

Conductivity elevation technology for polymer coating layer using self-assembly monolayer system

J. T. Kim*, J. R. Lee*

ABSTRACT

SAMs are themselves nanostructures with a number of useful properties. For example, the thickness of a SAM is typically 1-3 nm; they are the most elementary form of a nanometer-scale organic thin-film material. The composition of the molecular components of the SAM determines the atomic composition of the SAM perpendicular to the surface; this characteristic makes it possible to use organic synthesis to tailor organic and organometallic structures at the surface with positional control approaching ~0.1 nm.

In this paper, we got the best result for not only the homogeneous metal particle dispersity but also the low surface electric resistance of the polymer coated layer, by using mixed SAM system of mercaptoethanol and mercaptoundecanol.

Key word : Self assembly monolayer, Cu, Conductivity, Nano metal particle

1. Introduction

Bare surfaces of metals and metal oxides tend to adsorb adventitious organic materials readily because these adsorbates lower the free energy of the interface between the metal or metal oxide and the ambient environment.¹ These adsorbates also alter interfacial properties and can have a significant influence on the stability of nanostructures of metals and metal oxides; the organic material can act as a physical or electrostatic barrier against aggregation, decrease the reactivity of the surface atoms, or act as an electrically insulating film. Surfaces coated with adventitious materials are, however, not well-defined: they do not present specific chemical functionalities and do not have reproducible physical properties (e.g., conductivity,

wettability, or corrosion resistance).

Self-assembled monolayers (SAMs) provide a convenient, flexible, and simple system with which to tailor the interfacial properties of metals, metal oxides, and semiconductors. SAMs are organic assemblies formed by the adsorption of molecular constituents from solution or the gas phase onto the surface of solids or in regular arrays on the surface of liquids (in the case of mercury and probably other liquid metals and alloys); the adsorbates organize spontaneously (and sometimes epitaxially) into crystalline (or semicrystalline) structures. The molecules or ligands that form SAMs have a chemical functionality, or "headgroup", with a specific affinity for a substrate; in many cases, the headgroup also has a high affinity for the surface and displaces adsorbed adventitious organic materials from the surface. There are a number of headgroups that bind to specific metals, metal oxides, and semiconductors. The most

*

extensively studied class of SAMs is derived from the adsorption of alkanethiols on gold,²⁻¹⁰ silver,^{9,10,11} copper,⁹ palladium,^{13,14} platinum,¹⁵ and mercury.¹⁶ The high affinity of thiols for the surfaces of noble and coinage metals makes it possible to generate well-defined organic surfaces with useful and highly alterable chemical functionalities displayed at the exposed interface.^{6,17}

This paper focuses on the preparation, formation, structure, and applications of SAMs formed from alkanethiols (and derivatives of alkanethiols) on copper.

2. Experimental

2.1. Materials

Cu particle(Aldrich) is used as a conducting materials. The cu particle shape is spherical below 100nm. Mercaptoethanol, Mercaptoundecanol(Aldrich, First grade) were used for surface modification of metal particles using the self assembly process. Polymer resin as a coating binder is polyurethane.

The brief specifications of materials are as following tables;

1) Organothiols

Organothiol	Structure	Mw
Mercaptoethanol	SH-(CH ₂) ₂ -H	78.13
Mercaptoundecanol	SH-(CH ₂) ₁₁ -OH	204.3

2) Polyurethane resin

Type	Polyester-urethane dispersion
Color	Light yellow(almost colorless)
Solid Content	34%
pH	8
Solvent	Water
Specific gravity	1.06

2.2. Treatment of Cu particle through the self assembly process

Two different self assembly solutions were prepared for surface treatment. The solutions were as follows, all of them freshly prepared before use :

(a) the solution of Mercaptoethanol was obtained by the dissolution of 0.07813g of Mercaptoethanol (0.01mol) in 100 ml of ethanol; (b) the solution of Mercaptoundecanol was obtained by the dissolution of 0.2044g of Mercaptoundecanol (0.01mol) in 100 ml of ethanol. Temperature was kept at room temp. during all procedures. Self assembly surface treatments were repeated several times and the results showed good reproducibility. Before reacting organothiol and cu particle , Cu particle was sonicated in ethanol to disperse evenly for 10~20min. The organothiol solution was added dropwise (1~10ml) to the 0.5g Cu particle (ethanol based). And then, the mixture was kept under strong magnetic stirring for 24~48hr.

