Alignment of Gold Nanorods in Directionally Solidified Polymer Blends

Hiroataka Ejima^{1,2}, Ayako Sakurai², and Naoko Yoshie^{2*}

¹ Department of Materials Engineering, The University of Tokyo,
7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan

² Institute of Industrial Science, The University of Tokyo,
4-6-1 Komaba, Meguro-ku, Tokyo 153-8505, Japan

*yoshie@iis.u-tokyo.ac.jp

We studied the alignment of gold nanorods (Au NRs) in polymer blends that were directionally solidified in the crystallizable organic solvent trichlorobenzene (TCB). The polymer blends/Au NRs were dissolved or dispersed in TCB at 80 °C between two glass plates. By cooling the sample, the polymer blends and Au NRs were directionally solidified as the liquid TCB transformed into large single crystals. With poly(3-hexylthiophene-2,5-diyl)/polyethylene glycol (P3HT/PEG) used as the polymer blend pair, PEG-modified Au NRs predominantly localized inside the PEG domains of the solidified films. In contrast, with a P3HT/poly(2-vinylpyridine) blend, PEG-modified Au NRs mostly localized at the interface between the polymers. These results show that directional solidification in crystallizable organic solvents is an effective one-step process for the alignment of Au NRs in polymer matrices.

Keywords: Gold nanorods, Polymer blends, Directional solidification, Poly(3-hexylthiophene)

1. Introduction

Gold nanoparticles (Au NPs) are one of the most frequently used building blocks in nanotechnology owing to their facile synthesis, unique surface plasmon resonance (SPR)-derived properties, and potential applications in biomedical and optoelectronic fields [1–3]. Gold nanorods (Au NRs) are a subclass of Au NPs and of particular interest owing to their anisotropic properties [4,5]. Mulvaney et al. reported that the localized SPR of Au NRs is influenced by the orientation of individual Au NRs [6]. Thus, a key step between the synthesis and practical application of the Au NRs is their alignment within solid matrices such as polymers.

Block copolymers are suitable matrices, as they form microphase-separated domains with sizes comparable to the size of Au NRs (tens of nanometers). A significant effort has been devoted to the self-assembly of Au NRs through block-copolymer-templating methods [7–10]. Liu et al. used the following three steps to align Au NRs on

block copolymer templates: (i) Approximately 100 nm-thick polystyrene-*b*-poly(methyl methacrylate) (PS-*b*-PMMA) block copolymer films were prepared by spin coating on silicon wafers [9]. The silicon substrates were pre-modified with a neutral PS-*r*-PMMA brush to vertically align the lamellae [11]. (ii) The block copolymer films were exposed to air plasma. As PMMA is etched faster than the PS phase in air plasma, this process created nanochannels in the block copolymer thin films. (iii) An aqueous solution of Au NRs was then spin-coated on the etched block copolymer template. The Au NRs concentrated in the grooves of the templates; this concentration was driven by the evaporation-induced capillary force.

Although the quality of the alignment of Au NRs in block-copolymer-templated films is impressive, such multistep processes consisting of etching and filling are routinely required. Furthermore, block copolymers are usually synthesized by living anionic polymerization, which requires sophisticated experimental set-ups. The monomers

that are amenable to living anionic polymerization are limited to those without functional groups, as functional groups can react with the propagating active-end anions to terminate the living polymerization.

Recently, we developed a facile one-step method to obtain lamellar patterns with periodicities from several tens to hundreds of nanometers from polymer blends instead of block copolymers [12–16]. In this method, rapid freezing of the structure induced by the directional solidification of crystallizable organic solvents prevents the phase separation of the polymer blends from extending to the micrometer scale. As polymer blends are simply a mixture of at least two polymers, their preparation is much easier than that of block copolymers.

Here, we studied the alignment of Au NRs in directionally solidifying polymer blends. We used 1,3,5-trichlorobenzene (TCB) as a crystallizable organic solvent owing to its low melting temperature (T_m). The polymers PS, poly(2-vinylpyridine) (P2VP), poly(3-dodecylthiophene-2,5-diyl) (P3DDT) and polyethylene glycol (PEG) were blended with poly(3-hexylthiophene-2,5-diyl) (P3HT) (Fig. 1). We investigated the effect of different blend combinations on the alignment and localization of the Au NRs.

Fig. 1. Chemical structures of the crystallizable organic solvent and polymers used in this study.

