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Synthesis of Nanocomposites of Metal Nanoparticles Utilizing Miscible Polymers

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Summary

Gold nanoparticles modified with poly(2-methyl-2-oxazoline) have been prepared via chemical reduction of $HAuCl_4$ by $NaBH_4$. The gold nanoparticles were homogeneously dispersed in poly(vinyl chloride) as a polymer matrix by the miscibility between the protecting polymer of the nanoparticle and the polymer matrix. Differential scanning calorimetry and UV-vis absorption measurement clearly showed that the miscibility played an important role for incorporation of the metal nanoparticles in the polymer matrix.

Introduction

Metal nanoparticles have unusual chemical and physical properties due to the quantum size effect, which make them attractive for applications such as catalysis, electronics, optics and biotechnology [1-3]. Recently, incorporation of the nanoparticles in a polymer matrix is a field of particular interest for materials engineering and the study of nanoparticles-matrix interactions [4]. Polymers are considered a good choice as host materials, because they can be designed to yield a variety of bulk physical properties, and they normally exhibit long-term stability and possess flexible reprocessability. Tailor made nanocomposites exhibiting novel properties can be easily prepared by the careful selection and combination of both components. Interesting properties such as fluorescence, electroluminescence and optical nonlinearity have already been observed [5,6].

Various approaches have been employed to prepare nanopartices/polymer composites. A number of papers employ various *in situ* preparation of nanoparticles from a suitable metal precursor in a matrix [7-11]. However, the metal nanoparticles produced by these methods were of either uncontrollable size or wide size distribution, and aggregation in the matrix. To overcome these difficulties, a few papers design a coating of nanoparticles to make them compatible with a polymer matrix [12,13]. For example, Lennox *at el.* reported the synthesis of gold nanoparticles decorated with covalently bound thiol-capped polystyrene and the successful incorporation of the gold nanoparticles into a presynthesized polystyrene matrix [12]. Exploitation of more simple and convenient techniques of synthesis of homogeneous metallic nanodispersion with controllable particle size and narrow size distribution in a polymer matrix is still challenging.

In this report, we report a homogeneous dispersion of gold nanoparticles into a polymer matrix. Our strategy is based on the miscibility between polymers surrounding the nanoparticle surface and the polymer matrix [12,14]. The instability problem of the nanoparticles, resulting in their aggregation and subsequent precipitation from the dispersion, has been solved through surface-passivation by organic molecules such as polymers and alkanethiols. If the protective organic shells show miscibility with a polymer matrix at a molecular level, the metal nanoparticles would be thermodynamically favorable to their incorporation without aggregation. Here we used poly(2-methyl-2-oxazoline) (POZO) as a protecting polymer for metal nanoparticles [15-17]. POZO is regarded as a polymer homolog of *N, N*-dimethylacetamide, which is one of aprotic polar solvents. POZO actually shows the miscibility with several commodity polymers like poly(vinyl chloride), polystyrene, poly(vinylidene fluoride) and so on [18]. Accordingly, poly(vinyl chloride) (PVC) was selected as a polymer matrix in the present system. In addition, POZO having amide groups on the side chain is expected to work as a protective group for metal nanoparticles like poly(vinyl pyrrolidone) [19,20].

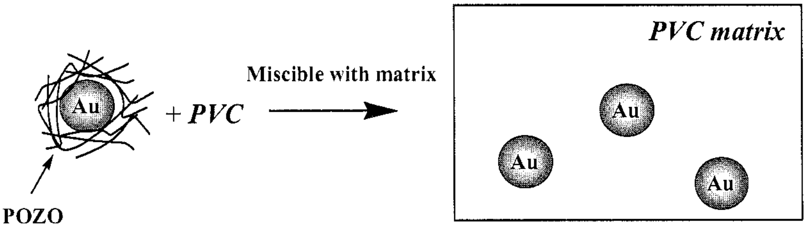

Figure 1. Schematic illustration of synthesis of nanocomposites of metal nanoparticles utilizing miscible polymer.

Results and Discussion

The gold nanoparticles were prepared by the reduction of 6 mg of $HAuCl_4$ with $NaBH_4$ in the presence of 0.25 g of POZO in methanol. The solution color immediately changed from yellow to dark red, indicating the formation of gold nanoparticles. The obtained solution of the gold nanoparticles modified with POZO (POZO-Au) was stable without precipitation for several months. This indicates that protecting ability of POZO for the gold nanoparticles is similar to that of poly(vinyl pyrolidone). The UV-vis absorption spectrum of the dark-red solution of POZO-Au showed the surface plasmon band at 527 nm. The average diameter of POZO-Au was 2.8 ± 1.0 nm as measured by transmission electron microscopy (TEM) (Figure 2). When 20 mg of $HAuCl_4$ was used, some precipitates were appeared in the solution after the reduction. We also prepared gold nanoparticles modified with 1-dodecanethiol (C_{12}-Au). A UV-vis absorption spectrum of a red solution after the chemical reduction with $NaBH_4$ indicated the formation of gold nanoparticles with the surface plasmon absorption band at 508 nm. TEM investigation showed C_{12}-Au with an average diameter of 2.2 ± 0.5 nm.

