Fabrication of $\text{C}_{60}$ assembly films via an fullerene-amine addition reaction by using stepwise immersion

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Abstract. Fullerene $\text{C}_{60}$ thin films were successfully fabricated on the surface of amino-substituted substrates via a reaction between $\text{C}_{60}$ and an $\text{NH}_2$ group of 1,2-diaminoethane (DAE) using simple immersion processes. The maximum thicknesses of the fullerene assembled films increased with the number of immersions into the fullerene solution. Layered fullerenes were obtained by a series of repeated processes. The aggregated $\text{C}_{60}$ thin films were evaluated using transmission absorption measurements, transmission electron microscopy, and atomic force microscopy. These analyses suggest the presence of $\text{C}_{60}$-DAE aggregates on the substrates.

1. Introduction

Fullerenes are highly attractive materials as both electron acceptors and organic n-type semiconductors. Indeed, fullerenes are widely used in artificial photosynthesis models [1, 2], organic solar cells [3], and organic transistors [4]. In organic solar cells (OSCs), the carrier mobility of the organic films is an important factor in the photoelectric conversion performance. Adjacent or aggregated fullerene structures feature efficient electron transport [5]; therefore, the development of a facile method for the preparation of fullerene aggregates or wire structures is important.

Chemical modification and assembling of fullerenes are fundamentally important for the application of fullerenes as novel functional molecules and in molecular devices and organic electronic devices. One of the simplest chemical modification methods is an addition reaction between amines and fullerenes [6-9]. Recently, we discovered that the reaction of fullerenes ($\text{C}_{60}$ and $\text{C}_{70}$) with a large excess of 1,2-diaminoethane (DAE) affords uniform sub-micrometer particles consisting of fullerenes and DAE [10-12]. Using these molecules, it was determined that the incorporation of the microparticles substantially enhanced the photocurrent generation of a polythiophene film [10].

The addition reaction between fullerenes and amines also occurs at the liquid/solid interface; this reaction can therefore be used to prepare ultra-thin fullerene films [13-15]. Furthermore, we found that fullerenes contribute to photocurrent generation as electron acceptors via photo-induced electron transfer even in ultra-thin films [16, 17].

The fabrication of assembled fullerene films with various morphologies should also be useful for the development of organic electronics materials. Accordingly, we fabricated $\text{C}_{60}$ assembly films by repeated fullerene-amine addition reactions. The structures of the resultant $\text{C}_{60}$ assembly films were investigated.
2. Experimental procedure

All chemicals and materials were used as received. Milli-Q water (18.2 MΩ cm) was used. All immersions of the substrates into the fullerene and amine solution were performed using hand-made alternating dip-coating equipment.

The procedure for the preparation of C₆₀ assembly films is as follows (Figure 1): The pre-cleaned quartz glass substrate was immersed in a toluene solution of 3-aminotrimethoxysilane. After the solution was refluxed for 12 h, the substrate was removed and washed with sufficient amounts of toluene, ethanol, aqueous NaHCO₃, and water to obtain a NH₂-modified substrate, which is denoted as Quartz/NH₂, where / represents the interface. The presence of amino groups on the surface of Quartz/NH₂ was confirmed via the formation of imine bonds between amino groups on the surface and 4-nitrobenzaldehyde [18].

After drying, Quartz/NH₂ was immersed in a toluene solution of C₆₀ (2.0 × 10⁻³ mol dm⁻³) for 5 min at room temperature and washed with enough amounts of toluene to obtain a C₆₀-modified quartz substrate, which is denoted as Quartz/[C₆₀]₁ (Step 1).

Then, Quartz/[C₆₀]₁ was immersed in a toluene solution of 1,2-diaminoethane (2.0 × 10⁻² mol dm⁻³) for 5 min to substitute the amino groups on the surface of the C₆₀ layer of Quartz/[C₆₀]₁ (Step 2). After washing this modified quartz substrate, it was immersed in the same C₆₀ toluene solution used in Step 1 to obtain a double layer of C₆₀; the resultant substrate is denoted as Quartz/[C₆₀]₂ (Step 3). Thus, through a similar process of alternating immersion in the toluene solutions of fullerene and amine (Steps 4 and 5), we obtained aggregated C₆₀ assembly films, which are denoted as Quartz/[C₆₀]ₙ, where n is the number of immersions into the C₆₀ toluene solution.

For the transmission electron microscopy measurements, a gold microgrid (400 mesh, 3.0 mm) was immersed in an ethanol solution of 2-aminoethanethiol (1.0 × 10⁻³ mol dm⁻³) for 1 day at room temperature. After withdrawal, the grid was washed with sufficient amounts of ethanol and then dried in order to obtain an amino-modified microgrid, which is denoted as Au/NH₂. C₆₀ and diamine modifications were also performed similarly to the preparation of Quartz/[C₆₀]ₙ, to obtain C₆₀-assembly-film-modified gold grids, which are denoted as Au/[C₆₀]ₙ.

The UV-Vis spectra of the C₆₀ assembly films were measured using a UV-Vis spectrophotometer (V-670, JASCO). The surface morphologies of the modified thin films were determined using atomic force microscopy (AFM; SPA400, SII). The thicknesses and cross-sectional images of C₆₀ assembly films were measured using transmission electron microscopy (TEM; H-8100, HITACHI).

Figure 1. Schematic illustration of the preparation of the C₆₀ assembly films.
3. Results and discussion

The surface coverage of Quartz/NH$_2$ with amino groups was $\sim 1.5 - 2.0 \times 10^{-10}$ mol cm$^{-2}$, as determined via comparison of the transmission absorption spectra before and after modification of Quartz/NH$_2$ with 4-nitrobenzaldehyde. The surface coverage was similar to that predicted for a monolayer of C$_{60}$ using a model based on crystallographic data (fcc; $1.9 \times 10^{-10}$ mol cm$^{-2}$) [13].