2. Experimental

2.1. Materials

P3HT ($M_n = 55 \text{ kg mol}^{-1}$, $M_w/M_n = 2.3$), P3DDT ($M_n = 102 \text{ kg mol}^{-1}$, $M_w/M_n = 2.1$), PEG ($M_n = 16 \text{ kg mol}^{-1}$, $M_w/M_n = 1.2$) and gold(III) chloride trihydrate were obtained from Sigma–Aldrich Co. (St. Louis, USA). L-Ascorbic acid was obtained from TCI Chemicals (Tokyo, Japan). PS ($M_n = 30 \text{ kg mol}^{-1}$, $M_w/M_n = 1.1$) was purchased from Showa Denko K.K. (Tokyo, Japan). Thiol-terminated PEG (PEG-SH; $M_n = 5.1 \text{ kg mol}^{-1}$) was obtained from NOF Corp. (Tokyo, Japan). P2VP ($M_n = 4.8 \text{ kg}$

mol^{-1} , $M_w/M_n = 1.1$) and hexadecyltrimethylammonium bromide (CTAB) were purchased from Fluka (Buchs, Switzerland). Sodium tetrahydroborate (NaBH_4), chloroform (CHCl_3), silver nitrate (AgNO_3) and gelatin were obtained from Wako Chemical Co. (Osaka, Japan). All these chemicals were used as received. TCB was purchased from Wako Chemical Co. (Osaka, Japan) and was purified by sublimation before use. Glass slides and silicon-coated glass slides ($18 \times 18 \text{ mm}$) were purchased from Matsunami Glass Ind., Ltd. (Osaka, Japan).

2.2. Synthesis of PEG-capped Au NRs

CTAB-capped Au NRs were synthesized by a slightly modified seed-mediated method [17], and then the ligand (CTAB) was exchanged with PEG-SH. Typically, an aqueous solution of HAuCl_4 (5.0 mL, 0.5 mM) was added to a solution of CTAB (5.0 mL, 0.2 M) in a glass vial. An ice-cold aqueous solution of NaBH_4 (0.6 mL, 0.01 M) was added to the solution under stirring (600 rpm) all at once, and stirring was continued for 2 min. This seed solution was kept at 25°C for future use.

A solution of CTAB (20 mL, 0.2 M), AgNO_3 (2.0 mL, 4.0 mM), L-ascorbic acid (280 μL , 79 mM), and 48 μL of the seed solution prepared earlier were added in this order to a glass vial and then stirred for 90 min. The obtained Au NRs were washed twice by centrifugation (10,000 g, 30 min) and redispersed in deionized (DI) water.

Ligand exchange was performed by adding 1 mL of an aqueous dispersion of CTAB-capped Au NRs to 3 mL of an aqueous PEG-SH solution (33 g L^{-1}) under constant stirring. The dispersion was stirred overnight then centrifuged to discard the supernatant. The solvent was changed from DI water to tetrahydrofuran and then to CHCl_3 through centrifugation/redispersion cycles.

2.3. Directional solidification

Glass substrates were first washed with DI water under sonication and then immersed in piranha solution (3/1 v/v mixture of 96% sulfuric acid and 30% H_2O_2) for 1 h to remove organic impurities. (CAUTION: Piranha solution can react violently with organic compounds and should be handled with extreme care.) To completely remove the piranha solution, the glass slides were rinsed with DI water, sonicated in DI water, and then dried in air. A polymer blend solution in chloroform (0.5 wt% of polymers in total) and a CHCl_3 dispersion of PEG-capped Au NRs (the absorbance at 525 nm was 0.5)

were spin-coated onto the washed glass slide at 2000 rpm for 20 s. Fine powders of TCB (ca. 5 mg) were scattered evenly on the spin-coated film of the polymer blend/Au NRs. This sample was covered with a silicone-coated glass slide to prevent extensive sublimation of the TCB during heating. This sandwiched sample (glass/polymer/Au NR/TCB/silicone-coated glass) was placed on a hotplate preheated to 80 °C and held there for approximately 20 s to melt the TCB. The sample was lifted with tweezers to initiate the directional solidification. The sandwiched sample was disassembled, and the non-silicone-coated glass substrate containing the polymer film was placed in a vacuum chamber and kept at room temperature for 2 h to remove TCB by sublimation.

