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Thin Film, Fullerene–Based Materials

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Abstract. A review of the literature pertaining to fullerene-based thin film materials is presented. Herein, a fullerene-based thin film material is defined as a thermally evaporated and/or solution cast film, a polymeric film, a Langmuir-Blodgett film, or a self-assembled monolayer.

Introduction

Since the discovery of methods for preparing macroscopic quantities of C_{60},[1] there has been a tremendous amount of research aimed at understanding C_{60}'s chemical and physical properties in a range of physical states. Although much of the organic chemistry involving C_{60} can be understood by analogy with less sophisticated electron deficient olefins,[2] many of the physical properties associated with fullerenes and materials formed from them are unusual and, in some cases, spectacular. For example, when reductively doped with the appropriate alkali metal, C_{60} becomes a high temperature superconductor;[3] with an onset T_c of 40 K, a Cs-based C_{60} salt holds the record for the highest critical temperature for molecule–based superconductors.[4] In thin film form, C_{60} exhibits an anomalously large second order non–linear optical response for a centrosymmetric molecule.[5] C_{60} also has proven to be an effective optical shutter and can absorb up to 100 photons per molecule in solution from a single seven nanosecond 532 nm laser pulse.[6] Polyvinylcarbazole and phenylmethylpolysilane doped with C_{60} (and C_{70}) yield excellent photoconducting materials with a wavelength dependence on the absorption spectrum of the fullerenes.[7] Additionally, C_{60} has 8 different electrochemically accessible and stable oxidation states (C_{60}^{-6} – C_{60}^{+}),[8] and it becomes a molecular magnet when reductively doped with a donor such as tetrakisdimethylaminoethylene (TDAE).[9] Reports from Wudl and Kenyon on HIV protease inhibition[10] and from Nakamura and Sugiura on the photoactivity of a modified fullerene[11] indicate modified fullerenes even have generated interest in the biological arena.

Because of C_{60}'s marvelous properties, many workers have focused on methods for preparing materials from it and its congeners in the hope that these materials also will possess unusual and potentially useful properties. Although it is still too early to determine whether or not such materials ultimately will evolve into technologically useful ones, initial studies have given entry into a new class of materials with properties as unusual as those for C_{60} and its doped forms. Furthermore, fullerenes, and C_{60} in particular, are being used to address many important fundamental issues in materials chemistry. These include the development of a better understanding of interfacial electron transfer and ion transport in thin films, the dynamics associated with monolayer self–assembly, and thin film structural characterization. The development of new fullerene–based materials relies on the development of new methodology for chemically modifying fullerenes. Such methodology is not only important for tailoring the fullerene to exhibit a desired optical or electronic response, but also for covalently attaching fullerenes to each other or to solid–state supports. Therefore, although some may argue that developing methodology for chemically modifying fullerenes is intrinsically uninteresting because of the similarity between C_{60}'s chemistry and that of electron deficient olefins, it is of paramount importance to those interested in constructing fullerene–based materials with properties and structures that may be tailored rationally.

The topic of fullerene–based materials is too large to cover adequately in this short review. Therefore, we will focus on C_{60} thin films; in our discussion of this area, we will divide it into four subsections according to class of thin film: thermally evaporated and solution cast films, polymeric films, Langmuir-Blodgett films, and self-assembled films.

Fullerene Films Prepared by Thermal Evaporation and Solution Casting. A variety of films formed from thermal evaporation and spin casting methods on a range of different substrates have been prepared and studied by many surface analytical methods.[12-21] Scanning tunneling microscopy (STM) has been a powerful tool in the characterization of fullerene thin films. In fact, very early STM studies of evaporated C_{60} films on Au[12] confirmed the postulated spherical structure for C_{60} and the 10 Å nearest neighbor distance for crystalline C_{60}. Since these initial papers, many researchers have reported being able to image some internal structure or "intramolecular contrasts" of C_{60} adsorbed onto Au, Ag, Cu, and Si surfaces.[13] Under ultra high vacuum (UHV) conditions, STM studies have shown that C_{60} chemisorbs onto a variety of crystalline substrates. These include Au(111),[13jk,14a] Ag(111),[13k,14a] GaAs(110),[14bc] Si(111),[14d] Si(100),[13f] Cu(111),[13hi] and Au(110).[14e] A wide range of techniques (e.g. AFM, TEM, TPD, x-ray methods) have been used to study C_{60} adsorption on a variety of substrates, including Si,[15] mica,[16,17,18c] alkali and alkaline earth halides,[17bc,18] $LaAlO_3$,[18d] $SrTiO_3$,[18d] ZrO_2,[18d] Rh(111),[19a] MoS_2,[18c,19bc] graphite,[18c] CdS,[20a] CdSe,[20a] Au(110),[20b] and Al_2O_3.[21] These studies are important because they provide valuable fundamental insight into the nucleation and growth phenomena associated with fullerene films and molecular substances in general.

