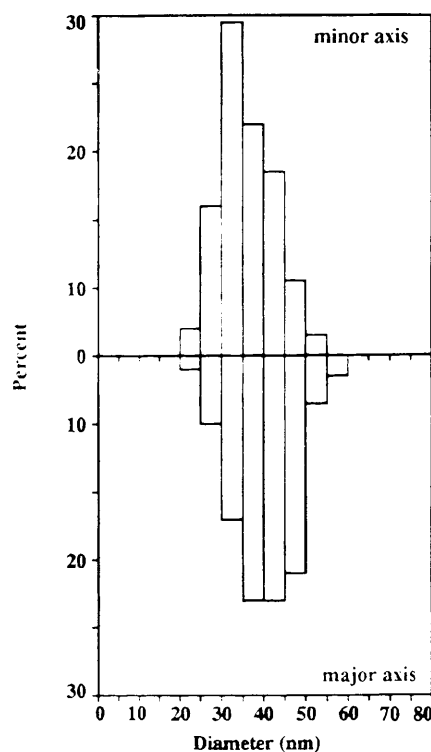
**Figure 1.** Possible mechanisms for the formation of SAMS on gold colloids. The surface charge of the initially formed colloidal particle,  $x$ , is primarily due to adsorbed hydroxide, chloride and citrate;  $m$  is the number of gold atoms in each particle. In pathway I, these ions are displaced by adsorbed thiols and hydrogen is eliminated as  $H^+$  to give  $Au_m^{(y+sy)-}$ ;  $y$  indicates the number of thiol molecules adsorbed, and  $s$  is a function of  $R$ . Oxidation of this intermediate ( $OX \rightarrow RED^+$ ) yields a final product,  $Au_m^{(z+sy)-}$  where  $z$  denotes the number of electrons lost. In mechanism II hydrogen is eliminated as  $H_2$  so that the final surface charge,  $sy$ , depends only on the identity of  $R$  and the number,  $y$ , of alkanethiols adsorbed.

by adsorption of polymers.<sup>11</sup> Functionalized gold colloids are electron dense, colored labeling reagents in electron microscopy and visible microscopy.<sup>12</sup> Finally, gold clusters have been studied as materials for quantum confinement;<sup>13</sup> Peschel and Schmid have recently reported progress in producing two-dimensional arrays of quantum dots based on ordered monolayers of ligand-stabilized gold clusters.<sup>14</sup>

## Results and Discussion

**Preparation of Colloids and Adsorption of Alkanethiols.** Dispersions of gold colloids were prepared by the reduction of tetrachloroauric acid ( $HAuCl_4$ ) in water using trisodium citrate ( $Na_3C_6H_5O_7$ ) as the reducing agent. The experimental conditions for adsorption of alkanethiols onto these gold colloids (approximately 2 nM in 50% aqueous ethanol) are included in Figure 1. The method of preparation, originally reported by Turkevich, Stevenson, and Hillier,<sup>15</sup> is well-known and often cited because of its simplicity and reproducibility. The mean size of the colloids may be controlled by varying the concentrations of the reactants;<sup>16</sup> in our experiments, the colloid particles typically had diameters of about 40 nm (Figure 2). The concentration of particles formed, about 70 pM, was calculated from the mean particle diameter and the weight of  $HAuCl_4$  used in the preparation.

**Mechanism of Alkanethiol Chemisorption.** SAMs of alkanethiols and their derivatives have been thoroughly studied on macroscopic gold films;<sup>17–20</sup> we expect formation



**Figure 2.** Representative distribution of dimensions in a sample of 150 particles of colloidal gold. Colloidal dispersions were evaporated to dryness onto thin carbon films and photographed in a transmission electron microscope. One large and one small diameter were measured on each particle in the distributions labeled 'major' and 'minor'. The particles are nearly isotropic. The mean of 300 measured diameters was 38 nm with a standard deviation of 7 nm.

of similar monolayers to result from exposure of gold colloids to alkanethiols. The chemistry of adsorption of thiols on extended flat gold substrates of infinite extent

(10) (a) Dorn, A.; Katz, E.; Willner, I. *Langmuir* **1995**, *11*, 1313–1317. (b) Brown, K. R.; Fox, A. P.; Natan, M. J. *J. Am. Chem. Soc.* **1996**, *118*, 1154–1157.

(11) (a) Magruder, R. H.; III; Yang, L.; Haglund, R. F., Jr. *Appl. Phys. Lett.* **1993**, *62*, 1730–1732. (b) Dutton, T.; VanWanterghem, B.; Saltiel, S.; Chestnoy, N. V.; Rentzepis, P. M.; Shen, T. P.; Rogovin, D. *J. Phys. Chem.* **1990**, *94*, 1100–1105.

(12) Beesley, J. E. *Colloidal Gold: A New Perspective for Cytochemical Marking*; Royal Microscopical Society Microscopy Handbook 17; Oxford University Press: Oxford, U.K. 1989.

(13) Hanna, A. E.; Tinkham, M. *Phys. Rev. B* **1991**, *44*, 5919–5922.

(14) Peschel, S.; Schmid, G. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1442–1443.

(15) Turkevich, J.; Stevenson, P. C.; Hillier, J. *Discuss. Faraday Soc.* **1951**, *11*, 55–75.

(16) Frens, G. *Nature Phys. Sci.* **1973**, *241*, 20–22.

(17) For reviews, see: (a) Whitesides, G. M.; Laibinis, P. E. *Langmuir* **1990**, *6*, 87–96. (b) Ulman, A. *Ultrathin Organic Films*; Academic Press: San Diego, CA, 1991.

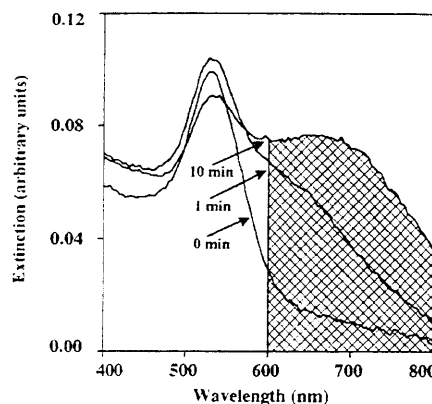
(18) Pale-Grosdemange, C. P.; Simon, E. S.; Prime, K. L.; Whitesides, G. M. *J. Am. Chem. Soc.* **1991**, *113*, 12–20.

(19) Abbott, N.; Whitesides, G. M. *Langmuir* **1994**, *10*, 1493–1497.

out of organic solvents is still debated;<sup>21</sup> the chemistry of adsorption on dispersed gold colloids of finite extent and the practicality of achieving conservation of the surface charge necessary to preserve the stability of the colloid are even less well understood. Porter<sup>22</sup> has produced evidence that adsorption of thiols on gold in both organic solvents and water is accompanied by elimination of  $H_2$  although the hydrogen might also be lost as  $H^+$  by oxidation. The presence or absence of oxygen may be a particularly important consideration; Henglein has demonstrated that adsorption of  $HS^-$  on silver colloids in degassed dispersions results in an accumulation of charge on the colloidal particles, which can be subsequently dissipated by exposure to air or to organic oxidants.<sup>23</sup> Karpovich and Blanchard have directly measured the kinetics and energetics of the adsorption of alkanethiols on gold,<sup>21</sup> and they concluded that their data are more consistent with elimination of  $H_2$  than with elimination of  $H^+$ .

Figure 1 shows these two possible mechanisms for the formation of a SAM of alkanethiolates on gold colloids in which the adsorption is accompanied by elimination of  $H^+$  (pathway I) or  $H_2$  (pathway II) and emphasizes the resultant charge on the colloids. The gold particles are depicted as spheres whose charges arise primarily from adsorbed hydroxide (from added NaOH to stabilize the colloid in 50% aqueous ethanol) and to a lesser extent from citrate and chloride (remaining from the preparation of the colloids). Since alkanethiols have  $pK_a$  values of approximately 9–11,<sup>24</sup> we assume that adsorption of thiols and not thiolates occurs in our solutions. Since oxygen was not rigorously excluded from our dispersions, dissipation of charge by oxidation of thiolate sulfur atoms in the manner proposed by Henglein has been included as a subsequent step in pathway I (OX/RED<sup>+</sup>). The importance of considering the mechanism here is that displacement of one hydroxide by one alkanethiol with elimination of  $H_2$  requires a net loss of one unit of negative charge from the surface of a colloidal particle; elimination of  $H^+$  does not require a net loss of charge. We could not directly determine the oxidation states of gold atoms on the colloidal surfaces in solution, but Herschbach and Sandroff concluded that Au(0) and Au(I) sites coexist on the colloidal surface,<sup>25</sup> and they speculated that the Au(I) sites form complexes with citrate. In contrast, Brust et al. determined by XPS that gold in dodecanethiol-stabilized gold clusters is present primarily, if not exclusively, as Au(0).<sup>1</sup>

**Determination of Flocculation.** The stability of colloidal dispersions in the presence of alkanethiols at different values of pH and ionic strength was evaluated by changes in their optical spectra. Experimentally, the dispersions were pipetted into cuvettes containing solutions of alkanethiols and the optical spectra monitored as a function of time. Qualitatively, flocculation was reflected in a change in color from red to violet or blue, followed by precipitation of colloids from the solution. We used the integrated extinction between 600 and 800 nm ( $I$ ) as a



**Figure 3.** Visible spectra of a flocculating dispersion. Flocculation was initiated by pipetting 28.5  $\mu$ L of a colloidal dispersion into 1.0 mL of 0.10 M  $NaNO_3$  at pH 4.0. Separately, the colloid was pipetted into 1.0 mM NaOH, in which it did not flocculate, to obtain a reference spectrum (0 min). The integrated extinction between 600 and 800 nm was used as a measure of flocculation.

quantitative measure of the extent of flocculation of the particles (see Figure 3).