The miscibility of POZO on the nanoparticle and PVC was studied by a differential scanning calorimetry (DSC). The degree of the miscibility was estimated by comparing glass transition temperatures of a mixture with those of the original polymers. Figure 3(a) shows DSC thermograms of the cast film of POZO-Au and PVC. The glass temperatures of POZO-Au and PVC were observed at 78 °C and 59 °C, respectively. Poly(vinyl chloride) (PVC) was added to the methanol solution of POZO-Au. The solution was evaporated at room temperature in air. The obtained film was homogeneous and transparent. Figure 3(b) shows DSC thermograms of the film of POZO-Au with PVC. From these results, it is obvious that the film shows one glass transition temperature at 66 °C, and accordingly that these polymers have good miscibility in the present system. These results strongly suggest the absence of phase separation in the polymer matrix and the formation of the homogeneous materials.

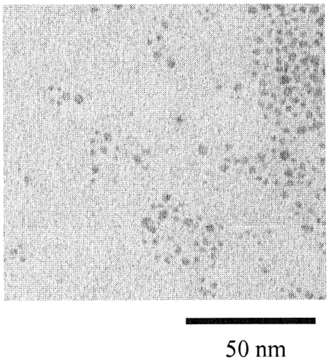

Figure 2. TEM iamge of the POZO-Au.

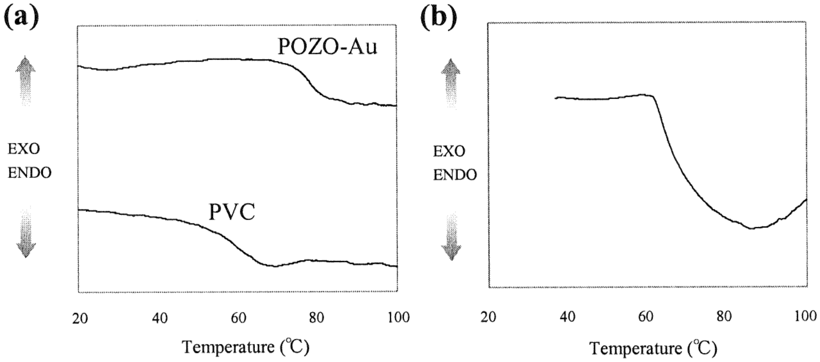

Figure 3. DSC thermograms of (a) POZO-Au and PVC and (b) the mixture of POZO-Au and PVC.

Incorporation of POZO-Au in the polymer matrix was studied. Gold nanoparticles display plasmon absorption bands that depend on their shapes and sizes [21-23]. As is generally known, particle aggregation results in further color changes of the gold nanoparticles due to mutually induced dipoles that depend on an interparticle distance and aggregation size. To investigate the state of the gold nanoparticles in the polymer matrix, A UV-vis absorption measurement is useful method. Several papers also reported spectroscopic technique to the study of dispersion phenomena of metal nanoparticles into polymer matrixes [12,24,25]. Figure 4(a) shows UV-vis absorption spectra of POZO-Au in dichloromethane and in the polymer matrix. The surface plasmon bands of both appeared at 527 nm. Comparison of (I) and (II) reveals that no red-shift of the surface plasmon band was observed, indicating the absence of aggregates of POZO-Au in the polymer matrix. The homogeneous distribution of the gold nanoparticles was further confirmed by TEM. Figure 5 shows the TEM image of the produced gold nanodispersion in the polymer matrix. It reveals that the gold nanoparticles were indeed homogeneously dispersed in the polymer matrix without change of the average particle size.

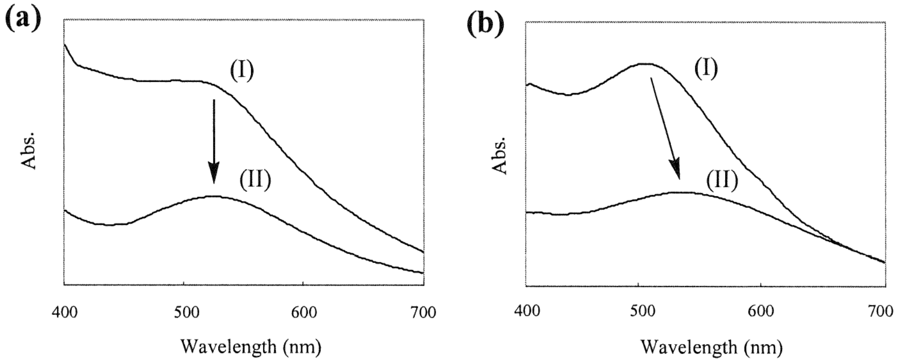

Figure 4. UV-vis absorption spectra of (a) POZO-Au in CH_2Cl_2 (I) and POZO-Au in PVC matrix (II) and (b) C_{12}-Au in CH_2Cl_2 (I) and C_{12}-Au in PVC matrix (II).

