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Preparation of Gold-Poly(propylene imine) Dendrimer Nanocomposites with UV irradiation

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Abstract

Gold nanoparticles were prepared in the presence of poly(propylene imine) dendrimers (PPI) (generation 2, 3, and 4) with surface amino groups by UV-irradiation. UV-vis absorption, dynamic light scattering, and transmission electron microscopy have been used to study the formation and structure of gold-PPI nanocomposites. The reduction of Au^{3+} ions proceeded with an increase of UV irradiation time and the average diameters of gold nanoparticles obtained increased with an increase of dendrimer concentration. It is suggested that the structure of gold-PPI nanocomposites is formed by adsorption of PPI dendrimers on the gold nanoparticles. In addition, studies of reduction reaction of 4-nitrophenol by the gold nanoparticles with NaBH_4 show that the rate constants are very similar even for different generations as well as the different concentrations of PPI dendrimers.

Key-words : Gold-dendrimer nanocomposite, Poly(propylene imine) dendrimer, Reduction of 4-nitrophenol, Dynamic light scattering

1. Introduction

Recently, metal-dendrimer nanocomposites have been prepared by reduction of metal precursors with chemical reducing agents or UV-irradiation.

In the chemical reduction, metal-poly(amidoamine) (PAMAM) dendrimer nanocomposites, such as copper, palladium, platinum, silver, and gold, have been obtained¹⁻⁹). Interestingly, the structure of nanocomposites depends on the generation; when the generation of dendrimer is small, the nanocomposites are formed by dendrimers adsorbing on the nanoparticles, while using high generations of dendrimers nanoparticles are encapsulated in the dendrimers. Using such nanocomposites several catalytic activities have been studied; the catalytic activities are significantly dependent on the generation of dendrimer^{7,9,10}).

On the other hand, only a few studies have been reported for photochemical methods to prepare metal-dendrimer nanocomposites^{3,11,12}). We have prepared gold-PAMAM dendrimer nanocomposites using UV irradiation and found that the average particle sizes decrease

with an increase of dendrimer concentration as well as the generation of dendrimer³). During the formation of gold-dendrimer nanocomposites a degradation of PAMAM dendrimers by UV irradiation is also suggested. Similarly, silver-PAMAM dendrimer nanocomposites have been prepared using PAMAM dendrimers with surface amino or carboxyl groups¹¹).

Poly(propylene imine) (PPI) dendrimers, which do not contain amide groups, are stable¹³) at high temperatures compared to PAMAM dendrimers. It would be expected that during UV-irradiation metal-PPI dendrimer nanocomposites are formed without degradation of PPI dendrimers.

In this study, gold-PPI dendrimer nanocomposites are prepared by photochemical reduction of Au^{3+} ions in the presence of PPI dendrimer. Also, catalytic activities of gold-PPI dendrimer nanocomposites are studied by a reduction reaction of 4-nitrophenol.

2. Experimental

2.1 Materials

PPI dendrimers (generation G, 2, 3, and 4) were obtained from Aldrich Chemical Co. HAuCl_4 was supplied by Tokyo Kasei Kogyo Co. Ltd. Milli-Q water was used in this study. All other chemicals were of reagent grade.

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2.2 Preparation of gold-PPI dendrimer nanocomposites

Since PPI dendrimers G (2-4) have surface amino groups, various mixtures of HAuCl_4 and PPI dendrimers (molar ratio of surface amino group of PPI dendrimer and HAuCl_4 from 1 : 1 to 4 : 1) were prepared under a constant feed concentration of HAuCl_4 (0.2 mmol dm^{-3}) and they were transferred to rectangular quartz vessels. UV irradiation was carried out with a 40 W low pressure mercury lamp ($\lambda_{\text{max}} = 253.7 \text{ nm}$). The solutions were irradiated during stirring in a dark box at ambient temperature.

