Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Synthesis and Optical Properties of Nano- Composite Particles

H. S. Zhou [a] , I. Honma [a] , H. Sasabe [b] & H. Komiyama [c]

[a] Electrotechnical Laboratory (ETL), 1-1-4, Umezono, Tsukuba, 305, Japan

[b] Nanophotonics Laboratory, The Institute of Physical and Chemical Research (RIKEN), Hirosawa 2-1, Wako-shi, Saitama, 351-01, Japan

[c] Department of Chemical System Engineering, Faculty of Engineering, The University of Tokyo, Bunkyo-Ku, Tokyo, 113, Japan

Version of record first published: 04 Oct 2006

To cite this article: H. S. Zhou, I. Honma, H. Sasabe & H. Komiyama (1998): Synthesis and Optical Properties of Nano- Composite Particles, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 314:1, 233-243

To link to this article: http://dx.doi.org/10.1080/10587259808042483

Mol. Cryst. Liq. Cryst., 1998, Vol. 314, pp. 233–243
Reprints available directly from the publisher
Photocopying permitted by license only

SYNTHESIS AND OPTICAL PROPERTIES OF NANO-COMPOSITE PARTICLES

H.S.ZHOU[a], I.HONMA[a], H.SASABE[b] and H.KOMIYAMA[c]

[a] Electrotechnical Laboratory (ETL) 1-1-4, Umezono, Tsukuba, 305, Japan

[b]Nanophotonics Laboratory, The Institute of Physical and Chemical Research (RIKEN), Hirosawa 2-1, Wako-shi, Saitama, 351-01, Japan

[c]Department of Chemical System Engineering, Faculty of Engineering, The University of Tokyo, Bunkyo-Ku, Tokyo, 113, Japan

Abstract Nanostructured composites provide a rich source of new advantage functional materials for fundamental research and application. Here, we disclose our recent research works on coated inorganic nanostructured composites materials by surface modification. For example, synthesis of gold thin layer coated on semiconductor nanoparticles; polydiacetylene(PDA) shell layer on a template of nanosize gold particles; and conformation's change of protein cytochrome b-562 on the surface of gold colloidal nano-particle. The optical properties of these nanostructured composites materials are also investigated.

Keywords: organic-inorganic nanostructure, nano- composite

INTRODUCTION

Nanomaterial is a new term describing recent research devoted to the generation of nanometer scaled structured functional material. The synthesis can be divided to two ways [1], "engineering down", whereas the nanophysicist tends to operate from bulk "down"; and "engineering up", whereas the nanochemist works toward this goal from atom "up". But, because further reduction of the currently available microsystems by "engineering down" (for example, photolithographic methods) is uneconomical, the chemical "engineering up" strategies are attracted more attention, and being explored for the assembly of small molecular building blocks to form devices [1-6].

Nanophase science is devoted to understandeding the changes in fundamental properties of materials as a function of the size, evolving from isolated atoms or assembled moleculae to a bulk phase. In the case of semiconductors or metals, this evolution is remarkable, whereas the electronic, optical and chemical properties depend on the particle size[2-6]. For example, the band gap of semiconductor particle goes blue shift as the size decreasing. Because surface atoms ration increases as the size decreasing, the surface treatment becomes a key point in nanomaterials synthesis[2,3,5,6]. The surface modification not only gives homogenieous uniform nanoparticles, but also controls the properties[7], and is emerging a new methods to synthesize nano-composite materials[2,5,6,7,8]. Here, we report several approaches to modify the surface of metal nanoparticles to obtain nano-composite materials with some new optical properties.

SEVERAL APPROACHES

1.Gold Coated Nanoparticles

We firstly report synthesis of Au_2S nanoparticles coated with thin gold layer by a colloidal method, and the optical properties are changed and controlled by the gold coated layer. The results are consistent with a theoretical approach that includes electromagnetic resonance effects[9] and the quantum confinement of the carriers in the thin gold shell layer[10]. Interest in metal coated particles comes from the expectation of large nonlinear optical response due to the surface plasmon resonance.[11,12]

The particles were prepared by a two-step colloidal process. First, we dissolved chloroauric acid ($HAuCl_4$ $4H_2O$) and sodium sulfide (Na_2S $9H_2O$) into superpure water at room temperature. We mixed the controlled amounts of the two solutions together to get the unstable gold sulfide Au_2S. The color of the Au2S solution was shallow brown. In the second step, we injected a little Na_2S solution into above Au_2S solution. The color changed from shallow brown to gray, shallow red, and dark red[13].

