Colloid Polym Sci (2009) 287:795–799
DOI 10.1007/s00396-009-2031-2

ORIGINAL CONTRIBUTION

Effect of composition of sucrose fatty acid esters on formation of palladium nanoparticles in reverse micelles

Hidetaka Noritomi · Kenji Kagitani · Yasutaka Muratsubaki · Satoru Kato

Received: 10 February 2009 / Revised: 23 March 2009 / Accepted: 27 March 2009 / Published online: 18 April 2009

Abstract Palladium (Pd) nanoparticles were prepared in the reverse micellar system containing sucrose fatty acid esters with various esterification degrees. The TEM showed that Pd nanoparticles were of spherical and relatively uniform. The size of Pd nanoparticles strongly depended upon the composition of sucrose fatty acid esters. The resultant Pd colloid could be preserved for at least 2 months without precipitation.

Keywords Reverse micelle · Sucrose fatty acid ester · Palladium nanoparticle

Introduction

In recent years, nanoparticles have been extensively investigated since their novel physical and chemical properties are quite different from those of bulk substances due to their extremely small sizes and large specific surface area [1–3]. They have many potential applications in optoelectronics, semiconductors, catalysts, photocatalysis, magnetic materials, drug delivery, and so on.

Many techniques such as coprecipitation, gas evaporation, sol–gel method, and sputtering have been developed in order to produce nanoparticles [4–7]. Additionally, more attention has been paid on the preparation of nanoparticles in reverse micelles [8, 9]. Reverse micelles are nanometer-sized aggregates of surfactant molecules dispersed in a hydrophobic organic phase like octane, which form thermodynamically stable w/o type microemulsions containing a small amount of water in their centers. This method does not require extreme conditions of temperature and pressure, and the particle size and shape can be controlled by simply varying the microemulsion composition and dynamics. In order to form reverse micelles, ionic surfactants such as sodium bis(2-ethylhexyl) sulfosuccinate (AOT) and cetyltrimethylammonium bromide (CTAB) have mainly been used [9]. However, it has been reported that those surfactants have several types of toxicity to aquatic organisms [10, 11].

In the present work, we examined the preparation of Pd nanoparticles in reverse micelles of sucrose fatty acid esters with various esterification degrees to address whether the structure of surfactants affects the formation of nanoparticles. Sucrose fatty acid esters are commercial food grade additives, and are biodegradable and non-hazardous to the environment [12]. We have reported that reverse micelles of sucrose fatty acid esters exhibit excellent solubilization and dispersion in the processes of the protein extraction and the protein refolding [13–16]. Pd nanoparticles were selected as a model nanoparticle, since Pd nanoparticles have been widely studied as a catalyst in chemical reactions and fuel cells [17–20].

Experimental

Palladium(II) chloride and hydrazinium hydroxide were the guaranteed reagents of Kanto Chemicals (Tokyo, Japan). As sucrose fatty acid esters, DK-F-10, DK-F-20W, DK-F-50, DK-F-110, and DK-SS were supplied from Dai-Ichi Kogyo Seiyaku (Kyoto, Japan). Table 1 represents the compositions

H. Noritomi (✉) · K. Kagitani · S. Kato
Department of Applied Chemistry,
Tokyo Metropolitan University,
Minami-Ohsawa, Hachioji,
Tokyo 192-0397, Japan
e-mail: noritomi@ecomp.metro-u.ac.jp

Y. Muratsubaki
Dai-Ichi Kogyo Seiyaku Co., Ltd.,
5 Oogawara-cho, Kisshoin, Minami-ku,
Kyoto 601-8391, Japan

Table 1 Compositions of sucrose fatty acid esters used in the present work

Product name	HLB (–)	Monoester (wt.%)	Diester and triester (wt.%)	More than tetraester (wt.%)	Average esterification degree (–)
DK-F-10[a]	1	1	13	86	4.85
DK-F-20W[a]	2	11	36	53	3.1
DK-F-50[a]	6	35	53	12	1.7
DK-F-110[a]	11	57	41	2	1.48
DK-SS[b]	19	99	1	0	1.01

[a] Fatty acid constituent consists of 70 wt.% stearic acid and 30 wt.% palmitic acid

[b] Fatty acid constituent consists of 60 wt.% stearic acid and 40 wt.% palmitic acid

of sucrose fatty acid esters used, and Fig. 1 shows the structure of sucrose monostearate as a typical structure of sucrose fatty acid ester. The surfactant was used without further purification. Isooctane and *n*-butanol were from Kanto Chemicals, and were of analytical grade.

