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[60]Fullerene-linked gold nanoparticles: synthesis and layer-by-layer growth on a solid surface†

Young-Seok Shon* and Hosun Choo
Department of Chemistry, Western Kentucky University, Bowling Green, KY 42101, USA

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The facile synthesis of soluble and isolable [60]fullerene-linked gold nanoparticles and layer-by-layer assembly of C_{60}/nanoparticle films on the solid surface were studied.

Since the discovery of C_{60} ([60]fullerene), there has been a tremendous amount of research focused on the synthesis of C_{60}-based organic or inorganic nanocomposites including C_{60} thin films.[1–4] Chemically modified C_{60} has been used for covalently attaching C_{60} to solid surfaces, polymeric organic matrixes and inorganic matrixes,[1–4] and they have exhibited interesting optical or electronic responses.[5] Recently, research involving colloidal nanoparticles has intensified with a focus on the adsorption of molecular species onto surfaces of metal nanocrystals such as gold, silver, platinum, palladium, copper and alloys.[6] These monolayer-protected nanoparticles have drawn remarkable academic and industrial interest due to their unique chemical, biological, catalytic, optical and electronic properties as well as their potential applications in molecular electronic devices, chemical sensors, biosensors, molecular reagents and electrocatalysts.[6,7] Incorporation of C_{60} to metal nanoparticles using a chemical methodology (*e.g.* covalent bonding or electrostatic interactions) can yield new materials having unique electrochemical, photochemical, and optical properties. We anticipate that the well designed assembly of C_{60}-linked nanoparticles on solid substrates would provide a tremendous opportunity for several device applications. There have been a few reports regarding the preparation of aggregated gold– or silver–C_{60} nanostructures[8–10] and covalently bonded C_{60}-functionalized nanoparticles.[11–13] However, to our knowledge, spatial layer-by-layer assembly of C_{60}-linked nanoparticles on solid surfaces has not been reported. The ability to generate controlled assemblies of C_{60}/nanoparticle films would allow for a systematic investigation of the physical properties of these novel structures.

The method adopted for the synthesis of C_{60}-linked gold nanoparticles as shown in Fig. 1 is described below.

4-Aminothiophenoxide/hexanethiolate-protected gold nanoparticles with an average core dimension of ~2 nm (obtained from TEM images) were synthesized using the modified Brust reaction followed by ligand place-exchange reaction of hexanethiolate-protected gold nanoparticles with 4-aminothiophenol.[14] The hexanethiols (1.6 mmol) were reacted with $AuCl_4^-$ (0.8 mmol), which was transferred to toluene layers using a phase-transfer reagent, yielding Au(I)–thiolate polymers. Subsequent reduction with $NaBH_4$ (8.0 mmol) generated hexanethiolate-protected gold nanoparticles. In the ligand place-exchange reaction, a new thiolate ligand (4-aminothiophenol) was incorporated into a nanoparticle by mixing its thiol and the hexanethiolate-protected gold nanoparticle in dichloromethane.[14] Unmodified C_{60} (10 mmol) was now reacted with 4-aminothiophenoxide/hexanethiolate-protected gold nanoparticles ~2.5 μmol) in 25 mL of toluene for 3 days at room temperature. Amination reaction of C_{60} with 4-aminothiophenoxide ligands generated C_{60}-linked gold nanoparticles. The C_{60}-linked gold nanoparticles are found to be soluble in various organic solvents including toluene, dichloromethane, ethanol and isopropanol.[15] Amination of C_{60} has been used for the preparation of C_{60} amine derivatives,[1] C_{60} organic–inorganic nanocomposites in sol–gel processing,[1] and C_{60} thin films.[2]

C_{60}-functionalized gold nanoparticles were self-assembled on the reactive surface such as glass slides functionalized with 3-aminopropyltrimethoxysilane.[16] Two different methods were used to prepare C_{60}/nanoparticle multilayer films (Fig. 2). First, the functionalized glass slides were alternately soaked in the toluene solution containing C_{60}-linked gold nanoparticles (~ 13 μM) and ethanol solution containing ethylene diamine (10 mM) for at least 24 h for the layer-by-layer growth of nanoparticle films (method 1). Second, the reactive slides were alternately soaked in the toluene solutions containing unmodified C_{60} (10 mM) and 4-aminothiophenoxide/hexanethiolate-protected gold nanoparticles (~ 14 μM) (method 2). The amination reaction of C_{60} facilitated self-assembly of nanoparticles on the glass surfaces for both assembly methods.[17]

The C_{60}-functionalized gold nanoparticles and 4-aminothiophenoxide/hexanethiolate-protected gold nanoparticles were characterized using UV-vis spectrocopy (Fig. A in ESI†) and TEM (Fig. B in ESI†). The average diameter of 4-aminothiophenoxide/hexanethiolate-protected gold nanoparticles was 2 nm. Although monolayer-protected gold nanoparticles with this small size fail to exhibit the sharp absorption peak corresponding to the surface plasmon (SP) band of gold, the broad absorption at 520 nm could be observed for gold nanoparticles. The UV-vis spectra of unmodified C_{60} in CH_2Cl_2 showed a strong absorption band at 330 nm. The disappearence of this band after the reaction with 4-aminothiophenoxide/hexanethiolate-protected gold nanoparticles indicated the saturation of one of the double bonds of C_{60} by the amination reaction.[17] The similar disappearence of C_{60} absorption band was observed

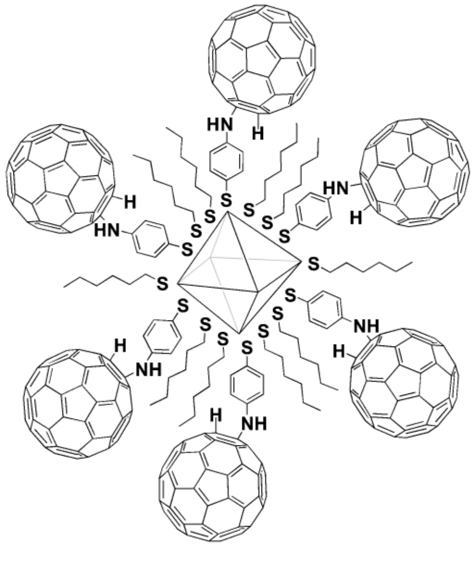

Fig. 1 C_{60}-Linked gold nanoparticle.

