

# Preparation of Ag Nanoparticles in the Presence of Low Generational Poly(ester-amine) Dendrimers

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**ABSTRACT:** Stable Ag nanoparticles of 10–20 nm were prepared by reduction of AgNO<sub>3</sub> with NaBH<sub>4</sub> in water solution in the presence of low generational hydroxyl-terminated poly(ester-amine) dendrimer G1.0 (OH)<sub>16</sub> and amino-terminated poly(ester-amine) dendrimer G1.5 (NH<sub>2</sub>)<sub>8</sub> by optimizing preparation conditions. UV–vis absorption spectra and transmission electron microscopy were adopted to characterize absorption properties of Ag<sup>+</sup>/dendrimer complex, Ag/dendrimer nanocomposite aqueous solutions, and the morphology of the formed Ag nanoparticles, respectively. The results showed that the

size of the Ag particles increased with Ag<sup>+</sup>/dendrimer molar ratio, and the size of Ag nanoparticles in Ag/G1.0 (OH)<sub>16</sub> system was larger than that of Ag nanoparticles in Ag/G1.5 (NH<sub>2</sub>)<sub>8</sub> system, while the polydispersities of two systems were similar. Moreover, the Ag/G1.5 (NH<sub>2</sub>)<sub>8</sub> nanocomposite system was more stable than the Ag/G1.0 (OH)<sub>16</sub> one. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 422–426, 2007

**Key words:** dendrimers; low generation; nanocomposite; Ag nanoparticles

## INTRODUCTION

Nanosized metal particles can be used in a broad range of fields, from catalysis to nonlinear optical devices,<sup>1</sup> among which, silver nanoparticles continue to be of great current research interest because of their unique catalytic, electronic, optical, fungicidal properties, and the surface-enhanced Raman effect, which has been explored in sensing biological molecules with extremely high sensitivity.<sup>2</sup> The formation of monodisperse metal colloids usually requires the presence of a protective agent, which can be organic molecules, linear polymers, and surfactants traditionally.<sup>3</sup> Recently, intensive research has been carried out on the synthesis of metal colloids using dendrimers as templates and stabilizers.<sup>4–6</sup>

Dendrimers are a new class of macromolecules and widely used in the fields of medicinal chemistry, hostguest chemistry, and catalysis.<sup>7–9</sup> They are particularly suitable for preparing metal nanoparticles because of their monodispersity, regular and highly branched architecture, multiple surface functionality, and cavities in the structure. It has been proved that the uniform, narrow polydispersity, and stable Ag nanoparticles are formed inside the high generational dendrimers.<sup>10–12</sup> But, the synthesis of high generation dendrimer is complicated and difficult, and some properties of nanoparticles, such as cata-

lytic activity, are limited because higher generation dendrimers have a spherical three-dimensional structure and inorganic molecules as catalyst active center are enveloped in their interior sites. Dendrimers of lower generation are easily prepared, and tend to exist in relative open forms, which provide reactive sites at the periphery of dendrimer, so, they attract attentions.<sup>13,14</sup>

