

Preparation and Characterization of Silver Nanoparticles with Dendrimers as Templates

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ABSTRACT: In this study, crystal silver nanoparticle clusters, prepared by the reduction of AgNO_3 in the presence of third-to-sixth-generation dendrimers with a trimesyl core, were characterized with ultraviolet–visible spectroscopy, transmission electron microscopy, and energy-dispersive X-ray spectroscopy. The results showed that the particle size of the silver nanoparticles was considerably affected by the generation of the dendrimers as well as the dendrimer concentration. When the concentration ratios of Ag^+ to the third-to-sixth-generation

dendrimers were all 4 : 1, the average diameters of the obtained particles were 6.7, 6.0, 5.2, and 4.3 nm, respectively. The data from high-resolution transmission electron microscopy and electron diffraction indicated that the particles belonged to a simple cubic crystal structure. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 4023–4028, 2008

Key words: composites; dendrimers; nanocomposites; nanotechnology; templates

INTRODUCTION

Many studies dealing with metal nanoparticles supported by polymeric materials have been reported for their interesting applications, such as catalysts, conductive materials, nonlinear optical devices, and color materials.^{1–4} Dendrimers, a new architecture of synthetic macromolecules, have a definite molecular weight and size. They are considered to be superb candidates for preparing nanoparticles because of their unique properties.^{5–7} Dendrimers have an intrinsically well-defined globular structure and highly modifiable surface groups. The dendritic branches and terminal groups can serve as gates to control the access of small substrates into the dendrimers and thus to obtain dendrimer-encapsulated nanoparticles (DENs). Therefore, dendrimers are monodispersed building blocks, ideal guest-molecule carriers,⁸ promising biocompatible materials,⁹ and

excellent templates for generating metal nanoparticles within their spacious interior.^{10,11}

Dendrimer-encapsulated metal nanoparticles are prepared in a two-step process. First, metal ions are sequestered within the dendrimers. Then, the ions are chemically reduced. Because the synthesis relies on dendrimer templates, the resulting metal nanoparticles (the replicas) can be quite monodisperse in size. The ability of high-generation poly(amido amine) (PAMAM) dendrimers to host copper, palladium, platinum, silver, and gold nanoparticles is attributable to the spheroidal structure of the dendrimers, which contains void spaces and functional groups that are able to complex with metal ions.^{12–17} The properties of metal–dendrimer nanocomposites depend on the nature of the terminal groups of the dendrimers. For example, amine peripheral groups usually (but not always) induce agglomeration and precipitation of large metal clusters. This is most likely because many metal ions complex with the periphery of amine-terminated dendrimers, and this typically results in rather large metal clusters stabilized by multiple dendrimers.¹⁸ This article reports the preparation and characterization of silver nanoparticles encapsulated within amine-terminated dendrimers of different generations with a trimesyl core.

EXPERIMENTAL

Materials

Dendrimers with a trimesyl core were synthesized according to ref. 19. The structures of the dendrimers