We could not distinguish aggregation (close, irreversible association) and agglomeration (loose, reversible association) of particles spectroscopically; we use "flocculation" generically to describe the instability of colloids. We paraphrase the following definitions from Ross and Morrison for the reader's clarification.<sup>26</sup> A "floc" is defined as any close association of primary particles, aggregates, and agglomerates, and "flocculation" is the process of forming them. The distinction between "aggregate" and "agglomerate" is that aggregates are more closely associated and cannot be separated once they are formed. We did confirm by electron microscopy that changes in the visible spectrum of gold colloids were directly related to flocculation. Flocs were stabilized by addition of gelatin to the flocculating dispersions; this addition inhibited further changes in the visible spectrum of the colloid. Following solvent evaporation, the dried residue observed in TEM images contained flocs of gold particles embedded in the gelatin which, we assume, were present prior to addition of gelatin. Centrifugation of dispersions at high speeds also sometimes produced the color changes that we associate with flocculation. Blue or black precipitates in the bottom of a centrifuge tube could not usually be redispersed; red precipitates were easily redispersed. The irreversibility of the color change suggests that flocculation occurs with fusion of the gold particles (in the sense of "aggregation").

The spectral changes accompanying flocculation of gold colloids have been studied extensively. The visible extinction (absorption of light plus scattering) in dispersions of nearly spherical metal colloids was first theoretically interpreted by Mie,<sup>27</sup> who showed that a metal sphere whose radius is much smaller than the wavelength of light will absorb certain wavelengths by resonant excitation of surface plasmons. For spherical gold colloids dispersed in water, this excitation occurs at approximately 520 nm. In general, the excitation wavelength depends upon the radius of the sphere and the dielectric constants of both the metal and the medium in which it is dispersed.<sup>28</sup> If the metal particle is sufficiently elongated in one or two dimensions to make it highly anisometric, red-shifting and broadening of the extinction spectrum results.<sup>29</sup>

(20) (a) DiMilla, P. A.; Folkers, J. P.; Biebuyck, H. A.; Harter, R.; Lopez, G. P.; Whitesides, G. M. *J. Am. Chem. Soc.* **1994**, *116*, 2225–2226. (b) Lopez, G. P.; Albers, M. W.; Srieber, S. L.; Carroll, R. W.; Peralta, E.; Whitesides, G. M. *J. Am. Chem. Soc.* **1993**, *115*, 5877–5878.

(21) Karpovich, D. S.; Blanchard, G. J. *Langmuir* **1994**, *10*, 3315–3322.

(22) Widrig, C. A.; Chung, C.; Porter, M. D. *J. Electroanal. Chem.* **1991**, *310*, 335–359.

(23) (a) Mulvaney, P.; Linnert, T.; Henglein, A. *J. Phys. Chem.* **1993**, *97*, 679–682; (b) **1991**, *95*, 7843–7846; (c) *Ber. Bunsen-Ges. Phys. Chem.* **1990**, *94*, 1449–1456.

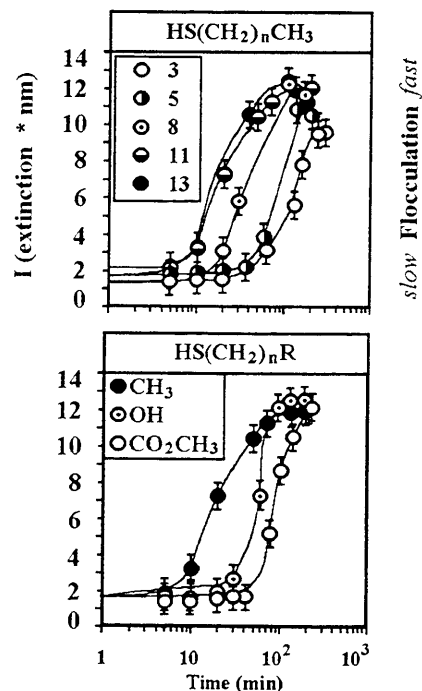
(24) Singh, R.; Whitesides, G. M. In *Thiol-Disulfide Interchange*; pp. 633–658, Patai, S., Ed.; John Wiley & Sons, Ltd.: New York, 1993; Chapter 13, pp 633–658.

(25) Sandroff, C. J.; Herschbach, D. R. *Langmuir* **1985**, *1*, 131–135.

(26) Ross, S.; Morrison, I. D. *Colloidal Systems and Interfaces*; John Wiley and Sons: New York, 1988, p 4.

(27) Mie, G. *Ann. Phys.* **1908**, *25*, 377–445.

(28) Underwood, S.; Mulvaney, P. *Langmuir* **1994**, *10*, 3427–3430.



**Figure 4.** Flocculation of colloids in solutions of several destabilizing thiols. Dispersions that had not previously been exposed to thiols were pipetted into cuvettes that contained 0.10 mM solutions of alkanethiols (upper plot) and into solutions of the thiols  $\text{HS}(\text{CH}_2)_{11}\text{CH}_3$ ,  $\text{HS}(\text{CH}_2)_{10}\text{OH}$ , and  $\text{HS}(\text{CH}_2)_{10}\text{CO}_2\text{CH}_3$  (lower plot). All thiols were dissolved in ethanol with 50% water and 0.5 mM NaOH. The concentration of gold particles in the cuvettes was estimated to be 15 pM. Lines have been drawn to guide the eye.

Flocculation of individual spheres also results in red-shifting and broadening in the visible spectrum. Quinten and Kriebig theoretically modeled the visible spectra of flocculating gold spheres with diameters of 10 or 56 nm for a series of small flocs with linear and nonlinear shapes and varying particle numbers.<sup>30</sup> They compared their modeled spectra to TEM images of flocculated aqueous gold colloids. They showed that when the distance between flocculating spheres is small compared to the radius of the spheres, additional resonances will occur at wavelengths that are longer than the resonance of the isolated spheres. These resonances are concentrated above 600 nm in the visible spectrum.

**Flocculation with  $\text{HS}(\text{CH}_2)_n\text{R}$ ,  $\text{R} = \text{CH}_3$ ,  $\text{OH}$ , or  $\text{CO}_2\text{CH}_3$ .** In Figure 4 (upper half) the quantity,  $I$  (our quantitative measure of flocculation) has been plotted as a function of time following addition of gold colloids to solutions containing 0.1 mM  $\text{HS}(\text{CH}_2)_n\text{CH}_3$ ,  $3 \leq n \leq 13$ . These data show that the dispersions flocculate at a rate that increases as the chain length of the alkanethiol increases. The rate of adsorption of a thiol on gold is known to increase with its chain length.<sup>31</sup> If charge dissipation is responsible for flocculation, we infer that most of the hydroxide and other ions on the surface of the gold particles were displaced within the 5 h window of observation and that thiols with long chain lengths displaced adsorbed ions faster than thiols with short chain lengths. We conclude, therefore, that pathway II in Figure 1 is consistent with the phenomenon of more rapid flocculation of colloids in the presence of thiols with longer chain lengths.

For pathway I (Figure 1) to be operative here, it would be necessary to explain why oxidation of the colloid by a

species in solution (designated as OX and which might, for example, be  $\text{O}_2$ ) occurs more rapidly as the thickness of the barrier (larger  $n$ ) increases on the colloid, particularly since SAMs derived from alkanethiols on gold and other metals have been shown to be effective barriers to oxidation.<sup>32</sup> If this mechanism were important, we would have expected the rate to increase in the presence of  $\text{O}_2$ . We found, however, no significant difference in the rates of flocculation of otherwise identical dispersions that had been purged with  $\text{N}_2$  or  $\text{O}_2$  just prior to mixing with alkanethiols.

Alternatively, the processes leading to the changes in the optical spectra that we are describing as flocculation may reflect the nucleation and/or precipitation of water insoluble alkanethiol-stabilized gold cluster compounds, similar to those formed by the reduction of tetrachloroaurate in the presence of alkanethiols.<sup>1,2</sup> Such a process would also lead to the observed increased rate of "flocculation" with increasing chain length. Even though this alternative pathway may be operating here, we will use the term "flocculation" throughout to refer to our observed spectral changes of the colloids in the presence of alkanethiols. Our experiments cannot distinguish between these alternative processes.