In the reaction, the gold atom in Au-S bond on the surface of Au_2S was reduced by S^{2-} ion[14] and the surface became gold coated shell layer. The gold

surface layer grew with time. This process is supported by TEM and electron diffraction.

TEM image shows Au_2S/Au coated particle with average diameter about 35nm. The average particle diameter is determined by the concentration of the solution and the time interval before the addition of more Na_2S solution in the second step. The lattice of the about 20A shell layer in Fig.1 is about 2.30A as similar to the Au(111) lattice 2.35A. The electron diffraction patterns of the particles include the pattern of gold mixed with that of Au_2S[14].

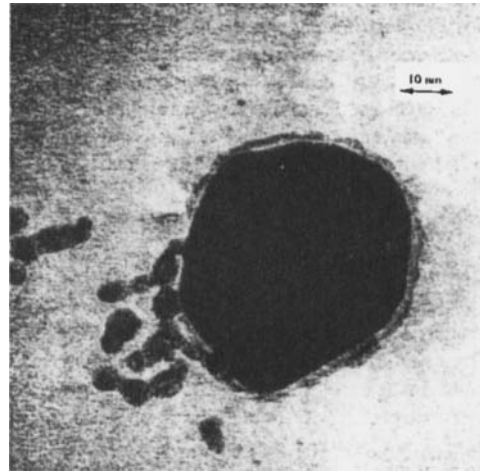

FIGURE 1 TEM image of Au_2S/Au coated nanoparticle

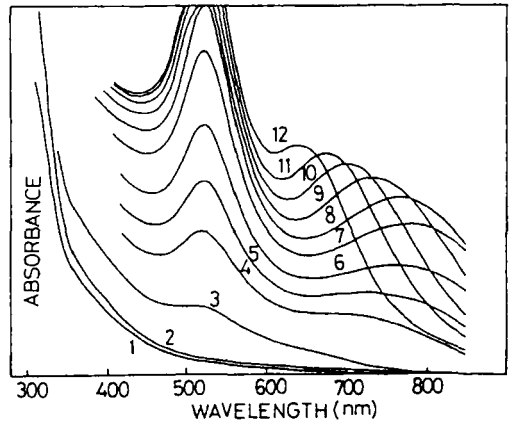

FIGURE 2 The modified surface plasmon resonance absorption of the Au_2S /Au coated particles.

Optical absorption experiments taken during the gold overcoat growth process are shown in Fig.2. Curve 1 is the absorption of the $HAuCl_4$ solution and curve 2 is from the Au_2S colloidal solution, and all the following sequences were taken after the addition of the Na_2S solution again in the second step.

There are two peaks in the spectra of Au_2S/Au coated nanoparticles. The

peak located on longer wavelength, which comes from the coated particles, shifts across the visible region and it shows two time regimes for all samples, the peak has a red shift in the initial time regime, and then a blue shift in the second time regime. The later time regime is described by the electromagnetic theory of a coated nanoparticles. The thicker the coating, then the closer the resonance is to that of a homogeneous gold particles[9]. There is an unexpected feature in the initial time regime of the absorption spectra; namely, the shift initially is toward longer wavelengths, which is attributed to quantum confinement of the electrons in the thin surface metal layer.

Generally, the dielectric constant of the metal is described by the Drude model; while the Drude model works well in the infrared regime, it is not directly applicable to the visible regime. Moreover, when the shell layer is as thin as several monolayers of gold, there is the very strong quantum confinement effect in the shell layer. Drs. Y. Silberberg and T. Sands[15] have done some works to calculate the dielectric constant of a thin metal layer on the quantum size effect. To simplify the analysis, the quantum properties of the free electrons are modeled by a modified form of the Drude model[13,10].