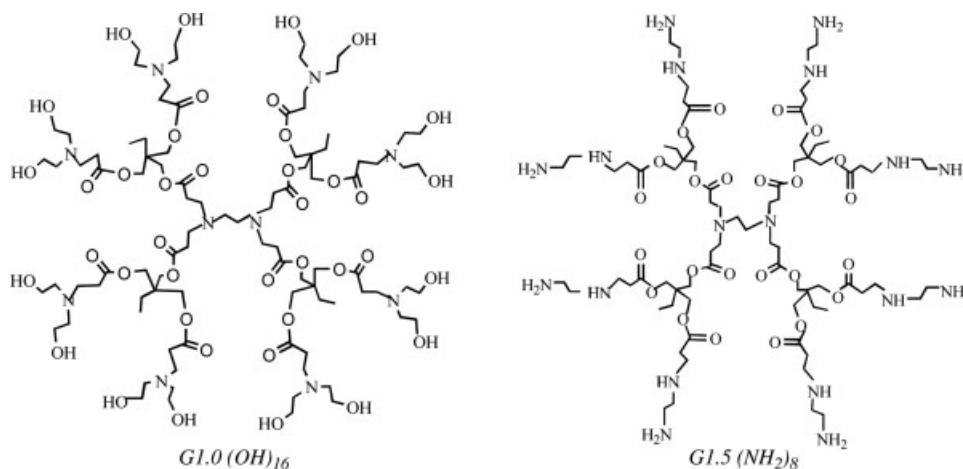
In this work, Ag nanoparticles were formed in the presence of low generational hydroxyl terminated poly(ester-amine) dendrimer G1.0 (OH)<sub>16</sub> and amino-terminated poly(ester-amine) dendrimer G1.5 (NH<sub>2</sub>)<sub>8</sub> synthesized by ourselves. It has been found that they are good templates and stabilizers for the synthesis of Ag nanoparticles. Our approach relies on the coordination between Ag ions and nitrogens of G1.0 (OH)<sub>16</sub> and G1.5 (NH<sub>2</sub>)<sub>8</sub> dendrimers. Reducing the Ag ions with NaBH<sub>4</sub> produced colloid solutions stabilized by the dendrimers. UV–vis absorption spectra, transmission electron microscopy (TEM) were employed to characterize the formation of the Ag nanoparticles and the morphology of the Ag nanoparticles.

## EXPERIMENTAL

### Materials

G1.0 (OH)<sub>16</sub> and G1.5 (NH<sub>2</sub>)<sub>8</sub> were prepared according to literature,<sup>15,16</sup> respectively. The structures of G1.0 (OH)<sub>16</sub> and G1.5 (NH<sub>2</sub>)<sub>8</sub> were given in Scheme 1. Silver nitrate (AgNO<sub>3</sub>), sodium borohydride (NaBH<sub>4</sub>), and 50% (mass) hydrazine aqueous were purchased

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**Scheme 1** The structure of G1.0 (OH)<sub>16</sub> and G1.5 (NH<sub>2</sub>)<sub>8</sub>.

from the Chemical Reagent Company of Shanghai (China) and were used without further purification. Deionized water was supplied by Special Chemical Reagent Company of Suzhou University (China).

### Synthesis of Ag nanoparticles

Preparation of Ag/G1.0 (OH)<sub>16</sub> and Ag/G1.5 (NH<sub>2</sub>)<sub>8</sub> colloids were carried out by mixing diluted aqueous solution of G1.0 (OH)<sub>16</sub> and G1.5 (NH<sub>2</sub>)<sub>8</sub> (1 mM) with aqueous solution of AgNO<sub>3</sub> (1 mM) at the molar ratio of 3 : 1, 1 : 1, 1 : 3, respectively, and reducing by sodium borohydride (NaBH<sub>4</sub>) (1 mM) or hydrazine (1 mM). It was found that NaBH<sub>4</sub> and hydrazine water solution could reduce the composites immediately.

### Measurements

UV-vis absorption spectra were recorded with a Shimadzu UV-240 UV-vis spectrophotometer (Shimadzu Co., Japan). Transmission electron microscopy (TEM) of Ag nanoparticles was taken with a Hitachi mode H-600 apparatus (Nicolet Co., USA). Samples for TEM were prepared by dropping of colloidal dispersion of Ag/G1.0 (OH)<sub>16</sub> and Ag/G1.5 (NH<sub>2</sub>)<sub>8</sub> onto a carbon-covered 200-mesh copper grid followed by naturally evaporating the solvent. The mean particle diameter was calculated by counting 100 particles from the enlarged photographs.

