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The structure of fullerene films and their metallocene doping

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Hexagonal close-packed (HCP) C_{60} and C_{70} films have been prepared by the Langmuir method and examined by electron microscopy and electron-diffraction analysis. It has been shown that the vacuum deposition of a $C_{60} + C_{70}$ mixture results in the formation of a film with small sized grains and a distorted C_{60}-HCP structure. The simultaneous deposition of C_{60} and ferrocene results in the formation of a film with a changed morphology and an electron-diffraction pattern that contains a variable amount of ferrocene depending on the experimental conditions. The electron-diffraction pattern corresponds to the presence of the known molecular complex $C_{60}[(C_5H_5)_2Fe]_2$. The analogous simultaneous deposition of fullerene C_{60} and cobaltocene results in the formation of a C_{60} film stable in air and water, which contains carbon and cobalt (from the data of X-ray fluorescence, electron microscopy and microdiffraction). It has a different morphology and different diffraction patterns than pure C_{60} films and, depending on the cobaltocene content (relative to that of fullerene), appears to be a fullerite film doped with various amounts of cobaltocenium fulleride, which is an ionic compound.

Key words: fullerenes, films doped by ferrocene and cobaltocene.

Fullerenes are of great interest as new film materials. Films of face-centered cubic (FCC) individual C_{60} and C_{70} have been obtained by evaporation from solution,[1] vacuum deposition,[1] or by the Langmuir—Blodgett method,[2] although there also exist hexagonal close-packed modifications of these fullerenes[1] as massive crystals of fullerites. The reproducibility of the structure and properties of these films depends on the degree of purity of the fullerenes (admixtures of C_{70} and higher fullerenes relative to C_{60}), and on the formation of insertion compounds with benzene,[3] gases,[4] or molecular complexes with iodine[5,6] and ferrocene.[7]

Fullerene acts as an electron acceptor, thus C_{60} can interact with electron donors to form charge-transfer complexes or systems with separated charges. Fullerene salts of alkaline metals, $C_{60}M_X$, are typical examples of these complexes. The nature of the complexes depends on the redox properties of the reagents. For example, there is a molecular complex of fullerene and ferrocene $C_{60}[(C_5H_5)_2Fe]_2$[7] obtained in a benzene solution in a crystalline form with triclinic syngony and $P\bar{1}$ space group and an ionic fulleride of cobaltocenium (1 : 1) similarly obtained from fullerene and cobaltocene in solution, whose structure was determined by elemental analysis, IR spectroscopy, and ESR.[8] It is noted in the latter work that the similarity of the redox potentials of cobaltocene and the fulleride anion (−2) allows one to expect the formation of the mentioned two-charge fulleride anion as the result of the interaction between cobaltocene and fullerene C_{60}. The possibilities of preparing cobalticenium $C_{60}{}^{1-}$ fulleride, decamethylenecobalticenium $C_{60}{}^{3-}$ fulleride[9], and cobalticenium $C_{70}{}^{1-}$ fulleride[10] are also briefly mentioned.

Analogously, the similarity between the redox potentials of ferrocene and iodine (0.5 V relative to SCE) demonstrated by the reversible oxidation of ferrocene with iodine[11] and the practical absence of charge transfer between polarized iodine and fullerene molecules in crystals of their complex[6] may attest to the possibility of the formation of a molecular complex[7] without charge separation by ferrocene and fullerene molecules.

It seemed interesting to compare the interaction of fullerene C_{60} with metallocenes with strongly different redox potentials, ferrocene (+0.5 V) and cobaltocene (−1.0 V relative to SCE) under the conditions of vacuum deposition and to test the possibility of doping fullerite thin films with metallocenes .

In this connection, the purpose of this work was the reproducible preparation of films of pure C_{60}, pure C_{70}, and of a mixture of C_{60} and C_{70} and the study of metallocene-doping of C_{60} films.

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Experimental

Films were prepared by vacuum deposition and the Langmuir method. Their compositions, morphology, and structures were studied.

