Fabrication of Au-Conjugated Polymer Hybridized Nanoparticles and Their Optical Properties*

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We have successfully fabricated well-defined Au-core and polydiacetylene-shell hybridized nanoparticles (NPs) having the suitable thickness of dielectric SiO$_2$ layer between Au-core and polydiacetylene-shell by co-precipitation/microwave irradiation method, and subsequent solid-state polymerization process. The resulting hybridized NPs exhibited the significant enhancement of fluorescence intensity, increase in fluorescence quantum yield, and decrease in fluorescence lifetime, compared with polydiacetylene nanocrystals, due to the “emission enhancement” by localized surface plasmon resonance effect, and then would be one of the promising plasmonic nanomaterials toward optical device applications such as intense and stable point light sources. [DOI: 10.1380/ejssnt.2018.436]

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I. INTRODUCTION

Many researches on intense and stable point light sources at nanoscale have attracted attention from scientific interest to strong interaction between fluorescence emitters and photons as well as practical applications to photonic devices and medical diagnosis [1–3]. Metal nanoparticles (NPs) have the ability to localize and strongly enhance the incident optical electric-field, when localized surface plasmon resonance (LSPR) is achieved [4–8]. Actually, there are a number of studies on enhanced fluorescence of dyes and quantum dots by LSPR effect [9, 10]. Especially, the distance between metal NPs and fluorescent dyes sensitively determines fluorescence kinetics and quantum yields [11, 12]. To our knowledge, however, there are not many reports on core-shell type hybridized NPs between conjugated-polymers and single metal NPs [13].

Polydiacetylene (PDA) is a kind of typical conjugated polymers, and PDA derivatives nanocrystals (NCs) and nanotubes have received tremendous attention, due to outstanding nonlinear optical and electronic properties [14–17]. Among PDA derivatives, polyADA [poly(10,12-heptacosadiynoic acid)] shows interesting chromism (usually from blue phase to red phase), when exposed to external stimuli such as heat, pH, organic solvent, and mechanical stress [18]. This colour change has been attributed to the restriction of effective conjugated length, owing to conformational change along main chain [19, 20]. PolyADA emits fluorescence in only red phase, and has been so far applied to chemosensors [21]. However, its high intense emission required for realistic applications have not been fully achieved [22].

In the present study, we have fabricated Au-core and PDA-shell hybridized NPs by co-precipitation/microwave irradiation methods, and the fluorescence enhancement effect will be discussed in detail.

II. EXPERIMENTAL

A. Reagents

All chemical reagents used in the present study were commercially available, and were used without further purification.

B. Fabrication of Au/SiO$_2$/polyADA hybridized NPs

As described in the literature [23], polyADA NCs were fabricated by the conventional reprecipitation method, followed by the solid-state polymerization process. A 200 μL of EtOH solution of ADA (5 mM) was quickly injected into 10 mL of ultra-pure water, and exposed to microwave (2.45 GHz, 500 W) for 1 min. Then, ADA was solid-state polymerized to convert into polyADA by UV-light (λ = 254 nm) irradiation for 100 min.

Au NPs as a core have been prepared as described elsewhere [24]. The diameter was controlled by changing the added amount of sodium citrate. Next, Au/SiO$_2$ NPs have been fabricated by coating the surface of Au NPs with silica layer as an insulator through biphasic process [25]. In addition, ADA shell was formed on the surface of Au/SiO$_2$ NPs by co-precipitation/microwave irradiation method [26] as follows. A 200 μL of EtOH solution of ADA (5 mM) was quickly injected into 10 mL of Au/SiO$_2$ NPs aqueous dispersion liquid, and exposed to microwave (2.45 GHz, 500 W) for 1 min. Then, ADA shell was solid-state polymerized to convert into polyADA by UV-light (λ = 254 nm) irradiation for 100 min. Finally, the resulting Au/SiO$_2$/polyADA hybridized NPs were centrifuged for 30 min at the rate of 6000 rpm, rinsed several times, and then re-dispersed in an aqueous medium.

