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Fluorescent gold nanoparticle superlattices

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Metal nanoparticles have a variety of interesting spectroscopic, electronic, and chemical properties that arise from their small sizes and high surface-to-volume ratios. Over the last several years, self-assembly of metal nanoparticles into two- or three-dimensional (2D or 3D) ordered arrays has become a topic of increasing interest in the field of nanotechnology. In this report, we prepared fluorescent gold nanoparticles and made fluorescent three-dimensional (3D) superlattices with them at an air/solution interface. Fluorescence spectral images of the superlattices have been examined and compared with those of reference superlattices［1］.

Fluorescein-labeled Au@MSA (abbreviated as Au@MSA/SAMSA) was prepared by ligand exchange. Figures 1a-1c show the absorption spectra of SAMSA, Au@MSA/SAMSA, and Au@MSA, respectively, and Figures 1d-1f are the emission spectra of SAMSA, Au@MSA/SAMSA and Au@MSA, respectively. The left and right ordinates are for absorption and fluorescence spectra, respectively. The spectral profile of Au@MSA was quite similar to that of Au@MSA/SAMSA (surface plasmon band = 540 nm), indicating that no size change of the core occurred. Although an absorption peak ascribed to the fluorescein moiety (490 nm) could not be observed in Figure 1b, we could detect distinct emission from the fluorescein moiety at 520 nm (Figure 1e); the peak maximum was unaffected upon binding on the nanoparticle surface (compare with Figure 1d). The absence of the absorption peak may be due to the very low concentration of the fluorescein molecules on the particle surface.

Figure 2A shows the fluorescence microscope images of the superlattice. There was no fluorescence for the suspended Au@MSA particle (Figure 1(f)). Although no fluorescence image could be obtained for the Au@MSA superlattices within the detection limit of our instrument, a weak Raman image accumulating the intensity in the entire Stokes shift range of 500-3500 cm^{-1} could be collected (Figure 2B). The optical microscope images and spectra at a single spot of respective superlattices are shown in insets I and II, respectively. The superlattice crystals typically appear as triangles with an edge length of 6.4 m. The emission peak of Au@MSA/SAMSA appears at 675 nm, largely red-shifted compared to the SAMSA solution sample or an isolated Au@MSA/SAMSA particle (~520 nm). The width of the emission has increased from 1731 cm^{-1} in the isolated particles to 3157 cm^{-1} in the superlattice. Both of these are probably due to the fact that the superlattices have different emission states compared to fluorophores in solution. In the superlattice, strong quenching might be expected because the fluorophores can be in contact not only with the attaching nanoparticles themselves but also with the adjacent nanoparticles to which they are not chemically linked. The present result clearly indicates that fluorescent superlattices can be built by using hydrophilic fluorescent gold nanoparticles.

[1] N.Nishida, E.S. Shibu, H.Yao, T.Oonishi, K.Kimura, T.Pradeep, Adv. Mater., (in press).

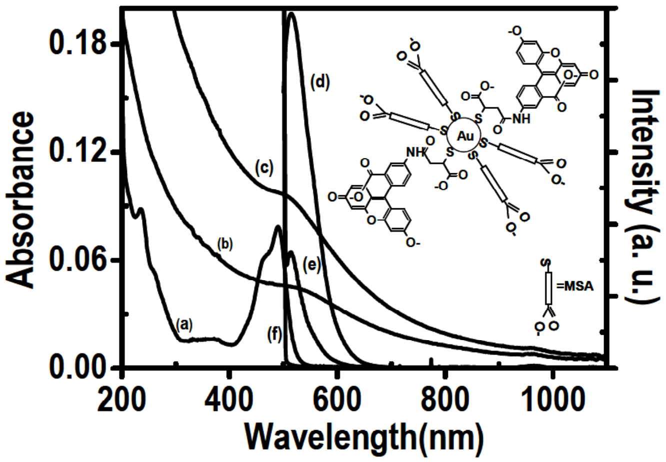

Figure 1. Absorbance spectra of (a) SAMSA, (b) Au@MSA/SAMSA and (c) Au@MSA and emission spectra of (d) SAMSA, (e) Au@MSA/SAMSA and (f) Au@MSA in water solutions. Inset shows a schematic of the fluorescent nanoparticle synthesized by exchanging MSA with SAMSA. The scale of ordinate on the right corresponds to fluorescence and that on the left is for absorption.

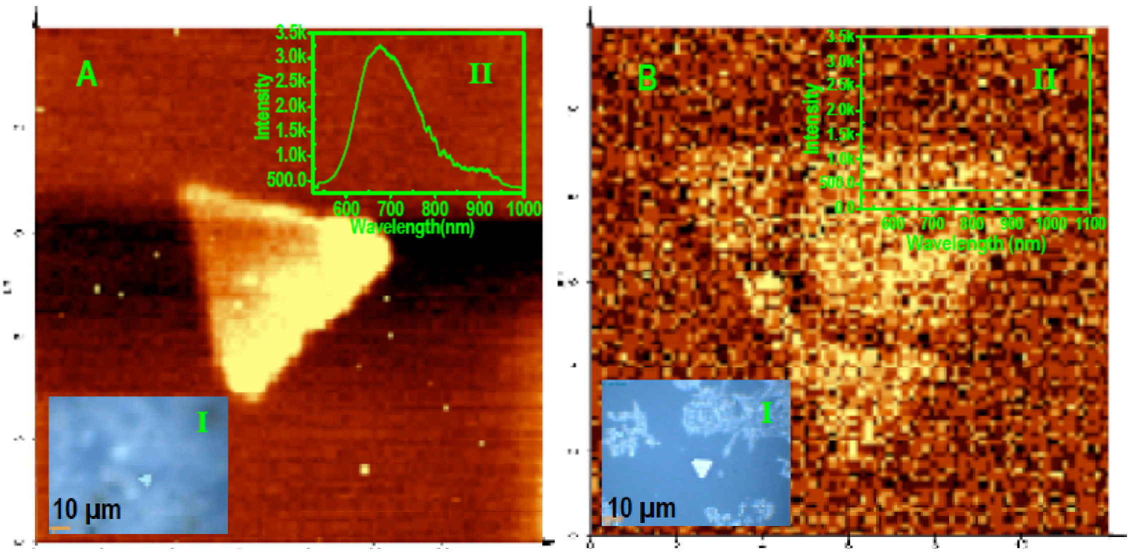

Figure 2. Fluorescence image of a superlattice crystal taken with the camera of a Raman microscope. The optical image of the superlattice crystal is shown in inset I and a single spot fluorescence spectrum is given in inset II. The excitation was at 514.5 nm. A is of Au@MSA/SAMSA superlattice and B is of Au@MSA superlattice.