Benzene solutions of C_{60} (purity 99.95 %) were used for the preparation of films by the Langmuir method. Unlike the Blodgett—Langmuir method, no compressing pressure was applied for the film preparation. A film was poured from water into a copper sieve 3 mm in diameter and dried. Films of pure C_{70} (99.95 %) and of a mixture of C_{60} + C_{70} (4 : 1) were prepared similarly.

Samples were examined on a JEOL JEM 2000 EX II electron microscope with accelerating voltage U = 200 kV. It was found that, due to their multilayer structure, films of C_{60} and C_{70} crystallized to form hexagonal and rectangular crystals.

C_{60} films were also prepared by vacuum deposition on a VUP-5 setup. Films of C_{60} and C_{60} + C_{70} deposited on NaCl were poured on a copper sieve after the usual preparation by dissolving in water. As seen on an electron microscope, all of the films were polycrystalline.

Vacuum co-condensation was performed by the thermal evaporation of fullerene C_{60} and metallocenes, and ferrocene and cobaltocene. Deposition was performed on both cool and hot supports. Evaporation temperatures were 150 to 200 °C for fullerene and no more than 100 °C for metallocenes. Monocrystals of NaCl and amorphous carbon films applied on copper sieves for PEM were used as supports. The elemental compositions of the films were confirmed by electron-fluorescent spectra obtained on a microprobe analyzer.

Fullerene and ferrocene were deposited on cool NaCl supports jointly and in turn. Judging by the morphology of the film of jointly deposited fullerene and ferrocene, some regions of the film were amorphous and some were polycrystalline.

Fullerene and cobaltocene were jointly deposited at 20, 60, and 100 °C on NaCl supports and amorphous carbon films caught by copper sieves. The films were examined by electron-microscopic and electron-fluorescent analyses. Judging both by the morphology and the microdiffraction pattern, the film was almost completely amorphous when deposited on a cool support. Deposition on hot supports resulted in polycrystalline and textured films. The microdiffraction patterns obtained did not differ for different support temperatures.

Results and Discussion

Films of pure C_{60} and pure C_{70} were crystallized in a hexagonal close-packed structure with a texture that agreed well with the literature data for crystals of C_{60}[12] and C_{70}[13] (Fig. 1).

