XPS study of ammonia-exposed C_{60} films both original and photopolymerized

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Surface of C_{60} films (original and photopolymerized with UV radiation) exposed to ammonia at different pressure was investigated by the method of X-ray photoelectron spectroscopy. Effect of X-ray stimulated interaction between films and adsorbed water, which resulted in bonds like C–O–H and enhanced by ammonia was detected. It was shown that ammonia unreacted chemically with C_{60} films, both original and photopolymerized.

Методом рентгеновской фотоэлектронной спектроскопии исследована поверхность фуллереновых пленок (не полимеризованных и полимеризованных с помощью ультрафиолетового облучения), выдержанных в аммиаке при различных давлениях газа. Обнаружен эффект взаимодействия пленок с адсорбированной водой с образованием связей типа С–О–Н, который стимулируется рентгеновским облучением и ускоряется аммиаком. Показано, что аммиак не взаимодействует химически с фуллереновой пленкой как полимеризованной, так и не полимеризованной.

The potential application of fullerene films as superhard coatings [1, 2] or building material to elaborate composite membrane for gas separation [3, 4] rises to a question concerning interaction between fullerene and different gases. As it was shown earlier [5−7], important industrial gases such as nitrogen, oxygen, and methane chemically unreact with fullerene under ambient conditions. But influence of such reactive gas as ammonia on C_{60} films does not study up today.

An effect of NH_3 adsorption on the electronic and structural properties of fullerene salts like A_3C_{60}, where A is alkali metal, has been investigated earlier [8−10]. The sorption of ammonia by these substances leads to charge transfer and expanding or distortion crystal lattice. No nucleophilic addition of ammonia to fullerene with formation C–N and C–H bonds was reported. Pure ammonia does not dissolve C_{60} under ambient conditions [11], but easy dissolve fullerene in the presence of reduction agents when solvated electron appeared [12]. Therefore dissolution effects of fullerene films have to pay attention too.

C_{60} in ground state has a closed shell of electrons and hence it is chemically stable compound. Chemical properties of C_{60} are determined mainly by 20 conjugated double carbon bonds. Photopolymerized fullerene consists on chains of C_{60} molecules fused by cyclobutane rings [13]. Each fusing reduces on 1 the number of double bonds in C_{60} molecule. In polymerized fullerene each C_{60} molecule bonds with 2 adjacent molecules, so the number of double bonds reduces to

18, not disturbing conjugation of other π-electrons. So polymerization must not have a sufficient influence on chemical properties of fullerene. In the same time, polymerization brings together C_{60} molecules, what results in different diffusion coefficient and gas solving in original and polymerized crystals or films of fullerene, so can be reason for difference in their chemical activity.

In this study we report XPS investigation of original and photopolymerized fullerene films after exposing to gas and liquid ammonia at room temperature and increased pressure.

The C_{60} films ~500 nm thick were deposed onto Si substrate in vacuum. C_{60} powder (purity 99.5 mass. %, purchased from Fullerene Technology Co, St. Petersburg, Russia) was evaporated from a graphite Knudsen cell at temperatures 450–500°C. Photopolymerized C_{60} films were grown using simultaneous deposition and irradiation with ultraviolet light. Obtained films were polycrystalline or amorphous. Details of films preparation have been reported in [14, 15]. The degree of photopolymerization was estimated as ~90 % after 20 h of irradiation [15]. Original and polymerized C_{60} films were exposed for 5–10 days to ammonia atmosphere at 300 K and pressure: 5 atm., 7.5 atm., 11 atm. It is should be noted that the latest ammonia pressure equals to pressure of its saturated vapor at this temperature, so ammonia vapor could condense on the film surface. Between preparation and XPS investigations films were on air. There were no any special conditions to defense films against air humidity.

