

Surface Attraction and Chemistry of Gold Nanoparticles

A Term Paper

Presented to

The Class of Applications of Nanomaterials (MatE 297),

Department of Chemical and Materials Engineering

San Jose State University

In Partial Fulfillment

of the Course Requirements for MatE 297, Spring 2006

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May 10, 2006

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Abstract

Entering the information age, scientists are discovering new applications and manipulating chemical composition of materials in nanometer scale. In such a tiny scale, surface electrons play a big role. Outmost electrons shielding an atom or a molecular represent the characteristics of the atom or the molecular. The characteristics include the electrical, chemical, and optical properties of the material. The characteristics also effect how the nano-material can be processed. On the surface of a gold nanoparticle composited by a minimum of eleven or more gold atoms, the negative electronic shielding the particle provide a Coulomb force to bind with the thiol-end copolymers or the bases of deoxyribonucleic acid (DNA). Then, the combination can be self-assembled by the electrical attraction on the addition materials. Gold nanoparticles have wide applications such as optical, magnetic, and medical applications. By understand its synthesis process of formation and binding mechanism to other additional materials, engineers will be able to develop more stable and useful products out of gold nanoparticles.

Introduction

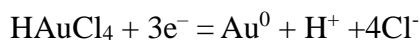
Interest of gold has got the attention of human since thousand years ago; application of gold nanoparticle has grabbed the concentration of researchers in the information age. Gold nanoparticle and nanocomposites can be used in many fields such as electrical, optical, magnetic, and medical applications, and those are the reason why it is so popular. In the electrical application, gold nanoparticle can be a single atom transistor by adjusting its quantum well. Another application can be that the electrode combining the gold nanoparticles with multiwall carbon nanotubes get the benefit of the excellent electroactivity from both of them.[1]

Optical properties of a gold nanoparticle are significant because its adsorption and emission of the wave length are within the visible range of light. A gold nanoparticle contains as less as eleven atoms which can be a perfect quantum dot, the zero dimension energy well for electron wave. Quantum confinement of a quantum dot can easily distinguish the energy levels of electronic state. The optical properties also have been changed under the change in geometry. Per the theory of linear combination of atomic orbital (LCAO), the energy states in a molecule are the molecule orbital (MO) for electrons in a molecule.[2] MOs are the linear combinations of each single atomic orbital (AO). Those energy states represent the bonding energy between atoms, the band gap energy for electrical current, and the work function of optical absorption. In bulk gold, there are infinite atoms to MOs no matter one gram or one kilogram of gold. In a size of nanoparticle, however, finite atoms from 11 to 10,000 impound the MOs in certain distributions. The optical properties of a particle which adsorb or emit light will be altered while the MOs are distorted. In other words, for colloidal gold, the change of size can be verified by visual inspecting its color from red to blue. Another application is that gold nanoparticles can adsorb the energy of laser and release energy in heat to kill cancer cells.

Gold nanoparticles can also be a core of magnetic materials such as AuNi alloy. By repeating a similar process, Nichol can be add on the core of gold and become nano-magnetic particles. By manipulating the ratio between of AuNi, the magnetic properties of the nano-alloy will be changed. The magnetization of high ratio of gold has slower response curve than that of a low ratio of gold. More and more magnetic applications such as AuCo have been investigated.[3]

Formation

Gold nanoparticles can be produced by the reduction of gold ions. In the solution of tetrachloroauric acid (HAuCl_4), addition of reducing agents nucleates the gold particles. Gold ions adsorb electrons from the reducing agents and become atoms as described as the chemical reaction below.



where the core of Au^0 nucleates when reducing agents provide e^- .