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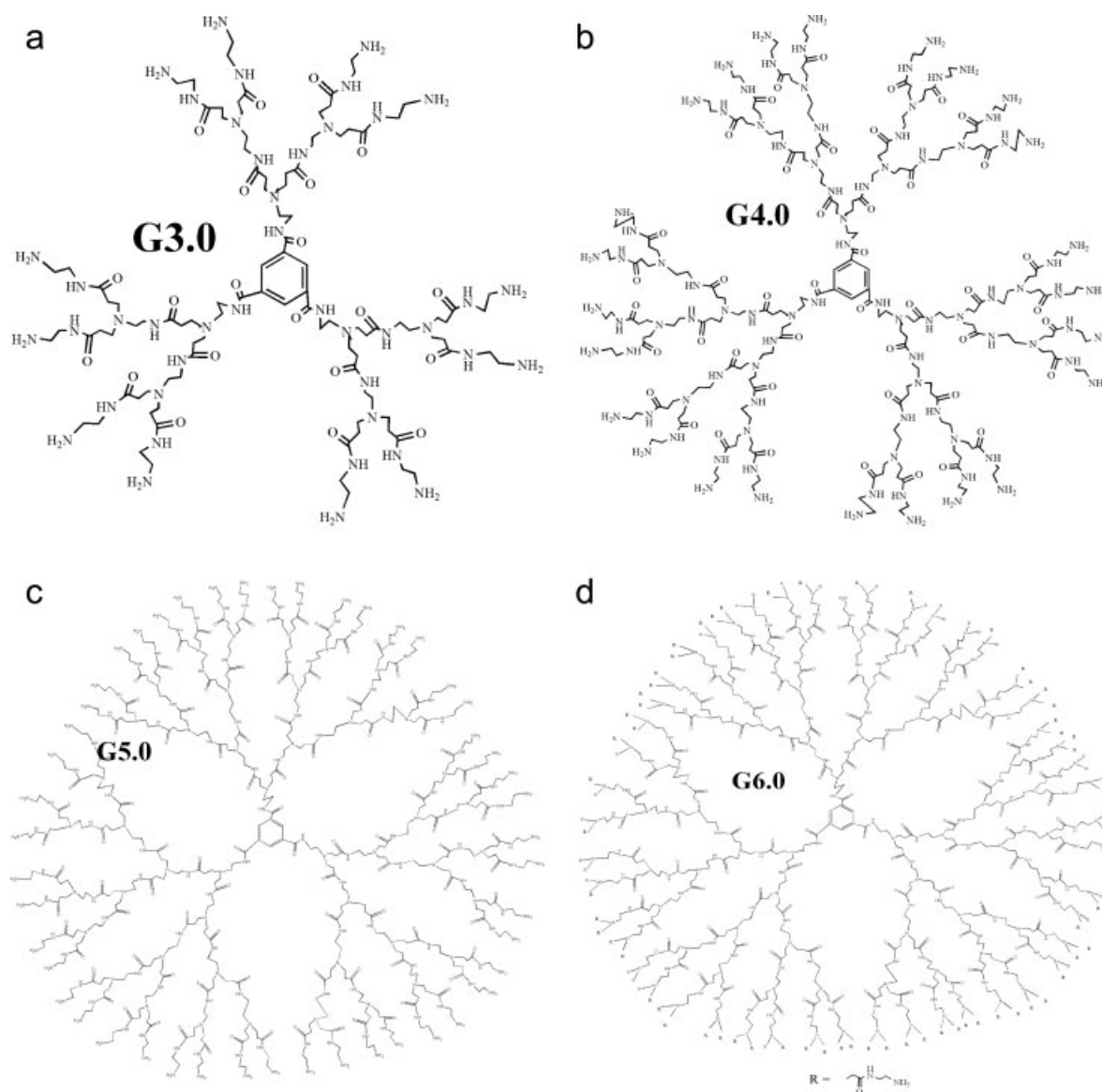
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Scheme 1 Structure of the G3.0–G6.0 dendrimers.

are presented in Scheme 1. The physical characteristics of the dendrimers are shown in Table I. Silver nitrate (AgNO_3) and sodium borohydride (NaBH_4) were purchased from Chemical Reagent Co. (Shanghai, China). All other chemicals were analytical-grade. Deionized water was used in all experiments.

Preparation of dendrimer-encapsulated silver nanoparticles

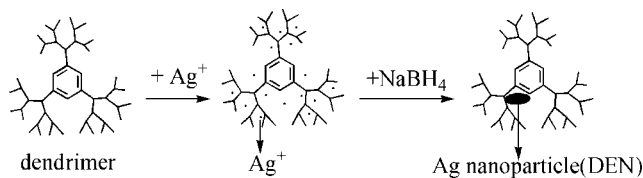
AgNO_3 and dendrimers were separately dissolved in deionized water. Both solutions were mixed with deionized water to make AgNO_3 and dendrimer solutions of the desired concentrations. Then, the AgNO_3 solutions were dropped into the aqueous dendrimer solutions, and the mixed solutions were

stirred for 2 h. Afterwards, freshly prepared NaBH_4 was added to the solutions quickly, and the solutions were stirred vigorously for 40 min. The synthesis of dendrimer-encapsulated silver nanoparticles is shown in Scheme 2.

