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SPECTRA OF PHOTOLUMINESCENCE OF CARBONCONTAINING NANOSTRUCTURED OBJECTS

Kumekov S. E.¹, Saitova N.K.¹, Syrgaliyev E.O.²

¹Hi-Tech Engineering Institute of Kazakh National Research Technical University named after K.I.Satpaev, Almaty, Kazakhstan, skumekov@mail.ru

²University of Power and Communication, Almaty, Kazakhstan

It is discussed the possible mechanism of photoluminescence of such objects as carbon quantum dots, layers of amorphous hydrogenated carbon, and the natural biopolymer – native collagen. Recently in some researches were observed the interesting features of photoluminescence of carbon quantum dots. The features were discovered in comparison of photoluminescence in layers of amorphous hydrogenated carbon and in natural biopolymer – native collagen. This article describes a method of experimental study of the absorption spectra, excitation and photoluminescence characteristics of collagen with using modern measuring devices. Fixed excitation of photoluminescence was carried by an argon laser. A nitrogen laser was used for pulsed excitation. It is found that some properties of the luminescent radiation may be explained by assuming the nature of excimer photoluminescence collagen.

Keywords: quantum dots, carbon, excitation, photoluminescence, collagen.

Introduction

Recently [1-4], there has been discovered an interesting feature of photoluminescence (PL) of carbon quantum dots (CD): a broad structure less band in the visible spectrum whose half width, photon energy at a maximum, and short-wave edge depend on the energy of excitation quantum. The long-wave edge of the band depends neither on the size of a quantum dot [1] nor on the energy of excitation quantum [1-4]. The decay of the luminescence typically follows first-order kinetics. Four respectable PL mechanisms have been confirmed: the quantum confinement effect or conjugated π -domains, which are determined by the carbon core; the surface state, which is determined by hybridization of the carbon backbone and connected chemical groups; the molecule state, which is determined solely by the fluorescent molecules connected on the surface or interior of the CDs; and the crosslink-enhanced emission (CEE) effect.

The similar behavior of photoluminescence spectra has been observed earlier in layers of amorphous hydrogenated carbon and in natural biopolymer – native collagen [5-6]. The present work proposes a unified mechanism for the photoluminescence characterized by the properties of spectrum established in [1-6].

In previous studies [5] the main properties of photoluminescence (PL) of a-C: H films were investigated. The investigation in [5] demonstrated that the spectra of PL of amorphous hydrogenated carbon depend on the position of the energy of the quantum of excitation and show that the temperature dependence of photoluminescence in those matters reveals anti-Stokes radiation at high temperatures. The kinetics of the decay of the luminescence typically is fluorescent. In [5] it was shown that all remarkable PL features, such as, a high emission quantum efficiency which is independent of temperature, electrical field and energy of the exciting light, and an extremely rapid excitonic –like PL decay which is also nearly independent of temperature and energy of both exciting and emitted quanta, are connected with micro- inhomogeneity of the materials. It was suggested that there exist light emitting nanograins of sp^2 phase inside a wide gap sp^3 and polymer matrix.

Earlier O'Reilly and Robertson [7, 8] have theoretically shown that π - bonding in a-C:H favours aromatic 6 - fold rings and clustering of separate rings into compact graphitic sheets. It is also well known that similar aromatic rings are contained in natural polymers. Hence one has to expect similar PL properties. From a-C:H and from such polymers, provided the sextets are the main centers of radioactive recombination.

1. Experimental technique

For the research of absorption spectra, excitation and characteristics of photoluminescence was used spectral, versatile and computing complex KSVU-23 spectro-fluorometer "Hitachi". PL measurements of spectra were performed in two excitation modes: in stationary and pulsed.

The sources of radiation which were used to investigate the photoluminescence excitation spectra were: d - lamp in the region of 250-350 nm, ultrahigh pressure mercury lamp DRSh-500 with lines of emission (254, 303, 312, 365, 405, 436, 546 nm). Stationary excitation of the PL was carried out by lines of an argon laser (459.2 nm, 476.9 nm, 488.2 nm, 496 nm, 502.02 nm, 514.5nm), He-Cd-laser (325 nm, 416 nm) Kr (645, 8 nm and 677.5 nm) and He-Ne (632,6 nm).