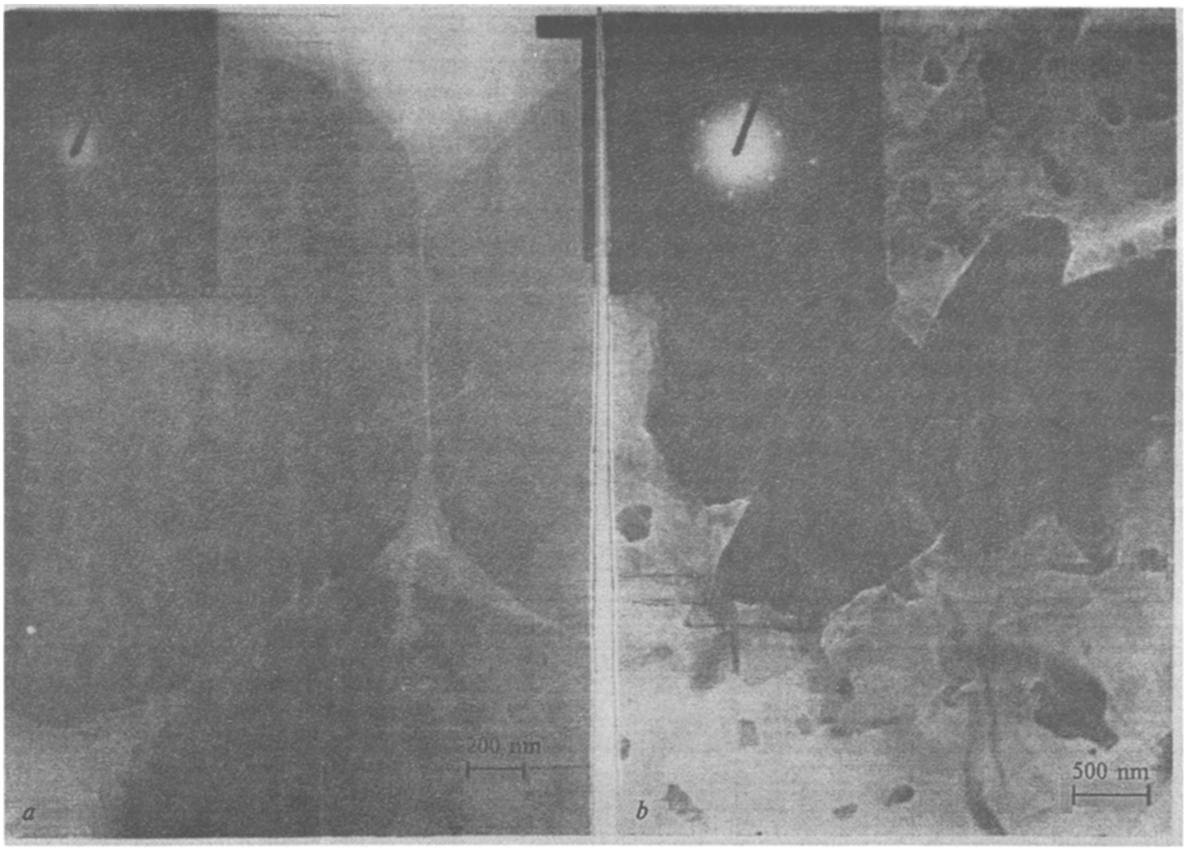

Fig. 1. Microstructures and electron-diffraction patterns of C_{60} (*a*) and C_{70} (*b*) films obtained by the Langmuir method (hexagonal close packing)

The diffraction patterns of pure C_{60} deposited *in vacuo* are similar to those of Langmuir films of C_{60} and correspond to the HCP-structure. The formation of the HCP-structure and not the FCC-structure demonstrated in Ref. 2 is apparently explained by the fact that in the latter work the Langmuir films were prepared under pressure and, therefore, the close-packed FCC structure was formed. In our case, so-called free Langmuir films were formed without any additional pressure. As a result, the less closely packed HCP structure was formed.

The electronograms of the C_{60} + C_{70} mixture obtained in the analysis of films deposited *in vacuo* and Langmuir films correspond to a solid solution of C_{70} in C_{60} with a distorted HCP structure and small grains (Fig. 2, *a*).

Ferrocene and fullerene form films with changed morphology and electronograms during joint vacuum deposition (Fig. 2, *b*). Depending on the conditions of deposition (temperatures of supports and evaporation), the films contained various amount of ferrocene (according to the data of X-ray fluorescent analysis). The electronograms of the films correspond to the presence of a compound identical to $C_{60}[(C_5H_5)_2Fe]_2$.[7] The symmetry is lower than that of fullerene. This is caused by the fact that ferrocene cannot occupy the tetrahedral and octahedral vacant sites in the HCP-lattice of fullerene like alkaline metals, because the diameter of the ferrocene molecule is larger than those of the tetrahedral and octahedral vacant sites and the alkaline cations. Therefore, ferrocene molecules can only occupy the sites between the fullerene layers, causing finally the symmetry to decrease to triclinic. The results of the identification of the electronogram allow one to believe that this compound is really formed but it can be crystallized with excess or deficient ferrocene, depending on the conditions of deposition. The compound easily dissociates in a vacuum to liberate ferrocene and produce deviations from stoichiometry.

It was believed that joint deposition of fullerene and cobaltocene could also result in the formation of a compound, and since the geometric factors for doping fullerite with metallocenes were similar (cobaltocene and ferrocene are isomorphous), the electronic factors must play an important role in the interaction between them and C_{60}. The experimental electronograms of fullerene C_{60} doped with ferrocene or cobaltocene are similar (Fig. 2, *b*, and 3). The X-ray analysis showed the existence of considerable amounts of cobalt, attesting to the existence of cobaltocene bound in the film, which is not oxidized in air and is not washed out with water in

