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Formation of Gold Nanorod Dimers and their Activity for Surface-Enhanced Raman Scattering

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Abstract

Side-by-side connected gold nanorod dimers were formed by ligand substitution of hexadecyltrimethylammonium bromide (C₁₆TAB) bilayer with 1-hexylamine. The addition of 1-hexylamine caused a gradual aggregation of gold nanorods, which was verified from blue shift of the longitudinal localized surface plasmon resonance (LSPR) band of gold nanorods. Dimers were found to be preponderant at about 4 h from the addition of 1-hexylamine. Raman intensity of Rhodamine 6G (R6G) molecules in the presence of gold nanorod dimers exhibited a 50-fold and a 15-fold enhancement compared with that of aqueous R6G solution without gold nanorods and with gold nanorod monomers, respectively.

Key-words: Gold nanorod, Dimer, 1-hexylamine, Surface-enhanced Raman scattering, Rhodamine 6G

1. Introduction

Gold nanorods have unique optical properties such as high light absorptivity from visible to near-infrared region and remarkable enhancement of the electric field at both ends^{1–3}. These properties are not only intriguing subjects for basic research^{4–6} but also important for various applications involving cancer diagnosis^{7–12}, plasmonic photocatalysis^{13,14} and optical recording^{15,16}. The spectral property and the electric field enhancement are a function of the aspect ratio (ratio of the longer axis length to the shorter axis length) of individual nanorods^{1–3}. Namely, gold nanorods with larger aspect ratio exhibit a larger extinction (sum of absorption and scattering) band at longer wavelengths as well as greater electric field enhancement^{17,18}. Meanwhile, both the optical extinction profile and electric field enhancement undergo a significant evolution when two gold nanorods approach together^{19–28}. The extinction band experiences a red-shift when the dimerization occurs by an end-to-end contact, while a side-by-side contact brings about a blue-shift of the optical extinction spectra. Extinction profiles for other dimer geometries like L-shape and V-shape have also been calculated. In all systems, the electric field is significantly enhanced at the interstice between two nanorod particles^{19–28}.

One important consequence of the large optical extinction and electric field enhancement by gold nanorods is surface-enhanced Raman scattering (SERS)^{29–32}. In addition to these two properties, the ability to tune the extinction maximum

wavelength to match the laser wavelength for excitation is also a benefit of using gold nanorods³³. SERS is, like ordinary Raman spectroscopy, based on vibrations accompanied with a polarizability change but the signals are greatly amplified due to two mechanisms, i.e., electromagnetic effect and chemical effect^{29–32}. Dimer formation of gold nanorods influences the electromagnetic effect on the signal enhancement.

Several studies have been reported so far on the formation of gold nanorod dimers with respect to their optical and SERS properties^{33–40}. Most of them are focused on the end-to-end connected dimers because of large enhancement of local electric field. However, side-by-side connected dimers could be intriguing because their contact surface area is much larger. Here we report a facile preparation procedure for side-by-side connected gold nanorod dimers by ligand substitution with 1-hexylamine and their application for SERS.

2. Experimental

2.1 Materials

Tetrachloroaurate tetrahydrate (HAuCl₄·4H₂O), silver nitrate (AgNO₃), acetone and cyclohexane were purchased from Wako Pure chemical Industries. Dodecyltrimethylammonium bromide (C₁₂TAB or DTAB), tetradecylammonium bromide (C₁₄TAB or TTAB) and hexadecyltrimethylammonium bromide (C₁₆TAB or CTAB) were obtained from Aldrich. L-ascorbic acid and 1-hexylamine were purchased from Tokyo Chemical Industries. All chemicals were of reagent grade and used as received. Water was deionized to the resistivity of