To designate the necessary band of the radiation lamps DDS-30 and DRSh-500 and to eliminate the stray light entering into the registering device were used filters: UFS 1-4. Isolation of excitation light lines was produced by using a double monochromatic prism DMR-4.

When measured spectra and kinetics decay of photoluminescence for pulsed excitation was used a pulsed nitrogen laser with a line at 337 nm and a pulse copper laser (510.3 nm and 579.4 nm). PL samples were carried out at three constant temperatures: 300, 70, 4.2 K.

When measuring the photoluminescence excitation spectra was registered the integral intensity of PL in the range of 1.6 to 2.0 eV. To excite the photoluminescence emission line was used a mercury lamp that stood with double prism monochromator DMR-4. Excitation spectra measurements of photoluminescence were performed at 78 and 300 K.

For measurements was used glass helium cryostat at 4.2 K. A sample was placed directly in liquid helium. To study the samples was used a nitrogen cryostat at 77 K: the sample was placed in liquid nitrogen. Experimental determination of the relative position of the photoluminescence spectra, excitation of photoluminescence spectra and absorption spectra is usually give opportunity to establish the nature of the energy levels that form these spectra. To this end, we measured the excitation spectra and absorption spectra.

The absorption spectra of native collagen is difficult to measure because of its optical heterogeneity. Therefore, according to the conventional approach, the absorption spectrum was measured with a model of collagen analogue - gelatin films, which is optically uniform material.

2. Results and discussion

Identical features of PL are characteristic of all objects investigated in [1-6]: shape of structure, dependence of position of a maximum of PL and of half-width of a PL band on energy of quantum of excitation (see Figures 1 and 2).

These features of PL as is well-known are inherent in an excimer luminescence [6, 9, 10]. Excimer in these objects can be formed in the sandwich structures of benzene rings, such as, in crystals of pyrene or naphthalene [9, 10]. In [6] are investigated the PL of the biopolymer – collagen. It is shown the anti-Stokes tail of spectra at high temperatures. The spectra are structure less at all temperatures. The kinetics of decay of PL has fluorescent behavior.

Fig.3 illustrates the spectra of absorption (1) of PL of collagen at excitation by quanta with $h\nu_{exc} = 3.68$ eV (2) and excitation of PL (3) at room temperature. Overlapping of spectral bands of a photoluminescence and excitation of PL of collagen in a wide interval of wavelengths of light demonstrate that the energy levels determining transitions of electrons in case of light absorption are at the same time levels between which there are radiating transitions.