2.3 Measurements

The UV-vis spectra of the solutions were measured with a Hewlett-Packard 8452 diode array spectrophotometer at 1-cm path length. Transmission electron microscope observation was performed for the samples dried on carbon-coated copper grids. A Hitachi H-9000 NAR transmission electron microscope was operated at accelerated voltage of 200 kV and direct magnification of 200,000 X. The size distributions of the gold nanoparticles were determined from about 100 particles. Dynamic light scattering (DLS) measurements were performed using a Photol dynamic light scattering spectrometer DLS-9000 (Otsuka Electronics Co., Ltd.) equipped with an argon laser. Analysis was performed using the software provided by the manufacture. In this analysis, the individual autocorrelation function was determined at a 90° angle and analyzed using a second-order cumulant analysis. The average decay rate is then converted to the collective diffusion coefficient and hydrodynamic radius is obtained from Einstein equation. Each solution was filtered over a $0.45 \mu\text{m}$ filter before measurements.

For reduction of 4-nitrophenol¹⁴⁾, solutions of gold-PPI dendrimer nanocomposites and 4-nitrophenol solution were mixed, and to this was added sodium borohydride solution. The final concentrations of gold-PPI dendrimer nanocomposites, 2-nitrophenol and sodium borohydride were 0.01 , 0.1 and 10 mmol dm^{-3} , respectively. The kinetics of 2-nitrophenol reduction was monitored spectrophotometrically following decrease in absorbance at $\lambda = 400 \text{ nm}$ at 15°C .

3. Results and Discussion

Before studying the preparation of gold-PPI dendrimer nanocomposites with UV irradiation, we have checked whether PPI dendrimers are stable against UV-irradiation. Since UV-spectra of PPI dendrimers in aqueous solution are hardly changed with UV-irradiation after more than 3 hr, it can be said that PPI dendrimers are very stable with UV-irradiation at the

condition of this study. This high stability may be due to the molecular structure since PPI dendrimers do not contain amido groups compared to PAMAM dendrimers.

Fig. 1 shows UV-spectra of Au^{3+} -PPI G 2 dendrimer solutions with UV-irradiation and their TEM images. In the case of $\text{PPI G 2} : \text{Au}^{3+} = 1 : 1$, a new band at around 520 nm assigned to plasmon band appears with an increase of UV irradiation time and the intensity of the band reaches a maximum at 60 min irradiation and then decreases with a further irradiation accompanying an increase of higher wavelength absorption (data not shown). This suggests that gold-PPI dendrimer nanocomposites are formed with UV-irradiation but their stability becomes low due to aggregation of gold particles. When the ratio of $\text{PPI G 2} : \text{Au}^{3+}$ increases from 1 : 1 to 2 : 1, a plasmon band appears and its intensity increases with the irradiation time accompanying a blue shift of the plasmon band and finally a complete reduction is attained at 2 hr irradiation. In the case of $\text{PPI G 2} : \text{Au}^{3+} = 4 : 1$, a plasmon band at around 520 nm appears and its intensity increases with the irradiation time without shifting the band and a complete reduction is attained at 2 h 45 min irradiation. Since it is suggested that Au^{3+} ions interact with surface amino groups of PPI dendrimers in aqueous solution³⁾, the nucleation and nuclear growth of gold are affected by the complex formation of Au^{3+} with PPI dendrimers. When the ratio of $\text{PPI} : \text{Au}^{3+}$ is small, the nucleation may predominantly occur from free Au^{3+} ions in aqueous solution. From the result that the complete reduction of Au^{3+} ions is delayed when the ratio increases, the complexes of Au^{3+} -amino groups are not so easily reduced with UV irradiation compared to free Au^{3+} ions. Actually, at the ratio more than 8 : 1, the formation of gold nanoparticles is hardly observed. In addition, from TEM images as shown in Fig. 1, one can see that the average size of gold is larger and the standard deviation is smaller when the ratio is increased. These results also suggest that the nucleation and nuclear growth are significantly affected by the ratio of $\text{PPI} : \text{Au}^{3+}$.