XPS study was conducted on a spectrometer XPS-800 Kratos. The vacuum in the chamber was 10^{-7} Torr. Photoelectrons were excited by MgK$_{\alpha\text{-radiation}}$ ($h\gamma = 1253.6$ eV). X-ray gun power was 15 kV×20 mA. The hemispherical electrostatic analyzer analyzed photoelectron kinetic energy. Instrument resolution was about 1 eV; accuracy of binding energy determination was 0.3 eV. The spectra were treated on computer: smoothing, subtraction of a constant and variable background (Shirley's method), removing expanding effect of the X-ray line (iterative deconvolution) and decomposition of complex line on its Gaussian component were made. The sample surface composition was determined using ratio of areas of photoelectron lines in spectra of *C1s*, *O1s*, *N1s* core levels taking into account their sensitivity factors.
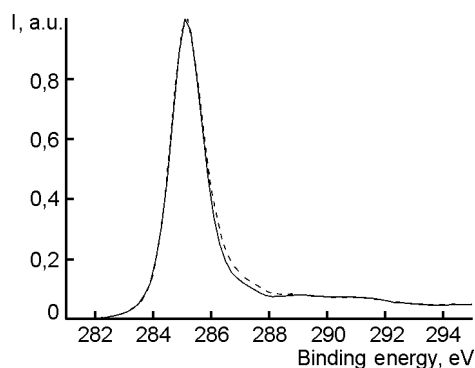

Fig. 1. XPS spectra of *C1s* core level of the original C_{60} film (sample No.1). Solid line — the first 30 min of measurement, dashed line — after 4 h of X-ray irradiation.

Fig. 1 shows XPS spectra of *C1s* core level for the original C_{60} film measured for the first 30 min. (solid line) and for 30 min. after 4 h of measurement (dashed line). The *C1s*-spectrum of C_{60} consists from a main line (binding energy $E_b = 285$ eV, full width at half maximum FWHM $\Delta E_b = 1.3$ eV) and a "shake-up" satellite peak ($E_b = 287$–291 eV). This satellite structure characterizes C_{60} and appears due to the π-electron transition from occupied to unoccupied valence molecular orbitals associated with the *C1s* core hole generation. The treatment of this spectra shows the same satellite structure and intensity as reported in [16]. During measurement at X-ray irradiation some small shoulder on main peak appeared at the higher binding energy side ($E_b \approx 286$ eV). Intensity of this shoulder increased and saturated at measurement time about 4 h.

The *C1s* spectrum of photopolymerized fullerene is very similar to one for original fullerene with small (about 5 %) decrease of the intensity of the shake-up satellite due to the reduction of π-electrons on a C_{60} molecule in the polimerization [17]. Shoulder at the higher binding energy also appeared in *C1s*-spectra of photopolymerized fullerene during measurement, but it was smaller and not for all samples. The intensity of this shoulder for different samples correlated with the intensity of *O1s* core level peak (Table).

O1s core level spectra for all samples (original and polymerized) presented a single peak with $E_b = 533.0\pm0.4$ eV, and $\Delta E_b = 2.2\pm0.2$ eV. The origin of this line was discussed in [18] and it was attributed to oxygen in H_2O molecules adsorbed on the

C_{60} film. Authors of [18, 19] considered that adsorbed O_2 mostly desorbed from the film at 300 К and high vacuum condition. This line also can be attributed to C–O–H groups, which have binding energy of *O1s* core level in the same region [20]. The shoulder at $E_b = 286$ eV (see Fig. 1) also can be also connected with C–O–H groups [21].

During XPS measurement under X-ray irradiation a lot of secondary electrons appear in fullerene film. It was shown in [19] that secondary low energy electrons, which appear in the system: solid O_2/C_{60}/GaAs substrate during photon irradiation at $T = 20$ К, can be captured by oxygen. Authors of [19] pay no attention to process of electron capturing by a C_{60} molecule. In our opinion such process plays an important role in the fullerene oxidation reaction, because electron affinities of O_2 and C_{60} equal to 0.45 eV [22] и 2.65 eV [23], respectively, hence fullerene can capture electron easier than oxygen. The decay of carbanion C_{60}^- at the presence of adsorbed H_2O molecules leads to partly fullerene oxidation with reaction products containing hydroxyl groups.