The lower half of Figure 4 compares dispersions in  $\text{HS}(\text{CH}_2)_{11}\text{CH}_3$ ,  $\text{HS}(\text{CH}_2)_{10}\text{OH}$ , and  $\text{HS}(\text{CH}_2)_{10}\text{CO}_2\text{CH}_3$  and shows that the terminal functional group of thiols with similar chain lengths also effects the rate of flocculation of colloids. We infer that  $\text{HS}(\text{CH}_2)_{10}\text{OH}$  adsorbed with its hydrophilic OH group exposed to the solvent and that the functionalized colloids flocculated at a slower rate than colloids that had been functionalized with the more hydrophobic  $\text{HS}(\text{CH}_2)_{11}\text{CH}_3$ . This variation in rates of flocculation of chemisorbed alkanethiols differing in their hydrophobicity cannot be readily ascribed to differences in charge dissipation but could result from the known differing solubilities of alkanethiol- and hydroxy-alkanethiol-gold clusters.<sup>5</sup> The slow rate of flocculation of colloids in  $\text{HS}(\text{CH}_2)_{10}\text{CO}_2\text{CH}_3$  may be the effect of partial hydrolysis of the ester in the basic solution to yield some ionizable carboxylic acid termini. Because of this possible hydrolysis, no further studies of alkanethiol carboxylate esters were pursued.

**Flocculation with  $\text{HS}(\text{CH}_2)_n\text{R}$ ,  $\text{R} = \text{CO}_2\text{H}$ .** SAMs on gold terminated by carboxylic acid groups constitute a paradigm in the engineering of interfacial properties of surfaces. These ionizable surfaces have been modeled theoretically<sup>33</sup> and characterized experimentally using the technique of contact-angle titration; this technique monitors wettability as a function of pH.<sup>34–36</sup> Surfaces covered with carboxylic acid groups were less wettable at pH values between 3 and 7 than at lower or higher pH values; we expect wettability to increase monotonically with increasing pH. This anomalous "hump" in the contact-angle titration curves between pH 3 and pH 7, previously observed on these surfaces, has been postulated to be the result of disorder induced in the SAMs by partial ionization of the termini and/or intermolecular hydrogen bonding of the termini that is energetically favorable only for intermediate pH values.<sup>36</sup> A similar broad minimum seen in the flocculation of gold colloids as a function of pH in the presence of  $\text{HS}(\text{CH}_2)_n\text{COOH}$  for  $n \geq 7$  (Figure 5) strongly supports our hypothesis that the chemisorption process

(32) Laibinis, P.; Whitesides, G. M. *J. Am. Chem. Soc.* **1992**, *114*, 9022–9028.

(33) Fawcett, W. R.; Fedurco, M.; Kovacova, Z. *Langmuir* **1994**, *10*, 2403–2408.

(34) Bain, C. D.; Whitesides, G. M. *Langmuir* **1989**, *5*, 1370–1378.

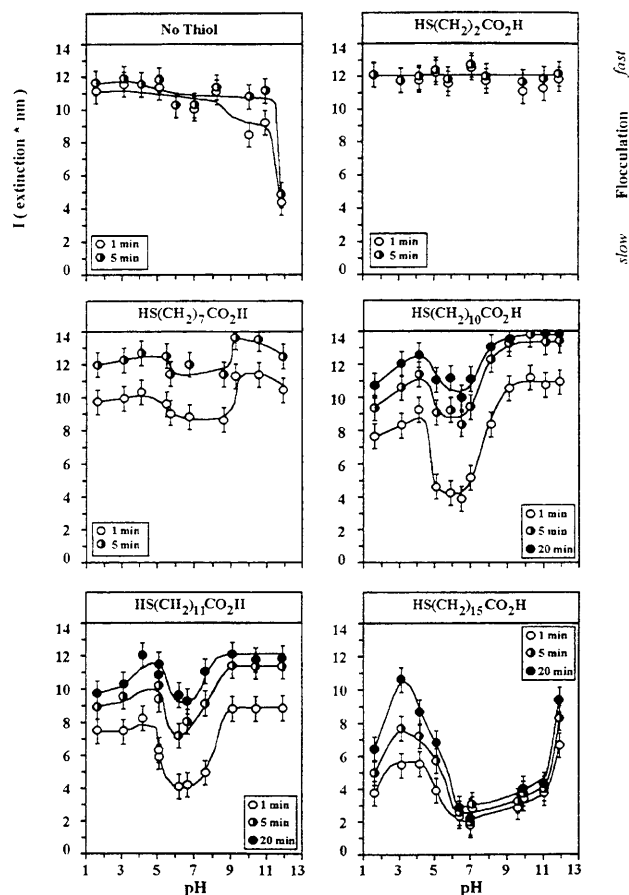
(35) Whitesides, G. M.; Biebuyck, H. A.; Folkers, J. P.; Prime, K. P. *J. Adhesion Sci. Technol.* **1991**, *5*, 57–69.

(36) Lee, T. R.; Carey, R. I.; Biebuyck, H. A.; Whitesides, G. M. *Langmuir* **1994**, *10*, 741–749.

(29) Wiesner, J.; Wokaun, A. *Chem. Phys. Lett.* **1989**, *157*, 569–575.

(30) Quinten, M.; Kriebig, U. *Surf. Sci.* **1986**, *172*, 557–577.

(31) Folkers, J. P.; Laibinis, P. E.; Deutch, J.; Whitesides, G. M. *J. Phys. Chem.* **1994**, *98*, 563–571.



**Figure 5.** Floculation of gold dispersions modified by reaction with  $\omega$ -mercaptoalkanecarboxylic acids in solutions of varying pH and  $m = 10^{-1}$ . Dispersions that had been previously exposed to  $\omega$ -mercaptoalkanecarboxylic acids were pipetted into aqueous solutions containing varying concentrations of  $\text{HNO}_3$ ,  $\text{NaOH}$ , and  $\text{NaNO}_3$ ,  $\mu = 0.10$ . The concentration of gold particles in the cuvette was estimated to be 15 pM. Lines have been drawn to guide the eye. Control dispersions that contained no thiol were also pipetted into the solutions.

produces monolayers on colloidal gold similar to SAMs on planar surfaces.

The control dispersion (no thiol, Figure 5) had a different profile from those of any of the functionalized colloids. If we assume that the rate of flocculation of the control is moderated by hydroxides adsorbed on the surface, as noted by others,<sup>37</sup> we can attribute the rapid flocculation seen with 3-mercaptopropionic acid (top right panel of Figure 5) relative to the control (top left panel) to its blocking sites for hydroxide adsorption. Although we had initially expected the carboxylic acids on the SAM derived from 3-mercaptopropionic acid to be ionized in basic solutions and, hence, to stabilize the colloid, they did not provide any measurable stability even at high pH with  $\mu = 10^{-1}$ . Figure 6 shows the results of flocculating dispersions in solutions with varying ionic strength. Here dispersions mixed with 3-mercaptopropionic acid flocculate at pH 10.5 when  $\mu \geq 10^{-2}$ .

It is evident in the intermediate pH range of Figure 5 and throughout the range of ionic strength both at pH 3 and at pH 10.5 in Figure 6 that the colloids flocculated more slowly as the chain length of the adsorbed thiol increased. There are at least two plausible reasons for this observed effect. The first results from an energy barrier, whose magnitude is dependent on chain length, associated with the processes required to separate the methylene chains in a SAM and to break the hydrogen

bonds among chain termini. Karpovich and Blanchard estimated the energy cost for the separation process to be 3–6 kcal/mol.<sup>21</sup> Collective chain–chain interactions in SAMs derived from alkanethiols generally cause the monolayers to become ordered and densely packed<sup>38</sup> when the alkane chain contains 10 or more methylene groups. The second explanation for the scaling of colloid stability with carboxyl-terminated alkanethiol chain length is suggested in Figure 7, which shows the effect of SAMs of differing thickness on the forces between colloid particles. The attractive force between two gold spheres in water is primarily due to van der Waals interactions<sup>39</sup> which cause aggregation in the absence of any other repulsive force. Repulsion between two colloidal spheres can arise because the interpenetration of diffuse layers of counterions that surround the charged colloidal particles occurs with an energetic cost.<sup>40,41</sup> The repulsive and attractive potentials drawn in Figure 7 are for the case of two gold spheres covered by SAMs of 2 nm thickness. The attractive potential is usually defined in terms of the distance of closest approach ( $h$ ) between the surfaces of two spheres (the distance between the gold surfaces) and does not depend on the monolayer thickness. The repulsive potential is defined in terms of the distance of closest approach between the two ionized surfaces ( $h - 2d$ ), where the thickness ( $d$ ) of the SAM separates the two ionized surfaces from the two gold surfaces. This repulsive force increases with increasing  $d$ , or alkanethiol chain length, consistent with the decrease in the rate of flocculation with chain length seen in Figure 6.

