Relaxation of the Energy of Optically Excited States in the Carbon Quantum Dots

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Article info

Abstract

Recently, in connection with the achievement of new technological opportunities for fabrication nanostructured carbon-containing objects, namely, carbon quantum dots (CQDs) and clusters, studies of their various physical properties have been intensively carried out. Investigation of the photoluminescence (PL) properties of these objects have revealed a number of unique features: a wide structureless band of the radiation in the ultraviolet and visible regions of the spectrum, the fluorescent kinetics of the luminescence decay, and the independence of the long-wavelength edge of the band on the excitation quantum energy. Similar features of PL are observed early in the different nanostructured carbon-containing materials. A common structural feature of the different nanostructured carbon-containing materials, such as CQD, liquid and solid aromatic hydrocarbons, amorphous hydrogenated carbon films, natural biopolymer – collagen is the existence of carbon sextets-aromatic rings connected by Van der Waals forces. This representation of the structure made it possible in the present work to develop a dimer-excimer model of radiative processes in the CQD. The studies are related to the prospects of application due to the unique combination of a number of key properties including tunable photoluminescence, important for the development of tunable lasers, biomedical applications where photostability, biocompatibility, molecular dimensions are essential to allow chemical connection with any biomolecule without compromising its functions. Further development of the theory of PL mechanisms in the CQD can help to identify other important features of the studied objects that will be of fundamental and practical importance.

1. Introduction

The increased interest in the study of photoluminescence (PL) in carbon quantum dots (CQD) is associated with a fundamental interest in their possible applications in solar energy, biotechnology, medicine, and nanoelectronic devices [1]. Recently, various methods have been developed for the fabrication of CQDs based on graphene, graphite, and polymers [2]. The experimental photoluminescence spectra of the CQD exhibit properties common to these objects: a structureless broad band of the radiation, a dependence of the photon energy at the maximum of band on the energy of the excitation quantum, the independence of long-wavelength boundary of the band on the excitation quantum energy, and the fluorescent kinetics of decay of PL [3–8]. In the literature [9] different mechanisms of PL in the CQD were discussed: the quantum size effect, fluorophores with various degrees of π – conjugation, recombination of electron-hole pairs localized within small sp^2 carbon clusters embedded within a sp^3 matrix, defects and surface states, surface groups, and surface passivation.

Similar features of PL were observed earlier in different carbon-containing materials, such as liquid and solid aromatic hydrocarbons [10, 11], films of amorphous hydrogenated carbon [12], biopolymer – collagen [13].

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A common structural feature of the above objects is the existence of carbon sextets-aromatic rings. The presence of these aromatic rings results in the creation of plane-parallel sandwich structures in the form of physical dimers in a medium containing molecules with a benzene nucleus [14]. On the basis of an analysis of the electronic terms of aromatic hydrocarbons, Birks [15] made conclusions about the excimer nature of PL. Collagen contains in its structure chromophore aromatic amino acids, which allowed the authors [13] also to explain the features of PL based on the excimer model.

2. Model

The excimer nature of PL of CQD, in particular graphite-based, can be assumed for the reason that for CQD sizes of the order of one nanometers, the electronic spectrum of graphite is significantly affected by size quantization (at an effective electron mass $m^* = 0.4\ m_0$ [16]). The energy interval between adjacent levels of size quantization is much higher than the thermal energy of the electrons in the conduction band. This circumstance suggests the dominant role of molecular terms in the formation of PL spectra. Here it is appropriate to note the analogy with crystals of pyrene and fluorene [10, 17]. The distance between adjacent graphene-like layers in graphite is 3.37 Å. In pyrene crystals, the distance between the monomers in the dimer calculated by the semi-empirical method [15] is 3.53 Å, while in the excimer the monomers are spaced at an average distance of 3.37 Å.