2.3. Preparation of resin solution

The resin solution was prepared by mixing of water soluble polyurthane solution and self assembled metal particle by weight. For this resin solution, the solid content of Polyurethane was changed to 3~17%, and the surface modified and unmodified metal particle contents were adjusted to the 0~8g/1L(polyurethane 1L).

2.4. Coated steel samples and its coating method

In this paper, steel sheet was used electrogalvanized (EG) steel plates. The steel plates were stored in a vacuum decicator to minimize the surface oxidation. The steel plates were coated with the polymer solution, mixture of polyurethane resin and self assembled metal particle, by a simple bar coating method. Before coating, the steel plates were cut into appropriate sizes (12×7.5 cm) and cleaned by immersing into

a cleaning solution for a desired period of time. And then it was taken out, washed, and dried by blowing a gentle stream of dried air. In the bar coating, we used #16 bar coater. The coated steel plates were cured in an oven at 100~120°C.

2.5. Analysis method

The change of UV-Vis. spectra before and after organothiol treatment were measured directly from the organothiol treated metal particle solution (after the washing step) by UV-VIS spectrophotometer (Perkin-Elmer, Lambda EZ 210), using ethanol as reference, in the range 200~800 nm.

Transmission electron microscope (TEM) was done with FEI/Philips CM-10 instrument. For TEM, the samples were prepared by dropping the organothiol treated metal particle solution on standard holey carbon grids.

The optical microscope was done with Nikon ECLPSE TE300 instrument. The samples were prepared by dropping or bar coating the organothiol treated metal particle solution and polyurethane with SAM metal particle on the glass.

3. Result & Discussion

3.1. Cu particle treatment

In all syntheses, the formation of Cu particle was not noticeable by a dramatic color change of the organic phase. But untreated sample was precipitated after a few minutes and treated sample was dispersed homogeneously for a long time.

Fig. 1~3 show the UV-Vis. absorption spectra of the as-made samples in ethanol solution. The spectra show the characteristic surface plasmon resonance band of Cu particle in ethanol at 603 nm. It is known that the maximum wavelength of the plasmon band and its bandwidth in metallic Cu particle depend on a number of factors, such as particle size, shape, and self

assembly agent. In Fig. 1~3, clear differences can be found among samples. They are mainly related to the wavelength band position and to the bandwidths. Once all the samples were prepared using the same solvent (ethanol) and different Organothiol self assembly agent, and the differences among the spectra may be attributed to variations in the Cu particle size, shape, and/or size distribution as well.

The samples were synthesized, washed, and characterized; they were kept in ethanol solution to verify their stability. We noted that after 7 days, the solution of sample such as Mercaptoethanol became unstable and the Cu particles were precipitated. On the other hand,

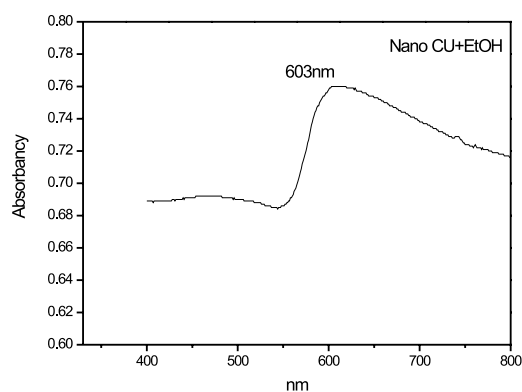


Fig. 1 UV-Vis. Spectrum of the as-made Cu nanoparticle samples dispersed in ethanol.