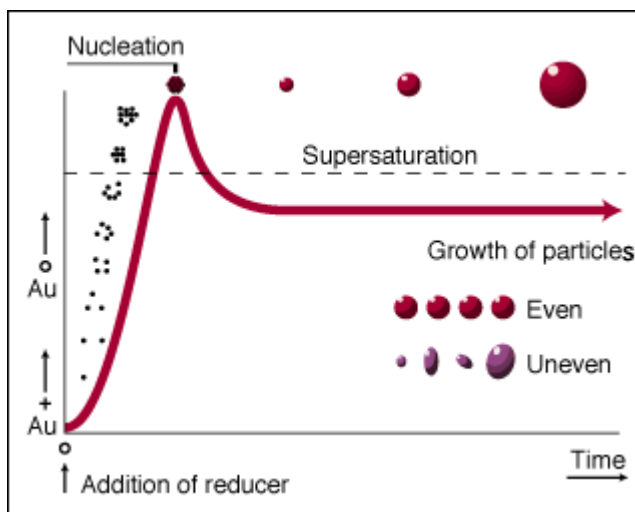


Figure 1. Nucleation of gold nanoparticles.[4]

Several atoms aggregate to nucleate the particle center in particular nanostructure. A minimum of 11 atoms form central icosahedral gold cores as shown in Figure 1, and the nanoparticles size depends on the process environment. The particles become gold colloid due to the electronic shield on the surface. The process of the colloidal gold particle can be completed in a polymer matrix. Polymer matrices trap the gold ions in the beginning of the process and prevent the nanoparticles from agglomerating at the end. The matrix immobilizes the gold ions to have the chemical reaction and barricades each single particle from growing by the electrostatic repulsion. Various polymers such as homopolymers, block copolymers and dendrimers have been investigated to assist the formation of gold.[4] Those polymers attached on the gold nanoparticle perform a monolayer protection to the core. The layer performs monolayer protected clusters (MPCs) and eases the handling of gold colloids. MPCs disperse readily and evenly into polymer matrices which provide specific sites for nanoparticles. On the other hand, the polymers are as ligands or functional groups for synthesizing of the nanoparticles with other components.

The bonding between gold nanoparticles and thiol-end polymers is held by the columbic force. Colloidal gold particle is surrounded by a double ionic layer as shown in Figure 2. The core of pure gold is shielded by a layer of adsorbed (AuCl_2^-) ions. Then, the hydrogen ions (H^+) in the solution are attracted by those negative charges and form the electrical double layers. The shield layer is as the function of preventing nanoparticles from aggregation by the electrostatic repulsion. The layer also provides chemical connections to its ligands. Ligands such as citrate and protein are used to bind the gold nanoparticles with different materials so various applications can be utilized. The native force is the initial charge attraction of the negative gold particle to the positive charged amino acids within the ligands.

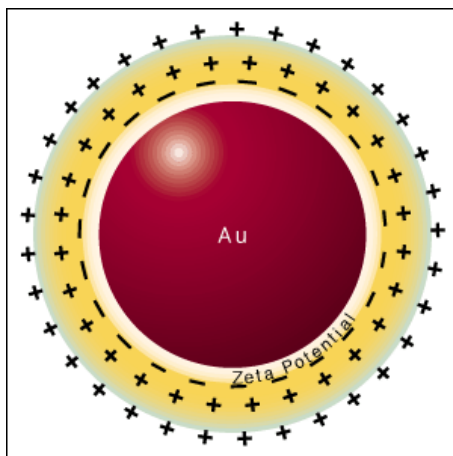


Figure 2. Colloidal gold particle surrounded by a double ionic layer.[4]

Gold nanoparticles present their color in the visible range of from wine red to blue or light green. The color in terms of wave length is from 510 nm to 550 nm. The energy absorbed by the gold particles is depended on the energy bands formed by each single particle. A single particle can be considered as a quantum well which has various molecular orbitals (MOs). The energy gaps between MOs in a nanoparticle will then be able to either adsorb or emit the energy from 1.0 to 1.7 eV. This feature helps to visually determine the size of gold nanoparticle.

By controlling the type of reducing agents and the surrounding polymers, monodispersed gold particles can be produced uniformly and steadily.[5] Through various methods, colloidal gold nanoparticles have stable and wide range in sizes. In Table 1, several citrate methods were listed to show their products of gold nanoparticles in various sizes.

