

Preparation and Characterization of Dendrimer-Templated Ag–Cu Bimetallic Nanoclusters

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Ag–Cu bimetallic nanoclusters with different shapes were prepared by a co-complexation method in the presence of PAMAM dendrimers. Small and evenly sized spherical Ag–Cu bimetallic nanoparticles were obtained with $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ as the reducing agent, and long rod-shaped bimetallic nanoclusters were prepared with NaBH_4 as the reducing agent. The mechanisms of formation of Ag–Cu bimetallic nanoclusters with different shapes were discussed. The different shapes of the cluster were likely caused by the differences in the reduction rate of metal ions with NaBH_4 and $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$. Structure characterization by TEM, UV–vis spectra, EDX, and TGA showed that, in the presence of PAMAM dendrimers, Ag–Cu alloy bimetallic nanorods were obtained with NaBH_4 reduction, and Ag–Cu bimetallic nanoparticles were prepared with $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ as the reducing agent.

1. Introduction

Transition-metal nanoclusters have attracted much attention over the past years because of their wide applications and interesting properties. Among these nanoclusters, silver and copper nanoclusters exhibit characteristic extinction bands in the visible region of the extinction spectra due to surface plasmon resonance.¹ Therefore, thin coating on glass substrates with metal nanoclusters (i.e., copper, silver, gold, and palladium) was used to make colored glasses.² Silver nanoclusters are known to produce intense yellow color, whereas copper nanoclusters produce ruby color.³ These intense colors produced by metal nanoclusters are attributed to their plasmon resonance bands. The plasmon bands of silver and copper nanoclusters in the visible region can be influenced by the concentration and geometry of the nanoparticles. In addition, it is known that the color produced by nanoparticles can be changed by altering the dielectric constant of the particles, and the dielectric constant can be changed by alloying or mixing two metals with different dielectric constants. Therefore, it is of great interest to prepare nanoparticles formed by the alloying or mixing of two different metals. Moreover, because the standard electrode potential of $\text{Cu}^{2+}/\text{Cu}^0$ is relatively low, the copper nanopar-

ticles are often easily oxidized and unstable. The addition of silver could prevent the oxidation of the copper and increases its stability. Several methods, such as chemical reduction and UV photo reduction of two metal salts, have been used for the preparation of bimetallic nanoparticles containing silver and copper in solution. Suyal⁴ synthesized the Ag–Cu bimetallic nanoparticles using the sol–gel route. Many researchers chose to study the bimetallic Cu–Ag nanoparticles because of their bactericidal^{5,6} and catalytic activities^{7,8} and their well-studied structure.

Dendrimers^{9–13} are symmetrical and spherical macromolecules, consisting of a relatively dense core, many branching sites, and terminal groups that usually form a well-defined surface. With dendrimers as the template for the formation

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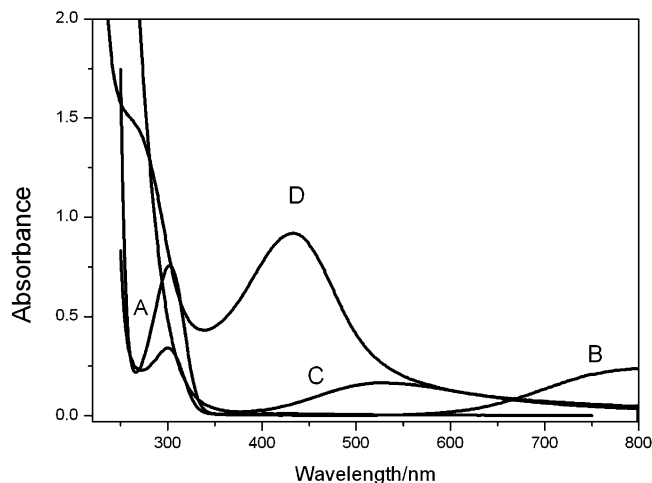


Figure 1. UV–vis spectra at different stages of the preparation of silver and copper nanoclusters. (A) 1 mM AgNO_3 , (B) 1 mM $\text{Cu}(\text{NO}_3)_2$, (C) complexation of metal mixture (15 mM AgNO_3 and 15 mM $\text{Cu}(\text{NO}_3)_2$) with 1 mM dendrimer, and (D) reduction with 0.5 M $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$. The dendrimers were G5.0-NH₂ PAMAM.

