

ARTICLE

Laying Gold Nanorods Monolayer down on Solid Surfaces for Surface Enhanced Raman Spectroscopy Applications

Haidong Zhao,^{a,b,c} Katsuhiro Isozaki,^{*c,d} Tomoya Taguchi,^c Shengchun Yang^b and Kazushi Miki^{*‡c}

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

Laying-down gold nanorods (GNRs) of a monolayer immobilized on a solid substrate was realized with the hybrid method, a combination of three elemental technologies: self-assembly, electrophoresis, and solvent evaporation. The self-assembly of CTAB-protected GNRs in the solution was induced by 0.05 mM of EDTA. The assembled GNRs were deposited in a laying form on the solid surface during the hybrid method. The final coverage is over 71 % on the substrate with an area being larger than 0.6 cm². The spacing between the sides of GNRs is fixed to be 4.6 ± 0.9 nm by the thermal annealing-promoted crystalline packing of the bilayer of CTAB salt-bridged with EDTA. The obtained laying-down GNRs of a monolayer on the gold substrate shows a small shift of the transverse LSPR around 550–570 nm (with a width of around 100 nm) and a large red shift of the longitudinal LSPR to be 900–1050 nm (with a width of 500 nm), because of the strong electromagnetic coupling between GNRs and gold substrate. Therefore it can be used in a wide range of wavelength for surface enhanced Raman spectroscopy (SERS) applications. The film has a high enhancement factor with 10⁵ for R6G.

1. Introduction

As one of the anisotropic noble metal nanomaterials, gold nanorods (GNRs) have received a great deal of attention in recent years because of their unique physical properties, such as optical, electronic, and catalytic properties.¹ By controlling the aspect ratio of the GNRs, it is possible to tune the localized surface plasmon resonance (LSPR) precisely in the visible to near-infrared range.² Among the applications of GNRs in the field of optics, the enhancement of Raman scattering signals of organic molecules using GNRs as a substrate has become one of the most focused subjects.^{1,3} Generally, the assembly of GNRs into two- or even three-dimensional functional superstructures would lead to a strong enhancement of Raman scattering of adsorbed molecules due to the collective behavior of nanorods and high density of hotspots.^{4–21}

The optical properties of the GNRs vary depending on the type of assembly.⁵ Various strategies have been employed to prepare a well-ordered assembly in the solution system. For example, the assembly of GNRs on carbon grids can be induced by the electrostatic interaction between

cetyltrimethylammonium bromide (CTAB) bilayers on the surface of GNRs.⁶ Moreover, well-ordered assemblies of GNRs can be fabricated by means of the intermolecular electrostatic interaction between CTAB and various molecules, such as ethylenediaminetetraacetic acid (EDTA),⁷ dimercaptosuccinic acid (DMSA),⁸ sodium phosphate (Na₃PO₄),⁹ and so on.¹⁰ However, in most cases, the well-ordered structure can only be transferred onto a very limited area, such as the TEM grid,^{6–10} which significantly restricts its applications, especially in the field of the optical device. Thus, up to date, many approaches have been developed to prepare the well-ordered GNRs array on the substrates such as glass and silicon. There are two main types of assembly for the GNRs monolayer film on a solid substrate, including standing-up and laying-down array.^{11–21} The construction of standing-up GNRs monolayer film mostly relies on alignment in applied electric or magnetic fields,¹¹ capillary forces during controlled solvent evaporation drying,¹² gravity-driven approach,¹³ and templating.¹⁴ With regard to the assemblies of laying-down GNRs monolayer film, the strategies include the solvent evaporation induced self-assembly of GNRs,¹⁵ self-assembly of GNRs at air/liquid or polar/nonpolar solvents,¹⁶ immobilization of GNRs monolayers via electrostatic interactions,^{8,17} orientation and organization of GNRs using a strong magnetic field,¹⁸ accumulation and alignment of GNRs driven by an electric field,¹⁹ *in situ* growth of the GNRs on the substrate surface using surfactant-assisted seed-mediated growth method,²⁰ and the Langmuir–Blodgett (LB) technique.²¹ Although these methods can produce laying-down GNRs monolayer and multilayer 3D array over large area with high coverage, the products of laying-down GNRs monolayer film are only attached to substrates and thus lack the mechanical strength required for several applications. Therefore, it remains a major challenge to develop a facile and efficient method to

^a School of Chemistry and Chemical Engineering, Shanxi Datong University, Datong 037009, Shan Xi, People's Republic of China.

^b School of Science, State Key Laboratory for Mechanical Behavior of Materials, Ministry of Education Key Laboratory for Non-Equilibrium Synthesis and Modulation of Condensed Matter, Xi'an Jiaotong University, Xi'an 710049, Shan Xi, People's Republic of China.

^c National Institute for Materials Science, 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan.

^d Institute for Chemical Research, Kyoto University, Gokasho, Uji, Kyoto 611-0011, Japan.

† Electronic Supplementary Information (ESI) available: See DOI: 10.1039/x0xx00000x

‡ Current address: Graduate School of Engineering, University of Hyogo, Shosya 2167, Himeji 671-2280, Japan.

fabricate large area and dense laying-down GNRs monolayer film immobilized on the solid substrate.