The aqueous solution of H_2PdCl_4 was prepared by dissolving palladium(II) chloride in 0.2 N HCl solution. The reverse micellar solutions containing hydrazine and H_2PdCl_4 were prepared by injecting the required amounts of the corresponding aqueous solution into the solution of *n*-butanol/isooctane (3:7 *v*/*v*) containing sucrose fatty acid esters and then were used for the preparation of nanoparticles within a few minutes.

The preparation of nanoparticles was achieved by mixing equal volumes of two reverse micellar solutions at the same water concentration, one containing an aqueous solution of H_2PdCl_4 and the other containing an aqueous solution of hydrazine. The reduction of H_2PdCl_4 was

$$2H_2PdCl_4 + N_2H_5OH \rightarrow 2Pd + 8HCl + N_2 + H_2O \quad (1)$$

The preliminary study indicated that the particles reached their final sizes within 1 h. Accordingly, the samples for various analyses were taken after 3 h. In this work, the concentration of sucrose fatty acid esters based on the overall volume of reverse micellar solution was fixed at 50 g/L. The concentrations of H_2PdCl_4 and hydrazine aqueous solutions were 0.1 and 1.0 M, respectively. The temperature was fixed at 25°C.

The TEM micrograph was obtained using a JEOL JEM-2000FX electron microscope operating at 200 kV. The sample for TEM was prepared by placing a drop of colloidal solution onto the standard carbon-coated copper grids and drying it under vacuum. The UV–vis spectra of the reverse micellar solutions containing nanoparticles were measured by UV/vis spectrophotometer (Ubest-55, Japan Spectroscopic Co. Ltd.) with a 10-mm quartz cell.

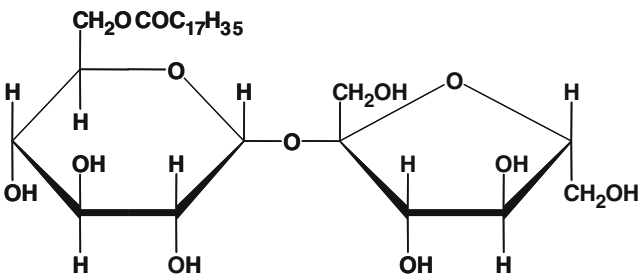

Fig. 1 Structure of sucrose monostearate

Results and discussion

Figure 2 shows the time course of the absorption at λ=500 nm when synthesizing Pd nanoparticles in reverse micellar system of DK-F-110 at 25°C. This absorption is not the characteristic absorption peak of Pd nanoparticles but the scattering due to the formation of Pd nanoparticles [21]. The absorption spectra increased with an increase in reaction time, and reached a plateau around 50 min. From this result, the preparation of Pd nanoparticles was carried out for 3 h.

Figure 3 shows the typical transmission electron micrograph and size distribution of Pd nanoparticles when preparing Pd nanoparticles in the reverse micellar system of DK-F-110 at 25°C for 3 h. The resultant particles were essentially monodisperse with a mean diameter of 4.1 nm and a standard deviation of 0.5 nm. It can be considered that, in the reverse micellar system, surfactants act as a solubilization agent for solubilizing the reactant aqueous