of inorganic nanoparticles, various metal nanoparticles made of gold,^{14–17} silver,¹⁸ copper,^{19,20} palladium,²¹ and platinum²² have been successfully prepared. However, most previous studies have been confined to the preparation of monometallic nanoparticles.^{23,24} In 2004, Rhee and co-workers^{25,26} reported the first preparation of Pt–Pd and Pd–Rh bimetallic nanoparticles in the presence of PAMAM dendrimers with surface hydroxyl groups. They applied these bimetallic nanoparticles as catalysts for the partial hydrogenation of 1,3-cyclooctadiene. Similar works have also been carried out by Scott.²⁷

Here, we report the synthesis and characterization of dendrimer-encapsulated bimetallic Ag–Cu nanoclusters. These materials are prepared by the co-complexation of Ag^+ and Cu^{2+} with the amines of amine-terminated PAMAM dendrimers followed by chemical reduction. Because the standard electrode potential of Ag^+/Ag^0 is relatively high, Ag^+ is reduced much more rapidly than the other metal ions, like Cu^{2+} , Pb^{2+} , Pd^{2+} , etc. Hence, the bimetallic nanoclusters containing silver and other metals are not easily formed. To obtain the bimetallic Ag–Cu nanoclusters with uniform size in the presence of PAMAM dendrimers, the reaction conditions have been carefully optimized.

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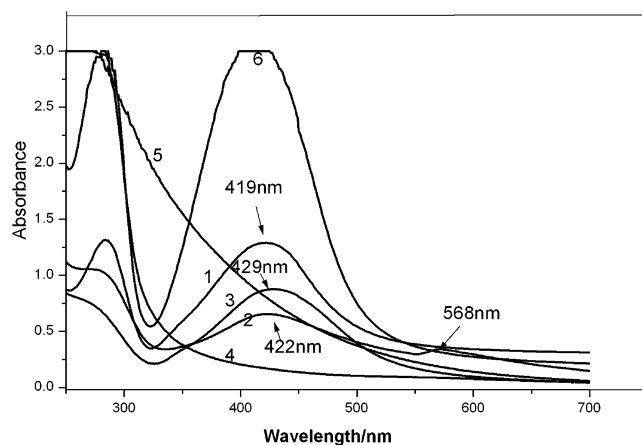


Figure 2. UV–vis spectra of G5.0-NH₂ PAMAM dendrimers-encapsulated Ag–Cu bimetallic nanoclusters ($\text{Ag}_n\text{Cu}_{30-n}$) made under different conditions. (1) Ag/Cu molar ratio 3:0, NaBH_4 as the reducing agent, (2) Ag/Cu molar ratio 1.5:1.5, NaBH_4 as the reducing agent, (3) Ag/Cu molar ratio 1.5:1.5, $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ as the reducing agent, (4) Ag/Cu molar ratio 0:3, NaBH_4 as the reducing agent, (5) Ag/Cu molar ratio 0:3, $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ as the reducing agent, (6) Ag/Cu molar ratio 3:0, $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ as the reducing agent.

2. Experimental Section

2.1. Chemicals. Amine-terminated fifth-generation poly(ami- doamine) (PAMAM) dendrimers (G5.0-NH₂ PAMAM) with a ethylenediamine core were synthesized according to the reported procedure.²⁸ AgNO_3 , $\text{Cu}(\text{NO}_3)_2$, NaBH_4 (99%), and $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ (50%) were purchased from China Beijing Chemical Company and used without further purification.

2.2. Preparation of Dendrimer-Templated Ag–Cu Bimetallic Nanoparticles. Dendrimer-templated Ag–Cu nanoparticles were prepared by simultaneous co-complexation of two different metal ions, followed by a single reduction step using NaBH_4 or $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ as the reducing agent, respectively. Complexation of metal ions with dendrimers was carried out by the addition of desired amounts of Ag^+ and Cu^{2+} (total metal concentration = 30 mM) to a 1 mM PAMAM dendrimer solution under vigorous stirring. After 8 h, 0.3 M NaBH_4 or $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ was slowly added under vigorous stirring.