2.4. Characterization

Height and phase images of directionally solidified films were obtained with an atomic force microscopy (AFM, Nanoscope, SII Nano Technology, Inc.) in dynamic force mode with a self-sensing microcantilever (PRC-DF40P). UV-Vis absorption spectra were obtained on a HITACHI U-3010 spectrophotometer at room temperature. Contact angles were measured (DMs-401, Kyowa Interface Science Co.) 10 s after 2 μ L drops of water or CH₂I₂ were dispensed onto the surface of the film.

For transmission electron microscopy (TEM) observations (JEM-2010, JEOL), the sample was first coated with a carbon film (ca. 40 nm) with a vacuum evaporator (VE-2012, Vacuum Device). Gelatin was dissolved in water (50 wt%) at 60 °C and then cast over the carbon-coated film. After the gelatin had hardened, the whole sample (gelatin-carbon-polymers/AuNRs) was peeled off from the glass substrate and floated on a stationary water surface at room temperature so that the polymers/AuNRs-side faced toward the air side. After the gelatin had dissolved in water, the sample was taken up on a copper grid and placed in a vacuum chamber for 24 h to remove residual water. The dried sample was kept inside the vacuum chamber until TEM observations.

3. Results and discussion

3.1. Synthesis of Au NRs

The seed-mediated synthesis of Au NRs is very sensitive to impurities in the CTAB surfactant [18]. We successfully obtained the Au NRs with the CTAB supplied from Fluka. TEM observations revealed that the Au NRs possessed longitudinal/transverse axes of 40/10 nm (Fig. 2a).

In the UV-Vis spectrum (Fig. 2b), the longitudinal peak (λ) was observed at 800 nm, which is consistent with the λ estimated from the aspect ratio and the discrete dipole approximation [19].

Structural changes of Au NRs have been observed at high temperatures. We initially tried to use hexamethylbenzene ($T_m = 164$ °C) [12–15] as a crystallizable organic solvent for alignment of the Au NR, but the T_m was too high and the Au NRs deformed. Mulvaney et al. [20] reported that Au NRs could be completely transformed into spherical particles in less than 1 h at 250 °C, which is much lower than the T_m of bulk Au (1064 °C). Thus, we used TCB as a crystallizable organic solvent, which has a relatively low T_m (63 °C) [16]. Because the as-prepared CTAB-capped Au NRs were not dispersible in TCB, we exchanged the capping agent from CTAB to PEG.

Fig. 2. (a) TEM image and (b) UV-Vis spectrum of the Au NRs.

3.2. Directional solidification in TCB

We have previously reported the formation of nanopatterns with polymer blends (P3HT/P3DDT and P3HT/PS) through directional solidification in TCB [16]: we used grazing-incidence wide-angle X-ray diffraction and polarized UV-Vis absorption spectroscopy to show that the P3HT crystalline lamellae were oriented edge-on in the nanopatterned thin films. For this paper, we prepared and tested two additional blend pairs, namely P3HT/P2VP and P3HT/PEG. Above the T_m (63 °C), TCB melted and served as a solvent to dissolve these polymers. When this solution was cooled to below the T_m , TCB rapidly crystallized directionally along its c -axis. The polymer blends were subsequently solidified on TCB crystals. By selectively removing the TCB from the polymers by sublimation, lamellar patterns were left on the glass substrates (Fig. 3).

These nanostructures were still obtained when a third component, PEG-capped Au NRs, was present (Fig. 4). However, some Au NR aggregates were observed after P3HT/P3DDT or P3HT/PS blends were used as matrix polymers (Fig. 4a,b); we attribute this aggregation to the PEG-capped Au NRs preferentially interacting with other PEG-

capped Au NRs rather than with the polymer matrices. In contrast, PEG-capped Au NRs were well-dispersed in the directionally solidified P3HT/P2VP and P3HT/PEG blends (Fig. 4c,d). Thus, these two blends were subsequently used as suitable matrix polymers for aligning the Au NRs. Interestingly, most PEG-capped Au NRs were localized inside the PEG domains in the P3HT/PEG films and at the interface in the P3HT/P2VP films.

Fig. 3. AFM images (top: phase, bottom: height) of directionally solidified (a) P3HT/P2VP (8:2, w/w) and (b) P3HT/PEG (8:2). The directions of solidification are indicated by arrows in the height images.

Fig. 4. TEM images of Au NRs within directionally solidified (a) P3HT/P3DDT (8:2), (b) P3HT/PS (8:2), (c) P3HT/P2VP (8:2) and (d) P3HT/PEG (8:2). The directions of the polymer solidification are indicated by arrows.

