

Preparation of Self-Assembled of α -D-Mannosyl Fullerene[C₆₀]-Gold Nanoparticle Films

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(Received October 27, 2008, Revised & Accepted November 17, 2008)

자기조립법에 의한 α -D-만노실 풀러렌[C₆₀]-금 나노입자 필름 제조

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(2008년 10월 27일 접수, 2008년 11월 17일 수정 및 채택)

ABSTRACT: α -D-mannosyl fullerene[C₆₀]-functionalized gold nanoparticle films were self-assembled using the layer-by-layer method on the reactive of glass slides functionlized with 3-aminopropyltrimethoxysilane. The functionalized glass slides were alternately soaked in the solutions containing α -D-mannosyl fullerene[C₆₀] and 4-aminothiophenoxide/hexanethiolate-protected gold nanoparticles. α -D-mannosyl fullerene[C₆₀]-functionalized gold nanoparticle films have grown up to 5 layers depending on the immersion time. The self-assembled nanoparticle films were characterized using UV-vis spectroscopy showed that the surface plasmon band of gold at 530 nm gradually became more evident as successive layers were added to the films.

요약: 3-아미노프로필메톡시 실란을 처리한 반응성 있는 유리표면 위에 “LbL” 방법을 사용하여 α -D-만노실 풀러렌[C₆₀]-금 나노입자를 자기조립 하였다. 표면 처리한 유리막을 α -D-만노실 풀러렌[C₆₀]과 핵산 티올레이트/아미노 티오페녹사이드-금나노입자를 포함하고 있는 용액속에 교대로 담그었다. α -D-만노실 풀러렌[C₆₀] -금 나노입자 필름을 시간에 따라 다중성(5층)막으로 제조하였다. 자외선-가시광선 분광기를 사용한 자기조립 나노입자 필름의 분석은 530 nm 일 때 금 나노입자의 표면 플라스몬 밴드로 인해 다중성(5층)막이 형성되는 것을 보여주었다.

Keywords: α -D-mannosyl fullerene[C₆₀]; gold nanoparticle; self-assembled; layer-by-layer method; UV-vis spectroscopy

I. Introduction

Fullerene functionalization has attracted much attention due to unique chemical and physical properties of fullerene derivatives, as well as their

potential applications in medicine, optics and material science, etc.¹ Ultrasound was applied to the synthesis of fullerene derivatives^{2,3} as a source of energy, since it has known to cause chemical reactions either in homogeneous or in heterogeneous systems. The chemical reactions are promoted by cavitation of liquid caused by ultrasonic waves

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traveling in the liquid. Here, cavitation implies the formation of micro-bubbles in a liquid subjected to sonication, which implode and generate high pressures and temperatures in their surroundings.^{4,5} Also, the self-assembly and organization of metal nanoparticles in multilayer films are one of the interesting research fields in material science due to the development of nanotechnology.⁶ Many of nanoparticles including Au, Ag, Pd and Pt were assembled into thin films for advanced electronic, magnetic, photonic and optoelectronic applications.⁷⁻⁹ The self-assembly of nanoparticles is mostly based on electrostatic interactions between adsorbed monolayers of nanoparticles and oppositely charged linker molecules.⁷⁻⁹ Recently, the strong affinity of C₆₀ to amine moieties was exploited to assemble multilayers of C₆₀ and gold nanoparticle bilayer structures.¹⁰⁻¹¹ The coupling (amination) of the C₆₀ molecules with peripheral amine moieties on the nanoparticle surface was the driving force for the layer-by-layer (LbL) assembly of these multilayer. The electrochemical studies on these multilayers revealed the compact nature of the surface assemblies. It is anticipated that the fabrication of organized surface assemblies of these nanocomposite materials might be exploited for optoelectronic applications. Here, we report sonochemical synthesis of α -D-Mannosyl fullerene[C₆₀] and preparation of self-assembled of α -D-mannosyl fullerene[C₆₀]-gold nanoparticle films.