2.3. Characterization. Absorption spectra were recorded on a Unico UV-2201 UV–vis spectrometer with deionized water as the reference for all of the measurements. Transmission electron microscopy (TEM) and the electron diffraction images of a selected area of Ag–Cu bimetallic nanoparticles were taken with a Hitachi transmission electron microscope (modes H700A-2). Samples for TEM and Energy Dispersive X-ray analysis (EDX) were prepared by dropping the colloidal dispersion of the nanoclusters onto a carbon-covered 200-mesh copper grid, followed by naturally evaporating the solvent. The mean particle diameter and standard derivation were calculated by counting 100 particles from the enlarged photographs. Thermogravimetric analysis (TGA) was carried out on a PerkinElmer TGA7 thermogravimetric analyzer in the temperature range of 50–500 °C.

3. Results and Discussion

We used the co-complexation method, which was done by preloading dendrimer nanoreactors with two types of suitable metal ions and then chemically reducing this composite in situ, to prepare the dendrimer-encapsulated

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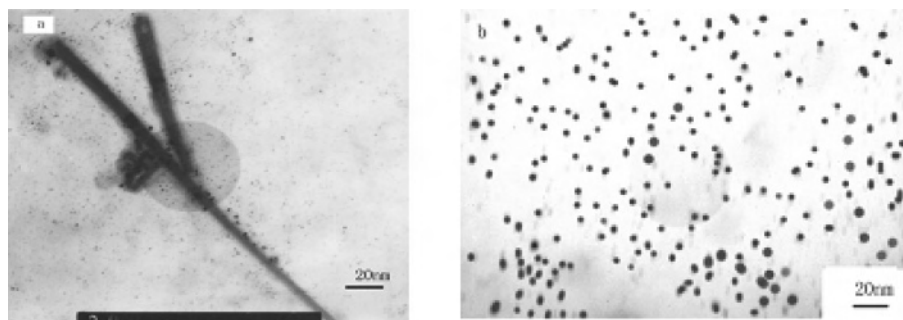


Figure 3. TEM of Ag–Cu bimetallic nanoclusters prepared by the reduction with NaBH_4 (a) and $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ (b) in the presence of G5.0- NH_2 PAMAM dendrimers with a Ag/Cu ratio of 1.5:1.5.

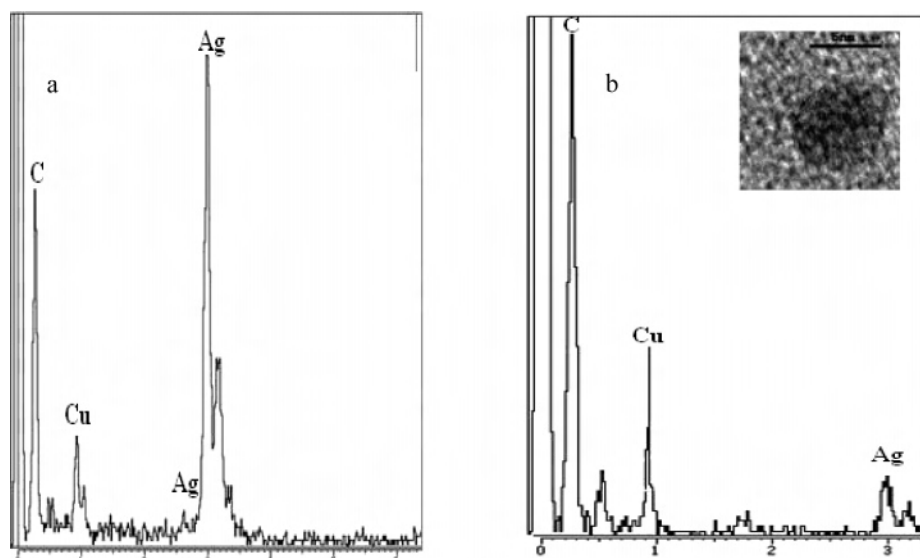


Figure 4. EDX of rod-shaped Ag–Cu nanoclusters (a) and a single Ag–Cu bimetallic nanoparticle (b) (Ag/Cu ratio of 1.5:1.5).

bimetallic nanoclusters. Specifically, PAMAM dendrimers in aqueous solution were mixed with Ag^+ and Cu^{2+} ions at controlled stoichiometries. During the co-complexation reaction, the reaction time for Ag^+ and Cu^{2+} to complex the nitrogen atoms of the dendrimers depended on the molar ratio of Ag^+ because Ag^+ ions were more difficult to be extracted by dendrimers than Cu^{2+} ions. After the solution was stirred for 6–9 h,²⁹ an aqueous solution of NaBH_4 (or N_2H_4) was slowly added to reduce the two metal ions simultaneously to zerovalent metal particles. The light-blue dendrimers/metal ion solution immediately turned yellow or golden brown during the reduction process, which indicated the formation of colloidal nanoclusters.