Figure 2(a) shows transmission absorption spectra of Quartz/[C$_{60}$]$_n$ (n = 1, 2, and 3). In each assembly film, the absorption profile decayed from shorter to longer wavelengths and the baseline increased from n = 1 to 3. These absorption characteristics are attributable to the sum of the $\pi-\pi^*$ absorption band of the C$_{60}$ structure and light scattering of the C$_{60}$ assemblies.

In Figure 2(b), the intensity of the absorbance at 350 nm, which is mainly attributed to the $\pi-\pi^*$ absorption, is plotted as a function of the number of immersions into the C$_{60}$ toluene solution: An approximately straight line results with an increasing slope from n = 1 to 3. This suggests that the amount of C$_{60}$ absorbed increases with increasing number of C$_{60}$ modification processes. The estimated absorbed amount of C$_{60}$ after one immersion is on the sub-monolayer level, as determined from the absorbance of Quartz/[C$_{60}$]$_n$ (n = 1, 2, and 3) at 350 nm.

![Figure 2. UV-Vis absorption spectra of (a) Quartz/[C$_{60}$]$_n$ (n = 1, 2, and 3) on both sides, (b) relationship between the absorbance of Quartz/[C$_{60}$]$_n$ (n = 1, 2, and 3) at 350 nm and the number of immersions (n) into the C$_{60}$ toluene solution.](image)

Figure 3. Contact-mode AFM images of (a) bare quartz, (b) Quartz/NH$_2$, (c) Quartz/[C$_{60}$]$_1$, (d) Quartz/[C$_{60}$]$_2$, (e) Quartz/[C$_{60}$]$_3$. All images display the top view.
AFM images of bare quartz, Quartz/NH₂, and Quartz/[C₆₀]ₙ (n = 1, 2 and 3) are shown in Figure 3. Very similar surface structures are observed for quartz and Quartz/NH₂, and the differences between the maximum and minimum heights in both samples are quite comparable. This is reasonable because the molecular length of 3-aminotrimethoxysilane is relatively short with respect to the surface roughness of quartz and Quartz/NH₂. In contrast, the surface morphology of Quartz/[C₆₀]₁ is dramatically different. Modification of C₆₀ increased the surface roughness from ~3 to ~8 nm. In addition, sub-micrometer aggregated structures were evident on the surface of Quartz/[C₆₀]₁. The 5 nm increase in the surface roughness is considerably larger than the diameter of C₆₀, which suggests that C₆₀ adsorbs onto the NH₂ surface of Quartz/NH₂ as aggregates or clusters [9]. The surface roughness increased to ~13 nm for Quartz/[C₆₀]₂, but was only ~6 nm for Quartz/[C₆₀]₃. The detailed mechanism for these changes in surface roughness has not yet been elucidated; one possibility is the formation of an amino-group domain in Quartz/NH₂, which may cause morphemic changes, as follows (Figure 4): 1) Oligomers of 3-aminotrimethoxysilane are formed on the surface of the quartz, 2) an uncoated quartz surface remains, 3) C₆₀ molecules attach to the amino groups of Quartz/NH₂ to give Quartz/[C₆₀]₁, and 4) C₆₀ assemblies grow in all directions.

![Figure 4](image.png)

**Figure 4.** Proposed reaction scheme and structural changes on the quartz surface following silanization, and the attachment of C₆₀ and DAE.

Typical cross-sectional TEM images of Quartz/[C₆₀]₁ and Quartz/[C₆₀]₃ are shown in Figure 5. The TEM images indicate that the densities of the organic layers are not equal, which is reasonable because C₆₀ assembly films have considerably larger surface roughness. The results of statistical analyses, including the average C₆₀ film thicknesses and standard deviations of the maximum thicknesses of the films, are summarized in Table 1.

![Figure 5](image.png)

**Figure 5.** TEM images of (a) Au/[C₆₀]₁ and (b) Au/[C₆₀]₃.
Table 1. Thicknesses of the $[\text{C}_{60}]_n$ layers.

| Sample | Average film thickness / nm | Standard deviation / nm |
|--------|----------------------------|-------------------------|
| Au/$[\text{C}_{60}]_1$ | 14 | 5 |
| Au/$[\text{C}_{60}]_3$ | 32 | 11 |

These results indicate that the facile stepwise chemical modification process yielded 10–30 nm thick $\text{C}_{60}$ assembly films. In addition, the obtained $\text{C}_{60}$ assembly films have rough surfaces. $\text{C}_{60}$ assembly films with these morphological characteristics are likely particularly suitable for electronic applications. Further investigations into controlling and expanding the $\text{C}_{60}$ assembly films are currently underway. In the near future, we will apply these $\text{C}_{60}$ assembly films as n-type semiconductors for organic electronics such as organic field effect transistors and organic solar cells.

4. Conclusion

$\text{C}_{60}$ assembly films were attached onto a Quartz/NH$_2$ surface via addition reactions between fullerenes and amines across double bonds of the $\text{C}_{60}$ molecules. The absorption spectra of the $\text{C}_{60}$ assembly films showed the sum of the $\pi-\pi^*$ absorption band from the $\text{C}_{60}$ structure and light scattering of the $\text{C}_{60}$ assemblies. Via AFM, it was determined that a homogeneous thin $\text{C}_{60}$ assembly film was obtained. The TEM images indicated that the film thickness increased with repeated immersions into the $\text{C}_{60}$ toluene solution.

Acknowledgement

This research was partially supported by a Grant-in-Aid for Scientific Research (C) (No. 22550123) from the Japan Society for the Promotion of Science (JSPS).

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