The fullerene adsorbate–surface interactions can be strong and play a significant role in determining film structure. For example, C_{60}, when adsorbed onto Au(111) and Ag(111) in ultrahigh vacuum, forms ordered films with fullerene-surface interactions of 50-60 kcal/mol.[13jk,14a] For Au(111), two distinct film structures were detected by STM; these structures were assigned by Colton to be $2\sqrt{3}x2\sqrt{3}R30^\circ$ and a 38 x 38 "in–phase structure," Figures 1a and 1b, respectively.[13jk,14a] For the "in–phase structure," unlike the $2\sqrt{3}x2\sqrt{3}R30^\circ$ structure, the lattice matching is poor and the molecules cannot all lie on equivalent surface sites. The formation of the in–phase structure was attributed to the kinetics for the film growth process on Au(111), and the nucleation sites, which were step-based, were believed to be different for the two observed structures. On Ag(111), fullerenes exclusively adopt the $2\sqrt{3}x2\sqrt{3}R30^\circ$ structure.[13k,14a] Although both substrates, which differ only slightly in lattice parameter, support a monolayer of C_{60} with a $2\sqrt{3}x2\sqrt{3}R30^\circ$ structure, there were some notable differences between the films formed on Au(111) and Ag(111). In addition to the greater tendency for C_{60} to form a film with a $2\sqrt{3}x2\sqrt{3}R30^\circ$ structure on Ag(111) as compared with Au(111), the rate of rotation of the fullerenes on the Ag(111) surface was significantly reduced as compared with that on Au(111).[13k,14a] This was initially attributed to the stronger interaction between the more reactive Ag(111) surface as compared with Au(111); however, in later work,

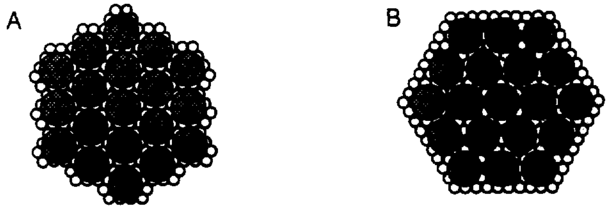


Figure 1. Models of observed structures for C_{60} on Au(111). A) $2\sqrt{3}x2\sqrt{3}R30°$; B) 38 x 38 in–phase structure.

Colton and coworkers determined that the fullerene adsorbate–surface interactions were comparable for the two different surfaces.[14a] Hamza and Balooch showed that C_{60} adsorbed onto Si(100) with a large fullerene–surface interaction of 56 kcal/mol and a C_{60}-C_{60} interaction of 31 kcal/mol; C_{60} adsorbs onto α-Al_2O_3 wtih a 25 kcal/mol fullerene-surface interaction.[15b,21a] J. Weaver and Smalley studied the adsorption of C_{60} on Si(111) at 300 K.[14d] They noted that at submonolayer coverages, the fullerenes showed no evidence for aggregation and remained randomly distributed on the surface. They attributed this phenomenon to unusually strong Si-C_{60} interactions, which hindered adsorbate mobility. They also reported that their ability to image adsorbed fullerenes was dependent on the bias voltages used in the process, attributing this phenomenon to multiple surface adsorption sites. In another study, J. Weaver and Smalley also showed that C_{60} formed well–ordered, commensurate, and structurally stable monolayers on GaAs;[14bc] two distinct adsorption sites were identified due to a regular periodic buckling in the monolayer. Consistent with the results of Hamza and Balooch,[15b] they estimated the cohesive energy of C_{60} to be 31 kcal/mol.[14b] Although there were no direct measurements of the C_{60}–GaAs interaction, based on the observation that fullerenes tend to form multilayers on GaAs, Colton later proposed that the C_{60}–GaAs interaction is weaker than the C_{60}-Au interaction and comparable to the C_{60} intermolecular interactions in the film.[14a]

