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Gold Nanoparticles

Preparation of Optical Resins Containing Dispersed Gold Nanoparticles by the Matrix Sputtering Method**

Yuichi Shishino, Tetsu Yonezawa, Satoshi Udagawa, Kaname Hase, and Hiroshi Nishihara**

Inorganic/organic hybrid optical materials have garnered much interest because they can display material properties, such as the index of refraction or thermal, mechanical, and luminescent properties, that are more desirable than the properties of pure organic materials.[1–12] To obtain transparent hybrid materials that include nanoparticles (NPs), it is necessary to avoid Rayleigh scattering from the NPs in the matrix. The size of NPs in the hybrid material should be smaller than one-tenth the wavelength of visible light.[13,14] However, NPs tend to aggregate if the affinity between the NP surfaces and the organic matrix is low. Hybrid optical materials may be prepared either by dispersing the NPs[1–7] or by synthesizing NPs[8–12] within a matrix. The former approach requires the addition of a dispersing agent to minimize aggregation of the NPs; the latter approach may introduce by-products into the matrix. Both methods have the drawback of requiring multistep processes.

Recently, we developed a simple technique, the molten matrix sputtering (MMS) method, for synthesizing inorganic NPs without the formation of by-products.[15] This method is based on vacuum metal evaporation using a liquid medium with a low vapor pressure. For example, we obtained AuNPs protected by (6-mercaptohexyl)trimethylammonium bromide (6-MTAB) with a metal core diameter of 1.3 nm and a narrow size distribution. These NPs exhibit red luminescence with a large Stokes shift.[16,17]

In the present study we have reaped the benefits of the matrix sputtering (MS) method, which does not require dispersing agents and produces no contaminating by-products, in the preparation of AuNPs/thiourethane and AuNPs/urethane hybrid optical resins. PEMP with thiol groups and PEEL with hydroxy groups (see Figure 1) were employed as substrates for generating thiourethane and urethane, respectively, because both compounds have a low vapor pressure at room temperature. Matrix sputtering afforded AuNPs/PEMP and AuNPs/PEEL hybrids, which could be transformed readily to thiourethane and urethane resins, respectively. The optical properties of the AuNPs/thiourethane and AuNPs/urethane hybrid resins were found to differ substantially; the former is almost colorless and exhibits red photoluminescence (PL), whereas the latter is red and shows no luminescence. Herein we describe the preparation, characterization, and physical properties of the AuNP hybrid resins.

Gold was sputtered into PEMP by application of a current of 40 mA under an air pressure of 10 Pa at room temperature in a sputter coater. The PEMP surface was positioned a distance of 40 mm from the Au target. The AuNPs/PEMP hybrid nanoparticles were prepared with a sputtering time (t_s) of 5–15 min. Next, AuNPs/thiourethane hybrid resins were prepared by heat polymerization of AuNPs/PEMP and *m*-xylylene diisocyanate (*m*-XDI; Figure 1). The amount of Au in the thiourethane hybrid resin for $t_s = 15$ min was 290 ppm (g g^{-1}) (see Figure S1 in the Supporting Information).

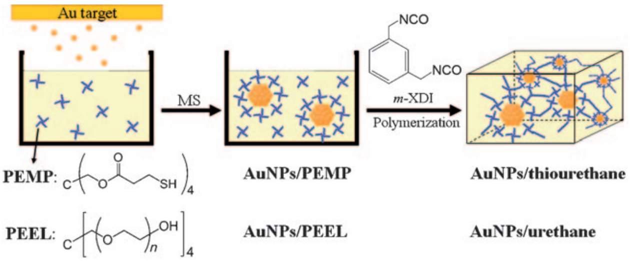

Figure 1. Preparation of the hybrid resins by the MS method.

