

## X-ray radiation influence on photoluminescence spectra of composite thin films based on C<sub>60</sub><CdTe>

M A Elistratova<sup>1,2</sup>, I B Zakharova<sup>1</sup> and N M Romanov<sup>1,2</sup>

<sup>1</sup> St. Petersburg Polytechnic University, 29 Polytechnicheskaya str., St. Petersburg 195251, Russia

<sup>2</sup> Lappeenranta University of Technology, 34 Skinnarilankatu, Lappeenranta 53850, Finland

E-mail: elistratovamari@yandex.ru

**Abstract.** Photoluminescence spectra of composite thin films based on C<sub>60</sub><CdTe> before and after X-ray irradiation, as well as the results of quantum-chemical calculations of corresponding molecular complexes are presented. Fullerene films doped by CdTe with various concentrations were obtained by means of vacuum co-evaporation in a Knudsen cell. Composition and surface morphology were measured by secondary electron microscopy and energy-dispersive X-ray spectroscopy. X-ray irradiated films were considered, and additional peaks in photoluminescence spectra were detected. These peaks appear as a result of molecular complexes formation from C<sub>60</sub>CdTe mixture and dimerization of the films. Density functional B3LYP quantum-chemical calculations for C<sub>60</sub>CdTe, molecular complexes, (C<sub>60</sub>)<sub>2</sub> and C<sub>120</sub>O dimers were performed to elucidate some experimental results.

### Introduction

Application of nanostructured materials in light energy conversion has emerged as an alternative to single-crystalline devices. Low material cost, easy methods of fabrication, high light absorption cross sections and ability to tune the optical response make organic-inorganic nanocomposites attractive candidates for optoelectronic devices. To achieve effective photoinduced charge separation, the bulk heterojunction can be used. To produce the bulk heterojunction the continuous interpenetrating network of donor and acceptor semiconductor is required. Nanoscale carbon, such as nanotubes and fullerene, represents a class of materials that are actively explored for solar energy applications [1]. For example, hybrid organic/inorganic composites combining C<sub>60</sub> with semiconductor CdSe quantum dots (QDs) were synthesized and tested for light-energy harvesting [2]. Due to the strong acceptor properties fullerene and its modifications are widely used to produce the molecular complexes, and various organic and inorganic materials are used as a donor. In the same way, A<sup>2</sup>B<sup>6</sup> group is of particular interest for their application in solar cell creation. Valuable information about the possibility of creation of new fullerene based composite materials can be obtained with use of ab initio quantum-chemical calculation [3]. It should be mentioned that numerous studies [4, 5] are dedicated to the structure, optical properties and the nature of various fullerene-inorganic clusters at the molecular and supramolecular level. However, irradiation effect on the material property is still out of sight of researchers. Therefore, the choice of the subject matter of this study is relevant from both the scientific and applied perspectives. We report the results of a study of photoluminescence spectra of the thin



composite  $C_{60}<CdTe>$  films before and after X-ray irradiation, as well as the results of quantum-chemical calculations of corresponding molecular complexes.

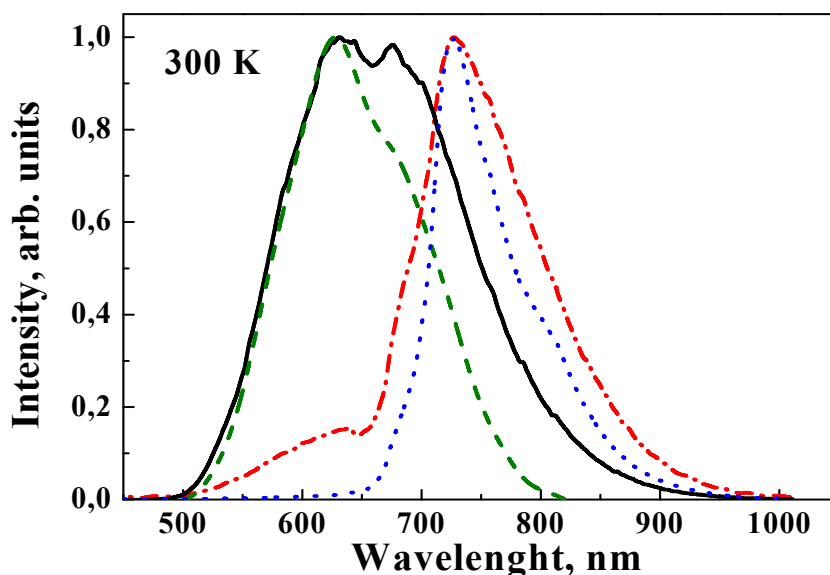
### Sample preparation and experimental methods