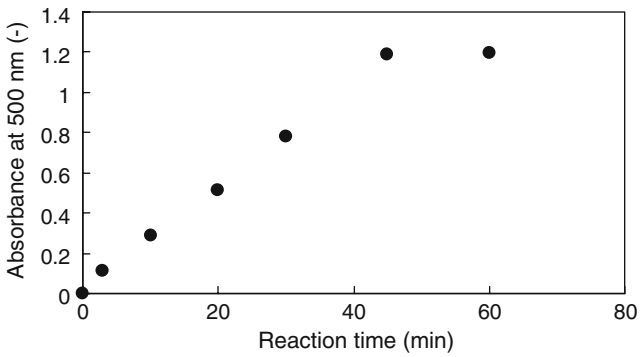

Fig. 2 Time course of absorption (500 nm) of Pd nanoparticles: $[H_2PdCl_4]$=0.1 M; $[N_2H_5OH]$=1.0 M; *n*-butanol/isooctane containing 50 g/L DK-F-110 and 7.6 g/L H_2O; reaction temperature=25°C

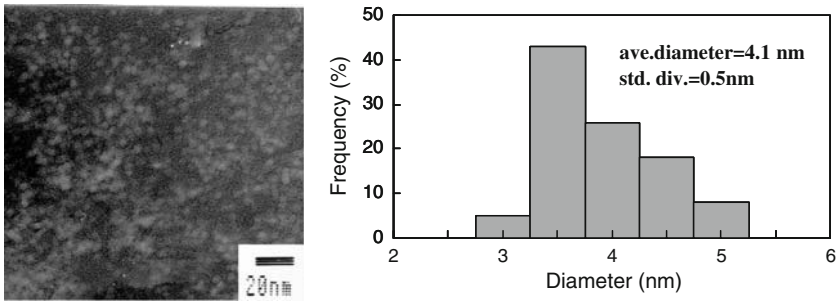

Fig. 3 Transmission electron micrograph and particle size distribution of Pd nanoparticles: $[H_2PdCl_4]$=0.1 M; $[N_2H_5OH]$= 1.0 M; *n*-butanol/isooctane containing 50 g/L DK-F-110 and 7.6 g/L H_2O; reaction temperature=25°C; reaction time=3 h

solution into the bulk organic phase, a growth inhibitor for inhibiting the growth of particles due to the adsorption of surfactants on the particle surface, and an aggregation inhibitor for inhibiting particle–particle aggregation. DK-F-110 exhibited the sufficient solubilization and dispersion capabilities in the present system, since reactant solutions could spontaneously be solubilized into the organic solution containing sucrose fatty acid esters and the generated Pd nanoparticles were relatively stabilized at room temperature for at least 2 months.

Figure 4 showed the plot of the mean diameter of Pd nanoparticles against the water content in the reverse micellar system of DK-F-110. As seen in Fig. 4, the sizes of Pd nanoparticles slightly increased with increasing the water content. It has been reported that the diameter of Pd nanoparticles increases with an increase in water content in AOT/isooctane reverse micelles, and that the tendency is similar to that for reverse micelles, since the size of water pool in a reverse micelle increased with an increase in the water content [22]. In the present system, the slight increase in the size of Pd nanoparticles might be interpreted by the fact that the surfactant molecules adsorb on the surface of particles formed in reverse micelles and restrict the growth of nanoparticles.

The formation and stability of micelles are attributable to the structure and/or HLB of surfactants [23–26]. In the case of sucrose fatty acid esters, the structure and HLB of sucrose fatty acid esters result from those esterification degree [12]. In order to elucidate the effect of those factors on the formation

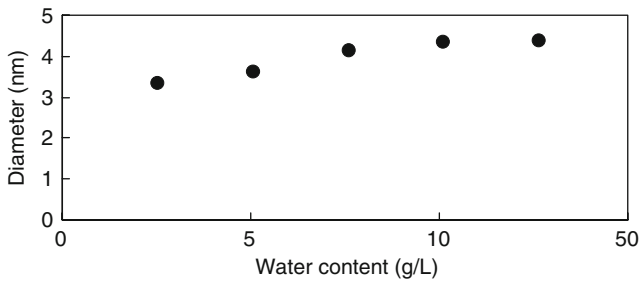

Fig. 4 Effect of water content on the size of Pd nanoparticles synthesized in DK-F-110 reverse micelles: $[H_2PdCl_4]$=0.1 M; $[N_2H_5OH]$=1.0 M; *n*-butanol/isooctane containing 50 g/L DK-F-110 and a certain amount of water; reaction temperature=25°C; reaction time=3 h

of Pd nanoparticles, we have examined the preparation of Pd nanoparticles in the reverse micellar system by using the mixture of DK-SS with DK-F-10, DK-F-20W, or DK-F-50. The mean diameters of Pd nanoparticles strongly depended