The  $\mu$  dependent plots of Figure 6 generally show stability at small values of  $\mu$  followed by a sharp onset of rapid flocculation. Such behavior is typical of colloids that are stabilized by charged double-layer repulsion.<sup>42,43</sup> A slight decrease in the rate of flocculation of colloids sometimes also occurs at very large values of  $\mu$ , but the behavior at very high ionic strength is difficult to interpret. At pH 3, the  $\mu$  dependence of flocculation in the control dispersion (no thiol) differs significantly from those of the functionalized dispersions, but no clear distinction can be observed at pH 10.5, probably because both functionalized and nonfunctionalized surfaces have high surface charge. In contrast to the thiol-containing solutions, at pH 3 and  $\mu = 10^{-3}$  the particles in the control dispersion alone do not flocculate. An explanation for this distinction might be adsorption of  $\text{NO}_3^-$  on the surface of the control dispersion and occupation of sites that are not available on the other functionalized surfaces. This contrast suggests that carboxylic acid groups are the main source of surface charge on the functionalized colloids. Given that a typical  $\text{pK}_a$  value for a carboxylic acid in solution is 4.5,<sup>44</sup> we would expect the surfaces to be neutral at pH 3.

#### Flocculation with $\text{HS}(\text{CH}_2)_n\text{R}$ , $\text{R} = \text{BO}_2\text{H}_2$ and

(38) Camillone, N., III; Chidsey, C. E. D.; Liu, G. Y.; Putvinsky, T. M.; Scoles, G. *J. Chem. Phys.* **1991**, *94*, 8493–8502.

(39) Clayfield, E. J.; Lumb, E. C.; Mackey, P. H. *J. Colloid Interface Sci.* **1971**, *37* (2), 382–39 and erratum **1972**, *38* (3), 677.

(40) Reference 18, pp 232–233, 249.

(41) A discussion of the repulsive interaction between charged double layers on spheres and flat surfaces is given in the book *Theory of The Stability of Lyophobic Colloids*; Verwey, E. J. W., Overbeek, J. Th. G., Eds.; Elsevier: New York, 1948.

(42) Reerink, H.; Overbeek, J. Th. G. *Trans. Faraday Soc.* **1954**, *74*–84.

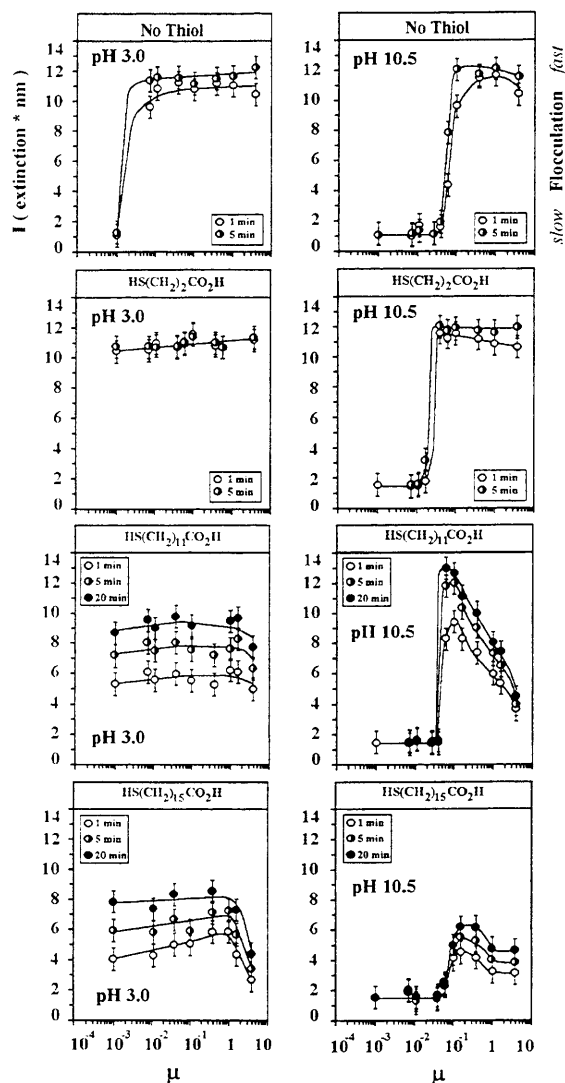
(43) Ottewill, R. H.; Walker, T. *Kolloid Z. Polym.* **1967**, *227*, 108–116.

(44) Smith, R. M.; Smith, A. E., Eds.; *Critical Stability Constants*; Plenum: New York, 1989. Perrin, D. D., *Dissociation Constants of Organic Acids In Aqueous Solution*; Butterworths: London, 1965.

(45) Yabroff, D. L.; Branch, G. E. K.; Bettman, B. *J. Am. Chem. Soc.* **1934**, *56*, 1850–1857.

(46) Carey, R. I.; Folkers, J. P.; Whitesides, G. M. *Langmuir* **1994**, *10*, 2228–2234. The value of  $\text{pK}_{12}$  is not explicitly stated here, but visual inspection of the data shows that ionization becomes significant at pH 12.

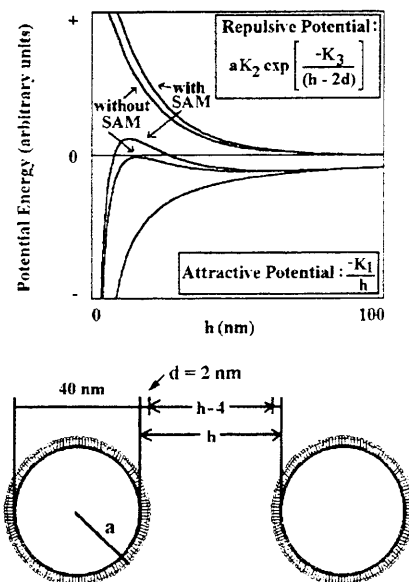
(37) Thompson, D. W.; Collins, I. R. *J. Colloid Interface Sci.* **1992**, *152*, 197–204.



**Figure 6.** Flocculation of gold dispersions modified by reaction with  $\omega$ -mercaptoalkancarboxylic acids in solutions of varying  $m$  and pH 3 or pH 10.5. Dispersions that had been previously exposed to  $\omega$ -mercaptoalkancarboxylic acids were pipetted into aqueous solutions containing varying concentrations of  $\text{NaNO}_3$  in addition to 1.0 mM  $\text{HNO}_3$  (pH 3) or  $\text{NaOH}$  (pH 10.5). The concentration of gold particles in the cuvettes was estimated to be 15 pM. Lines have been drawn to guide the eye. Control dispersions that contained no thiol were also pipetted into the solutions.

**$\text{PO}_3\text{H}_2$ .** Figure 8 summarizes flocculation experiments with dispersions mixed with (11-mercaptopundecanyl)-boronic acid and (11-mercaptopundecanyl)phosphonic acid. The stability at intermediate pH values (broad minima in Figure 5), observed with the carboxylic acid-terminated alkanethiols, was absent in both of these dispersions. Typical  $\text{pK}_a$  values for alkylphosphonic acids in solution are 2.8 and 8.2;<sup>44</sup> the  $\text{pK}_a$  of  $n$ -butylboronic acid is 10.7.<sup>45</sup> The analogous  $\text{pK}_{1/2}$  value of a SAM terminated by phosphonic acid groups on a planar gold film (obtained from contact-angle titration), corresponding to the first  $\text{pK}_a$ , is approximately 7;<sup>36</sup> for a SAM terminated by boronic acids,  $\text{pK}_{1/2}$  is 12.<sup>46</sup> The value of  $\text{pK}_{1/2}$  is undefined for a SAM terminated by carboxylic acids because of the anomalous feature—similar to the broad minima of Figure 5—in the contact-angle titration curves.<sup>36</sup>

The value  $\text{pK}_{1/2}$  is an estimate of the pH at which half of the functional groups on a surface are ionized. It typically exceeds the  $\text{pK}_a$  of acids in solution by at least 2 pH units because deprotonation occurs in the potential established by other deprotonated acids on the surface. Contact-angle titration data cannot generate a value



**Figure 7.** Double-layer repulsion of charged colloids increases as the thickness of SAMs increases. The drawing depicts the shape of the van der Waals attractive potential between colloidal spheres and of the double-layer repulsive potential between spheres with and without a SAM of thickness  $d = 2$  nm possessing ionizable R groups. The distance of closest separation of gold surfaces is  $h$ , the sphere radius is  $a$ , and  $K_1$ ,  $K_2$ , and  $K_3$  are positive constants. The colloidal spheres possess the same surface charge with and without the SAM. The net interaction potentials (refer to ref 26, pp. 249–250) are also plotted, and the shift of the repulsive potential due to the SAM raises the height of the barrier in the net potential.

