Colloid Polym Sci (2005) 283: 583–586
DOI 10.1007/s00396-004-1222-0

SHORT COMMUNICATIONS

Hideo Sawada
Ayumu Sasaki
Kazuo Sasazawa
Tokuzo Kawase
Katsuya Ueno
Kazuo Hamazaki

Dispersion of gold nanoparticles above the poly(methyl methacrylate) surface by the use of fluoroalkyl end-capped oligomeric aggregates

Received: 11 June 2004
Accepted: 20 September 2004

H. Sawada (✉) · A. Sasaki
Department of Materials Science and Technology, Faculty of Science and Technology, Hirosaki University,
Bunkyo-cho, Hirosaki 036-8561, Japan
E-mail: hideosaw@cc.hirosaki-u.ac.jp
Tel.: +81-172-393578
Fax: +81-172-393541

K. Sasazawa
Central R & D Laboratories,
Taiyo Yuden Co. Ltd., 8-1 Sakae-cho,
Takasaki, Gunma 370-8522, Japan

T. Kawase
Department of Chemistry and Materials Technology, Kyoto Institute
of Technology, Matsugasaki, Sakyo-ku,
Kyoto 606-8585, Japan

K. Ueno · K. Hamazaki
Asahi Glass Co. Ltd., Yurakucho,
Chiyoda-ku, Tokyo 100-8405, Japan

Abstract Nanometer size-controlled gold particles were prepared under mild conditions by reducing the corresponding metal precursor in the presence of self-assembled molecular aggregates formed by fluoroalkyl end-capped *N*-(1,1-dimethyl-3-oxobutyl)acrylamide oligomers. The stable gold nanoparticles protected by these fluorinated molecular aggregates were applied to the dispersion above the poly(methyl methacrylate) film surface.

Keywords Gold nanoparticle · Surface dispersion · PMMA surface · Fluorinated molecular aggregates · XPS

Hitherto, there has been a considerable interest in colloidal transition metals such as gold and silver because they exhibit different colors of the colloidal metal particles depending on particle size, shape, and agglomeration [1]. Colloidal nanometer size-controlled metal particles are also interesting from the viewpoints of chemical and medical technologies [2–4]. Therefore, it is of particular interest to develop novel colloidal transition metals, which could exhibit surface active properties imparted by fluorine. However, studies on the preparation and the development of fluorinated metal nanoparticles have been, hitherto, very limited except for the report on the preparation of 1*H*, 1*H*, 2*H*, and 2*H*-perfluorodecanethiol-stabilized silver nanoparticles [5]. We have already reported that fluoroalkyl end-capped oligomers can form self-assembled molecular aggregates with nanometer size levels in aqueous and organic media [6, 7]. This finding suggests that these fluorinated aggregates should provide a suitable host moiety to interact with transition metals as guest molecules. In this communication, we would like to report on the preparation and applications of gold nanoparticles by the use of self-assembled molecular aggregates formed by fluoroalkyl end-capped oligomers, with a particular emphasis on a new approach to the dispersion of gold nanoparticles above the common organic polymer surface such as poly(methyl methacrylate) (PMMA).

