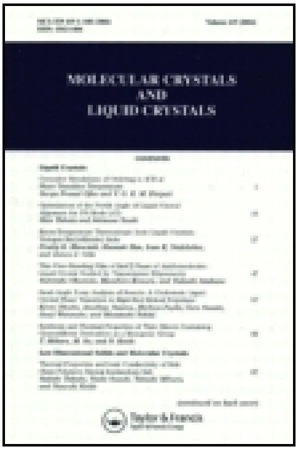

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A Convinient Method to Prepare Gold-Coated C_{60} Nanocrystals

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A Convinient Method to Prepare Gold-Coated C_{60} Nanocrystals

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Gold-coated C_{60} nanocrystals were first fabricated successfully. C_{60} nanocrystals as a core were prepared previously by the reprecipitation method using CS_2 as a good solvent and ethanol as a poor solvent. Gold nanoparticles were interestingly deposited on the surface of the C_{60} nanocrystals core without using any reducing reagent, after adding of $HAuCl_4$ aqueous solution into 10 ml of C_{60} nanocrystals dispersion. SEM images and powder X-ray diffraction proved the formation of gold nanoparticles. By changing temperature of C_{60} nanocrystals dispersion liquid after adding $HAuCl_4$ solution, we could control the gold-coating coverage of C_{60} nanocrystals.

Keywords: C_{60}; core-shell structure; gold; nanocrystals; reprecipitation method

INTRODUCTION

Both fullerene C_{60} molecule and their aggregates like clusters and micro/nanocrystals are now of much interest, because of their great potential applications in many research field such as physics, chemistry, and electronics [1–3]. On the other hand, recently, the core-shell type nanostructures have also attracted much attention [4–6].

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In particular, metal nanoshell formed on a core could provide novel optical, electronic and chemical properties [7,8]. It is the most important to choose suitable core and shell materials, and to fabricate well-defined interfacial nanostructures to control an interfacial interaction. In fact, the enhancement of nonlinear optical properties of hybridized nanomaterials was theoretically predicted [9,10], and has been actually revealed to occur in the gold nanoparticle-dispersed polydiacetylene thin film [11]. We have already prepared the hybridized nanocrystals composed of silver nanoparticles and polydiacetylene nanocrystals by means of the co-reprecipitation method [12], which was the developed ordinary reprecipitation method [13], and investigated their hybridized nanostructure and unconventional optical properties. Up to the date, there was few reports on metal-coated C_{60} nanocrystals [14,15]. C_{60} derivatives were used in these cases, not C_{60} itself, to fabricate metal-fullerene composites. However, the surface coverage of metal nanoparticles deposited on fullerene nanoparticles was still much low.

In the present article, we will report the fabrication of gold-coated C_{60} nanocrystals by means of the reprecipitation method and subsequent chemical reduction process without adding the reducing agent. Their crystal structure was evaluated using X-ray diffraction patterns as well as transmission and scanning electron microscopes (TEM and SEM).

EXPERIMENTAL

Materials

Fullerene C_{60} powder ($> 99.9\%$) was purchased from Tokyo Kasei Co., Ltd. Carbon disulfide (CS_2, 98 V/V%), ethanol (99.8%), and methanol (99.8%) were purchased from Kanto Chemical Industries Co., Inc. C_{60} and the solvents were used without further purification. Hydrogen tetrachloroaurate trihydrate [$HAuCl_4 \cdot 3H_2O$ (99.9%)] was purchased from Sigma-Aldrich, Inc. Water used in this experiment was purified up to $18.2\,M\Omega \cdot cm^{-1}$.

Preparation of C_{60} Nanocrystals as a Core

C_{60} nanocrystals were prepared by reprecipitation method [13]. A $200\,\mu l$ of C_{60} solution (2.5 mM), in which good solvent was CS_2, was quickly injected into vigorously stirred ethanol (10 ml) as a poor solvent. The color of the obtained dispersion liquid was slowly changed from colorless to weak brownish yellow, which indicates the formation of C_{60} nanocrystals. C_{60} nanocrystals dispersion liquid should be further allowed to stand for several hours to completely finish nanocrystallization.