It is tempting to correlate the strength of the fullerene-surface interaction to its ligating properties towards those surfaces, but there are several inconsistencies with this postulate, suggesting that the bonding situation is more complicated than simple adsorbate–surface coordination chemistry. One of the most glaring inconsistencies is that the C_{60} interactions with Au(111) and Ag(111) are comparable,[13jk,14a] yet based on reactivity towards olefins, Ag should be the more reactive metal and the one that exhibits stronger adsorbate–surface interactions.[22a] This suggests that for some of these substrates, there must be other contributors to the adsorbate-surface interaction. One possibility is a charge transfer interaction between some of the surfaces and C_{60}. Indeed, tunneling spectroscopy[13k] and luminescence studies[23] of C_{60} adsorbed onto Ag provide evidence for a charge transfer interaction between the fullerene and the Ag(111) surface.

Recently, Van Duyne has developed a new technique which allows one to do temperature dependent UHV-surface-enhanced resonance Raman spectroscopy (SERRS) on SERS-active substrates.[24] This has allowed him to characterize fullerene thin films (submonolayer to 100 monolayers) adsorbed onto Ag, Cu, and Au as a function of temperature. For example, a temperature dependent SERS experiment performed on a 1.5 monolayer film of C_{60} on SERS-active Ag shows spectral shifts associated with C_{60}'s

A_g pentagonal pinch mode (1460 cm^{-1}) as a function of substrate temperature, Figure 2. At 550 °C, which is the temperature at which the fullerenes desorb from the surface, spectral features associated with the film disappear. He preliminarily attributes the shifts in intensity and position of the A_g pentagonal pinch mode in the 350-550 °C temperature range to a change in the interaction of the fullerenes with the Ag surface. As it develops, this method will be important in the further understanding of the structures for and interactions within fullerene thin films and molecular films in general.[24]

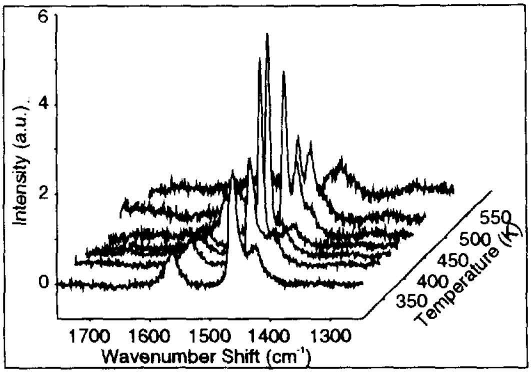
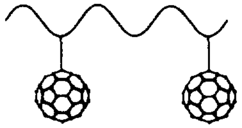


Figure 2. UHV SERRS-detected thermal desorption experiment for a 1.5 ML film of C_{60} on Ag.

As stated earlier, C_{60} can be reversibly reduced in solution in sequential, reversible fashion to the hexaanion, but the electrochemistry of evaporated or solution cast fullerene films has proven to be vastly different. Bard,[25] Compton,[26] and Kadish[27] have explored the electrochemical properties of solution cast and electrodeposited films of C_{60}, respectively. These films have similar electrochemical responses; their cyclic voltammetry shows extremely large potential separations for the first and second reduction and corresponding reoxidation processes. Furthermore, the current associated with the reoxidation of these films did not compare well with the current associated with their reduction. This was attributed to the resistivity associated with the more compact reduced forms of the film, which became, in part, electrochemically inaccessible. The increased compactness apparently comes from the incorporation of charge compensating counterions into the film. This area has been reviewed elsewhere.[28]

Other novel properties discovered in the study of evaporated fullerene films are superconductivity and second harmonic generation (SHG). Fullerene films were discovered to exhibit superconductivity by Hebard and coworkers at AT&T in 1991.[3a] Initial studies by the AT&T group reported that vapor phase alkali metals could be intercalated into evaporated C_{60} films to form conducting materials, of which a K-doped film provided the highest conductivity (500 S/cm) at room temperature.[29a] Once studied at low temperature, these films exhibited a decrease in resistivity at a temperature of 16 K, reaching zero resistivity at 5 K.[3a] Further studies by several groups focusing on: 1) various mixtures of metals and C_{60}; and 2) the purification of the reductively-doped fullerene compositions have led to the discovery of materials that exhibit superconducting behavior at much higher temperatures,[3b,29bc] with 40 K being the highest reported so far.[4] SHG is forbidden for centrosymmetric molecules such as C_{60}, but evaporated fullerene films have shown SHG signals,[5] which are postulated to arise from a combination of: a bulk magnetic dipole, an electric quadrupole, a surface electric dipole, and an electric field contribution involving the third harmonic properties of C_{60}.[30]