A typical procedure for the preparation of gold nanoparticles by the use of fluoroalkyl end-capped oligomers is as follows: to a 1,2-dichloroethane solution of fluoroalkyl end-capped *N*-(1,1-dimethyl-3-oxobutyl)acrylamide oligomer [R_F-[$CH_2CHC(=O)NHCMe_2CH_2C(=O)Me$]$_n$-$R_F$: R_F-(DOBAA)$_n$-R_F; R_F = $CF(CF_3)OC_3F_7$; Mn = 3710 [8]), 4 g/dm^3: 20 ml] was added 1,2-dichloroethane (5 ml) containing $HAuCl_4$ (2.4 mmol/dm^3). The mixture was stirred with a magnetic stirring bar at room temperature for 1 h. A 1,2-dichloroethane solution (12 ml) containing $NaBH_4$ (200 mg) was mixed with this solution, and then the mixture was stirred for 2 h at 45 °C. The 1,2-dichloroethane solution thus obtained was centrifuged for 5 min, and then filtered through a 0.45-μm PTFE membrane to obtain a transparent wine-red solution. As shown in Fig. 1, UV-vis spectra of this solution displayed a plasmon absorption in the visible region (λ_{max}: ca. 540 nm). Longer fluoroalkyl end-capped DOBAA oligomer [R_F = $CF(CF_3)OCF_2CF(CF_3)OC_3F_7$] also afforded a similar plasmon absorption; however, an extremely decreased plasmon absorption was observed in the corresponding nonfluorinated DOBAA oligomer as in Fig. 1. This finding suggests that fluorinated DOBAA oligomers can form self-assembled fluorinated molecular aggregates (Fig. 1) with the aggregations of the end-capped fluoroalkyl segments in organic media to interact with gold nanoparticles as guest molecules. Our present fluorinated molecular aggregates lead to stabilization and prevent further agglomeration of the gold nanoparticles. In contrast, the interaction of the molecular aggregates with gold particles would be extremely decreased in the case of nonfluorinated DOBAA oligomer, because this oligomer is not likely to form self assemblies in organic media. Transmission electron microscopy (TEM) image of a freshly prepared sample by the use of fluorinated DOBAA oligomer under similar conditions is shown in Fig. 2. Gold nanoparticles protected by fluorinated molecular (Fig. 2) aggregates are well dispersed and possess an average diameter of 7.1 nm (see Fig. 3) (Fig. 3). In addition, we have measured the size of fluorinated molecular aggregates in the presence of gold nanoparticles, which were prepared under similar

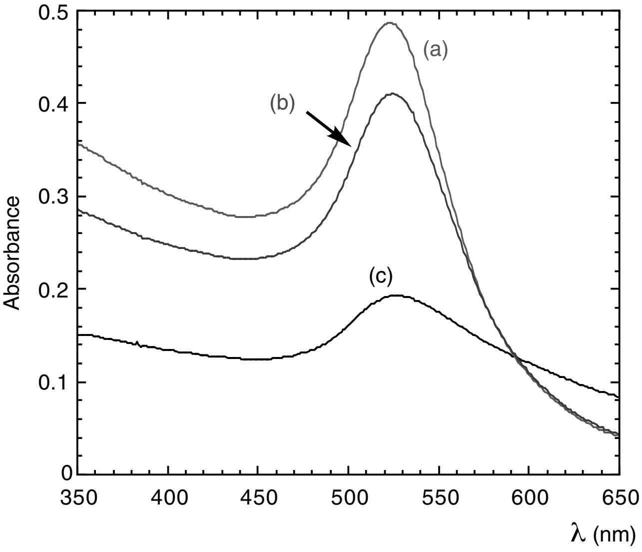

Fig. 1 UV-vis spectra of colloidal gold prepared by the use of fluoroalkyl end-capped oligomers (2.1 g/dm^3) in CH_2ClCH_2Cl. **a** R_F-(DOBAA)$_n$-R_F[R_F = $CF(CF_3)OC_3F_7$, Mn = 3710]. **b** R_F-(DOBAA)$_n$-R_F [R_F = $CF(CF_3)OCF_2CF(CF_3)OC_3F_7$, Mn = 6770]. **c** -(DOBAA)$_n$-[Mn = 5820]

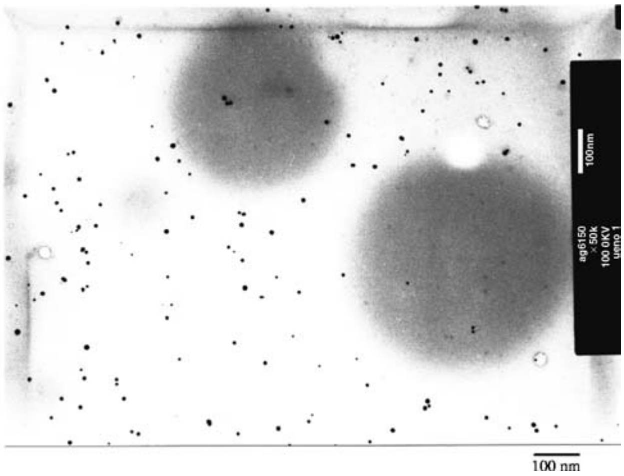

Fig. 2 Transmission electron microscopy image of freshly prepared fluorinated molecular aggregates—stabilized Au nanoparticles. R_F-(DOBAA)$_n$-R_F, R_F = $CF(CF_3)OCF_2CF(CF_3)OC_3F_7$ [2.1 g/dm^3 in CH_2ClCH_2Cl]

