Fabrication and Luminescent Properties of Silver Nanoparticles Passivated by Fullerodendrons

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Spherical silver nanoparticles (diameter: 7–10 nm) were fabricated through passivation by fullerodendrons (C_{60}(Gn-COOK) ($n = 0.5, 1.5, 2.5$)), which were synthesized from fullerene and anthracenyl focal poly(amido amine) dendrons with carboxylate terminals and different generations (G). The resultant nanocomposites presented unique luminescence, which was contributed by not only anthracenyl moiety but also poly(amido amine) dendron moiety, although the latter has no traditional fluorophore. Furthermore, fluorescence of C_{60}(G2.5-COOK) was quenched by the silver nanoparticles, indicating that the excitation energy transferred to silver particles.

Recently, considerable numbers of studies focus on the possibility of the construction of new materials from nanoparticles and other components in order to yield composite nanomaterials with unique properties, which go beyond properties of single elements. There are several reports concerning C_{60} derivative-stabilized nanometals, which reveal unusual optoelectronic properties.[1] However, these nanometals could not be dispersed in water, which limited the application. On the other hand, utilizing poly(amido amine) (PAMAM) dendrimers as a protector, water-soluble metal and metal derivative nanoparticles have been synthesized for purposes of providing the industrial materials and medical therapeutic agents.[2]

In the present work, silver nanoparticles are fabricated in the presence of PAMAM dendron with a fullerene-focal point (fullerodendron)[3] as a stabilizer agent, which is a useful way to produce water-soluble nanometals passivated by fullerene derivatives. The size and morphology of resultant nanoparticles are observed, and the influence of dendron generation on fabrication of nanoparticles is compared. Furthermore, luminescent properties of silver nanoparticles passivated by fullerodendrons are examined.

According to the previously reported method,[3a] fullerodendrons (C_{60}(Gn-COOK) ($n = 0.5, 1.5, 2.5$)) (Figure 1) were synthesized by Diels–Alder reaction of C_{60} with anthracenyl focal PAMAM dendrons, which have potassium carboxylate terminal groups and different generations (Gn). C_{60}(Gn-COOK)-passivated silver (Ag-C_{60}(Gn-COOK)) nanoparticles were prepared through the reduction of Ag^+ by $NaBH_4$ in the presence of C_{60}(Gn-COOK) in water at $0\,°C$ according to literature.[2b] Then silver ion concentration in a mother suspension was 8×10^{-5} M, and a number ratio of silver ion to terminal carboxyl group of the fullerodendron was 1:25.

The UV–visible absorption spectra were measured in a 1 mm quartz cell on a Shimadzu UV-2200 spectrometer. The transmission electron microscopic (TEM) observations were carried out on a Hitachi H-7000 microscope operated at
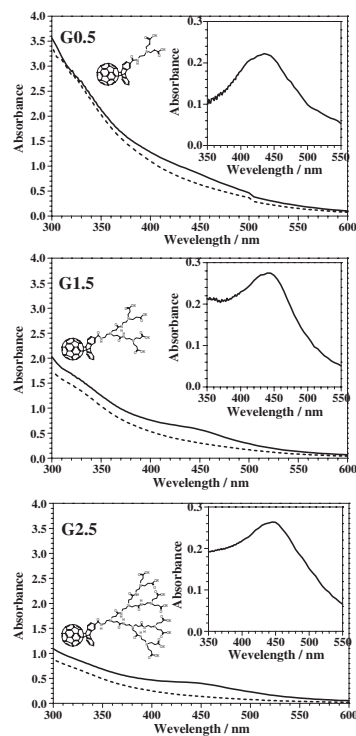

Figure 1. UV–vis absorption spectra of C_{60}(Gn-COOK) (broken line) and Ag-C_{60}(Gn-COOK) nanoparticles (solid line) in water. Insets: differential spectra and chemical structures of fullerodendrons.

100 kV. Liquid film of the suspension was dried on a carbon-deposited copper grid. Fluorescence spectra were recorded in a quartz cell (1 cm path) with a Hitachi F-3010 fluorometer.

In Figure 1, UV–vis absorption spectra of aqueous suspensions of Ag-C_{60}(Gn-COOK) nanoparticles are compared to solution spectra of C_{60}(Gn-COOK). While spectra of C_{60}(Gn-COOK) solutions at 300–600 nm region displayed the tail of a UV band, spectra of Ag-C_{60}(Gn-COOK) nanoparticle suspensions showed a weak band at 440 nm (see the inserted differential spectra in Figure 1). The position of this band, which was attributed to a plasmon band of silver nanoparticles,[2b] was independent of the dendron generation.