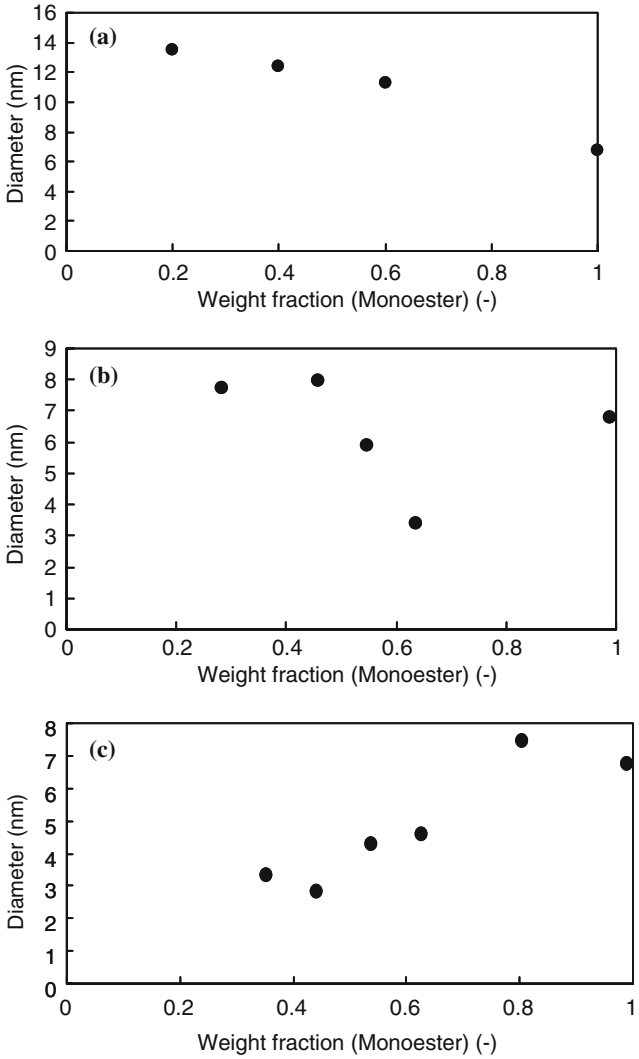

Fig. 5 Effect of composition of sucrose fatty acid esters on the size of Pd nanoparticles synthesized in reverse micelles of sucrose fatty acid esters: **a** DK-SS/DK-F-10; **b** DK-SS/DK-F-20W; **c** DK-SS/DK-F-50. $[H_2PdCl_4]$=0.1 M; $[N_2H_5OH]$=1.0 M; *n*-butanol/isooctane containing 50 g/L sucrose fatty acid ester and 7.6 g/L H_2O; reaction temperature= 25°C; reaction time=3 h

Table 2 Experimental and calculation values on the size of Pd nanoparticles synthesized in reverse micelles of various compositions

Weight fraction of surfactant (–)				Diameter (nm)	
Mixing ratio (wt/wt)	Monoester	Diester and triester	More than tetraester	Experimental value	Calculation value
SS:F-10					
2:8	0.207	0.102	0.691	13.5	12.0
4:6	0.403	0.079	0.518	12.4	10.6
6:4	0.598	0.056	0.346	11.3	9.2
10:0	0.990	0.010	0	6.8	6.3
SS:F-20W					
2:8	0.282	0.293	0.425	7.7	7.9
4:6	0.459	0.222	0.319	8.0	7.5
5:5	0.548	0.187	0.265	5.9	7.3
6:4	0.636	0.152	0.212	3.4	7.1
SS:F-50					
0:10	0.352	0.534	0.114	3.3	2.8
1.4:8.6	0.442	0.461	0.097	2.8	3.3
2.8:7.2	0.537	0.382	0.081	4.2	3.8
4.3:5.7	0.627	0.308	0.065	4.6	4.3
7.1:2.9	0.805	0.162	0.033	7.5	5.3