II. Experimental

Fullerene[C₆₀] used in this work was golden grade from Hoechst and Southern chemical group Inc.. All solvents and chemical reagents were purchased from Aldrich and Fluka. The ultrasonication of all samples was conducted in continuous mode with an ultrasonic generator UG 1200 made by Hanil Ultrasonic CO. LTD.. Ultrasonic equipment having frequency 20 kHz, power 750 W was employed in this research. The configuration of the equipment is horn type system, and the size of the horn tip

is 13 mm in diameter. ¹H- and ¹³C-NMR spectra were recorded with a Varian Inova AS400 and Bruker avance digital 400 spectrometers on solutions in CDCl₃ with tetramethylsilane as the internal standard. IR spectra were recorded on JASCO FT/IR-4100 spectrometer (JASCO, Japan) using thin film on KBr plates. FAB-MS spectra were measured on a JMS-700 Mass spectrometer (JEOL, Japan) using metanitrobenzyl alcohol (NBA) and polyethylene glycol as a matrix, respectively. The UV-vis spectra were obtained by a Varian Cary 100 UV-visible spectrophotometer. Flash chromatography was carried out with silica gel (E. Merck, Art 9385, 230-400 mesh). The reactions were monitored by thin layer chromatography (TLC). TLC was performed using precoated silica gel plates (60F-254, E. Merck) and the spots were detected by charring with 5% sulfuric acid in ethanol.

1. Sonochemical synthesis of α -D-Mannosyl fullerene[C₆₀]

General procedure for mannosyl fullerene[C₆₀] synthesis - The solution of C₆₀ (20 mg, 0.028 mmol) in benzene (15 mL) was reacted by ultrasonication with 2'-azidoethyl mannoside 1a¹² (0.056 mmol) for 2 days at room temperature. The resulting solution was evaporated and then separated by flash chromatography (toluene/EtOAc = 10:1.5:1) to give mannosyl fullerene[C₆₀] **2a** and recovered C₆₀ (eluent: toluene).

α -D-mannosyl fullerene[C₆₀] (2a): R_f 0.50 (Tol:EtOAc 5/1); 5.8 % yield; ¹H-NMR (400MHz, CDCl₃) δ 5.34-5.27 (m, 3 H), 5.01 (d, 1 H, J_{1,2}=1.20 Hz, H-1), 4.70-4.53 (m, 3 H), 4.34 (dd, 1 H, J=5.6, 12.4 Hz), 4.25-4.15 (m, 3 H), 2.15, 2.146, 2.01. 1.95 (4 s, each 3 H, CH₃CO); ¹³C-NMR (100 MHz, CDCl₃) δ 170.94, 170.24, 169.93, 169.33 (C=O), 147.91, 146.51, 146.31, 146.24, 146.19, 146.03, 145.61, 145.46, 145.41, 144.61, 144.46, 144.41, 144.20, 144.14, 144.07, 143.33, 143.25, 143.22, 143.11, 142.98, 142.87, 142.73, 142.51, 142.43, 142.35, 142.32, 142.21, 141.01, 140.85, 140.55, 136.87, 136.35, 98.23 (C-1), 81.72, 69.65, 69.36,

69.19, 66.80, 66.30, 62.66, 47.73 ($\text{CH}_2\text{NC}_{60}$), 21.13, 21.08, 20.88, 19.96 (CH_3CO); UV-vis (CHCl_3): λ_{max} [nm] = 260, 326, 424; FT-IR (KBr, cm^{-1}): 2919, 1739, 1539, 1459, 1368, 1221, 1136, 1085, 1044; MS (FAB) m/z : 1109.2, 720.1 (C_{60}); HRMS (FAB⁺, polyethylene glycol matrix): m/z calcd for $\text{C}_{76}\text{H}_{23}\text{NO}_{10}$ 1109.36, found 1109.1334.