18.2 M Ω cm using a Barnstead Nanopure system.

2.2 Procedure

Gold nanorods were synthesized by a coupled chemical and photochemical reduction of Au³⁺ developed by Niidome *et al.*⁴¹⁾. Typically, 1.2 mL of 2 mM aqueous tetrachloroauric acid (HAuCl₄) was mixed with 1.8 mL of 500 mM alkyltrimethylammonium bromide (C_nTAB; n = 12 ~ 16). The mixed solution was stirred for 10 min at 25 °C to completely dissolve the complex. Successively, acetone (65 μ L), cyclohexane (45 μ L) and 10 mM silver nitrate (200 μ L) were added to the solution and stirred for 10 min. When 200 μ L of 40 mM ascorbic acid was added, color of the solution turned from orange to colorless, indicating a partial reduction from Au³⁺ to Au⁺. For the complete reduction to Au⁰, the colorless solution was placed in a rectangular quartz vessel (50 $\times$ 50 $\times$ 1 mm) and irradiated with UV light for 20 min. The light source used was a 200 W low pressure mercury lamp (Sen Tokushu Kogen, Japan) whose main wavelength was 253.7 nm. Visible components of the light were removed with a cut filter (Kenko U-330). Irradiance at the sample position was 700 μ W cm⁻².

After the reduction to Au⁰ was completed, a 3 mL aliquot of the sample was diluted with water to 30 mL and centrifuged at 10000 rpm for 60 min to remove the excess surfactant and other impurities. Precipitated gold nanorods (ca. 12 mL) were suspended in 1 mM C_nTAB and centrifuged again at 20000 rpm for 20 min. Then the precipitate was re-dispersed in 0.5 mM C_nTAB and centrifuged again at 20000 rpm for 20 min. The final precipitates were re-suspended in water to make 3 mL of the dispersion. The final concentration of Au⁰ was determined to be 1.41 mM from an ICP measurement.

In order to form gold nanorod dimers, 0.75 mL of 10 mM 1-hexylamine was added to 1.5 mL of the gold nanorods dispersion. After gentle agitation for several seconds, the samples were left standing for a given period at ambient temperature.

UV-visible extinction spectra were recorded on an Agilent 8453A diode array UV-vis spectrophotometer using a quartz vessel with a 1 mm light path length.

For the SERS measurement, 1.5 mL of gold nanorod dispersion containing 1.41 mM Au⁰ was mixed with 0.75 mL of water and 0.75 mL of 10 mM 1-hexylamine and left to stand for 4 h at ambient temperature. Then 60 μ L of 25.5 mM Rhodamine 6G (R6G) was added and left to stand for 1 h at ambient temperature. Successively, a 90 μ L portion of the sample was mounted on a glass slide. For control samples, i) a solution comprising 3 mL of water and 60 μ L of 25.5 mM R6G and ii) a solution comprising 1.5 mL of gold nanorod dispersion, 1.5 mL of water and 60 μ L of 25.5 mM R6G were prepared. Raman scattering was performed with a Jasco

NRS-2000 system equipped with a 100 mW Kr laser (wavelength: 647 nm).

3. Results and Discussion

During the formation of gold nanorods, cationic surfactants such as alkyltrimethylammonium bromides play a crucial role not only as stabilizer but also as structure-directing agent.

Therefore, firstly the effect of alkyl chain lengths of alkyltrimethylammonium bromide (C_nTAB) was investigated with regard to the yield of gold nanorods. **Fig. 1** (a) compares UV-vis extinction spectra of gold nanoparticles formed in 300 mM C_nTAB with different alkyl chain lengths (n = 12, 14, 16) after a consecutive chemical and photochemical reduction of Au³⁺ to Au⁰. Two extinction bands are observed for all systems, at 510 nm and 710 ~ 720 nm. The origin of these extinction bands is the resonance between the incident electric field of light and collective oscillation of conduction electrons at the surface of gold nanorods, referred to as localized surface plasmon resonance (LSPR)¹⁻³⁾. Existence of the two LSPR bands stems from two directions of electronic oscillation, indicative of rod like particles. The LSPR band at shorter wavelength corresponds to transverse electronic oscillation, and the other band at longer wavelength is ascribed to longitudinal electronic oscillation¹⁻³⁾. For the longitudinal LSPR band it can be seen that the C₁₆TAB system shows a more intense peak at a slightly longer wavelength compared with C₁₂TAB and C₁₄TAB systems, while for the transverse LSPR band peak intensity and peak wavelength are similar for three surfactant systems.

Taking into account that the transverse LSPR band at about 510 nm is observed not only for gold nanorods but also for

Fig. 1 UV-visible extinction spectra (a) and TEM images (b) of gold nanorods prepared in the presence of alkyltrimethylammonium bromide (300 mM) with different alkyl chain lengths. Bars represent 100 nm.

