

## Complexation of Dendrimer-protected Silver Nanoparticles with Hydrotalcite

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The preparation of nanocomposites of dendrimer-protected silver nanoparticles and their complexation with hydrotalcite clay has been reported. Stable, water-soluble silver nanoparticles with an average particle size of 1.7–3.4 nm were prepared from the reduction of silver nitrate by sodium boron hydride in the presence of poly(amido amine) dendrimer with carboxylate terminals. The complexation of nanocomposites with hydrotalcite was achieved by ion exchange process by incubating at 70 °C for 24 hours. The transmission electron micrographs clarified the coexistence of nanocomposites with clay. It was revealed from X-ray diffraction that the spacing between the clay layers (sheets) increased from their intrinsic value (0.32 nm) to 1.9–2.2 nm, indicating the diffusion of dendrimer-protected silver nanoparticles into the clay galleries.

Key words: Dendrimer-protected silver nanoparticle, poly(amido amine) dendrimer, hydrotalcite, transmission electron microscopy, X-ray diffractometry

### 1. INTRODUCTION

The preparation of particles in range of nanometer size has been extensively studied in the past few decades due to their attractive electronic and optical properties. Nanosized metal particles can be utilized in a broad range of fields, including catalyses and nonlinear optics devices [1-3]. Stable particles are achieved by capping the particles with suitable surface-passivating agents, which determine the stability, solubility, reactivity, size and shape of the particles [4,5].

Dendrimers are highly branched polymers with a topologically regular structure, since repeating units are sequentially covalent-bonded, starting from a central core [6]. Amine terminated poly(amido amine) (PAMAM) dendrimer is a water-soluble molecule, which may behave as an unimolecular micelle in solution. The preparation of PAMAM dendrimer-stabilized gold, silver and copper nanoparticles has been extensively reported [7-10].

The organization of nanoparticles in monolayers results in materials that can be applied as scaffolds for posterior elaborations. Clay minerals have been used for the stabilization and organization of nanoparticles [11,12]. The hydrotalcite exhibits a lamellar structure with exchangeable anions like  $\text{Cl}^-$  and  $\text{CO}_3^{2-}$ , which are sandwiched between the lamellas and can easily be replaced by many other anions. The anion exchange properties of hydrotalcite [13] have been explored for the intercalation of various molecules [14-18].

Herein we describe a novel route for the complexation of dendrimer-protected silver nanoparticles with hydrotalcite clay. A PAMAM dendrimer with carboxylate terminals used in this study acts as a stabilizer of silver nanoparticles. The nanoparticles prepared at different silver-to-dendrimer ratios were characterized by UV/visible spectroscopy and transmission electron microscopy (TEM). The diffusion of nanoparticles in hydrotalcite was achieved by hot-incubating mixtures of hydrotalcites and nanoparticles. In order to assess the intercalation, the

structural changes were monitored by X-ray diffraction (XRD) and TEM.

### 2. EXPERIMENTAL SECTION

Methanol solution (5 wt%) of 4.5<sup>th</sup> generation PAMAM dendrimer with carboxyl-terminated groups (molecular weight = 26,258, number of terminal groups = 128), silver nitrate ( $\text{AgNO}_3$ ), and sodium borohydride ( $\text{NaBH}_4$ ) were purchased from Aldrich. Hydrotalcite ( $[\text{Mg}_{4.5}\text{Al}_2(\text{OH})_{13}\text{Cl}_2]3.5\text{H}_2\text{O}$ ) was donated from Kyowa Chemical Co. Ltd. Its anion exchange capacity (AEC) is 350 milli equivalent/100g. MilliQ water was used throughout the experiment.