In our previous research, we have developed a hybrid method, which has been proven to be a facile and efficient way for the fabrication of chemically immobilized gold nanoparticles (GNPs) arrays on large substrates with high coverage and well-ordered assembly.²² This method includes three elemental technologies: chemical modification of both GNPs with alkanethiol and the substrate with thiol-termination, electrophoresis, and solvent evaporation. Therefore, the hybrid method is an excellent choice for immobilizing the monolayer GNRs arrays onto the substrate surface. Herein, we apply the hybrid method to the fabrication of laying-down GNRs monolayer film with side-by-side assembly of high coverage over 71% on the large area (>0.6 cm²) gold-coated quartz substrate (Figure 1). We used a method including chemical modifications of both the GNR with CTAB and the substrate with thiol-termination, electrophoresis, and solvent evaporation. The applicability of the laying-down GNRs monolayer film was demonstrated by the surface-enhanced Raman scattering (SERS) with rhodamine 6G (R6G) showing the high enhancement factor with 10⁵.

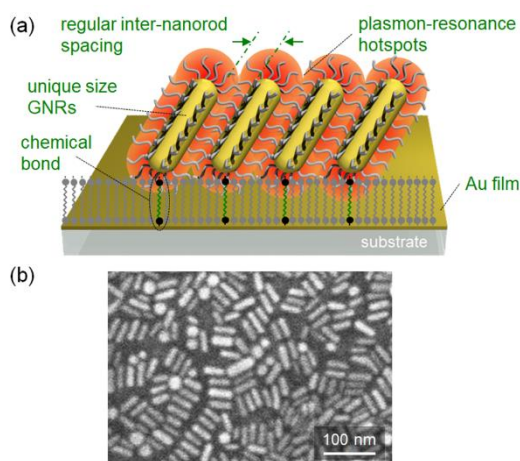


Fig. 1 (a) Schematic illustration of side-by-side assembled laying-down monolayer film of GNRs. (b) SEM image of laying-down monolayer film of I-GNRs on 1,6-hexanedithiol-coated gold substrate using the hybrid method.

2. Experimental Section

2.1 Materials

Tetrachloroauric acid trihydrate (HAuCl₄·3H₂O), silver nitrate (AgNO₃), and CTAB were purchased from Sigma-Aldrich. Sodium borohydride (NaBH₄), EDTA, ascorbic acid, 1,6-hexanedithiol, sodium hydroxide (NaOH), hydrochloric acid (HCl) were commercially available (from NACALAI TESQUE, INC Kyoto, Japan). All chemicals were used as received without further purification. Milli-Q water was used throughout the experiments.

2.2 Synthesis of GNRs

GNRs were synthesized by using the seeding mediate growth method established by El-Sayed.^{2a} Briefly, the as-prepared

CTAB-capped seeds were added to a growth solution containing specific amounts of CTAB, AgNO₃, HAuCl₄, and ascorbic acid. This mixture was kept undisturbed for 24 h. The as-prepared GNR samples were centrifuged at 11,000 rpm for 15 min. The supernatant was discarded, and the residue was re-dispersed in distilled water. This process was repeated twice to remove the excess CTAB and other residual reactants.

2.3 Assembly of GNRs in solution with different concentration of EDTA

Initially, the GNR concentrations were maintained constant in all samples by diluting the purified GNRs to an optical density with 0.44 of transverse localized surface plasmon resonance (transverse LSPR) at 515 nm, and the pH values of the GNRs solutions and EDTA (1 mM and 10 mM) solutions were adjusted to 6.8 by using HCl or NaOH, respectively.⁷ Then, the GNRs solutions were centrifuged at 11,000 rpm for 10 min and a predetermined volume of the supernatant was removed. The GNRs were re-dispersed by sonication and diluted to the original volume by adding EDTA (1 mM and 10 mM) solution. The resultant GNR solutions, which have the same GNR concentration but with EDTA concentrations of 0.01, 0.05, 0.1, 0.5 mM, were obtained. The spectral changes were analyzed by UV–Vis–NIR extinction spectra.

2.4 Fabrication of monolayer film of laying-down GNRs by hybrid method

The 1,6-hexanedithiol-coated substrate and plastic formed carbon (PFC) plate (10×10×1.0 mm) were used as the cathode and anode, respectively. In a typical procedure, the substrates were prepared by vapor-depositing chromium (10 nm) and gold (40 nm) metal onto quartz plates (10×10×0.6 mm). Then, the gold-coated quartz glass substrates were immersed in 1,6-hexanedithiol solution in ethanol (3.27×10⁻¹ M) at room temperature for 24 h. After washing with ethanol and acetone, and dried with flowing nitrogen, the dithiol-coated electrodes were obtained. The PFC electrodes were cleaned by sonication in water and hexane before being used. The solutions containing GNRs and EDTA were used for the hybrid method. The electrophoresis parameters were performed with the interelectrode distance of 1.2 mm and the applied DC voltage of 1.0 V. The electrophoresis vessel was opened to increase the rate of solvent evaporation. After the solvent was evaporated completely, the cathode was annealed on the hot plate at 50 °C for 12 h. After annealing, the substrate was washed by sonication in hexane for 1 min to remove the loosely adsorbed GNRs and then dried with flowing nitrogen to produce the monolayer film of laying-down GNRs on the substrate.

