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pH-Dependent Adsorption of Gold Nanoparticles on *p*-Aminothiophenol-Modified Gold Substrates

Tao Zhu, Xiaoyi Fu, Tao Mu, Jian Wang, and Zhongfan Liu*

Center for Nanoscale Science and Technology (CNST), College of Chemistry & Molecular Engineering, Peking University, Beijing 100871, China

Colloidal Au nanoparticles were assembled on a gold substrate via a *p*-aminothiophenol coupling layer. The surface coverage of Au nanoparticles was found to be closely related to the pH value of gold colloids. In alkaline solution, where the amino group was not protonated, Au nanoparticles could not be adsorbed on the substrate, while, under acidic conditions, protonation makes the amino group positively charged and the adsorption becomes easier. The interaction between Au colloids and the substrate is believed to be electrostatic.

Introduction

To date, various strategies have been proposed to assemble nanostructures with metal and semiconductor nanoparticles as building blocks.[1] Among them, much attention has been paid to the covalent or noncovalent immobilization of nanoparticles onto a functionalized solid surface to obtain ultrathin nanoparticulate films. Work along this line was pioneered by Colvin et al.,[2] who reported the chemisorption of CdS nanocrystals onto a metal surface by using bifunctional self-assembled monolayers (SAMs) as adhesion layers. Since then, similar approaches have also been proposed to immobilize synthesized nanoparticles onto solid surfaces for various purposes. For example, Ogawa et al.[3] have reported monolayer formation of Q-CdS nanoparticles on gold substrates via dithiol SAMs and studied the photoelectrochemical characteristics of such composite structures. Gold nanoparticles immobilized on thiol- or amino-terminated surfaces of SAMs have been used as active substrates in surface-enhanced Raman scattering (SERS),[4–6] as novel nanoelectrodes for electrochemical studies,[7] and as the coulomb islands in the study of single-electron tunneling,[8] respectively.

There are also some works on the formation mechanism of nanoparticulate films. Grabar et al.[9] have studied the time-dependent adsorption of gold nanoparticles onto thiol- and amino-terminated surfaces. Fan and Lopez[10] have studied the effect of surface hydrophobicity on nanoparticle adsorption, by using nanoparticles and substrates, both modified with mixed functional monolayers, as a model system. Although most previous work on the colloidal gold nanoparticle adsorption has been performed in the aqueous phase, where the pH is believed to be an important factor, no systematic study on the pH effect has been reported. On the other hand, few proofs are available to distinguish the binding nature between nanoparticles and the surface functional groups, especially in the case of gold nanoparticles and amino groups.

In this Letter, we studied the effects of pH on the adsorption of gold colloidal nanoparticles onto the amino-terminated surface. It will give some insight into the adsorption mechanism, as well as the nature of interactions between the colloidal gold nanoparticles and amino groups.

Experimental Section

p-Aminothiophenol (*p*-ATP) and $HAuCl_4 \cdot 3H_2O$ were purchased from Aldrich and used as received. Ultrapure water (>17 MΩ·cm) was used throughout the experiments. Other reagents are of analytical grade.

An aqueous gold colloid, with an average particle size of 39.3 ± 5.3 nm (determined from the TEM image) and a particle concentration of 1.28×10^{-10} mol·L^{-1},[11] was synthesized by the method proposed by Frens.[12] After centrifugation, the colorless supernatant was carefully decanted and the remaining colloid increased its concentration by a factor of 16. It was used as the stock colloid in the present study. Aliquots of the stock colloid were redispersed in buffered solutions at different pH values. UV–vis absorption at 520 nm, where the surface plasmon excitation band of nanosized gold particles appears,[13] was kept at the same level for each buffered colloid so that all the resulted colloids will have a nearly identical particle concentration (ca. 8.06×10^{-11} mol·L^{-1}). Citrate buffer (1 mmol·L^{-1}) and NaOH solution (10 mmol·L^{-1}) were used as buffers at pH < 8.0 and pH > 8.0, respectively.

The scheme for gold nanoparticles assembling was similar to that previously reported.[14] Gold substrates were modified with a *p*-aminothiophenol (*p*-ATP) self-assembled monolayer by immersing them into a *p*-ATP/ethanol solution for 24 h. Gold nanoparticles were deposited onto the *p*-ATP-modified substrate surface by simple dipping into the colloidal solution at different pH values for a given time.

* To whom correspondence should be addressed. Telephone and Fax: +86-10-62757157. E-mail: lzf@chemms.chem.pku.edu.cn.

