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Preparation of gold–, gold/silver–dendrimer nanocomposites in the presence of benzoin in ethanol by UV irradiation

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Abstract

Gold– and gold/silver–dendrimer nanocomposites have been synthesized by UV irradiation of their salts dissolved in ethanol containing dendrimers. As dendrimers, poly(amidomaine) PAMAM dendrimers and poly(propyleneimine) PPI dendrimers of various generations were used. The photoreduction of their salts is greatly accelerated by using benzoin as a photoinitiator. The sizes of gold in the nanocomposites are affected by the concentration of benzoin as well as the concentration of dendrimers, but are hardly changed with the kind of dendrimers. For gold/silver–dendrimer nanocomposites, the absorption spectra of gold/silver nanoparticles in the nanocomposites are very similar to the theoretical spectra of gold/silver alloy nanoparticles, suggesting the formation of gold/silver alloy nanoparticles. From the comparison of TEM and DLS measurements, it is found that the metal–dendrimer nanocomposites consist of metal nanoparticles covering by dendrimer molecules.

Keywords: Gold–dendrimer nanocomposite; Gold/silver–dendrimer nanocomposites; UV irradiation; Benzoin

1. Introduction

Recently, metal–dendrimer nanocomposites have been prepared [1–7] and characterized by transmission electron microscopy (TEM) and UV–visible spectroscopy. Their composite structures are mainly classified into two categories: one is that metal nanoparticles are encapsulated in the dendrimers and the other is that nanoparticles are covered by dendrimers adsorbing. Both nanocomposites can be obtained in aqueous solutions or nonaqueous solutions using various kinds of dendrimers such as hydrophilic and hydrophobic ones. Most metal ions are reduced by addition of reductants such as sodium borohydride.

In photochemical reduction, hydrated electrons or free organic radicals formed by irradiation by γ-rays [8,9] or UV light reduce metal ions to metals. We have prepared gold–poly(amidomaine) PAMAM dendrimer nanocomposites by UV irradiation in aqueous solutions and found that the average gold sizes decrease with increased dendrimer concentration as well as with the dendrimer generation [10]. Similarly, photoinitiators absorb light in the UV–visible region and form reactive intermediates such as free radicals. Benzoin derivatives represents the most important classes of initiators for photopolymerization and undergo primarily γ-cleavage to produce benzoyl and benzyl radicals [11–13] by UV irradiation. Indeed, metal nanoparticles such as copper, silver, gold, and their bimetallic nanoparticles have been prepared [14] in ethanol by UV irradiation using benzoin as a photoinitiator, where poly(vinyl pyrrolidone) has been used as a stabilizer. Ethanol is a very attractive solvent because it is a nontoxic solvent and easily eliminated by evaporation.

In this work, we describe the formation of gold– and gold/silver–dendrimer nanocomposites in ethanol by UV irradiation using benzoin. Here, poly(amidoamine) PAMAM dendrimers and poly(propyleneimine) PPI dendrimers are used.

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2. Experimental

2.1. Materials

Silver perchlorate and chloroauric acid of high purity were kindly supplied by Tanaka Kikinzoku Kogyo K.K. Poly(amidoamine) (PAMAM) dendrimers (G3.0 and 5.0) were prepared according to the literature [15]. Their purity was confirmed by ^{1}H NMR, FTIR, and elemental analysis. Poly(propyleneimine) (PPI) dendrimers (G2.0 and G4.0) were purchased from Aldrich Chemicals Co. Benzoin obtained from Tokyo Kasei Co. was used after recrystallization twice from ethanol. All other chemicals were of reagent grade.

2.2. Preparation of gold– and gold/silver–dendrimer nanocomposites

An ethanol solution of $HAuCl_4$ (0.2 mmol dm^{-3}) containing dendrimer and benzoin was deaerated by bubbling with nitrogen for 1 h. A 3-cm^3 portion of the solution was transferred to a rectangular quartz vessel in a glovebox under nitrogen. UV irradiation was carried out with a 40-W low-pressure mercury lamp. The solution was irradiated in a dark box at ambient temperature. In order to prepare composite particles of gold/silver, ethanol solutions dissolving $HAuCl_4$ and $AgClO_4$ (0.2 mmol dm^{-3}) in various mixed rations were used. Here, the concentration of dendrimer was expressed as its surface function group.