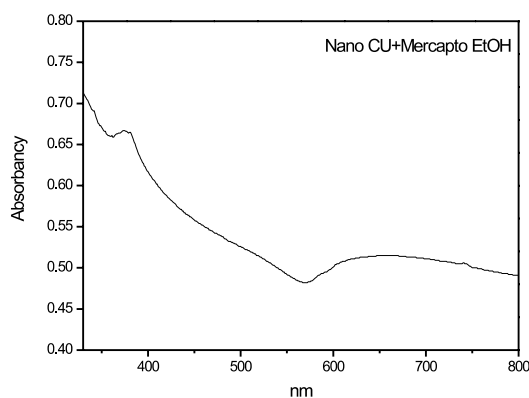


Fig. 2 UV-Vis. spectrum of the as-made Cu nanoparticles/Mercaptoethanol samples dispersed in ethanol.

Mercaptoundecanol treated Cu particle remained stable in solution, and their absorption spectra did change, comparing with non-treated Cu particle. In this case, the spectrum showed a dramatic shift and band widths in the plasmon band position, which was a sign that the particles were modification in solution.

Figs. 4 shows the TEM images of the Cu nanoparticle/Organothiols samples. The differences in the mean size and dispersion are evident. It is noticeable that the more stable Mercaptoethanol, and

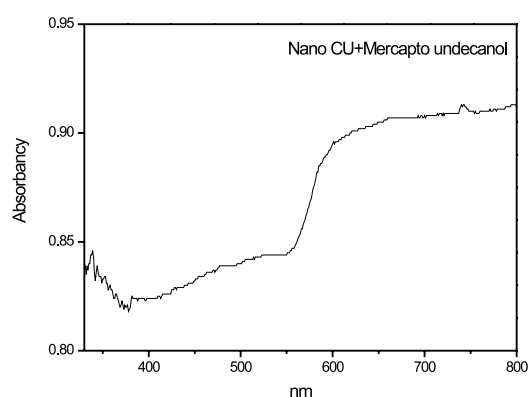


Fig. 3 UV-Vis. spectrum of the as-made Cu nanoparticles/Mercaptoundecanol samples dispersed in ethanol.

Mercaptoundecanol treated Cu particles presented the homogeneous distributions, whereas the unstable non-treated Cu particle presented a large non-homogeneous distribution.

The TEM images of the solids resulting from the precipitation of all the unstable samples presented a rich population of large and non-homogeneous particles, indicating that the precipitation resulted from the random growth of the Cu particle. So it is very important to sonicate Cu particle before self assembly reaction, indicating that preventing aggregation resulted from self assembly reaction on the Cu particle surface could be possible after sonication.

3.2. Cu particle treatment using mixed self assembly agents

In order to get more improved degree of dispersion of Cu particle, the mixed self assembly system was used; that is, coadsorption from solutions containing mixtures of thiols ($RSH + R'SH$).

The mole fraction of a specific adsorbate on the particles in the SAM reflects the mole fraction of the adsorbate in the solution through all ranges of concentration. Experimental conditions can bias the relative ratio of the molecular components constituting the SAM: for