TABLE I
Physical Characteristic of the Dendrimers

Generation	Surface groups	Tertiary amines	Molecular weight ^a
2	6	3	1,020
3	12	9	2,388
4	24	21	5,124
5	48	45	10,596
6	96	93	21,540

^a The molecular weight is based on defect-free, ideal-structure, amine-terminated dendrimers.



Scheme 2 Synthesis of dendrimer-encapsulated silver nanoparticles.

Characterization

The obtained nanoparticles were characterized with transmission electron microscopy (TEM; JEM-2100, JEOL, Japan). For the preparation of TEM specimens, the liquid samples were dropped onto carbon-coated copper grids, and the drops were allowed to dry in air. The mean particle diameter was calculated through the counting of 100 particles from the enlarged photographs. Ultraviolet–visible (UV–vis) spectra of the solutions before and after the reduction of the dendrimer–metal salts were measured with a UV spectrophotometer (UV-8500, Shanghai, China).

RESULTS AND DISCUSSION

UV–vis spectra of silver nanoparticles

UV–vis spectra of silver nanoparticles in the presence of dendrimers [generation 3 (G3) to generation 6 (G6)] are shown in Figure 1. When silver nanoparticles formed in G3 dendrimers, a new band centered at about 419 nm appeared. This band is assigned to the characteristic plasmon resonance band of silver nanoparticles²⁰ and shows that silver clusters gained in this way are greater than 4 nm in diameter.^{21–23} Plasmon resonance cannot be detected for very small metal clusters because the peak is flattened on account of the large imaginary dielectric constant of such materials.²⁴ The complex dielectric function of the nanoparticles can be approximated with a modified Drude theory. For silver nanoparticles prepared in a higher generation (G6), this band in the visible region is blueshifted, and this indicates the formation of smaller silver nanoparticles.

TEM

G3–G6 dendrimers were used as templates for the synthesis of silver nanoparticles. TEM micrographs and particle size distributions of the silver nanoparticles are shown in Figure 2(a–d) for G3–G6. The formation of silver nanoclusters was further confirmed with TEM data. The photographs show that all of the particles are almost spherical. The average diameter of the particles in a lower generation is larger than that of those in a higher generation [G3, 6.7 nm; generation 4 (G4), 6.0 nm; generation 5 (G5),

5.2 nm; and G6, 4.3 nm], and particles prepared with higher generation dendrimers are well dispersed. Lower generation dendrimers (G3) are highly asymmetric, tend to exist in an open and extended form, and have an expanded or open configuration; they do not hold confined structures. Thus, silver nanoparticles can easily transfer to the outside of dendrimers and aggregate. Hence, it is hard to form lower generation DENs. This result indicates that low-generation dendrimers may act as surface stabilizers. On the other hand, higher generation dendrimers have a spherical, three-dimensional structure,²⁵ and their interiors are rather hollow; moreover, they are more sterically crowded on their exterior. Silver particles are confined in their interior sites with little chance to aggregate with other particles, so silver nanoparticles encapsulated by a higher generation dendrimer can be formed and well dispersed. Therefore, higher generation dendrimers can operate as very effective protective templates for the preparation of silver particles.

Not only does the generation of the dendrimer influence the size of the silver nanoparticles as described previously, but the concentration ratio of Ag^+ to the dendrimer can also affect the particle size. To obtain the relationship between the size of the silver nanoparticles and the concentration ratio of Ag^+ to the dendrimer, the average diameters of the silver particles are plotted against the concentration ratios of Ag^+ to the dendrimer for G3–G6 dendrimers. As shown in Figure 3, the average diameter increases with an increase in the concentration ratio of Ag^+ to the dendrimer. For example, when the concentration ratio of Ag^+ to the dendrimer is 2 : 1, the average diameter of the silver nanoparticles is 5.9 nm for G3, 5.5 nm for G4, 4.4 nm for G5, and 3.8 nm for G6. With the concentration ratio of Ag^+ to