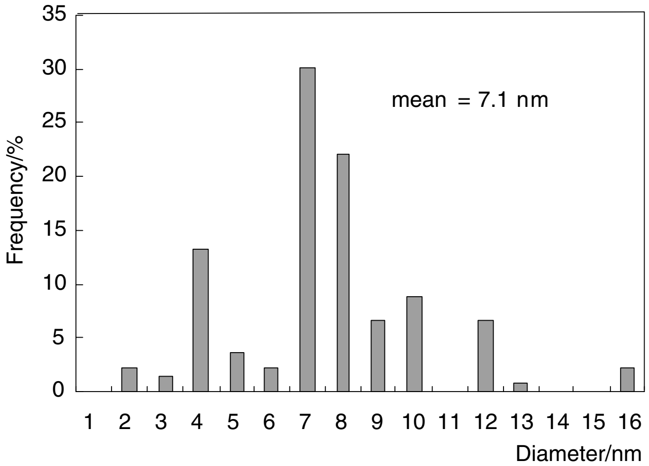

Fig. 3 Size distributions of gold particles in the presence of R_F-(DOBAA)$_n$-R_F [R_F = $CF(CF_3)OCF_2CF(CF_3)OC_3F_7$] in CH_2ClCH_2Cl

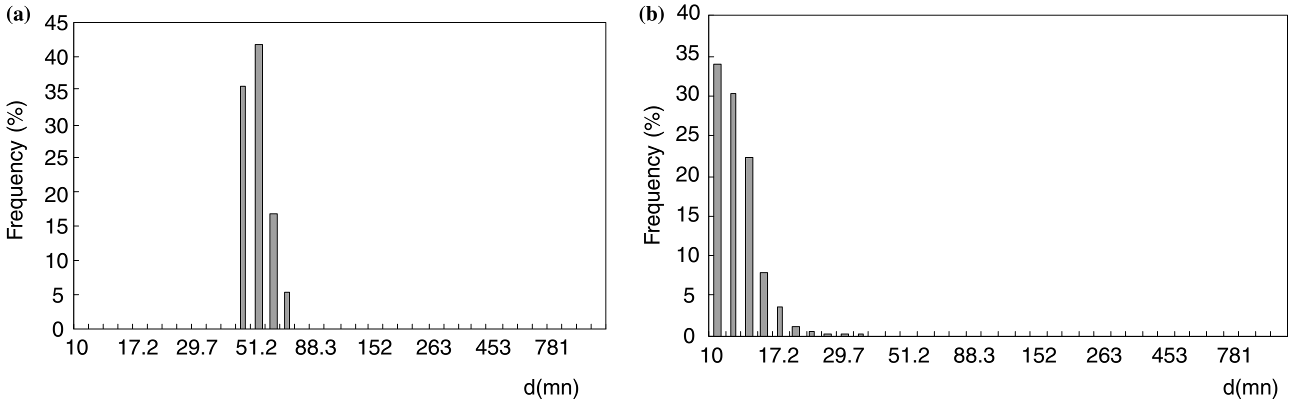

Fig. 4 Histogram of self-assembled molecular aggregates formed by R_F-(DOBAA)$_n$-R_F [R_F = $CF(CF_3)OC_3F_7$] in the absence (**a**) and the presence (**b**) of gold nanoparticles in 1,2-dichloroethane solutions by dynamic light-scattering measurments