**Table 1**

SAM	$\text{pK}_a^1$	$\text{pK}_{1/2}$	$\text{pK}_f$	$\log [\mu_f(10.5)]$
$\text{HS}(\text{CH}_2)_{11}\text{BO}_2\text{H}_2$	10.7 <sup>a</sup>	12 <sup>d</sup>	11–12 <sup>f</sup>	−1.1 <sup>g</sup>
$\text{HS}(\text{CH}_2)_{11}\text{CO}_2\text{H}$	4.5 <sup>b</sup>			−1.3 <sup>g</sup>
$\text{HS}(\text{CH}_2)_{11}\text{PO}_3\text{H}_2$	2.8 <sup>c</sup>	7 <sup>e</sup>	5.5–6.5 <sup>f</sup>	−1.2 <sup>g</sup>

<sup>a</sup> See ref 45. <sup>b</sup> See ref 34. <sup>c</sup> See ref 44. <sup>d</sup> See ref 45. <sup>e</sup> See ref 36.

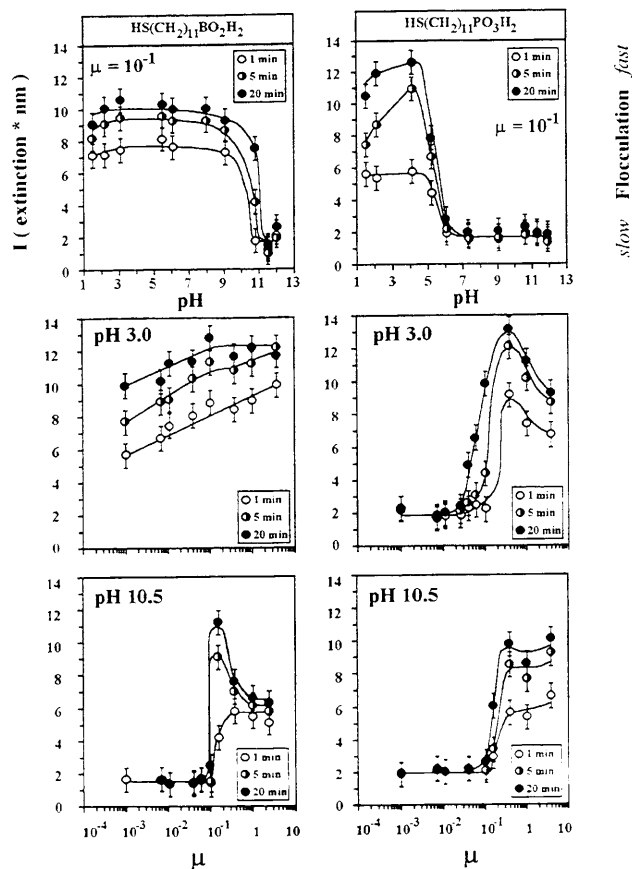
<sup>f</sup> The value  $\text{pK}_f$  is the lower limit of pH in which dispersions are stable when  $\mu = 10^{-1}$ . <sup>g</sup> The value  $\mu_f(10.5)$  is the upper limit of ionic strength in which dispersions are stable at pH 10.5.

analogous to the second  $\text{pK}_a$  of an acid; the data only suggest an onset of ionization, as do the flocculation data for our gold colloids.

A reasonable expectation about the three acidic SAMs would, therefore, be that dispersions functionalized by them flocculate more rapidly as  $\text{pK}_a$  and  $\text{pK}_{1/2}$  increase (in the order  $\text{PO}_3\text{H}_2 < \text{CO}_2\text{H} < \text{BO}_2\text{H}_2$ ). We can define two metrics from our data (see Table 1):  $\text{pK}_f$  is the lower limit of pH in which dispersions were stable when  $\mu = 10^{-1}$ , and  $\mu_f(10.5)$  is the upper limit of ionic strength in which dispersions were stable at pH 10.5. This latter parameter,  $\mu_f(10.5)$ , is nearly invariant and, consequently, is a poor gauge of surface acidity. Evidently, each of the dispersions has a high surface charge at pH 10.5, and small differences are not measurable by our spectroscopic method. Even though the parameter  $\text{pK}_f$  could not be defined for  $\text{R} = \text{CO}_2\text{H}$ , it does quantify the difference in acidity of the other two surfaces. The similarity between  $\text{pK}_f$  and  $\text{pK}_{1/2}$  for the two cases, where it is defined, shows that  $\text{pK}_f$  is a useful parameter for characterizing modified colloids.

**Flocculation with  $\text{HS}(\text{CH}_2)_{11}(\text{OCH}_2\text{CH}_2)_y\text{OH}$ .** Colloidal dispersions that had been mixed with oligo(ethylene oxide)-terminated thiols did not flocculate when the number of ethylene oxides in the thiol exceeded 3 ( $y > 3$ ); the cases that we observed encompassed  $1 \leq y \leq 6$ . Depicted on the left side of Figure 9 are plots of the induced flocculation of colloids that had been mixed with  $\text{HS}(\text{CH}_2)_{11}(\text{OCH}_2\text{CH}_2)_6\text{OH}$ . The stabilization of colloids by

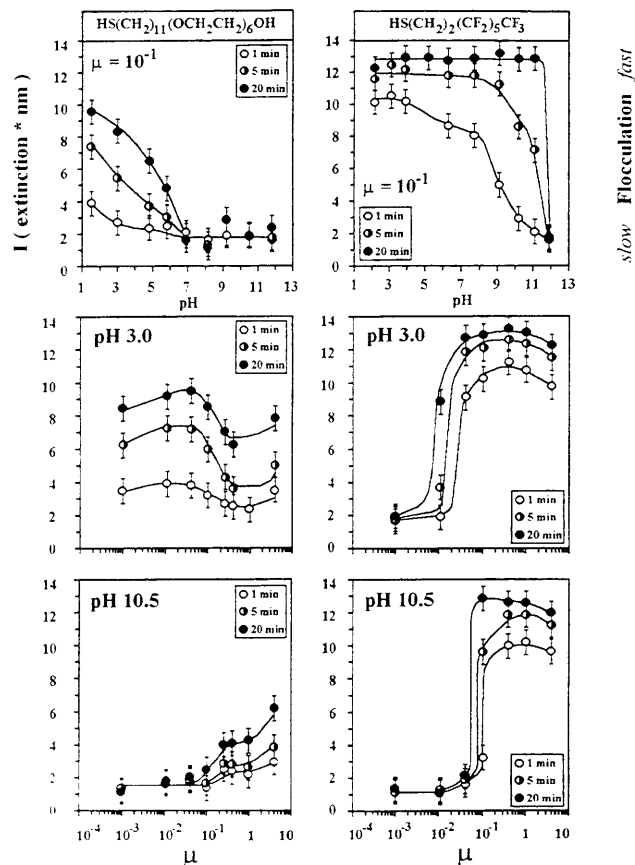




**Figure 8.** Flocculation of gold dispersions modified by reaction with  $\text{HS}(\text{CH}_2)_{11}\text{BO}_2\text{H}_2$  and  $\text{HS}(\text{CH}_2)_{11}\text{PO}_3\text{H}_2$ . Dispersions that had been previously exposed to thiols were pipetted into aqueous solutions containing varying concentrations of  $\text{HNO}_3$ ,  $\text{NaOH}$ , and  $\text{NaNO}_3$ ,  $\mu = 10^{-1}$ . The concentration of gold particles in the cuvette was estimated to be 15 pM.

adsorbed derivatives of polyethylene oxide is documented, and oligo(ethylene oxide) surfaces have interesting 'non-stick' properties that have been applied to the preparation of biocompatible materials.<sup>47</sup> Solvation and entropic effects in the polymer chains<sup>48</sup> are known to be important in their behavior. The pH dependence of the rate of flocculation is weaker in this case than in any other case that we observed, and the rate of flocculation at fixed pH is nearly independent of ionic strength in either acid or base. Our expectation would be that full monolayer coverage on the colloidal surfaces should completely inhibit flocculation in good solvents, such as water; instead, the weak pH dependence suggests that coverage may be incomplete.

**Flocculation with Perfluorinated Thiols.** On mixing colloidal dispersions with  $\text{HSCH}_2\text{CF}_3$  and  $\text{HS}(\text{CH}_2)_2(\text{CF}_2)_5\text{CF}_3$ , we were surprised that these perfluorinated thiols did not destabilize colloidal dispersions at all. In fact, these dispersions were stable for as long as they were observed (i.e. many months). Perfluorinated SAMs are known to be more hydrophobic than methyl-terminated SAMs,<sup>49</sup> and neither solvation nor surface charging seems to be a plausible mechanism of colloidal stability. The right side of Figure 9 summarizes flocculation experiments performed on dispersions mixed with



**Figure 9.** Flocculation of gold dispersions modified by reaction with  $\text{HS}(\text{CH}_2)_2(\text{CF}_2)_5\text{CF}_3$  and  $\text{HS}(\text{CH}_2)_{11}(\text{OCH}_2\text{CH}_2)_6\text{OH}$ . Dispersions that had been previously exposed to thiols were pipetted into aqueous solutions containing varying concentrations of  $\text{HNO}_3$ ,  $\text{NaOH}$ , and  $\text{NaNO}_3$ ,  $\mu = 10^{-1}$ .

