

## Ultrasonic, Chemical Stability and Preparation of Self-Assembled Fullerene[C<sub>70</sub>]-Gold Nanoparticle Films

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### 자기조립 풀러렌 [C<sub>70</sub>]-금 나노입자 필름 제조와 초음파적, 화학적 안정성

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**ABSTRACT** : C<sub>70</sub>-gold nanoparticle multilayer films were self-assembled using a "dirt-ball" method on the reactive surface of glass slides functionalized with 3-aminopropyltrimethoxysilane. The functionalized glass slides were soaked in the solution containing both unmodified C<sub>70</sub> and  $\omega$ -amino-functionalized gold nanoparticles. Organic reaction (amination) facilitated the assembly of multilayer C<sub>70</sub>-gold nanoparticle films, which have grown up to several layers. Chemical stability of C<sub>70</sub>-gold nanoparticle films was studied by monitoring the changes in absorbance after the immersion of the films in acidic solution. In addition, ultrasonic stability of these nanoparticle films was studied by exposing them to ultrasonic irradiated surrounding, which resulted in partial desorption and a little aggregation of nanoparticles on solid surfaces.

**요약** : 3-aminopropyltrimethoxysilane을 처리한 반응성 있는 유리표면 위에 "dirt-ball" 방법을 사용하여 C<sub>70</sub>-금 나노입자 다중성막 필름을 자기조립하였다. 표면처리한 유리막을 C<sub>70</sub> 과  $\omega$ -아미노기를 가진 금 나노입자를 포함하고 있는 용액속에 담그었다. 유기반응(아민화 반응)은 여러층으로 쌓인 다중성막 C<sub>70</sub>-금 나노입자 필름을 용이하게 자기조립 할 수 있었다. C<sub>70</sub>-금 나노입자 필름의 화학적 안정성은 산성용액에 필름을 담근후 흡수도의 변화를 측정함으로 조사되었다. 또한 나노입자 필름의 초음파적 안정성은 초음파 조건에 C<sub>70</sub>-금 나노입자 필름을 노출하여 초음파를 조사시킨후 고체 표면 위에 부분적인 탈착도의 변화와 작은 정도의 응집성이 일어남을 알 수 있었다.

**Keywords** : nanoparticle, fullerene[C<sub>70</sub>], multilayer, assembly

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## I. Introduction

There is considerable current interest in the self-assembly and organization of metal nanoparticles in thin films.<sup>1</sup> Various nanoparticles including Au, Ag, CdS, and FePt were assembled into thin films for advanced electronic, photonic, magnetic, and optoelectronic applications.<sup>2-4</sup> The self-assembly of nanoparticles is mostly based on electrostatic interactions between adsorbed monolayers of nanoparticles and oppositely charged linker molecules.<sup>2-4</sup> However, despite the ease of preparation, the stability of these multilayer films depends on several factors such as pH and polyelectrolyte concentration.

Recently, the strong affinity of C<sub>60</sub> to amine moieties was exploited to assemble multilayers of C<sub>60</sub> and gold nanoparticle bilayer structures.<sup>5,6</sup> The coupling (amination) of the C<sub>60</sub> molecules with peripheral amine moieties on the nanoparticle surface was the driving force for the layer-by-layer (LbL) assembly of these multilayers. 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 introduce a slightly different approach to prepare C<sub>70</sub>-gold nanoparticle composite films. Although the reported LbL assembly of C<sub>60</sub>-gold nanoparticle multilayers is effective, the build-up of each bilayer takes at least two days to achieve more than 80 % of a full surface coverage.<sup>6</sup> Faster formation of fullerene-gold nanoparticle assembly was necessary for technological applications of these nanocomposite materials. We also report chemical and ultrasonic stability of C<sub>70</sub>-gold nanoparticle composite films generated from the "dirt-ball" assembly method. Although understanding of the stability of hybrid nanostructures is critical for technological applications, to our knowledge, the systematic research focusing on the stability of nanoparticle multilayer films has not been reported.

## II. Experimental

### 1. "Dirt-ball" Assembly of C<sub>70</sub>-Gold Nanoparticle Multilayer Films

First, 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.<sup>5</sup> Second, C<sub>70</sub> and functionalized gold nanoparticles were self-assembled on the reactive surface such as glass slides functionalized with 3-aminopropyl trimethoxysilane. The reactive slides were soaked in the toluene solutions containing both unmodified C<sub>70</sub> (10 mM) and 4-aminothiophenoxide/hexanethiolate-protected gold nanoparticles (~14 μM).