According to the procedure previously reported [10], silver nanoparticles protected by PAMAM dendrimer were prepared: An aqueous solution of  $\text{AgNO}_3$  was mixed with a methanol solution of dendrimer at mixing silver/dendrimer ratios ( $\text{Ag}^+$  to carboxylate group of dendrimer) of 1:10, 1:100 and 1:1000. An orangish color developed immediately upon mixing of the  $\text{AgNO}_3$ /PAMAM solution with an aqueous solution of  $\text{NaBH}_4$  (equimolar to  $\text{Ag}^+$ ) under stirring. The stirring was continued for ~ 1 hour to complete the reaction. No precipitation was observed even after several months, indicating the stability of the nanoparticles.

Hydrotalcite was added to the silver nanoparticles protected with dendrimer in water in order to prepare hydrotalcite/nanoparticles mixture. Composition number ratio (anionic charge of clay/carboxylate group of dendrimer) was set to 1:4. The mixtures were incubated at 70 °C for 24 hours under shaking. The resulting suspension was filtered using a Millipore filter (0.22  $\mu\text{m}$  pore size), washed a few times with water to remove the possible excess of nanoparticles, and dried.

UV/visible absorption spectra were recorded at room temperature on a Shimadzu UV 2200 UV/visible spectrometer using a quartz cell of 1 mm path. The spectral background was subtracted by using a UV/visible spectrum of water. TEM photographs were taken on a Hitachi H-7000 electron microscope



equipped with a Hamamatsu C4742-95 digital camera. The specimens were prepared by spreading a small drop of sample solutions (or dispersions) onto standard copper grids coated with carbon film, and letting the drop dry completely for a few minutes. The XRD patterns were recorded by a Rigaku RINT 2500 PC X-ray diffractometer possessing a CuK $\alpha$  radiation of a wavelength  $\lambda = 0.154$  nm, operating at 40 kV and 200 mA and scanning at a rate of 0.1 °/min. The scattering intensity  $I(2\theta)$  as a function of  $2\theta$  was converted to the intensity  $I(q)q^2$  as a function of  $q$  (Kratky representation), where  $2\theta$  is the scattering angle and  $q = 4\pi\sin(2\theta/2)/\lambda$  is the scalar of the scattering vector. The spacings between the reflection planes were calculated by using an indexed Bragg peak position  $q_{hkl}$ , where  $hkl$  are the Miller indices, and an equation  $d_{hkl} = 2\pi/q_{hkl}$ .

### 3. RESULTS AND DISCUSSION

#### 3.1 Characterization of dendrimer-protected silver nanoparticles (nanocomposites)

UV/visible spectra of the dendrimer-protected silver nanoparticles in water were taken. Solutions at silver/dendrimer ratios of 1:10 and 1:100 displayed surface plasmon bands of the silver clusters [10] at 417.6 and 403.5 nm, respectively, supporting the formation of "quantum dot particles". The blue shift of the plasmon band with decreasing in the silver/dendrimer ratio indicates the decrease in the particles size [10].

TEM images of dendrimer-protected silver nanoparticles and histograms of particle size are shown in Figure 1. TEM images indicate that the silver nanoparticles are almost spherical. The average particle size (3.4, 1.8 and