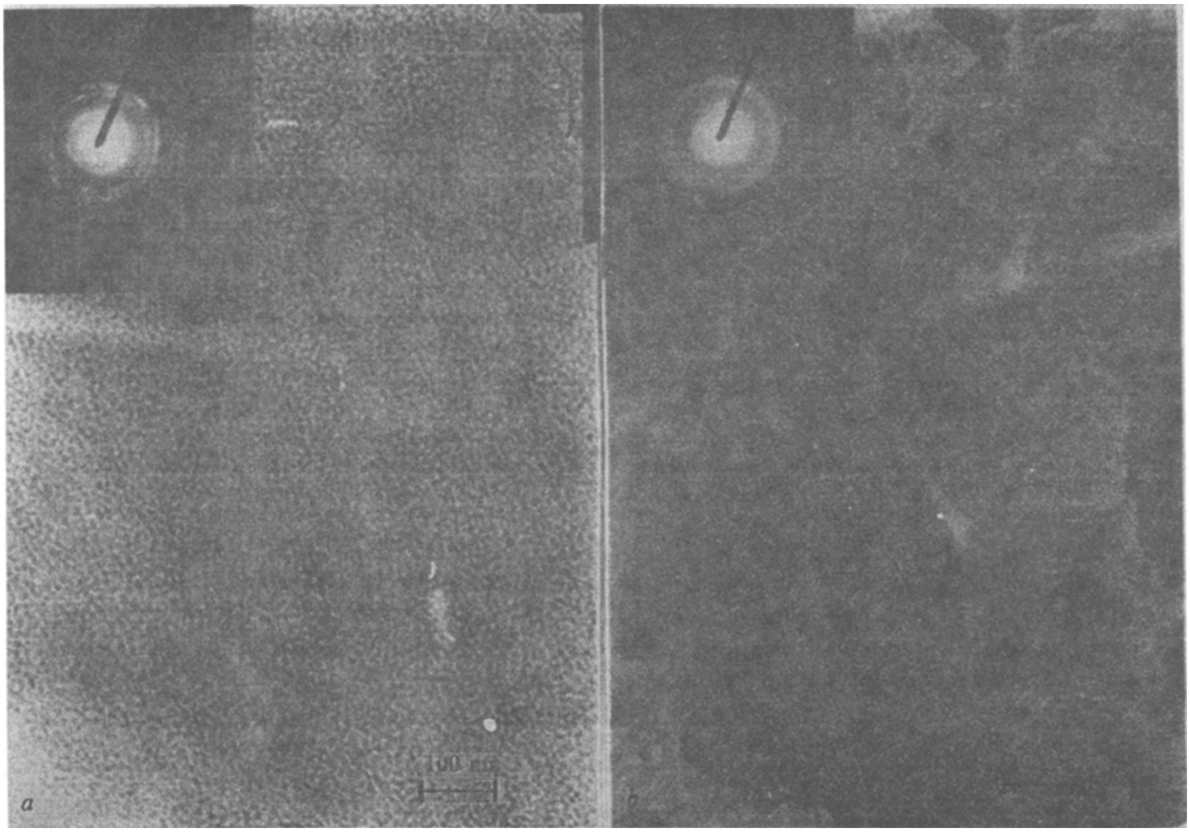

Fig. 2. Microstructures and electron-diffraction patterns of C_{60} films doped with C_{70} (HCP-C_{60} structure (*a*)) and ferrocene (*b*)

