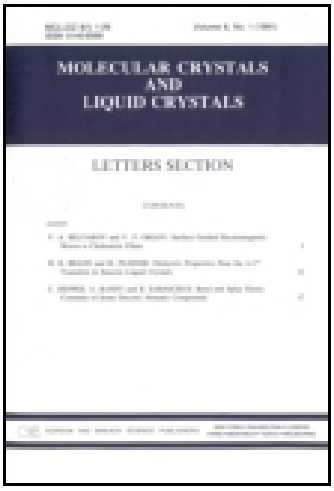

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Effects of Strong Magnetic Processing on Orientation and Photoproperties of Gold Nanowires on a Substrate

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We have investigated the effect of magnetic processing on orientation of gold nanowires (AuNWs) using a strong magnetic field. The results in the extinction spectra due to surface plasmon and SEM images in the presence of magnetic processing (10 T) showed that the long axes of AuNWs in side-by-side aggregation of AuNWs were oriented perpendicular to the magnetic field. On the other hand, in the absence of magnetic processing, random orientation of the side-by-side aggregation of AuNWs was observed. The magnetic orientation of the aggregation is most likely attributable to the anisotropy in the magnetic susceptibilities of the pristine AuNWs.

Keywords gold nanowire; surface plasmon; side-by-side aggregation; magnetic orientation; anisotropy; magnetic susceptibilities

Introduction

The application of strong magnetic fields on materials induces strong magnetic field effects. This can lead to the creation of highly functional nanomaterials with new properties, which result from the new interfaces or nanostructures formed by the strong magnetic fields [1].

We have reported the effects of magnetic processing on the morphological, electrochemical, and photoelectrochemical properties of electrodes modified with nanoclusters of phenothiazine-C_{60} systems [2–4]. We have also reported that the magnetic orientation of single-walled carbon nanotubes or their composites using polymer wrapping [5] and nanowires consisting of regioregular poly(3-alkylthiophene) (poly(3-hexylthiophene) [6] and poly(3-butylthiophene) [7]).

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Recently, we reported the effects of magnetic processing on the orientation and the organization of gold nanorod (AuNR) / poly(styrenesulfonate) (PSS) composites [8] or AuNRs with three different the aspect ratios (ARs : the ratio of the longitudinal-to-transverse length) [l-AuNR (AR) = 8.3), m-AuNR (AR = 5.0), and s-AuNR (AR = 2.5)] [9] on a substrate. The magnetic processing resulted in magnetic organization via the side-by-side aggregation of AuNR/PSS composites or AuNRs and the long axes of l- and m-AuNRs oriented parallel to the magnetic field. However, magnetic orientation of s-AuNR was observed. The magnetic orientation is most likely because of the anisotropy in the magnetic susceptibilities of the adsorbed hexadecyltrimethylammonium bromide (CTAB) on AuNRs [8,9]. On the other hand, when the magnetic processing was performed using the dilute concentration of aqueous solutions of m-AuNR, the opposite magnetic orientation, that the long axes of m-AuNRs were oriented perpendicular to the magnetic field, was obtained. The magnetic orientation is probably responsible for the magnetic property of the pristine m-AuNR [9].

However, the effect of magnetic processing on orientation and organization of gold nanowires (AuNWs), which have AR up to 10, have not yet been examined. In this study, we examined the magnetic processing on magnetic orientation and organization of AuNWs.

Experimental

AuNWs were prepared with nitrogen bubbling and without Cu(I) using the previously reported method [10]. The AuNWs were supplied by Dai Nippon Toryo Co. Ltd. (Osaka, Japan) and Mitsubishi Materials Co. Ltd. (Tokyo, Japan). The AuNWs in aqueous solution contain an excess amount of CTAB, which serves as a stabilizing agent. Centrifugation (3,000 rpm, 5 min) of the aqueous AuNWs solution was carried out twice to remove the excess CTAB.