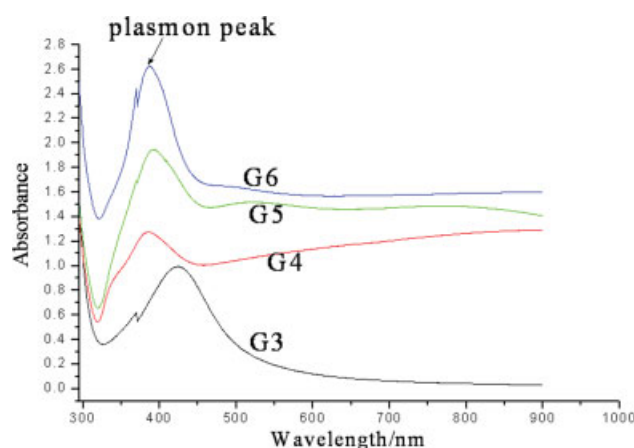


Figure 1 UV–vis spectra of silver nanoparticles in the presence of dendrimers G3–G6 ($[\text{Ag}^+]/[\text{dendrimer}] = 4 : 1$). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

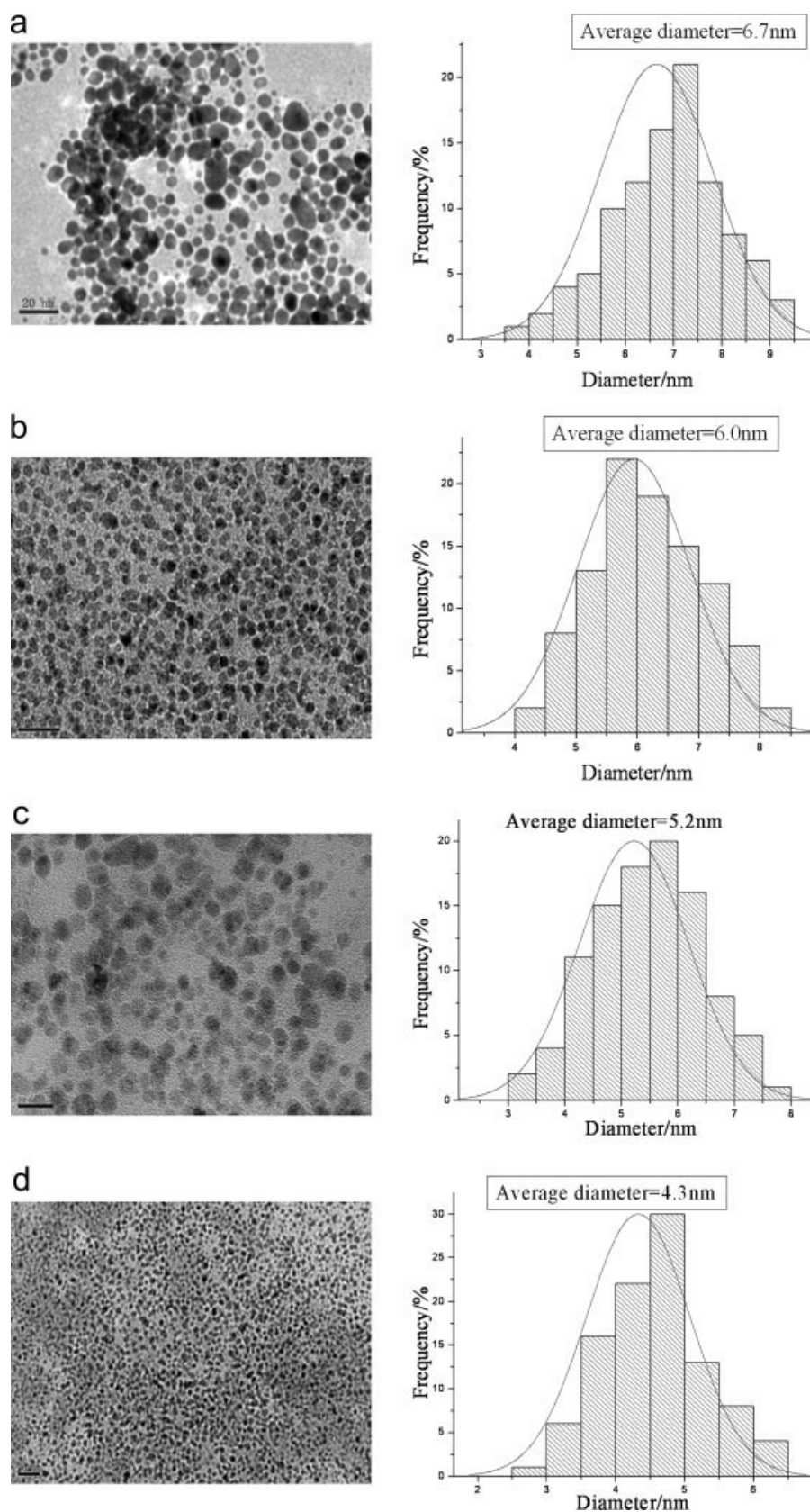


Figure 2 TEM images and particle size distributions of silver nanoparticles obtained in the presence of dendrimers (a) G3, (b) G4, (c) G5, and (d) G6 ($[AgNO_3] = 4 \text{ mmol/L}$, $[G3-G6] = 0.5 \text{ mmol/L}$, $[NaBH_4] = 0.15 \text{ mol/L}$).

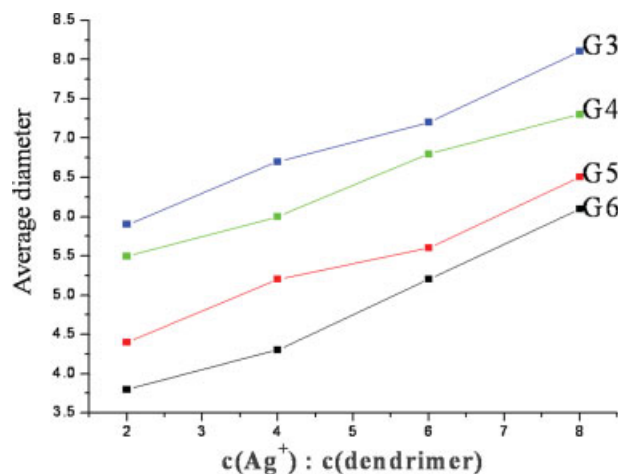


Figure 3 Changes in the average particle diameter of silver nanoparticles with the $[\text{Ag}^+]/[\text{dendrimer}]$ ratio. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