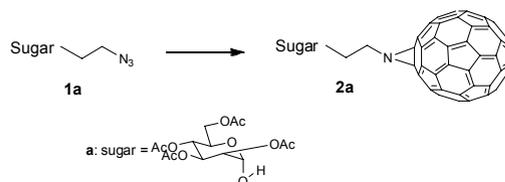
2. Layer-by-layer assembly of α -D-mannosyl fullerene[C_{60}]-gold nanoparticle films

4-aminothiophenoxide/hexanethiolate-protected gold nanoparticles with an average core dimension of ~ 3.2 nm were synthesized using the modified Brust reaction followed by ligand place-exchange reaction of hexanethiolate-protected gold nanoparticles with 4-aminothiophenol.¹³ α -D-mannosyl fullerene[C_{60}]-gold nanoparticle films and functionalized gold nanoparticle were self-assembled on the reactive surface such as glass slides functionalized with 3-aminopropyl trimethoxysilane. The functionalized glass slides were alternately soaked into the toluene solutions containing α -D-mannosyl fullerene[C_{60}] (10 mM) and 4-aminothiophenoxide/hexanethiolate-protected gold nanoparticles (~ 14 μM).

III. Results and discussion

1. Sonochemical synthesis of α -D-Mannosyl fullerene[C_{60}]

For the application of ultrasound in the synthesis of mannosyl fullerene[C_{60}], a cycloadditive reaction of fullerene[C_{60}] with 2'-azidoethyl mannoside **1a**¹² was performed as described in Scheme 1. First, 2'-azidoethyl mannoside **1a** was reacted with one equivalent of fullerene[C_{60}] in benzene under ultrasonic irradiation for 2 days. The silica gel TLC indicated that a new brownish-purple spot ($R_f = 0.50$) appeared between fullerene[C_{60}] and 2'-azidoethyl mannoside **1a** ($R_f = 0.23$). After evaporation of the solvent, the residue was separated by silica gel column chromatography (eluent:



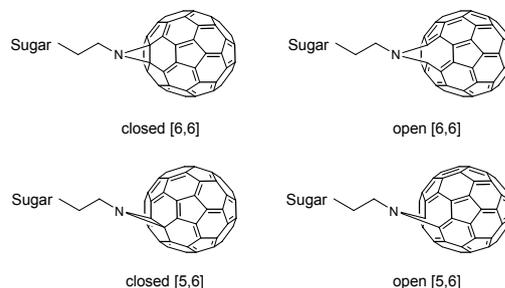
Scheme 1. Synthesis of α -D-mannosyl fullerene[C_{60}]. Reaction condition; C_{60} , benzene, ultrasound, rt, 2 days.

toluene/ethyl acetate = 10/1) to give mono-adducts **2a** (5.8 % yield). Unreacted fullerene[C_{60}] was recovered to 39% at the first stage of the chromatography (eluent: toluene).

For the characterization of mono-adducts **2a**, FAB-MS, ^1H - and ^{13}C -NMR, FT-IR, and UV-vis spectra characterizations were performed. The FAB-MS spectrum of **2a** shows a molecular peak at m/z 1109.1334 (M) with the base peak for fullerene[C_{60}] at m/z 720 (Figure 1). From the FAB-MS, ^1H - and ^{13}C -NMR spectra, **2a** was determined to be a 1:1 mannose-fullerene[C_{60}] adduct.

In general, there are four possible isomers for mono-adducts in cycloaddition of fullerene[C_{60}]¹⁴ in scheme 2. In the synthesis of the substituted methanofullerenes, thermolysis leads to an open [5,6] addition product, while photolysis gives a mixture of the close [6,6] and the open [5,6] products.¹

In order to identify the nature of the bonding in mono-adducts **2a**, we performed an analysis of the ^{13}C -NMR and UV-vis spectroscopic data for the fullerene cage. The ^{13}C -NMR spectrum of **2a** from



Scheme 2. Four possible isomers for mono-adducts in cycloaddition of fullerene[C_{60}]; close [6,6], open [5,6], close [5,6], and open [6,6] adducts