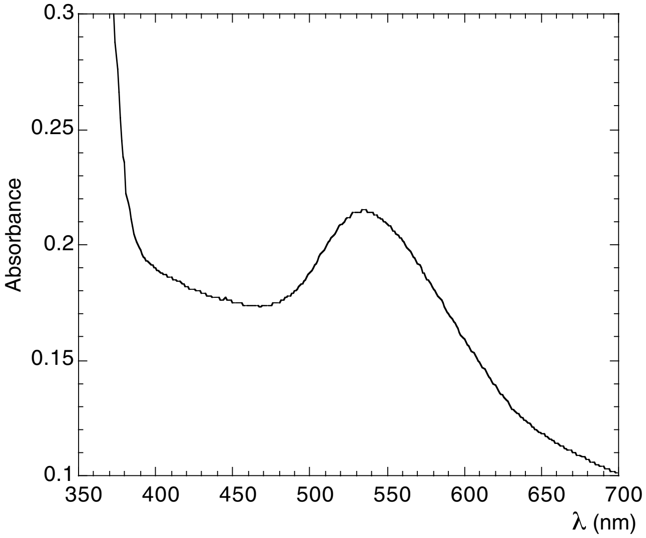

Fig. 5 UV-vis spectra of gold nanoparticles—containig PMMA film treated with fluoroalky end-capped DOBAA oligomer [R_F = $CF(CF_3)OC_3F_7$]

conditions as in Fig. 1, by dynamic light-scattering measurements (DLS-6000 HL: Otsuka Electronics Co., Ltd., Japan). The size of the fluorinated molecular aggregates in the absence of gold nanoparticles was also measured under similar conditions for comparison (see Fig. 4). Figure 4 shows that the number-average diameter of fluorinated molecular aggregates is 51.2 ± 6.2 nm, and the (Fig. 4) size (number-average diameter) of fluorinated aggregates—gold nanoparticle complexes—was decreased from 51.2 to 12.1 ± 2.5 nm. The obtained number-average diameter (12.1 nm) demonstrates the mean-diameter of gold particles. In addition, nanometer size-controlled gold particles could interact with fluorinated molecular aggregates to afford the stable gold nanoparticles in the molecular aggregate cores.

Previously, we reported that fluoroalkyl end-capped oligomers containing cationic segments could be arranged regularly above the PMMA surface to exhibit not only a strong oleophobicity imparted by fluorine but also a good surface antibacterial activity related to the cationic segments [9]. This suggests that gold nanoparticles should be dispersed above the PMMA surface through the interaction of self-assembled molecular aggregates formed by fluorinated DOBAA oligomers with gold nanoparticles. From the viewpoint of developing metal nanoparticles into the material sciences, it is of considerable interest to apply these fluorinated molecular aggregates into the dispersion of gold nanoparticles above the common polymeric materials such as PMMA. In fact, the PMMA film (film thickness: 196 μm) was prepared by casting the homogeneous 1,2-dichloroethane PMMA (1.0 g) solutions (32 ml) containing R_F-(DOBAA)$_n$-R_F oligomer [R_F = $CF(CF_3)OC_3F_7$: 0.04 g]—gold nanoparticle complexes [$HAuCl_4$ (5.9 μmol); $NaBH_4$ (100 mg)]—on a glass plate. We have measured the UV-vis spectra of the obtained film in which the surface color is wine-red, and the result is shown in Fig. 5.

As shown in Fig. 5, the modified cast PMMA film exhibited a similar plasmon absorption at around 540 nm, the same as for the 1,2-dichloroethane solution system in Fig. 1. This finding suggests that gold nanoparticles should be well dispersed without the agglomeration between the metal particles in the cast film. Furthermore, we have measured the contact angles for dodecane and the conduct electricity of both the surface and the reverse sides of this film at room temperature, and the results are as follows:

	Surface side	Reverse side
Contact angle (°)	30	19
Conduct electricity (S/cm)	$\mathbf{1.02}\times10^{-10}$	$\mathbf{2.05}\times10^{-12}$