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FIG. 1. STEM/EDS mapping images of Au/SiO$_2$/polyADA hybridized NPs: (a) C element mapping, and (b) Si, Au, O, and C elements mappings. See the color codes of elements in the mapping images.

FIG. 2. (a) Extinction (solid line) and excitation (dash line) spectra of polyADA NCs (blue) and Au/SiO$_2$/polyADA hybridized NPs (red) dispersed in an aqueous medium, (b) extinction spectrum of Au NPs, and (c) fluorescence spectra of polyADA NCs (blue) and Au/SiO$_2$/polyADA hybridized NPs (red) dispersed in an aqueous medium. The detection wavelength in excitation spectra is 640 nm, and the excitation wavelength in the fluorescence spectra is 480 nm in any case.

C. Characterization methods

The resulting hybridized NPs were observed by using both transmission electron microscope (TEM: FEI Titan$^3$ G2 60-300 DoubleCsCorrector, EDS Super-X ProbeCsCorrector, 300 keV) and scanning electron microscope (SEM: JEOL, JSM-6700F). Extinction and fluorescence spectra were measured with spectrophotometer (JASCO, V-570) and with spectrofluorometer (Hitachi High-Tech Science Co. Ltd., F-7000), respectively. Fluorescence quantum yield (FQY) was determined by spectrofluorometer equipped with integrating sphere (Bunkoukeiki, IZ-CT-25TP). Fluorescence lifetime (FLT) was evaluated by FLT measurement apparatus with Ti-sapphire laser [Spectra-Physics, MaiTai: $\lambda = 460$ nm, 160 fs and 80 MHz, 5–1300 $\mu$W (0.063–16 pJ pulse$^{-1}$)] and pico-second streak camera system (Hamamatsu Photonics Inc., C10627). The spot diameter of incident laser light was typically 27 $\mu$m, and the excitation power per unit area was around 0.9–227 W cm$^{-2}$. The obtained fluorescence decay curves were fitted well with double-exponential functions so as to determine FLT. The all samples were adjusted to the same absorbance (extinction) before spectroscopic measurements.

III. RESULTS AND DISCUSSION

Figure 1(a, b) shows the STEM/EDS mapping images of Au/SiO$_2$/polyADA hybridized NPs. The overall shape was basically spherical, and the overall size of hybridized NPs was estimated to be 140$\pm$16 nm. In addition, Au NPs as a core and SiO$_2$ layer were clearly observed, and polyADA shell was further formed finely on the surface of SiO$_2$ layer. The average thicknesses of SiO$_2$ layer and polyADA shell are estimated roughly to be 25$\pm$7 nm and 3$\pm$2 nm, respectively (Fig. S1 in Supplementary Material). Interestingly, the thickness of polyADA shell was reported to be also about 3 nm in the similar hybridized NPs having Ag NPs as a core [17].

Figure 2(a) indicates the extinction and excitation spectra of polyADA NCs and Au/SiO$_2$/polyADA hybridized NPs. The extinction peaks at around 480 nm and 530 nm are, respectively, assigned to phonon-side band and excitonic absorption band of red-phase polyADA [19, 27]. In addition, monodispersed Au NPs with 85 nm in the almost same size as Au NPs (Fig. S1) core exhibit the LSPR peak at 560 nm in wavelength [Fig. 2(b)] [28]. The LSPR peak of Au/SiO$_2$/polyADA hybridized NPs are usually red-shifted with increasing the thickness of SiO$_2$ layer [29]. However, no clear extinction peak and/or shoulder based upon LSPR appeared at around 560 nm and/or longer.
wavelength region in the present hybridized NPs. The LSPR peak would be hidden with the relatively stronger excitonic absorption of polyADA shell on the surface of Au/SiO$_2$ hybridized NPs.