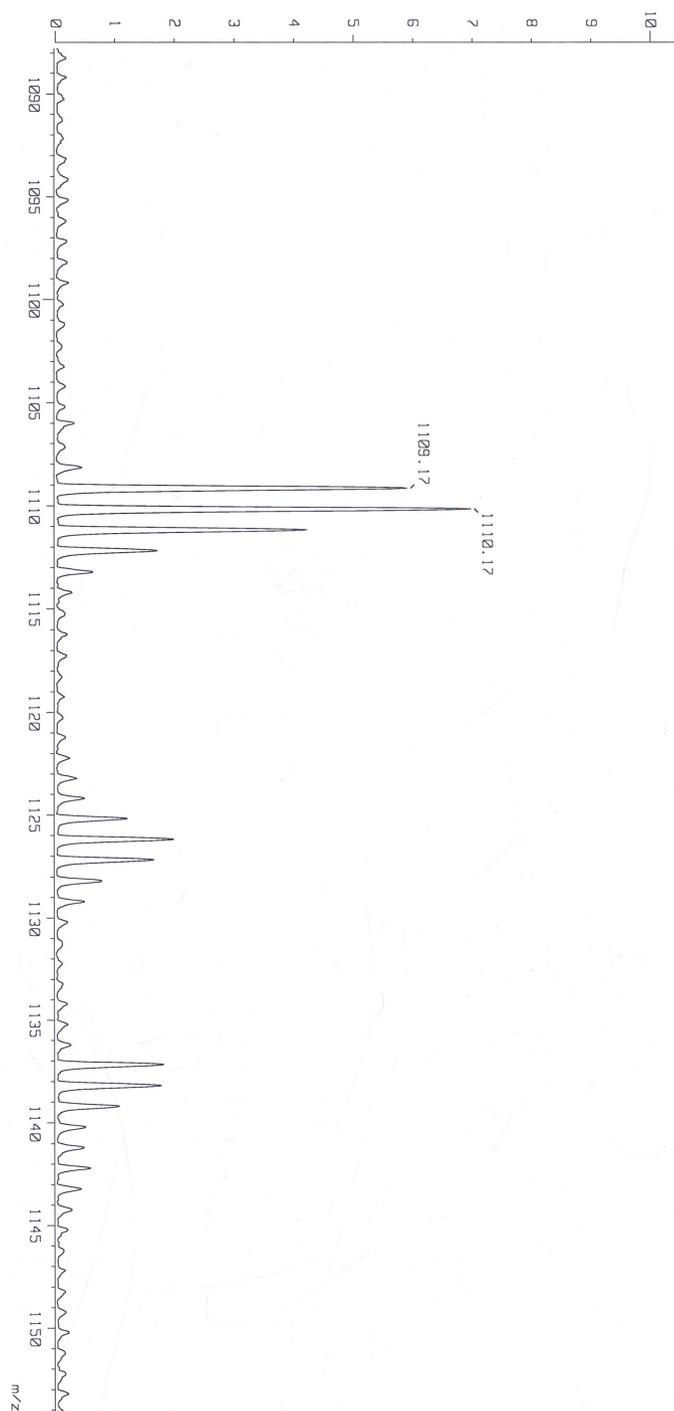


Figure 1. FAB-MS spectrum of α -D-mannosyl fullerene[C₆₀] (2a).

ultrasonication consists of 34 resonances in the 147.91-136.35 ppm region with an additional peak at 81.72 ppm corresponding to the sp^3 carbon atom. Particularly, M. R. Banks *et al.* also have reported a similar phenomenon that the ^{13}C -NMR spectra of the closed [5,6] adducts consisted of 31 resonances for the sp^2 carbons of the fullerene cage in 146-132 ppm region with a single and diagnostically significant line assigned to the two equivalent sp^3 carbon atoms attached to the aziridine nitrogen in the 104.2-80.4 ppm region.¹⁴ It is also worth noting that these values are distinctly different to that reported for the opened [5,6]-junction isomer.¹⁵ Comparison of the ^{13}C -NMR spectrum of **2a** from ultrasonication with the 47 peak pattern of the mono-mannosyl adducts from thermolysis showed that the peak pattern of **2a** is different feature to the mono-mannosyl adducts in 135-150 ppm region. Furthermore, this spectrum also shows that mono-adducts **2a** have more resonance peaks than the closed [5,6] adduct but less than the opened [5,6] adduct in this region. Thus, these results indicate that the mono-adducts **2a** may be a mixture composed of predominantly the closed [5,6] adduct.