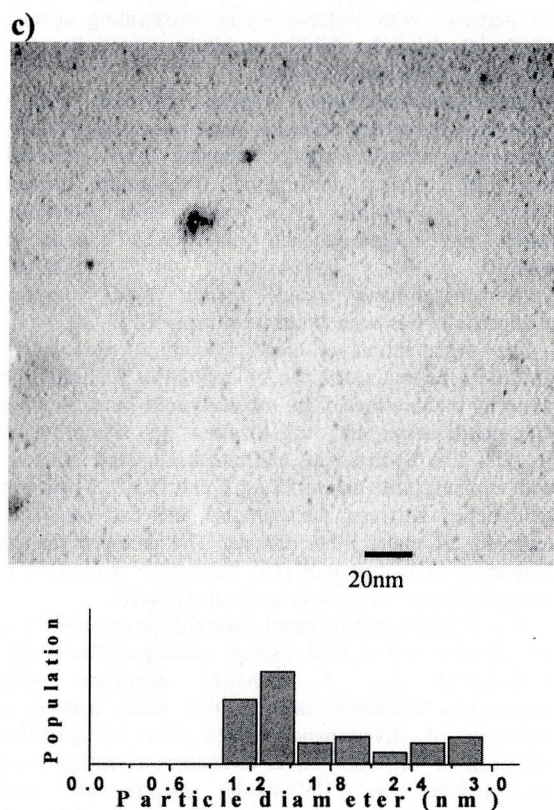
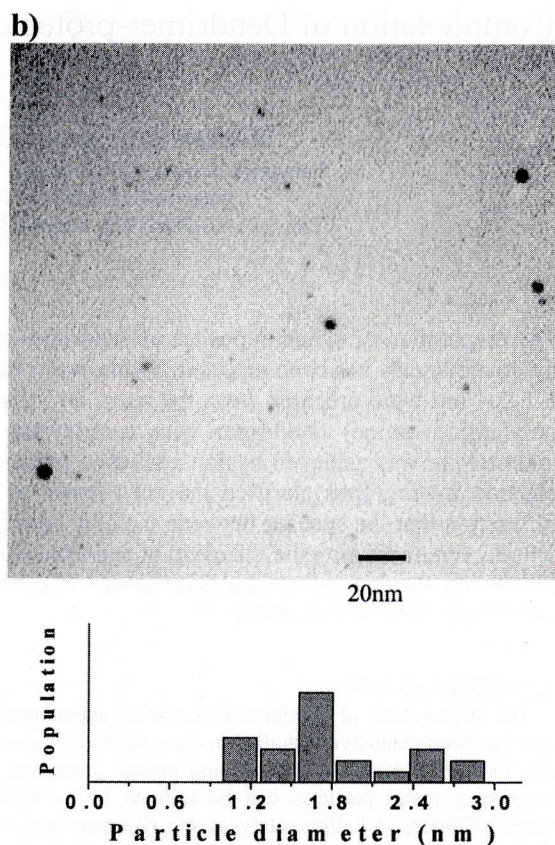
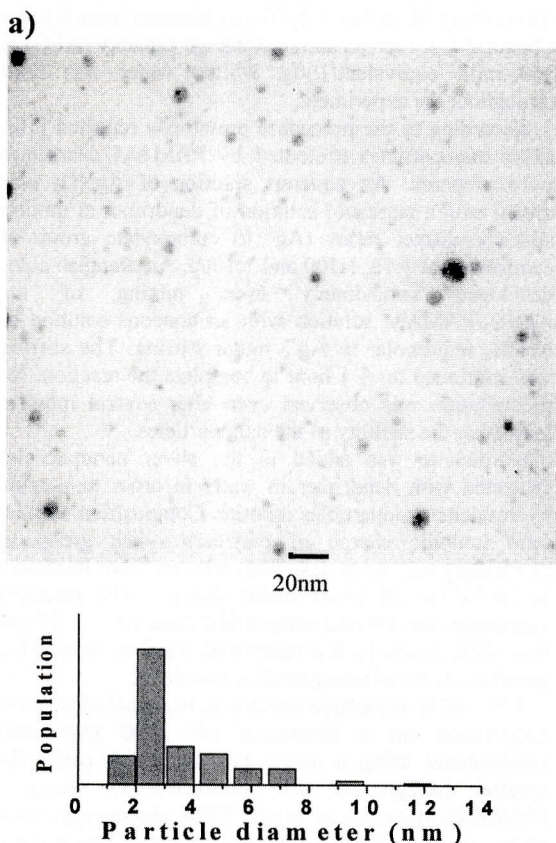


Figure 1. TEM of dendrimer-protected silver nanoparticles prepared at different silver/dendrimer ratios. a) 1:10, b) 1:100, c) 1:1000.