Here it is believed that the crystalline structure of graphite clusters contains graphene-like monomer layers that form dimer-like structures. Similar structures are described in [11]. Dimer contains two benzene like monomer that created sandwich structure. The geometry of dimer structure is showed on insert of Fig. 1. In these structures, the monomers are linked together in the direction of the **c**-axis of the crystal by weak long-range Van der Waals forces [18, 19]. The Van der Waals forces compensate for the repulsive forces. The repulsive forces exist due to the exchange and Coulomb interactions between the graphene-like layers. These circumstances lead to a stable ground state of the dimer with an insignificant potential barrier [18, 19]. The anisotropy of the mechanical and electrical properties of graphite [16] is explained by the large difference in the geometric parameters of the crystal in the direction of the **c**-axis from directions perpendicular to it.
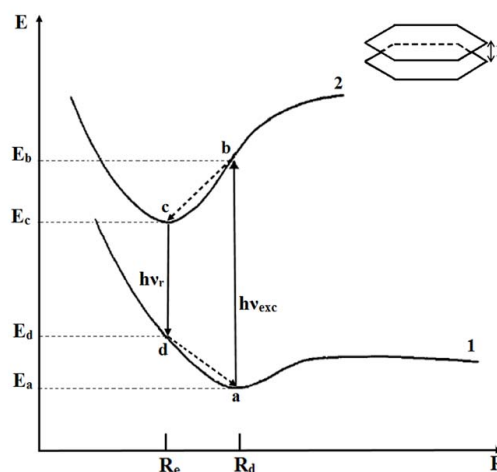

Fig. 1. Configuration diagram of the dimer-excimer complex: 1 – potential energy of the dimer; 2 – potential energy of the excimer are shown in the dependence on distance R between the monomers. Rectifier arrows show non-radiative transitions. Stokes shift $\Delta = E_b + E_d - E_c - E_a$. R_d is the coordinate of the stable state of the dimer, R_e is the coordinate of the stable state of the excimer.

3. Results and Discussions

The excited state of the dimer, which represents the excimer state, also corresponds to a stable state due to the Coulomb interaction [14], but at distances between layers in the excited dimer R_e that are smaller than in the stable ground state of the dimer R_d ($R_e < R_d$). The Hamiltonian of the physical dimer H can be written [14]

$$H = H_1 + H_2 + V_{12} \qquad (1)$$

where H_1 and H_2 are the Hamiltonians of the individual monomers, and V_{12} (R) is the interaction energy between the monomers, depending on the distance between the monomers R.

In the general case, V_{12} (R) is composed of the exchange, Coulomb, and van der Waals interactions. The forces of exchange interaction are short-range and have the character of repulsion. Van der Waals interaction is a long-range interaction and manifests itself as attractive forces. The sign of the Coulomb interaction is different for the ground state of the dimer and the excited state of the dimer (excimer). In the first case, the Coulomb forces will be repulsive, in the second case the character of the Coulomb interaction has the character of attractive forces. For this reason, the stable ground state of the dimer is reached at $R_d > R_e$ (Fig. 1).

If the eigenvalues of the Hamiltonian (1) are written for the dimer and excimer as E_1 and E_2, respectively, then the stable state will satisfy to the equations:

$$\frac{dE_1}{dR} = 0 \quad at \ R = R_d \qquad \frac{dE_2}{dR} = 0 \quad at \ R = R_e \qquad (2)$$

According to (2) the depth of the potential well at $R = R_d$ determines the bond energy of the dimer and can be measured as the dissociation energy of the dimer in spectroscopic studies. The depth of the potential well at $R = R_e$ can be estimated from the longwave edge of the excimer radiation band. This feature of radiative processes during transitions from the discrete state to the states of the continuous spectrum was noted in [20]. The repulsive term of the ground state refers to the states of the continuous spectrum.

In the adiabatic approximation of the description of the electron-nuclear system [14, 20], the potential energies of the ground and excited states of electrons are depicted graphically as functions of the inter-nuclear or intermolecular distance in the configuration diagram. In Fig. 1 schematically are shown the electronic terms of the ground and excited states of the dimer-excimer complex as a function of the distance R between the monomers.