the dendrimer increased from 4 : 1 to 8 : 1 to 16 : 1, the average diameter of the silver nanoparticles increases to 6.7, 6.0, 5.2, and 4.3 nm, 7.2, 6.8, 5.6, and 5.2 nm, and 8.1, 7.3, 6.5, and 6.1 nm for G4, G5, and G6, respectively.

High-resolution transmission electron microscopy (HRTEM) and electron diffraction

The HRTEM measurements were performed on stabilized silver nanoparticles with dendrimers as templates. Figure 4 shows that the silver nanoparticles and their shapes are spherical. Also, we can see the lattice fringes of the particles, which suggest that silver nanoparticles are crystal structures and that their crystalline order is clear. The growth orientation of

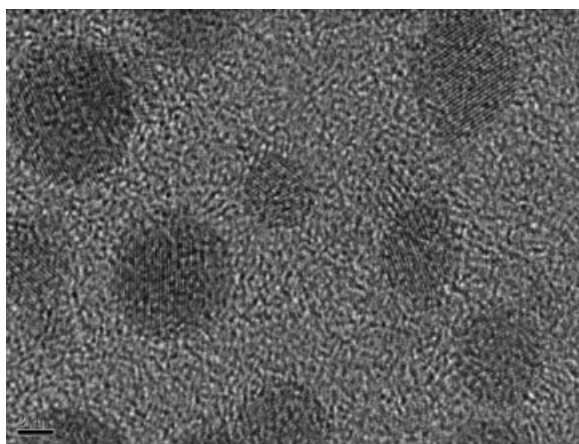


Figure 4 HRTEM image of the silver nanoparticles obtained in the presence of G5.

