Immobilization of Gold Nanorods on the Glass Substrate by the Electrostatic Interactions for Localized Plasmon Sensing

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(Received January 8, 2004; CL-040036)

Gold nanorods (NRs) have two localized surface plasmon bands in the visible–near infrared region. We have succeeded in well-dispersed deposition and immobilization of the gold nanorods on the surface of a glass substrate by the electrostatic interactions. The outermost PDDA layer was effective to prevent the lateral diffusion of NRs on the PSS layer. The longitudinal plasmon band showed clear shifts with solvents in the near-infrared region.

Since the pioneering works about DNA detection using gold nanoparticles by Mirkin et al.,[1] gold nanoparticles have attracted much attention as spectroscopic analytical tools. Because the gold nanoparticles have characteristic absorption bands in the visible–near infrared region based on the localized plasmon resonance (surface plasmon (SP) band), they are especially attractive for photometric applications.[2] To increase the photometric sensitivity using gold nanoparticles, the peak positions of the SP bands should be sensitive to the surrounding medium. From these viewpoints, gold nanorods (NRs: rod-like nanoparticles) that have two SP bands corresponding to the transverse and longitudinal oscillation modes are promising materials, because the peak position of the latter is theoretically much sensitive to the surrounding medium as compared with that of spherical particles.[3,4] Recently, several approaches for preparing the gold NRs have been reported.[5–9] The gold NRs have been applied as some sensing tools such as DNA-sensing as in the case of gold nanoparticles[10] and for surface-enhanced Raman scattering.[11,12] However, the deposition of gold NRs on a substrate was limited only by a precipitation procedure,[11] and no useful methods for depositing the gold NRs without aggregation have been reported yet.

In the present study, we have first succeeded in well-dispersed fixing of the gold NRs onto a glass substrate by electrostatic interactions.[13] Appreciable spectral shifts of the longitudinal SP band with solvents were obtained.

Gold NRs were prepared in our laboratory.[9] The NRs were fairly uniform in shape (aspect ratio (length divided by width): 2 ± 0.5), and well dispersed in water without appreciable aggregation. It is known that hexadecyltrimethylammonium bromide (CTAB) stabilizes the NRs.[12] Thionicotineamide (TNA) (1 mg/mL) was added in the NR solution as an additional stabilizer. The NRs solution was centrifuged three times to decrease the excess CTAB. After the centrifugations, the absorption peak intensity of the longitudinal SP band decreased less than 10% of the initial NR solution, nevertheless the absorption spectrum of the solution showed characteristics of the gold NRs having a couple of SP bands. The surface of the NR retained positive charge even after the centrifugations, as was confirmed from the measurements of zeta-potentials (ca. +30 mV).

A glass substrate was first made hydrophilic by treating with the mixed solution (1:1) of aqueous hydrogen peroxide (31%) and ammonia (28%). The degree of the direct electrostatic deposition of NRs on this glass substrate was low, even on immersion into the aqueous colloidal solution of NRs for one day. Thus, the surface of glass substrate was modified with polyions as follows. First, the glass substrate was immersed into an aqueous solution (1 mg/mL) of polycation polymer, poly(allylamine hydrochloride) (PAH), for 20 min, to generate positive charges on the surface. Then, the PAH-modified substrate was immersed into an aqueous solution (3 mg/mL) of poly(sodium styrene sulfonate) (PSS) for 20 min, so that the outermost layer of the substrate was negatively charged. This PSS–PAH-modified precursor substrate was immersed into the aqueous colloidal solution of NRs for 30 min. All these treatments were performed at room temperature. Electrostatic deposition of NRs was confirmed from absorption spectral measurements. Characteristic SP bands due to the NRs were clearly seen. Scanning electron micrograph (SEM) observations confirmed that almost all of the deposited NRs were isolated without appreciable aggregation. However,

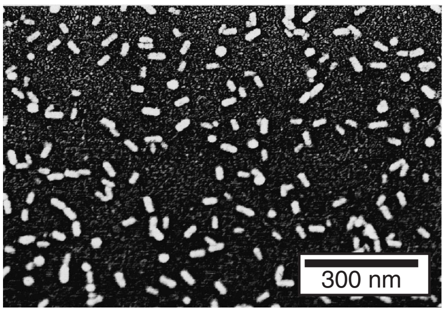

Figure 1. SEM image of PDDA-NR modified substrate.

