Nanocarbons and quantum dots formation in new hybrid materials

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Abstract

We present technique of obtaining complex hybrid structures combining the multi-walled carbon nanotubes or multi-layer graphene and luminescent hydrophobic semiconductor core/shell quantum dots CdSe/ZnS. As a result, a formation of quantum dot decorated carbon nanotubes and graphene films is evidenced by 2D microluminescence and micro-Raman mapping of quantum dots and nanocarbons, respectively, where a spatial correlation between the luminescence and Raman signals is found.

Keyword list graphene, multi-wall carbon nanotubes, quantum dots, hybrid structures.

1. Introduction.

Nanostructured carbon materials, such as nanotubes and graphene, have great potential for applications in many scientific and technological fields [1,2]. They are considered as "building blocks" for electronic and photonic devices, such as nanotransistors, power converters, energy storage devices, sensors for various substances, etc. [3-6].

Nowadays the idea of creating hybrid materials with new and unique electrooptical, electrochemical and optical properties basen on nanostructured carbon materials and metal and semiconductor nanoparticles, as well as various organic compounds is at the peak of popularity [7-15]. Among them, the complex hybrid structures combining the multi-walled carbon nanotubes (MWNT) or multi-layer graphene (MLG) and luminescent semiconductor nanocrystals, or quantum dots (QDs), attract especial attention because of unique electric properties of MWNT and MLG [16] and size-dependent optical properties of QDs. At the same time, formation of quantum dot decorated carbon nanotubes and graphene films with desired electro-optical properties is a problem of primary importance.

In this work we report method of formation of complex hybrid structures combining nanocarbons (MWNT or MLG) and highly luminescent hydrophobic semiconductor core/shell quantum dots CdSe/ZnS. The samples of the nanocarbons with surface decorated by luminescent nanocrystals were fabricated by the mixing of solutions of nanocrystals and nanocarbon particles in a hydrophobic solvents. The resulting structures were characterized by optical methods of 2D micro-luminescent and micro-Raman mapping.

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2. Materials and methods

Colloidal core/shell CdSe/ZnS quantum dots of two different sizes were prepared by high temperature organometallic synthesis, accordingly to the procedure described in. The dots have sizes of about 2.5 nm and 5.3 nm with luminescence peaks at 530 nm and 625 nm, respectively. Their surface was passivated by mixture of trioctylphosphine oxide (TOPO) and oleic acid molecules. For the formation of the hybrid structures a colloidal solution of CdSe/ZnS QDs in toluene with concentration of 10^{-4} M was prepared.

Initial solutions of the multilayer graphene and multi-walled carbon nanotubes were prepared in two solvents - isopropanol and toluene. First one is most suitable for preparation of multilayer graphene with optimal characteristics by sonication of natural graphite. Second one is known as a best solvent for preparation of colloidal solution of highly luminescent CdSe/ZnS quantum dots. The prepared MLG flakes have lateral dimensions in the range of 1-3 μm and thickness from a few nm to ~50 nm. The MWNT have diameter of 20-30 nm and length of 2-5 mm. After preparation the solution of multi-walled carbon nanotubes was sonicated in an ultrasonic bath "Unique lavadora ultrasonica" for 2 minutes and centrifuged in "Eppendorf MiniSpin" at 1000 rpm for exclude nanocarbon agglomerates. The MWNT isopropanol and toluene solutions with concentration of 10^{-3} mg/mL were prepared. For the formation of the hybrid structures a 10:1 volume mixture of MWNT and 2.5 nm QD solutions was deposited on silicon substrate.

Hybrid structures with MLG were prepared by dripping of the 1:1 volume mixture of 10^{-3} mg/mL MLG solution and 5.3 nm QD solutions on a glass slide surface.

Decoration of the nanocarbon surfaces by quantum dots were visualized by 2D micro-luminescence and micro-Raman mapping where signals of the QD photoluminescence and Raman G-band of the nanocarbons (at 1580 cm^{-1}) were used for the luminescence and Raman mapping, respectively. The 2D mapping was performed with "inVia" Renishaw micro-Raman spectrometer with 457.9 and 514.5 nm laser lines and NT-MDT micro-Raman spectrometer equipped with 473 and 633 nm lasers. For the luminescence mapping of MLG/QDs structures with 405 nm excitation a laser scanning luminescence microscope LSM-710 (Carl Zeiss) was also used.