1.7 nm for ratios 1:10, 1:100 and 1:1000, respectively) decreased with the decreasing of the silver/dendrimer ratio from 1:10 to 1:100. This result is consistent with the estimation from UV/visible absorption spectra described above. Same result was also reported on the cases used PAMAM dendrimers with amine terminals [8-10]. Nucleation of silver nanoparticles arises from competition between tertiary amine and carboxyl groups in carboxylate terminated PAMAM dendrimers [19]. The more dendrimer fraction increases, the more number of nuclei increases, resulting in particles with smaller size. The presence of well separated particles in the TEM images at a ratio 1:10 enforces the assumption that the dendrimer encapsulate nanoparticles. However, very small decreasing was observed from ratio 1:100 to 1:1000. This is an indication that at a ratio 1:100 the large excess of dendrimer does not promote more stabilization of particles in comparison to ratio 1:100 because of too small amount of  $\text{Ag}^+$ .

### 3.2 Complexation of nanocomposites with clay

Complexation of dendrimer-protected silver nanoparticles with clay can be determined from XRD measurement. The XRD patterns of hydrotalcite and hydrotalcite/nanocomposites are shown in Figure 2. The hydrotalcite spectrum exhibits sharp diffraction peaks at  $q = 7.88, 16.00$  and  $24.40 \text{ nm}^{-1}$ , which correspond to indexes 003, 006 and 009, respectively, of a lamellar array. A basal spacing ( $d_{003}$ ) was evaluated to be  $0.797 \text{ nm}$ .

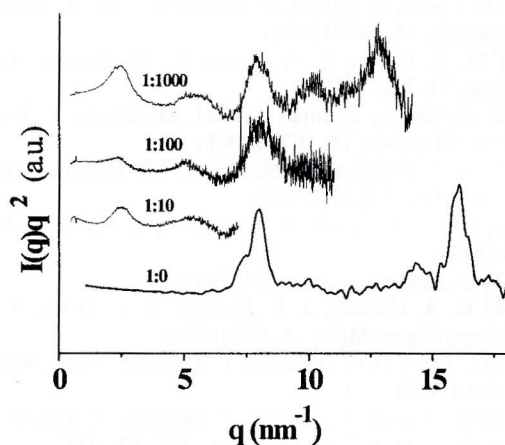


Figure 2. X-ray diffraction patterns of hydrotalcite and complexes of hydrotalcite and dendrimer-protected silver nanoparticles prepared at different silver/dendrimer ratios

All mixtures of hydrotalcite/nanocomposites present new diffracting peaks, besides the diffraction of the crude hydrotalcite, as listed in table I. The new peak can be indexed as the spacing ( $d_{003}$ ) of clay intercalated by dendrimer-protected silver nanoparticles. The brucite-like sheet thickness ( $0.477 \text{ nm}$ ) can be well approximated to the hydrotalcite layer thickness [20]. To obtain interlayer distance, the brucite layer thickness is subtracted from the basal distances of complexes, which are  $2.463, 2.662$  and  $2.565 \text{ nm}$  for silver/dendrimer ratio

Table I: Bragg peak positions in  $\text{nm}^{-1}$  for complexes of hydrotalcite and nanocomposites at different silver/dendrimer ratios, with the indexes according to rhombohedral  $R(-3)m$  symmetry in brackets.

Silver /dendrimer ratio	Hydrotalcite	hydrotalcite /nanocomposite
1:0	7.88 (003)	
	16.0 (006)	
	24.40(009)	
1:10		2.55 (003)
		5.16 (006)
1:100		2.36 (003)
	7.90 (003)	4.90 (006)
		overlapped (009)
1:1000		2.45 (003)
		5.30 (006)
	7.88 (003)	overlapped (009)
		10.00 (0012)
		12.70 (0015)

