Adsorption of Colloid Gold Nanoparticles on Charged Surface

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ABSTRACT

Colloidal gold nanoparticles have many important applications, such as bio-molecular sensors and electronic devices. To fabricate devices, one of the most significant processes is to assemble gold nanoparticles on the substrate surface. In this work, we use the advanced random sequential adsorption (ARSA) model to simulate the adsorption properties of gold nanoparticles on a surface with positively charged self-assembled monolayer (SAM). By comparing the results of experiment and ARSA simulation, we can deduce some properties of the colloid system. Besides, we demonstrate that the saturation density and the radial distribution function of adsorbed nanoparticles can be well predicted from the ARSA simulation. The influence of Hamaker constants used in the simulation is also discussed. These results will be advantageous on the understanding and control of the self-assembly of nanoparticles on charged surface.

Keywords: nanoparticle, self-assembly, colloid

1 INTRODUCTION

Colloidal particles have many applications and attractive properties for the fabrication of nano-structures and nano-devices. Their ability of self-assembly can be used to form not only ordered structures, but also semi-disordered structures on the surface. The formation properties of self-assembled nanoparticle structures allow us to study the particle-particle interactions or particle-surface interactions with a variety of conditions. Such study is important for the understanding of many physical and biological phenomenon. In this work, we introduce the advanced random sequential adsorption (ARSA) simulation method to study the interactions of gold nanoparticles in colloidal solution. When a strong attractive interactions present between particle and substrate, the adsorption of particle on surface will be highly irreversible, and the adsorbed particles have low lateral mobility, resulting in a random spatial distribution. Their adsorption curves, densities, and radial distribution functions can be calculated and compared to the experiment results. These compares could give useful information about the properties of the colloid system.

2 MATERIALS

2.1 Colloidal Gold Solution

A commercial colloidal gold solution (Sigma, G1527) is used as the source of nanoparticles. The diameter of particles is 8.8 ± 0.6 nm. The solution is first diluted by deionized water, and then the ionic strength and pH value are adjusted by adding NaCl and HCl aqueous solutions, respectively. The ionic strength I_C is 2.91 mM, and pH value is 6. The density of nanoparticles in the solution is estimated to be 1.1×10^{12} particles/cm^3.

2.2 APTMS Substrates

Silicon substrates functionalized with 3-aminopropyl-trimethoxysilane (APTMS) are used as the substrate for the assembly of colloidal gold nanoparticles. Silicon substrates are cleaned by water, ethanol, acetone, and then treated in an oxygen plasma cleaner to activate the silicon oxide surfaces. After plasma treated, the substrates are immersed into APTMS for about 1 day to form an amine-terminated self-assembled monolayer on the surface. The excess APTMS molecules on the surface are washed away by water. Then, the substrates are placed into prior colloidal gold solution for about 24 hours to adsorb gold nanoparticles.

3 ADVANCED RANDOM SEQUENTIAL ADSORPTION (ARSA) MODEL

A 3-D RSA simulation method used for simulate the adsorption of colloidal particles has been reported by Lenhoff *et al*.[1]. Particles with radius a are attempted to placed on the surface at random position sequentially. The probability of a successful adsorption is $\exp(-U_b/k_BT)$, where U_b is the maximum of the total interacting energy U, which includes the electrostatic and van der Waals potential energies. The electrostatic potential between the substrate and the approaching particle is $U_{PS}^{el}(h) = B_{PS}\, e^{-\kappa a h}$. The van der Waals potential between the substrate and the approaching particle is

$$U_{PS}^{vdW}(h) = -\frac{A_{132}}{6k_BT}\left[\frac{1}{h}+\frac{1}{h+2}+\ln\left(\frac{h}{h+2}\right)\right].$$

The electrostatic potential between the approaching particle and the particle already at the surface is $U_{PP}^{el}(r) = \frac{B_{PP}}{r} e^{-\kappa a(r-2)}$. The van der Waals potential between the approaching particle and the particle already at the surface is

$$U_{PP}^{vdW}(r) = -\frac{A_{131}}{6k_BT}\left[\frac{2}{r^2-4} + \frac{2}{r^2} + \ln\left(1-\frac{4}{r^2}\right)\right].$$