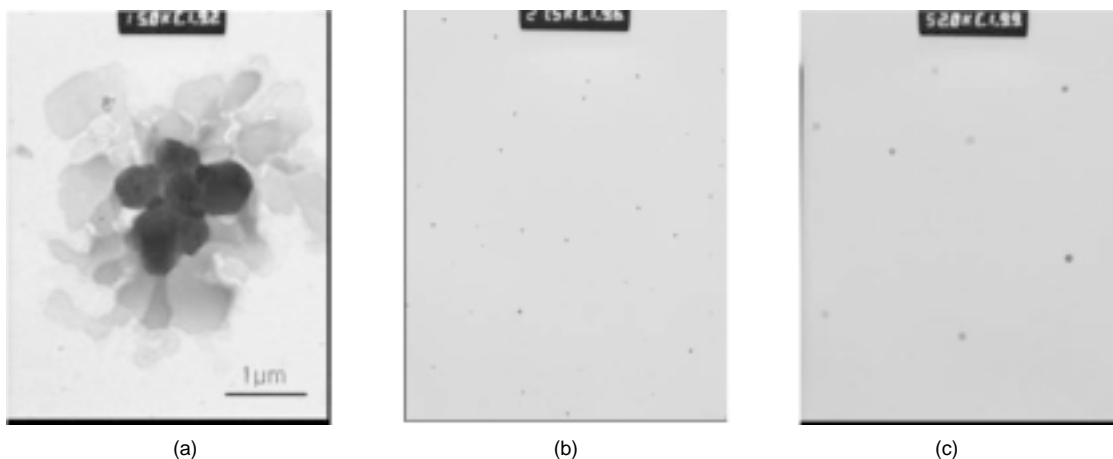


Fig. 4 TEM images from the as-made Cu nanoparticles samples:
(a) Cu particle (b) Cu particles/Mercaptoethanol (c) Cu particle /Mercaptoundecanol

example, the choice of solvent can modify the relative mole fractions of adsorbates on the particles in the SAMs formed from a mixture of polar and nonpolar molecules. Similarly, the mixture of *n*-alkanethiols with different chain lengths will form SAMs with a composition enriched with the longer alkanethiol; this bias increases over time. There has been some attention given to the homogeneity of the local composition of SAMs formed from mixtures of thiols

At first, when the single thiol compound was used, the stable sample was dispersed homogeneously for a long time (about 7days). But after 7 days, it is happened the aggregation and precipitation of self assembled Cu particle. When the short chain thiol was used, degree of dispersion was superior to non-treatment Cu particle, but it was difficult to prevent the aggregation of Cu particles because the thiol chain was too short. On the other hand, when the long chain thiol was used, it is difficult to form dense self assembly layer on the Cu particle because of its steric hindrance, so it was also easy to precipitate.

By using the mixed self assembly system (Mercaptoethanol and Mercapto undecanol), the precipitation time was increased longer and degree of dispersion was more improved homogeneously than the single organotiol self assembly system.

3.3. Dispersion of metal particles

Microscopic analysis could provide the information in real space on the spatial distribution of the Cu particle in the self assembled metal particles/polyurethane resin solution.

Fig. 5 shows the Microscopic images of the self assembled Cu nanoparticle/Polyurethane Coating samples with increasing Cu contents. The differences in the degree of dispersion and density of Cu particle between all samples are evident. Actually, the size of particles was about 0.5 ~ 3 μ m in the microscopic images. And there

was no aggregation between particles and it showed homogeneous dispersion. The particles below 1~100nm were difficult to observe in the microscopic image.

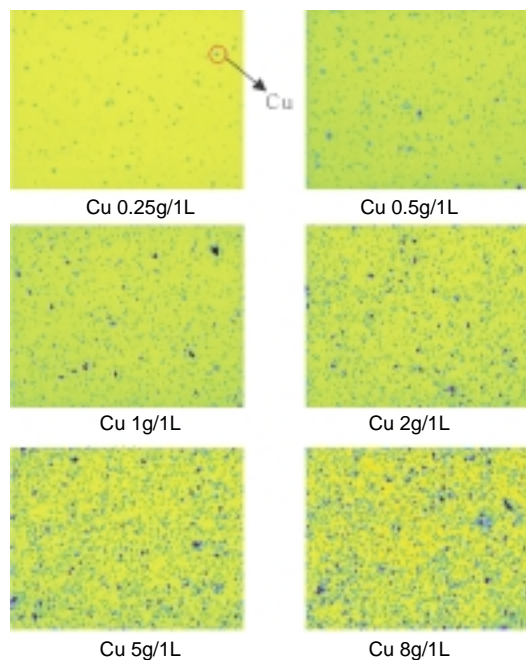


Fig. 5 Microscopic analysis of degree of dispersion of self assembled Cu particle in the coating layer.