2.5 Characterization methods

UV–Vis–NIR extinction spectra of the GNRs solution were measured on a JASCO MSV-370 spectrometer using distilled water as a reference. For the laying-down GNRs monolayer-coated substrate, UV–Vis–NIR extinction spectra in reflection geometry were obtained with a 1,6-hexanedithiol-coated substrate as a reference. Scanning electron microscope (SEM) images were taken on a Hitachi S-4800 electron microscope

without metal sputtering. The coverage values of GNRs on the substrate were calculated from 7 different points by analyzing the SEM images with ImageJ 1.44p software, as similar to the previous works.²²

2.6 SERS measurement

SERS measurements were carried out on a confocal microprobe Raman spectrometer (Lab RAM HR800, HORIBA JOBIN YVON) with the 633 nm irradiation from He-Ne laser at room temperature. The laser was focused by a 100× objective (numerical aperture (NA) = 0.9) to a $\sim 1\ \mu\text{m}$ spot on the sample. The power of the laser beam on the sample was 0.05 mW and all spectra were integrated for 10 s. For SERS signals measurement, R6G was adopted as the analyte. To ensure the same amount of R6G molecules adsorbed onto different substrates, samples for SERS were prepared by immersing the substrates with GNRs monolayer into the aqueous solution of R6G ($1 \times 10^{-7}\ \text{M}$) for 12 h, and dried with putting the substrates into the desiccator.

3. Results and discussion

In the current research, the hybrid method for immobilization of Au nanoparticles as reported by Isozaki et al.^{22a} was applied to prepare a monolayer film of laying-down GNRs on substrates, which is schematically illustrated in Figure 2. At first, the 1,6-hexanedithiol-coated Au substrate and plastic formed carbon (PFC) plate were used as the cathode and anode, respectively. The self-assembly of CTAB-protected GNRs in the solution was induced by 0.05 mM of EDTA. The hybrid method including electrophoresis and solvent evaporation was used to accelerate the self-assembly of GNRs at the air-liquid interface and transfer the self-assembled GNRs onto the substrate (Figure 2a). The positively charged GNRs and their assemblies are attracted to the cathode substrate by the electric field. The electrophoresis vessel was opened for increasing the rate of solvent evaporation until the solution level lowered to the bottom of the cathode, enabling the formation of the well-ordered GNRs arrays onto the large area of the substrate (Figure 2a). After the solvent was evaporated completely, the self-assembled aggregates of GNRs were physisorbed on the substrate (Figure 2b). The self-assembled aggregates of GNRs were reported to have the spacing between the sides of GNRs with $8.7\ \text{nm}$ ⁷ composed of the bilayer of CTAB with the width of $3.9\ \text{nm}$ ⁸ and the salt-forming EDTA layer with $0.9\ \text{nm}$ ²³ (Figure 2c).

Finally, the substrate was annealed on the hot plate for covalent anchoring the monolayer film of laying-down GNRs. After the annealing, the substrate was sonicated to remove the adsorbed over-layers of GNRs on the monolayer film of GNRs. During the annealing process, the weakly physisorbed GNRs were covalently anchored on the substrate by the ligand exchange from CTAB to thiolate at the surface, giving sufficient mechanical strength for device applications (Figure 2d). In addition, the thermal annealing process accelerates the further self-assembly of CTAB-protected GNRs, producing the closely arrayed laying-down GNRs monolayer with $4.5\ \text{nm}$ inter-nanorod spacing (Figure 2e). The driving force to form such a

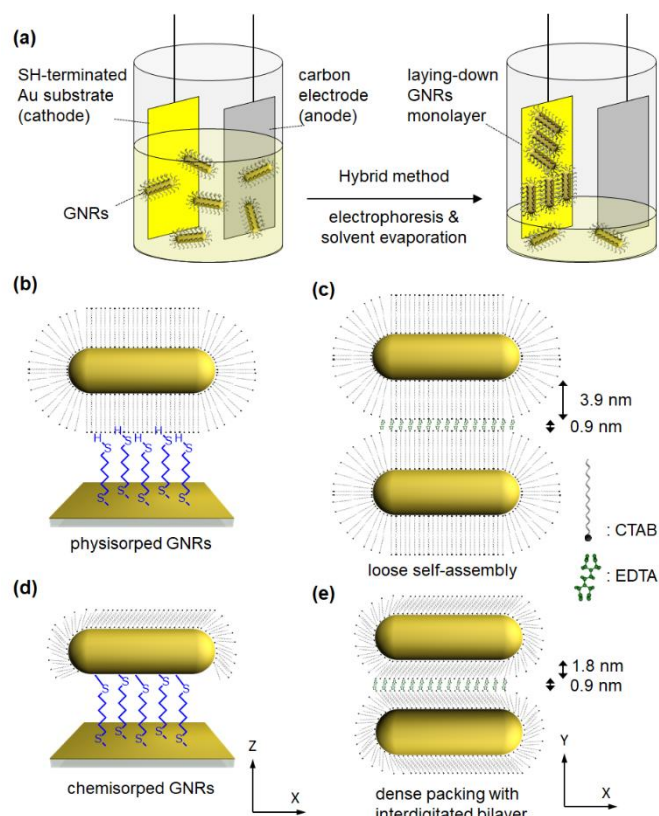


Fig. 2 (a) Fabrication process of laying-down monolayer film of GNRs. Schematic illustration of self-assembled GNRs before (b, c)⁷ and after (d, e) thermal annealing. Side (b, d) and top views (c, e).