The UV-vis spectrum of **2a** was observed the characteristic absorption bands of fullerene[C₆₀] derivatives at 260 and 326 nm with the weak but sharp band at 424 nm that was highly characteristic band for the closed [6,6]-junction isomers (Figure 2). It is proved that the closed [6,6]-junction isomers is included in the mono-adducts **2a**, since the characteristic sharp band is not observed in the UV-vis spectrum for the closed [5,6]-junction isomers as well as the opened [5,6]-junction isomers.¹² Therefore, these results strongly establish that **2a** is a mixture of the closed [5,6] and the closed

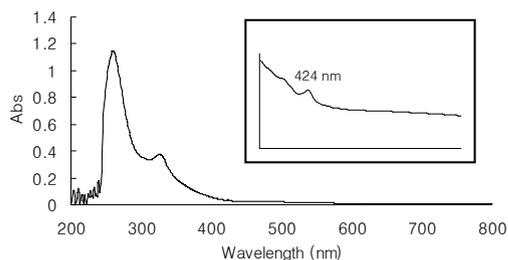


Figure 2. UV-vis spectrum of α -D-mannosyl fullerene[C₆₀] (**2a**).

[6,6]-junction isomers.

Based on analyses using FAB-MS, UV-vis, FT-IR, 1H - and ^{13}C -NMR spectroscopies, the mono-adducts **2a** is supposed to be a mixture of the closed [5,6]- and the closed [6,6]-junction isomers and composed of predominantly the closed [5,6]-junction isomer. Moreover, ultrasonication promoted reaction of fullerene[C₆₀] with **1a** leading to only a mono- adducts, while the thermal reaction afforded the mixture of mono- and bis-mannosyl adducts. The results of **2a** are presented in Table 1.

2. Layer-by-layer assembly of α -D-mannosyl fullerene[C₆₀]-gold nanoparticle films

UV-vis spectroscopy was used to monitor multi-layer α -D-mannosyl fullerene[C₆₀]- gold nanoparticle films. The data were collected multiple times and fell in the absorbance range of $\pm 10\%$. The reactive slides were alternately immersed in the toluene solution containing α -D-mannosyl fullerene[C₆₀] (10 mM) and 4-aminothiophenoxide/hexanethiolate-protected gold nanoparticles ($\sim 14 \mu M$) for indicated period.

UV-vis spectra of nanoparticle multilayer films showed that the surface plasmon (SP) band of gold

Table 1. Characterization of Reaction Products Between 2'-Azidoethyl Mannoside **1a** and Fullerene[C₆₀]

| 2'-Azidoethyl Mannoside | Product | Isolated Yield (%) | FAB-MS (m/z) | FT-IR (KBr, cm^{-1}) | UV-vis (CH ₂ Cl ₂ , nm) |
|-------------------------|-----------|--------------------|---------------|--|---|
| 1a | 2a | 5.8 | 1109.2, 720.1 | 2919, 1739, 1539, 1459, 1368, 1221, 1136, 1085, 1044 | 260, 326, 424 |

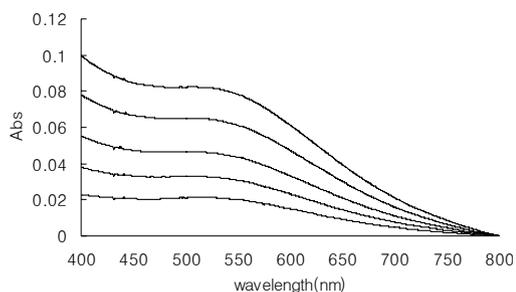


Figure 3. UV-vis absorption spectrum of the layer-by-layer assemblies of α -D-mannosyl fullerene[C₆₀]-gold nanoparticle multilayer films for the indicated time; +24h, +24h, +24h, +24h, +24h (from bottom to top).

at 530 nm gradually became more evident as successive layers were added to the films. This enhancement (and shift from \sim 520 nm) suggested that nanoparticle cores were induced to approach one another through interactions between α -D-mannosyl fullerene[C₆₀] and amine moieties (Figure 3.).