Magnetic processing of the samples was performed using a superconducting magnet with a vertical magnetic field (B_{max} = 10 T) [4,6–9] (Oxford Ltd., S10-76.5 (60 RT)-B) or a superconducting magnet with a horizontal magnetic field (B_{max} = 10 T) (Oxford Ltd., 14Tr70) [11]. For comparison, a sample was placed outside the tube. The temperatures of the samples in the absence and the presence of the magnetic field were kept constant using a temperature regulated circulating water-bath system (NESLAB RTE-8, Thermo Scientific, Waltham, MA).

Magnetic processing of the samples was performed using the component of the magnetic field parallel to the surface of the glass or ITO plate in magnet with a vertical or horizontal magnetic field, respectively. The glass or ITO plate was immersed in an aqueous solution of AuNW (concentration: Extiction = 0.3 at 520 nm). After evaporating water at 323 K at atmospheric pressure, SEM measurement of the sample on the ITO plates, and extinction spectra or polarized extinction spectra measurements of the samples on the glass plates were performed. SEM and TEM images were obtained using a Hitachi S-5000 microscope images and a JEOL JEM-2010 TEM, respectively.

Results and Discussion

One surface plasmon (SP) band of AuNW was observed at 528 nm in the aqueous solution at wavelength range (300–1750 nm). In contrast, the AuNRs (ARs < 8.4) had a couple of localized SP bands, that one SP band corresponding to the transverse oscillation mode locates at 520 nm, while the another corresponding to the longitudinal oscillation mode between near-infrared region, that are dependent on the AR ratios [8, 9, 12]. These results

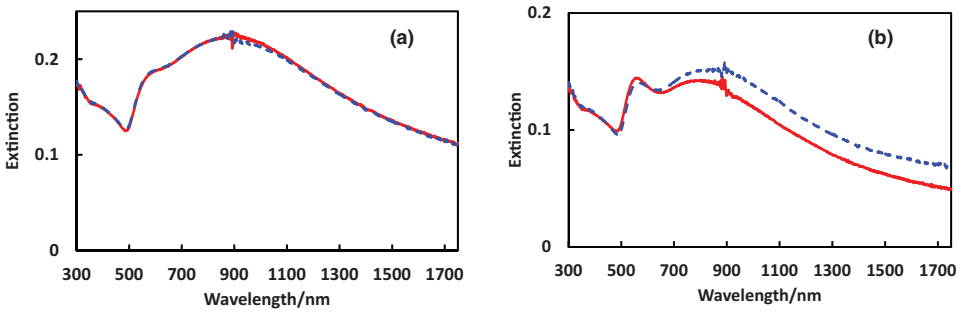

Figure 1. Polarized extinction spectra for AuNWs in (a) the absence of magnetic processing and (b) the presence of magnetic processing (10 T) using a superconducting magnet with a vertical magnetic field at 323 K with the magnetic field directed horizontally to the surface of the glass plate. In the absence of magnetic processing, both polarization parallel (red solid line) and perpendicular (blue dashed line) to gravity were investigated. In the presence of magnetic processing (10 T), the polarization direction of the light is parallel B(//); red solid line) or perpendicular (B(⊥); blue dashed line) to the applied magnetic-field direction on glass plate.

suggested that the SP band corresponding to the longitudinal oscillation mode in AuNWs locates at far-red region up to1750 nm. In TEM images of AuNWs, a number of AuNWs (AR>10) were observed.

The broaden extinction bands due to SP band in the near-infrared region (700−1750 nm) were clearly observed in extinction spectra of glass plates (Fig. 1). The result indicates that the SP bands corresponding to the longitudinal oscillation mode of the AuNWs were remarkably blue-shifted due to side-by-side aggregation of the AuNWs, as compared with those in aqueous solutions [8, 9, 13–17].

Magnetic processing of AuNWs was examined using the magnetic field directed horizontally to the surface with a vertical magnetic field (10 T) by polarized extinction measurements. In the extinction spectrum of the AuNWs on the glass plate, two SP bands (580 (shoulder) and 882 nm) corresponding to the transverse and the longitudinal modes were observed in the absence of magnetic processing (Fig. 1(a)). In the extinction spectrum of the AuNWs on the glass plate, two SP bands (554 and 800 nm) corresponding to the transverse and the longitudinal modes were observed in the presence of magnetic processing (10 T) (Fig. 1(b)). The extinction spectra of the AuNWs in the presence of magnetic processing are different from those in the absence of magnetic processing. In the presence of magnetic processing, the peaks of the SP band corresponding to the longitudinal mode were dramatically blue-shifted and those to the transverse mode were red-shifted. The results strongly indicate that large side-by-side aggregations of the AuNWs were generated by the magnetic processing as compared with those in the absence of magnetic processing [8, 9].