Thin films of  $(C_{60})_{1-x}(CdTe)_x$  were prepared by co-deposition technique from a Knudsen cell or quasi-closed volume. A possibility of large area film fabrication is an advantage of the Knudsen cell. The mixture of  $C_{60}$  with 10-50 wt.% of CdTe was evaporated at 520–650 °C on Si, a glass with ITO, KBr or mica substrate. This process may give rise to a significant changing of a film composition in comparison with the initial charge. Changes in the composition are much less in the case of quasi-closed volume evaporator than in the case of the Knudsen cell. The substrates were kept at room temperature during the process. Sputtering on a cold substrate leads to amorphous and polycrystalline structure formation and possibly to alignment of randomly distributed semiconductor clusters or molecular complexes. A scanning electron microscope Jeol JSM-6390 with resolution of 3 nm was used to study the surface morphology. The films composition in the selected area was measured by an energy dispersive micro-analysis console “Oxford INCA Energy” with the utmost sensitivity of 0.1 wt%. These studies confirmed the high homogeneity of the impurity distribution and the absence of the mosaic structure of the composite films.

The samples were subjected to X-ray irradiation in REIS-D equipment with a rhenium anode. X-ray energy flux was  $5 \cdot 10^{-3}$  J/s during 6 hour. Photoluminescence (PL) spectra were obtained by automated equipment based on a FHR 640 monochromator with a grating of  $1200 \text{ mm}^{-1}$  and the Symphony II (1024×256) Cryogenic Open - Electrode CCD detector. Samples were fixed at the angle of  $45^\circ$  to the laser beam. A quartz cryostat was used to make measurements at 77 K in liquid nitrogen.

### Results and discussion

PL spectra obtained at 300 K are shown in figure 1. The wide PL peak with 730 nm maximum is detected in pristine fullerene films. Since singlet transitions for the  $C_{60}$  molecule are prohibited for the

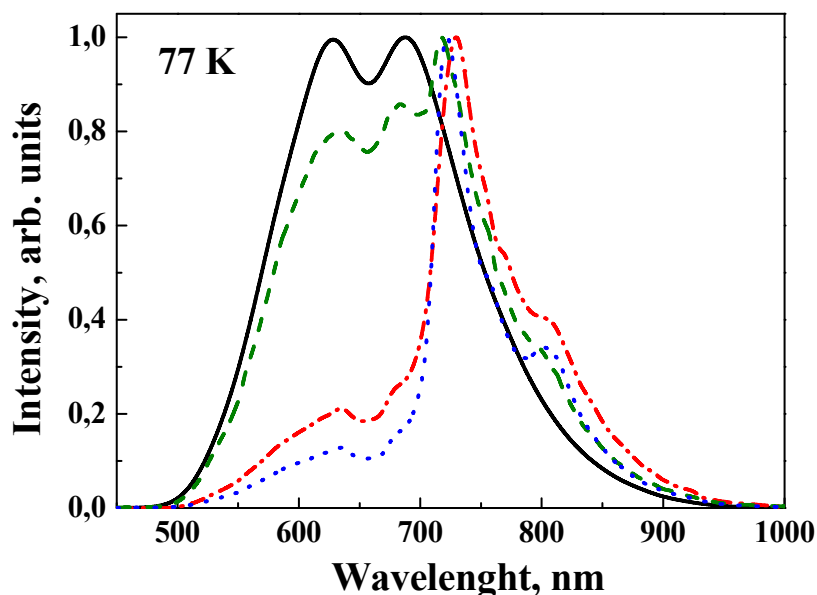


**Figure 1.** Photoluminescence spectra obtained at 300 K. X-ray irradiated pure  $C_{60}$  spectrum is shown by dash line. X-ray irradiated  $C_{60}$  with 50% CdTe is shown by solid line. Unexposed  $C_{60}$  with 50% CdTe and pure  $C_{60}$  PL spectra is dash-dot and dot line accordingly.

reason of symmetry, the wide peak can be interpreted as the superposition of two fullerene peaks:  $T_1-T_0$  at 730 nm and its vibration recurrence at 820 nm.