In Figure 1 the parts of Raman spectra of multi-walled carbon nanotubes (a) and multilayer graphene (b) with characteristic for nanocarbon materials D-band (~1348 cm^{-1}) and G-band (~1574 cm^{-1}) [17] are shown together with luminescence band (530 nm and 625 nm) of used CdSe/ZnS QDs. D-band indicates breathing mode of sixfold aromatic rings in carbon network. The G-band in Raman spectra of carbon materials indicates a presence of graphitic sp^2-phase the in-plane bond stretching of sp^2 bonded C atoms in hexagonal rings. Presented in Figure 1 characteristic optical responses from components of studied hybrid structures were used for 2D mapping of prepared nanocarbons/QDs samples.

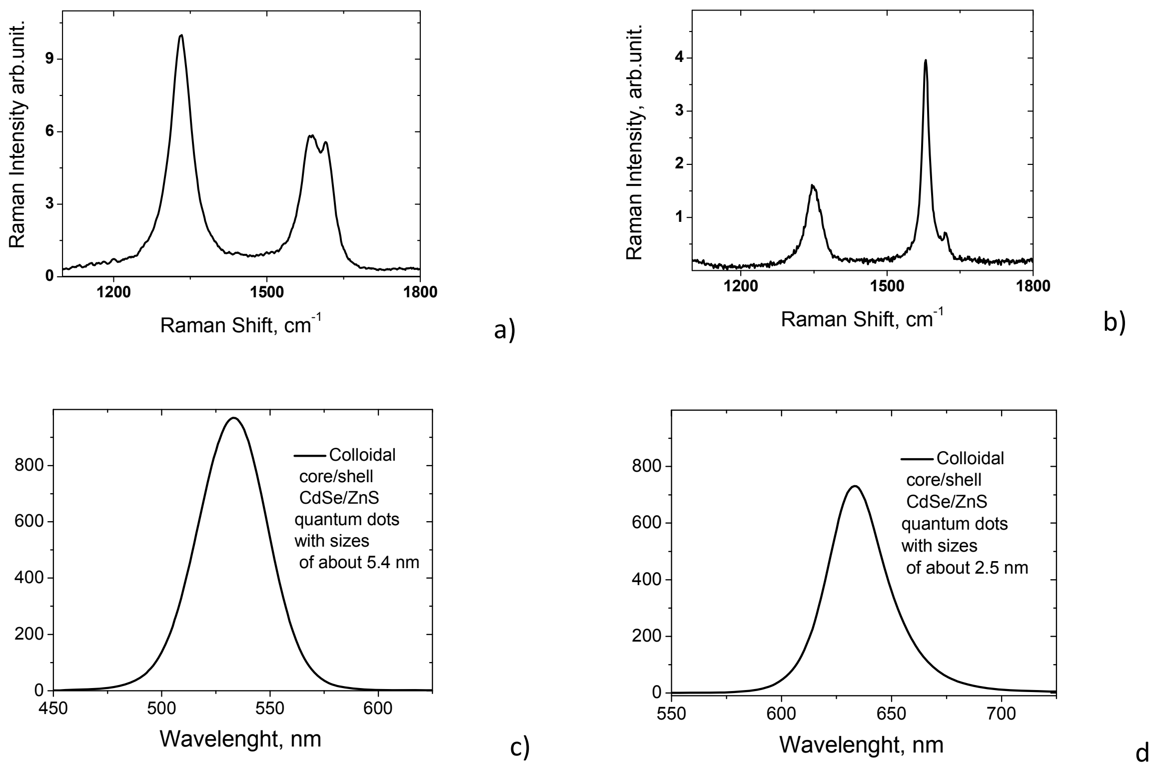

Figure 1. The parts of Raman spectra of multi-walled carbon nanotubes (a) and multilayer graphene (b) with characteristic for nanocarbon materials D-band (~1348 cm^{-1}) and G-band (~1574 cm^{-1}) are shown together with luminescence bands at 530 nm (c) and 625 nm (d) of used CdSe/ZnS QDs with average sizes of 2.5 nm and 5.4 nm, respectively.