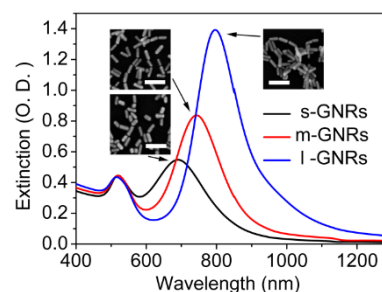


Fig. 3 UV-Vis-NIR extinction spectra of aqueous solution of s-GNRs, m-GNRs, and l-GNRs. The transverse LSPR optical densities were kept at 0.44 at 515 nm. The insets are corresponding SEM images. The scale bar is 100 nm.

closer arrayed GNRs monolayer is considered to originate from the crystalline packing of the colloid particles at the substrate surface where a higher degree of interdigitation of alkyl chains²⁴ is induced to form a thermodynamically stable densely packed structure.²⁵

Figure 3 shows the UV-Vis-NIR extinction spectra of as-prepared three kinds of GNRs solutions with different aspect ratios, such as 2.2, 2.8, and 3.1, named short-GNRs (s-GNRs), middle-GNRs (m-GNRs), and long-GNRs (l-GNRs), respectively. The obtained GNRs show two maxima in the UV-Vis-NIR extinction spectra, as similar to the well-known spectral feature of GNRs.^{2a,b,26} One of them is the transverse LSPR at 515 nm,

which is due to the plasmon excitation along the short axis. The other one is longitudinal LSPR ranging from 691 to 797 nm, which is due to the excitation along the long axis. Their peak positions shift depending on the aspect ratios of the GNRs. The insets in Figure 3 show SEM images of GNRs with different aspect ratios. The structural and spectral parameters of the as-prepared GNRs are summarized in Table S1. It can be seen that the longitudinal LSPR band redshifts from 691 to 797 nm with increasing the aspect ratio of the GNRs, indeed the negligible shift of the transverse LSPR band, as similar to the previous reports.^{2a}

The self-assembly of CTAB-protected GNRs in aqueous solution was reported to be induced depending on the concentration of EDTA.⁷ The UV–Vis–NIR extinction spectra were used to monitor the self-assembly of GNRs in solution before and after the addition of EDTA. Figure S1 shows the spectral change in LSPR bands of the s- and l-GNRs dispersed in aqueous solution in the presence of EDTA with different concentrations. In the case of s-GNRs with the EDTA concentration lower than 0.01 mM, no significant change in the position and intensity of the longitudinal LSPR band is observed even after 24 h (Figure S1a and S1b). With the EDTA concentration of 0.05 mM, the intensity of the longitudinal LSPR band at around 690 nm presents a slight decrease after 24 h. When EDTA concentration increased to 0.1 mM, the longitudinal LSPR band only shows a slight redshift and decrease in intensity at 5 min, then shifts from 694 to 732 nm with a significant decrease in intensity after 24 h (Figure S1b), indicating the aggregation of GNRs has occurred. When EDTA concentration is higher than 0.5 mM, the longitudinal LSPR band becomes broad and accompanied by a great reduction in intensity even within 5 min (Figure S1a) and almost no absorption can be observed after 24 h due to the significant degree of aggregation (Figure S1b). As the concentration of EDTA increases further, the GNRs precipitated at the bottom of the container within a very short time. The redshift of the LSPR band with the addition of EDTA indicates the partial anion exchange of CTAB with EDTA to form $\text{CTA}^+-\text{EDTA}^-$ complexes, which induces the self-assembly of GNRs in solution by edge-to-edge interaction, as similar to previous reports.^{5a,7} Figure S1c and S1d show a similar spectral change in LSPR bands of l-GNRs, which reveals a similar, but more significant self-assembly nature of l-GNRs compared with those of s-GNRs with a smaller aspect ratio (Figure S1a and S1b).

Figure 4 shows the SEM images of monolayer films of laying-down l-GNRs on the substrate by the hybrid method in the absence or presence of EDTA with 0.05 and 0.10 mM, respectively. Without the addition of EDTA, no characteristic assembly was observed to show the coverage of 58% (Figure 4a). When the concentration of EDTA was 0.05 mM, the dense monolayer GNRs-array with high coverage of 87% was obtained (Figure 4b). The observed laying-down l-GNRs were composed of small islands of side-by-side assemblies which were randomly contacted each other, suggesting the structural shift of the self-assembled GNRs from the edge-to-edge assembly in the solution by the self-assembly on the substrate due to the stronger side-by-side interaction than that of edge-to-edge on

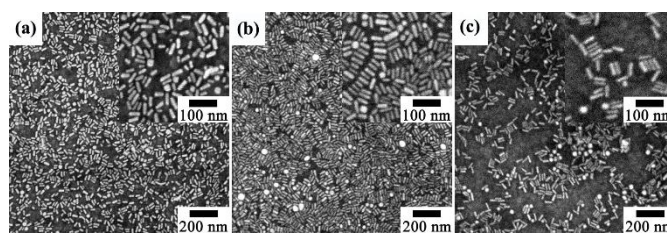


Fig. 4 SEM images of monolayer film of laying-down l-GNRs on gold coated quartz glass substrate prepared without (a), with 0.05 (b) and 0.10 (c) mM EDTA. The insets show magnified SEM images.

