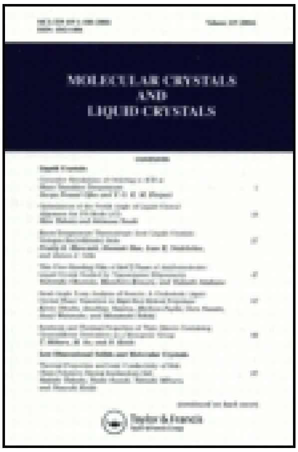

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Fabrication and Optical Properties of Gold Nanorod-Polymer Composite Films

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Fabrication and Optical Properties of Gold Nanorod-Polymer Composite Films

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Gold nanorods are fascinating nanomaterials for electro-optical applications in nanotechnology, but the basic drawbacks have been thermally unstable and the difficulty in incorporating into the film. In this study, we have developed a simple and highly-reproducible method for large-scale fabrication of composite films consisting of gold nanorods and an organic polymer. The film could be easily casted for more than $10 \times 10\text{-cm}^2$ area and the shape (that is, optical characteristic) of gold nanorods could withstand up to ca. 200°C. The composite film was also sensitive to the dielectric constant of the surrounding medium.

Keywords Composite film; gold nanorod; localized plasmon resonance; optical property; polymer

1. Introduction

One-dimensional metal nanostructures such as gold nanorods (AuNRs) and nanowires have been attracting much attention because of promising practical applications in electronic and optical devices [1]. A noteworthy characteristic of AuNRs is that they show unique optical properties depending on the size and the aspect ratio, as exemplified with a couple of plasmon bands corresponding to the longitudinal oscillation mode in the far-red to near-infrared region (SP_L band) and the transverse oscillation mode in the visible region (SP_T band) [2,3]. However, the basic problems of those materials are thermal instability and difficulty in incorporating into the organic (inorganic) films. From the practical point of view, large-scale fabrication of AuNR-polymer composite films with thermal stability and film homogeneity is primarily important.

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As to the composite films incorporating metal nanorods, some kinds of composite films consisting of metal nanorods and organic polymers have been reported [4–6]. However, those studies showed no distinct thermal properties, large-scale fabrication, and further sensing applications based on localized plasmon resonance (LPR).

In the present study, we have succeeded in the large-scale fabrication of the composite film consisting of AuNRs and an organic polymer. The film could be casted for more than 10 × 10-cm^2 area and the optical property of gold nanorods could withstand up to ca. 200°C. In addition, the composite film was sensitive to the dielectric constant of the surrounding medium.

2. Experimental

Gold Nanorods (AuNRs) were prepared in an aqueous solution containing large excess of cetyltrimethylammonium bromide by slightly modifying the method reported previously [7]. In order to disperse the resultant AuNRs in methy isobuthyl ketone (MIBK), they were further capped with a hydrophobic aminopolymer, making a AuNR-dispersed MIBK solution (5 wt%). COMPOCERAN (AC601, Arakawa Chemical In. Ltd., poly(methylmethacrylate) (PMMA) derivative) was used as a polymer matrix. This polymer has been prepared by graft co-polymerization of PMMA with alkoxysilyl groups, and has the characteristics of causing the sol-gel reaction among the alkoxysilyl groups above 120°C. Thus, the film of this polymer can encapsulate AuNRs by dispersed silica moieties. The MIBK solution of AuNRs and COMPOCERAN was simply spread on the surface of a glass plate (12 × 12-cm^2). The thickness of the film was 3–4 μm, and the content of AuNRs was 25 wt%, respectively. A transmission electron microscope (TEM: JEOL LEM-3200FSK) image and the extinction spectra (JASCO V-670 spectrophotometer) of the MIBK solution and the composite film fabricated on the glass plate are shown in Figure 1. Aspect ratios of AuNRs somewhat dispersed and the mean value was 8.5. The extinction spectrum of the MIBK solution showed a couple of plasmon band around 510 and 1300 nm (A). These bands showed somewhat broadening in the film (B), probably due to interparticle plasmon coupling. However, these results do not necessarily affect to the present study.