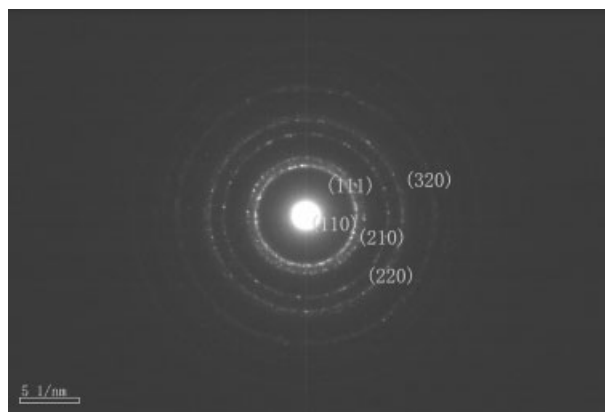


Figure 5 Electron diffraction of the silver nanoparticles obtained in the presence of G5.

the crystal is vertical to the lattice fringes, which reflect the crystalline order of the silver nanoparticles.²⁶ Figure 5 presents the electron diffraction of the crystal (the same sample shown in Fig. 4). The data from five Debye rings show that the silver nanoparticles are spathic structures. The ratio of these Debye ring radii is nearly 2 : 3 : 5 : 8 : 13, which corresponds to the surfaces of 110, 111, 210, 220, and 320, respectively, as shown in Figure 5. According to the literature, this kind of crystal belongs to a simple cubic crystal structure.²⁷

Energy-dispersive X-ray spectroscopy (EDS)

Elemental composition analyses were initially carried out with EDS to verify the presence of the following in the Ag-DEN samples: (1) silver (from the nanoparticle core) and (2) carbon, oxygen, and nitrogen (arising from the dendrimer component). As

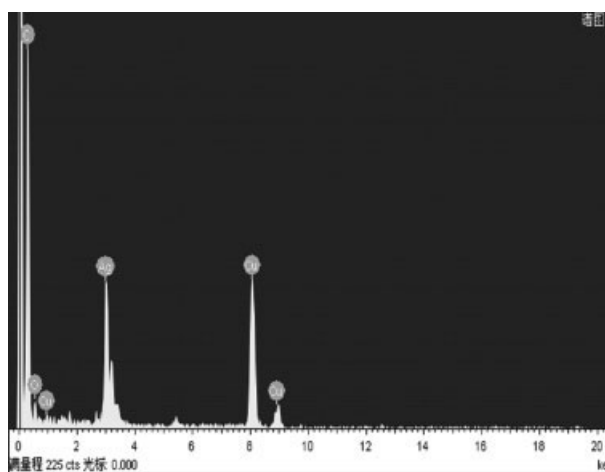


Figure 6 EDS of the silver nanoparticles obtained in the presence of G5.

expected, the resulting EDS spectrum (Fig. 6) shows a strong copper and carbon peak. Copper arises from the supporting copper grids, and carbon arises from both the supporting carbon film in the copper grids and the dendrimer component. The small oxygen peak in the spectrum is likely due to both the PAMAM dendrimer component in the Ag-DEN sample and the oxygen atoms present in the native oxide layer of the copper grids. Significantly, the EDS spectrum does not contain any obvious nitrogen or hydrogen signals. It is possible that in these samples the nitrogen and hydrogen peak is simply obscured by the more dominant carbon and oxygen signals present. On the other hand, the absence of any visible nitrogen or hydrogen signals may have also been due to the relatively poor sensitivity of the EDS technique for detecting light elements, particularly nitrogen²⁸ (because nitrogen X-ray emissions tend to become strongly absorbed by any carbon present).

CONCLUSIONS

In this article, we have described the synthesis and characterization of silver nanoparticles using dendrimers with a trimesyl core as templates. All of the particles that we have obtained are less than 10 nm in diameter. The diameter of the silver cluster nanoparticles obtained in lower generation dendrimers are large, whereas they become smaller in higher generations because of the different structures of the dendrimers. In addition, the diameter of the nanoparticles can also be affected by the concentration ratio of Ag⁺ to the dendrimers. The diameter of the silver nanoparticles increases when the concentration ratio of Ag⁺ to the dendrimers is raised. The EDS results suggest that the nanoparticles that we have obtained are silver particles. Electron diffraction shows that these silver nanoparticles encapsulated by dendrimers belong to a simple cubic crystal structure.