## RESULTS AND DISCUSSION

### Optimization of the reaction conditions

In the first step, the Ag<sup>+</sup> ions concentration, the dendrimer concentration, and the Ag<sup>+</sup>/G1.0 (OH)<sub>16</sub> and Ag<sup>+</sup>/G1.5 (NH<sub>2</sub>)<sub>8</sub> molar ratio in solution had to be adjusted so that no precipitation occurred. At higher concentration, [Ag<sup>+</sup> ≥ 5 mM, G1.0 (OH)<sub>16</sub> ≥ 5 mM, G1.5 (NH<sub>2</sub>)<sub>8</sub> ≥ 10 mM] and larger molar ratio of

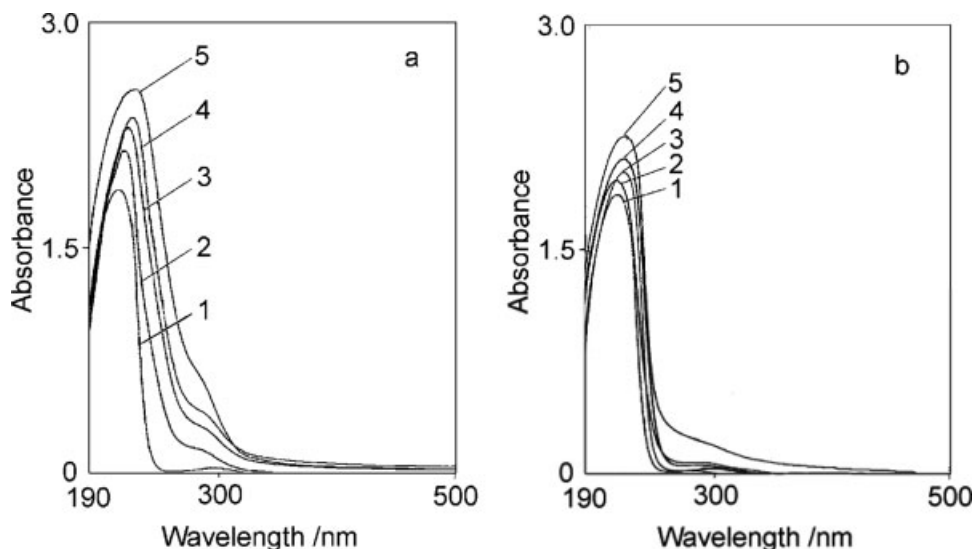
Ag<sup>+</sup>/G1.0 (OH)<sub>16</sub> (≥5/1) and Ag<sup>+</sup>/G1.5 (NH<sub>2</sub>)<sub>8</sub> (≥7/1), precipitation occurred upon reduction of the Ag<sup>+</sup>/G1.0 (OH)<sub>16</sub> and Ag<sup>+</sup>/G1.5 (NH<sub>2</sub>)<sub>8</sub> water solutions. Therefore, the mixing aqueous solutions of G1.0 (OH)<sub>16</sub> and G1.5 (NH<sub>2</sub>)<sub>8</sub> (1 mM) with AgNO<sub>3</sub> (1 mM) at the molar ratio of 1 : 3, 1 : 1, 3 : 1 Ag<sup>+</sup> : dendrimer were chosen to be reduced.

The second step was to select reducing agent, the concentration of the reducing agent, and the reduction rate. It was found that NaBH<sub>4</sub> as reductant needed shorter reaction time and could produce more stable Ag colloids in aqueous solution than hydrazine in this work. Lower concentration of NaBH<sub>4</sub> was beneficial to form stable Ag colloids. Higher concentration of NaBH<sub>4</sub> (≥1 mM) resulted in stable time of Ag colloids decreasing and precipitation occurring. The reduction rate was controlled by adding reductant dropwise into the Ag<sup>+</sup>/G1.0 (OH)<sub>16</sub> and Ag<sup>+</sup>/G1.5 (NH<sub>2</sub>)<sub>8</sub> solution under well stirring. The appropriate molar ratio of NaBH<sub>4</sub> : Ag<sup>+</sup> (0.8 : 1) was obtained by adding NaBH<sub>4</sub> to Ag<sup>+</sup>/G1.0 (OH)<sub>16</sub> and Ag<sup>+</sup>/G1.5 (NH<sub>2</sub>)<sub>8</sub> in water solutions until no further increases in area of the plasmon absorption peak were observed.