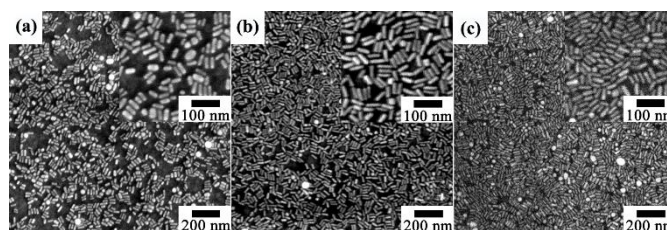


Fig. 5 SEM images of s-GNRs (a), m-GNRs (b), and l-GNRs (c) monolayers on gold coated quartz glass substrate prepared with 0.05 mM EDTA by hybrid method. The insets show magnified SEM images.

the substrate. Previously, Pradeep reported the higher concentration of EDTA induces the structural shift of GNR assembly from edge-to-edge to side-by-side in the solution.⁷ In our case, local high concentration could be induced at the air-liquid interface during the self-assembly process, enabling the structural shift of GNR assembly from edge-to-edge to side-by-side on the substrate. In contrast to 0.05 mM result, excess EDTA with 0.10 mM accelerated the significant aggregation of GNRs in the solution (Figure S1c and S1d), thus resulted in a decreased coverage of 41% (Figure 4c). These results indicate the existence of optimal concentration of EDTA for balancing the aggregation and immobilization of GNRs into the monolayer state on the solid substrate.

Figure 5 shows SEM images of as-obtained s-GNRs, m-GNRs, and l-GNRs monolayers on the substrate by the hybrid method with 0.05 mM EDTA. The monolayer films of laying-down GNRs are composed of small islands of well-ordered structures and cover large area over 0.6 cm² with high coverages: 71% for s-GNRs (Figure 5a), 81% for m-GNRs (Figure 5b), and 87% for l-GNRs (Figure 5c, Figure S2). The typical spacing between the sides of GNRs arranged in a side-by-side fashion is measured to be 4.5 nm from the SEM images (Figure 5 insets and Figure S3), which is much smaller than the reported side-by-side spacing of GNR monolayers with 8.7 nm prepared by drop-casting of CTAB-capped GNRs in the presence of EDTA.⁷ Such a shorter spacing is considered to be induced by the hybrid method including the thermal annealing process, which accelerates the formation of the densely packed crystalline state of CTAB bilayers. Herein, we obtained closely arrayed GNRs monolayer having a much smaller spacing between side faces which is the critical parameter for plasmonic applications.

The driving force to form the densely packed GNRs monolayer was investigated by preparing GNRs monolayers with different methods: the hybrid method consisted both of the electrophoresis and the solvent evaporation, only the electrophoresis without the solvent evaporation, and only the solvent evaporation without the electrophoresis. In all methods, the obtained substrates were thermally annealed at 50 °C for 24 h and then sonicated in hexane for 1 min. The hybrid method, the combination of electrophoresis and solvent evaporation gave large area, dense and high coverage monolayer on the substrate (Figure S4a). The proportion of the GNRs monolayer relative to the entire substrate area reached around 60%. At the bottom side of the reaction vessel, the sparsely adsorbed GNRs were observed due to the consumption of colloidal GNRs in the solution during the preparation process. With regard to the sample prepared by the electrophoresis without the solvent evaporation, multilayer GNRs assembly was formed only at the gas-liquid interface, and no assemblies were observed under the interface (Figure S4b). The proportion of GNRs monolayer was estimated to be around 10%. In the case of the sample obtained by the solvent evaporation without the electrophoresis, only a few bands of GNRs assembly were observed (Figure S4c), and the proportion of GNRs monolayer was decreased to less than 5%. In all samples, SEM observation clarifies the inter-nanorod spacing with ca 4.5 nm (Figure S3, S5 and S6) shorter than that of the reported CTAB-capped GNR aggregate in the presence of EDTA. This result reveals that both of the electrophoresis and the solvent evaporation don't affect the inter-nanorod spacing, suggesting that the dense packing is accelerated by the thermal annealing step after the self-assembly of GNRs.

Figure 6 shows the UV–Vis–NIR extinction spectra of monolayer films of laying-down s-GNRs, m-GNRs, and l-GNRs on gold-coated quartz glass substrates. As shown in Figure 6, both transverse and longitudinal LSPR bands are red-shifted to 570 and 892 nm for the s-GNRs, 550 and 1016 nm for the m-GNRs, and 565 and 1036 nm for the l-GNRs. El-Sayed previously reported that a side-by-side association of GNRs gives rise to a blue-shift of the longitudinal LSPR and a red-shift of the transverse LSPR, whereas an end-to-end association only gives rise to a red-shift of the longitudinal LSPR with a negligible shift of the transverse LSPR by DDA simulation.^{5a} In fact, this

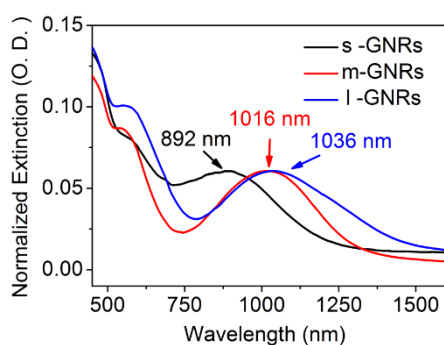


Fig. 6 UV–Vis–NIR extinction spectra of monolayer film of laying-down s-GNRs, m-GNRs, and l-GNRs on gold coated quartz glass substrates.