$\text{HS}(\text{CH}_2)_2(\text{CF}_2)_5\text{CF}_3$ . Contrary to our expectations, the plots have a strong dependence upon pH and ionic strength. If "flocculation" results from nucleation and precipitation of alkanethiol-stabilized gold clusters, we would expect rapid flocculation as observed for the similarly hydrophobic normal alkanethiols. We do not have an explanation for our observations at this time.

**Chemical Etching of Colloids.** SAMs formed from alkanethiols retard the rate of oxidation of macroscopic gold films by chemical etchants.<sup>50</sup> In fact, monolayers of hexadecanethiol are effective monolayer resists that can be used to pattern gold films with a  $\text{CN}^-/\text{O}_2$  or ferricyanide etchant.<sup>51</sup> We mixed colloidal dispersions with solutions of *aqua regia* or KCN and found that functionalized dispersions were partially protected during the time when the control dispersion was completely etched and dissolved. We again used the visible spectra of the dispersions to monitor etching. Although the spectral changes that are due to flocculation complicate attempts to quantify rates of etching, the extinction at 400 nm is well separated from the spectral changes above 600 nm that are due to flocculation. Its value as a function of time seems to be satisfactory for a rough comparison of the relative rates of etching of colloidal dispersions, although it does vary due to flocculation alone (Figure 3). Figure 10 shows spectra that were collected at times up to 1 h after adding dispersions to solutions of 0.1 M KCN, and Figure 11 traces out the intensity at 400 nm for these dispersions and for some others. The extinction of all the dispersions that had been functionalized with  $\text{HS}(\text{CH}_2)_n\text{R}$ , where  $n \geq 10$ ,

(47) (a) Mrksich, M.; Whitesides, G. M. *Trends Biotech.* **1995**, *13*, 228–235. (b) Lopez, G. P.; Albers, M. W.; Schreiber, S. L.; Carroll, R. W.; Peralta, E.; Whitesides, G. M. *J. Am. Chem. Soc.* **1993**, *115*, 5877–5878.

(48) (a) Prime, K.; Whitesides, G. M. *J. Am. Chem. Soc.* **1993**, *115*, 10714–10721. (b) Tadros, Th. F., Ed. *The Effect of Polymers on Dispersion Properties*; Academic Press: London, 1982.

(49) Bain, C. D.; Troughton, E. B.; Tao, Y.-T.; Evall, J.; Whitesides, G. M.; Nuzzo, R. G. *J. Am. Chem. Soc.* **1989**, *111*, 322–335.

(50) Kumar, A.; Whitesides, G. M. *Appl. Phys. Lett.* **1993**, *63*, 2002–2004.

(51) Gorman, C. B.; Biebuyck, H. A.; Whitesides, G. M. *Chem. Mater.* **1995**, *7*, 252–254.



**Table 2. Spectra of SAMS Adsorbed on Macroscopic Gold Films from the Thiol  $\text{HS}(\text{CH}_2)_{11}\text{PO}_3\text{H}_2$  Used as Standards To Estimate the Monolayer Coverage of SAMs on Dried Residues of Colloidal Dispersions**

	element	core level	binding energy (eV)	intensity ratio <sup>a</sup>		% coverage <sup>b</sup>
				S/Au	P/Au	
Au/mica	S	2p	164	0.0502	0.0349	100 <sup>c</sup>
	P	2p	134			
	Au	4f <sub>7/2</sub>	84			
Au/Ti/Si	S	2p	164	0.0523	0.0339	100 <sup>c</sup>
	P	2p	134			
	Au	4f <sub>7/2</sub>	84			
Au/colloid	S	2p	164	0.0133	0.0432 <sup>d</sup>	26, <sup>e</sup> 126, <sup>f</sup> (76) <sup>g</sup>
	P	2p	134			
	Au	4f <sub>7/2</sub>	84			

<sup>a</sup> The integrated intensities of peaks such as those depicted in Figure 13 were normalized with respect to the number of scans used to acquire the signals. <sup>b</sup> The theoretical coverage of a SAM on Au(111) is 0.77 nmol/cm<sup>2</sup>. <sup>c</sup> We used the SAMs on two types of gold films as standards and assumed their coverage to be complete. <sup>d</sup> This ratio was obtained using the sum of the integrated intensities of both P 2p peaks. <sup>e</sup> This estimate was obtained by comparing the intensity ratio S 2p/Au 4f<sub>7/2</sub> for the colloid to the average of that ratio for the two standards. <sup>f</sup> The intensity ratio, P 2p/Au 4f<sub>7/2</sub> for the colloid was compared to the average of that ratio for the two standards. <sup>g</sup> The estimate of coverage in parentheses is the average of the two estimates.

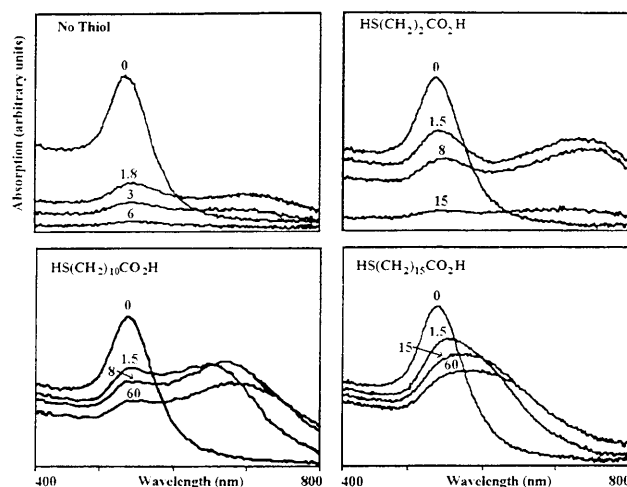
decreased only slightly over time. These dispersions were protected, in part, by the alkanethiol. The control dispersion dissolved rapidly, and so did others more slowly in proportion to the chain length of the thiol.

#### TEM Images and XPS Spectra of Gold Colloids.

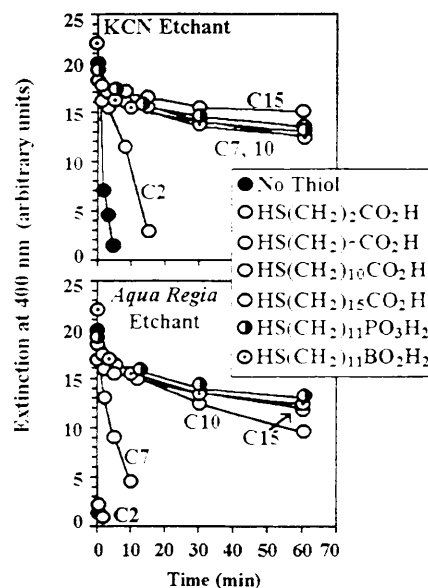
The flocculation experiments indirectly suggested that the gold particles in our dispersions were functionalized with SAMs in the manner suggested by the drawing in Figure 1. We also looked at the dried precipitate of some of these dispersions via TEM and XPS to provide further evidence that the particles were chemically transformed. The gold colloids were equilibrated with thiols for 24 h prior to removing excess thiols by centrifugation and washing with 1 mM NaOH; the estimated concentrations of colloidal particles and free thiol in the final preparations were 1 and 8 nM, respectively. Drops of these dispersions were evaporated to dryness and examined by TEM and XPS.

The residues in Figure 12 show differences typical of those observed between functionalized dispersions (a) and the control (b). The dispersion (a) was mixed with  $\text{HS}(\text{CH}_2)_{11}\text{PO}_3\text{H}_2$ . These latter flocs (a) were packed together more loosely than flocs of the control dispersion and resemble those of the 36-nm ligand-stabilized gold colloids of Schmid.<sup>6a</sup> A surface coating was visible in profile c. We estimate that the thickness of this monolayer should be 22.4 Å on the basis of strictly the van der Waals radii of sulfur, oxygen, and phosphorus atoms<sup>52</sup> and of the incremental chain length of methylene groups in *trans* extended chains with a 30° cant angle (estimated to be 1.1 Å).<sup>53</sup> The thickness of the coating observed in the TEM is qualitatively consistent with expectations for a SAM on gold.

The expected sulfur and phosphorus signals from  $\text{HS}(\text{CH}_2)_{11}\text{PO}_3\text{H}_2$  were observed in the XPS spectra of gold



**Figure 10.** Spectra collected after adding dispersions to solutions of 0.1 M KCN. Dispersions that had been previously exposed to the indicated thiols were pipetted into aqueous solutions containing 1.0 M KOH and 0.10 M KCN. Spectra were recorded starting at the indicated times (measured in minutes). The spectrum that is labeled '0' was obtained from a dispersion pipetted into 1.0 mM NaOH. Similar spectra were obtained in *aqua regia* (not shown).