Fig. 2 (a) Evolution of UV-vis extinction spectra of gold nanorods dispersion immediately after the addition of 1-hexylamine of different concentrations. (b) Magnification of the peak region of (a) showing a blue shift. (c) Time course of UV-vis extinction spectra of gold nanorods after the addition of 30.4 mM 1-hexylamine.

Fig. 3 Photographs showing color change of gold nanorods dispersions at 4 h after the addition of 1-hexanol at various concentrations.

Fig. 4 TEM images of gold nanorods at 4 h after the addition of 1-hexylamine of various concentrations. Circles indicate dimers.

Fig. 5 TEM images of (a) incidentally approached C₁₆TAB-ligated gold nanorods on the TEM grid showing an inter-surface distance of 5.8 nm, and (b) a side-by-side connected nanorod dimer induced by 1-hexylamine showing an inter-surface distance of 1.4 nm.

Fig. 6 Raman spectra of (a) Rhodamine 6G (R6G) in aqueous solution and glass slide as background, (b) R6G in the presence of Au nanorod dimers, (c) R6G in the presence of Au nanorod, and (d) chemical structure of R6G molecule.

spherical gold nanoparticles, the intensity ratio of the longer wavelength peak to the shorter wavelength one can be an index for the yield of rodlike nanoparticles. Meanwhile, the peak wavelength is proportional to the aspect ratio defined as the ratio of longer axis length to the shorter axis length¹⁾. Accordingly, the UV-vis extinction spectra suggest that the C₁₆TAB system provides the longest nanorods at the highest yield among these three surfactants. Indeed, TEM images (Fig. 2 (b)) indicate many quasi-spherical gold nanoparticles in the C₁₂TAB and C₁₄TAB systems, whereas most particles have elongated shape for the C₁₆TAB system. Therefore, all the experiments were performed hereafter by using C₁₆TAB as capping ligand. For the nanorod particles capped with C₁₆TAB, the mean lengths of shorter and longer axes were 9.5 nm and 26.0 nm, respectively, and the mean aspect ratio is 2.7.

Subsequently, 1-hexylamine was added to the C₁₆TAB-ligated gold nanorods to induce aggregation. Fig. 2 displays UV-vis extinction spectra at different concentration of added 1-hexylamine. Fig. 2 (a) and (b) indicate that even immediately after the addition of 1-hexylamine a distinct blue shift is observed for the longitudinal LSPR band of gold nanorods. Furthermore, the blue shift is more significant at higher concentration of 1-hexylamine. As mentioned above, peak wavelength of the longitudinal LSPR peak is proportional to the aspect ratio of gold nanorods¹⁻³⁾. Hence the blue-shift observed here can be attributed to an apparent decrease in the aspect ratio of gold nanorods, i.e., side-by-side connection between the nanorods.

Although the aggregation of gold nanorods sets in immediately after the addition of 1-hexylamine, it proceeds over a long time. Fig. 2 (c) displays time course of UV-vis extinction spectra indicating a continuous blue shift of the longitudinal LSPR band of gold nanorods accompanied with a slight decrease in the peak intensity. The blue shift and decrease of peak intensity are consistent with the side-by-side connection of gold nanorods.

Aggregation of gold nanorods can also be verified from a color change of nanorods dispersion. As shown in Fig. 3, the color of nanorods dispersion changes from brown to green with increasing concentration of added 1-hexanol, which corresponds to an increasing number and / or degree of aggregates.

Fig. 4 presents TEM images of gold nanorods at 4 h after the addition of 1-hexylamine in various concentrations. It clearly indicates that higher concentration of 1-hexylamine induces more significant aggregation of gold nanorods. Dimers are predominant when the concentration of 1-hexylamine ranges between 2 and 5 mM. Higher concentration of 1-hexylamine resulted in larger aggregates of gold nanorods.

It is known from various measurements that C₁₆TAB forms a bilayer on the surface of gold nanorods^{42,43)}. However, these data suggest that the C₁₆TAB bilayer can be replaced

with 1-hexylamine despite the latter having a shorter alkyl chain.