The Ag/G1.0 (OH)<sub>16</sub> and Ag/G1.5 (NH<sub>2</sub>)<sub>8</sub> solutions were pH dependent, as reported by Zheng et al.<sup>12</sup> Excess NaBH<sub>4</sub> was to raise the pH of the solutions and reduce their stability against flocculation. On the other hand, red brown precipitation of Ag particle aggregates appeared as NaBH<sub>4</sub> added to the Ag<sup>+</sup>/G1.0 (OH)<sub>16</sub> and Ag<sup>+</sup>/G1.5 (NH<sub>2</sub>)<sub>8</sub> aqueous solutions with pH below 5. The Ag/G1.0 (OH)<sub>16</sub> and Ag/G1.5 (NH<sub>2</sub>)<sub>8</sub> colloids were stable when the pH was between 5 and 8.

### UV-vis absorption spectra characterizing the formation of the Ag nanoparticles

When NaBH<sub>4</sub> was added to Ag<sup>+</sup>/G1.0 (OH)<sub>16</sub> and Ag<sup>+</sup>/G1.5 (NH<sub>2</sub>)<sub>8</sub> water solutions, the colorless Ag<sup>+</sup>/G1.0 (OH)<sub>16</sub> and Ag<sup>+</sup>/G1.5 (NH<sub>2</sub>)<sub>8</sub> solutions



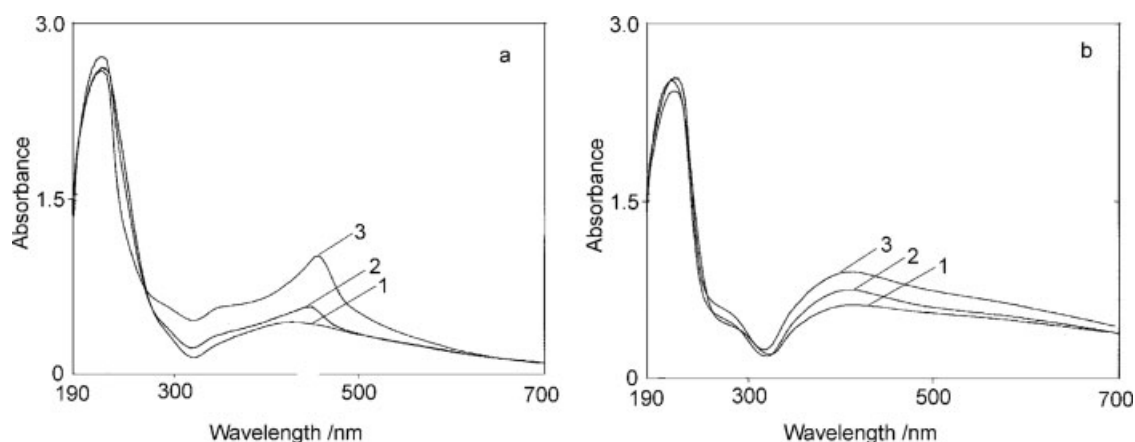
**Figure 1** UV-vis absorption spectra of  $\text{Ag}^+$ /dendrimer in aqueous solutions: (a) 1,  $\text{AgNO}_3$ ; 2–4,  $\text{Ag}^+ : \text{G1.0 (OH)}_{16} = 1 : 3, 1 : 1, 3 : 1$  (molar ratio); 5,  $\text{G1.0 (OH)}_{16}$ ; (b) 1,  $\text{AgNO}_3$ ; 2,  $\text{G1.5 (NH}_2)_8$ ; 3–5,  $\text{Ag}^+ : \text{G1.5 (NH}_2)_8 = 1 : 3, 1 : 1, 3 : 1$  (molar ratio).