Figure 1 shows the changes in the absorption spectra of silver and copper nanoclusters (Ag/Cu molar ratio = 1.5:1.5) during the course of the complexation with dendrimers and the subsequent reduction. For the individual ions, the characteristic absorption peaks arising from the d–d transition were clearly observed. After the addition of PAMAM dendrimers to the solution of the metal ions, a new absorption peak around 550 nm appeared, indicating that the two metals ions were complexed with the internal functional groups of dendrimers. After reduction, the spectrum changed dramati-

cally. There was a new high intensity absorption peak at about 430 nm, which results from the surface plasmon resonance of the encapsulated zerovalent metal nanoclusters.

Figure 2 shows a series of UV–vis spectra of nanoparticles made with various Ag/Cu ratios using NaBH_4 and $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ as the reducing agents. The UV–vis spectra varied greatly depending on the Ag/Cu ratios and reducing agents. There was a strong adsorption peak at about 425 nm of silver nanoclusters due to surface plasmon adsorption. These silver nanoparticles were obtained at the molar Ag/Cu ratio of 3:0. However, reduction with $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ generated the particles with much higher absorption than those from the reduction with NaBH_4 . The copper nanoclusters, which were prepared at a molar Ag/Cu ratio of 0:3, showed no absorption band at greater than 300 nm in wavelength but displayed a monotonic spectrum increasing exponentially toward shorter wavelengths.¹⁹ For the bimetallic nanoclusters (Ag/Cu = 1.5:1.5), the spectra are not only from those of the monometallic silver or copper nanoclusters but also from their physical interactions. The differences in the absorption spectra of the bimetallic nanoclusters from those of individual silver or copper were primarily attributed to the changes in the dielectric properties caused by the mixing of the two metals. The different characteristics of the spectra of bimetallic nanoclusters strongly suggested that bimetallic nanoclusters

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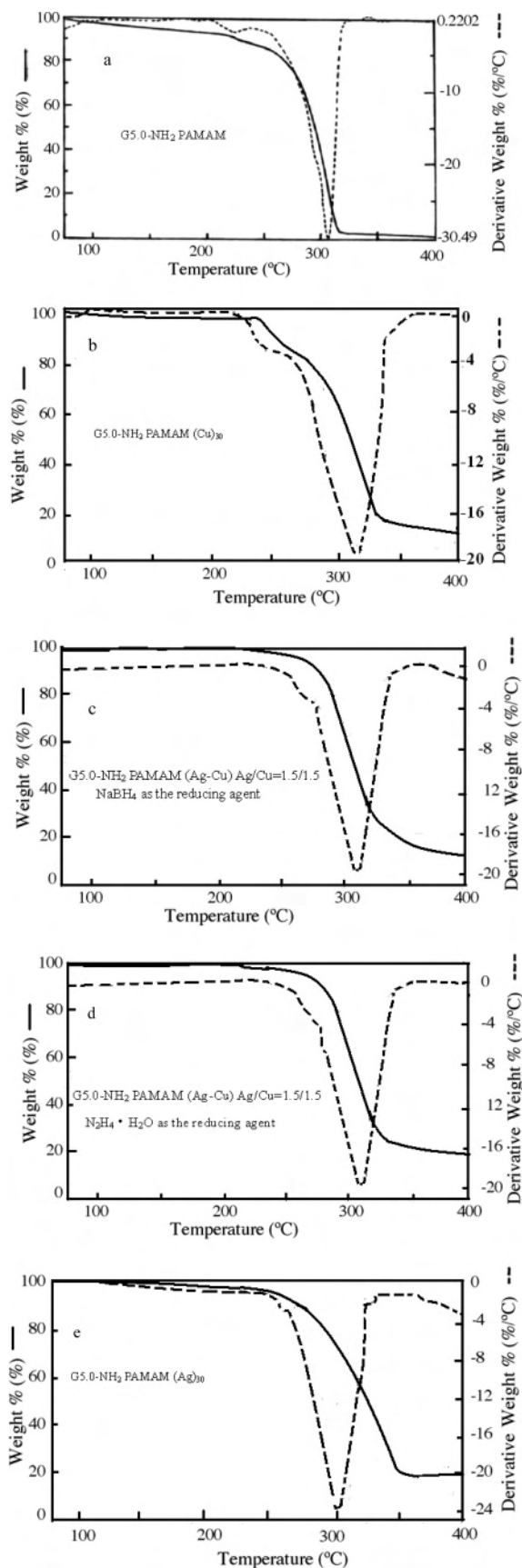