Fig. 2 shows UV-vis spectra of Au^{3+} -PPI G 4 dendrimer in aqueous solution with UV-irradiation and their TEM images. The intensity of plasmon band increases with UV-irradiation time for both cases and the time for saturating the intensity is also increased with an increase of the ratio of $\text{PPI} : \text{Au}^{3+}$. In addition, the particle size distribution becomes narrower when the ratio is increased. This suggests that the growth of gold nanoparticles is also controlled by the concentration of PPI dendrimers. Similar results are obtained

Fig. 1 UV-vis spectra of Au³⁺-PPI G 2 dendrimer in aqueous solution with UV irradiation and TEM images with size distribution ; (a) PPI : Au³⁺ = 2 : 1, TEM = 120 min ; (b) PPI : Au³⁺ = 4 : 1, TEM = 165 min.

using PPI G 3 dendrimers.

To characterize the structure of the gold-PPI dendrimer nanocomposites in aqueous solution, hydrodynamic radius of the composites was determined by DLS measurements. Since the DLS measurements are sensitive to the size of the whole gold-dendrimer nanocomposites or association of their composites, they will include this organic matter. On the other hand, the TEM measurements are sensitive only to the electron-dense metal particles. **Table 1** shows the hydrodynamic diameters of the gold-PPI dendrimer nanocomposites and their sizes determined from TEM. Here, the diameters of PPI dendrimer are 1.9 (G 2), 2.4 (G 3), and 2.8

nm (G 4)¹⁵⁾. If the metal particles are covered with dendrimers as a monolayer, the difference in the measurements will correspond to two times the hydrodynamic diameter of the dendrimer. From Table 1, it is found that the TEM and DLS data are in good agreement except G 3 : Au³⁺ = 4 : 1 and G 4 : Au³⁺ = 4 : 1, indicating that the gold-PPI dendrimer nanocomposites prepared by UV irradiation consist of gold nanoparticles covered with PPI dendrimers as a monolayer.

The formation of gold nanoparticles by UV irradiation of Au³⁺ ions may occur through the photolysis of water and formation of radicals in the solution^{16,17)}.

Fig. 2 UV-vis spectra of Au³⁺-PPI G 4 dendrimer in aqueous solution with UV irradiation and TEM images with size distribution ; (a) PPI : Au³⁺ = 2 : 1, TEM = 105 min ; (b) PPI : Au³⁺ = 4 : 1, TEM = 165 min.

Table 1 Average diameter (nm) of gold nanoparticles determined by TEM and hydrodynamic diameter (nm) of gold-PPI dendrimer nanocomposites determined by DLS

PPI : Au ³⁺	Average diameter	Hydrodynamic diameter
2 : 1 G 2	8.1±4.3	12.2±2.7
4 : 1 G 2	10.9±3.3	13.3±2.9
2 : 1 G 3	8.9±1.9	13.1±2.8
4 : 1 G 3	11.4±2.6	12.0±2.6
2 : 1 G 4	8.8±2.3	14.4±3.2
4 : 1 G 4	11.2±2.8	11.6±2.5

Although mechanisms for formation of gold nanoparticles with UV irradiation using PPI dendrimers seem very complex, primary reaction products are assumed as Au⁰ and chloride. The conversion of AuCl₄⁻ ions to

Au⁰ may proceed through complex reactions involving AuCl₃⁻ ions and AuCl₂⁻ ions¹⁸⁾. Also, there is a possibility that amino groups of PPI dendrimers act as electron-transfer agents¹¹⁾.