Polymeric Fullerene Films. There are two general types of fullerene-containing polymers: "pearl necklace" polymers (below, left) where the fullerenes are part of the backbone of the polymer, and "charm bracelet" polymers (below, right) where the fullerenes are attached to the polymer but are not part of the backbone.[31] There are many examples in the literature of both types of polymers. It has been reported that evaporated C_{60} films can be polymerized into "pearl necklace" structures by irradiation with visible or ultraviolet light,[32] pressure,[33] electron stimulation,[34] and ion bombardment.[35] Eklund showed that the photoirradiation of films of C_{60} induced an oligomerization reaction; $(C_{60})_n$ species (n= 1-10) were detected using laser desorption mass spectroscopy. Raman and IR spectra of these materials exhibited many more lines than those for pure C_{60} films, indicating a reduction in symmetry of the fullerenes. A 2+2 reaction between the parallel double bonds of adjacent fullerenes to form a four membered ring was suggested as the mechanism of polymerization.[32abc] Later work by Eklund showed this polymerization to be a reversible process; as the film was heated to higher temperatures, the Raman signatures for C_{60} returned.[32d] Akselrod and coworkers reported that the depolymerization also could be induced by high intensity light.[32ef] When subjected to high pressures and high temperatures, the lattice constant for the fullerenes in the fcc cell shrinks; a reduction in the symmetry of the fullerenes comprising the film is also observed through vibrational spectroscopy. This polymerization is reversible by heating at ambient pressures.[33] J. Weaver demonstrated that electron irradiation could polymerize such fullerene films.[34] Like the photopolymerization, this process also could be reversed by heating a polymerized film to 470 K for 2 hours.[34] Ion bombardment also has been noted by Palmetshofer to broaden Raman spectra and produce new lines, possibly indicating a polymerization is occurring.[35] There have also been reports that polymeric chains of AC_{60} (A=K, Rb) exist and act as quasi-one-dimensional metals above 50 K. A contraction of the lattice along the a direction of the unit cell was observed.[36a,b] $(KC_{60})_n$ can be grown through coevaporation of the reagents in a tube furnace into single crystalline fibers up to 1 mm in length.[36c]



As new fullerene chemistry has developed, new types of "pearl necklace" polymers have been created. The reactivity of fullerenes with the diradical species *p*-xylylene was utilized by Loy and Assink to create the first fullerene copolymer. This material was reported to be highly cross-linked and have a xylylene:C_{60} ratio of 3.4:1.[37] A living polymerization via carbanion attack of an anionic polystyrene chain on C_{60} has yielded "flagellenes," where a fullerene is modified with multiple polystyrene "arms."[38] Wudl assembled "two-pearl" sections of a "pearl necklace" polymer through the reaction of C_{60} with molecules containing two diazo moieties. The cyclic voltammetry of these bisfulleroid species show reversible two-electron waves, indicating the reduction of one fullerene moiety does not affect the reduction of the other in this polymer section.[39] Nagashima has reported the preparation of an organometallic polymer with the formula $C_{60}Pd_n$, where n was dependent on the initial reagent ratios. The thermodynamic product was reported to have n = 3, which would have 6 Pd atoms around each fullerene.[40a] Polymers with n > 3 were reported to catalyze the hydrogenation of olefins.[40b] C_{60} also has been incorporated into the backbone of a polymer as reported by Geckeler and Hirsch through the reaction of C_{60} with amines.[41a] Li reported the modification of C_{60} with multiple amines functionalized with silane groups.[41b] The silane groups allowed for polymerization on surface acoustic wave resonators. These modified resonators were reported to sense volatile organic molecules in air by trapping the molecules in free space within the polymer.