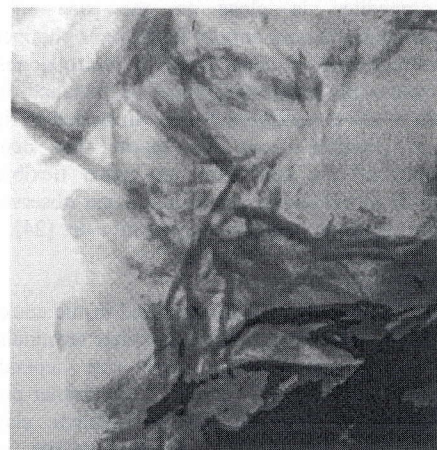
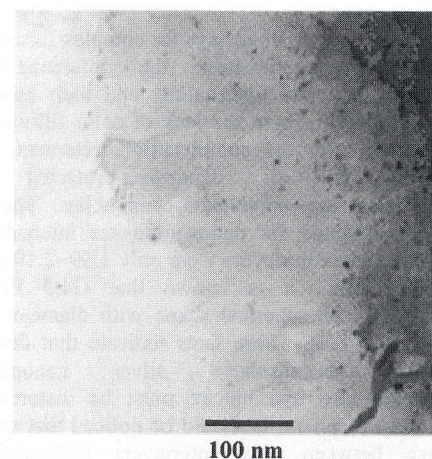


Figure 3. TEM images of hydrotalcite (Top) and hydrotalcite/nanocomposite (silver/dendrimer ratio 1:10) (bottom).



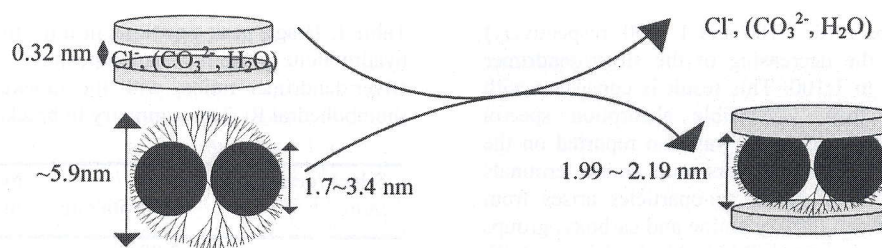


Figure 4. Schematic representation of complexation of dendrimer-protected silver nanoparticle in hydrotalcite

of 1:10, 1:100 and 1:1000, respectively. The resulting interlayer distances are 1.987, 2.185 and 2.090 nm. The dendrimer-protected silver nanoparticles may be intercalated into the clay interlayers. However, the coexistence of diffraction peaks of crude hydrotalcite suggests that there are interlayers in which the  $\text{Cl}^-$  or  $\text{CO}_3^{2-}$  anions were not replaced by the nanocomposites. TEM images of hydrotalcite and its complex with nanocomposites at silver/dendrimer ratio 1:10 are shown in Figure 3. The crude hydrotalcite does not have any small dark spots but the complex presents them, which are assigned to be silver nanoparticles. This indicates the complex formation between hydrotalcite and nanocomposites.

There are two possible ways for complex formation of hydrotalcite/nanocomposites; the intercalation of nanocomposites into hydrotalcite and their adsorption onto hydrotalcite. From the lack of color filtrate of the suspensions, after the complexation treatment, it was assumed that all dendrimer-protected silver nanoparticles are complexed with clay. The basal distances obtained for nanocomposites intercalated in the hydrotalcite interlayers were only 1.99–2.19 nm. On the other hand, it is known that G4.5 PAMAM dendrimer keeps spherical shape with diameter of 5.9 nm in water [21]. These facts indicate that dendrimer molecules (encapsulated silver nanoparticles) intercalated into hydrotalcite must be distorted their shape from a sphere. It should be noticed that the basal distance between clay interlayers intercalated by nanocomposites is close to the size of silver nanoparticles and very similar to the ones obtained from the intercalation of dendrimers in hydrotalcites [22]. This means that dendrimers must be flattened down to the size of silver nanoparticles, as illustrated in figure 4. This is possible from the report that dendrimer molecules of low generation are rather flexible [23]. Similar distorted dendrimer structure was observed even between lyotropic lamellar bilayers in water [24].

