A Simple In Situ Hydrogen Bond Interaction to Homogeneous Dispersion of Gold Nanoparticles in SiO_2 Matrix Using Dendrimer as Template

Yong Zhou,* Chenghuan Ma,† Hideaki Itoh, Kensuke Naka, and Yoshiki Chujo*
Department of Polymer Chemistry, Graduate School of Engineering, Kyoto University, Yoshida, Sakyo-ku, Kyoto 606-8501
†*Department of Polymer Science and Engineering, Kyoto Institute of Technology, Matsugasaki, Sakyo-ku, Kyoto 606-8585*

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A novel dendrimer-templated gold nanoparticle was homogeneously dispersed in SiO_2 matrix via in situ hydrogen bond interaction between the dendrimer and silica matrix.

Dispersion of metal nanoparticles in silica glass with large third-order optical non-linearity has attracted much interest as materials for all optical functional devices,[1,2] such as optical switches, shutters or wave guides. Many techniques have been exploited for the preparation of the metal nanoparticle-dispersed SiO_2 matrix nanocomposites.[3–8] Sequential reduction of gold salt and sol-gel processing in inverse micelle solution was used for the preparation of metal-silicate nanodispersion, termed as the dispersion of the nanoparticle in silicate.[7] Kozuka et al reported direct addition of $HAuCl_4$ in tetramethoxysilane (TMOS) without additional stabilizing agents,[9] followed by heating treatment at 500 °C of the solution, producing the gold dispersion in silicate matrix. However, all of the metallic nanoparticles produced with the above methods were of either uncontrollable size or wide size distribution, and aggregation in silica matrices. Exploitation of more simple and convenient techniques of large-scaled synthesis of homogeneous metallic nanodispersion of controllable particle size and narrow size distribution in silica matrix is still challenging.

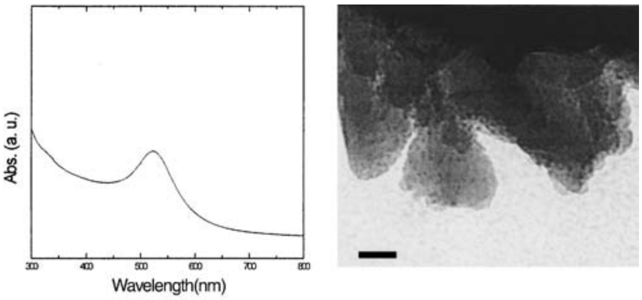
Dendrimers are quasispherical organic molecules that have well-defined, branched and compartmentalized structures in the nano-size range and unique properties.[10] Recently, utilization of dendrimers as templates for the synthesis of nanoparticles has attracted considerable research interest.[11] Several noble metals,[12] metal sulfides[13] and metal oxides[14] of nano-scale size have been synthesized with the dendrimers of various generations and surface terminal groups as templates. Incorporation of dendrimers into SiO_2 matrix has been reported to create novel functional hybrid materials of the combination of the fascinating structure of the dendrimer with the silica network, which maybe has wide application in membrane separation and catalysis.[15–17]

Recently, noncovalent bonds have widely been applied to the molecular-level incorporation of organic polymers in the framework of silica gel, represented by hydrogen bonds,[18] in which the polymer of the strong hydrogen bond-accepting groups (e.g., amide or urethane) can interact and form hydrogen bonds with the silanol groups of silica gel generated by the hydrolysis of alkoxysilane.

In this letter, we first extend the hydrogen bond interaction between polymers and silica to synthesis of homogeneous gold nanodispersion in SiO_2 matrix. Here, we choose poly(amidoamine) (PAMAM) dendrimers (G 4.5) with 128 surface carboxylate groups as template for the formation of gold nanoparticles. The *N*-alkylamide functional group in the repeating unit of the dendrimer can form hydrogen bonds with the silanol groups of silica gel,[15] further resulting in homogeneous incorporation of the templated gold nanoparticle into silica. Of the most important advantages using the PAMAM dendrimer as template, the size, size distribution and number density of the dispersed gold nanoparticle in the SiO_2 matrix can be controlled easily and precisely via varying the dendrimer generation and loading ratio of the dendrimer to the metal source.[12] It is expected that the present in situ hydrogen bond interaction can provide a general and convenient way to prepare homogeneous dispersion of metal, metal sulfide and metal oxide nanoparticles in silica matrices.

In a typical procedure, 0.2 g of methanol solution of 5 wt% of the dendrimer with 128 surface carboxylate groups (Generation 4.5) supplied from Dendritech Inc. was mixed with 0.5 ml of methanol solution of 1 mM $HAuCl_4$ under stirring. The formation of the gold nanoparticle was achieved by subsequent addition of 0.1 M $NaBH_4$ dissolved in methanol under vigorously stirring. The solution exhibited an instantaneous change from yellow to purple, indicative of the formation of the gold colloidal nanoparticle. The mixture solution was added dropwise into 5 ml of methanol solution containing 1.0 ml of TMOS and 0.5 ml of aqueous solution of 0.1 M HCl as an acid catalyst. The resulting mixture was stirred at room temperature for 2 h, allowing the sol-gel reaction of the silica. Complete gelation process was accomplished by casting the resultant into a plastic vessel covered with aluminum foil of a few pinholes and standing it for three days at room temperature under air. After another two days of removal of the solvent in vacuo at 60 °C, a transparent purple monolith was obtained with no visible cracks. The transparency of the hybrid material strongly suggests the homogeneity of the gold nanoparticle in the silica matrix. The product was washed with distilled water and absolute methanol, dried at room temperature and ground into powders for characterization. For comparison, a similar gold dispersion in the silica matrix was also prepared in the absence of the PAMAM dendrimer. A turbid film was obtained, indicating that the produced gold particles in absence of the dendrimer caused phase separation in the matrix and formed heterogeneous materials.