3. Results and discussion

3.1 Formation of hybrid structure based on multi-walled carbon nanotubes and quantum dots.

It has been found that using an isopropanol solvent, suitable for preparing multilayer graphene, was not good for quantum dots, since the were poorly dissolved in the isopropanol and QD photoluminescence was strongly quenched. Therefore, for further experiments we used only toluene solution of QDs and nanocarbons.

We supposed that increasing number of defects on multi-walled carbon nanotubes can cause better surface decoration by nanocrystals. Multi-walled carbon nanotubes have undergone a procedure of oxidation in 65% HNO_3 acid for ~8 hours at T= 80^{o}C. But oxidation of nanotubes wasn't made sufficient different which was expected. Probably defects appeared only on the top of tubes. Oxidation has not made significant changes in the Raman spectra of multi-walled carbon nanotubes.

Figure 2 shows the QD luminescence (a) and MWNT Raman (b) mapping of the same area of sample. A correlated increasing of the luminescence and Raman intensities presented in Figure 2c shown that multi-walled carbon nanotubes and CdSe/ZnS QDs are in the same areas. The fact of location of QDs and MWNT in the same areas of the sample confirms formation of hybrid material.

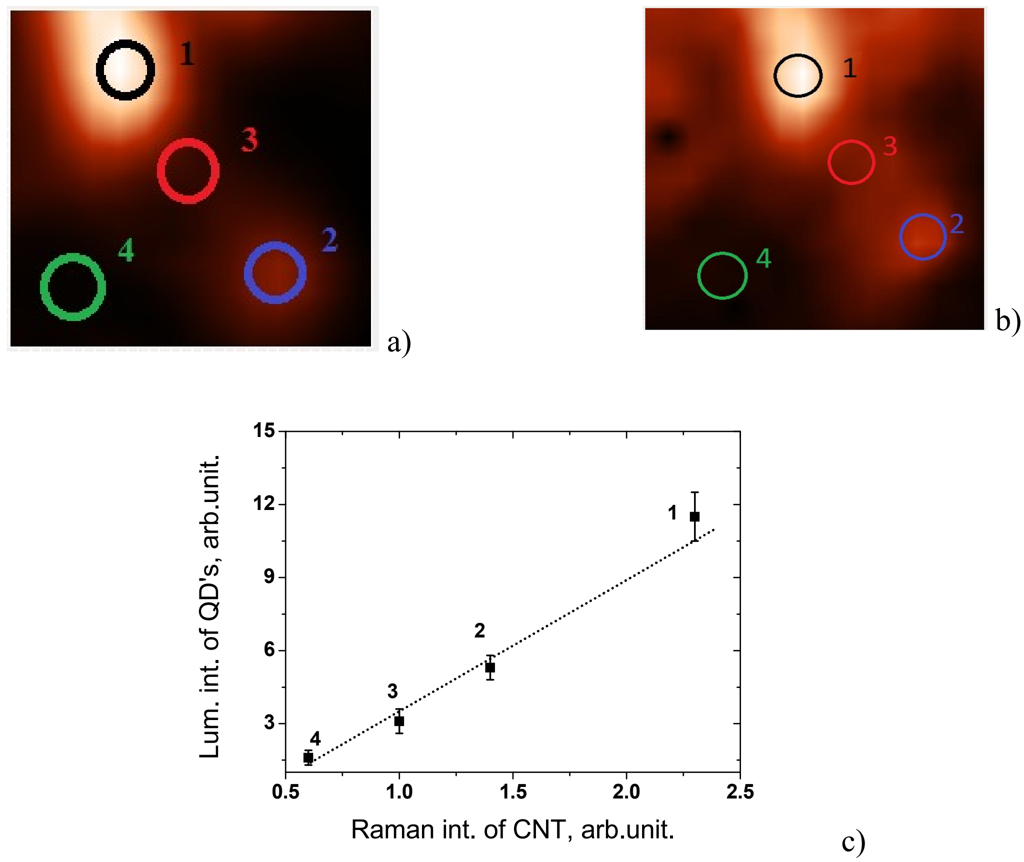

Fig. 2. Two-dimensional maps of hybrid carbon MWNT/QDs structures: a) is the 2D map of the quantum dot luminescence intensity, b) is the 2D map of the the MWNT G-band Raman intensity obtained from areas marked by circles with the same numbers in a) and b). c) Correlation between the intensities of quantum dot luminescence and Raman signal from multi-walled carbon nanotubes in studied hybrid material is shown

