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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 ends¹⁻³. These properties are not only intriguing subjects for basic research⁴⁻⁶ but also important for various applications involving cancer diagnosis⁷⁻¹², 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 nanorods¹⁻³. 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 together¹⁹⁻²⁸. 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 particles¹⁹⁻²⁸.

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 effect²⁹⁻³². 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 properties³³⁻⁴⁰. 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