(corresponding to Fig. 1) changed into golden yellow solutions (corresponding to Fig. 2), which indicated the reduction of  $\text{Ag}^+$  ions coordinated to nitrogen atoms in amino groups of the  $\text{G1.0 (OH)}_{16}$  and  $\text{G1.5 (NH}_2)_8$  into zerovalent Ag. In the case of  $\text{G1.0 (OH)}_{16}$  and  $\text{G1.5 (NH}_2)_8$  free system, the separate dark precipitates appeared and the solution turned colorless within several minutes. These facts showed that low generational dendrimer  $\text{G1.0 (OH)}_{16}$  and  $\text{G1.5 (NH}_2)_8$  could be used as template and stabilizer for preparing Ag nanoparticles.

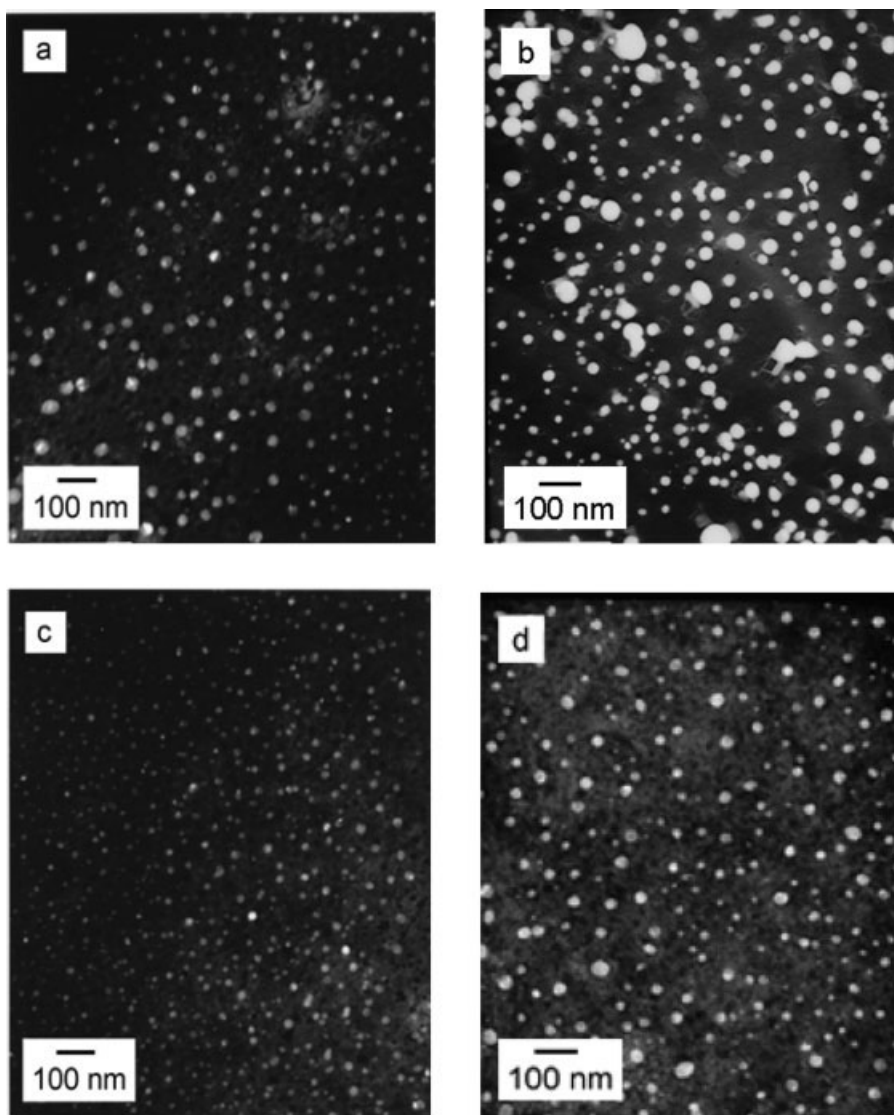
It was further seen that the maximum absorbing wavelength  $\lambda_{\text{max}}$  belonging to the characteristic plasmon resonance band of Ag nanoparticles<sup>17</sup> shifted from 440 to 460 nm and 400 to 410 nm when the molar ratio of  $\text{Ag}^+/\text{G1.0 (OH)}_{16}$  and  $\text{Ag}^+/\text{G1.5 (NH}_2)_8$  changed from 1 : 3 to 3 : 1, respectively, at the same time, the absorbance increased. From this phenomenon, it could be deduced that the size of Ag/dendrimer nanoparticles became larger with  $\text{Ag}^+/\text{dendrimer}$  molar ratio in the reduced solution, which was consistent with the results of Li et al.<sup>10</sup> The size of Ag nanoparticles in  $\text{Ag}/\text{G1.0 (OH)}_{16}$  system was larger than that of Ag nanoparticles in  $\text{Ag}/\text{G1.5 (NH}_2)_8$  system, since the  $\lambda_{\text{max}}$  of the characteristic plasmon resonance peak was in accordance with the diameter of nanoparticles.<sup>10</sup>