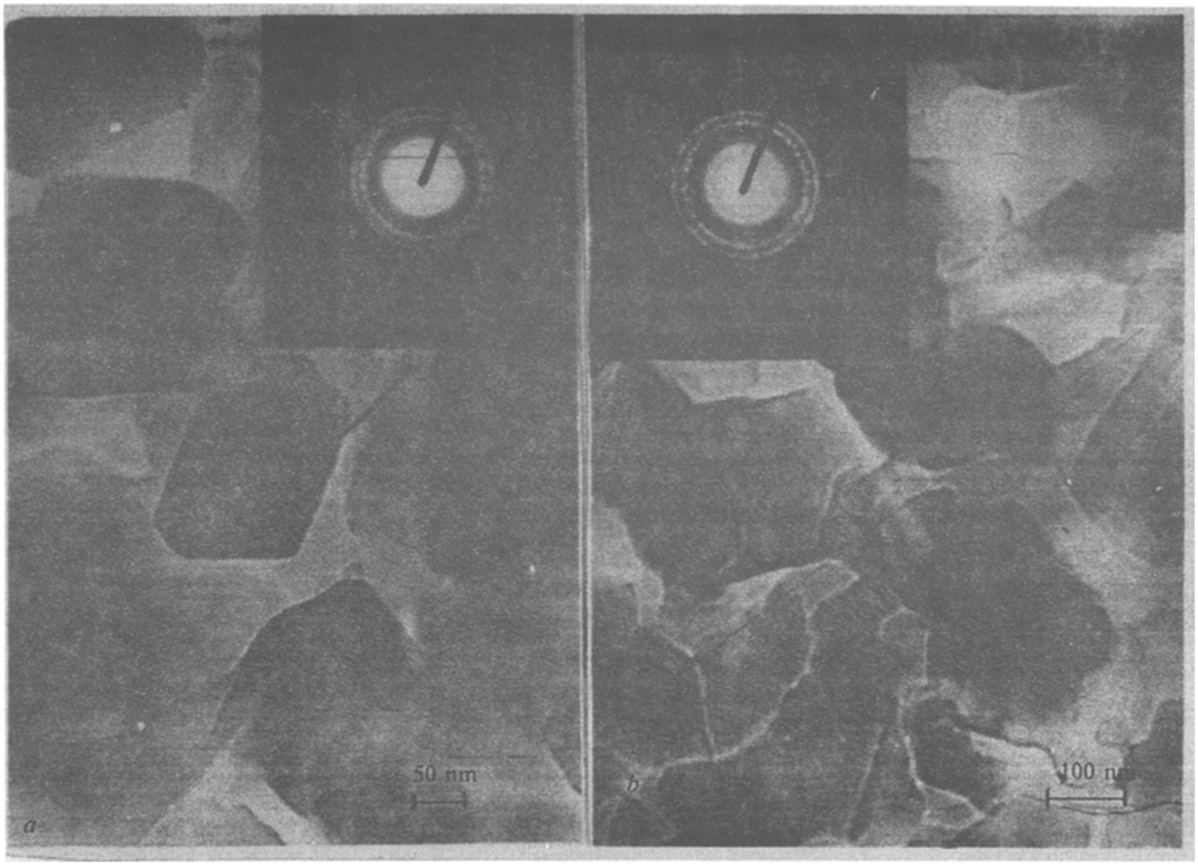

Fig. 3. Microstructures and electron-diffraction patterns of C_{60} films doped with cobaltocene (temperatures of the support are 60 °C (*a*) and 90 °C (*b*))

the preparation of samples for analysis. Cobaltocene that is not chemically bound in the fullerite film should be easily oxidized to the cobalticenium cation and washed out with water in the deposition of the film on a water-soluble NaCl support.

The differences between fullerite films doped with ferrocene and those doped with cobaltocene appear in their stability and solubility. The ferrocene derivative is apparently a reversibly dissociating molecular complex (variable Fe/carbon ratio at various temperatures in a vacuum and volatility in a vacuum), whereas the cobaltocene derivative is more stable at various elevated temperatures, is insoluble in nonpolar solvents, is stable in the solid state (a crystalline film) to air and water, retains the Co/carbon ratio, and, apparently, the fullerite film contains chemically bound cobaltocene as an ionic complex of cobalticenium(I) cations with fulleride-anions.

Thus, the analysis of Langmuir "free" films has elucidated that only one phase, a hexagonal closed-packed structure, is formed both for C_{60} and C_{70}.

The formation of the film of the C_{60} + C_{70} mixture both by vacuum deposition and the Langmuir method results in their solid solution with a distorted C_{60} structure (HCP).

The joint vacuum deposition of films of fullerene and metallocenes, in particular, ferrocene and cobaltocene, results in doping of the films of C_{60} fullerene with metallocenes to form films with morphology and electron-diffraction patterns different from those of pure C_{60}-fullerite and with properties that depend on the nature of the metallocene, in particular, on the redox properties of the metallocene-fullerene system.

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