Absorption spectrum of carbon nanocages

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In the current research, hollow carbon nanocages are synthesized and characterized by electronic microscopy. It shown that the nanocages have $3-5$ nm size and consist of few carbon layers with oxygen addition. The experimental and theoretical study of their absorption spectrum is provided. A simple model of electron energy spectrum is supposed. It is used for calculation of optical absorption spectrum. We have found that the theoretical results are in qualitative agreement with the experimental measurements in IR-band. Thus, the analysis of optical properties of nanocages is provided. They can be used as a pretty optical absorber in IR-band in integral photonics devices.

Introduction

Hollow carbon nanospheres have subnanometer channels, a high specific area of the surface with a defective outer shell, and an adjustable electronic structure, which makes them very different from carbon nanotubes and graphene. These structural and morphological characteristics make such fullerene-like materials a new platform for energy conversion and storage [1], optical absorption [2], and drug delivery [3].

The optical properties of carbon materials are the subject of active study. The specifics of the energy spectrum and density of states of electrons determine the structure of the optical reflection and polarizability peaks [4,5]. An essential feature of carbon nanotubes is the absence of IR absorption, because they do not contain C-H bonds, unlike organic molecules, and a common feature of all carbon materials is the pronounced absorption in the UV range at wavelengths around $200-300$ nm associated with energy transitions in the ensemble of unpaired π-electrons [6–8]. On the other hand, for structures such as quantum dots, an expansion of the absorption spectrum towards the near-IR range is observed, due to the contribution of surface states. An important role in the formation of the IR spectrum of compact nanostructures, in particular fullerenes, is played by vibration modes [9,10] and the presence of defects and impurities [11–13].

This study presents a comparison of the experimentally measured and theoretically calculated IR spectrum of a system of hollow carbon nanospheres, and also characterizes their structure.

Research methods

The carbon nanospheres were synthesized according to the following procedure. First, an array of cobalt nanoparticles coated with several layers of carbon (graphite) was synthesized by pyrolysis in a nitrogen atmosphere at $600°$C. Then, the metal was etched out of the material structure by nitric acid and an array of hollow carbon nanospheres was produced. The synthesis technique is described in more detail in [14].

The nanostructure of the samples under study was characterized using a JEOL JEM 2010 high-resolution transmission electron microscopy (TEM) system with an accelerating voltage of 200 kV with a Gatan Multiscan CCD matrix. The samples were prepared by dropping of 2μl of the solution of carbon nanospheres onto a carbon-coated copper grid for TEM, followed by drying at room conditions.

The samples were analyzed by scanning electron microscopy (SEM) using a Quattro Thermo Fisher Scientific setup in the secondary electron mode at an accelerating voltage of 30 kV and an Everhart-Thornley detector. Elemental analysis was carried out using an energy-dispersive INCA attachment (Oxford Instruments).

IR spectroscopy was carried out using a Spectrum Two PerkinElmer Fourier spectrometer in the range of $1000-4000$ cm^{-1} with a resolution of 1.0 cm^{-1}. To obtain an IR absorption spectrum, a thin layer of the sample was placed between two glasses.
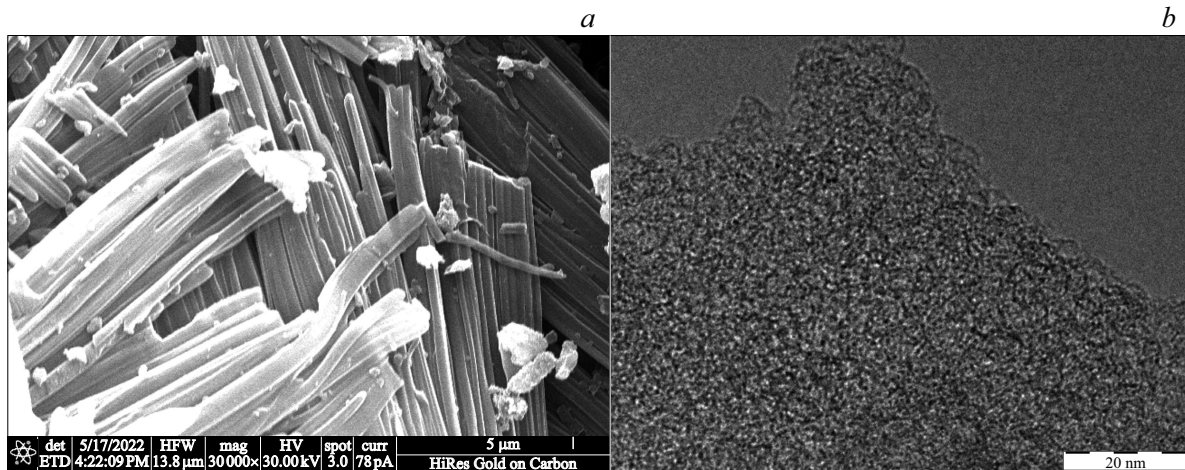
Figure 1. Samples of carbon nanospheres: *a* — microstructure, *b* — nanostructure.