Figure 1(a) shows the UV-vis absorption spectrum of the produced dendrimer-templated gold homogeneous nanodispersion in SiO_2 matrix using the PAMAM dendrimer-dispersed SiO_2 as reference. The peak centering at 526 nm can be assigned to the surface plasmon resonance of the produced gold colloid.[19] Generally, the gold colloids of size bigger than 3 nm are supposed to be capable of exhibiting the distinguished surface plasmon resonance. In our case, the produced gold nanoparticle was of 2 nm in average size (See the TEM image discussed below). We believe that the unordinarily high intensity of surface plasma resonance in the present sample may result from the influence of the dendrimer and silica matrix on the distribution or motion state of the electrons of the produced gold nanoparticle, e.g. electron



(a) (b)

Figure 1. (a) UV-vis absorption spectrum of the produced dendrimer-templated gold homogeneous nanodispersion in SiO_2 matrix. (b) TEM image of the produced dendrimer-templated gold homogeneous nanodispersion in SiO_2 matrix. Scale bar is 20 nm.

mean-free path, an important parameter for the UV-vis absorption spectrum of a metal.[19]

In addition, it is well known that agglomeration of metal colloids results in increasing absorption at longer wavelengths and broadening of the primary absorption band, and often to the appearance of a secondary absorption peak that is red-shift relative to the primary absorption band. In the present study, no absorption at longer wavelengths was observed, and the absorption band displayed finely symmetrical configuration, implying that the template-synthesized gold nanoparticle was homogeneously dispersed in the SiO_2 matrix.

The homogeneous distribution of the formed gold nanoparticles was further confirmed by a transmission electron microscopy (TEM) image. Figure 1(b) shows the TEM image of the produced gold nanodispersion in the SiO_2 matrix. It reveals that the formed gold nanoparticles were indeed homogeneously dispersed in the SiO_2 matrix. The average particle size was approximately 2 nm with narrow distribution in the range of 1–3 nm, calculated by averaging the sizes of 300 particles directly from the TEM images. The average size of the gold nanoparticle is well consistent with that of the pore by means of pyrolysis of the PAMAM dendrimer-incorporated silica hybrid,[15] further confirming that the gold nanoparticle was templatedly produced within the dendrimer.

The *N*-alkylamide functional groups in the repeating unit of the dendrimer can interact and form hydrogen bonds with the silanol groups of silica gel generated by the hydrolysis of alkoxysilane,[15] resulting in homogeneous dispersion of the templated gold nanoparticle in silica. It is expected that there may also exist the hydrogen bonds between the carboxy groups generated under the present acidic condition and silanol group, which maybe partially contributed to the homogeneous dispersion. It is important to note that the terminal functional group of the PAMAM dendrimer was found to play a crucial role on the homogeneity of the dendrimer in silica gel.[15] Employment of the PAMAM dendrimer having surface amino groups has been demonstrated to cause phase separation to produce only turbid or heterogeneous materials. The possible reason is that besides the hydrogen bonds formed between the dendrimer and silica in the present system, surface carboxy or amino groups of the dendrimer molecules maybe formed preferentially the inter-dendrimer hydrogen bonds via the carboxy or amino groups of the neighboring denderimers. Nevertheless, we believe that the intensity of the inter-dendrimer hydrogen bonds formed via amino groups of the neighboring denderimers may be much stronger than that of the dendrimer and silica, resulting in the aggregation of the dendrimers.[20]

In summary, a simple and convenient way has been exploited to large scale synthesis of homogeneous gold nanodispersion in SiO_2 monoliths by utilization of in situ hydrogen bond interaction between the *N*-alkylamide functional group in the repeating unit of the poly(amidoamine) (PAMAM) dendrimer with 128 surface carboxylate groups and the silanol groups of silica gel generated by the hydrolysis of alkoxysilane. The average particle size was approximately 2 nm with narrow distribution in the range of 1–3 nm. Very importantly, since the dendrimer-encapsulated metal nanoparticle contained the same number of atoms as initially preloaded into the dendrimer, thus, in the preparation of the present silica-based hybrid, the size, size distribution and number density of the dispersed gold nanoparticle can be precisely and easily controlled via varying the dendrimer generation and loading ratio of the dendrimer to the metal source. In addition, until now, many metal, metal sulfide and metal oxide nanoparticles can be synthesized with the dendrimers as template, thus, it is expected that the present in situ hydrogen bond interaction can provide a general and convenient way to large scale preparation of homogeneous dispersion of metal, metal sulfide and metal oxide nanoparticles in silica matrices.

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