Pd nanoparticles were prepared under the following condition: $[H_2PdCl_4]$=0.1 M; $[N_2H_5OH]$=1.0 M; *n*-butanol/isooctane containing 50 g/L sucrose fatty acid esters and 7.6 g/L H_2O; reaction temperature=25°C; reaction time=3 h. Calculation values were obtained by Eq. (2)

upon the composition of sucrose fatty acid esters, as shown in Fig. 5. The average esterification degree of mixed sucrose fatty acid esters decreases with an increase in the weight fraction of monoesters. When using only DK-F-10 or DK-F-20W, the precipitate was formed as the reaction proceeded. Therefore, it is suggested that these surfactants cannot sufficiently function as an aggregation inhibitor for inhibiting particle–particle aggregation. As seen in Table 1, the average esterification degrees of DK-F-10 and DK-F-20W are much greater than those in DK-F-50 and DK-F-110. Sucrose fatty acid esters with high esterification degrees might be unsuitable for preparing nanoparticles in the present system, since highly esterified ones are too bulky [12]. On the other hand, Pd nanoparticles were formed by using DK-SS although this surfactant has high HLB, compared to AOT and CTAB, which are widely used to form the reverse micelles. It is suggested that a certain amount of monoesters are necessary to stably form Pd nanoparticles. When using the mixture of DK-SS with DK-F-10 or DK-F-20W, the diameter of Pd nanoparticles tended to decrease with increasing the weight fraction of monoesters, while that increased when using the mixture of DK-SS with DK-F-50. From the results obtained, it is considered that the weight fraction of monoesters to polyesters is not a suitable parameter to estimate the behavior of the formation of Pd nanoparticles.

Table 2 represents the composition of sucrose fatty acid esters and the diameter of Pd nanoparticles shown in Fig. 5. From these data, the regression equation showing the relationship between the diameter of Pd nanoparticles and the composition of sucrose fatty acid esters is obtained as

$$d = 6.364x - 2.281y + 15.866z \quad (2)$$

where d is the mean diameter of Pd nanoparticles, x the weight fraction of monoester, y the weight fraction of

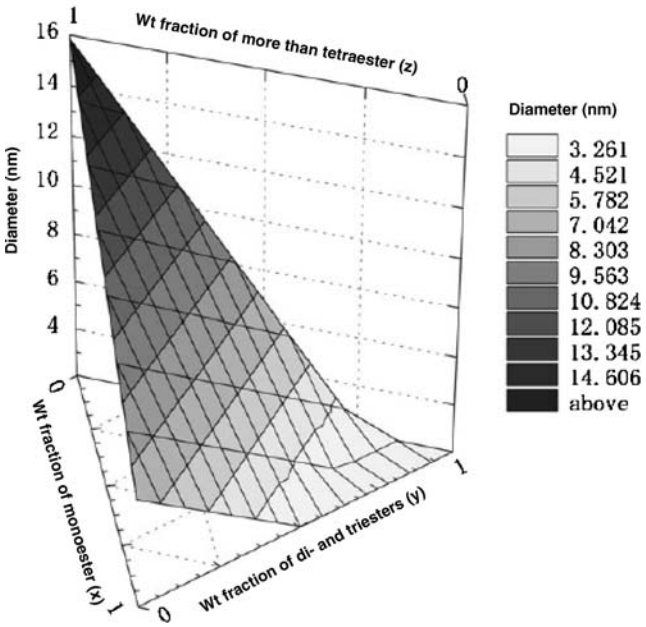

Fig. 6 Triangle graph on the relationship between the diameter of Pd nanoparticles and the composition of sucrose fatty acid esters. The data in Table 2 was plotted