Table 1. Methods for colloidal gold synthesis.[5]

Methods	Size of particles
Undercagold clusters	0.82 nm
Thiocyanate	2.6 nm
White Phosphorous	3 nm
Citrate plus Tannic Acid	3 – 17 nm
Sodium Borohydride	4.2 nm
White Phosphorus	5.2 nm
Sodium Citrate	8.5 nm
Ethyl Alcohol	10 nm
Ascorbic Acid	12 nm
Sodium Citrate	12 – 64 nm

Synthesis of gold nanoparticles with other materials

As mentioned above, the polymers are as ligands or functional groups for synthesizing of the nanoparticles with other components. The appropriate ligands and functional groups result in various nanoparticles in shape and size as varied building blocks. The building blocks then can have different chemical and mechanical behaviors incorporating with components. Once the particles form building blocks, the functional groups on the other side can synthesize with other attractive polymer groups and become useful composites. For instance, a thiol-end polymer bonds with gold and forms a Thy-Au structure. The other side of the polymer has hydrogen bondings with a polymer 1 as shown in Figure 3(a). And, the polymer 1 can be a functional group of random copolymer which is a matrix of a composite material as shown in Figure 3(b).

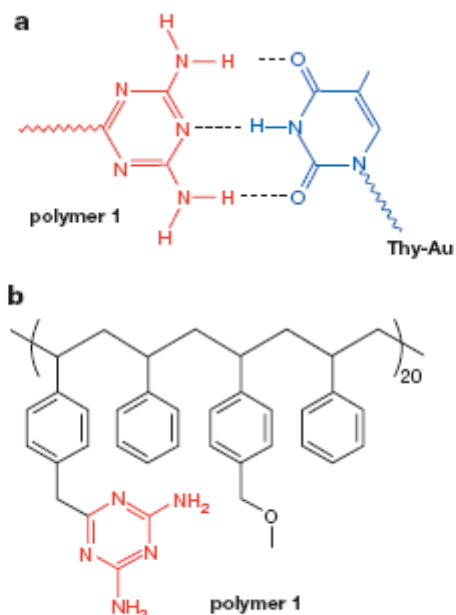


Figure 3. Recognition motif and polymer ‘mortar’. a. Diaminotriazine-thymine recognition; b, triazin-functionalized random copolymer 1. [6]

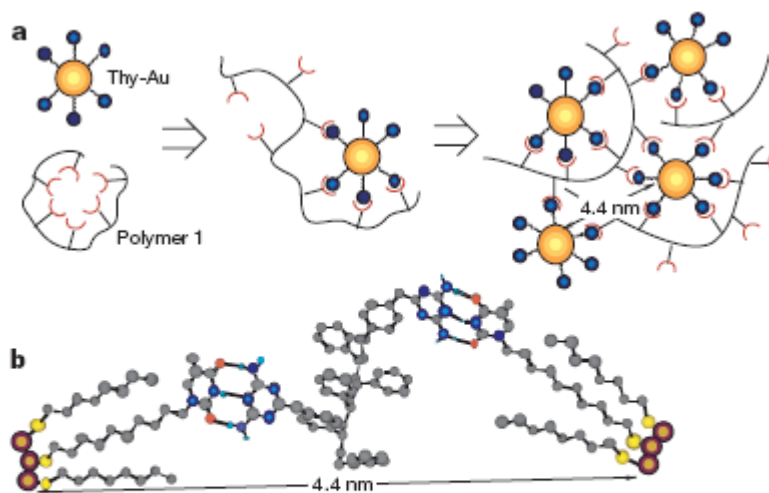


Figure 4. Mechanism for the aggregation of polymer 1-Thy-Au. (a) Polymer mediated self-assembly of Thy-Au, showing the experimentally determined interparticle distance. (b) Proposed polymer 1-Thy-Au self-assembled structure (using AMBER force field as implemented by Micromodel 4.0), showing the computationally predicted interparticle distance. [6]

As shown in Figure 4(a), the citrate (alkanethiols) surrounds the colloidal gold by the superficial bonding. The protein as the polymer 1 then has been hydrophobic adsorbed to the gold colloid. The other side of polymer 1 can have different functional groups to bind to other groups or materials. Once a DNA has the functional group as polymer 1, a bio-application can be accomplished through the same idea.

Conclusion

The bottom-up process of manufacturing gold nanomaterials is well developed, and the difficulties are that how well the productivity and uniformity of colloids that we can have. The reducing agents and surrounding polymers are the key parameters of the synthesis process of gold nanoparticles. As long as the gold nanoparticles are ready, the next step then will be to develop as many as possible of versatile applications that the gold nanoparticles can have. By understanding of the chemical reactivity of ligands and functional groups, the applications of gold nanoparticles can be well developed.

References

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