Figure 2a shows the UV/Vis absorption spectrum of AuNPs/PEMP with $t_s = 5$–15 min. A surface plasmon band at 520 nm is not observed in the spectrum.[16,18,19] However, the absorbance at 380 nm increases in proportion to t_s. The spectrum profile is similar to that of AuNPs/6-MTAB reported in our previous study.[15] Accordingly, it is expected that only AuNPs/PEMP with a diameter less than 2 nm are produced in PEMP, and the number of NPs increases linearly with t_s. The thiol groups of PEMP, which strongly coordinate the gold surface, effectively constrict the growth and aggregation of the AuNPs during sputtering. The size of AuNPs in PEMP could not be determined by standard transmission

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[*] Y. Shishino, Prof. H. Nishihara
Department of Chemistry, School of Science, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033 (Japan)
Fax: (+81) 3-5841-8063
E-mail: nisihara@chem.s.u-tokyo.ac.jp
Homepage: http://www.chem.s.u-tokyo.ac.jp/users/inorg/indexe.htm

Prof. T. Yonezawa, S. Udagawa
Division of Materials Science and Engineering
Faculty of Engineering, Hokkaido University (Japan)
E-mail: tetsu@eng.hokudai.ac.jp

K. Hase
Tokai Optical Co., Ltd. (Japan)

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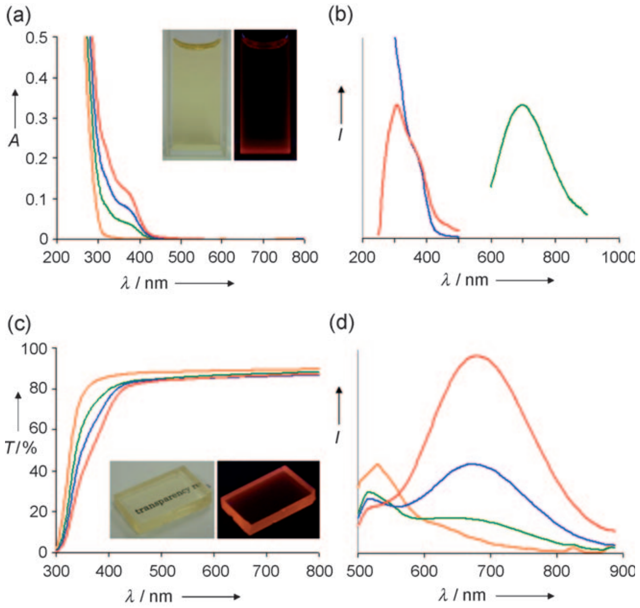

Figure 2. a) UV/Vis absorption spectra of AuNPs/PEMP generated with $t_s = 0$, 5, 10, and 15 min for orange, green, blue, and red curves, respectively; inset: photograph of AuNPs/PEMP with $t_s = 15$ min. b) UV/Vis absorption (blue), PL (green), and PL excitation (red) spectra of AuNPs/PEMP with $t_s = 15$ min. c) Transmittance and d) PL spectra of AuNPs/thiourethane resin (thickness: 1.3 mm) with $t_s = 0$, 5, 10, and 15 min for orange, green, blue, and red curves, respectively; inset: photograph of the AuNPs/thiourethane resin with $t_s = 15$ min under daylight (left) and under 365 nm UV irradiation (right).

electron microscopy (TEM) techniques because the NPs are smaller than the detection limit of TEM. However, the size of AuNPs/PEMP was expected to be less than 1 nm given the high angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) characterization of the AuNPs after transformation to a hybrid resin, as discussed below.[20,21] This size (< 1 nm) is smaller than that of AuNPs/6-MTAB, (1.3 ± 0.3) nm, reported previously.[15] The difference can be explained as arising from the discrepancy between the number of thiol groups in PEMP and 6-MTAB. Because PEMP has four -SH groups per molecule, protection of the sputtered Au atoms by PEMP is most likely more rapid than protection by 6-MTAB, which has only one -SH group per molecule.

AuNPs/PEMP exhibit photoluminescence at a wavelength of 690 nm, as shown in Figure 2b. The PL spectra are similar irrespective of t_s (Figure S2). This result also supports the constancy of the NP size for varying t_s. The PL peak wavelength for AuNPs/PEMP is shorter than that of AuNPs/6-MTAB, 770 nm.[15] This difference is understandable because PL from the AuNPs is sensitive to the particle size and shape, which are affected by the nature of the protecting agents.[22]

The UV/Vis transmittance spectra of AuNPs/thiourethane hybrid resins made from AuNPs/PEMP with a t_s between 5 and 15 min exhibit good transparency at wavelengths longer than 450 nm (Figure 2c). Similar to AuNPs/PEMP, the resins show no surface plasmon band and exhibit PL (Figure 2d). The PL peak wavelength (690 nm) and the increase in PL intensity as a function of t_s were not altered by the polymerization heating process at 130 °C, which was necessary to form the resins. The HAADF-STEM images of the hybrid thiourethane resin indicate that AuNPs of diameter less than 1 nm are well-dispersed in the resin (Figure S3). This result is consistent with the UV/Vis transmittance and the PL spectra described above.