3.2 Hybrid structure based on multilayer graphene and quantum dots

The spectra of absorption of quantum dots, multilayer graphene and mixed solution presence on Figure 3. We expect that defects on the surface of multilayer graphene can physically interact with free end of QD molecular solubilizer. The quenching of quantum dot luminescence above 50% was observed in mixing solutions of QDs and MLG. Luminescence quenching in a mixture in our opinion caused by interaction between multilayer graphene and quantum dots and indicates formation of hybrid structure from multilayer graphene and quantum dots.

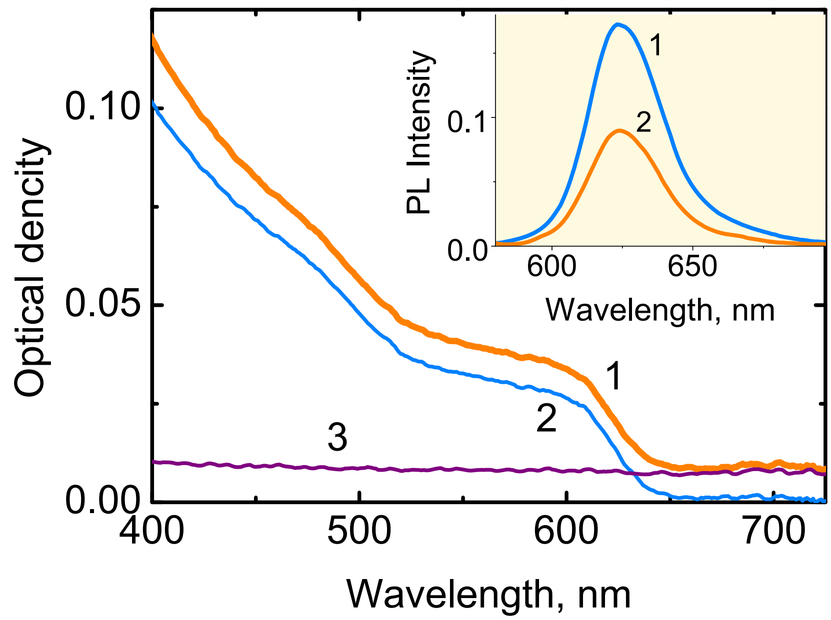

Fig. 3 Absorption spectra of toluene solutions of quantum dots (1), of mixture of multilayer graphene and quantum dots (2) and of multilayer graphene. Inset shows luminescence spectra of QDs and mixture of QDs and MLG.

Formed in toluene solution hybrid structure of MLG and quantum dots were investigated by micro-luminescence and micro-Raman spectroscopy. For this purpose mixture solution was deposited on the glass slide surface under normal conditions. Examples of the luminescence and transmittance micro-images of the slide sample obtained with a scanning confocal microscope are presented in Fig. 4. It is clearly seen from comparison of the luminescence and transmittance micro-images that QDs are localized in the small dark areas in the transmittance image, which can be attributed to the graphene flakes. This attribution is evidently supported by characteristic Raman spectrum of graphene observed only from these dark areas. Really, the Raman mapping characterized this areas as multilayer graphene by presents of standard nanocarbon materials peaks: D and G lines. It should be noted that the layers of quantum dots deposited on the slide surface from toluene solution in the absence of MLG particles did not show such a spatial inhomogeneity. This fact confirms that most of the quantum dots are adsorbed onto the surface of graphene confirming the formation of hybrid structures based of multilayer graphene and quantum dots.