When the shell layer is thin enough, the resonance frequency, ($\omega_0=V_F/d$, where V_F is the Femi velocity and d is the thickness of the metal layer) occurs in the visible regime and becomes small as the shell thickness increasing. This strongly modifies the dielectric constant so that the absorption resonance peak moves to longer wavelengths as the shell layer d becomes thicker. This is the reason that the first regime has a red shift. This model approaches Drude's model when d is large enough. In the Drude's model regime, the thicker the coating, then the closer the resonance is to that of a homogeneous gold particle[9].

We find that the results on the quantum size model is difference from the classical Drude model and show a red shift as the ratio in the beginning. We compare the theoretical and experimental results, and find the theoretical results agree with the experimental one[13].

2.Cytochrome b562 Coated Nanoparticles

Aqueous gold colloidal particles solution was prepared by reduction of HAuCl4 with citric acid[16]. In this condition, the particle size can be controlled

from 10nm to 40nm with a narrow size distribution according to both transmission electron microscopy (TEM) and dynamic light scattering method[17,18].

A series of cytochrome b-562 solution with various concentration was prepared and added to the gold colloidal solution with stirring vigorously. The cytochrome b-562 is a small haem protein found in the periplasm of *Escherichia coli*.. It is of a cylindrical shape[19] (height is 5.0nm and diameter is 2.5nm, shown in Fig.3) and has the chromophore (protoheme IX) at the position of about 3.5nm from the bottom.

The surface plasma resonant absorption band of Au particles is located at about 530nm[9]. The plasmon absorption band (at 530nm) of a original 31.0nm gold particles was red-shifted and broadened by increasing adsorption of the protein.

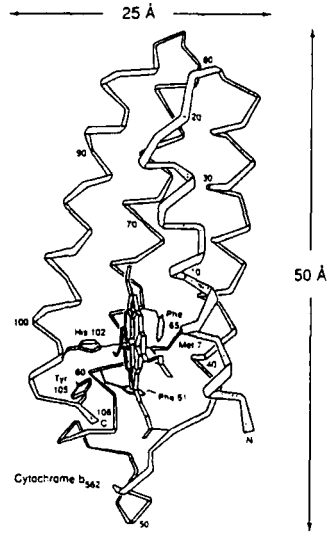

FIGURE 3 Schematic structure of cytochrome b-562.

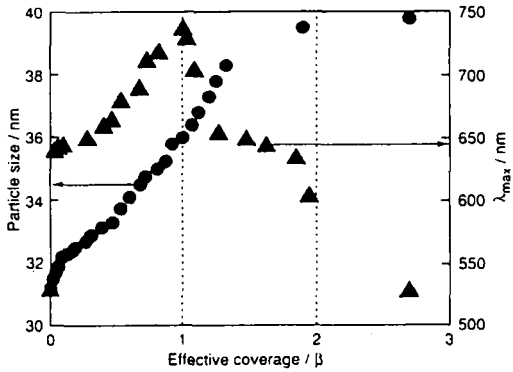

FIGURE 4 Relationship of whole particle size and peak position of longer wavelength band with respect to protein effective coverage.

In the first stage, when a small amount of the protein was added, which was much less than the protein's monolayer full coverage around the particle surface, the interaction was weak. Only a small shoulder emerged at about 650nm. We found that, with increasing quantity of the protein, the effect became strong and the new peak was shifted to longer wavelength up to 750 nm and broadened.

There was an unexpected feature with further increasing quantity of the protein in the second stage. The absorption spectrum returned to that of the original colloidal solution. It showed that the interaction became weak and disappeared as further increasing quantity of the protein.

We introduced effective coverage to describe the status of adsorbed protein cytochrome b-562 on the surface of gold particles. The effective coverage β=1.0, and β=2.0 were just the full coverage of cytochrome b-562 on the surface of gold particles in "side-on" and "tail-on" conformation manner, respectively.