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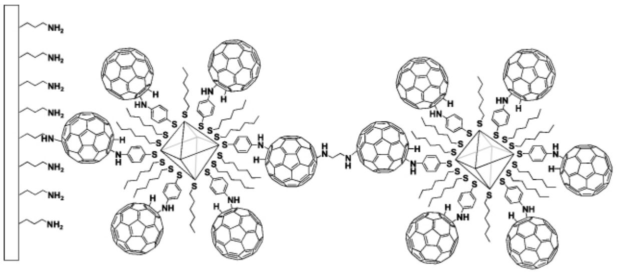
† Electronic supplementary information (ESI) available: supporting data including UV-vis spectroscopy and transmission electron microscopy results. See http://www.rsc.org/suppdata/cc/b2/b207246g/

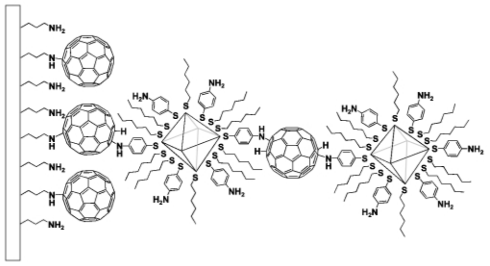
when C_{60} was interacted with gold nanoparticles capped with γ-cyclodextrin hosts.[10] We observed a slight increase and red-shift of gold SP band of C_{60}-linked gold nanoparticles. This might indicate a decreasing of the spacing (due to interactions between C_{60} units) between gold nanoparticles. TEM images of C_{60}-linked gold nanoparticles also showed the presence of C_{60}-induced small aggregates of nanoparticles upon the evaporation of solvents.

The UV-vis spectra of the nanoparticle films, which were layer-by-layer grown on the modified glass surfaces, are shown in Fig. C in ESI.† The data were collected multiple times and fell in the absorbance range of ±10 % for both methods.

UV-vis spectra of nanoparticle multilayer films showed that the SP band of gold at ~580 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_{60} and amine moieties. Since C_{60}-linked gold nanoparticle have a structure of several C_{60} units surrounding the metal cluster core, we expected that method 1 would yield multilayer films with relatively lower concentration of gold nanoparticles in the films. Method 2 would generate films with higher concentration of gold nanoparticles compared to method 1, because every other layer of these films would be composed of 4-aminothiophenoxide/hexanethiolate-protected gold nanoparticles without participation of C_{60}. The results clearly showed that the absorbance of UV-vis spectra for samples from method 2 was much stronger than that of UV-vis spectra for method 1 after each nanoparticle layer growth on the glass surface (up to 5 layers were examined). This supports the idea that the method 2 yielded nanoparticle films with a higher concentration (and likely higher packing density) of gold nanoparticles than method 1. The variation of film contents on these materials might provide an opportunity to obtain nanostructured films with distinct optical and electrical properties. We could not observe any evident deterioration in film growth after five repeated cycles evidenced by the linear regression plots of UV absorbance at 520 nm (Fig. D in ESI†). This suggests that we might be able to grow C_{60}/nanoparticle multilayer films continuously beyond 5 layers. For comparison, we attempted the preparation of nanoparticle films by alternative immersion of glass slides in each solution containing 4-aminothiophenoxide/hexanethiolate-protected gold nanoparticles and ethylenediamine. The failure to yield nanoparticle multilayer films by this approach suggested that the presence of C_{60} in solution and on glass surface was critical for successful results. UV-vis spectra of nanoparticle films generated by exposing the slide to solutions of 4-aminothiophenoxide/hexanethiolate-protected gold nanoparticles and poly(styrene sulfonic acid) showed relatively lower absorbance in the 300–400 nm region but similar absorbance in the 500–600 nm region compared to that of nanoparticle films obtained by method 1 (Fig. E in ESI†). The presence of C_{60} caused this stronger absorbance at 300–400 nm region in the nanoparticle film generated by method 1. The structural characterizations and characterization of electronic properties of C_{60}-linked nanoparticles and C_{60}/nanoparticle films are currently underway using X-ray diffraction, STM, and electrochemical studies and will be reported in the near future. The kinetics and thermodynamic stability of these films are also currently under investigation.



Method 1



Method 2

Fig. 2 C_{60}/nanoparticle multilayer films.

In summary, C_{60}-linked gold nanoparticles and C_{60}/gold nanoparticle films with distinct compositions can be prepared. The synthesis does not involve a chemical modification of C_{60} prior to the adsorption onto the surface of gold nanoparticles. This eliminates many difficult reactions and purification processes concerning the low solubility of C_{60}. This research might provide control over the optical, photochemical and electrical properties by modifying nanoparticle core size and/or composition (*e.g.* Ag, Pd, alloy). The understanding of properties of these nanomaterials may lead to various device applications.

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