3.3. Localization of the Au NRs in the polymer blend films

To investigate the localization of the Au NRs in the polymer blends, we prepared spin-coated films of the AuNRs and the polymer blends (Fig. 5). No

contrast was evident in the TEM image of P3HT/P3DDT (Fig. 5a), which suggests that P3HT/P3DDT is a miscible pair owing to their similar chemical structures. For other blend pairs, spherical domains were formed by phase separation (Fig. 5b,c,d), corresponding to either PS, P2VP or PEG domains: in these films, the localization of the PEG-capped Au NRs were markedly different. The Au NRs were inside the P3HT domains in P3HT/PS (Fig. 5b), at the interfaces of P3HT/P2VP (Fig. 5c) and inside the PEG domains in P3HT/PEG (Fig. 5d).

Fig. 5. TEM images of Au NRs spin-coated with (a) P3HT/P3DDT (8:2), (b) P3HT/PS (8:2), (c) P3HT/P2VP (8:2) and (d) P3HT/PEG (8:2).

To investigate the difference in localization, the surface free energy (γ) of each polymer was estimated by measuring the contact angles. Table 1 shows the static contact angles of water and diiodomethane (CH_2I_2) on each polymer surface used in this study. The γ values of each polymer were calculated based on the Owens–Wendt equation, which divides γ into the dispersive (γ^d) and polar surface free energy (γ^p) [21], and are listed in Table 2.

$$\gamma_L(1 + \cos \theta) = 2\sqrt{\gamma^d \gamma_L^d} + 2\sqrt{\gamma^p \gamma_L^p} \quad (1)$$

where θ is the measured contact angle of a liquid on the surface of the polymers and γ_L is the surface tension of the liquid. We then calculated the interfacial energy between the two polymers used in the blend (polymers A and B ($\gamma_{A/B}$)) with the following equation:

$$\gamma_{A/B} = \gamma_A + \gamma_B - 2\sqrt{\gamma_A^d \gamma_B^d} - 2\sqrt{\gamma_A^p \gamma_B^p} \quad (2)$$

where γ_A and γ_B are the surface free energies of polymers A and B, respectively (Table 3).

Based on these calculations, we prepared a schematic illustration of the localization of Au NRs

Table 1. Static water and CH₂I₂ contact angles on the polymer films.

Polymers	Water contact angle (°)	CH ₂ I ₂ contact angle (°)
P3HT	105.7	56.5
P3DDT	115.5	58.1
PS	86.1	21.2
P2VP	46.8	8.8

Table 2. Surface free energies of the polymers.

Polymers	γ^d (mJ m ⁻²)	γ^p (mJ m ⁻²)	γ (mJ m ⁻²)
P3HT	31.3	0.0	31.3
P3DDT	26.9	0.0	26.9
PS	46.5	1.0	47.5
P2VP	41.9	19.0	60.9
PEG	29.3 ^{a)}	19.0 ^{a)}	48.3 ^{a)}

^{a)} These values are adopted from Ref. [22].

Table 3. Interfacial energies of the polymer pairs.

Polymer A/B	γ^d (mJ m ⁻²)
P3HT/P3DDT	0.17
P3HT/PS	2.50
P3HT/P2VP	19.8
P3HT/PEG	19.0
PEG/P2VP	1.12
PEG/PS	13.3
PEG/P3DDT	19.1

in the polymer blends (Fig. 6). The interfacial energy of P3HT/P2VP (19.8 mJ m⁻²) was the largest among the calculated values. Thus, the PEG-capped Au NRs preferentially localized at the interfaces of P3HT/P2VP to decrease the contact area between P3HT and P2VP (Fig. 6a). In the P3HT/PEG blend, PEG-capped Au NRs were well-dispersed in the PEG domains (Fig. 6b).

Fig. 6. Schematic illustration of the localized PEG-capped Au NRs in (a) P3HT/P2VP and (b) P3HT/PEG with interfacial energy values.