### 2. Chemical and Ultrasonic Stability of C<sub>70</sub>-Gold Nanoparticle Multilayer Films

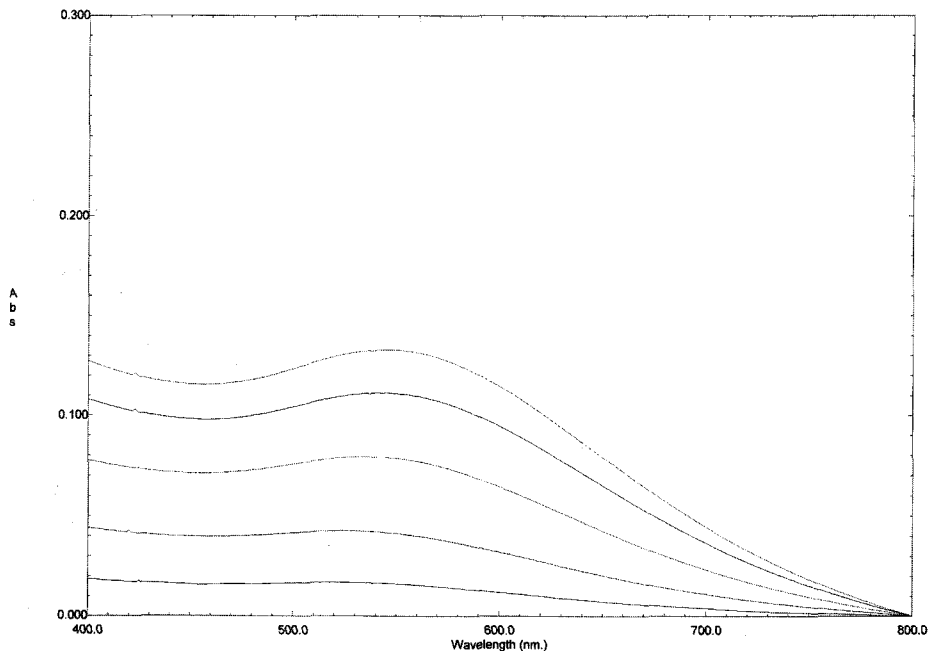
Chemical stability of nanoparticle multilayer films was studied by monitoring the changes in the absorbance by UV-vis spectroscopy before and after the immersion of nanoparticle films in the solution containing 0.1M-HCl. UV-vis spectra were acquired on a Shimadzu UV-1601 PC spectrophotometer.

The ultrasonic stability of these nanoparticle films was studied by exposing them to ultrasonic irradiated surrounding. The ultrasonic irradiation of all samples was conducted in continuous mode with an Ultrasonic Generator UG 1200 made by Hanil Ultrasonic Co, Ltd.

## III. Results and discussion

### 1. "Dirt-ball" Assembly of C<sub>70</sub>-Gold Nanoparticle Multilayer Films

UV-vis spectroscopy was used to monitor multilayer C<sub>70</sub>-gold nanoparticle film formation (Figure 1). The data were collected multiple times and fell in the absorbance range of ±10 %. The reactive slides were immersed in the solution containing both C<sub>70</sub> and 4-aminothiophenoxide-functionalized gold



**Figure 1.** UV-vis absorption spectra of the "dirt-ball" assemblies of  $C_{70}$ -gold nanoparticle multilayer films for the indicated time ; +30min, +180min,+360min, +720min, +1440min (from bottom to top).

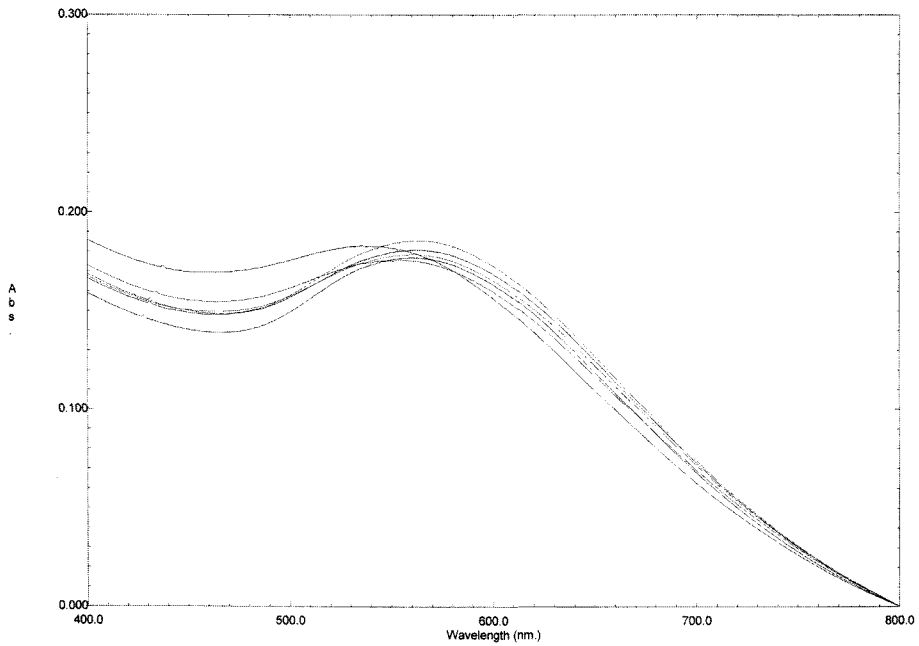
nanoparticles for indicated periods.