On addition of CdTe to fullerene the extra peak appears at the wavelength of 630 nm. The extra peak intensity increases with impurity content. This peak may be attributed to the emergence of singlet excitation in  $C_{60}$  electron spectrum. The corresponding optical transition is forbidden for a fullerene molecule in fullerite at room temperature for the reason of symmetry ( $T_h$  point group). However, CdTe doping leads to molecular complex formation and reduces the symmetry of  $C_{60}$ , so that the transition becomes allowed. The changes in PL spectra for irradiated CdTe-doped and pristine  $C_{60}$  films were investigated. The results have shown significant changes in the photoluminescence spectra after X-ray irradiation dose. A wide peak is observed only at 600–650 nm in the case of exposed samples. Therefore, after X-ray exposition the wide peak ( $T_1-T_0$ ) at 730 nm disappears and another wide peak ( $S_1-S_0$ ) emerges at 630 nm.  $T_1-T_0$  is a transition between triplet fullerene levels and  $S_1-S_0$  is a transition between singlet levels. More detailed information on the electronic structure comes from PL measurements at 77 K (see figure 2). One can see the weak peak at 630 nm in pristine fullerene films. The corresponding optical transition appears because the symmetry of fullerite is reduced at temperatures below 260 K and 90 K and a simple cubic lattice and glass phase are respectively formed.

All additional peaks mentioned above are detected in X-ray exposed pristine fullerene. The energy position of the peaks does not change significantly but for 630 and 680 nm peaks the relative intensity increases after irradiation. In the case of composite films the changes are significantly stronger and initial emission peaks (730 nm and 820 nm) almost disappear. To explain the results, one can suggest that X-ray irradiation promotes dimerization in the fullerene matrix and reduces the symmetry, so that some optical transitions become possible.



**Figure 2.** Photoluminescence spectra obtained at 77 K. X-ray irradiated pure  $C_{60}$  spectrum is shown by dash line. X-ray irradiated  $C_{60}$  with 50% CdTe is shown by solid line. Unexposed  $C_{60}$  with 50% CdTe and pure  $C_{60}$  PL spectra is dash-dot and dot line accordingly.

Quantum chemical calculations of the optimum geometry, total energy and electronic structure of  $C_{60}$ CdTe molecular complex, CA (cyclo-adduct) and SB (single-bonded) dimers  $(C_{60})_2$  and  $(C_{60})_2O$

were performed by the DFT-B3LYP method. It is shown that in electronic spectra of dimers and complexes allowed singlet-singlet transitions of about 1.91 eV appear in accordance with the experimental data.

### Conclusions

The novel method for the production of thin composite fullerene films was developed. The samples were investigated using the optical spectroscopy technique. In this work it was revealed that X-ray irradiation affects significantly the electronic structure of both pristine fullerene films and the films doped by CdTe. The photoluminescence spectra measured have shown the appearance of some extra peaks related to the supramolecular complex formation. It was revealed that the 630 nm (1.97 eV) line appears in the doped films, which is absent in pure fullerene. Quantum-chemical calculations have shown that this line may be attributed to  $S_1$ - $S_0$  transition in electron excitation spectrum which is forbidden in pristine fullerene. It is found that intensive X-ray irradiation of the films gives rise to considerable enhancement of intensity of the additional peak which becomes prevalent in spectra of composite films. The possible reason is that X-ray irradiation brings to dimerization of the  $C_{60}$  matrix.

### References

- [1] Shibu E S *et al* 2012 *ACS Nano* **6** 1601
- [2] Bang J H and Kamat P V 2011 *ACS Nano* **5** 9421
- [3] Chaban V V, Prezhdo V V and Prezhdo O V 2013 *J. Phys. Chem. Lett.* **4** 1
- [4] Guldi D M, Zilbermann I, Anderson G, Kotov N A, Tagmatarchis N and Prato M 2004 *J. Am. Chem. Soc.* **126** 14340
- [5] Brown P and Kamat P V 2008 *J. Am. Chem. Soc.* **130** 8890