Figure 2 displays TEM images of Ag-C_{60}(Gn-COOK) nanoparticles. The observed spherical silver nanoparticles were 9 ± 1, 10 ± 5, and 7 ± 3 nm in diameter for $n = 0.5, 1.5$, and 2.5, respectively. It has been reported that the size of silver nanoparticles became small as increasing generation of PAMAM dendrimer.[2a] However, in the present case, it is apparent that the size and shape of nanoparticles did not depend on generation
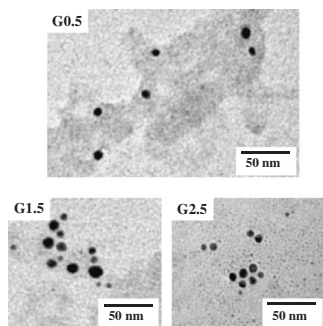
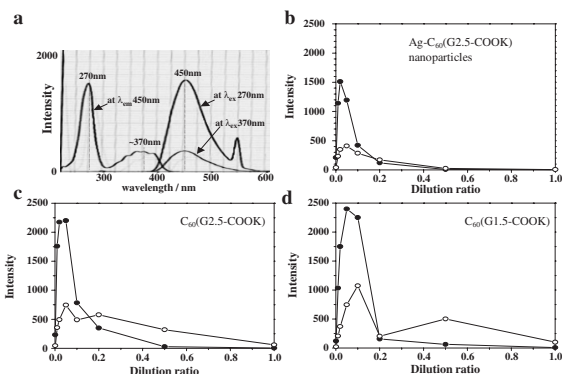**Figure 2.** TEM images of Ag-C_{60}(Gn-COOK) nanoparticles.

Figure 3. Fluorescence spectra for aqueous suspensions of Ag-C_{60}(G2.5-COOK) nanoparticles at 50 times dilution (a) and plots of emission fluorescence intensities at 450 nm versus dilution ratio (b–d). Solid circles: excited at 270 nm, open circles: excited at 370 nm.

of dendritic moiety. This independency on generation is consistent with the result from plasmon bands.

Fluorescence excitation and emission spectra for aqueous suspensions of Ag-C_{60}(G2.5-COOK) nanoparticles were measured at various dilution of the mother suspension. Typical spectra at 50 times dilution were shown in Figure 3a. Whereas there were a strong excitation band at 270 nm and weak excitation bands at 320–400 nm, an emission band was at 450 nm. A peak at 540 nm is attributed to second-order scattering of irradiation light at 270 nm. Fluorescence bands of aqueous suspensions of Ag-C_{60}(G2.5-COOK) nanoparticles were at the same position as those of aqueous solutions of not only C_{60}(G2.5-COOK) but also C_{60}(G1.5-COOK) without silver nanoparticles. These results mean that a fluorophore was not silver nanoparticles but fullerodendrons.

It has been reported that fullerene derivatives emit fluorescence in 700–800 nm region, when excited at 370 nm.[4] Because fluorescence lifetime of fullerene derivatives is very short (1.2–1.5 ns),[5] an emission band was not measured in 700–800 nm region on our fluorometer. On the other hand, luminescent behavior of C_{60}(Gn-COOK) was consistent with that (excitation bands at 270 nm and 320–400 nm, an emission band at 450 nm) of PAMAM dendron moiety with an anthracenyl focal point and amine terminal groups. Then, it can be claimed that anthracenyl-focal PAMAM dendron moiety in fullerodendron plays an important role as a fluorophore.

Fluorescence emission intensity at 450 nm versus dilution

ratio is plotted for Ag-C_{60}(G2.5-COOK) nanoparticles, C_{60}-(G2.5-COOK), and C_{60}(G1.5-COOK) in Figure 3b, 3c, and 3d, respectively. All of them revealed that after fluorescence was intensified up to ≈0.05 dilution, strong quenching occurred at high concentrations. Moreover, maximum fluorescence of Ag-C_{60}(G2.5-COOK) nanoparticles was two-third as compared to that of C_{60}(G2.5-COOK). At the presence of silver nanoparticles, the excitation energy may transfer to silver particles.

On the other hand, there was no obvious difference in maximum emission intensity between 1.5th and 2.5th generation dendron. Wang and Imae[6] have reported that PAMAM dendrimers presented luminescence and their emission fluorescence shifted from 415 to 450 nm with increasing generation from second to fourth, although PAMAM dendrimers have no traditional fluorophores. Furthermore, anthracene molecule in methanol was excited at 250 and 310–380 nm and generated blue emission (390–480 nm). These facts suggest that fluorophores may be anthracenyl moieties. However, since chemical structure of anthracenyl group at focal point in PAMAM dendron is changed to 9,10-dewar anthracenyl group in C_{60}(Gn-COOK), fluorescence of latter group should be different from that of former one. Nevertheless, observed fluorescence spectra of C_{60}(Gn-COOK) were alike those of anthracenyl-focal PAMAM dendron. In terms of this point, it is presumable that PAMAM dendron moiety acts as a fluorophore. It might be one of interpretations that fluorescence from two different fluorophores, namely anthracene and PAMAM dendron, is overlapped on the observed fluorescence region. This interpretation was supported by the fact that the dilution ratio dependence of emission intensity was different between 270 and 370 nm excitation: The intensity of emission band excited at 370 nm overtook the intensity at 270 nm excitation, as the concentration increases over 0.2 dilution.

In the present study, silver nanoparticles have been fabricated by using a reducer in the presence of C_{60}(Gn-COOK) as a stabilizer. It was found that the size and shape of Ag-C_{60}(Gn-COOK) nanoparticles did not depend on generation of dendritic moiety. The Ag-C_{60}(Gn-COOK) suspensions emitted fluorescence, which was attributed to anthracenyl moiety and PAMAM dendron moiety without traditional fluorophore. The fluorescence was quenched from that of C_{60}(Gn-COOK) by the presence of silver nanoparticles, indicating the excitation energy transfer to silver nanoparticles.

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