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Atomic force microscopy (AFM) (Nanoscope IIIa, DI Inc.) was used to characterize the morphology of the adsorbed nanoparticulate monolayers. The surface coverage of the particles was determined by counting the number of particles in an area of 2 μm $\times$ 2 μm size in the AFM image. At least three different areas were counted and averaged to get a more reliable value for each surface coverage.

Results and Discussion

Adsorption of gold nanoparticles onto a solid surface is a very complicated process, where many experimental factors, such as pH, ionic strength, and particle concentration of the colloid, as well as immersion time, are expected to influence the overall surface coverage.[9,10] However, not all factors listed here have been fully explored. Grabar et al. studied the kinetics of gold nanoparticle adsorption on organosilane surfaces by changing the immersion times (t). They found that the surface coverage at an early stage could be nicely predicted by a $t^{1/2}$ dependence, which is derived from an equation that describes diffusion of spherical particles to a planar surface. A negative deviation from the $t^{1/2}$ kinetics at longer time was also noticed and attributed to the interparticle repulsion, which decreases the sticking probability of the particles at higher surface coverage ($>1.2 \times 10^{11}$ particles/cm^2 for 15 nm gold nanoparticles).[9] In a very recent work on the preparation and characterization of Ag colloid monolayers, Natan et al. reported that increasing concentrations of silver nanoparticles could lead to the increase of surface coverage.[15] As to pH and ionic strength, they were only mentioned as possible factors by Fan and Lopez in discussions on the effect of surface hydrophobicity on nanoparticle adsorption.[10]

To study the pH effects independently, the concentration and the ionic strength of the colloids were intentionally kept identical (but not optimized) in the present Letter. The time dependence of surface coverage at selected pH was examined to get some kinetic information, which will enable us to derive a reasonable immersion time for the pH-dependence experiments.

Figure 1 gives the plots of surface coverage against immersion times for two different pH values. The solid lines are the $t^{1/2}$ curves obtained by fitting the measured surface coverage following the method in ref 9. As Figure 1 shows, the measured surface coverage is in good agreement with the $t^{1/2}$ dependence within the time range explored (up to 18 h), while the rates of particle immobilization are quite different for pH 4.0 (upper trace) and pH 5.8 (lower trace). Both the agreement and the difference are significant, and they can be explained in terms of the *sticking probability*, a factor defined by Grabar et al. as the ratio of *the number of surface bound particles* to *the number that reached the surface.*[9] The proportional growth of surface coverage with $t^{1/2}$ shown in Figure 1 suggested that the interparticle repulsion did not take its effect in the period of time <18 h. This is reasonable because the surface coverage in our case is 1–2 magnitudes lower than 1.2 $\times$ 10^{11} particles/cm^2, which was the threshold reported for the 15 nm gold nanoparticles by Grabar et al.[9] It should be noted that the particle concentration in the colloids we used is 8.06 $\times$ 10^{-11} mol·L^{-1}, also 2 magnitudes lower than that used in ref 9 (8.86 $\times$ 10^{-9} mol·L^{-1}). In the $t^{1/2}$-dependent regime, since other variables remained constant and only pH changed, the difference in the rates of particle adhesion at different pH values could be attributed to the different sticking