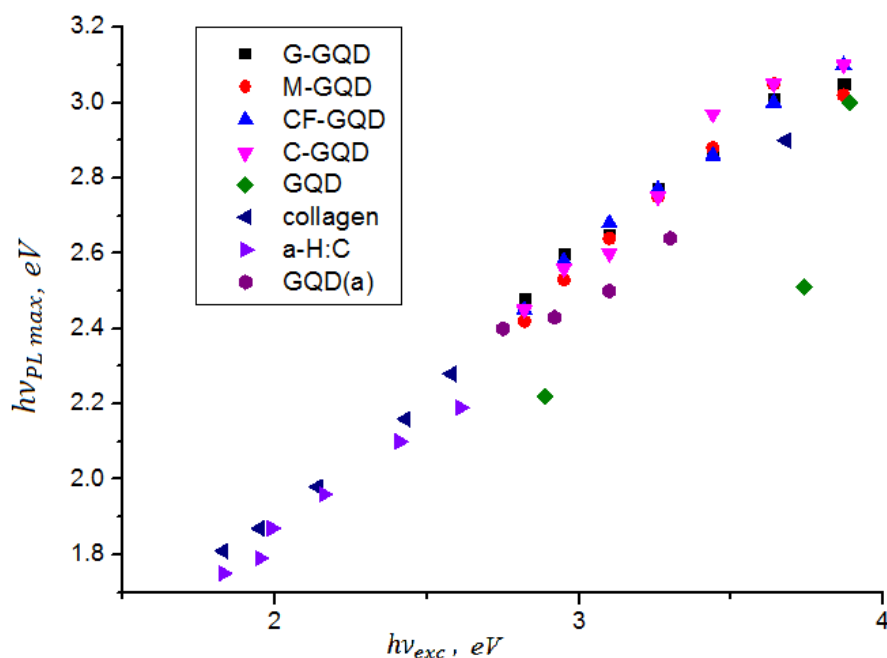


Fig. 1. The dependence of the position of the maximum of spectra of PL of different objects on the energy of quantum of excitation observed in [1-6]. Objects: G-GQD, M- GQD, CF- GQD, C- GQD, GQD are grafen quantum dots performed by different technologies, a-C: H films, collagen.

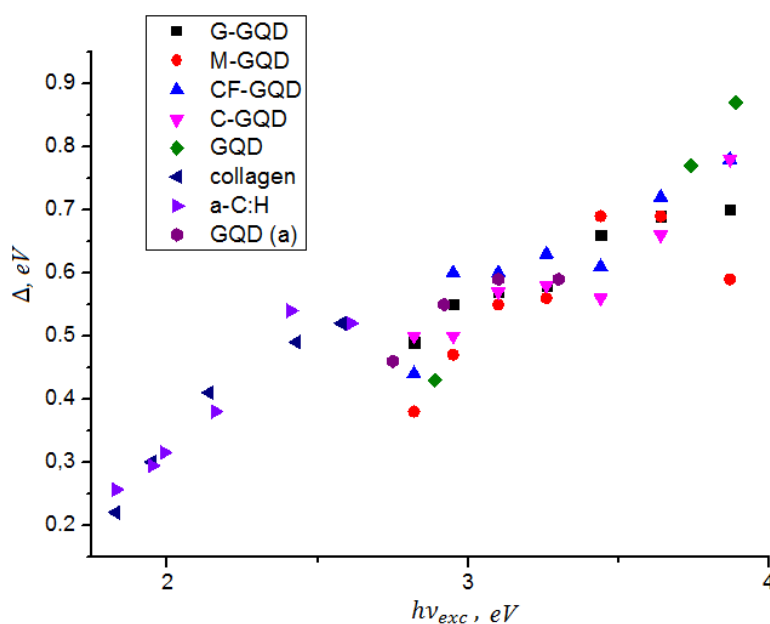


Fig. 2. The dependence of the halfwidth of spectra of PL of different objects on the energy of quantum of excitation observed in [1-6]. G-GQD, M- GQD, CF- GQD, C- GQD, GQD are grafen quantum dots performed by different technologies, a-C: H films, collagen.

This circumstance in a complex with the found and described properties of luminescent radiation can be explained within the assumption about excimer in a complex with the found and described properties of luminescent radiation can be explained within the assumption of the excimer nature of PL of collagen.

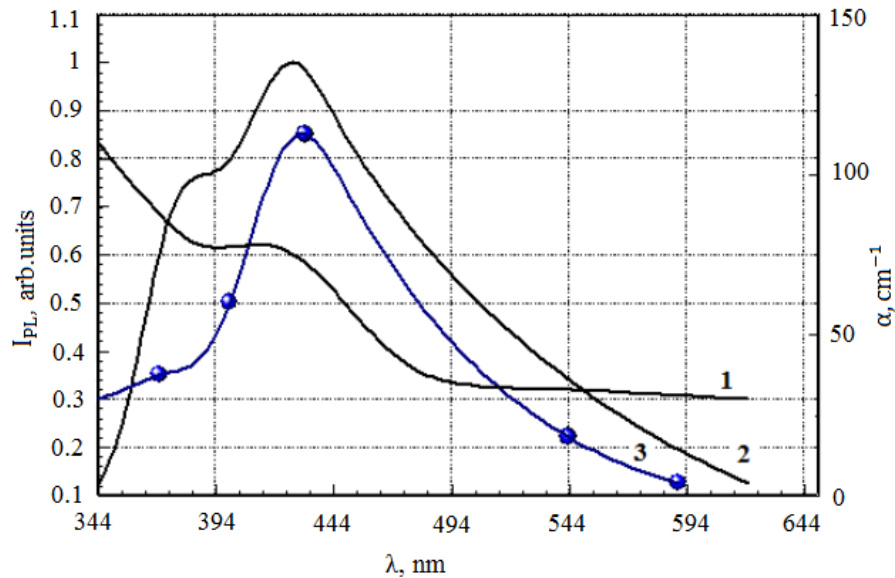


Fig.3. The spectra of absorption (1), of PL of collagen at excitation by quanta with $h\nu_{exc} = 3.68$ eV (2) and excitation of PL (3) at room temperature.

