End-to-end Assemblies of Gold Nanorods Adsorbed on a Glass Substrate Modified with Polyanion Polymers

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Phosphatidylcholine-passivated gold nanorods (NRs) adsorbed on polyanion-modified glass substrates. The NRs on glass substrates formed end-to-end assemblies showing red-shifted and broaden longitudinal surface plasmon (SP) bands. Addition of aminohexanethiol (AHT) induced dumping of SP bands but increased the density of NRs on glass surfaces. Thiol groups of AHT were effective to change the properties of NR assemblies on glass surfaces.

Gold nanorods (NRs) are rod-shaped gold nanoparticles that present extraordinary spectroscopic characteristics. That is, NRs show two surface plasmon bands; one in the visible region and another in the near infrared (near-IR) region[1] (see Supporting Information). The visible band is assigned to transverse SP oscillation, and the near-IR band is assigned to longitudinal SP oscillation, which can be tunable depending on the shapes of the NRs. Longitudinal SP bands are very sensitive to surroundings and aggregation.[1,2] Thus, they are advantageous to monitoring assembling (aggregation) of NRs, which have already been reported using linker molecules.[3,4] Biotin–avidin interaction[3] and α,ω-alkanedithiol[4] were useful to realize end-to-end assembled NRs.[3]

In previous papers, we deposited NRs on a glass substrate using electrostatic interaction[5] and transfer from liquid–liquid interfaces;[6] however, in both cases, density and alignment of NRs could not be controlled. In this study, NRs were deposited on a glass substrate through electrostatic interaction between phosphatidylcholine (PC)-passivated NRs and polyanion-modified surfaces. Alignment of the PC-passivated NRs on a glass surface is also discussed.

NRs, prepared by a modification of our previously reported method,[6] were supplied by Mitsubishi Materials Co., Ltd. Some of the precipitated hexadecyltrimethylammonium bromide (CTAB) was removed using a membrane filter (pore size, 0.8 μm). Initial zeta potential of NRs was +50 mV, which originated from the CTAB bilayer on the NR surfaces. The residual CTAB in the NR solution (20 mL) was extracted into 10 mL of a chloroform solution PC (10 mg/mL; from egg yolk; Nacalai Tesque). After repeating the extraction procedures a further two times, NRs passivated PC layers were obtained.[7] The NR-solution was centrifuged once, and then NRs were redispersed in water or an aminohexanethiol hydrochloride (AHT) solution. The final concentration of NRs was 4.0 mM (Au atoms) in every case. The NR solutions could be kept for at least one month without forming aggregations.

A glass substrate to deposit NRs was modified with water-soluble polymers using layer-by-layer methods.[5] A glass substrate was first made hydrophilic by treating with the mixed solution (1:1) of an aqueous hydrogen peroxide (31%) and ammonia (28%). A hydrophilic glass substrate was immersed in an aqueous solution (1 mg/mL) of polycation polymer and poly(allylamine hydrochloride) (PAH) for 20 min to generate positive charges on the surface. Then, the PAH-modified substrate was immersed in an aqueous solution (3 mg/mL) of poly(sodium styrene sulfonate) (PSS) for 20 min. After these treatments, the outermost layer of the substrate was negatively charged. Polyion-modified substrates were immersed in aqueous colloidal solutions of NRs containing different concentrations of AHT. After the immersion for one week, substrates were washed with water and dried in air. All treatments were performed at room temperature.

Absorption spectra of NRs deposited on substrates were obtained by a spectrophotometer (V-570, JASCO). The zeta potentials of NRs were evaluated using a Zetasizer NanoZS (MALVERN, He–Ne laser). Zeta potential was calculated using a theoretical model with spherical particles. Thus, the value qualitatively indicated the sign and magnitude of the zeta potential of the NRs. This was sufficient for the relative evaluation of the surface charge of NRs. A field emission scanning electron microscope (SEM, S-5000, Hitachi) was used for observation of NRs on the substrates.

Zeta potentials of NRs dispersed in AHT solutions are shown in Table 1. In the absence of AHT, NRs showed positive zeta potential (+15 mV) because of residual CTAB on NRs surfaces.[7] Addition of AHT in the solutions increased the zeta potentials; when 1 mM of AHT was added in an NR solution, the zeta potential was +46 mV. This value was comparable with the initial NRs capped with a CTAB bilayer (+50 mV). This indicates that AHT was adsorbed on NRs.