The two SP bands of AuNWs were approximately the same for both polarization directions (parallel and perpendicular) in the absence of magnetic processing (Fig. 1(a)). In contrast, while the extinction band of the longitudinal SP (700–1750 nm) of the AuNWs on the glass plate with the polarization direction perpendicular to the magnetic field (B(⊥)) was larger than that with the polarization direction parallel to the magnetic field (B(//)) after magnetic processing (10 T). The extinction band of the transverse SP (500–600 nm) with the polarization direction perpendicular to the magnetic field (B(⊥)) was appreciably weaker than that with the polarization direction parallel to the magnetic field (B(//)).The results strongly indicate that the long axes of in side-by-side aggregation of AuNWs were oriented perpendicular to the magnetic field.

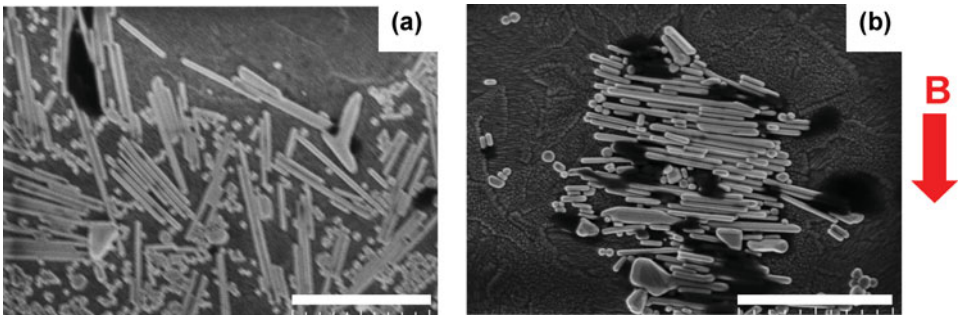

Figure 2. SEM images of AuNWs on ITO plates in (a) the absence and (b) presence of magnetic processing (10 T) using a superconducting magnet with a vertical magnetic field. (scale bar = 1 μm).

Figure 2 shows SEM images of AuNWs on ITO plates in (a) the absence and (b) presence of magnetic processing (10 T). In the absence of magnetic processing, random orientation of the AuNWs was observed (Fig. 2(a)). By contrast, magnetic orientation of AuNWs was observed in the presence of magnetic processing (10 T). The long axes of AuNWs in the large side-by-side aggregates of them were oriented perpendicular to the magnetic field (Fig. 2(b)). These results seen in the SEM images are in fair agreement with those of the polarized extinction spectra (Fig. 1). All of these experimental results strongly indicate the formation of side-by-side aggregates of many AuNWs, which the long axes of the AuNWs are oriented perpendicular to the magnetic field used for processing. Same magnetic orientation of side-by-side aggregates of AuNWs were observed in the presence of magnetic processing using a superconducting magnet with a horizontal magnetic field (10 T).

Magnetic orientation of AuNWs is similar to those in the magnetic processing using dilute concentration of aqueous solutions of m-AuNR in previous paper [9]. Therefore, the magnetic orientation of side-by-side aggregates of AuNWs in this paper is most likely attributable to the anisotropy in the magnetic susceptibilities of the pristine AuNWs [9, 18–20]. From comparison of magnetic orientation of side-by-side aggregates between AuNW and AuNR [9], the effect of AR on the magnetic orientation of anisotropic gold nanoparticle (AuNWs or AuNR) are clearly observed. In other words, the origin of magnetic orientation probably switches from the anisotropy in the magnetic susceptibilities of the adsorbed CTAB to that of the gold nanoparticle with increasing AR from AuNR to AuNW. Further investigations on the side-by-side aggregation and orientation of the AuNWs on a substrate using gradient fields of strong magnetic fields are now in progress.

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