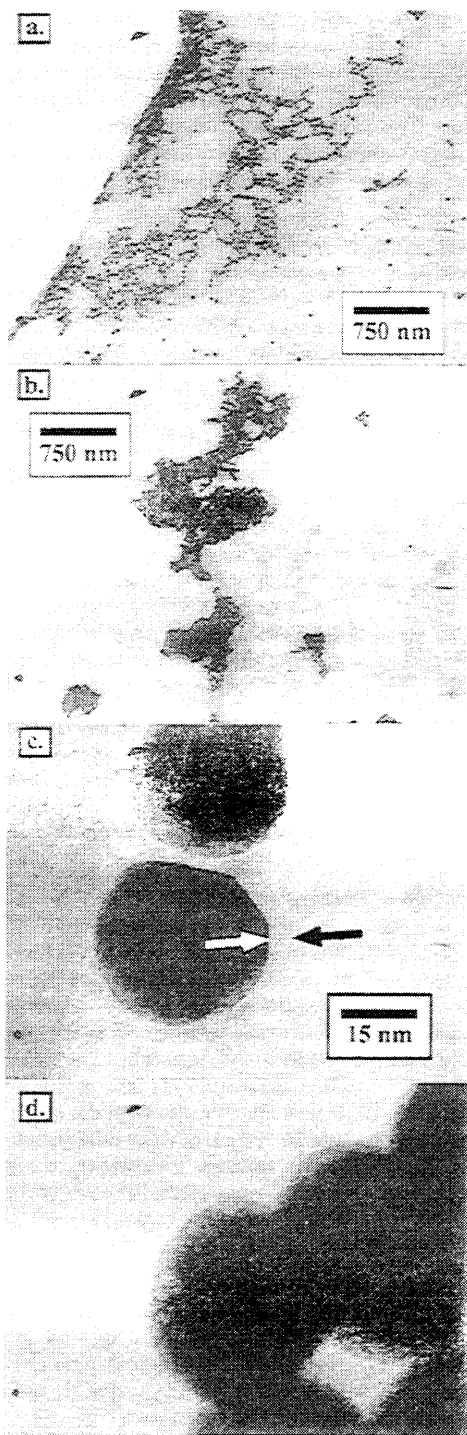


**Figure 11.** Time dependence of extinction at 400 nm for several dispersions in *aqua regia* and KCN. The decreases in intensity indicate that the gold particles are dissolving in the etchant solution. The symbols C2, C7, C10, and C15 indicate the chain lengths of the  $\omega$ -mercaptoalkancarboxylic acids that the dispersions were exposed to before they were pipetted into etchant solutions.

residues (see Figure 13). The ratio of the intensities of sulfur 2p or phosphorus 2p to those of gold 4f<sub>7/2</sub> from the colloidal spectra relative to these ratios for macroscopic gold films exposed to  $\text{HS}(\text{CH}_2)_{11}\text{PO}_3\text{H}_2$  was used to estimate the thiolate coverage of the colloidal surface (see Table 2, last column). These data indicate that the coverage approximates that of a monolayer if the thiolate/Au ratio is the same on the colloids as on planar gold: 26% from the S/Au data; 126% from the P/Au data; 76%, mean of these two estimates. The large difference in estimated coverage obtained from the sulfur and phosphorus data cannot be attributed to surface roughness. Although the two planar Au substrates used to prepare the monolayer standards vary in roughness, the S/Au and P/Au intensity ratios of the XPS data from these two types of gold films were similar. The smooth Au/Ti/Si substrate was formed by e-beam evaporation of a 500 Å gold layer

(52) Huheey, J. E. *Inorganic Chemistry: Principles of Structure and Reactivity*, 2nd ed.; Harper & Row: New York, 1978.

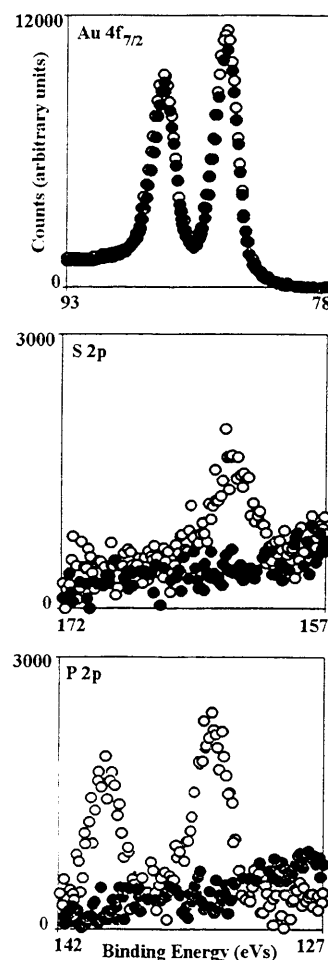
(53) In Laibinis, P. E.; Bain, C. D.; Whitesides, G. M. *J. Phys. Chem.* **1991**, 95 (18), 7017–21, the equation  $\lambda = 9.0 + (0.022)(\text{KE})$  (where  $\lambda$  is the attenuation length in angstroms, and KE is the kinetic energy of a photoelectron in electronvolts) was shown to be a good fit to the XPS data of SAMs. We used this equation to estimate  $\lambda = 38$  Å for both S(2p) and P(2p) photoelectrons.



**Figure 12.** Electron microscopy of dried flocs of gold colloids. The images depict the following structures: (a) a floc of colloids that had been previously exposed to  $\text{HS}(\text{CH}_2)_{11}\text{PO}_3\text{H}_2$ ; (b) a floc of colloids that had not been exposed to any thiol; (c) a coating of material approximately 2 nm thick surrounding colloids that were exposed to  $\text{HS}(\text{CH}_2)_{11}\text{PO}_3\text{H}_2$ ; (d) unexposed colloids that became fused together.

onto Si(100) with a 10 Å layer of Ti deposited on the silicon as an adhesion promoter; whereas, the rougher Au/mica substrate was prepared by deposition of 1200 Å of gold onto freshly cleaved mica at 300 °C. Flat terraces of gold on this latter surface were observed by atomic force microscopy.

In comparing the coverage on the colloids with the coverage on gold films, we assumed that all of the XPS signals came from the top surfaces even though the colloids have thiolates attached on all sides. This assumption is reasonable, as the 40 nm diameter thickness of the gold particles would be sufficient to mask the molecules



**Figure 13.** XPS Spectra of colloids dispersed on an indium substrate. Open circles are for colloids exposed to  $\text{HS}(\text{CH}_2)_{11}\text{PO}_3\text{H}_2$ ; closed circles are for colloids alone. Spectra of the Au 4f, S 2p, and P 2p regions are shown.

adsorbed on the lower surface; the attenuation length of sulfur 2p or phosphorus 2p electrons is about 4 nm.<sup>54</sup>

The phosphorus 2p region of gold colloids differs from that of gold films due to an additional peak at 139 eV (Figure 13). The colloidal precipitates were evaporated to dryness in the presence of NaOH, so that the two peaks may reflect the presence of two chemical species, i.e.  $\text{PO}_3\text{H}_2$  and  $\text{PO}_3\text{HNa}$ . In the gold films not exposed to base, the P 2p regions of the films contained only one peak at 134 eV.

### Summary and Conclusions

Aliphatic thiols form SAMs on gold colloids. Gold dispersions flocculate following their addition to solutions of alkanethiols. Flocculation suggests a loss of surface charge, which itself suggests that the thiols adsorb onto the surface of the gold colloids. "Flocculation" may occur by pathway II in Figure 1 (by elimination of  $\text{H}_2$ ) or may reflect nucleation and precipitation of alkanethiol-stabilized gold clusters similar to those reported by Brust and colleagues.<sup>1,2</sup> Alternatively, the spectral changes reported here may reflect a combination of these two processes. The evidence for formation of SAMs via chemisorption of alkanethiols on gold colloids includes the following: (1) The pH dependence of the colloidal

(54) Details of the preparation of methyl 11-mercaptoundecanoate, 11-mercapto-1-undecanol, and thiols of the form  $\text{HS}(\text{CH}_2)_n\text{CO}_2\text{H}$  are located in the supplementary material for *J. Am. Chem. Soc.* **1989**, *111*, 321–335. Details of the preparation of (11-mercaptoundecanyl)-1-boronic acid and (11-mercaptoundecanyl)-1-phosphonic acid are located in ref 45. Details of the preparation of thiols of the form  $\text{HS}(\text{CH}_2)_{11}(\text{OCH}_2\text{CH}_2)_2\text{OH}$  are located in ref 18.

flocculation in the presence of  $\text{HS}(\text{CH}_2)_n\text{COOH}$  is similar to the anomalous pH dependence of wetting as measured by the contact angles of carboxylic acid alkanethiolate monolayers on planar gold surfaces.<sup>35,36</sup> (2) The pH dependence of colloid flocculation in the presence of the acidic (11-mercaptopundecanyl)boronic acid and (11-mercaptopundecanyl)phosphonic acid differs from that in  $\text{HS}(\text{CH}_2)_n\text{COOH}$ -containing solutions and parallels the pH dependence of SAMs formed from these compounds on planar gold.<sup>36</sup> (3) Chemisorbed long chain ( $n \geq 10$ ) alkanethiols on gold colloids retarded the etching of gold particles with KCN and  $\text{CN}^-/\text{O}_2$  in a manner similar to the protection afforded to planar gold surfaces from these etchants by alkanethiolate SAMs.<sup>50</sup> (4) The TEM images of gold colloids dispersed in alkanethiols differ from those of control colloids, resemble those of ligand-stabilized gold clusters,<sup>6a</sup> and show evidence of a surface coating of the gold particles. (5) XPS spectra of the dried residues of gold colloids that had been mixed with  $\text{HS}(\text{CH}_2)_{11}\text{PO}_3\text{H}_2$  show the presence of sulfur and phosphorus on the surface.