Figure 5. TGA (solid line) and DTG (dotted line) thermograms for samples of G5.0-NH₂ PAMAM dendrimers (a), G5.0-NH₂ PAMAM (Cu)₃₀ (b), G5.0-NH₂ PAMAM (Ag–Cu) Ag/Cu = 1.5:1.5, NaBH₄ as the reducing agent (c), G5.0-NH₂ PAMAM (Ag–Cu) Ag/Cu = 1.5:1.5, N₂H₄·H₂O as the reducing agent (d), and G5.0-NH₂ PAMAM (Ag)₃₀(d).

were formed in the cavity of the dendrimers. It was also noticed that the spectra of the bimetallic nanoclusters made with different reducing agents (NaBH₄ or N₂H₄·H₂O) under the same Ag/Cu ratio were different. There was a new peak at 568 nm in the absorption spectra of the bimetallic nanoclusters made by using NaBH₄ as the reducing agent. Generally, from Mie's theory³⁰ the nanoclusters with diameters below 5 nm have no absorption peak at the longer wavelength. With the increase in particle size, the absorption peak will be broadened and shifted to a higher wavelength. Particularly, the Ag–Cu bimetallic nanoclusters with over 10 nm diameters will exhibit bands at over 500 nm. It is likely that the size or the shape of Ag–Cu bimetallic nanoclusters prepared using NaBH₄ as the reducing agent is different from those using N₂H₄·H₂O as the reducing agent. To confirm if there is a difference, the Ag–Cu bimetallic nanoclusters were examined by TEM, and the results are shown in Figure 3.

It is interesting to notice that rod-shaped and spherical Ag–Cu bimetallic nanoclusters were obtained with reducing agent NaBH₄ and N₂H₄·H₂O, respectively. The microscopic examination of Ag–Cu bimetallic nanoclusters prepared by N₂H₄·H₂O reduction showed that the particle size was uniform and the shape was nearly spherical. The diameters of Ag–Cu bimetallic nanoparticles were about 5.6 ± 0.4 nm, a little larger than the diameter of G5.0-NH₂ PAMAM dendrimers (4.5 nm),³¹ which indicated that the dendrimers acted as an outer template for the formation of the clusters. The formation of almost homogeneously dispersed nanoparticles also demonstrated the effectiveness of dendrimers acting as both nanoreactors for the preparation of nanoclusters and stabilizers to prevent aggregation. Moreover, the size of the Ag–Cu nanoclusters is smaller than that of the monometallic silver nanoclusters or the copper nanoclusters obtained under the same conditions, suggesting that the specific interactions between the two metals affected the particle sizes. Under the same experimental conditions but with the reducing agent NaBH₄, rod-shaped Ag–Cu bimetallic nanoclusters were obtained (part a of Figure 3). The average diameter and length of these rod-shaped nanoclusters were 7.1 nm and 0.5 μ m, respectively.

The formation of two different shapes of Ag–Cu nanoclusters must be due to the effects of the reducing agents. The standard electrode potential of Ag⁺/Ag⁰ (0.78 eV) is higher than that of Cu²⁺/Cu⁰ (0.34 eV). Therefore, Ag⁺ is reduced more rapidly than Cu²⁺ and silver core-copper shell type of the bimetallic particles are easily formed by this co-complexation method. But the addition of a large amount of the potent reducing agent, NaBH₄, could make Cu²⁺ and Ag⁺ both reduced to Cu⁰ and Ag⁰ simultaneously and immediately. As a result, both silver and copper atoms acted as the nuclei for the formation of Ag–Cu bimetallic nanoclusters. Moreover, the high rate of reduction induced aggregation of nanoclusters. Although dendrimers might prevent this aggregation, the sphere-linking-sphere type of

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Table 1. Thermal Degradation of Samples at Different Temperature Regions

