Enhanced Absorption and Emission in a Copper Phthalocyanine–Gold Nanoparticle System Assisted by Localized Surface Plasmon

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Localized surface plasmon resonance leads to an increase in the degree of photon absorption and concomitant emission in copper phthalocyanine–gold nanoparticle systems.

Localized surface plasmon resonance (SPR) leads to generation of locally enhanced electric field at a metal/medium interface and is promising for the application of surface-enhanced Raman scattering (SERS)[1] and fluorescence[2] of organic molecules.

As to fluorescence enhancement, the effect of SPR is highly dependent on the distance between a metal nanoparticle surface and a molecule.[3] Considerable enhancement of absorption of organic molecules adjacent to silver island film,[4] hole arrays,[5] and nanoparticles[6] has also been found to be induced by local electric fields.

As can also be recognized from the aforementioned reports, the special distance between organic molecules and metal nanoparticle surfaces is very important for controlling the optical responses of organic molecules. This may also open up new applications of gold nanoparticles to photonics.

From these viewpoints, we have precisely controlled the distance between a gold nanoparticle surface and a nonfluorescent copper phthalocyanine derivative by incorporating polyion films between them. A remarkable correlation of absorption and emission changes with the special distance was found.

An aqueous solution of gold nanoparticles (AuPs) capped with citric ion was prepared by the reduction of $HAuCl_4$ with sodium citrate as described previously.[7] The mean diameter evaluated from transmission electron micrograph (TEM) image was 18 ± 1 nm. A copper(II) complex of phthalocyanine derivative (CuPc) was supplied from Mitsui Chemicals, Inc.

The surface of a glass substrate was made hydrophilic as described previously.[8] The hydrophilic substrate was then modified with polyions as a precursor film. Namely, the substrate was successively immersed into an aqueous solution of 1.5 mM polyethyleneimine (PEI, MW: 50000–100000) for 30 min at room temperature, an aqueous solution of 3 mM poly(styrene sulfonate) (PSS, MW: 70000) for 30 min at room temperature, and again the 1.5 mM PEI solution, with intermediate water washing. Accordingly, the (PEI/PSS/PEI) layers were adsorbed on a glass surface as the precursor film (Figure 1). An AuP film prepared at the liquid/liquid interface was then deposited on the precursor film, denoted as AuP/Glass. The preparation procedure for a AuP film at a liquid/liquid interface has been reported previously (detailed procedures are shown in Supporting Information[9]).[2b,10] Next, the CuPc solution (0.1 mM, 10 μL) was spin-coated on AuP/Glass, giving a CuPc–AuP assembly on the substrate denoted as CuPc/AuP/Glass (Figure 1a), in which the distance between CuPc and AuP is assumed to be zero.

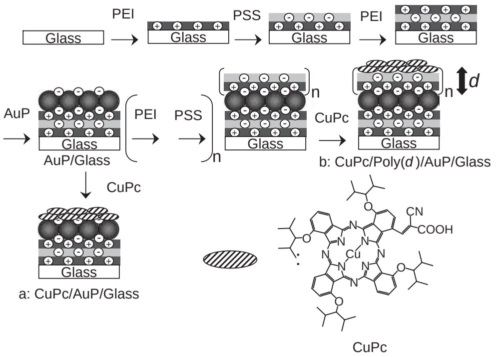

Figure 1. Preparation procedures of a: CuPc/AuP/Glass, b: CuPc/Poly(*d*)/AuP/Glass.

On the other hand, the distance between AuP and CuPc was changed by incorporating the interlayers of polyions between them. Namely, AuP/Glass was immersed into 1.5 or 0.15 mM PEI solution for 30 min and then 3 or 0.3 mM PSS solution for 30 min, with intermediate water rinsing. By repeating these procedures, the thickness of the polyion films, Poly(*d*), could be controlled by the number of deposited layers. Finally, the CuPc solution was spin-coated on the surface of polyion-coated AuP/Glass, denoted as CuPc/Poly(*d*)/AuP/Glass, where *d* represents the thickness (nm) of (PEI/PSS) interlayers (Figure 1b).

As a reference sample, the CuPc solution was spin-coated directly on the surface of the precursor-coated glass substrate, denoted as CuPc/Glass. The amount of spin-coated CuPc on every substrate was roughly identical (see Supporting Information[9]).

The thickness of polyion layers was evaluated to be 5.8 ± 0.3 or 0.9 ± 0.4 nm by using ellipsometry when the solutions of 1.5 mM PEI/3 mM PSS and 0.15 mM PEI/0.3 mM PSS were used, respectively (detailed information is shown in Supporting Information[9]). The method of fabricating two-dimensional AuP films using the liquid–liquid interface is convenient (Figure S1), and the resultant AuP film can be readily transferred onto the glass substrate. Figure 2A shows the SEM image of AuP/Glass. It is clear that AuPs are arranged two-dimensionally with densely packed structure. The coverage of AuPs was evaluated to be ca. 70%.