Preparation of Gold-Coated C_{60} Nanocrystals

A 200 µl of $HAuCl_4$ aqueous solution (22.2 mM) was added into the 10 ml of the resulting C_{60} nanocrystals dispersion liquid, and the mixed dispersion was kept at given temperatures under slowly stirring for 2 hours. The colored dispersion liquid was further turned to raw umber, which suggests the formation of Au nanoparticles. After stirring for 2 hours, the dispersion liquid was cooled to room temperature.

Characterization

A few droplets of the resulting C_{60} and/or gold-coated C_{60} nanocrystals dispersion liquids were put on the Millipore membrane filter (VMTP, 50 nm of hole size), and then dried in air for measurements of electron microscope and powder X-ray diffraction pattern. Scanning electron microscope (SEM) image was taken by JSM-6700F (JEOL), and transmission electron microscope (TEM) by JEM-2000 EX (JEOL). XRD pattern was obtained by M18XHF22 (Bruker Axs).

RESULTS AND DISCUSSION

Figure 1(a) shows the SEM image of the resulting C_{60} nanocrystals as a core, and C_{60} nanocrystals are not entirely aggregated. The size distribution is in the range from 80 nm to 200 nm, and the average size is about 120 nm in this case. By adding $HAuCl_4$ aqueous solution, gold nanoparticles were deposited on the surface of C_{60} nanocrystal without using any binder and chemically modifying C_{60} molecule. As a result, novel metal coated core-shell type nanocrystals are demonstrated as shown in Figures 1(b)–1(d). In Figure 1(b), the average size of gold nanoparticles deposited at room temperature is about 10 nm, but the coverage is still low. Namely, the deposited Au nanoparticles are isolated each other on the surface of C_{60} nanocrystals. To control the coverage in gold-coated C_{60} nanocrystals, the deposition temperature of was elevated. The coverage and the size of deposited gold nanoparticles increased with deposition temperatures. Actually, Figures 1(c) and (d) indicate gold-coated C_{60} nanocrystals prepared at 40°C and 80°C, respectively. We can evidently observe the increase of coverage and gold nanoparticles size at the elevated temperatures, compared with at room temperature. Gold nanoparticles could be

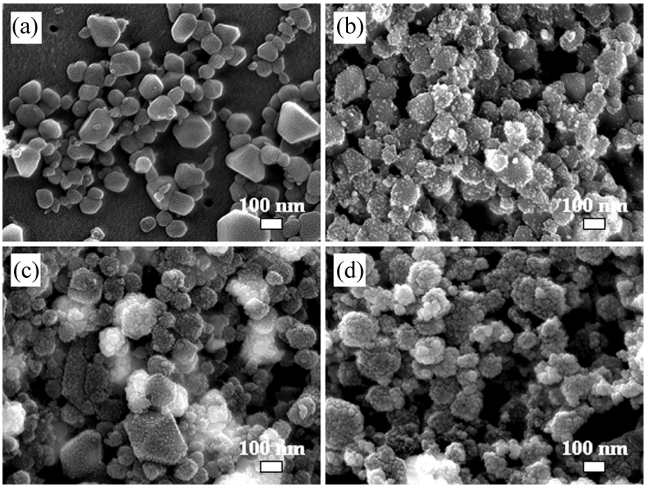

FIGURE 1 SEM images of (a) C_{60} nanocrystals prepared by the reprecipitation method (good solvent: CS_2/poor solvent: ethanol), and gold-coated C_{60} nanocrystals prepared at (b) room temperature, (c) 40°C, and (d) 80°C, respectively.

deposited densely at 80°C (Fig. 1(d)), and the surface of C_{60} nanocrystals core was almost covered with gold nanoparticles having 20 nm in size. In addition, there are no isolated gold nanoparticles (Figs. 1(b)–(d)), which means that gold nanoparticles were all deposited selectively on the surface of C_{60} nanocrystals.

Figure 2 indicates the relationship between average size of the deposited gold nanoparticles and deposition temperature, and the linear relation within experimental errors. From Figure 2, we could confirm that the size of the gold-coated C_{60} nanocrystals increased with deposition temperature.