Results and discussion

A. Structure of carbon nanospheres

The results of electron microscopic research methods are presented in Fig. 1. The samples have a form of black dispersed powder. The microstructure has a layered shape (Fig. 1, *a*) in the form of rods or shapeless particles, which consist at the nanoscale level of hollow spheres with a diameter of $3-5$ nm containing $2-5$ layers of carbon (Fig. 1, *b*). A qualitative assessment of the degree of defectiveness of the nanosphere structure was carried out using elemental analysis. According to the results of this analysis, the nanospheres contain $80\pm3\%$ of carbon atoms and $20\pm3\%$ of oxygen. It should be noted that the nanospheres contain absolutely no cobalt residues and a high oxygen content. This results in an increased degree of defectiveness of the material and distortion of the nanospheres' shape from the ideal one. Thus, the real structure of the synthesized carbon nanospheres has been characterized, which makes it possible to compare the experimentally obtained optical absorption/transmission spectra with theoretical calculations for a defect-free structure.

B. Optical absorption spectrum: theory and experiment

In [15] a scalable model was proposed for the approximate calculation of the energy spectrum and wave functions of free electrons in a monolayer of carbon closed into a sphere of finite radius R. The model is built on the basis of the strong-binding approximation in combination with the limiting transition to a continuous medium. The hexagonal structure of graphite is disrupted when the shell is closed into a sphere, however, with a large radius of curvature, amounting to a few nanometers in the synthesized samples, the lattice can be assumed to be locally flat everywhere and differing little from hexagonal. Then the elements of the structure different from this symmetry are „averaged", and the coordination number approximately remains equal to 3. The energy spectrum calculated in this model, with neglecting the Coulomb interaction and without impurities in the shell, is given by the following relationship:

$$E_l = \pm tZ \left(1 - \frac{a_0^2 l(l+1)}{2R^2} \right), \qquad (1)$$

where l is orbital quantum number, t is averaged hopping integral ($t \approx 2.7$ eV for a flat lattice), $Z \approx 3$ is coordination number, $a_0 = 0.14$ nm is lattice constant. Each l corresponds to $2(2l+1)$ states taking into account the degeneracy in the azimuthal quantum number and spin orientation. It is limited from top and is related to R and to the number of atoms in the shell N by the following estimates:

$$l_{max} \sim \sqrt{\frac{16}{3}} \frac{R}{a_0} - 1 \sim \sqrt{\frac{N}{2}} - 1. \qquad (2)$$

For nanoshells with a radius of $2 \div 3$ nm, it yields $N \sim 9 \cdot 10^2 \div 2 \cdot 10^3$, $l_{max} \sim 29 \div 45$. The electron wave functions can be represented by a superposition of spherical harmonics:

$$c_\sigma(r_j, t) = \sum_{i=0}^{\infty} \sum_{m=-l}^{l} c_{\sigma,lm}(t) Y_{lm}(\vartheta, \phi). \qquad (3)$$

To calculate the model absorption spectrum of an electromagnetic wave, it is sufficient to take into account the influence of the z-component of its electric field E_0 on the shell and consider the corresponding dipole transitions, whose matrix elements are

$$\langle \psi_f | \hat{V} | \psi_i \rangle = \frac{eE_0}{2} \langle \psi_f | z | \psi_i \rangle \qquad (4)$$