Wudl also prepared "charm bracelet" polymers by modifying fullerenes with functionality that formed polyester and polyurethane chains.[42] Bergbreiter lithiated polyethylene to generate an anionic material which would react with fullerenes; this reaction was confirmed via X-ray photoelectron, UV-vis, and fluorescence spectroscopies.[43] Many groups have used the reactivity of C_{60} towards amine- and azide-functionalized polymer supports to produce "charm bracelet" polymers; some polymer supports studied were an ethylene propylene terpolymer,[44] polystyrene,[45] and poly(oxyethylene).[46] Diederich *et al.* reported the synthesis of a fullerene modified with butadiyne pendant chains.[47] This compound was electrochemically polymerized from solution onto platinum electrodes, forming an electrically conducting polymer which continued to grow on Pt electrodes even after 200 electrochemical cycles. Rotello has reported the reversible attachment of C_{60} to a polymer backbone modified with cyclopentadienyl moieties.[48] The addition of C_{60} to the polymer was achieved through a Diels-Alder reaction between C_{60} molecules in solution and the pendant cyclopentadienyl moieties of the polymer, and fullerene removal was achieved by polymer thermolysis. Polycarbazole has been modified by an acid-catalyzed alkylation reaction with C_{60} and by a Friedel-Crafts addition reaction with a brominated fullerene.[49] The fullerene-modified polycarbazole polymers were shown to have charge storage capabilities. A ring opening metathesis polymerization was recently reported by Prato using a norbornene-modified fullerene and norbornene in solution with a Mo carbene catalyst.[50] The *cis:trans* ratio for the polymer was found to be dependent on the fullerene concentration in solution, and the electronic configuration of the polynorbornene was retained in the polymer as evidenced by UV-vis spectroscopy. It is apparent that work in this area has focused on polymer preparation with less attention on polymer properties. This remains a relatively unexplored area that will undoubtedly be the focus of much attention in years to come.

Preparation of Fullerene Langmuir and Langmuir-Blodgett (LB) films. Many workers have been interested in methods for organizing fullerenes into highly ordered monolayer materials. Being able to construct such highly ordered monolayer structures from fullerene adsorbate molecules is of paramount importance to understanding how to assemble, in a step–by–step fashion, multilayered fullerene materials with definable structures. Preparing materials with definable structures is critical if meaningful conclusions regarding the relationship between a material's structure and function are to be made. In this regard, two techniques may be used: Langmuir-Blodgett and monolayer self-assembly. Both have been used to assemble fullerenes into two and three dimensional materials. The former will be discussed in this section of the review while the latter will be addressed in the subsequent section.

A Langmuir film typically is formed by spreading an amphiphilic compound on the surface of a water trough and compressing the molecules. The monolayer formation process may be monitored by following the surface pressure as a function of trough surface area.[51] As the surface pressure increases, the distances between the molecules comprising the film decrease and intermolecular interactions increase. When a Langmuir film is transferred to a solid substrate, it is then referred to as a LB film.[51] Amphiphilic molecules which possess a hydrophilic end to interact with the water and a hydrophobic end which avoids the water layer are typically used in the formation of Langmuir and LB films.[51] Even though C_{60} is not amphiphilic, several researchers have explored its suitability in the preparation of Langmuir and LB films.[25b,52-63] There have been mixed results in this area. Bard initially reported success in preparing a Langmuir film of C_{60} with a limiting molecular area of 98 Å^2, which is consistent with the molecular footprint of C_{60}, but he attained this value only if extremely dilute solutions of C_{60} were used.[25b,52] Otherwise, crystallites on the water subphase would appear, which indicated the formation of multilayered materials. Once transferred to hydrophobic substrates, the electrochemical responses of the films were reported to be dependent upon the pressure at which the transfers occurred; an increase in the peak current and a decrease in the peak widths were observed with an increase in transfer pressure.[53] Many other groups also reported attempts to form Langmuir and LB films of C_{60} using a range of conditions without success.[54] However, Heiney and Smith were able to reproduce the Bard Langmuir studies with C_{60}.[55] It would appear that although monolayer films may be prepared from C_{60} by the Langmuir and LB methods, it is not straightforward and is highly condition dependent.