Au sputtering into PEEL, which presents hydroxy groups, was carried out for $t_s = 3$ min. The size of the AuNPs immediately after sputtering (fresh AuNPs/PEEL) was estimated to be (2.1 ± 0.7) nm from the TEM image (Figure 3a), which is consistent with the slight appearance of a surface plasmon band at 520 nm in the UV/Vis absorption spectrum (Figure 3c). The difference in the size of the AuNPs/PEMP and fresh AuNPs/PEEL is attributed to the different coordination affinities of the thiol and hydroxy groups to gold surface. The interaction of the gold particles with the hydroxylated surface is weaker than with the thiolated surface, so that coalescence and aggregation of AuNPs on PEEL proceeds at a faster rate. In fact, the size of the AuNPs/PEEL after 65 days (matured AuNPs/PEEL) was (4.5 ± 3.4) nm, which is twice the size of freshly formed AuNPs (Figure 3b). This result was consistent with the absorption spectrum of matured AuNPs/PEEL, in which a surface plasmon absorption peak clearly appears at 520 nm (Figure 3c).

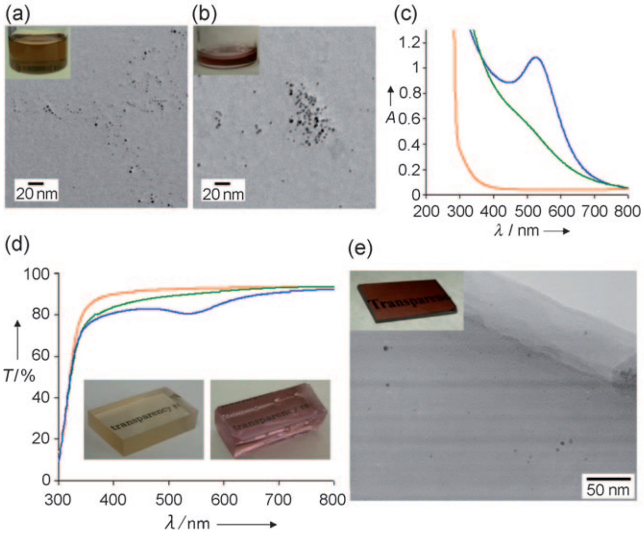

Figure 3. TEM images and photographs of a) fresh and b) matured AuNPs with $t_s = 3$ min; c) UV/Vis absorption spectra of (orange) PEEL, (green) fresh AuNPs, and (blue) matured AuNPs with $t_s = 3$ min; d) UV/Vis transmittance spectra of (orange) urethane, (green) fresh AuNPs/urethane, and (blue) matured AuNPs/urethane with $t_s = 3$ min (thickness: 1.3 mm); inset: photographs of fresh (left) and matured (right) AuNPs/urethane; e) TEM image and a photograph of AuNPs/urethane resin with $t_s = 30$ min.

Figure 3d shows the UV/Vis transmittance spectra of fresh and matured AuNPs/urethane hybrid resins, which were prepared by heat polymerization of fresh and matured AuNPs/PEEL, respectively, and *m*-XDI. These resins show

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good transparency, and their absorption properties are similar to the fresh and matured AuNPs/PEEL materials, respectively. Once the resin had formed, no further UV/vis spectral changes were detected, indicating that coalescence and aggregation of AuNPs in the solid matrix ceased. Figure 3e shows a TEM image of a fresh AuNPs/urethane resin with $t_s =$ 30 min. The TEM image confirms that AuNPs of size (3.2 ± 1.3) nm are well-dispersed in the urethane resin, consistent with the transparency of the resin.

In conclusion, we have presented a simple technique, matrix sputtering, for obtaining AuNPs/thiourethane and AuNPs/urethane hybrid resins with high transparency. AuNPs/thiourethane hybrid resins do not show surface plasmon absorption, but they do show luminescence at 690 nm. In contrast, AuNPs/urethane hybrid resins exhibit a surface plasmon absorption, the intensity of which can be tuned by changing the size of the AuNPs/PEEL by way of the maturation time before polymerization. This study demonstrates that the MS method may be utilized for the preparation of hybrid resins with various functional properties by controlling the interaction strength between the metal surface and the matrix material.

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