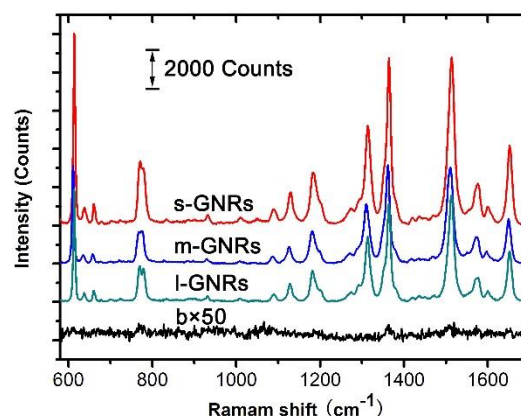


Fig. 7 SERS spectra of R6G (10^{-7} M) adsorbed on the surface of GNRs monolayer with different aspect ratio (red line: s-GNRs, blue line: m-GNRs, green line: l-GNRs), and the gold coated quartz glass without GNRs monolayer (black line: 50 times expanded background).

tendency of LSPR shift of GNRs was experimentally confirmed in the recent papers.²⁷ In contrast, the monolayer films of laying-down s-GNRs, m-GNRs, and l-GNRs exhibit the red-shifted longitudinal LSPR, although mostly composed of side-by-side aggregates (Figure 5), suggesting the strong contribution of plasmonic coupling between the immobilized GNRs and the supporting gold film.²⁸ In the monolayer films, GNRs are immobilized to the gold film through 1,6-hexanedithiolate whose molecular length is 1.2~1.3 nm,²⁹ much shorter than the inter-nanorod spacing with 4.5 nm. Such shorter distance between the immobilized GNRs and the gold film than the inter-nanorod spacing results in the strong plasmon coupling of GNRs with gold films, as similar to the electronic coupling between GNPs and the gold film accelerating the catalytic turnover of silane alcoholysis.³⁰ Thus, the observed red-shift of LSPR bands is considered to originate from the plasmonic coupling both between GNRs, and between GNRs and the gold film.

The monolayer film of laying-down GNRs on the solid substrate is expected as SERS substrate for molecular detections with high sensitivity,^{7,27e,31} because the electromagnetic field is strongly enhanced by plasmon coupling when particles are placed close to each other, generating hotspots at the gaps between particles.^{3,32} The hybrid method for immobilizing the dense GNRs monolayer onto the substrate provides a guide for strong enhancement of Raman scattering of adsorbed molecules because of the high density of hotspots. As shown in Figure 7, the intense Raman signals of R6G molecules are observed at about 1652, 1513, 1364 cm^{-1} (C–C stretching modes of aromatic rings), 771 cm^{-1} (C–H out-of-plane bending), and 613 (C–C–C in-plane bending) cm^{-1} , in fair agreement with previously reported results.^{15b,28,33} The relative SERS enhancement factor (the ratio of Raman signals intensity at 1364 cm^{-1} for gold-coated quartz glass substrates with and without GNRs monolayer) of s-, m-, and l-GNRs monolayer are obtained to be 3.93×10^5 , 2.32×10^5 , and 2.31×10^5 with 1.0×10^{-7} M concentration of R6G, indicating the potent applicability with the remarkably low detection limit less than 1.0×10^{-12} M.

Although there have been reports on higher SERS enhancement factor of 10^7 – 10^8 order with cross-linked or metal-decorated gold nanomaterials, the obtained values are comparable or higher than reported GNR assemblies.^{3a,7,15a,31,34} It is noteworthy that a slightly higher enhancement in SERS was observed for s-GNRs monolayer than that of m- and l-GNRs, although the s-GNRs monolayer has the lower coverage of 71% than those of m- and l-GNRs monolayers of 81 and 87%. The higher enhancement of the s-GNRs monolayer is considered to originate from the stronger plasmon coupling between s-GNRs than other GNRs, because the width of s-GNRs with 16.0 nm is wider than that of m- and l-GNRs with 15.2 and 14.2 nm (Table S1), despite the same spacing with 4.5 nm between the sides of all GNRs (Figure S4 and S3). Thus, the more highly enhanced electromagnetic field is generated at the gap between s-GNRs than other GNRs. This result demonstrates the tunability and high applicability of the monolayer film of GNRs for sensor applications.

4. Conclusions

In summary, we developed a novel methodology for the immobilization of monolayer film of laying-down GNRs on the solid substrate. This method enables the formation of GNR monolayer films on a large area over 0.6 cm² with high coverage over 71% and regular spacing of 4.5 nm between the sides of GNRs. The closely arrayed GNR monolayers were obtained by the thermal annealing process, which accelerates the crystalline packing of CTAB-protected GNRs in the solid state. The densely arrayed feature of the monolayer film of laying-down GNRs was demonstrated by the SERS activity, showing the remarkably high enhancement factors of 10^5 order toward R6G with 1.0×10^{-7} M. This work demonstrates the applicability of the hybrid method for fabricating 2D arrays of various types and shapes of nanoparticles from the solution onto large area substrate.

Author Contributions

All authors have given approval to the final version of the manuscript.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

We thank Natural Science Foundation of Shanxi Province of China (grant no. 201801D121073), the Scientific and Technological Innovation Programs of Higher Education Institutions in Shanxi Province (No. 2019L0749), and Ph.D. Research Startup Foundation of Shanxi Datong University (grant no. 2013-B-16). We also thank the Japan Society for the Promotion of Science (JSPS) and the Ministry of Education, Culture, Sports, Science and Technology of Japan (MEXT) for

financial support; MEXT KAKENHI Grant Number JP24106746 (K.M.: Grant-in-Aid for Scientific Research on Innovative Areas “Integrated Organic Synthesis”); JSPS KAKENHI Grant Number JP24656040, JP30455274 (K.M.: a Grant-in-Aid for Challenging Exploratory Research, K. I.: Grant-in-Aid for Young Scientists). A part of our research was supported by the Research Foundation for Opto-Science and Technology. T.T. thanks the Japan Society for the Promotion of Science for the Young Scientist Fellowship. H.Z., and S.Y., were supported by NIMS, and also K.M. was supported by XJTU University during which this research was carried out.