When the Cu particle of same weight in the polyurethane solution was used, the degree of dispersion and the size of Cu particle showed remarkable differences. In case of non-treatment Cu, although we used nanosized Cu particle, the size of Cu particle was about 5~15 μ m and most of the Cu was precipitated, because of the aggregation. But, in this case, the most of self assembled Cu particles were dispersed homogeneously, and its size was below 1~3 μ m.

3.4. Electric surface resistance of coated layer

It is well known that electric surface resistance of an organic coated layer depends on the composition, structure, and the thickness of the coated layer, which affects a flow of

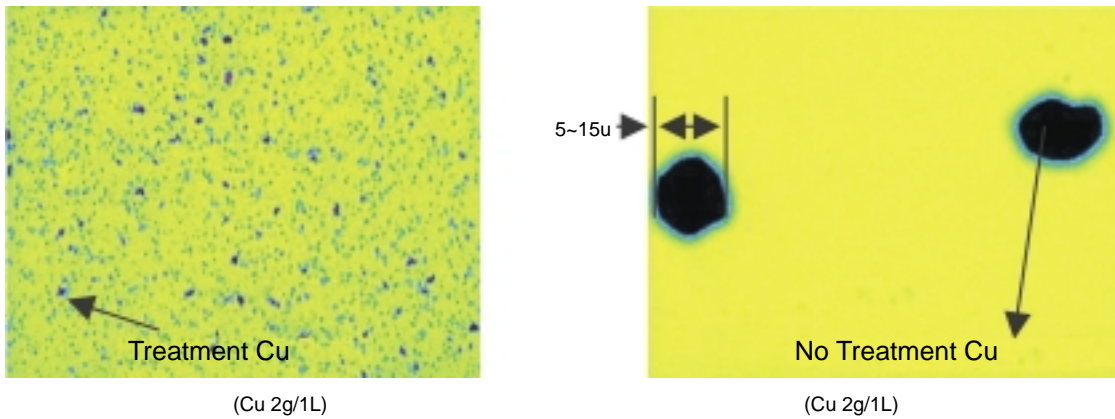


Fig. 6 Comparison of self assembly treated and non-treated Cu particles

electricity. It also depends on the distance, density and dispersibility of metal particles over the metal/resin coat. A thin organic coated layer must have less electric surface resistance to show the electrical conductivity, and if these coated layers have metal particles, it could be more effective to the conductivity.

Generally, a thick organic coating tends to show more electric surface resistance. As a matter of fact, it was hard to measure the value of electric surface resistance because of over load caused from high surface resistance. However, by adding metal particle, the electric surface resistance was much decreased. Finally, the condition for lower surface resistance was found at about $3\mu\text{m}$ as the same level of thin coated layer (below $1\mu\text{m}$).

This means that the preventing of aggregation resulted from self assembly reaction on the Cu particle surface after sonication made metal particles floating longer and well dispersed state in the coating solution.

When it was compared with non-treatment metal particle and self assembled treatment one, if we would want to get low electric surface resistance using non-treatment metal, we should add above 10 times more amount of Cu particles.

Table 1. The detail experimental conditions and brief results are as below table.

Composition of solution		Degree of dispersion	Surface electrical resistance (mΩ)
Polyurethane solid content (%)	Treated Cu content(g/1L)		
2.5	0	-	0.06
2.5	0.5	excellent	0.06
2.5	1	excellent	0.06
2.5	2	excellent	0.06
2.5	3	excellent	0.06
2.5	4	excellent	0.06
2.5	5	excellent	0.06
2.5	8	excellent	0.06

Coating thickness : below 1000mg/m²

Composition of solution		Degree of dispersion	Surface electrical resistance (mΩ)
Polyurethane solid content (%)	Treated Cu content(g/1L)		
5	0	-	Over load
5	0.5	excellent	Over load
5	1	excellent	Over load
5	2	excellent	Over load
5	3	excellent	Over load
5	4	excellent	0.06
5	5	excellent	0.06
5	8	excellent	0.06

Coating thickness : about 3200mg/m²

4. Conclusion

It was evident, according to the results presented in this work, that the characteristics of Cu nanoparticles were strongly affected by the synthetic parameters. Properties such as stability, structure, and size distribution were able to be drastically changed by a simple modification, SAM method. In respect to the different samples studied in this work, we can make the following considerations: there was evidence that the stability of the Cu particles was directly related to homogeneity (both in size and structure) of the as made samples.