2.3. Characterization of gold– and gold/silver–dendrimer nanocomposites

The UV–visible spectra of the metal–dendrimer nanocomposites in ethanol were measured with a Hewlett–Packard 8452 A diode array spectrophotometer at path length 1 cm. Electron micrographs of the metal nanoparticles were taken with a Hitachi 9000 NAR transmission electron microscope, operating at 200 kV. The particle sizes and their distributions were determined by counting about 200 particles. The hydrodynamic radius of the metal–dendrimer nanocomposites in ethanol was measured using a Photal DLS-9000 dynamic light scattering spectrometer (Otsuka electronics Co., Ltd.) equipped with an argon ion laser. 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 was then converted to the collective diffusion coefficient and the hydrodynamic radius was obtained from the Einstein equation.

3. Results and discussion

Before studying the preparation of metal–dendrimer nanocomposites in the presence of benzoin in ethanol by UV irradiation, we discuss at first how benzoin molecules

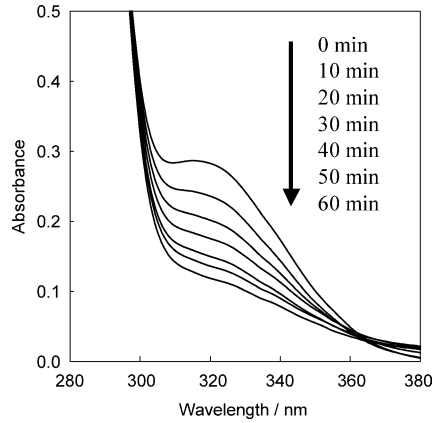
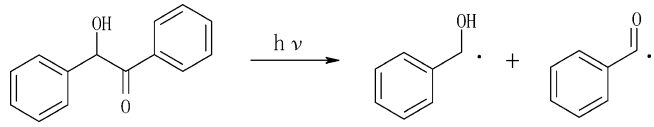


Fig. 1. Change in the optical spectra of benzoin (1 mmol dm^{-3}) in ethanol with UV irradiation (40 W).

change in ethanol by UV irradiation. Fig. 1 shows the spectral change of benzoin in ethanol with UV irradiation time. An absorption peak at around 315 nm is assigned to the excitation of benzoin between the ground state and the excited one. This absorbance decreases gradually with the irradiation time and this spectrum change is due to γ-cleavage of benzoin, as follows [11–13]:



A quantitative analysis of the spectral change by taking the intensity with the molar extinction coefficient of benzoin leads to the conclusion that the photoreaction of benzoin in ethanol proceeds at least more than 40% at 60 min of UV irradiation (40 W).

In order to confirm whether these benzoin and/or benzyl radicals can reduce auric ions, the spectral changes of the auric ions through photoreduction by these radicals was investigated. Fig. 2a shows the spectrum change of $HAuCl_4$–ethanol solutions containing benzoin and poly(amidoamine) (PAMAM) dendrimer G3.0 with UV irradiation time. In the absence of benzoin, no spectral change in the presence of the dendrimer was observed. However, in the presence of benzoin (1 mmol dm^{-3}), a distinct peak of gold nanoparticles at around 520 nm appears and the intensity increases above 70 min of UV irradiation time. During irradiation, within 1 h, the intensity of the absorption band at 320 nm assigned to Au–Cl decreases with increased of UV irradiation time. This indicates that the reduction of $AuCl_4^-$ occurs by elimination of chloro ligands during an early stage of UV irradiation but these changes do not affect the reduction of auric ions. Then, benzoin accelerates the reduction of AuCl species, resulting in the formation of gold nanoparticles. Thus, gold nanoparticles are formed in the presence of both benzoin and dendrimer, where benzoin works for the promotion of the photoreduction of $HAuCl_4$ via photolytically produced benzol and benzyl radicals or benzaldehyde and dendrimer acts as a stabilizer. A TEM image shows that the particle