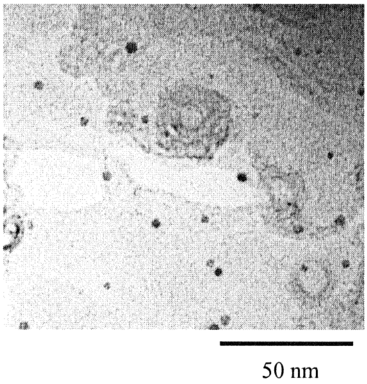

Figure 5. TEM image of the resulting mixture of POZO-Au and PVC.

As a control experiment we used C_{12}-Au instead of POZO-Au under the same experimental condition. In this case, the shift of the surface plasmon band based on nanoparticles aggregation is expected by the low miscibility between the alkyl group surrounding the nanoparticle surface and the polymer matrix. Figure 4(b) shows UV-vis absorption spectra of C_{12}-Au in dichloromethane and in the polymer matrix. In contrast with the described result as shown in Figure 4(a), the shift of the surface plasmon band from 508 nm to 537 nm was clearly observed, which can be explained by the changes in the effective dielectric constant of the composite film, due to the increase of effect of dipole interaction between the neighboring particles. That is, the aggregates of C_{12}-Au were formed. This result is in accordance with the described expectation. Based on the fact that the mixture of POZO-Au with PVC shows good miscibility, these results clearly suggest that POZO-Au was homogeneously dispersed in the polymer matrix by the miscibility between POZO on the nanoparticle and PVC.

Conclusion

In conclusion, we describe a simple and convenient method for synthesis of homogenous dispersion of the gold nanoparticles in the polymer matrix by the miscibility between the polymers on the nanoparticle and the polymer matrix. Many metal, metal sulfide, semiconductor, metal oxide nanoparticles would be protected with POZO [26-28]. We expect that the POZO protected metal nanoparticles give a powerful and general strategy for the creation of polymer/metal nanoparticles nanocomposites.

Experimental

Measurement

^{1}H NMR spectra were obtained with a JEOL JNM-270 spectrometer (270MHz for ^{1}H NMR) in chloroform-d. UV-visible spectra were measured on a Jasco V-530 spectrometer. Transmission electron microscopy was performed using a JEOL JEM-100SX operated at 100 kV. DSC analyses were carried out on a Seiko DSC200 instrument by using about 10 mg of exactly weighted samples at heating and cooling rate of 10 °C / min. The midpoint of T_g peak in the thermogram of the second heating scan was adopted as the value of the glass transition temperature.

Materials

All solvents and reagents were obtained from commercial source and used as supplied except the following. 2-Methyl-2-oxazoline was dried and distilled from KOH and stored under nitrogen.

Preparation of Gold Nanoparticles Modified with Poly(2-methyl-2-oxazoline)

Poly(2-methyl-2-oxazoline) (POZO) was prepared according to the previous method [14-16]. POZO of M_n = 8,500 (degree of polymerization = 100) was used. $HAuCl_4$ (6 mg, 0.014 mmol) was added to 20 mL of dichloromethane in the presence of POZO (0.25 g). To the solution, a methanol solution (2 mL) of $NaBH_4$ (3 mg, 0.073 mmol) was subsequently added. This caused an immediate color change to dark black. The mixture was vigorously stirred for 30 min.

Preparation of Gold Nanoparticles Modified with 1-Dodecanethiol

Gold nanoparticles were prepared according to the procedure described by Brust [29]. $HAuCl_4$ (20.0 mg, 0.048 mmol) was dissolved in 30 mL H_2O. Tetraoctylammonium bromide (26.5 mg, 0.048 mmol) was then added as a solution in 30 mL toluene, and the reaction mixture was stirred until the yellow aqueous layer was clear and the organic layer was red. 1-Dodecanethiol (6 mg, 6.3×10^{-3} mmol) was then added, followed by the dropwise addition of $NaBH_4$ (5.23 mg, 0.14 mmol) as a solution in 5 mL H_2O. This caused an immediate color change to dark black. The reaction mixture was stirred for 10 min, and the organic phase was collected and added to MeOH (100 mL). The precipitates were isolated by centrifugation. The gold nanopartices modified with 1-dodecanethiol was obtained as a black powder.

Preparation of a Mixture of PVC and Gold Nanoparticles
PVC (0.5 g) was added to the described solution of gold nanoparticles modified with POZO. The solution was evaporated at room temperature in air.

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