As the instability of the samples was related to the particle growth, the importance of the organothiol in this process could be verified when we compared the stability of treated Cu samples, in which the only difference was the kinds of organothiol at the Cu particle treatment.

The mixed self assembly system works well metal particle for the preventing aggregation each other and dispersing homogeneously than single organothiol self assembly system. In this work, the mixture of mercaptoethanol and mercaptoundecanol was applied for the surface of metal particle.

Finally, we got the best result for not only the homogeneous metal particle dispersity but also the low surface electric resistance of the polymer coated layer, by using mixed SAM system of mercaptoethanol and mercaptoundecanol.

Reference

- (1) Adamson, A. W.; Gast, A. P. *Physical Chemistry of Surfaces*, 6th ed.; Wiley-Interscience: New York, 1997.
- (2) Poirier, G. E.; Pylant, E. D. *Science (Washington, D.C.)* 1996, 272, 1145.
- (3) Nuzzo, R. G.; Allara, D. L. *J. Am. Chem. Soc.* 1983, 105, 4481.
- (4) Porter, M. D.; Bright, T. B.; Allara, D. L.; Chidsey, C. E. D. *J. Am. Chem. Soc.* 1987, 109, 3559.
- (5) Dubois, L. H.; Nuzzo, R. G. *Annu. Rev. Phys. Chem.* 1992, 43, 437.
- (6) Laibinis, P. E.; Whitesides, G. M.; Allara, D. L.; Tao, Y. T.; Parikh, A. N.; Nuzzo, R. G. *J. Am. Chem. Soc.* 1991, 113, 7152.
- (7) Dubois, L. H.; Zegarski, B. R.; Nuzzo, R. G. *J. Chem. Phys.* 1993, 98, 678.
- (8) Love, J. C.; Wolfe, D. B.; Haasch, R.; Chabiny, M. L.; Paul, K. E.; Whitesides, G. M.; Nuzzo, R. G. *J. Am. Chem. Soc.* 2003, 125, 2597.
- (9) Laibinis, P. E.; Whitesides, G. M.; Allara, D. L.; Tao, Y. T.; Parikh, A. N.; Nuzzo, R. G. *J. Am. Chem. Soc.* 1991, 113, 7152.
- (10) Dubois, L. H.; Zegarski, B. R.; Nuzzo, R. G. *J. Chem. Phys.* 1993, 98, 678.
- (11) Walczak, M. M.; Chung, C.; Stole, S. M.; Widrig, C. A.; Porter, M. D. *J. Am. Chem. Soc.* 1991, 113, 2370.
- (12) Fenter, P.; Eisenberger, P.; Li, J.; Camillone, N., III; Bernasek, S.; Scoles, G.; Ramanarayanan, T. A.; Liang, K. S. *Langmuir* 1991, 7, 2013.
- (13) Love, J. C.; Wolfe, D. B.; Haasch, R.; Chabiny, M. L.; Paul, K. E.; Whitesides, G. M.; Nuzzo, R. G. *J. Am. Chem. Soc.* 2003, 125, 2597.
- (14) Carvalho, A.; Geissler, M.; Schmid, H.; Micel, B.; Delamarche, E. *Langmuir* 2002, 18, 2406.
- (15) Li, Z.; Chang, S.-C.; Williams, R. S. *Langmuir* 2003, 19, 6744.
- (16) Muskal, N.; Turyan, I.; Mandler, D. *J. Electroanal. Chem.* 1996, 409, 131.
- (17) Laibinis, P. E.; Whitesides, G. M. *J. Am. Chem. Soc.* 1992, 114, 1990.