Temperature (°C)	Mass Change (%)				
	a	b	c	d	e
50–100	4.2	2.3	2.4	2.3	2.5
100–350	89.1	79.9	76.2	75.9	73.2
residue left at 400 °C (R_{400})	5.7	17.9	21.4	21.6	24.3
weight percentage of metal (P_M) ^a	0	12.2	15.7	15.9	18.6
theory weight percentage of metal (TP_M) ^b	0	11.8	15.3	15.3	18.5

^a $P_M = (R_{400}(\text{b, c, or d}) - R_{400}(\text{a}))/100 \times 100$. ^b $TP_M = (n(\text{Cu}) \times 63.5 + n(\text{Ag}) \times 107.8)/(n(\text{Cu}) \times 63.5 + n(\text{Ag}) \times 107.8 + n(\text{PAMAM}) \times 14\ 215)$. 14 215 is the molecular weight of G5.0-NH₂ PAMAM.³¹ For a, b, c, d, or e, see Figure 5 legend.

nanostructure was formed, and the Ag–Cu alloy nanoclusters were assembled to a rod. The stability of the rods was high because of the stabilizing effects of the dendrimers.

When N₂H₄·H₂O was added to the solution of Ag⁺–Cu²⁺/PAMAM dendrimers, Cu²⁺ likely complexed with N₂H₄·H₂O to form (PAMAM–Cu–NH₃)²⁺. Because the redox potential of (PAMAM–Cu–NH₃)²⁺/Cu⁰ (0.05 v)³² is far less than that of Ag⁺/Ag⁰, the apparent rate of reduction of Cu²⁺ into Cu⁰ should be far lower than that of the reduction of Ag⁺ to Ag⁰. It was probably that the formation of Cu⁰ only starts after the complete reduction of Ag⁺ to Ag⁰, which resulted in the formation of the silver core-copper shell nanoparticles.

To confirm the composition and structure of the rod-shaped and spherical nanoparticles as argued above, EDX analysis was carried out. As shown in Figure 4, both silver and copper elements were detected. But the EDX of the rod-shaped Ag–Cu nanoclusters (part a of Figure 4) was different from that of the spherical ones (part b of Figure 4). The atomic percentage of silver and copper of the rod-shaped nanoclusters were 63 and 37%, respectively, in agreement with the expected values. This indicated that the Ag–Cu bimetallic nanoclusters prepared with NaBH₄ were Ag–Cu alloy nanoclusters. The atomic percentage of silver and copper of the spherical nanoclusters were 21 and 79%, respectively, indicating that the surface of nanoparticles was made of Cu⁰.

Regardless of the reducing agents, the color of the solution of Ag–Cu nanoclusters/PAMAM dendrimers remained

henna for over 2 months. There was no observable absorption band at about 800 nm, which resulted from the formation of copper oxide particles, after 2 months, suggesting that both the Ag–Cu bimetallic nanorods and the Ag–Cu bimetallic nanoparticles were highly stable.

The effects of metal nanoclusters on the thermal stability of G5.0-NH₂ PAMAM dendrimers was determined by TGA as shown in Figure 5. It was observed that the presence of metal nanoclusters did not affect the maximum decomposition temperature, but the residue weight at 400 °C varied with the types of metal nanoclusters in the metal nanocluster/PAMAM dendrimer nanocompositions as shown in Table 1. We found that the weight of the composition (b, c, d, and e in Table 1) subtracting the weight of pure PAMAM dendrimers (a) was similar to the theoretical percentage of metal nanoclusters, indicating that all of the added metal ions were reduced to form the metal nanoclusters when the ratio of metal ions to dendrimers was less than the maximum complex ratio and complexation time was sufficient.³³ It also indicated that the different reducing agent did not affect the percentage of the metal nanoclusters in the nanocomposition when the other conditions were same.

4. Conclusion

We prepared Ag–Cu bimetallic nanoclusters with different shapes stabilized with PAMAM dendrimers by a co-complexation method with different reducing agents. Ag–Cu bimetallic nanoparticles with a narrow size distribution and uniform shape were prepared by N₂H₄·H₂O reduction, and long Ag–Cu bimetallic nanorods were prepared using NaBH₄ as the reducing agent. The reducing power of the reducing agents and the reduction rate of Ag⁺ to Ag⁰ and Cu²⁺ to Cu⁰ determined the shapes of the formed Ag–Cu bimetallic nanoclusters.

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