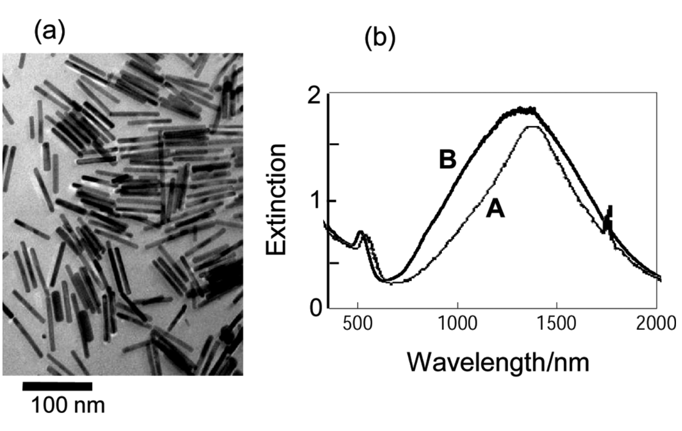

Figure 1. (a) TEM image of AuNRs. (b) Extinction spectra of AuNRs cast on the glass plate (A) and embedded in the polymer (COMPOCERAN) film (B).

3. Results and Discussion

The thermal stability of AuNRs is essentially important in their practical applications. However, AuNRs gradually change into spherical particles even in the colloidal solution at room temperature. In spite that we had capped AuNRs (core) with silica layer (shell), it could not keep their shapes above 150°C [8]. In this study, we have tried to utilize the thermosetting polymer (COMPOCERAN) as a matrix (see experimental section), intended for improving the heatproof property of AuNRs. As has been described in the experimental section, this polymer contains alkoxysilyl groups, and causes the sol-gel reaction among the alkoxysilyl groups above 120°C. Thus, the film of this polymer can encapsulate AuNRs by the dispersed silica moieties generated by the sol-gel reaction. Thus, the thermal stability of the AuNRs embedded in the polymer matrix will be expected.

In order to realize the above-described attempt, the composite was annealed at different temperatures intended for proceeding the sol-gel reaction. Figure 2 shows the comparison of thermal stabilities between the composite film (Fig. 2a) and the cast sample (AuNR alone, fabricated by casting the AuNR-MIBK solution on the glass plate) (Fig. 2b). In the composite film, the $\mathrm{SP_L}$ band appeared around 1300 nm, while that of the cast film shifted in longer wavelength region than 1400 nm, because of interparticle plasmon coupling effects owing to aggregation. It is clear that the $\mathrm{SP_L}$ band did not change appreciably up to 200°C in the composite film (Fig. 2a), while the cast sample showed appreciable spectral changes even around 100°C (Fig. 2b). The results strongly suggest that AuNRs are snugly embedded in the hard polymer matrix, by the generation of silica moieties by the sol-gel reaction.

Another important property of AuNRs is that the $\mathrm{SP_L}$ band is sensitive to the dielectric constant of the surrounding medium, so that AuNRs can be applied as a tool for localized plasmon resonance (LPR) sensing [9]. In the present composite film, we also investigated the spectral shifts of both plasmon bands ($\mathrm{SP_L}$ and $\mathrm{SP_T}$), as shown in Figure 3. The $\mathrm{SP_L}$ band showed no appreciable spectral shifts (Fig. 3a). In contrast, the $\mathrm{SP_L}$ band showed clear spectral shifts, depending on the local field of solvent expressed by $(n^2-1)/(n^2+2)$, as shown in Figures 3b and 3c, though some fluctuation could not be avoided. The results clearly indicate that the AuNRs incorporated in the polymer film can sense the surrounding medium, and thus can be applicable to LPR sensing.