Fig.4 shows the shifting absorption peak position in longer wavelength and the whole particle size as a function of the protein's effective coverage β. As the protein coverage increases, the peak position moves to longer wavelength until it reaches 750nm and the effective coverage just reaches 1.0, where particle surface is covered by proteins in a "side-on" conformation. The whole size measured by dynamic light scattering supported it. Then, a further addition of the protein moves the peak back to the original position at 530nm, although the composite particle size increases monotonously with the protein coverage. This monotonously increasing of the whole size indicates that the phenomenon of the peak back to the original position does not result from separating of the protein and gold particles. The behavior is apparently non-linear with respect to the protein coverage. A model is proposed which considers two adsorption conformation of cytochrome b-562 on the gold surface. Namely, the "side-on" conformation dominates at low concentrations ($\beta < 1.0$) while the "tail-on" conformation dominates at high concentrations ($1.0 < \beta < 2.0$). The protein's conformation caused difference of the interaction distance between the gold surface and the interior chromophore of cytochrome b-562. For other words, the interaction between gold particles and cytochrome b-562 depends strongly on the distance between the surface

and chromophore. The red-shift to 750nm and spectral broadening occurred only by "side-on" conformation because the distance is short at this case.

The model of the conformation change of the protein was supported by the particle size determined by the dynamic light scattering method. In fig.4, at first, a diameter of original gold particles was 31.0nm and it increases with the protein coverage. The composite particle size, when a maximum spectral shift of the plasmon absorption appeared, was 36nm. In this stage, the protein b-562 was in "side-on" conformation on the gold surface. This size is exactly identical to the size of protein's "side-on" monolayer coverage around the particles because the increment of the particles size is exactly twice the width of the protein of 2.5nm. From 36nm to 40nm, where the concentration increases more than the protein "side-on" full coverage region, a model for protein's adsorption conformation is that all the absorbed protein molecules start shifting altogether with angle to the surface. In the optical absorption measurement, when the diameter of the whole particles was 40nm, the interaction was so weak that the optical absorption spectrum was almost the same as the intrinsic absorption spectrum of gold particles. The effective coverage β was equal to 2.0, which was just the full coverage of cytochrome b-562 on the surface of gold particles in "tail-on" conformation. The size of 40 of diameter is about the diameter of gold adding twice of the height length of cytochrome b-562. After the particle size reaches 40nm, the diameter of the composite particle doesn't change even if further addition of the protein. In this stage, the protein b-562 seems adsorbed on the surface with a "tail-on" monolayer coverage around the gold particle. Therefore, a further addition of the protein can not give second layer coverage, keeping the particle size same and just leave proteins isolated in the solution. The absorption peak of isolated cytochrome b-562 appeared at 418nm.

The conformation's changes of adsorbed protein have been optically detected by the shift of the resonant plasmon absorption arising from the distance sensitive dielectric interaction between the protoheam whin the protein and the gold surface.

3.Polydiacetylene Coated Nanoparticles

A colloidal gold particles dispensed in water is prepared. The size of gold colloidal particles is 20nm with a very good distribution. The diacetylene monocarboxylic acid (10,12-pentacosadiynoic acid,

$CH_3(CH_2)_{11}CCCC(CH_2)_8COOH$) (12,8-DA) is commercially available.

At first, the solution I { ethanol solution of 12,8-DA monomer ($5.0X10^{-3}$ M/L, 1.5ml)}; solution II { 300ml above colloidal gold solution } and solution III { 300ml deionized water } are prepared.

For method A, we mix solution I and II with stirring. For method B, we mix solution I and III with stirring. For method C, we mix the solution I and III just like the method B, but, the mixture solution is treated by ultrasonic wave for about one hour. Then, these mixture solutions are exposed to UV irradiation by a high pressure mercury lamp for photopolymerization at room temperature.