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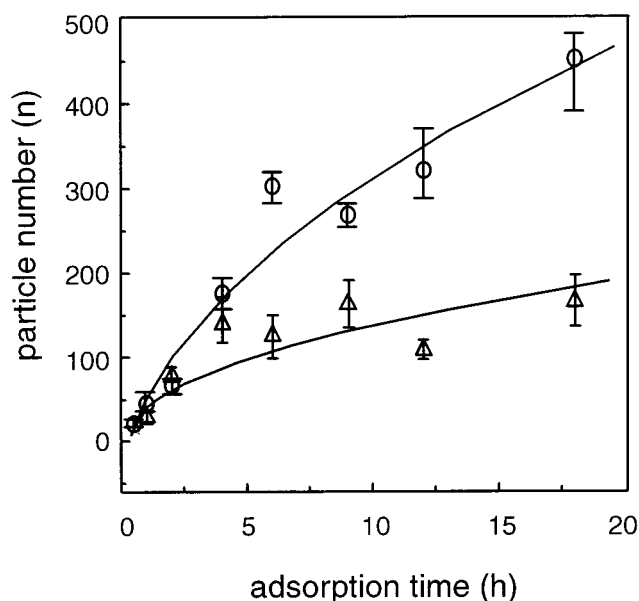
Figure 1. Time dependence of the surface coverage of gold nanoparticles (an averaged number of particles in an area of 2 μm $\times$ 2 μm). The solid lines are the best fit to [particle coverage/cm^2] = $kt^{1/2}$, treated by the method reported in ref 9. $\bigcirc$, pH = 4.0; $\triangle$, pH = 5.8.
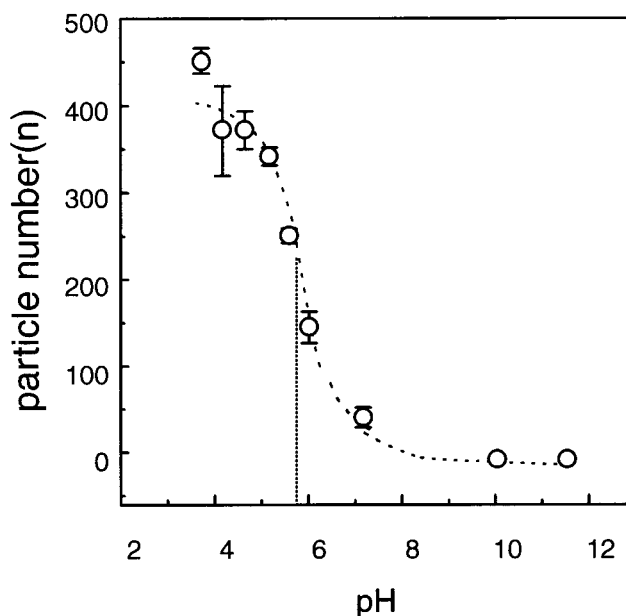
Figure 2. pH-dependence of the surface coverage of gold nanoparticles (an averaged number of particles in an area of 2 μm $\times$ 2 μm. For each pH, the particle statistics were carried out on three distinct surface areas of the same size on a single sample.). The line is meant only as a guide to the eye.

probabilities, which is an indication of substrate–particle interactions. On the basis of the above arguments, to get comparable results for all the pH values investigated, the immersion time was controlled to be 6 h.

Figure 2 gives the plot of the surface coverage (after a 6-h immersion) against the colloid pH. At pH < 5, the surface coverage shows only a slight change. However, it shows a drastic decrease with the increase of solution pH when pH > 5. Finally, it drops to nearly zero after pH > 8.

Since the interparticle repulsion does not take its effect in the present system (see above), the measured surface coverage was far from the "saturated value" for each pH. In this case, the measured surface coverage would be

mainly determined by the particle–substrate interactions. The pH-dependence of surface coverage indicates that these interactions are strongly affected by solution pH. The pH may take its effect in two ways. First, since the gold colloids have an isoelectric point of about 2,[16] they are dominantly negatively charged due to adsorption of anions within the pH range studied.

Second, the protonation degree of amino groups depends on the solution pH. The surface $pK_{1/2}$ of the amino group in *p*-ATP SAMs is 5.3, as measured by chemical force titration.[17] Therefore, at pH $\ll pK_{1/2}$, amino groups will dominantly be positively charged due to protonation, which will promote the adsorption of negatively charged gold nanoparticles by strong electrostatic interaction. At pH around $pK_{1/2}$, amino groups are partially protonated and the surface charge density will drastically decrease with pH increase, leading to the decrease in attractive electrostatic interactions between surface and particles. At pH $\gg pK_{1/2}$, amino groups are fully deprotonated, producing a nearly neutral surface, where the attractive electrostatic interactions between particles and the surface can be negligible.

The pH dependence we observed is reasonably consistent with the above discussion. Actually, the curve

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shown in Figure 2 is very similar to the force titration curve of *p*-ATP SAMs,[17] which characterizes the dissociation properties of the surface amino-groups. The pH-dependent surface coverage curve also has a deflection point around pH 5.6, in nice agreement with the $pK_{1/2}$ value (5.3) of the surface amino groups. This fact indicates that the adsorption of nanoparticles has strong relations to the charging states of the surface amino groups, suggesting that the particle–amino group interaction is electrostatic.

In summary, we have studied the effect of pH on the adsorption of colloidal Au nanoparticles onto gold substrate via the *p*-aminothiophenol coupling layer. The coverage of Au nanoparticles is found to be closely related to the pH value of the colloidal solution. In alkaline solution, where the amino group was not protonated, Au nanoparticles could not be adsorbed on the substrate, while under acidic conditions, protonation makes the amino group positively charged and the adsorption becomes easier. The interaction between Au colloids and the substrate is believed to be electrostatic.