Notes and references

- (a) S. E. Lohse and C. J. Murphy, *Chem. Mater.*, 2013, **25**, 1250; (b) H. Chen, L. Shao, Q. Li and J. Wang, *Chem. Soc. Rev.*, 2013, **42**, 2679; (c) L. Vigdeman, B. P. Khanal and E. R. Zubarev, *Adv. Mater.*, 2012, **24**, 4811.
- (a) B. Nikoobakht and M. A. El-Sayed, *Chem. Mater.* 2003, **15**, 1957; (b) T. K. Sau and C. J. Murphy, *Langmuir*, 2004, **20**, 6414; (c) C. J. Murphy, T. K. Sau, A. M. Gole, C. J. Orendorff, J. Gao, L. Gou, S. E. Hunyadi and T. Li, *J. Phys. Chem. B*, 2005, **109**, 13857; (d) W. Ni, X. Kou, Z. Yang and J. Wang, *ACS Nano*, 2008, **2**, 677; (e) A. McLintock, N. Hunt and A. W. Wark, *Chem. Commun.*, 2011, **47**, 3757; (f) S. Kaushal, S. S. Nanda, D. K. Yi and H. Ju, *J. Phys. Chem. Lett.*, 2020, **11**, 5972.
- (a) L. Dai, L. Song, Y. Huang, L. Zhang, X. Lu, J. Zhang and T. Chen, *Langmuir*, 2017, **33**, 5378; (b) C. J. Orendorff, L. Gearheart, N. R. Jana and C. J. Murphy, *Phys. Chem. Chem. Phys.*, 2006, **8**, 165.
- (a) L. Song, Y. Huang, Z. Nie and T. Chen, *Nanoscale*, 2020, **12**, 7433; (b) W. Wei, F. Bai and H. Fan, *Angew. Chem. Int. Ed.*, 2019, **58**, 11956; (c) L. Scarabelli, C. Hamon, and L. M. Liz-Marzán, *Chem. Mater.*, 2017, **29**, 15.
- (a) P. K. Jain, E. Eustis and M. A. El-Sayed, *J. Phys. Chem. B*, 2006, **110**, 18243; (b) X. Hu, W. Cheng, T. Wang, Y. Wang, E. Wang and S. Dong, *J. Phys. Chem. B*, 2005, **109**, 19385.
- (a) T. K. Sau and C. J. Murphy, *Langmuir*, 2005, **21**, 2923; (b) B. Nikoobakht, Z. L. Wang and M. A. El-Sayed, *J. Phys. Chem. B*, 2000, **104**, 8635.
- T. S. Sreeprasad and T. Pradeep, *Langmuir*, 2011, **27**, 3381.
- T. S. Sreeprasad, A. K. Samal and T. Pradeep, *Langmuir* 2008, **24**, 4589.
- H. Huang, C. Qu, X. Liu, S. Huang, Z. Xu, Y. Zhu and P. K. Chu, *Chem. Commun.*, 2011, **47**, 6897.
- C. J. Orendorff, P. L. Hankins and C. J. Murphy, *Langmuir*, 2005, **21**, 2022.
- (a) J. Wang, M. Scampicchio, R. Laocharoensuk, F. Valentini, O. González-García and J. Burdick, *J. Am. Chem. Soc.*, 2006, **128**, 4562; (b) Q. Liu, Y. Cui, D. Gardner, X. Li, S. He and I. I. Smalyukh, *Nano Lett.*, 2010, **10**, 1347.
- (a) X. Zhang and T. Imae, *J. Phys. Chem. C*, 2009, **113**, 5947; (b) A. Guerrero-Martínez, J. Pérez-Juste, E. Carbó-Argibay, G. Tardajos and L. M. Liz-Marzán, *Angew. Chem. Int. Ed.*, 2009, **48**, 9484.
- B. D. Smith, D. J. Kirby, I. O. Rivera and C. D. Keating, *ACS nano*, 2013, **7**, 825.
- J. W. Cizdek, L. Huang, S. Tsonchev, Y. Wang, K. R. Shull, M. A. Ratner, G. C. Schatz and C. A. Mirkin, *ACS nano*, 2010, **4**, 259.
- (a) R. Rong, L. Song, P. Si, L. Zhang, X. Lu, J. Zhang, Z. Nie, Y. Huang, T. Chen, *Langmuir*, 2017, **33**, 13867. (b) Y. Huang, L. Dai, L. Song, L. Zhang, Y. Rong, J. Zhang, Z. Nie and T. Chen, *ACS Appl. Mater. Interfaces*, 2016, **8**, 27949; (c) Y. Xie, S. Guo, Y. Ji, C. Guo, X. Liu, Z. Chen, X. Wu and Q. Liu, *Langmuir*, 2011,