3.4. Orientation of the Au NRs in the polymer blend films

The angle distribution of the Au NRs, whereby we define the direction parallel to the lamella as $\theta = 0^\circ$, is shown in Fig. 7. More than 60% of the Au NRs in the P3HT/P2VP film were oriented in the range of $\theta = 0-10^\circ$, whereas only 30% of the Au NRs in

the P3HT/PEG films were oriented in the same angle range. In the P3HT/PEG films, the Au NRs oriented to some extent under directional flow, but little confinement effect led to a low degree of orientation, as the width of the PEG domains in the P3HT/PEG films were larger than the length of the Au NRs. Better orientation was achieved by the geometrical confinement effect caused by the localization of Au NRs at the interface in the P3HT/P2VP films. This result indicates that the choice of polymer blends is an important factor for the effective ordering of Au NRs.

Fig. 7. Histograms showing angle distribution of Au NRs in (a) P3HT/P2VP (8:2) and (b) P3HT/PEG (8:2) films.

4. Conclusion

In this study, Au NRs were aligned in polymer blend films through a rapid directional solidification in the crystallizable organic solvent TCB. TCB is a relatively inexpensive chemical that can easily be removed by sublimation under vacuum. The equipment required to carry out this method is common and accessible in a standard laboratory. Thus, only the careful choice of the components of the polymer blend is required to control the localization of Au NRs. This technique could be widely used to obtain polymer composite films containing oriented Au NRs.

Acknowledgement

This work was partly supported by a Grant-in-Aid for Scientific Research (No. 25600023) from the Japan Society for the Promotion of Science.

References

1. R. Sardar, A. M. Funston, P. Mulvaney, and R. W. Murray, *Langmuir*, **25** (2009) 13840.
2. C. Y. Yeh, B. C. Creran, and V. M. Rotello, *Nanoscale*, **4** (2012) 1871.
3. C. J. Murphy, A. M. Gole, J. W. Stone, P. N. Sisco, A. M. Alkilany, E. C. Goldsmith, and S. C. Baxter, *Acc. Chem. Res.*, **41** (2008) 1721.
4. H. Chen, L. Shao, Q. Li, and J. Wang, *Chem. Soc. Rev.*, **42** (2013) 2679.
5. S. E. Lohse and C. J. Murphy, *Chem. Mater.*, **25** (2013) 1250.
6. A. M. Funston, C. Novo, T. J. Davis, and P. Mulvaney, *Nano Lett.*, **9** (2009) 1651.

7. R. D. Deshmukh, Y. Liu, and R. J. Composto, *Nano Lett.*, **7** (2007) 3662.
8. D. Nepal, M. S. Onses, K. Park, M. Jespersen, C. J. Thode, P. F. Nealey, and R. A. Vaia, *ACS Nano*, **6** (2012) 5693.
9. Z. Liu, H. Huang, and T. He, *Small*, **9** (2013) 505.
10. Q. Tong, E. W. Malachosky, J. Raybin, P. Guyot-Sionnest, and S. J. Sibener, *J. Phys. Chem. C*, **118** (2014) 19259.
11. P. Mansky, Y. Liu, E. Huang, T. P. Russell, and C. Hawker, *Science*, **275** (1997) 1458.
12. H. Ejima, J. E. Itako, K. Ishida, and N. Yoshie, *Macromolecules*, **40** (2007) 6445.
13. S. Kodama, X. Zhang, and N. Yoshie, *Colloid Polym. Sci.*, **293** (2015) 2165.
14. X. Zhang, H. Ejima, and N. Yoshie, *Polym. J.*, **47** (2015) 498.
15. X. Zhang, H. Ejima, and N. Yoshie, *Macromol. Rapid Commun.*, **36** (2015) 1664.
16. H. Ejima, K. Ogita, M. Yamamoto, S. Sasaki, T. Hikima, M. Takata, and N. Yoshie, *Chem. Lett.*, **45** (2016) 604.
17. T. K. Sau and C. J. Murphy, *Langmuir*, **20** (2004) 6414.
18. D. K. Smith and B. A. Korgel, *Langmuir*, **24** (2008) 644.
19. P. K. Jain, K. S. Lee, I. H. El-Sayed, and M. A. El-Sayed, *J. Phys. Chem. B*, **110** (2006) 7238.
20. H. Petrova, J. P. Juste, I. Pastoriza-Santos, G. V. Hartland, L. M. Liz-Marzán, and P. Mulvaney, *Phys. Chem. Chem. Phys.*, **8** (2006) 814.
21. D. K. Owens and R. C. Wendt, *J. Appl. Polym. Sci.*, **13** (1969) 1741.
22. S. Nuriel, L. Liu, A. H. Barber, and H. D. Wagner, *Chem. Phys. Lett.*, **404** (2005) 263.