More stable monolayer films containing C_{60} were prepared with the introduction of amphiphilic matrix molecules, which serve to dilute the fullerenes in the resulting film. For example, Bard reported that stable two component monolayer films were formed from mixtures of C_{60} and eicosanoic acid.[25b,52,53] The limiting area per molecule was equal to that of pure eicosanoic acid, indicating that the fullerenes were pushed away from the air–water interface. Nakamura reported the transfer of fullerene Langmuir multilayers using eicosanoic acid as a matrix molecule onto graphite substrates.[56a] Atomic force microscopy (AFM) images of the resulting surfaces showed large crystallites if no diluent molecule was used but a smooth film if eicosanoic acid was used as a diluent molecule. Milliken used octadecanol as a matrix and was able to transfer successfully C_{60}/octadecanol multilayered films onto fused silica substrates.[57] Ringsdorf used more complicated matrix molecules, such as hexa– and octaazacrowns that were designed to possess lipophilic cavities in which fullerenes could reside within a Langmuir film.[58] Efforts to transfer these films to substrates as monolayers in sequential fashion were successful as determined by X–ray studies. Attempts by Tomioka to produce Langmuir monolayers of C_{60} in a different manner, using an aqueous phenol solution as the subphase instead of pure water, were unsuccessful at providing a fullerene Langmuir *mono*layer.[59] But interestingly, *tri*layer films were formed and transferred to hydrophobic substrates, which when studied by electron microscopy were shown to be highly crystalline with polymorphic domain structure.

As the chemistry of C_{60} has developed, there have been an increasing number of reports of the preparation of new fullerene derivatives suitable for Langmuir and LB methods. Heiney and Smith reported Langmuir monolayer film formation from $C_{60}O$ and $C_{61}H_2$ with limiting areas per fullerene of 96 and 94 Å^2 per molecule, respectively; however, they concluded that these monolayers were difficult to transfer successfully to substrates.[55] Bryce and Petty reported the formation of stable Langmuir mono– and multilayer films from a t–butyl derivatized fullerene, but only the multilayered films could be transferred to substrates.[60] Their electrochemical studies exhibit reversible waves for the first three reductions of a LB film (multilayer not monolayer), with considerable wave broadening as additional layers are deposited. They attribute this phenomenon to increased difficulty in transporting ions into the film. Langmuir monolayer formation from fullerenes modified with multiple amines has been reported by Vaknin.[61ab] Xiao and coworkers formed Langmuir and LB films from $C_{60}Br_8$. The quality of the films was again concentration dependent; low concentration spreading solutions produced monolayers and higher concentration solutions produced multilayers. These films could be transferred to hydrophilic substrates easily, and the conductivity of these LB films was measured to be higher than the conductivity of pure C_{60} films.[61c] Pasimeni studied the concentration dependence of Langmuir film formation from a series of pyrrolidine-containing fullerenes.[62] He reported a steady decrease in the limiting area per fullerene as the concentration of spreading solution increased, and three fullerenes containing amide functionality showed limiting areas in accordance with monolayer formation. However, only a short chain amide could be transferred to substrates.

In an elegant study, Matsumoto and Nakamura prepared an amphiphilic, carboxylic acid-terminated fullerene that formed stable Langmuir and LB monolayers,[63] Figure 3. The limiting area per fullerene in these films was reported to be 78 Å^2, yielding a nearest neighbor distance within the films of 1.0 nm. LB mono- and multilayers, which were characterized with a variety of methods, could be formed from these Langmuir films. It was concluded from IR spectroscopy that the carboxylic acid moieties in a multilayer film were hydrogen bonded in a dimeric fashion. An AFM image of a LB monolayer shows an extremely smooth surface on a macroscopic scale with an undulation of ~1 nm over most of the surface. X-ray diffraction gave a thickness of 26 Å for each layer, which is consistent with the length of the molecule. This is an excellent example of how fullerenes, when chemically modified with the appropriate functionalities, can be organized into interesting materials in a rational manner. It underscores the importance of the relationship between the efforts to chemically modify C_{60} and prepare materials from it.

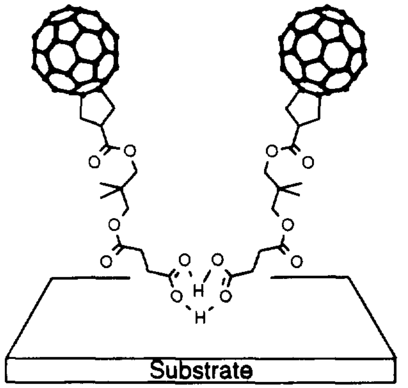


Figure 3. An LB monolayer of an amphiphilic, carboxylic acid terminated fullerene showing the postulated dimerization of the adsorbate molecules.