To study the catalytic activities of the gold-PPI dendrimer nanocomposites the reduction reaction of 4-nitrophenol using these nanocomposites was spectroscopically monitored. **Fig. 3** shows successive UV-vis absorption spectra of the reduction of 4-nitrophenol by gold-PPI G 4 dendrimer nanocomposites. Similar spectra changes were also obtained for the other systems. In the absence of any catalysis, the peak due to 4-nitrophenol at 400 nm remains unaltered. Addition of an aliquot of gold nanoparticles to the reaction mixture causes the fading and ultimate bleaching of the yellow color of the 4-nitrophenol in aqueous solution. Since the amount of the gold nanoparticles added is very small, the absorption spectra of 4-nitrophenol are hardly interfered with by the gold nanoparticles. The reduction can be visualized by the disappearance of the 400 nm peak with the concomitant appearance of a new peak at 300 nm which has been attributed to 4-aminophenol¹⁴⁾. As the concentration of BH_4^- is very high, it remains essentially constant during the reaction. Accordingly pseudo-first-order kinetics with respect to 4-nitrophenol could be used in this case to evaluate the catalytic rate. A good linear correlation with time was obtained for all the systems studied. The values of

Fig. 3 Successive UV-vis spectra of the reduction of 4-nitrophenol by gold-PPI G 4 dendrimer nanocomposite; PPI : Au^{3+} = 4 : 1, irradiation time = 165 min.

pseudo-first-order rate constants determined from these plots are given in **Table 2**. It is apparent that the rate constants for all the systems are very similar. From the results using gold-dendrimer nanocomposites obtained by chemical reduction of Au^{3+} ions with NaBH_4 , it has been reported that the rate constants decrease with increasing dendrimer concentration as well as increasing generation¹⁰⁾. This result has been interpreted by the view that the dendrimers adsorbed on the gold nanoparticles interfere the reduction reaction to some extent and the magnitude of the interference becomes large when both the concentration and generation of dendrimers increase. However, in this study the rate constants for all the systems are almost same. It is conceivable that PPI dendrimers with different generations covered on the gold nanoparticles provide a similar hindrance effect on the catalytic reaction.

4. Conclusions

Gold-PPI dendrimer nanocomposites have been prepared by the reduction of Au^{3+} in the presence of PPI dendrimers with UV-irradiation. When the ratio of [dendrimer] : $[\text{Au}^{3+}]$ is increased, the complete reduction is achieved in a longer irradiation time and the average size of gold nanoparticles becomes large, whereas the average size of gold obtained is not dependent on the generation of PPI dendrimers. Dynamic light scattering and TEM measurements suggest that gold-PPI dendrimer nanocomposites are formed by PPI dendrimers adsorbing on gold nanoparticles. Further, the reduction reaction of 4-nitrophenol using the gold-PPI dendrimer nanocomposites is hardly affected by the size of PPI dendrimers.

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Table 2 Rate constants for reduction reaction of 4-nitrophenol

PPI : Au^{3+}	Rate constant ($\times 10^{-3} \text{ sec}^{-1}$)
2 : 1 G 2	2.95
4 : 1 G 2	2.87
2 : 1 G 3	2.82
4 : 1 G 3	2.72
2 : 1 G 4	2.67
4 : 1 G 4	2.51

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UV 照射による金-ポリプロピレンイミンデンドリマーナノコンポジットの調製

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要 旨

表面アミノ基を有するポリプロピレンイミンデンドリマー(PPI) (世代 2, 3 または 4) の存在下, UV 照射により金ナノ粒子を調製した。紫外可視吸収スペクトル, 動的光散乱法ならびに透過型電子顕微鏡を用いて金-PPI ナノコンポジットの生成ならびに構造をしらべた。金イオンの還元は UV 照射時間の増加にともない進み, また得られた金ナノ粒子の平均粒子径はデンドリマーの濃度が増えると増加した。金-PPI ナノコンポジットの構造は PPI 分子が金ナノ粒子に吸着することにより形成されることが示唆された。さらに, 金-PPI ナノコンポジットによる 4-ニトロフェノールの還元反応における反応定数は PPI デンドリマーの世代ならびに濃度に関係なくほぼ同じであることがわかった。