References

1. Liao, F. *Chem Lett* 2004, 33, 1020.
2. Levy, R.; Than, N. T. K.; Doty, R. C.; Hussain, I.; Nichois, R. J.; Schiffrin, D. J.; Brust, M.; Fernig, D. G. *J Am Chem Soc* 2004, 126, 10076.
3. Esumi, K.; Hosoya, T.; Suzuki, A.; Torigoe, K. *Langmuir* 2000, 16, 2978.
4. Crooks, R. M.; Lemon, B.; Sun, L.; Yeung, L. K.; Zhao, M. *Top Curr Chem* 2001, 212, 81.
5. Tomalia, D. A.; Frechet, J. M. J. *J Polym Sci Part A: Polym Chem* 2002, 40, 2719.
6. Grayson, S. K.; Frechet, J. M. J. *Chem Rev* 2001, 101, 3819.
7. *Dendrimers and Other Dendritic Polymers*; Frechet, J. M. J.; Tomalia, D. A., Eds.; Wiley: New York, 2001.
8. Zimmerman, S. C.; Lawless, L. J. *Top Curr Chem* 2001, 217, 95.
9. Malik, N.; Wiwattanapatapee, R.; Klopsch, R.; Lorenz, K.; Frey, H.; Weener, J. W.; Meijer, E. W.; Paulus, W.; Duncan, R. *J Controlled Release* 2000, 65, 133.
10. Zhao, M. Q.; Sun, L.; Crooks, R. M. *J Am Chem Soc* 1998, 120, 4877.
11. Jansen, J. F. G. A.; de Brabander-van den Berg, E. M. M.; Meijer, E. W. *Science* 1994, 266, 1226.
12. Zhao, M.; Crooks, R. M. *Angew Chem Int Ed* 1999, 38, 364.
13. Zhao, M.; Sun, L.; Crooks, R. M. *J Am Chem Soc* 1998, 120, 4877.
14. Esumi, K.; Suzuki, A.; Yamahira, A.; Torigoe, K. *Langmuir* 2000, 16, 2604.
15. Esumi, K.; Hosoya, T.; Suzuki, A.; Torigoe, K. *J Colloid Interface Sci* 2000, 226, 346.
16. Balogh, L.; Tomalia, D. A. *J Am Chem Soc* 1998, 120, 7355.
17. Gröhn, F.; Bauer, B. J.; Akpalu, Y. A.; Jackson, C. L.; Amis, E. J. *Macromolecules* 2000, 33, 6042.
18. Manna, A.; Imae, T.; Aoi, K.; Okada, M.; Yogo, T. *Chem Mater* 2001, 13, 1674.
19. Zhang, X.-Q.; Wang, X.-L. *Biomacromolecules* 2005, 6, 341.
20. Kreibig, U.; Vollmer, M. *Optical Properties of Metal Clusters*; Springer: Berlin, 1995.
21. Abe, H.; Charle, K.-P.; Twsche, B.; Schulze, W. *Chem Phys* 1982, 68, 137.
22. Curtis, A. C.; Duff, D. G.; Edwards, P. P.; Jefferson, D. A.; Johnson, B. F. G.; Firkland, A. I.; Wallace, A. S. A. *Angew Chem Int Ed* 1988, 27, 1530.
23. Lisiecki, I.; Pileni, M. P. *J Am Chem Soc* 1993, 115, 3887.
24. Kreibig, U.; Vollmer, M. *Optical Properties of Metal Clusters*; Springer: Berlin, 1995.
25. Esumi, K.; Torige, K. *Prog Colloid Polym Sci* 2001, 117, 80.
26. Sonny, S.; Magno, B. *Biomacromolecules* 2006, 7, 1884.
27. Zhang, X. Z. *Electron Microscopy and Analysis*; Tsinghua University Press: Beijing, 2007.
28. Statham, P. J. *J Microsc Microanal* 1998, 4, 605.