These potentials have been scaled by thermal energy k_BT. Where r is the dimensionless distance between the approaching particle and the particle already at the surface, h is the dimensionless distance between the surface of particle and the planar surface (scaled by the particle radius a), $\kappa^{-1} \sim 5.6$ nm is the Debye length corresponding to 2.91 mM ionic strength. A_{131} is the Hamaker constant for two particles interacting through the solution, and A_{132} is for the particle interacting with the substrate through the solution. A_{131} and A_{132} are assumed to be 11.5×10^{-20} J and 2.5×10^{-20} J. B_{PS} and B_{PP} are the characteristic energies given by [2]

$$B_{PS} = \left(\frac{4\pi\varepsilon\varepsilon_0 k_B T a}{e^2}\right)\left(\frac{y_P + 4\gamma\Omega\,\kappa a}{1+\Omega\,\kappa a}\right)\left(4\tanh\left(\frac{y_S}{4}\right)\right),$$

and $B_{PP} = \left(\frac{4\pi\varepsilon\varepsilon_0 k_B T a}{e^2}\right)\left(\frac{y_P + 4\gamma\Omega\,\kappa a}{1+\Omega\,\kappa a}\right)^2$, where $y_P \sim -3.7$ is the dimensionless potential (scaled by k_BT/e) of the particle. $y_S \sim +0.04$ is the dimensionless potential of the APTMS substrate surface at pH6. γ and Ω are defined by $\gamma = \tanh\left(\frac{y_p}{4}\right)$ and $\Omega = \left(\frac{y_P - 4\gamma}{2\gamma^3}\right)$. The area used for the RSA simulation is 1 μm × 1 μm with a periodic boundary condition.

Figure 1(a) shows a typical result of RSA simulation. The density of particles is only about 1350 μm^{-2} and there is no aggregation of these particles. However, the actual adsorption result with experimental conditions corresponding to the simulation, as shown in Figure 1(b), has much higher particle density (~1750 μm^{-2}), and there is some aggregation of particles. More obvious difference between RSA simulation and experiment can be seen on their corresponding radial distribution functions $g(r)$, as shown in Figure 1(c). The peak value of $g(r)$ at $r \sim 24$ nm corresponds to simulation is much larger than that to experiment. Besides, the latter is broader. Moreover, there is a peak appear at distance $r \sim 2a =$ 8.8 nm, which is related to the aggregation of particles.

To improve the 3-D RSA simulation results, we introduce an advanced RSA (ARSA) simulation [3]. Some additional modifications are applied in the 3-D RSA simulation. They are related to the consideration of the size distribution of nanoparticles, the potential distribution of nanoparticles, and the treatment of the overlap of adsorbed particles.

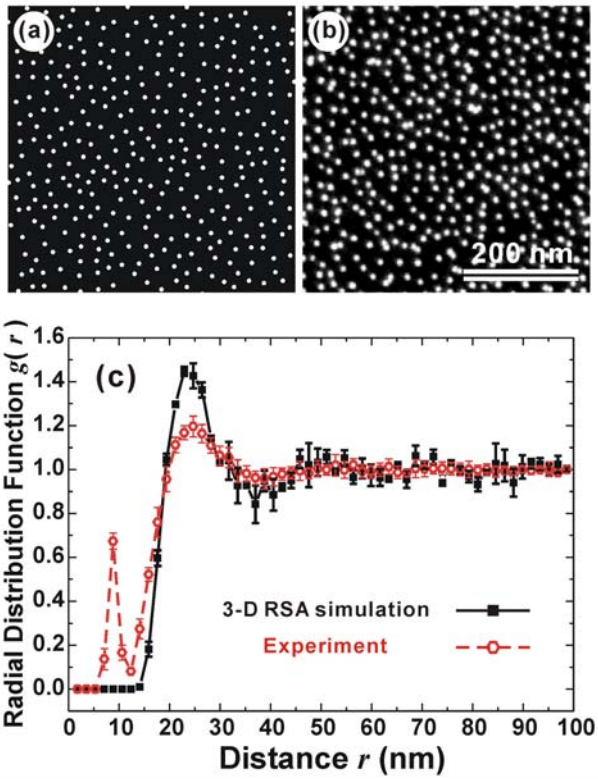

Figure 1: (a) RSA simulation result, (b) SEM image of gold nanoparticles on APTMS/Si substrate. (c) Radial distribution functions $g(r)$ corresponding to the results of RSA simulation and experiment.

Figure 2(a) shows the result of ARSA simulation. Although the density of particles (~1520 μm^{-2}) is still quite lower than the result of experiment, the radial distribution function is very similar to that of experiment, except the peak of $g(r)$ at $r \sim 2a$. We think the additional value of $g(r)$ at $r \sim 2a$ is related to the additional aggregation of particles, which is caused by the contamination of some particles.

Some parameters used in the prior ARSA simulation are very critical, such as the potential of particles, the potential of substrate, and the ionic strength of the solution. For example, the adsorption density decreases about 50% when the ionic strength changes from 2.91 mM to 0.58 mM, as shown in Figure 3. By contrast, some parameters such as the Hamaker constants A_{131} and A_{132} have larger permissible range for simulation. As A_{132} changes from 1×10^{-20} J to10×10^{-20} J, the adsorption density increases less than 10%. The influence of A_{132} is even less than A_{132}. This means that we don't have to know the exact value of Hamaker constants for the simulation.