Self-Assembled Fullerene Monolayers (SAMs). SAMs are monolayer films formed from the spontaneous adsorption of molecules onto a variety of surfaces of interest. Substrates that have been explored include metals,[64] semiconductors,[51,65] insulators,[51] and, very recently, cuprate-based high temperature superconductors (HTSCs).[66] The term self-assembly, at least as we use it, implies that the adsorbate molecules have not only chemically adsorbed onto the surface of interest but also have organized themselves into a definable surface structure. There are few classes of molecules known to form such structures:[67,68] azobenzenes, linear alkanes, fluorinated alkanes, and now fullerenes. In the most rigorous use of the word, "self-assembly" refers to a two-dimensional crystallization of the adsorbate molecules that make up a monolayer film.

Because C_{60} has remarkable electronic, spectroscopic, and structural properties, it may be the quintessential SAM building block. Some of its attractive features are: 1) It can be easily modified with surface tethering functionality.[2,68,69] 2) It has unusually large intermolecular interactions which are manifested in its cohesive energy.[13-15,21,70] 3) Its spherical shape and 10 Å van der Waals' radius[71] make it possible to easily image a surface adsorbed fullerene by scanning probe microscopies.[12-14] 4) It is redox-active,[8] making electrochemical characterization of monolayer films formed from it straightforward. 5) It has large cross-section Raman and IR spectroscopic signatures.[1,22bcd,72]

Two approaches may be taken towards fullerene self-assembly on surfaces, Figure 4. In the first approach, a surface is chemically modified with a reagent which undergoes a bond forming reaction with a particular fullerene in solution, Figure 4A. Alternatively, a fullerene may be modified to undergo a chemical reaction with a particular surface that results in its immobilization on that surface, Figure 4B. From a materials preparation standpoint, Strategy A from Figure 4 has the advantage in that pure C_{60} may be used as the adsorbate molecule. However, this strategy often leads to films which are difficult to characterize due to the possibility of multiple additions to C_{60}. On the other hand, Strategy B from Figure 4, which is synthetically more involved than Strategy A, leads to more chemically homogeneous materials that can be characterized in a more straightforward fashion.

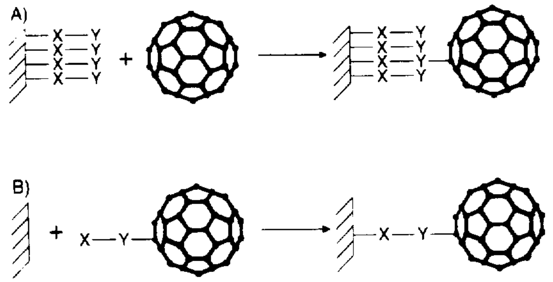


Figure 4. Two strategies used to prepare chemisorbed fullerene monolayer films.

There have been several reports of fullerene monolayers formed via Strategy A. Mirkin initially reported the covalent attachment of fullerenes to aminopropylsilanized oxide substrates.[73] The cyclic voltammetry of these films yielded broad reversible reductions which were attributed to the redox-active surface-confined fullerenes. Fullerene films were subsequently formed in an analogous manner on polycrystalline Au substrates.[74] A quartz crystal microbalance experiment was used to follow the fullerene adsorption process and confirm the formation of a monolayer film. Also, the redox-inactivity of the monolayer was shown to be a consequence of dense fullerene packing and ion transport inhibition, although coulombic interactions also may contribute to the observed response. These results suggest that higher quality films can be formed on Au substrates via thiol adsorption chemistry as compared with the films formed on oxide surfaces by trichlorosilane adsorption chemistry. Smith and Blasie prepared a fullerene monolayer by adsorbing C_{60} onto a pyridyl-terminated surface which had been exposed to OsO_4.[75] In an elegant use of x-ray methodology, Smith and Blasie were able to show that the fullerenes had formed a primitive hexagonal lattice resting over the pyridyl-terminated surface. Tsukruk and Brittain utilized the reactivity of fullerenes with surface-confined azides to prepare and study monolayers on oxide substrates.[76a]

AFM images of a C_{60} monolayer formed on an azide terminated silicon substrate showed a regular, closed packed multidomain structure. A statistical analysis of multiple molecular resolution images was consistent with the fullerenes forming a face centered cubic cell with an edge length of 14 Å. Later work by Brittain and coworkers with these monolayers has focused on their blood contact properties and resistance to friction and wear; however, the C_{60} monolayers did not exhibit any unusual properties in these regards.[76bc] Lee used amine-terminated surfaces similar to those prepared by Mirkin[73] to produce fullerene monolayers, then grew multilayered structures using 1,12-diaminododecane as a linking agent between the fullerene layers.[77]