Excimer is the dimer which exists only in an excited state [9, 10]. The main condition of such couple is unstable as in case of distance between molecules of an order of the size of an excimer of force of interaction have repulsive character. For the excimer-forming connections a characteristic sign is that circumstance that features of optical absorption correspond to monomers (molecular bands), and in a range of fluorescence wide structure less bands are found.

Hamiltonian of dimer of two sandwich benzene rings is expressed as [10]: $\mathbf{H} = \mathbf{H}_1 + \mathbf{H}_2 + \langle \mathbf{V} \rangle_{12}$. $\langle \mathbf{V} \rangle_{12}$ is defined by Coulomb interaction. For ground state of dimer the Coulomb interaction is negative (repulsive interaction) and for excited state of excimer the Coulomb interaction is positive (attractive interaction). Fig.4 illustrates the dependence of ground state of dimer and of excited state of excimer on distance between a benzene rings.

The shape of a band of a luminescence and fast kinetics of decay are caused by nature of electronic terms of the initiated and main conditions a dimer which are schematically represented in the figure 4. Optical transitions in case of absorption and radiation of light in such system happen between two terms.

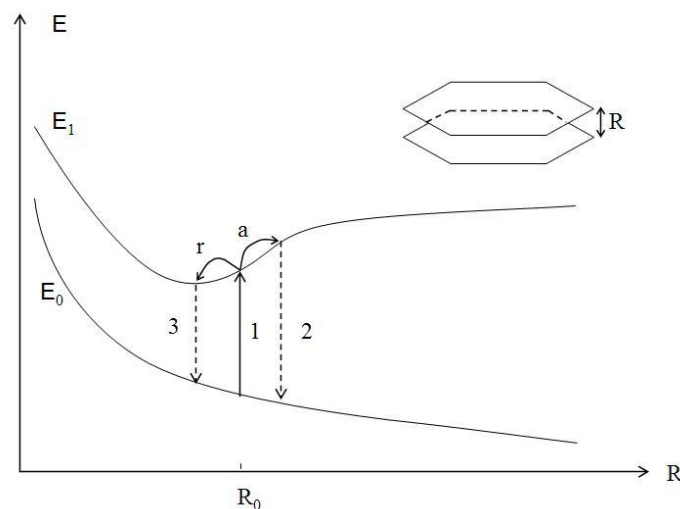


Fig.4. Energetic levels E of dimer-excimer complex as a function of R : 1 – transition of electron at absorption of light, 2 – anti Stokes transition, 3 – Stokes transition; a – thermoactivation, r – relaxation.

On fig. 4 the value of R is a distance between two benzene rings. E_0 and E_1 are the terms of ground and excited states of dimer. Excimer radiation of systems of aromatic molecules is well known to [10]. The experiments described in these reviews showed that almost all flat aromatic molecules are formed by excimer. Experiments were conducted in different systems: solutions, liquids, organic crystals, solid polymers.

Mainly excimer in system of flat aromatic molecules spatially represent sandwich structures (see a figure 4 insert) which in case of a crystal are formed along the plane of sliding of dislocations [10], and in case of liquids and solutions are created in case of absorption of light in one of aromatic rings, accidentally appeared at a short distance, sufficient for forming of an excimer.

Conclusion

The features of PL of native collagen are observed: structure less shape at high and low temperatures, great values of halfwidth, and fast kinetic of decay. Experimentally observed the overlapping the spectra of excitation of PL and spectra of PL gave possibility to propose the excimer model of PL. In frame of this model it is shown the create of the anti-Stokes tail of spectra at high temperatures [6]. It is proposed the excimer model of luminescence. Given mechanism will have possible relation to the nature of PL of objects observed in [1-5].

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