Figure 1 shows absorption spectra of surface-modified glass substrates after immersions in NR solutions containing different concentrations of AHT. Figures 1e and 1f are magnified spectra of Figures 1c and 1d, respectively. In every case, absorption peaks are clearly seen in near-IR regions. These peaks can be assigned to the longitudinal SP bands of NRs deposited on the glass substrates. In the absence of AHT (Figure 1a), the SP band shifted to a longer wavelength region (≈1200 nm) and showed a very broad profile. This suggested that NRs formed kinds of assemblies on the substrates. Addition of AHT in NR solutions decreased the intensities of the SP bands of deposited NRs, and the SP bands shifted to a shorter wavelength region. The

Table 1. Zeta potentials of NRs

AHT/mM	Zeta potential/mV
0	+15
0.125	+18
0.500	+42
1.000	+46

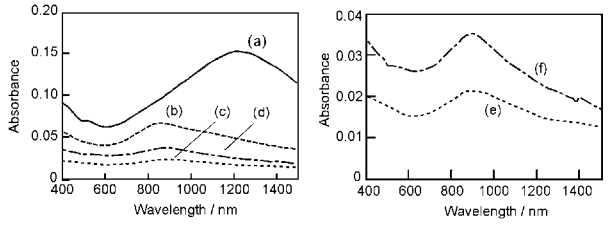

Figure 1. Absorption spectra of NRs deposited on glass substrates in the absence (a) and presence (b–d) of AHT. (e) and (f) are magnified spectra of (c) and (d), respectively. AHT concentrations: (a) 0, (b) 0.125, (c) 0.5, (d) 1.0 mM. The glass substrates were immersed in NR solution (4 mM) for one week.

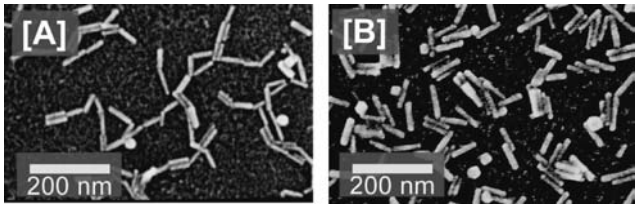

Figure 2. SEM images of deposited NRs on glass substrates. NRs were deposited in the absence [A] and presence ([B], 0.5 mM) of AHT.

peak positions of Figures 1e and 1d were close to those of the initial NRs dispersed in water (see Supporting Information). This indicates that the addition of AHT in NR solutions suppresses assemblies of NRs on a glass substrate.

Figure 2 shows SEM images of deposited NRs in the presence (Figure 2A) and absence (Figure 2B) of AHT. It is remarkable that NRs formed end-to-end assemblies in the absence of AHT (Figure 2A). This was a typical image of the substrate immersed in an NRs solution in the absence of AHT; most NRs formed end-to-end assemblies on the substrate. It was found that the absorption spectrum in Figure 1a originated from these NR assemblies. The red shift and broadening of the SP band can be explained by the interactions of SP oscillations of NRs that were aligned linearly.[2,4] CTAB-passivated NRs did not form such end-to-end assemblies on the glass surface.[5,8] PC layers on NRs may be effective to linearly align the NRs.

In contrast, the SEM image of NRs deposited from an NR-solution containing AHT (0.5 mM) exhibited randomly distributed NRs (Figure 2B). Addition of AHT in the NR solution was effective to disturb the end-to-end NR-assemblies. This indicates that the adsorbed layers of PC molecules on NRs were a crucial factor for end-to-end alignment. Continuous PC-layers, which align NRs linearly, may be formed on the end-to-end NR-assemblies. The density of the NRs in the case of Figure 2B was about 480 rod/μm^2, which was larger than that of case of Figure 2A (210 rod/μm^2). However, this is not consistent with the absorption spectra of the substrates; as shown in Figure 1, the addition of AHT decreased the SP bands of deposited NRs. This contradiction is probably induced because some NRs contacted each other on their longitudinal sides as shown in Figure 2. Gloudents et al. indicated that SP oscillations of NRs in a neighborhood resonated with each other.[2] That is, if NRs contacted at their ends, longitudinal SP bands would shift to a longer wavelength region. In contrast, if NRs contacted on their longitudinal side, longitudinal SP bands would be dumped and shifted to a shorter wavelength region. The SP oscillation of the side-by-side NR-assemblies would be same as that of square gold nanoplates. It is reasonable that the SP bands in Figures 1e and 1f would originate from a few isolated-NRs on the substrates.

The most plausible interaction between NRs and a glass surface was electrostatic interaction. From this perspective, the larger positive zeta potentials that were given by excess AHT (0.5 and 1 mM) seem to be advantageous to the deposition of NRs; however, excess AHT probably formed an adsorbed layer of AHT on the polyanion layer. These AHT layers were disadvantageous to electrostatic adsorption of NRs, but NR deposition was enhanced by the addition of AHT, as shown in Figure 2. This strongly suggested that the thiol groups of AHT were effective for depositing NRs on the AHT layers. If NRs were deposited through different interactions, the alignment of NRs on glass surfaces would not be the same. The different NR assemblies shown in Figure 2 would have originated from the different interactions between NRs and the substrates.

End-to-end NR-assemblies were achieved by adsorption of PC-passivated NRs on polyanionic surfaces without linker molecules to connect NRs. Addition of AHT in NR solutions increased the zeta potentials of NRs and changed the properties of NR assemblies. Detailed mechanisms of the formation of end-to-end NR assemblies and their deformation have remained to be clarified. Further characterization of NR and polyanion surfaces in the absence and presence of AHT should give definitive information about why PC-passivated NRs form such linear assemblies.

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