**Morphology of the formed Ag nanoparticles**

The results coming from UV-vis absorption spectra were in good agreement with TEM, which is pre-



**Figure 2** UV-vis absorption spectra of Ag/dendrimer in aqueous solutions: (a) 1–3,  $\text{Ag}^+ : \text{G1.0 (OH)}_{16} = 1 : 3, 1 : 1, 3 : 1$  (molar ratio), after reduction; (b) 1–3,  $\text{Ag}^+ : \text{G1.5 (NH}_2)_8 = 1 : 3, 1 : 1, 3 : 1$  (molar ratio), after reduction.



**Figure 3** TEM image of Ag nanoparticles: (a) and (b) Ag/G1.0 (OH)<sub>16</sub>, the molar ratio of Ag<sup>+</sup> : G1.0 (OH)<sub>16</sub> = 1 : 1, 3 : 1, respectively; (c) and (d) Ag/G1.5 (NH<sub>2</sub>)<sub>8</sub>, the molar ratio of Ag<sup>+</sup> : G1.5 (NH<sub>2</sub>)<sub>8</sub> = 1 : 1, 3 : 1, respectively.

sented in Figure 3. It could be seen that the particles in the pictures are isolated and disperse. The mean diameter of Ag nanoparticles in the reduced systems with the molar ratio of Ag<sup>+</sup> : G1.0 (OH)<sub>16</sub> 1 : 1 and 3 : 1 was about 15 nm [Fig. 3(a)] and 20 nm [Fig. 3(b)]; While the average diameter of Ag nanoparticles in the reduced systems with the molar ratio of Ag<sup>+</sup> : G1.5 (NH<sub>2</sub>)<sub>8</sub> 1 : 1 and 3 : 1 was about 10 nm [Fig. 3(c)] and 16 nm [Fig. 3(d)]. It was obvious that the size of the formed Ag particles increased with Ag<sup>+</sup>/dendrimer molar ratio.

The size of G1.0 (OH)<sub>16</sub> (calculated molecular mass: 2084) and G1.5 (NH<sub>2</sub>)<sub>8</sub> (calculated molecular mass: 1724) should be close to that of the OH-PAMAM-1.5 dendrimer (calculated molecular mass: 3744)<sup>14</sup> and the first generation PAMAM dendrimer (calculated molecular mass: 1430)<sup>18</sup> because of their

structure similarity. The diameter of OH-PAMAM-1.5 and the first generation PAMAM were approximately 2.8 nm<sup>14</sup> and 2.2 nm,<sup>18</sup> respectively; therefore, the diameter of G1.0 (OH)<sub>16</sub> and G1.5 (NH<sub>2</sub>)<sub>8</sub> was smaller than the diameter of the formed Ag nanoparticles. On the basis of these facts, most of the Ag nanoparticles in the image were surrounded by G1.0 (OH)<sub>16</sub> and G1.5 (NH<sub>2</sub>)<sub>8</sub> dendrimer,<sup>14</sup> and aggregation of the Ag/dendrimer nanocomposite existed because of hydrogen bonds among the peripheral hydroxyl and amino groups of dendrimer and the intrinsic aggregation tendency of nanoparticles.

