INTERACTION OF PARTIALLY FLUORINATED GRAPHITE WITH PHOTONS

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Fluorination of graphite using inorganic fluorides at room temperature produces compounds with a composition CF_x, where x is usually below 0.5. We have prepared a set of CF_x samples with $0.3<x<0.5$ by changing the concentration of the fluorinating agent BrF_3 in Br_2 and the duration of its contact with graphite in sealed reactors at room temperature. According to the XPS data, the C–F bonds are covalent regardless of the fluorine content. The fluorinated layers were spaced by acetonitrile, which is transparent in the visible range and therefore does not affect the color and luminescence of the sample. Optical properties were studied on solid samples to exclude their modification during dispersion in a solvent. The optical absorption spectra of CF_x samples showed a band in the UV range (~270 nm) and a weaker band in the visible range (~380–650 nm). The latter band was redshifted with a decrease in the fluorine content. The photoluminescence (PL) spectra of the samples were fitted by the green, green-yellow, orange-red, and red components. The weakest green band and the highest orange-red band were observed in the spectrum of $CF_{0.33}$. To interpret the experimental spectra, we used time-dependent density functional theory (TDDFT) calculations of polyaromatic and polyene structures in the fluorographene surrounding. It was shown that these sp^2-carbon regions are mainly responsible for the optical absorption in the ultraviolet and visible regions, respectively. The electron-hole recombination within branched aromatic rings or long carbon chains produces orange-red emission, while green-yellow PL is due to transitions of excited polyene electrons to half-occupied levels of aromatic carbon [1].

Photolysis of CF_x with embedded acetonitrile was studied using the radiation from a synchrotron source, which covers a wide range of photon energies and the UV light. Under exposure to non-monochromatized synchrotron radiation light, CF_x layers lose a part of fluorine and acquire nitrogen atoms from acetonitrile. These atoms are located at the boundaries of vacancies, produced when fluorine atoms are removed from the layer together with carbon. The photolysis of acetonitrile yields N_2 and HCN molecules. The study shows that the products of the photolysis of CH_3CN depend on the time of irradiation and the fluorine loading of the fluorographitic matrix [2]. The kinetics of photodegradation of CF_x samples under UV irradiation was shown to be also dependent on the fluorine content and the nature of guest molecules in the interlayer space. A reversible and reproducible increase (decrease) in the PL intensity was found upon adsorption of acetonitrile (acetone) vapors on the surface of fluorinated layers.

Our results demonstrate the prospect of fluorinated graphite crystallites as anisotropic optical elements. Layers of fluorinated graphite are promising as sensitive elements of optical chemosensors.

References

1. Okotrub A.V. et. al. / Carbon 2022. Vol. 193. P. 98–106.
2. Semushkina G.I. et. al. / Nanomaterials 2022. Vol. 12. P. 231.