diester and triester, and z the weight fraction of more than tetraester. Figure 6 shows the diameter of Pd nanoparticles against the composition of sucrose fatty acid esters. When comparing the mean diameters obtained experimentally with the diameters calculated by Eq. (2) in Table 2, it is considered that Eq. (2) as a whole has a good correlation between the diameter of Pd nanoparticles and the composition of sucrose fatty acid esters, since the correlation coefficient of the regression equation is 0.90. However, when the mixing ratio of DK-SS to DK-F-20W was 6 to 4, the calculation value was twice greater than the experimental value as shown in Table 2. Equation (2) indicates that sucrose fatty acid esters with monoester and more than tetraester work for an increase in the diameter of Pd nanoparticles while those with di- and triesters work for a decrease in the diameter. It has been well known that the morphology of surfactant assemblies is strongly dependent upon the structure of surfactants [24]. When reverse micelles are formed in an organic solvent, surfactant molecules are packed in the vicinity of the interface between the oil and water phases of reverse micelles [25, 26]. The structure of surfactants affects the size, stability, and properties of reverse micelles such as solubilization capacity and dispersibility. Sucrose fatty acid esters with monoester have a rather large hydrophilic group relatively to a hydrophobic group, while those with more than tetraesters have bulky hydrophobic groups [12]. Sucrose fatty acid esters with di- and triesters might tend to be densely packed compared to those with monoester and more than tetraester when forming reverse micelles.

Conclusion

It has been demonstrated that the sucrose fatty acid ester/*n*-butanol/isooctane system is suitable for the preparation of monodisperse Pd nanoparticles. The size of the generated Pd nanoparticles was strongly dependent upon the composition of sucrose fatty acid esters. Therefore, it has been found that it is possible to control the size of Pd nanoparticles by changing the composition of sucrose fatty acid esters.

Acknowledgment We wish to thank Mr. Misaki for taking TEM micrographs.

References

1. Ozin GA (1992) Adv Mater 4:612
2. Toshima N, Yonezawa T (1998) New J Chem 22:1179
3. Fendler JH (1998) Nanoparticles and nanostructured films: preparation, characterization and applications. Wiley-VCH, Weinheim
4. Tang ZX, Sorensen CM, Klabunde KJ, Hadjipanayis GC (1991) J Colloid Interf Sci 146:38
5. Siegel RW (1998) J Mater Res 3:1367
6. Fegley B Jr, White P, Bowen HK (1985) Am Ceram Soc Bull 64:1115
7. Fayet P, Woste LZ (1986) Phys D 3:177
8. Boutonnet M, Kizling J, Stenius P (1982) Colloids Surf A 5:209
9. Uskokovic V, Drofenik M (2005) Surface Review Lett 12:239
10. Singh RP, Swaroop D, Annie K (1999) J Ecotoxicol Environ Monit 9:117
11. Okumura Y (1998) Chuo Suisan Kenkyusho Kenkyu Hokoku 11:113
12. Otomo N (2003) Jpn J Food Eng 4:1
13. Noritomi H, Ito S, Kojima N, Kato S, Nagahama K (2006) Colloid Polym Sci 284:604
14. Noritomi H, Kowata H, Kojima N, Kato S, Nagahama K (2006) Colloid Polym Sci 284:677
15. Noritomi H, Kojima N, Kato S, Nagahama K (2006) Colloid Polym Sci 284:683
16. Noritomi H, Takasugi T, Kato S (2008) Biotechnol Lett 30:689
17. Durand J, Teuma E, Gomez M (2008) Eur J Inorg Chem 23:3577
18. Astruc D (2007) Inorg Chem 46:1884
19. Trzeciak AM, Ziolkowski JJ (2007) Coodinat Chem Rev 251:1281
20. Zhu Y, Khan Z, Masel RI (2005) J Power Sources 139:15
21. Wang C-C, Chen D-H, Huang T-C (2001) Colloid Surf A 189:145
22. Chen D-H, Wang C-C, Huang T-C (1999) J Colloid Interf Sci 210:123
23. Shaw DJ (1992) Introduction to colloid and surface chemistry. Butterworth-Heinemann, Oxford
24. Israelachvili JN (1985) Intermolecular and surface forces. Academic, London
25. Mitchell DJ, Ninham BW (1981) J Chem Soc Faraday Trans II 77:601
26. Hou M-J, Shah DO (1987) Langmuir 3:1086