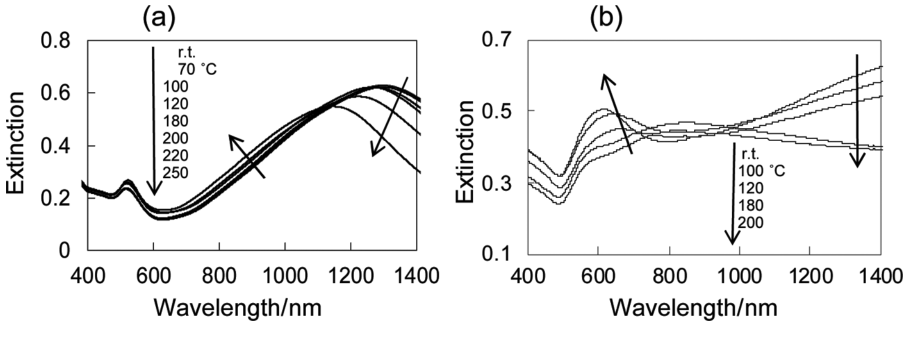

Figure 2. Effects of annealing on the optical properties of AuNR-polymer composite film. Annealing temperatures: (a) r.t., 70, 100, 120, 180, 200, 220, 250°C; (b) r.t., 100, 120, 180, 200°C.

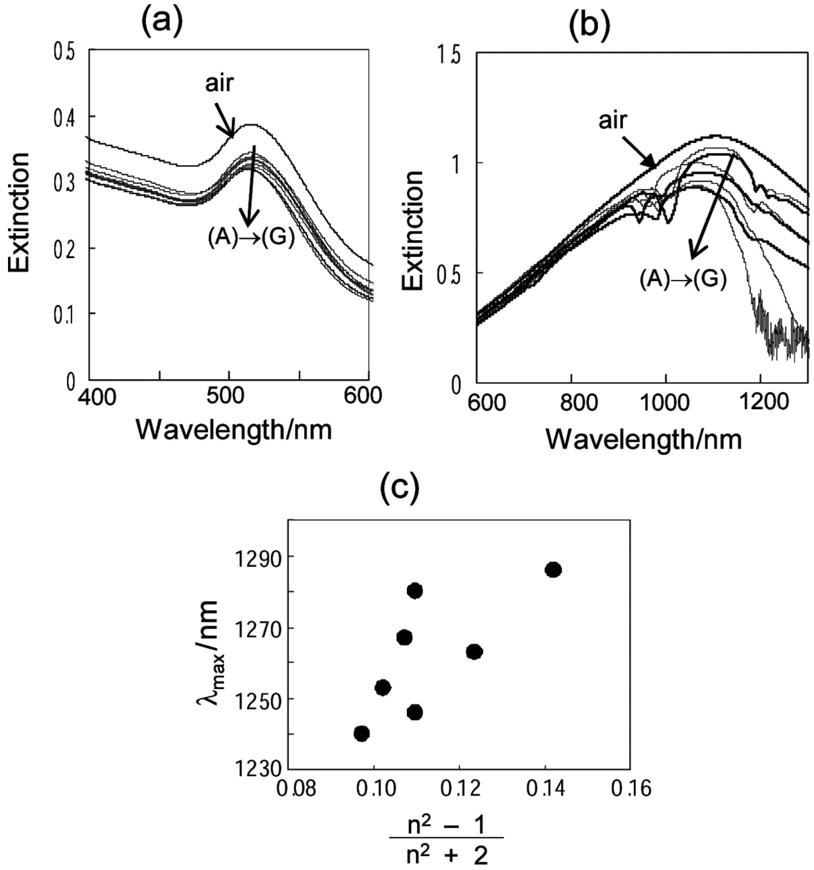

Figure 3. Extinction spectra of AuNR-polymer film in various solvents: plasmon bands of transverse (a) and longitudinal (b) modes. The relationship between peak positions of longitudinal bands and refractive indices of solvents (c). Solvents: (A) hexane, (B) cyclohexane, (C) acetonitrile, (D) toluene, (E) ethylacetate, (F) ethanol, (G) water.

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