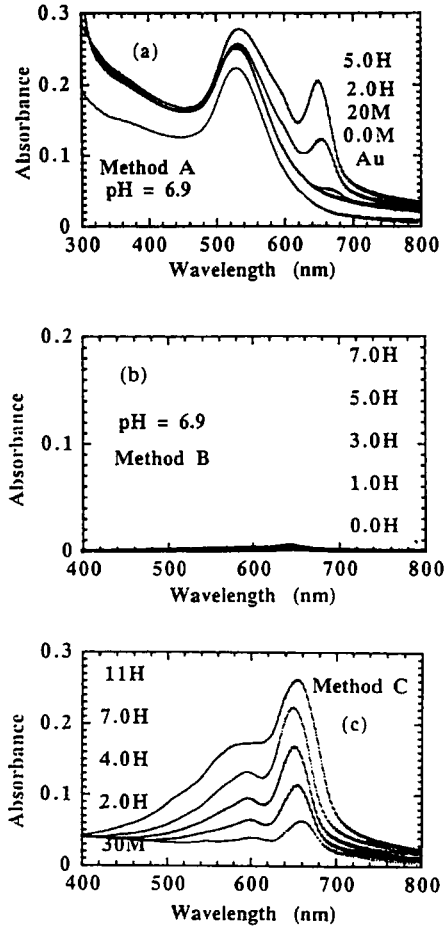

FIGURE 5 (a), (b), and (c) show the optical spectra of the mixture solution by method A, B, and C, respectively, during UV irradiation. The numbers show the irradiation time from the down to up.

The optical spectra of the mixture solution by method A during the photopolymerization process are shown in Fig.5(a). The absorption band at about 530nm results from the surface plasma resonance of gold particles. The

intensity increases, and position of the surface plasma absorption band shifts to longer wavelength slightly after adding the PDA ethanol solution. These changes result from the interaction between surfactant hydrophilic group of 12,8-DA and the surface of gold nanoparticles, when the hydrophilic group -$(CH_2)_8$-$COO^-$of 12-8, DA monomer form a capped shell layer at the surface of the gold particle.

The excitonic absorption band of π conjugated polymer backbone of 12,8-PDA appears slightly at 640nm[21] after about 20 minutes irradiation, and increases as time. The spectra are as same as the typical absorption band of π conjugated polymer backbone of the blue state 12,8-PDA[21,22], which has a main peak at 640nm and a broad subpeak at about 600nm. It proves that the 12, 8-DA can be photopolymerized on the surface of the colloidal gold particles.

There are unexpected no any absorption spectra of the mixture solution by the method B in Fig.5(b). It indicates that 12,8-DA monomer can not be polymerized only in pure water solution without any pretreatment. Furthermore, The surprised results are very strong absorption spectra of the mixture solutions by the method C in Fig.5(c). The order of intensity in Fig.5(c) is as same as that in Fig.5(a), which shows that the 12,8-PDA can also be photopolymerized by the method C under UV irradiation.

The experimental results show that the 12,8-PDA can be obtained by photopolymerization in the method A and C except B. In method A, the gold nanoparticles take a key role as template for polymerization of 12,8-DA monomer. The nuclear forming process can be explained that, at first, the hydrophilic group -$(CH_2)_8$-COO^- of 12,8-DA monomer is attracted at the surface of the gold nanoparticle to form a molecular capped shell layer to shorten the distance between the adjacent 12,8-DA monomers, so, 12,8-DA in colloidal gold solution is much more easily photopolymerized than that in aqueous solution.

In the method B, the 12,8-DA monomer molecule is in a random state in only water solution without any template materials. The interaction between the adjacent DA monomers is too weak to polymerize. That is why the polymerization process is failed in the mixture solution of Method B.

In the method C, the polymerization process results from forming of the

vesicles of 12,8-DA by the long time ultrasonic treatment[23], which shorten the distance between the adjacent 12,8-DA monomers. That is why the spectra of absorption band in Fig.5 (c) shows a same order as that in Fig.5 (a).

CONCLUSION

The surface modification of nanoparticles provides a new way to synthesize nano-composite materials. Recently, DNA gold nano-composite materials[24,25] have been synthesized by modification surface with thiolate 18-mer oligonucleotides. We envision that this technique will because a useful synthetic tool for the conveninent and economic manufacture of nano-composite materials.