UV-vis spectra of nanoparticle multilayer films showed that the surface plasmon (SP) band of gold at 548 nm gradually became more evident as successive layers were added to the films. This plasmon band enhancement (and shift from ~520 nm) suggested that nanoparticle cores were induced to approach one another through interactions between  $C_{70}$  and amine moieties. The results also showed that the longer the immersion time, the stronger the absorbance of UV-vis spectra. This suggests the continuous adsorption of both  $C_{70}$  and functionalized gold nanoparticles due to the amination of  $C_{70}$ . The overall absorbance of UV-vis spectra obtained from the "dirt-ball" assembly was quite comparable to that of UV-vis spectra obtained from LbL assembly of  $C_{70}$ -gold nanoparticle multilayers. This supports the idea that the "dirt-ball" assembly method is a convenient way to build nanoparticle multilayer films with a comparable layer thickness within 24 hours compared to several

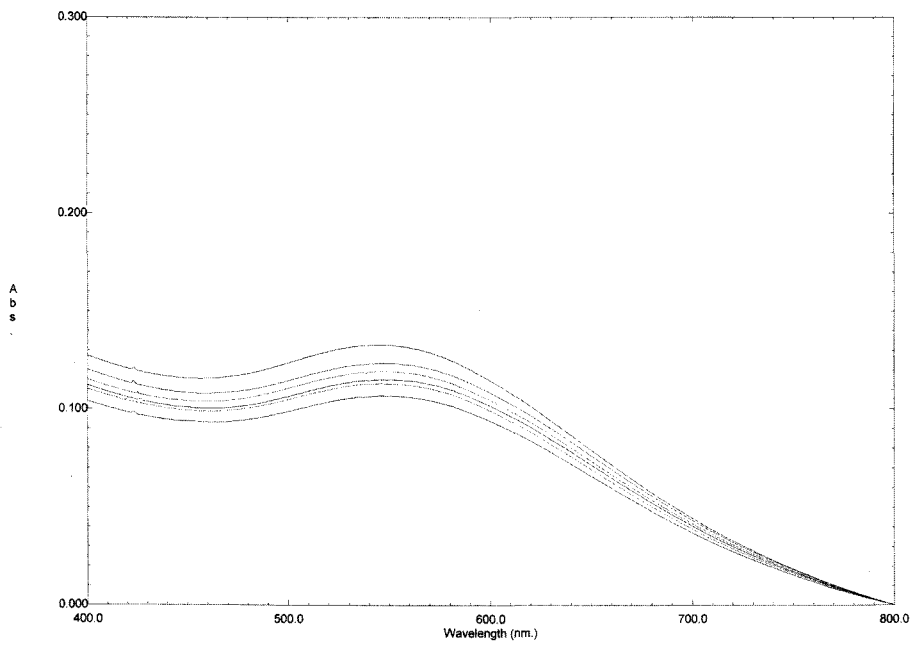
days with LbL assembly.

## 2. Chemical and Ultrasonic Stability of $C_{70}$ -Gold Nanoparticle Multilayer Films

Chemical stability of  $C_{70}$ -gold nanoparticle multilayer films was examined by monitoring desorption kinetics in acidic (dil. HCl) solution. HCl can either disrupt the bonding between  $C_{70}$  and amine moieties or cause the dissociation of the monolayer with possible etching of the gold underlayer. Desorption of the films was monitored with UV-vis spectroscopy. The result showed that HCl desorbed less than ~15 % of  $C_{70}$ -gold nanoparticle multilayers in 24 hours. Also, UV-vis spectra of  $C_{70}$  gold nanoparticle multilayer films showed that the surface plasmon band of gold moved into red shift (from 548 to 568) in figure 2. It may be represent aggregation of nanoparticles after the films immersion for indicated time in 0.1M-HCl solution. Compared to other hybrid nanoparticle multilayers,<sup>7</sup> this result indicated that  $C_{70}$ -gold nanoparticle multilayers were more stable



**Figure 2.** UV-vis absorption spectra of C<sub>70</sub>-gold nanoparticle multilayer films in 0.1M-HCl solution for the indicated time; 0min, +60min, +180min, +360min, +720min, +1440min (from top to bottom).



**Figure 3.** UV-vis absorption spectra of C<sub>70</sub>-gold nanoparticle multilayers before and after exposing the films to ultrasonic irradiated surrounding for the indicated time; 0min, +60min, +180min, +360min, +720min, +1440min (from top to bottom).

in acidic condition (figure 2).

Ultrasonic stability of C<sub>70</sub>-gold nanoparticle multilayers was examined by monitoring the changes in the absorbance by UV-vis spectroscopy after exposing the films to ultrasonic irradiated surrounding for the indicated times (Figure 3).

The results showed that the multilayer films undergo only partial desorption (~18%) with very little red-shift (from 548 to 550 nm) in SP band of gold, indicating minimal desorption and aggregation of nanoparticles after ultrasonic irradiation.

#### IV. Conclusions

C<sub>70</sub>-gold nanoparticle multilayer films were prepared using the "dirt-ball" assembly method. Studies on chemical and ultrasonic stability of these films suggested that C<sub>70</sub>-gold nanoparticle multilayer films were quite stable in acidic condition and ultrasonic irradiated surrounding. Further understanding of properties of these nanostructures may lead to various device applications.

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