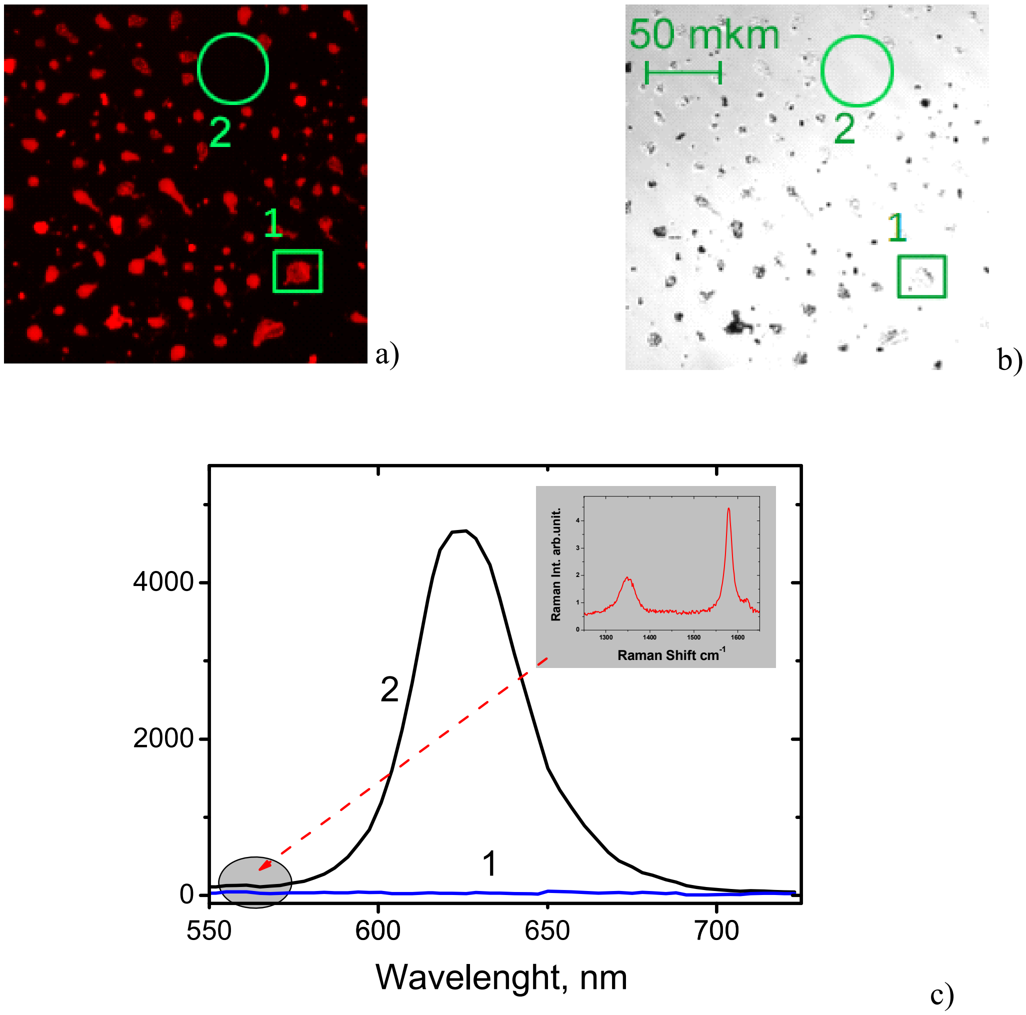

Fig. 4. Luminescence (a) and transmission (b) micro-images of hybrid structures based on multilayer graphene and quantum dots. Micro-images and spectra obtained from selected areas (1) and (2) marked as circles in (a) and (b). Luminescent spectra of QD in hybrid structure (c) with MLG Raman from area 2 (inset in (c)). Hybrid structures were obtained by mixing toluene solutions. Micro-Images were obtained with a scanning luminescence microscope LSM-710.

Conclusion.

We demonstrated method of formation of hybrid structures based on multilayer graphenes or multi-walled carbon nanotubes and core/shall CdSe/ZnS quantum dots with surface passivated by mixture of trioctylphosphine oxide and oleic acid molecules. The samples of the nanocarbons with surface decorated by luminescent quantum dots were fabricated by the mixing of solutions of nanocrystals and nanocarbon particles in a toluene solution. The formation of the hybrid structures were proved by optical methods of 2D micro-luminescent and micro-Raman mapping and micro-spectroscopy.

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