#### 4. CONCLUSIONS

Silver nanoparticles were prepared in the coexistence of PAMAM dendrimer with carboxylate terminals. They were almost spherical and their size depended on dendrimer content. The dendrimer-protected nanoparticles complexed with hydrotalcite clay. The assembly of nanoparticles in hydrotalcite can be developed into materials, which are used in catalytic process. This approach is possible to use for storing nanoparticles in solid state.

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#### 6. REFERENCES

- [1] A. Henglein, J. Lillie, *J. Phys. Chem.*, **85**, 1246 (1981)
- [2] M. Suzuki, Y. Taga, *J. Appl. Phys.*, **71**, 2848 (1992)
- [3] K. Puech, W. Blau, A. Grund, C. Bubeck, G. Cardenas, *Opt. Lett.*, **20**, 1613 (1995)
- [4] T. G. Shaaff, R. L. Whetten, *J. Phys. Chem. B*, **104**, 2630 (2000)
- [5] A. N. Shipway, E. Katz, I. Willner, *ChemPhysChem*, **1**, 18 (2000)
- [6] D. A. Tomalia, H. Baker, J. Dewald, M. Hall, G. Kallos, S. Martin, J. Roeck, J. Ryder, P. Smith, *Polymer J.*, **17**, 117 (1985)
- [7] L. Balogh, D. R. Swanson, R. Spindler, D. A. Tomalia, *Polymer Mater. Sci. Eng.*, **77**, 118 (1997)
- [8] K. Esumi, A. Suzuki, N. Aihara, K. Usui, K. Torigoe, *Langmuir*, **14**, 3157 (1998)
- [9] M. E. Garcia, L. A. Baker, R. M. Crooks, *Anal. Chem.*, **71**, 256, (1999)
- [10] A. Manna, T. Imae, K. Aoi, M. Okada, T. Yogo, *Chem. Materials*, **13**, 1674 (2001)
- [11] S. Yamanaka, T. Nishihara, M. Hattori, *Mater. Chem. Phys.*, **17**, 87, (1987)
- [12] H. L. D. Castillo, P. Grange, *Appl. Catal. A*, **103**, 23 (1993)
- [13] K. Allmann, *Chimia*, **24**, 99 (1970)
- [14] K. A. Carrado, J. E. Forman, R. E. Botto, R. E. Winans, *Chem. Mater.*, **5**, 472 (1993)
- [15] L. Raki, D. G. Rancourt, C. Detellier, *Chem. Mater.*, **7**, 221 (1995)
- [16] K. Takagi, E. Harata, T. Shicchi, T. Kanoh, Y. Sawaki, *J. Photochem. Photobio.*, **105**, 47 (1997)
- [17] E. A. Gardner, S. K. Yun, T. Kwon, T. Pinnavaia, *J. Appl. Clay Sci.*, **13**, 479 (1998)
- [18] I. Chatti, A. Ghorbel, P. Grange, J. M. Colin, *Catal. Today*, **75**, 113 (2002)
- [19] K. Esumi, A. Suzuki, A. Yamahira, K. Torigoe, *Langmuir*, **16**, 2604 (2000)
- [20] A. Ookubo, K. Ooi, H. Hayashi, *Langmuir*, **9**, 1418 (1993)
- [21] T. J. Prosa, B. J. Bauer, I. J. Amis, *Macromolecules*, **34**, 4897 (2001)
- [22] A. S. Costa, T. Imae, K. Takagi, K. Kikuta, submitted
- [23] J. Li, T. Piehler, D. Qin, J.R. Baker Jr., D. A. Tomalia, D. J. Meier, *Langmuir*, **16**, 5613 (2000)
- [24] X. Li, T. Imae, D. Leisner, M. A. López-Quintela, *J. Phys. Chem.*, **106**, 12170 (2002)