- 27, 11394; (d) S. Yun, M. K. Oh, S. K. Kim and S. Park, *J. Phys. Chem. C*, 2009, **113**, 13551; (e) H. Nakashima, K. Furukawa, Y. Kashimura and K. Torimitsu, *Langmuir*, 2008, **24**, 5654.
- 16 (a) L. Song, N. Qiu, Y. Huang, Q. Cheng, Y. Yang, H. Lin, F. Su and T. Chen, *Adv. Opt. Mater.*, 2020, **8**, 1902082; (b) Q. Cheng, L. Song, H. Lin, Y. Yang, Y. Huang, F. Su and T. Chen, *Langmuir*, 2020, **36**, 250.
- 17 (a) A. Gole, C. J. Orendorff and C. J. Murphy, *Langmuir*, 2004, **20**, 7117; (b) S. Vial, I. Pastoriza-Santos, J. Pérez-Juste and L. M. Liz-Marzán, *Langmuir*, 2007, **23**, 4606; (c) L. Guo, X. Zhou and D.-H. Kim, *Biosens. Bioelectronics*, 2011, **26**, 2246; (d) A. Gole and C. J. Murphy, *Chem. Mater.*, 2005, **17**, 1325; (e) H. J. Kim, W. Wang, A. Traveset, S. K. Mallapragada and D. Vaknin, *ACS nano*, 2020, **14**, 6007.
- 18 (a) H. Yonemura, S. Natsuko, J. Suyama and S. Yamada, *J. Photochem. Photobiol. A*, 2011, **220**, 179; (b) H. Yonemura, J. Suyama, T. Arakawa and S. Yamada, *Thin Solid Films*, 2009, **518**, 668.
- 19 W. Ahmed, E. S. Kooij, A. Van Silfhout and B. Poelsema, *Nano Lett.*, 2009, **9**, 3786.
- 20 P. Kannan, S. Sampath and S. A. John, *J. Phys. Chem. C*, 2010, **114**, 21114.
- 21 P. Yang and F. Kim, *ChemPhysChem*, 2002, **3**, 503.
- 22 (a) K. Isozaki, T. Ochiai, T. Taguchi, K. Nittoh and K. Miki, *Appl. Phys. Lett.*, 2010, **97**, 221101; (b) T. Taguchi, K. Isozaki and K. Miki, *Adv. Mater.*, 2012, **24**, 6462; (c) F. Pincella, Y. Song, T. Ochiai, K. Isozaki, K. Sakamoto and K. Miki, *Chem. Phys. Lett.*, 2014, **605**, 115.
- 23 M. Pérez, I. Pavlovic, C. Barriga, J. Cornejo, M. Hermosin and M. Ulibarri, *Appl. Clay Sci.*, 2006, **32**, 245.
- 24 M. Giersig and P. Mulvaney, *Langmuir*, 1993, **9**, 3408.
- 25 B. Dusemund, A. Hoffmann, T. Salzmann, U. Kreibig and G. Schmid, *Z. Phys. D Atom. Mol. Cl.*, 1991, **20**, 305.
- 26 (a) Y.-Y. Yu, S.-S. Chang, C.-L. Lee and C. R. C. Wang, *J. Phys. Chem. B*, 1997, **101**, 6661; (b) K. Esumi, K. Matsuhisa and K. Torigoe, *Langmuir*, 1995, **11**, 3285.
- 27 (a) G. Cheng, D. Xu, Z. Lu and K. Liu, *ACS nano*, 2019, **13**, 1479; (b) Z. Zhu, W. Liu, Z. Li, B. Han, Y. Zhou, Y. Gao and Z. Tang, *ACS nano*, 2012, **6**, 2326; (c) J. Lu, Y.-X. Chang, N.-N. Zhang, Y. Wei, A.-J. Li, J. Tai, Y. Xue, Z.-Y. Wang, Y. Yang, L. Zhao, Z.-Y. Lu and K. Liu, *ACS nano*, 2017, **11**, 3463; (d) F. C.-M. Leung, S. Y.-L. Leung, C. Y.-S. Chung and V. W.-W. Yam, *J. Am. Chem. Soc.*, 2016, **138**, 2989; (e) P. Li, Y. Li, Z.-K. Zhou, S. Tang, X.-F. Yu, S. Xiao, Z. Wu, Q. Xiao, Y. Zhao, H. Wang and P. K. Chu, *Adv. Mater.*, 2016, **28**, 2511.
- 28 J. D. Driskell, R. J. Lipert and M. D. Porter, *J. Phys. Chem. B*, 2006, **110**, 17444.
- 29 T. Y. B. Leung, M. C. Gerstenberg, D. J. Lavrich, G. Scoles, F. Schreiber and G. Poirier, *Langmuir*, 2000, **16**, 549.
- 30 K. Isozaki, T. Taguchi, K. Ishibashi, T. Shimoaka, W. Kurashige, Y. Negishi, T. Hasegawa, M. Nakamura and K. Miki, *Catalysts*, 2020, **10**, 908.
- 31 (a) C. Hanske, E. H. Hill, D. Vila-Liarte, G. González-Rubio, C. Matricardi, A. Mihi and L. M. Liz-Marzán, *ACS Appl. Mater. Interfaces*, 2019, **11**, 11763; (b) X. Lin, W.-L.-J. Hasi, S.-Q.-G.-W. Han, X.-T. Lou, D.-Y. Lin and Z.-W. Lu, *Phys. Chem. Chem. Phys.*, 2015, **17**, 31324.
- 32 F. Pincella, K. Isozaki, T. Taguchi, Y. Song and K. Miki, *J. Nanosci. Nanotechnol.*, 2015, **15**, 1171.
- 33 J. A. Dieringer, K. L. Wustholz, D. J. Masiello, J. P. Camden, S. L. Kleinman, G. C. Schatz and R. P. van Duyne, *J. Am. Chem. Soc.*, 2009, **131**, 849.
- 34 X. Lu, Y. Huang, B. Liu, L. Zhang, L. Song, J. Zhang, A. Zhang, T. Chen, *Chem. Mater.*, 2018, **30**, 1989.