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Photoreactivity of As-Fabricated Au Clusters at the Single-Cluster Level

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Metal clusters with a size comparable to the Fermi wavelength exhibit characteristics that are different from those of both bulk and large nanoparticles. In this size regime, metal clusters exhibit molecule-like transitions owing to the discretion of the density of states.[1−3] Noble-metal clusters, composed of several tens of atoms, have attracted considerable attention for a variety of reasons, ranging from a fundamental scientific interest in nanoscopic materials to technological applications.[1−9]

The discrete states of noble-metal clusters along with the fluorescence initiate an investigation into the behavior and reactivity of these metal clusters by using spectroscopic techniques. Single-molecule fluorescence spectroscopy (SMS)[10] is a powerful method to reach the individual clusters underlying the heterogeneous characteristics of materials. There have been a few attempts to investigate the Ag clusters at the single-cluster level; however, these studies concentrate primarily on the optical properties of the clusters.[6,7] Here, we fabricated Au clusters (Au_n, n = atom number) using a photochemical method in a polymer matrix and concurrently investigated the photoreactivity of newly formed clusters at the single-cluster level. This novel approach gave us an opportunity to achieve a better understanding of the following subjects of interest. (1) The fluorescence spectra of Au_n were characteristic to the n, which motivated us to identify a Au_n sample with a clear resolution of the number of atoms during the growth process.[3,4] The study has provided new insight into the growing process of clusters and the synthesis of metal clusters with a strictly controlled atom number. (2) Due to the molecular-like transitions, the photochemical reactivity of quantized Au_n is a subject of great interest. However, there have been no reports regarding the reactivity of excited Au_n due to its instability without a protective ligand. In this study, we have investigated the photoinduced reaction between the ligand-free Au_n and O_2.

A poly(vinyl acetate) (PVAc) film containing a radical precursor (2-hydroxy-4′-(2-hydroxyethoxy)-2-methylpropiophenone) and $HAuCl_4$ (denoted as **PVAc**) was prepared (see Supporting Information, SI). PVAc can disperse and stabilize Au_n. Upon photoexcitation, the radical precursor yields radicals via a Norrish-type-I α-cleavage.[11] These radicals work as reducing agents for the Au ion to generate Au_n (see SI).

Figure 1a shows the absorption spectra of **PVAc** before and after UV-light irradiation. It was observed that the broad absorption band at 420 nm appeared after the irradiation. The UV-light-irradiated **PVAc** matrix exhibited luminescence with the excitation and emission maxima at 409 (∼80 nm for fwhm) and 490 (∼100 nm for fwhm) nm, respectively (Figure 1a and b).

No such fluorescence was observed when the UV light was irradiated to the polymer matrix containing either the radical precursor or $HAuCl_4$. The transmission electron microscopy (TEM) image of **PVAc** after UV-light irradiation showed Au_n that were ∼1 nm in diameter (Figure 1c).[12] Since small Au_n exhibited fluorescence owing to the discrete energy levels, the fluorescence was derived from the generated Au_n.[3,4]

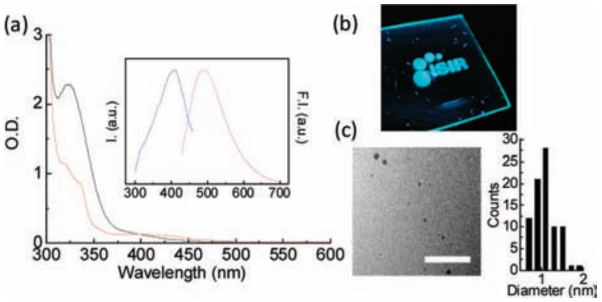

Figure 1. (a) UV−vis absorption spectra of **PVAc** before and after the 2 h irradiation of UV light (black and red, respectively). Inset shows the excitation (blue) and fluorescence (pink) spectra of UV-light-irradiated **PVAc**. (b) Au_n pattern of ISIR logo in the **PVAc** under irradiation of UV light. (c) TEM image and size distribution of Au_n fabricated in the **PVAc**. Scale bar = 20 nm.

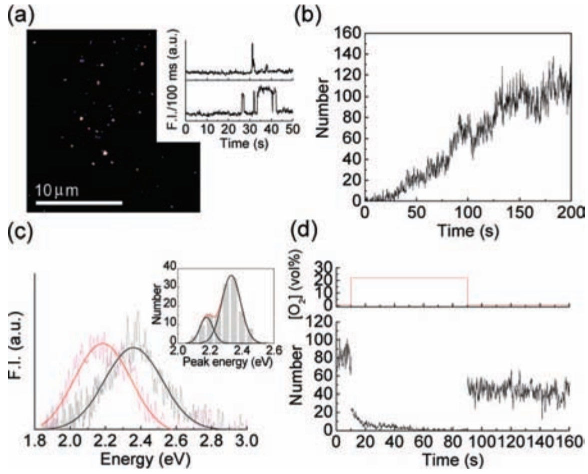

Figure 2. (a) SMS image under excitation of a 405-nm laser for 60 s showing the photofabricated Au_n. Inset shows the typical fluorescence trajectories observed for single Au_n. (b) Time-dependent change in the number of fluorescent species. (c) Single-cluster fluorescence spectra. Inset shows the histogram of single-cluster emission peak. Emission maxima for typical single Au_n are ca. 2.2 and >2.4 eV. (d) Dependence of the change in the number of fluorescent species on O_2 concentration ($[O_2]$). The number of fluorescent species before O_2 exposure was ∼80, and this number decreased to almost 0 after exposure to O_2 ($[O_2]$ = 22 vol%). ∼50% of the decreased number of the species was recovered by decreasing the $[O_2]$ to 0.3 vol%.