Since the adsorption properties strongly depend on the electric properties of the system, we can well control the nanoparticle assembly by adjusting the electric-related conditions, and predict by the ARSA simulation. Figure 4 shows that the experiment results are well predicted by the ARSA simulation with different ionic strength.

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4 SUMMARY

In summary, we have shown that the advanced random sequential adsorption simulation (ARSA) method can be used to well simulate the adsorption properties of nanoparticles on a charged surface. Some electric-related parameters, such as the ionic strength of the solution, obviously influence the adsorption properties. By contrast, the Hamaker constants show relatively small influence.

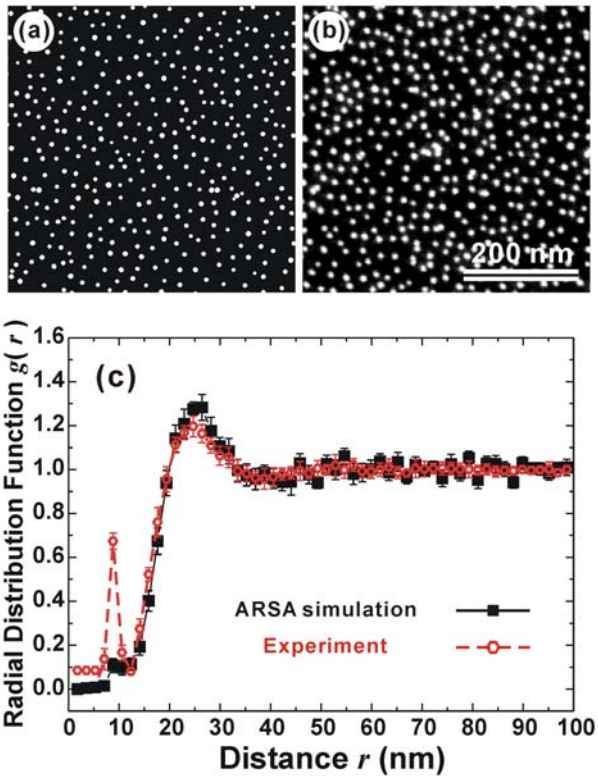

Figure 2: (a) ARSA simulation result, (b) SEM image of gold nanoparticles on APTMS/Si substrate. (c) Radial distribution functions $g(r)$ corresponding to the results of ARSA simulation and experiment.

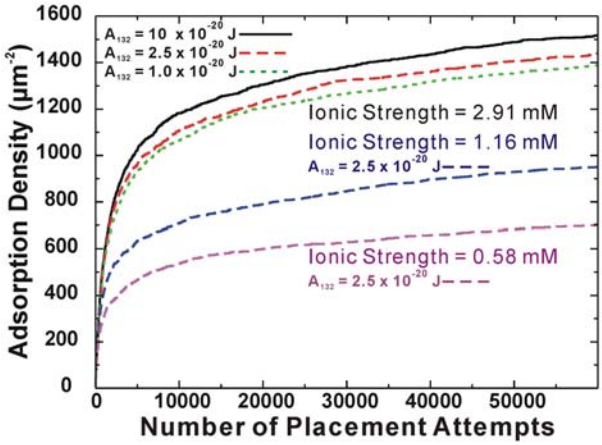

Figure 3: Some adsorption curves calculated by ARSA simulation with different values of ionic strength or Hamaker constant.

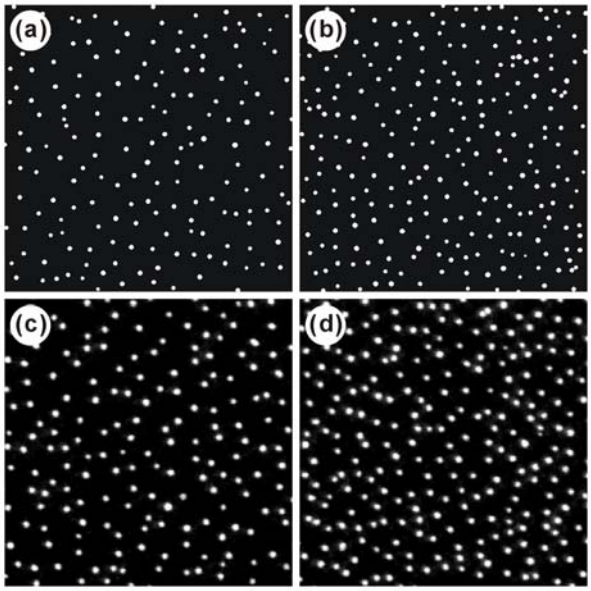

Figure 4: (a)-(b) ARSA simulation result, (c)-(d) SEM images of gold nanoparticles on APTMS/Si substrate. The ionic strength for (a) and (c) is 0.58 mM. The ionic strength for (b) and (d) is 1.16 mM. Potential of particles used for simulation is $y_P = -3.7 \pm 1.3$.

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