So, the fullerene oxidation reaction with reaction products containing hydroxyl groups can occur on the surface of C_{60} films not exposed to ammonia under X-ray irradiation during XPS measurement. This process leads to increasing of the *O1s* peak intensity in XPS spectra during measurement. Element atomic concentrations in analyzed layer (which thickness was estimated in [18] as 18 Å) and content of oxygen and nitrogen atoms per one C_{60} molecule are shown in Table.

The mean van der Waals diameter of water has been reported as 2.82 Å [24]. The diameters of tetrahedral and octahedral cavities for the lattice parameter of fullerene are 2.24 Å and 4.15 Å, respectively [25]. So, H_2O molecule can occupy only octahedral cavities of fullerene lattice and only one H_2O molecule can be in one cavity, hence the ratio between oxygen and C_{60} can not be more than 1. But it was 2.5 for original film (Table, sample No.1, the first 30 min. of measurement). Apparently, the most amount of water was adsorbed on the surface edges of crystallites forming fullerene films. Further X-ray irradiation leads to increasing of oxygen content and its saturation on the level of about 3 oxygen atoms per one C_{60} molecule.

This increasing suggests that, at first, water adsorbed on the crystallite surface reacts with fullerene, then water, adsorbed deeper in film. Low diffusion coefficient for water in fullerene lattice limits this process.

Polymerized films contented sufficiently less amount of oxygen (see Table, sample No.2) and were more stable to X-ray irradiation during XPS measurement. This can

Table. Atomic concentration of elements and their ratio to C_{60} molecule (estimation of stochastic error shown)

| Sample	Condition	C, at % ±0.3	O, at % ±0.2	N, at % ±0.2	C_{60}, mol.	O, mol.	N, mol. ±0.1
No.1 (original.)	30 min X-ray	96.2	3.6	0.2	1	2.5	0.1
No.1 (original.)	4 h X-ray	95.1	4.6	0.3	1	2.9	0.2
No.2 (polymer)	30 min. X-ray	98.9	1.1	0	1	0.7	0
No.3 (original)	NH_3 7.5 atm., 30 min. X-ray	96.5	2.1	1.4	1	1.3	0.9
No.4 (original)	NH_3 11 atm., 30 min. X-ray	96.6	2.3	1.1	1	1.4	0.7
No.4 (original)	NH_3 11 atm., 4 h X-ray	94.0	5.0	1.0	1	3.1	0.6
No.5 (polymer)	NH_3 5 atm., 30 min. X-ray	97.1	1.8	1.1	1	1.1	0.7
No.6 (polymer)	NH_3 7.5 atm., 30 min. X-ray	96.4	2.0	1.6	1	1.2	1.0
No.7 (polymer)	NH_3 11 atm., 30 min. X-ray	94.1	4.3	1.6	1	2.7	1.0
No.7 (polymer)	NH_3 11 atm., 4 h X-ray	93.0	5.4	1.6	1	3.5	1.0
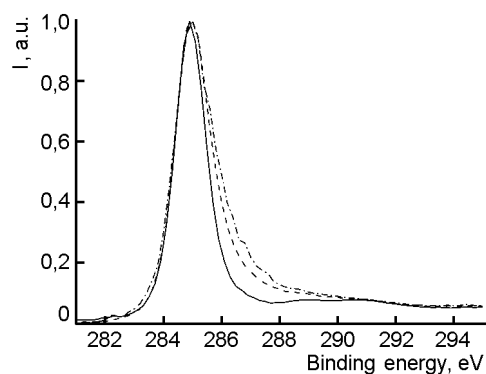
Fig. 2. XPS spectra of *C1s* core level of the polymerized C_{60} film before exposition to ammonia (sample No.2 — solid line) and after exposition at 11 atm. (sample No.7, dashed line — the first 30 min. of measurement, dashed-dotted line — after 4 h of X-ray irradiation).

be explained by difference in morphology and structure between original and polymerized films.

