Influence of the QD luminescence quantum yield on photocurrent in QD/graphene hybrid structures

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Abstract

Photoinduced changes in luminescent and photoelectrical properties of the hybrid structure based on CdSe/ZnS QDs and multilayer graphene nanobelts were studied. It was shown that an irradiation of the structures by 365 nm mercury line in doses up to 23 J led to growth of QD luminescent quantum yield and photocurrent in the QD/graphene structures. This confirms the proximity of the rates of the QD luminescence decay and energy/charge transfer from QDs to graphene, and opens an opportunity to photoinduced control of the photoelectric response of the graphene based hybrid structures with semiconductor quantum dots.

Keywords: CdSe/ZnS QDs, QD/graphene hybrid structures, QD luminescent quantum yield, photoresponse, photoinduced processes.

1.   INTRODUCTION

Graphene is a two-dimensional allotropic form of carbon remarkable by high mechanical strength, high thermal conductivity and huge carrier mobility. Due to its outstanding electrical properties graphene is promising material for developing of new generation of phototransistors and photodetectors[1 - 3]. However, the low absorption capacity of graphene in the visible and near-infrared ranges is the main restriction for its direct application in photoactive device. One way for solving this problem is formation of hybrid structures based on graphene with surface covered by quantum dots (QDs) strongly absorbing light. The QDs are the semiconductor nanocrystals with unique optical properties. In particular the positions of absorption and photoluminescence (PL) bands depends on particle size, also QDs have high PL quantum yield and high photostability[4].

Previously it was demonstrated that conductivity of QD/graphene hybrid structures increases under irradiation into QD absorption band[5 - 7]. The exact mechanism of photoinduced conductivity in QD/graphene structures is not clear yet. In the literature photocurrent in these structures is associated with photoinduced hole transfer from QD to graphene[8]. In Ref.[9] it is shown that the rate of this process are much lower than the rate of dipole-dipole energy transfer from QD to graphene and it is comparable with the exciton lifetime in QDs. At the same time, it is well known that photoluminescence intensity of QDs could be increased significantly due to minimize of trap states on their surface under photo irradiation[10, 11]. Then, a decreasing of the number of nonradiative channels in QDs will be accompanied by enlarge of QD contribution in QD/graphene structure photoconductivity.

In this work a photopassivation of the QD surface was used to establish correlation between the nonradiative dissipation of the excitons in QDs and QD/graphene structure photoconductivity. It was shown that photoinduced QD brightening leads to multiple increasing of the hybrid structure photoconductivity.

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2. MATERIALS AND METHODS

CdSe/ZnS core/shell QDs with diameter of 5.5 nm and PL maximum at 630 nm were synthesized by hot ejection method[12 - 14]. QD surface was passivated by oleic acid[15, 16]. Initially QDs was dissolved in chloroform with concentration of $2 \cdot 10^{-5}$ mol/l. Multilayer graphene (MLG) nanobelts have been received from «Nacional de Grafite» Ltd. (Brazil). Nanobelts, according to the vendor and SEM data, have a length of 20-50 μm, width of 1-5 μm and thickness of about 10 nm. Solution with concentration of 0.5 mg/ml was prepared by 4h sonification of nanobelts in N-methyl-2-pyrrolidone.

The hybrid structures were formed on the planar electrodes by subsequent deposition of the nanobelts and QDs layers. Before deposition the MLG solutions were sonicated at least 30 minutes to avoid nanobelts aggregation. The glass slides were cleaned by sonification in 1M hydrochloric acid, and then they were rinsed with plenty of water and finely immersed in isopropyl alcohol where they stored before use. Ti electrodes were sputtered on glass slides by physical vacuum deposition using Kurt Lesker PVD setup. The 10 μm gap between electrodes was cut by laser ablation. The graphene films were deposited on the electrodes by modified Langmuir-Blodgett (L-B) technique[17, 18]. Then the samples were annealed at 150°C in air to eliminate solvent residues and to improve adhesion to the glass slides. At the last, QD films were deposited by modified L-B technique. The surface concentration of QD was estimated as $\sim 3.01 \cdot 10^{14}$ mm^{-2}.