The probability of absorption of a quantum of light is greatest in the stable ground state of the dimer. The emission of a photon of light occurs with the greatest probability in a stable excimer state. The optical transitions are shown in Fig. 1 by vertical arrows in accordance with the Franck-Condon principle. According to adiabatic approximation the optical transition between ground and excimer states occurs at the same distance R (Franck-Condon principle). Transitions of excitations within terms occur through non-radiative channels: from state *b* to *c* and from *d* to *a*. The difference in the energies of the quanta of the exciting and radiative photons is the Stokes shift $\Delta = h\nu_{exc} - h\nu_r$, observed in the experiments.

As can be seen from Fig. 1 the part of the energy of the exciting photon, wasted through the non-radiative channel, is equal to the Stokes shift Δ. The Stokes shift depends on the structure of the potential curves of the ground and excited states of the dimer and can characterize the rate of relaxation of the energy of the exciting photon along the nonradiative channel due to the electron-phonon interaction. In Fig. 2 are presented the results of a generalization of the Stokes shift measurements as a function of the energy of the exciting

quantum, obtained at different carbon-containing nanostructured objects. As can be seen from Fig. 2, the parameter $\delta = \frac{\Delta}{E_{exc}}$, equal to the ratio of the Stokes shift to the energy of the exciting quantum, has a spread in values relative to the mean value. The spread of δ may be due to the difference in the technology of the CQD preparation. Different technologies cause differences in the CQD in terms of geometric dimensions, chemical structure of the CQD surface. As shown in [9], CQDs were obtained by different methods, including technologies for the synthesis of CQDs based on graphene, graphite and polymers. The common properties of luminescent characteristics of these objects were described in the introduction to this article. Also in [9] various PL mechanisms proposed by different authors are given. However, these papers do not pay attention to the general feature of the PL spectra manifested in the independence of the long-wave edge of the spectra from the energy of the excitation quantum. The model proposed in this article explains all the features of the photoluminescence spectra of the CQDs [3–8]. A broad structureless band of PL is characteristically for excimer systems [11, 15]. Because the radiative optical transition occurs in the repulsive ground state the band of luminescence is observed to be structureless and fluorescent. The long-wavelength edge of the reduced dependence can be associated with radiative transitions from excimer states, whose energy is higher than the level corresponding to the dissociation energy of the excimer [20, 22].
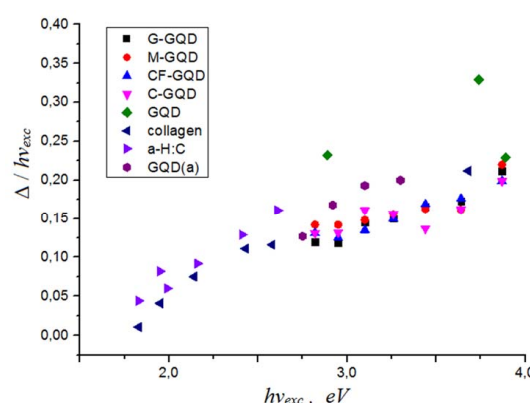

Fig. 2. Dependence of the parameter δ on the energy of the exciting quantum for various objects. The insertion contains the notation for the objects studied in the works: G-GQD – graphite quantum dots [5], M-GQD – quantum dots from multilayered carbon nanotubes [5], CF-CQD – quantum dots from carbon fibers [5], C-GQD – carbon quantum dots [5], GQD – graphene quantum dots obtained by the synthetic method [21], collagen [13], a-H:C – amorphous hydrogenated carbon [12], GQD (a) – graphene quantum dots from carbon fibers [22].

4. Conclusions

Based on the concept of structural features of carbon-containing objects, the dimer-excimer model of radiative processes in the CQD is developed. A part of the absorbed quantum of light is determined, which is dissipated due nonradiative channel of energy relaxation as a function of the energy of the excitation quantum. The independence of the long-wave edge of PL on the energy of the excitation quantum is explained.

Acknowledgements

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