where $z = R\cos\vartheta$ is electron coordinate relative to the shell center. The conditions for orthogonality of wave
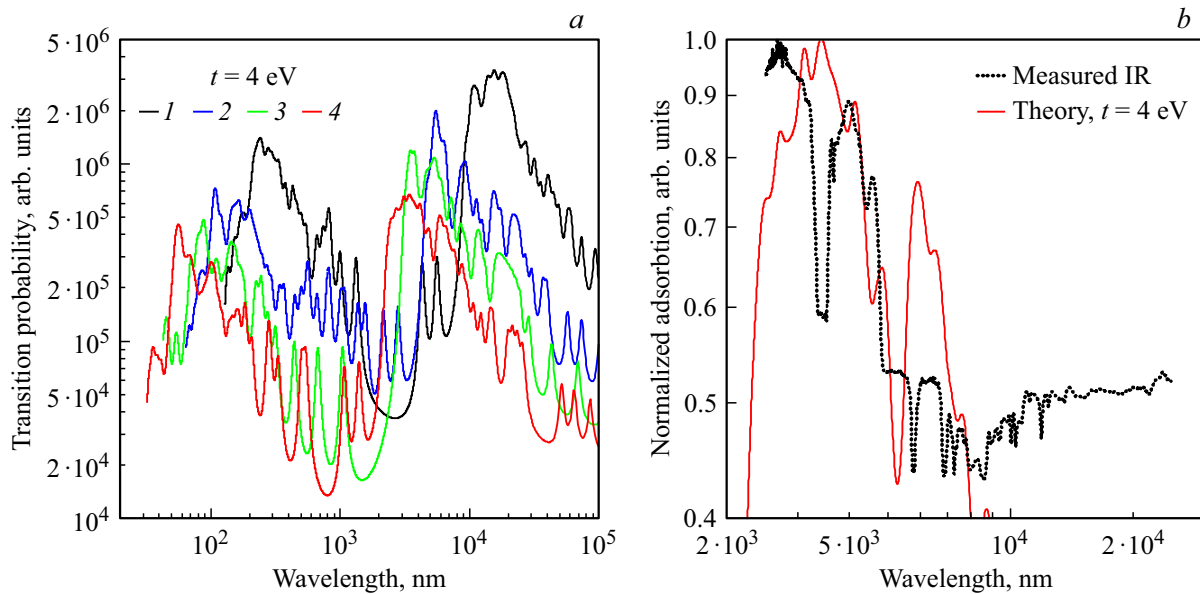
Figure 2. Absorption spectra of an ensemble of carbon nanospheres: *a* — calculation, individual spectral lines are approximated by Lorentz curves with a relative half-width of 5%; *b* — comparison of IR spectroscopy data and the theoretically found IR branch of the spectrum; the model dependence has been obtained for the hopping integral of $t = 4$ eV.

functions determine the rule for selecting allowed transitions $\Delta l = \pm 1$, and direct calculation of matrix elements makes it possible to determine their specific probabilities.

The resulting pattern of the model absorption spectrum for an ensemble of non-interacting nanospheres, for example in glass, is shown in Fig. 2, *a*. The absorption spectrum was calculated for the following values of the hopping integral: $t = 1$, 2, 3 and 4 eV. Its increase results in a shift of absorption peaks towards shorter wavelengths. Due to the fact that the energy spectrum of the system shell is a discrete spectrum, in the modeling of the observed optical absorption spectrum each line of the spectrum is approximated by a Lorentz curve with a relative half-width of 5%, the contributions of all lines are summed. Two absorption bands are clearly distinguished being localized in the near-IR region and at the interface between UV and visible regions. The absorption band in the ultraviolet region at wavelengths near $100-300$ nm is located close to the position of the absorption peak for graphene [6–8]. In the region of near-IR radiation, the absorption band is narrower with a maximum near the wavelength of 3000 nm.

Experimental results show that there are indeed two predominant absorption peaks in the wavelength region of 2000 nm and 4000 nm. The absolute value of their intensity is more than twice the absorption in the long-wave region of the measured spectrum. Thus, the results of the theoretical calculation at $t = 4$ eV are in qualitative agreement with the location and width of the absorption bands found by IR spectroscopy of nanoshells in glass (Fig. 2, *b*).

The approximate nature of the averaged model used and the implementation of the calculation assuming an ideal spherical shell shape and its single-layer structure

increases the number of possible transitions, some of which will be prohibited in a real material due to a different symmetry. In addition, the model does not take into account the contribution of oxygen in the composition of the material, which role was noted, for example, in [11]. Oxygen may be responsible, in particular, for the ensuring uniform absorption at wavelengths greater than 10^4 nm. It is assumed that the above-listed features, along with the lack of information about the exact values of the control parameters for spherical shells, determine the existing discrepancy in the location of absorption peaks. Nevertheless, when performing a theoretical analysis, the use of a simple and easily scalable model of the energy spectrum of electrons in the shell was implemented, which opens up the possibility of predicting optical and other properties determined by the electronic structure of carbon nanospheres.

Conclusion

In an array of hollow carbon nanospheres, absorption peaks in the near-IR region were theoretically calculated and experimentally confirmed. When calculating on the basis of a model that considers the surface states of electrons on a sphere, a pronounced absorption in the near-IR range is realized. The characteristic absorption wavelengths correspond to the results of spectroscopy of the synthesized nanosphere samples. The developed model for calculating the energy spectrum of such materials allows investigating other properties that depend on their electronic structure. The presence of a clearly distinguished absorption peak in the near-IR region of the spectrum, along with a rod-like microstructure, makes the composite based on hollow

carbon nanospheres a promising material for absorbing IR radiation for problems in photonics, nanophotonics, and integrated optics.

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Conflict of interest

The authors declare that they have no conflict of interest.

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