Steady state absorption and PL spectra of QD solution were registered with spectrophotometer Shimadzu (Japan) and spectrofluorometer Cary Eclipse (Varian, Australia), respectively. PL and morphology of QD films were investigated with laser confocal microscope LSM-710 (Zeiss, Germany).

Time-resolved PL measurement was performed on fluorescence microscope MicroTime100 (Pico Quant, Germany). The decay curves were fitted by multiexponential function and the average PL decay time was calculated by formula:

$$\langle \tau \rangle = \frac{\sum_i A_i \tau_i^2}{\sum_i A_i \tau_i} \tag{1}$$

where A_i and τ_i are the amplitude and PL decay time for of the i-component.
The SEM images were recorded on Merlin scanning electron microscope (Ziess, Germany). The photoelectrical properties of QD/graphene structures were investigated with picoammeter Keithley 6487 (Keithley Instruments Inc), synchronized with 405 nm diode laser.
The samples were exposed with 365 nm line of mercury lamp. The lamp emission in other spectral range, especially in infrared region, was cut off by optical filters. The exposure dose per hour was 14.4 J. Samples were irradiated for an hour three times with measurement of their optical and photoelectrical characteristics between expositing.

3. RESULTS AND DISCUSSION

Figure 1 demonstrates the absorption and PL spectra of a colloidal solution of CdSe/ZnS QDs in chloroform that was used for QD/graphene structure formation.
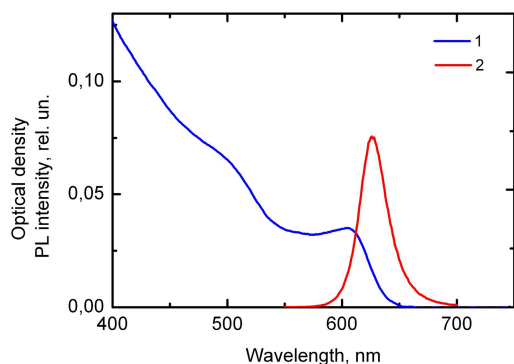
Figure 1. The absorption (1) and PL (2) spectra of colloidal solution of CdSe/ZnS quantum dots. PL excitation is 405 nm.

Figure 2 shows the PL spectrum of the QD/graphene structures on the Ti electrodes captured with the luminescent confocal microscope. Inset shows PL image of the structures (a) and SEM image of graphene nanobelts (b) used in the QD/graphene structures. The gap between the electrodes is highlighted by green.
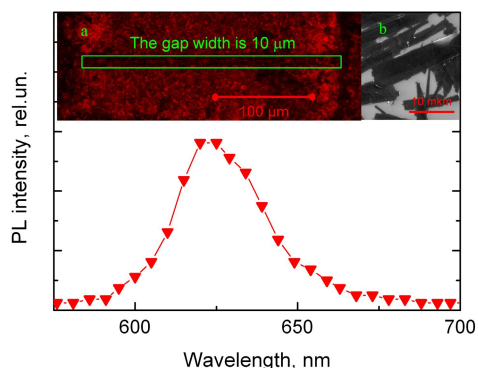

Figure 2. The PL spectrum of QD/graphene structures. The inset: (a) is the PL image of QD/graphene structure. (b) is the SEM image of graphene nanobelts. The PL excitation was performed by a diode laser with a 405 nm wavelength. The data were obtained with luminescent scanning microscope using a 20x objective lens.

The photoluminescent data of QD/graphene structures presented in Figure 2 clearly demonstrate that the structures are characterized by bright QD luminescence, the spectrum of which has the shape and position like QDs in chloroform solution (see Figure 1).

It should be noted that the QD/graphene structures deposited on Ti electrodes do not transmit light and have planar sizes about several millimeters. These make it difficult to determine of PL quantum yield of these samples using standard procedure[19]. Therefore, we will analyzed the QD PL kinetic because it's uniquely associated with QD PL quantum yields:

$$\varphi = \tau \cdot k_r \tag{2}$$

where τ is PL decay time of QDs and k_r is radiative rate of QDs.

Obviously, in assumption of invariability of k_r, any change in τ should be accompanied by change of the PL quantum yield.

Analysis of PL decay of QDs in the structures has shown that the PL kinetic is well fitted by tree exponential function and the characteristic times (τ_i) are shorter than that of in chloroform solution and in QD dry layers on glass slides (see

Table 1). This indicates that QD photoluminescence in the QD/graphene structures is quenched due to interaction with graphene.