Shape and relative intensity of XPS spectra of *C1s*, *O1s* and *N1s*-core levels were analyzed also for samples exposed to ammonia. Fig. 2 shows *C1s* spectra of polymerized fullerene before (1 — solid line) and after (2 — dashed line) exposition to ammonia at pressure 11 atm. for 10 days. Spectrum 2 measured for the first 30 min., spectrum 3 (dashed-dotted line) — for 30 min. after 4 h of X-ray irradiation. *C1s*-spectra for original fullerene exposed to ammonia had the same form. No dependence of *C1s*-spectra shape on exposition time and pressure was detected. The high-energy shoulder in *C1s* spectra was observed for all samples exposed to ammonia (even in the first 5 min. of measurement). This shoulder also increased during X-ray irradiation (see Fig. 2).

C1s spectra treated on computer (Fig. 3) show, that this shoulder can be attributed to small peak at binding energy $E_b = 286.2$ eV. Maximum of its intensity was about 7 % from intensity of main peak at $E_b = 285$ eV. Literature data analysis [21, 26] shows that peak at 286.2 eV can be attributed as to a bond between carbon and oxygen (like –C–O–C– or C–O–H), as to an imine bond between carbon and nitrogen (–N=C<). Possibility of the latest bond will be discussed later on the base of an elements concentration analysis.

The *O1s* core level spectrum for exposed to ammonia films was the same as one for original films and has $E_b = 533.0\pm0.4$ eV.
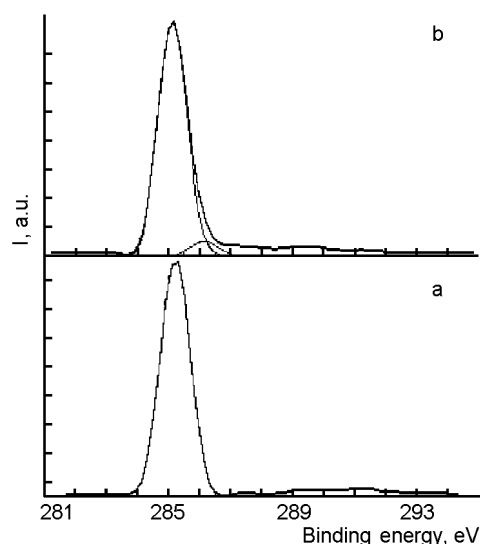

Fig. 3. Treated on computer XPS spectra of *C1s* core level of the polymerized C_{60} film before exposition to ammonia (a — sample No.2) and after exposition at 11 atm. pressure, the first 30 min. measurement (b — sample No.7).

The *O1s* signal indicates the presence of adsorbed water or hydroxyl groups in the analyzed layer of ammonia-exposed films.

Increasing of oxygen atoms amount during X-ray irradiation also observed for all types of films (see Table). The shape of *N1s* core level spectra depended on ammonia pressure. Fig. 4 shows *N1s*-spectra for polymerized fullerene exposed to ammonia at pressure 5 atm. (a) and 11 atm. (b). The spectrum on Fig. 4b consists from the main peak at binding energy 399.4 eV and a peak at $E_b = 401.0$ eV, which appeared at pressure 7.5 atm. The main peak can be connected with ammonia molecule NH_3, adsorbed by fullerene film. The peak at $E_b = 401.0$ eV can be attributed to ion NH_4^+. This peak also was observed in [27] during investigation of interaction between C_{60} and nitrogen containing polymers and was attributed to protonited nitrogen atom. The nitrogen concentration showed weak dependence on ammonia pressure and did not change during X-ray irradiation (see Table). Its maximum was about 1 atom per one C_{60} molecule. We assumed that this nitrogen is connected with adsorbed ammonia, so its concentration depends on film adsorption ability, i.e. film structure and morphology.