An SMS image during the 405-nm cw laser excitation in an Ar atmosphere is shown in Figure 2a. The sample for SMS (a film of ca. 5-μm thickness) was fabricated by spin coating (3000 rpm, 40 s) an acetonitrile solution of PVAc (1 wt%) containing the precursor (2.5 mM) and $HAuCl_4$ (1 mM). The laser excited both the radical

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precursor and Au_n, and hence a real-time observation of the newly formed Au_n clusters was possible.

Initially, no fluorescence was observed, while successive laser excitation clearly displayed an increase in individual fluorescent blinking species with a long off-time (Figure 2a inset, b). Similar blinking behavior was also observed for the thiol-capped Au_n, supporting the hypothesis that the emissive species were single Au_n (see SI).

While the bulk fluorescence spectrum of **PVAc** was quite broad and indistinguishable, the single Au_n exhibited much narrower fluorescence spectra (Figure 2c). By taking the spectral response of the detection system, in particular, the effect of cutoff filters, into account, we concluded that the bulk spectrum of **PVAc** was composed of two main fluorescence spectra with a peak at 2.2 or >2.4 eV.[13] Since the stability of Au_n, as well as its emission energy, depended on n due to the closing of the electronic shell and the structure of the cluster,[1] the histogram of the fluorescence maxima indicated that the distribution of the generated clusters was biased toward the favorable n (Figure 2c, inset). No time-dependent spectral change in single Au_n was observed, indicating that these clusters were very stable without further growth and/or decomposition during the experimental duration (~5 min).

Interestingly, the number of fluorescent species decreased dramatically when the samples were exposed to O_2 (Figure 2d). ~50% of the decreased number was recovered by removing O_2. The fluorescence spectra and the histogram of the fluorescence maxima did not change significantly after the recovery. Therefore, it was concluded that there were two different quenching processes, that is, a reversible process and an irreversible process.[14] Fluorescence quenching by O_2 was prohibited by capping the clusters with octadecanethiol, inferring that the access of O_2 to the surface of the Au_n played a key role (see SI).

Various theoretical and experimental results have indicated that the stable O_2-adsorption on negatively charged Au_n occurs through a (partial) charge transfer.[15,16] However, the reversibility of the observed reaction indicated that the fluorescence quenching did not proceed through a strong interaction such as chemisorption but through a weak interaction. The binding energy of O_2 for Au_n with an odd n was dramatically smaller than that for Au_n with an even n; therefore, the observed fluorescent species would be odd-numbered Au_n.[15] Otherwise, the polymer might prohibit stable adsorption because Au_n are partially stabilized through the multiple coordination of the polymers.[16]

We examined the fluorescence quenching by using several electron acceptors (nitrobenzene, 1,4-dinitrobenzene, and nitrobenzaldehyde; $E_{\mathrm{red}} = -1.06$, -0.69, and -0.86 V vs SCE, respectively).[17] Because the reduction potentials of these compounds are similar to that of O_2 ($E_{\mathrm{red}} = -0.87$ V vs SCE),[18] they quenched the fluorescence (see SI). Therefore, it can be speculated that photoinduced electron transfer was one of the reasons for the fluorescence quenching by O_2. The charge separation with and without recombination would be responsible for the reversible and irreversible processes, respectively.

In conclusion, we observed the as-fabricated Au_n at the single-cluster level. The approach successfully captured the optical characteristics of individual Au_n during the growth process. It was revealed that Au_n composed of a different number of atoms were fabricated during the formation/growth process and the distribution was significantly biased toward the stable clusters. Although further improvements are necessary, the proposed procedure would be a powerful method for in situ observation of the formation and growth of noble-metal clusters.

We discovered the reversible and irreversible quenching of fluorescence from ligand-free Au_n by using O_2 for the first time. The electron transfer played an important role in the fluorescence quenching of Au_n. Our attempt detected a new photoinduced reaction via weak interaction, which had been overlooked in previous studies. Although a Ag cluster is considered to be a powerful fluorescent probe,[7,8] Au_n is unfavorable due to the blinking character and reactivity toward O_2, unfortunately. However, our findings would eventually lead to further applications of Au_n, for example, as photocatalysts and in three-dimensional photoprocessing.[9,19]

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Supporting Information Available: Experimental section, characterization of emitters, SMS study for the thiol-capped Au_n and blinking behavior of Au_n, τ_f measurement, and fluorescence quenching. This material is available free of charge via the Internet at http://pubs.acs.org.

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(12) Furthermore, we extracted the emitting component by using the thiol capping and chromatography technique and identified the Au_n (see SI).
(13) According to the jellium model (emission energy $= E_{\mathrm{Fermi}}/n^{1/3}$, where E_{Fermi} is the Fermi energy of bulk Au),[3,4] several Au_n ($n = 9-20$) would exhibit emissions in the region 2.1 to 2.6 eV. Au_{17} and $Au_{n<12}$ may correspond to the clusters emitting at 2.2 and >2.4 eV, respectively.
(14) The fluorescence lifetimes of Au_n (τ_f) in the Ar- or O_2-saturated acetone solution were measured by using the laser flash photolysis technique (see SI). The τ_f value decreased significantly in the presence of O_2 and recovered completely when purged with Ar.
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