Very recently, the synthesis of a well-defined, surface-confinable fullerene was reported, Figure 5.[68] This compound was prepared via the condensation of 2-(4-mercaptobutyl)benzaldehyde, sarcosine, and C_{60}; the condensation reaction was based on work reported by Prato and coworkers.[69] This compound was designed so that the fullerene cage would be the dominant moiety of the molecule and therefore would govern its packing within the monolayer. The molecule was shown to spontaneously adsorb from a benzene solution onto Au(111)/mica substrates[78] and self-assemble into a highly ordered monolayer structure. Monolayer films of the fullerene adduct were characterized via SERS, AFM, and cyclic voltammetry. The AFM image of a monolayer of the fullerene adduct clearly exhibited a distorted hexagonal array of bright spots which was attributed to the fullerene molecules comprising the film, Figure 6. The lattice parameter (10.9 +/- 0.8 Å) was in excellent agreement with the nearest neighbor distance for the fullerenes that make up a (111) face of crystalline C_{60} (10.7 +/- 1.3 Å) as determined by AFM.[79] Note that this packing arrangement is different from that observed by Brittain and Tsukruk for C_{60} adsorbed onto an azide terminated silicon surface.[76a] The origin of this difference is not understood. Mirkin further showed that the redox properties of the fullerenes which comprise the monolayers were drastically

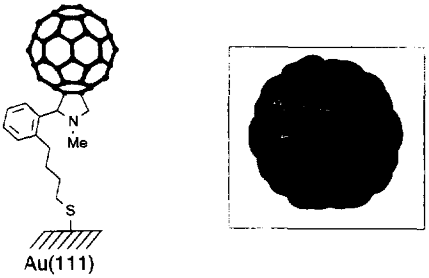


Figure 5. A surface-confined fullerene on Au(111)/mica. The fullerene cage dominates the structure of the molecule (inset) and drives the self-assembly process.

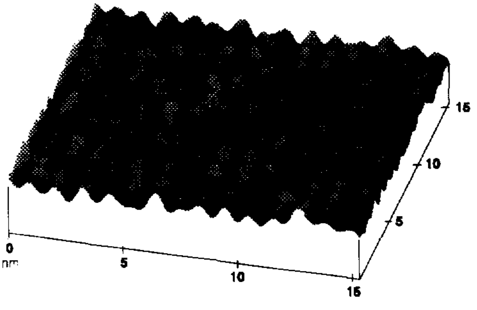


Figure 6. AFM image of a C_{60} SAM on an Au(111)/mica substrate. The fullerene intermolecular distance is 10.9 Å.

dependent on film structure and often did not reflect the redox properties of the adsorbate molecules in solution.[68] It was shown that the dense packing of the molecules that comprised the monolayer inhibited ion transport within the film. The energetic consequences of separating charge compensating cations from the reduced forms of the fullerene adsorbate molecules caused anomalously large shifts in the reduction potentials for the immobilized fullerenes. It is important to note that the effects of restricted ionic motion in chemisorbed monolayer films of redox-active molecules like C_{60} were not generally recognized by the monolayer community prior to these studies. Through related work by Mirkin[67a,80] and others,[81] the observation has now become quite general and extends beyond fullerene adsorbate molecules. It is also worthwhile noting that LB films, which are physisorbed rather than chemisorbed to surfaces, do not suffer as significantly from this problem because there is an inherent lateral flexibility for the molecules that make up an LB film.

Conclusion

Although significant initial strides have been made, it is clear that the development of fullerene-based materials, and thin films in particular, is still in its infancy. However, when one considers that facile methods to cleanly modify C_{60} have only been around for the past three years (some discovered only in the past year), it is amazing how much progress has already been made in this area. Methods for preparing sophisticated polymers and highly ordered monolayer structures have been developed. Promising properties for these materials have been discovered and are beginning to be explored in depth. It is clear that one of the most promising aspects of C_{60} for materials chemistry is its use as a marker molecule for materials characterization. It has already provided a wealth of fundamental insight into the nucleation and growth processes for thin films in UHV environments. Similarly, it will be useful in addressing many important fundamental issues concerning the dynamics of the monolayer self-assembly process. The development of technologically useful fullerene-based materials will not only rely on clever ways to organize fullerenes into two and three-dimensional structures but also on the development of clean methods for chemically modifying fullerenes.

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