As we discussed above, low energy electrons, which appears at X-ray irradiation during XPS measurement influence on the C_{60}^- oxidation process. Ammonia liquates in
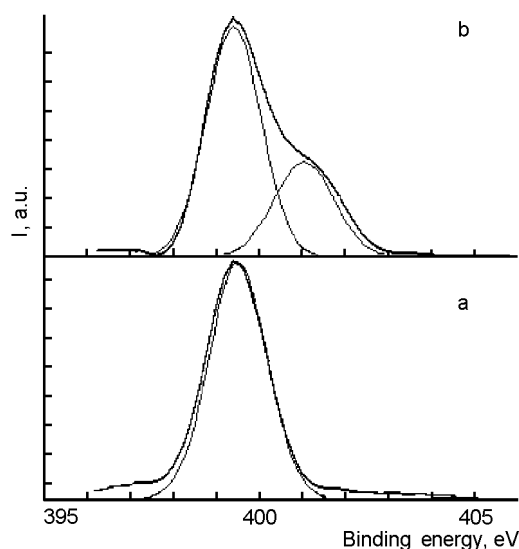
Fig. 4. Treated on computer XPS spectra of *N1s* core level of the polymerized C_{60} film exposed to ammonia at pressure 5 atm.(a — sample No.5) and 11 atm. (b — sample No.7).

film pores at high pressure. Secondary electrons can be solvated by liquid ammonia; hence their lifetime and concentration in film increase. Solvated electrons interact with a C_{60} molecule producing a carbanion C_{60}^-, which decay leads to fullerene oxidation with reaction products containing hydroxyl groups.

Water and ammonia, adsorbed by the film surface, are in the ion-molecular equilibrium (reaction: $NH_3 + H_2O = NH_4^+ + OH^-$). A carbanion C_{60}^- can be stabilized by forming ion salt $C_{60}^- NH_4^+$ with ammonia ion, which can penetrate to crystal octahedral cavities at high ammonia pressure. So, a carbanion bonds an ammonia ion, i.e. removes it from the equilibrium shown above, making for increasing of an amount of hydroxyl ions in the film. So ammonia ion concentration depends on carbanion C_{60}^- concentration and can not be more then amount of C_{60} molecules, because the process of two electrons capturing by a fullerene molecule has low probability. This explains saturation of *N1s* signal in XPS spectra for ammonia-exposed films. If imine bonds like –N=C< formed during interaction, the saturation would not observe, because in this case forming more then one nitrogen bond per one C_{60} molecule would be possible. So, evidently, ammonia unreacts chemically with fullerene, both during exposition, and at further X-ray irradiation.

Hydroxyl ions reacts with C_{60} by mechanism of nucleophile attachment and the re-

action results in fulleroles $C_{60}(OH)_n$, n mainly depends on amount of adsorbed water, which is a source of hydroxyl ions, and does not depend on amount of C_{60} molecules. Therefore the intensity of the *O1s* signal and the peak at $E_b = 286.2$ eV in *C1s* spectra of the films increased during X-ray irradiation.

To eliminate effects connected with possible hydrocarbons contamination of the fullerene film surface, samples of Si substrate were investigated before and after exposition to ammonia. No changing in atomic concentration of elements and shape of the *C1s* spectrum for hydrocarbons contamination on the Si surface during exposition and X-ray irradiation observed. We observe no sufficient difference in XPS spectra for original and polymerized fullerene films exposed to ammonia. No chemical interaction C_{60} with ammonia for both types of films was observed.

So, this study shows, that ammonia does not interact chemically with the fullerene film, both original and polymerized. This result expands the range of practical application of fullerene films, which are chemically stable to active gases. However, air humidity can lead to accessory effects, connected with appearance of ammonia ions and formation of hydroxyl ions, which can enhance film photooxidation.

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Рентгенівська фотоелектронна спектроскопія вихідних та фотополімеризованих плівок C_{60}, що були експоновані в аміаку

М.В.Добротворська, В.О.Карачевцев, О.М.Вовк, А.М.Рао

Методом рентгенівської фотоелектронної спектроскопії досліджено поверхню фулеренових плівок (не полімеризованих і полімеризованих за допомогою ультрафіолетового опромінення), витриманих в аміаку при різних тисках газу. Виявлено ефект взаємодії плівок з адсорбованою водою з утворенням зв'язків типу C-O-H, що стимулюється рентгенівським опроміненням і прискорюється аміаком. Показано, що аміак не взаємодіє хімічно з фулереновою плівкою як полімеризованою так і не полімеризованою.