REFERENCES

(1) Geoffrey A. Ozin, Adv. Mater. 4, 612, (1992).
(2) A. Henglein, Chem. Rev. 89, 1861, (1989)
(3) H.S.Zhou, I.Honma, J. Haus, H.Sasabe, H.Komiyama; J. Lumin. 70, 21, (1996)
(4) A.P.Alivisatos, Science 271, 937, (1996)
(5) C.B.Murray, C.R.Kagan, M.G.Bawendi, Science 270, 1335, (1995)
(6)R.P.Andres, T.Bein, M.Dorogi, S.Feng, J.I.Henderson, C.P.Kubiak, W.J.Mahoney, R.G.Osifchin, R.Reifenberger, Science, 272, 1323, (1996); R.P.Andres, J.D.Bielefeld, J.I.Henderson, D.B.Janes, V.R.Kolagunta, C.P.Kubiak, W.J.Mahoney, R.G.Osifchin, Science, 273, 1690, (1996)
(7) B.O'Regan and M.Gratzel, Nature, 353, 737, (1991); A. Kay, M.Gratzel, J. Phys. Chem., 97, 6272, (1993)
(8) H.S.Zhou, T.Wada, H.Sasabe, H.Komiyama, Appl. Phys. Lett. 68, 1288, (1996)
(9) Bohren, C. F., and Huffman, D. R., Absorption and Scattering of Light by Small Particles, (Wiley, New York, 1983)
(10) U.Kreibig, and L.Genzel, Surf. Sci. 156, 678 (1985); L.Genzel, T. P. Martin and U.Kreibig, Z. Phys. B21, 339 (1975)
(11). A. E. Neeves and M. H. Birnboim, Opt. Lett. 13, 1087 (1988); J. Opt. Soc. Am. B6, 787 (1989); N. Kalyaniwalla, J. W. Haus, R. Inguva, and M.H. Birnboim, Phys. Rev. A42, 5613 (1990)

(12). J. W. Haus, H. S. Zhou, S. Takami, M. Hirasawa, I. Honma, and H. Komiyama J. Appl. Phys. 73, 1043, (1993)

(13). H. S. Zhou, I. Honma, H. Komiyama and J. W. Haus, Phys. Rev. B. 50, 12052, (1994)

(14) Swift, E. H., and Schaefer, W. P., Quantitative Elemental Analysis, (W. H. Freeman, San Francisco, 1962) p.280

(15) Y. Silberberg, and T. Sands, IEEE J. Quantum Electronics, 28, 1663, (1992)

(16) G.Frens Nature (London), 241, 20, (1973)

(17) B.E.Dahneke, D.K.Hutchins J. Chem Phys. 100, 7890, (1994); J. Chem Phys. 100, 7903, (1994).

(18) C.L.Gettinger, A.J.Heeger, D.J.Pine, Y.Cao, Synth. Met. 74, 81, (1995).

(19) P.C.Weber, F.R.Salemme, F.S.Mathews, P.H.Bethge, J.Biol. Chem. 256, 7702, (1981); Adam P. Brunet, Enoch S. Huang, Mary Elizabeth Huffine, Jonathan E. Loeb, Robert J. Weltman and Michael H.Hecht, Nature, 364, 355, (1993)

(20) H.S.Zhou, S.Aoki, I.Honma, M.Hirasawa, T.Nagamune, and H.Komiyama, Chem. Commun., 605, (1997)

(21) B.Tieke, G.Lieser, G.Wegner, J.Polym. Sci. Polym. Chem. Ed. 17, 1631 (1979)

(22) H.Bassler, Advances in Polymer Science Vol63, (Spring-Verlag, 1984)

(23) H.Hub, B.Hupfer, H.Koch, H.Ringsdorf, Angew. Chem. Int. Ed. Engl. 19, 938 (1980)

(24) C.M.Niemeyer Angew. Chem. Int. Ed. Engl. 36, 585, (1997)

(25) C.A.Mirkin, R.L.Letsinger, R.C.Mucic, J.J.Storhoff, Nature, 382, 607, (1996); A.P. Alivisatos, K.P.Johnsson, X.Peng, T.E.Wilson, C.J.Loweth, M.P.BruchezJr, P.G.Schultz, Nature, 382, 609, (1996)