Fig. 5 compares TEM images of gold nanorods at close approach. Shown in (a) are C₁₆TAB-ligated gold nanorods which incidentally come close to each other in the course of drying on a grid. The inter-surface distance is 5.8 ± 1.7 nm which is shorter than twice the bilayer thickness taking the molecular length of 2.1 nm of C₁₆TAB into account, but it is significantly longer than the thickness of one bilayer. Meanwhile, gold nanorod dimers induced by 1-hexylamine show a significantly shorter inter-surface distance of 1.4 ± 0.4 nm, which is in good agreement with twice the molecular length of 1-hexylamine at all-trans conformation (0.78 nm). The result that inter-surface distance after the addition of 1-hexylamine becomes shorter than the molecular length of C₁₆TAB supports the ligand substitution of C₁₆TAB bilayer with a 1-hexylamine monolayer. It is easily imagined that once C₁₆TAB bilayer was replaced with 1-hexylamine monolayer, the surface becomes hydrophobic, which leads to formation of dimers.

Finally, Raman spectra of Rhodamine 6G (R6G) and their assignment are presented in Fig. 6 and Table 1, respectively. Six distinct peaks other than those of glass substrate are visible for aqueous R6G solution. Peak intensity of the most prominent peak at 1508 cm⁻¹ assigned to aromatic C-C stretching vibration⁴⁴⁾ is about 0.06. This peak is intensified to 0.2 (after the background subtraction) in the presence of gold nanorod monomers and further enhanced to 3.0 (after the background subtraction) in the presence of nanorod dimers. Thus the signal enhancement in the presence of gold nanorod dimers is calculated to be 50-fold and 15-fold compared with the R6G solution without gold nanorods and with nanorod monomers, respectively.

The SERS enhancement factor (EF) is given by the following equation³⁰⁾:

$$EF = \frac{I_{SERS}}{I_{NRS}} \frac{N_{vol}}{N_{surf}}$$

where I_{SERS} denotes the surface-enhanced Raman intensity, I_{NRS}

Table 1 Raman signals of Rhodamine 6G and their assignment⁴⁴⁾

Raman shift (cm ⁻¹)	Assignment
1086	γ (C-H)
1123	δ (C-H)
1180	δ (C-H)
1308	ν (C-O-C)
1362	ν (aromatic C-C)
1433	ν (aromatic C-C)
1508	ν (aromatic C-C)
1572	ν (aromatic C-C)
1599	ν (aromatic C-C)
1648	ν (aromatic C-C)

γ : out-of-plane bending vibration, δ : in-plane bending vibration, ν : stretching vibration.

represents the normal Raman intensity, N_{vol} is the number of R6G molecules in the scattering volume, and N_{surf} is the number of R6G molecules adsorbed on the metal surface in the scattering volume.

With this formula, the ratio I_{SERS} / I_{NRS} can be determined from the above discussion. However, it is difficult to determine the ratio N_{vol} / N_{surf} because of i) ambiguity in the number of gold nanorods forming dimers and ii) difficulty in the determination of Rhodamine 6G molecules residing in the interstitial region of gold nanorod dimers. Therefore, we report here only the intensity ratio of the Raman signals.

4. Conclusions

In this study, we showed that the addition of 1-hexylamine induces a gradual aggregation of C₁₆TAB-capped gold nanorods, as evidenced from the blue-shift of longitudinal LSPR band and TEM images. In the course of aggregation, there is a certain time (~ 4 h after the addition of 1-hexylamine) when the dimers are preponderant, while longer elapsed time results in formation of larger aggregates of gold nanorods. In the presence of gold nanorod dimers, Raman intensity of Rhodamine 6G experiences a 50-fold and a 15-fold enhancement compared with that of aqueous R6G solution without gold nanorods and with gold nanorod monomers, respectively.

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金ナノロッド二量体の形成とその表面増強ラマン散乱活性

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要 旨

側面同士が連結した金ナノロッド二量体をヘキサデシルアンモニウムブロミド (CTAB) 二分子層を1-ヘキシルアミンでリガンド置換することによって形成させた。1-ヘキシルアミン添加により金ナノロッドは徐々に凝集し、それは金ナノロッドの縦の局在表面プラズモン (LSPR) バンドがブルーシフトすることから確かめられた。1-ヘキシルアミンの添加後約4時間で二量体がおもに生成することがわかった。金ナノロッド二量体存在下でのローダミン6G (R6G) 分子のラマン散乱は金ナノロッドなしのR6G水溶液および金ナノロッド単量体存在下と比較して50倍および15倍の増強を示した。

キーワード：金ナノロッド，二量体，1-ヘキシルアミン，表面増強ラマン散乱，ローダミン6G