The results also showed that the longer the immersion time, the stronger the absorbance of UV-vis spectra. This suggests alternately the continuous adsorption of α -D-mannosyl fullerene[C₆₀] and functionalized gold nanoparticles due to the amination of α -D-mannosyl fullerene[C₆₀].

IV. Conclusions

1. Sonochemical synthesis of α -D-Mannosyl fullerene[C₆₀]

Cycloadditive reactions of fullerene[C₆₀] with 2'-azidoethyl mannoside **1a** at room temperature were promoted by ultrasonication to give the mannosyl fullerene[C₆₀] derivatives **2a**. ¹H-NMR, FAB-MS and FT-IR spectra revealed that the products were a 1:1 sugar-fullerene[C₆₀] adduct. The analysis of the ¹³C-NMR and UV-vis spectroscopic data indicated that the mono-adducts **2a** were a mixture of the closed [5,6]- and the closed [6,6]-junction isomers and composed of mainly the closed [5,6]-junction isomer. Although the products were obtained in low yields (5.6-9.0%), an ultrasonication

can be a simple method under mild condition.

2. Layer-by-layer assembly of α -D-mannosyl fullerene[C₆₀]-gold nanoparticle films

α -D-mannosyl fullerene[C₆₀]-gold nanoparticle films were prepared using the layer-by-layer assembly method. UV-vis spectra of nanoparticle multilayer films showed that the surface plasmon (SP) band of gold at 530 nm gradually became more evident as successive layers were added to the films. This plasmon band enhancement (and shift from \sim 520 nm) suggested that nanoparticle cores were induced to approach one another through interactions between α -D-mannosyl fullerene[C₆₀] and amine moieties.

Acknowledgements

This work was supported by Sahmyook University funding in Korea.

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 - General Procedure for 2'-Azidoethyl Mannoside Synthesis** - A solution of 2'-chloroethyl mannoside (1.46 g, 3.55 mmol) and sodium azide (443 mg, 7.10 mmol) in DMF (70 mL) was stirred for 4 h at 110°C. The reaction mixture was cooled to room temperature and then the solvent removed in vacuo. The residual syrup was diluted with CH₂Cl₂, washed with water, dried, and concentrated to a syrup. The crude product was purified by silica gel column chromatography (Tol:EtOAc 5/1) to give 2'-azidoethyl glycosides **1a**.
 - 2'-Azidoethyl 2,3,4,6-Tetra-O-Acetyl- α -D-Mannopyranoside (1a)**: R_f 0.29 (Tol:EtOAc 5/3); 90% yield; m.p. 78.6-79.6 °C (EtOAc-Hex, lit.¹³ m.p. 75-77 °C); ¹H-NMR (400MHz, CDCl₃) δ 5.33-5.23 (m, 3 H), 4.83 (d, 1 H, J_{1,2}=2.0 Hz, H-1), 4.25 (dd, 1 H, J=5.2, 12.4 Hz, H-6a), 4.08 (dd, 1 H, J=2.8, 12.2 Hz, H-6b), 4.03-3.99 (m, 1 H, H-5), 3.86-3.81 and 3.66-3.60 (2m, each 1 H, OCH₂), 3.45-3.40 (m, 2 H, CH₂N₃), 2.12, 2.07, 2.01, 1.95 (4 s, each 3 H, CH₃CO); ¹³C-NMR (100MHz, CDCl₃) δ 170.7-169.9 (C=O), 97.9 (C-1), 69.6 (C-2), 69.05, 69.02 (C-3,5), 66.1 (C-4), 67.3 (OCH₂), 62.6 (C-6), 50.6 (CH₂N₃), 21.2-21.0 (CH₃CO).
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