Figure 2B shows absorption spectra of the colloidal solution of AuPs, AuP/Glass, and CuPc/Glass. The colloidal solution

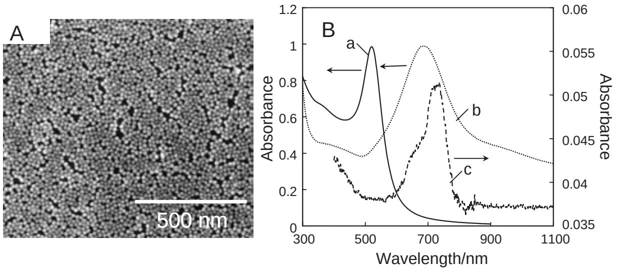

Figure 2. A: SEM image of AuP/Glass. B: Absorption spectra of aqueous colloidal gold solution (a: —), AuP/Glass (b: ···), and CuPc/Glass (c: - - -).

shows a plasmon band at 520 nm. On the other hand, considerable red shift and broadening of the plasmon band with a peak at 680 nm were observed in AuP/Glass. These spectral features are usually observed when the particles are densely arranged on a substrate with high refractive index, so that interparticle plasmon coupling is responsible.[11]

As shown in Figure 2B (line c), CuPc/Glass shows characteristic peaks of CuPc at 655 and 730 nm which considerably overlap with the plasmon band of AuP/Glass. Thus, the interaction between the electronic transition dipole of CuPc and the locally enhanced electric field based on surface plasmon resonance (SPR) is expected in the present CuPc–AuP systems.

Figures 3a–3c show typical transmission absorption spectra of CuPc/AuP/Glass (a) and CuPc/Poly(d)/AuP/Glass where the d values of (PEI/PSS) interlayers are 0.9 (b) and 2.7 nm (c), respectively. As shown in Figure 3a, the spectrum of CuPc/AuP/Glass exhibits two peaks based on AuP at 680 nm and CuPc at 730 nm. Note that appreciable damping of the former peak (680 nm) while clear absorption of the latter (730 nm) was observed. Although the reason of this damping is not clear at this stage, the degree of the damping (680 nm) and the peak intensity (730 nm) decreased steeply with increasing d value of the polyion interlayer (Figures 3b and 3c). To clarify this, the value of absorbance difference between Poly/AuP/Glass and CuPc/Poly/AuP/Glass at 750.5 nm (ΔAbs) was plotted as a function of the d value (Figure 3d). It is clear that the ΔAbs value dramatically decreased with increasing the d value in less than $\approx$3 nm and showed no appreciable enhancement above $\approx$3 nm.

The inset of Figure 3d shows emission spectra of CuPc/Glass and CuPc/Poly/AuP/Glass excited at 680 nm. Though the emission from CuPc was hardly detectable for CuPc/Glass, CuPc/AuP/Glass showed considerable emission signals especially when the CuPc layer was close to AuP. The emission intensity at 750 nm was also plotted against the d values, as shown in Figure 3d. It is noteworthy that the profile of absorbance change with the d value is quite well correlated with the corresponding emission change. These results suggest that when the distance between CuPc and AuP is close (less than 3 nm) the coupling of the nonradiative excited state(s) of CuPc and the LSPR state of AuP accelerates (enhances) the nonradiative decay process of the excited state(s) of CuPc. This must enhance the emission from CuPc–AuP assembly via AuP and the concomitant photon absorption of CuPc caused by the degradation of the nonradiative excited state(s) of CuPc.

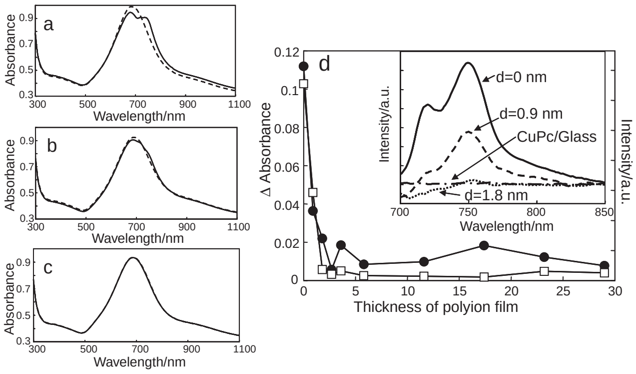

Figure 3. a–c: Absorption spectra of Poly(a: $d = 0$, b: $d = 0.9$, c: $d = 2.7$ nm)/AuP/Glass, before (- - -) and after (—) the modification with CuPc respectively. d: plots the absorbance change (ΔAbs) at 750.5 nm (●), before and after the modification with CuPc, and emission intensity at 750 nm (□) for CuPc/Poly/AuP/Glass against the thickness of polyion film. (Inset: emission spectra for CuPc/Poly($d = 0, 0.9, 1.8$ nm)/AuP/Glass and CuPc/Glass.)

In conclusion, we have succeeded in controlling absorptivity as well as emission intensity of a CuPc–AuP assembly by precisely changing the distance between CuPc and AuP surface, by utilizing the localized electric field based on SPR of AuP.

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