The formation of SAMs on colloidal gold via chemisorption of alkanethiols on extant gold colloids reported here and that of alkanethiol-stabilized gold cluster compounds via reduction of tetrachloroaurate in the presence of alkanethiols<sup>1,2</sup> appear to be complementary methods of producing functionalized nanoparticles for potential applications in biosensors, catalysis, and optoelectronics.

## Experimental Section

**General.**  $\text{HAuCl}_4 \cdot x\text{H}_2\text{O}$  (99.999%), 2,2,2-trifluoroethanethiol, and 3-mercaptopropionic acid were obtained from Aldrich and used as received. Trisodium citrate (99.9%) and ACS reagent grade sodium nitrate were obtained from Mallinckrodt. Methyl 11-mercaptopundecanoate, 11-mercapto-1-undecanol, the carboxylic acid-terminated thiols [ $\text{HS}(\text{CH}_2)_n\text{CO}_2\text{H}$ ], (11-mercaptopundecanyl)-1-boronic acid, (11-mercaptopundecanyl)-1-phosphonic acid, and ethylene glycol-containing thiols [ $\text{HS}(\text{CH}_2)_{11}(\text{OCH}_2\text{CH}_2)_2\text{OH}$ ] were synthesized using published procedures.<sup>54</sup> The thiol  $\text{HS}(\text{CH}_2)_2(\text{CF}_2)_5\text{CH}_3$  was a gift from Dr. Nandan Rao (DuPont). Other alkanethiols were obtained from Aldrich and were used as received.

**Preparation of Modified Colloidal Surfaces.** All glassware used in the preparation and storage of colloidal Au was treated with *aqua regia*, rinsed with water, cleaned in a bath consisting of seven parts concentrated sulfuric acid and three parts 30% hydrogen peroxide (piranha solution), rinsed, and dried at 100 °C. *Use caution when cleaning glassware with piranha solution because it reacts violently with organic materials.*<sup>55</sup> Aqueous reagents were filtered through 0.2  $\mu\text{m}$  filters. Colloidal gold was prepared following the procedure reported by Turkevich, Stevenson, and Hillier:<sup>15</sup> 10 mL of 1.0 mg/mL  $\text{HAuCl}_4$  was added with vigorous stirring to 180 mL of boiling water. When the pale-yellow solution resumed boiling, 10 mL of a 10.0 mg/mL sodium citrate solution was quickly added with continued stirring. The boiling solution turned to a deep red color within about 20 min, at which time the dispersion was removed from the heat and allowed to cool to room temperature.

The colloidal dispersions were filtered through 0.2  $\mu\text{m}$  filters (Millipore GS) to trap any large particles and transferred to sterile polypropylene centrifuge tubes; the dispersions were washed twice (using centrifugation) with 200 mL of 1.0 mM NaOH. The concentration of the colloidal particles, based on a mean particle diameter of 40 nm and the weight of  $\text{HAuCl}_4$  used in the preparation, was 70 pM. The gold colloids were then concentrated to approximately 2.0 nM by additional centrifugation and resuspension in 1 mM NaOH; the sol was deoxygenated with Ar or  $\text{N}_2$ . Thiol solutions in ethanol at 0.2 mM, also similarly

deoxygenated, were mixed with equal volumes of the aqueous dispersions. We prepared a nonfunctionalized control by mixing a portion of deoxygenated colloid with an equal volume of deoxygenated ethanol. We stored both this control and the functionalized gold dispersions in polypropylene centrifuge tubes in the dark to prevent light-induced flocculation of the colloids<sup>56</sup> and oxidation of the alkanethiols.<sup>57</sup>

**Observations of Colloidal Flocculation.** The effect of pH and ionic strength on the flocculation of functionalized colloids was evaluated from changes in the absorbance spectrum in the 400–800 nm region. We obtained the spectral data of colloids at ambient temperature with a Hitachi U-3210 spectrophotometer. The extinction (absorbance and scatter) between 600 and 800 nm was integrated digitally using the instrument software; this integral,  $I$ , was our measure of flocculation. Data were collected at timed intervals to determine the rate of flocculation.

The spectral measurements were obtained on colloid dispersions of approximately 15 pM, which were made by pipetting 10–20  $\mu\text{L}$  of the concentrated sol (1 nM in 0.5 M NaOH, 50% ethanol) into 1.0 mL of the test solution contained in a standard cuvette (either quartz or disposable plastic) in the spectrophotometer. The solution was stirred briefly with the pipet tip and the absorbance at 528 nm measured. This initial absorbance value was used to determine the colloid concentration; data for all experiments were normalized to an initial value of 0.1.

The pH of the test solutions was adjusted with 0.10 M NaOH or 0.10 M HCl and was measured with a pH meter prior to adding the colloid. Sodium nitrate was used to adjust ionic strength. The ionic strength of each test solution was calculated from the quantities of  $\text{NaNO}_3$ ,  $\text{HNO}_3$ , and NaOH in the electrolyte solutions.

**Wet Chemical Etching of Modified Colloids.** *Aqua regia* consisting of one part each of concentrated HCl (37%) and concentrated  $\text{HNO}_3$  (70%) was diluted twofold. We then pipetted 200  $\mu\text{L}$  of this acid into a quartz cuvette containing 800 mL of distilled water and stirred the solution briefly. We added 10–20 mL of a colloidal dispersion to the cuvette and recorded the visible spectra of the dispersion at timed intervals. The time required to complete each scan was approximately 20 s. A solution of 0.10 M KCN in 1.0 M KOH was also used to etch the gold particles. In this case, we pipetted 10–20  $\mu\text{L}$  of a colloidal dispersion into 1.0 mL of this KCN/KOH solution in a quartz cuvette. The spectrum labeled '0' in each set (Figure 10) was obtained when the same dispersion was pipetted into 1.0 mM NaOH (in which it neither flocculated nor dissolved).

**TEM Imaging of Colloidal Surfaces.** Gold particles in dried residues of aqueous dispersions were imaged in a Phillips 420 Transmission Electron Microscope after placing drops of a dispersion onto carbon-coated TEM sample grids from Structure Probes, Inc. and allowing the liquid to dry in air at room temperature. The accelerating voltage was 120 kV.

**Quantitative XPS of Modified Colloidal Surfaces.** Drops of colloidal dispersions were pipetted onto indium foil and allowed to dry in air. The indium foil contributed a flat background signal to the XPS spectra. XPS spectra of colloids were obtained on a Surface Science SSX-1000 spectrophotometer that focused monochromatic Al K $\alpha$  X-rays onto the sample. The X-ray spot size was 600  $\mu\text{m}$ . The detector pass energy was 100 eV, so that the analyzer resolution was therefore 1.0 eV. We collected 5 scans of the Au 4f<sub>7/2</sub> region and 50 scans each of the S 2p and P 2p regions in a 15 eV window.

**Acknowledgment.** This work was supported in part by the ONR and ARPA. The XPS spectra and the TEM images were obtained at The Harvard MRL Facility.

LA950776R

(55) Published warnings concerning "piranha solution": (a) Dobbs, D. A.; Bergman, R. G.; Theopold, K. H. *Chem. Eng. News* **1990**, 68 (17), 2. (b) Wnuk, T. *Chem. Eng. News* **1990**, 68 (26), 2. (c) Matlow, S. L. *Chem. Eng. News* **1990**, 68 (30), 2.

(56) Satoh, N.; Hasegawa, H.; Tsujii, K.; Kimura, K. *J. Phys. Chem.* **1994**, 98, 2143–2147. Nakao, Y. *J. Chem. Soc., Chem. Commun.* **1994**, 2067–8.

(57) Hemminger, J. C.; Huang, J. J. *Am. Chem. Soc.* **1993**, 115, 3342–3343.