Figure 2(c) displays the corresponding fluorescence spectra. Fluorescence in red-phase PDA is assigned to transition from the lowest excited B$_u$ state [30]. It has become apparent that the fluorescence intensity (FI) of the hybridized NPs was much stronger than that of polyADA NCs, and so enhanced by about 5-fold. On the contrary, no fluorescence was observed in the case of Au/polyADA hybridized NPs without SiO$_2$ layer. In other words, the suitable thickness of dielectric SiO$_2$ layer between Au-core and polydiacetylene-shell in the present hybridized NPs plays a very important role to enhance FI, due to “emission enhancement” induced by LSPR as discussed later [31, 32]. In any NPs, the excitation spectra were in good agreement with the extinction spectra as shown in Fig. 2(a), which suggests that the emission in Fig. 2(c) would originate from polyADA shell. The FQY was still low but significantly increased from less than 0.05% in polyADA NCs to 1.2% in the hybridized NPs. In addition, the FLT of the hybridized NPs was $\tau_1 = 0.04$ ns (77%), $\tau_2 = 0.12$ ns (23%), which was evidently shorter than those of polyADA NCs [$\tau_1 = 0.06$ ns (73%), $\tau_2 = 0.20$ ns (27%)] by means of double exponential fitting to the decay curves of FI (decay curves not shown)]. In general, the LSPR effects would strongly accelerate the radiative process of fluorophore adsorbed through spacer with optimum thickness on the surface of metal NPs under the condition of overlapping between LSPR and fluorescence peaks. This is because excitation energy resonantly transfers from fluorophore to metal NPs and induces LSPR, followed by shorter radiative decay of LSPR than that of fluorophore [31, 32]. Actually, the LSPR of hybridized NPs would be overlapped with fluorescence peak from polyADA, so that fluorescence enhancement was caused by “emission enhancement” [31, 32].

Figure 3(a, b) indicate the dependence of FI and FLT on excitation light intensity. The FI increased gradually and FLT clearly became shorter with increasing excitation light intensity: $\tau_{\text{AV}} = 0.14$ ns at 5 $\mu$W (low intensity limit) and $\tau_{\text{AV}} = 0.08$ ns at 1300 $\mu$W (high intensity limit). The decay curves of FI were expeditiously fitted to analyze FLT by using double exponential function in the present study. However, this fitting does not simply the existence of the two kinds of excited emission level, or rather the distribution of FLT, owing to thermal motion and/or structural fluctuation of polyADA inside the present hybridized NPs [33]. In principle, excitation energy resonantly transfers from excited polyADA shell to Au NPs core, and excited localized surface plasmon was not only radiatively decayed but also induced spontaneous emission of polyADA [34, 35]. Actually, the hybridized NPs took typical linear correlation in the double logarithm plot within the range of applied excitation light intensity (slope = 0.99) in Fig. 3(c). So, this fact suggests that singlet-singlet annihilation could be ignored in substance even under the conditions of the present excitation light intensity. The dependence of FLT on excitation light intensity in Fig. 3(b) is still unclear, and more details should be investigated.

These facts provide useful insight that non-emitted nanomaterials such as polyADA NCs are made fluorescent by constructing optimum hybridized structure, which would develop novel element materials toward various photonic device applications.

IV. CONCLUSION

In the present study, we have successfully fabricated Au/SiO$_2$/polyADA hybridized NPs through the co-precipitation/microwave irradiation method and the subsequent solid-state polymerization. The decrease in FLT as well as the increase in FQY of the resulting hybridized NPs were clearly observed at the same time, compared with the polyADA NCs control. These experimental facts could be explained reasonably in terms of “emission enhancement” induced by LSPR effect, which occurrence would be controlled by well-defined and suitable thickness of dielectric SiO$_2$ layer introduced between Au-core and polydiacetylene-shell in the present hybridized NPs. As one of the important instances, the present results would further contribute to the development of nano-optics and nano-photonics. In fact, intense and stable point light sources such as the present hybridized NPs will be possibly used in some fields of photos-science, bio-science, and nonlinear optics.
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APPENDIX

The histogram of the hybridized NPs is available in Supplementary Material at https://doi.org/10.1380/ejssnt.2018.436.