High deposition temperature could lead to the large size of gold nanoparticles and to the higher coverage. The present process is the simple way to fabricate gold nanoshell with controllable thickness at a given temperature.

On the other hand, we found that the impurities such as sulfide would produce at high deposition temperature and multiplied with the increasing deposition temperature. Figure 3 shows the powder XRD patterns of C_{60} and gold-coated C_{60} nanocrystals prepared at several temperatures. From these XRD patterns, C_{60} nanocrystals has the same hexagonal phase of C_{60} bulk crystal (*hcp* structure, with $c/a = 1.633$) [16]. For example, one can see clearly the XRD diffraction

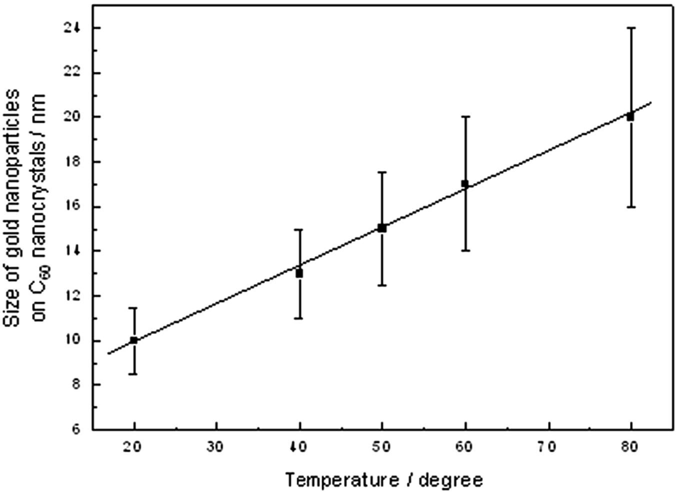

FIGURE 2 Relationship between average size of the gold nanoparticles on C_{60} nanocrystals and deposition temperature.

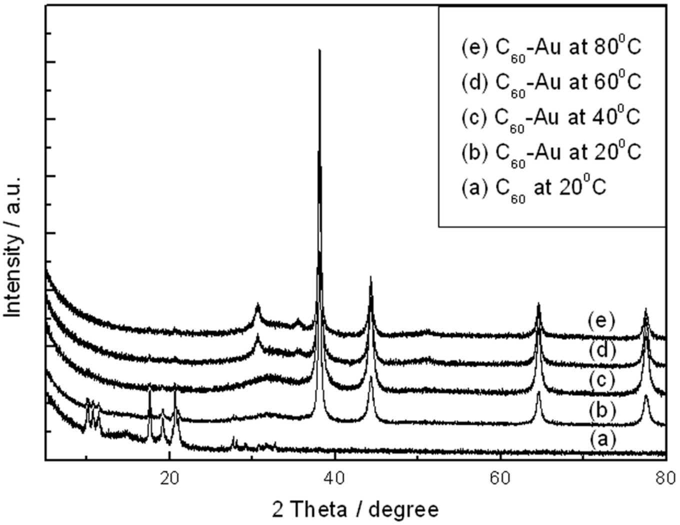

FIGURE 3 Powder XRD patterns of C_{60} and gold-coated C_{60} nanocrystals prepared at different deposition temperature. The peaks from C_{60} around $2\theta = 10°$ and $20°$ apparently disappeared at the more than 40°C, due to the strong peaks from gold around $2\theta = 40°$.

peaks of Au (111), (200), (220), and (311) as shown in Figure 3(b). Unexpectedly, the small weak peaks from Au_2S around $2\theta = 30^\circ$ appeared at the high deposition temperature.

We suggest that the deposition temperature is better at lower less than 60°C to avoid the production of impurity such as Au_2S. It was speculated that the residual CS_2 in C_{60} nanocrystal, that is to say, crystal solvates, may play a role of the reducing agent.

CONCLUSION

We could prepare successfully the C_{60} nanocrystals by the reprecipitation method. The resulting C_{60} nanocrystal had *hcp* structure and is a kind of crystal solvates [16].

In addition, we have also succeeded in gold-coated C_{60} nanocrystals only by addition of $HAuCl_4$ and the subsequent heating treatment. In particular, we could control the surface coverage of gold-coated C_{60} nanocrystals.

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