An aqueous solution of Ag/G1.0 (OH)<sub>16</sub> and Ag/G1.5 (NH<sub>2</sub>)<sub>8</sub> nanocomposite prepared under the same conditions stored for weeks and months, respectively, at room temperature remained stable and could not agglomerate. The fact that the size of

Ag nanoparticles was smaller and the Ag/G1.5 (NH<sub>2</sub>)<sub>8</sub> colloid was more stable indicated that G1.5 (NH<sub>2</sub>)<sub>8</sub> be a more effective template and stabilizer than G1.0 (OH)<sub>16</sub>. The difference between the structures of two dendrimers only existed in the variety and number of their terminated groups. G1.0 (OH)<sub>16</sub> contained 16 peripheral hydroxyl groups, while G1.5 (NH<sub>2</sub>)<sub>8</sub> had 8 primary amino groups on the periphery. Therefore, it was suggested that amino groups have more important contribution than hydroxyl groups in dendrimer structure when the dendrimer was used as template and stabilizer in preparing metal nanoparticles.

### CONCLUSIONS

In this work, using low generational hydroxyl-terminated poly(ester-amine) dendrimer G1.0 (OH)<sub>16</sub> and amino-terminated poly(ester-amine) dendrimer G1.5 (NH<sub>2</sub>)<sub>8</sub> as template and stabilizer, Ag nanoparticles were prepared through mixing aqueous solution of AgNO<sub>3</sub> and G1.0 (OH)<sub>16</sub> or G1.5 (NH<sub>2</sub>)<sub>8</sub> reduced by NaBH<sub>4</sub>. The formation and growth of Ag nanoparticles and the stability of Ag/dendrimer colloid were greatly affected by the concentration of Ag<sup>+</sup> ions and dendrimer, the Ag<sup>+</sup>/G1.0 (OH)<sub>16</sub> and Ag<sup>+</sup>/G1.5 (NH<sub>2</sub>)<sub>8</sub> molar ratio in solution, the variety and concentration of reductant, the reduction rate, and the pH value. Stable Ag nanoparticles were obtained when the mixing solutions of 1 mM AgNO<sub>3</sub> and 1 mM G1.0 (OH)<sub>16</sub> or G1.5 (NH<sub>2</sub>)<sub>8</sub> at molar ratio 3 : 1, 1 : 1, 1 : 3 Ag<sup>+</sup> : dendrimer were reduced with 1 mM NaBH<sub>4</sub> water solution at the molar ratio of 0.8 : 1 NaBH<sub>4</sub> : Ag<sup>+</sup> within pH 5–8. Most of Ag nanoparticles were surrounded with G1.0 (OH)<sub>16</sub> or G1.5 (NH<sub>2</sub>)<sub>8</sub> dendrimers. An aqueous solution of Ag/G1.0 (OH)<sub>16</sub> and Ag/G1.5 (NH<sub>2</sub>)<sub>8</sub> nanocomposite stored for weeks and months, respectively, without coagulation at room temperature. G1.5 (NH<sub>2</sub>)<sub>8</sub> was a more effective template and stabilizer than G1.0 (OH)<sub>16</sub>. Compared to hydroxyl groups, amino groups in dendrimer structure played a more impor-

tant role in preparing metal nanoparticles. We believed that many other low generational dendrimers could also be used as template and stabilizer for the preparation of metal nanoparticles, and the obtained nanocomposites uniquely suited for catalysis. Experiments are underway to test this idea.

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