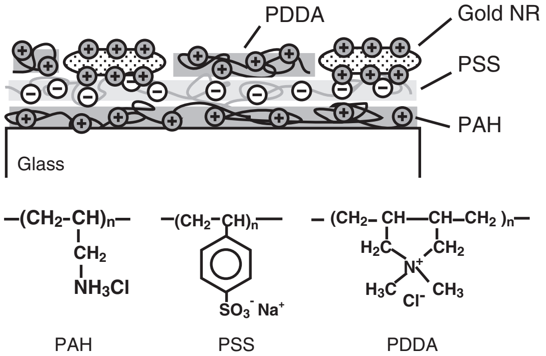

Figure 2. Estimated structure of gold NR–polyion assembly.

when this NR-modified substrate was immersed into organic solvents, substantial aggregation of NRs was observed.

The NR-modified substrate was again immersed for 20 min into an aqueous solution of another polycation polymer, poly(diallyldimethylammonium chloride) (PDDA, 1 mg/mL), to give PDDA–NR-modified substrate. By treating with PDDA, the deposited NRs showed no appreciable aggregation even on immersion into the organic solvents. It is certain that the adsorption of PDDA on the NR-modified substrate is effective to avoid the aggregation of the NRs. The SEM image of the PDDA–NR-modified substrate (Figure 1) shows that most NRs are isolated each other and distributed randomly on the substrate. The outermost PDDA layer may fill the spaces among NRs. A possible structure of the PDDA–NR-modified substrate is illustrated in Figure 2.

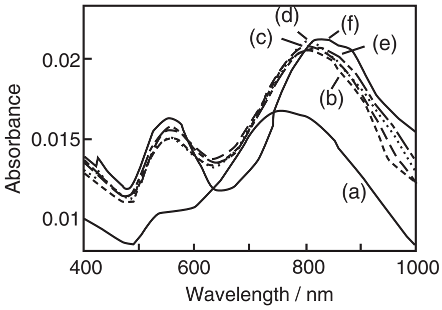

Figure 3. Absorption spectra of PDDA–NR-modified substrate in air (a) and in solvents: (b), water; (c), ethanol; (d) acetone; (e), cyclohexane; (f), chloroform.

Table 1. Peak positions of the longitudinal SP bands and the refractive indices of solvents

solvent	refractive index (n_d^{20})	peak position/nm
air	1.000	762
water	1.333	805
acetone	1.359	807
ethanol	1.361	806
cyclohexane	1.425	818
chloroform	1.447	841

Figure 3 shows spectral changes of the PDDA–NR-modified substrate, when the substrate was sequentially immersed in several solvents. The spectrum of the substrate in air shows clear SP bands around 550 (transverse mode) and 760 nm (longitudinal mode), respectively. On immersion into the solvents, the longitudinal SP band showed substantial red shift. Table 1 summarizes the peak positions of the longitudinal SP bands and the refractive indices of the solvents. Degrees of red-shift were in the order: water < ethanol < acetone < cyclohexane < chloroform. This is roughly correlated with the order of refractive index (dielectric constant) of the solvent. The spectral change in the longitudinal SP band was satisfactorily reproducible even for repeated immersions in the solvents. Accordingly, the outermost PDDA layer was effective to prevent the lateral diffusion of NRs on the PSS layer.

As shown in Table 1, the value of the red-shift from air to chloroform ($\Delta n = 0.447$) was ca. 80 nm. This is not so large as the value estimated from the theoretical calculation according to the previous paper (ca. 200 nm).[3] It is plausible that the polymers underneath and beside the NRs affect the refractive index that is sensed by the deposited gold NRs. The NRs were further deposited with PSS and NRs + PDDA layers by the layer-by-layer technique.[14] In that case, the SP bands of the NRs were quite less sensitive to the solvents, probably because the most of the NRs fixed in the layer-by-layer structure were thoroughly wrapped with the polymers. Accordingly, in the PDDA–NR-modified substrate, the NRs were fixed in a favorable condition to prevent aggregation yet to sense the refractive index of the solvents.

In summary, chemical immobilization of gold NRs without substantial aggregation could be realized. The present system can be very powerful for the sensing in the longer wavelength region, since the longitudinal SP band locates in the near-infrared region. Thus, applications to biosensing are fascinating. Further improvements for increasing the degree of deposition as well as optimization of the longitudinal SP band are now in progress.

The present study was partially supported by the Grant-in-Aids Scientific Research (Grant Nos. 15350085, 15655026), from the Ministry of Education, Culture, Sports, Science and Technology (MEXT) of the Japanese Government, and Industrial Technology Research Grant Program in '03 from New Energy and Industrial Technology Development Organization (NEDO) of Japan.

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14 The PDDA–NR-modified substrate was further immersed in a series of the PSS, the NRs, and the PDDA solution, repeatedly. Absorption peak intensities originating from the NRs increased almost linearly with the series of the deposition cycles.

Published on the web (Advance View) March 20, 2004; DOI 10.1246/cl.2004.454