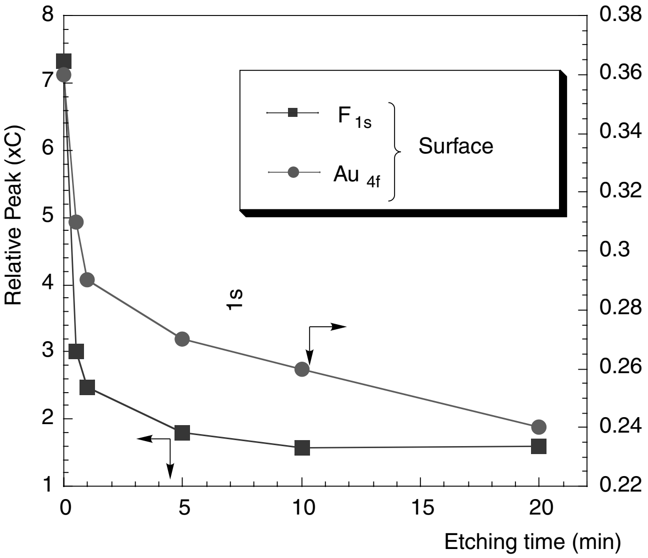

Fig. 6 Depth profiles of PMMA surface treated with R_F-(DOBAA)$_n$-R_F oligomer-protected gold nanoparticles measured by XPS [$R_F = CF(CF_3)OC_3F_7$]

We have obtained higher values for the contact angles and conduct electricity of the surface side of this cast film compared to that of the reverse side. Contact angle measurements show that fluoralkyl end-capped DOBAA oligomer could exhibit a markedly strong oleophobicity imparted by fluoroalkyl segments above the surface. In addition, higher conduct electricity of the surface side suggests that gold nanoparticles could be well dispersed above the PMMA surface during the cast film formation.

In order to clarify the dispersion of gold nanoparticles on the PMMA surface, we have analyzed the PMMA film (film thickness: 196 μm) modified by fluorinated DOBAA oligomeric aggregates [$R_F = CF(CF_3)OC_3F_7$] (gold nanoparticle complexes) by the use of the X-ray photoelectron spectroscopy (XPS) technique, and the amounts of gold (Au_{4f}) and fluorine (F_{1s}) at the surface were also estimated. These results are shown in Fig. 6.

Interestingly, as shown in Fig. 6, the relative peak area of fluorine was found to decrease extremely with the increase of etching time (etching rate is about 50 Å/min). A similar tendency was observed in the peaks of Au_{4f}, and the relative peak area of this peak decreased with the increase of etching time. More interestingly, the relative peak areas of F_{1s} (7.33) and Au_{4f} (0.36) of the modified PMMA film surface side were demonstrated to become extremely higher compared to those [F_{1s} (3.07) and Au_{4f} (0.06)] of the reverse side. Thus, it was verified that gold nanoparticles should be well dispersed above the polymer surface as well as fluorinated DOBAA oligomers (Fig. 6).

In conclusion, fluoroalkyl end-capped DOBAA oligomers are clarified to be a convenient tool for the preparation of nanometer size-controlled gold particles, and in particular these oligomers are applicable for the dispersion of gold nanoparticles above the polymer surface. Further studies are actively in progress.

References

1. Puddephatt RJ (1978) The chemistry of gold. Elsevier, Amsterdam
2. Henglein A (1989) Chem Rev 89:1861
3. Ogawa S, Hayashi Y, Kobayashi N, Tokizaki T, Nakamura A (1994) J Appl Phys 33:L331
4. Lewis LN (1993) Chem Rev 93:2693
5. Yonezawa T, Onoue S, Kimizuka N (2001) Adv Mater 13:140
6. Sawada H (1996) Chem Rev 96:1779
7. Sawada H (2003) J Fluorine Chem 121:111
8. Sawada H, Yoshino Y, Kurach M, Kawase T, Takishita K, Tanedani T (2000) Fluoroalkyl end-capped *N*-(1, 1-dimethyl-3-oxobutyl)acrylamide oligomers were prepared by the reactions of fluoroalkanoyl peroxides with the corresponding monomer according to our previously reported method. Polymer 41:397
9. Sawada H, Yanagida K, Inaba Y, Sugiya M, Kawase T, Tomita T (2001) Eur Polym J 37:1433