Table 1. Kinetic parameters of CdSe/ZnS QD photoluminescence.

Samples	τ_1, ns	A_1, %	τ_2, ns	A_2, %	τ_3, ns	A_3, %	$<\tau>$, ns
QD/graphene structures	0.7	74.1	2.8	22.7	12.6	3.1	4.6
QD dry layers on glass slides	0.8	71.2	4.5	27.1	11.4	1.5	5.7
QD solution in chloroform	-	-	1.7	61	10	39	8.3

Further, the photoelectric properties of the QD/graphene structures with 405 nm laser irradiation were investigated. A typical photoresponse from the structures is shown in Figure 3. The data presented in Figure 3 clearly demonstrate the presence of photoresponse in the hybrid structures under external radiation. An analysis of the photoelectric properties of the structures has shown that they are characterized by the photoresponse in 0.2%, which was estimated as ΔI/I (where ΔI is the increase in conductivity under irradiation, I is the conductivity of structures in the darkness). Enlarged graph of the photoresponse is presented in the inset in Figure 3. Three typical ranges in photocurrent behavior can be distinguished. The first range is the increase of the photoresponse, the rate of this process is 0.013 µA·s⁻¹. The second range is characterized by the photocurrent saturation of the hybrid structures. The third range is the current drops after external light off.
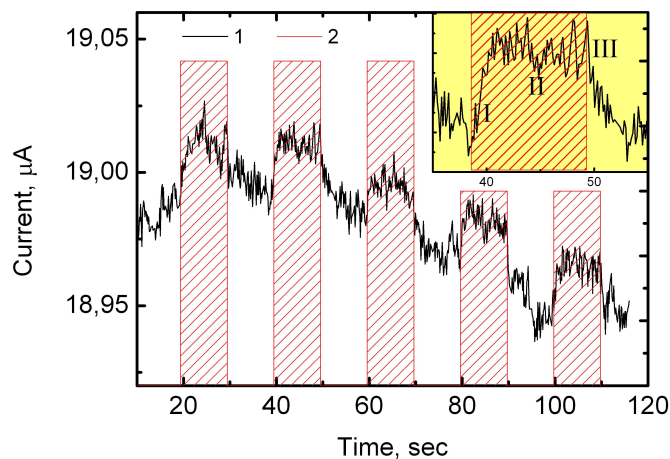

Figure 3. A photoresponse of QD/graphene hybrid structures on Ti-electrodes under voltage of 10 mV (1). The crosshatched area (2) shows the periods of sample irradiation. Inset is an enlarged graph of the photoresponse. Three components of different current behavior indicate: I is the increase of the photoresponse, II is the photocurrent saturation, III is the current drops.

To investigate the influence of external radiation on the photoelectric properties of the structures they were irradiated by the 365 nm mercury line. The duration of one session of radiation was 1 hour that is corresponding to a radiation dose of 14.4 J. After each exposure the photoluminescent and photoelectrical properties of the structures were examined. Characteristic decay times and its amplitudes for CdSe/ZnS QDs in the hybrid structures for different exposure doses are presented in the Table 2.

Table 2. Kinetic parameters of CdSe/ZnS QD PL in the QD/graphene structures irradiated by 365 nm-lines of mercury lamp.

Dose, J	τ_1, ns	A_1, %	τ_2, ns	A_2, %	τ_3, ns	A_3, %	$<\tau>$, ns
0	0.7	74.1	2.8	22.7	12.6	3.1	4.6
14.4	0.8	77.4	3.1	20.2	14.5	2.3	4.7
28.8	0.7	70.1	2.9	26.5	14.5	3.3	5.5
43.2	0.6	76.7	2.4	20.9	14.5	2.2	4.9

Analysis of QD PL kinetics in the hybrid structures showed that irradiation of samples during the first two hours led to a gradual increase in the QD PL decay time. Photoinduced growth of PL quantum yield or PL decay time of QDs usually is attributed to photopassivation of their surface[10]. Increasing the external irradiation dose up to ~ 43 J led to the shortening QD PL decay time in the structures, which reflects photodestruction of the ZnS shell or CdSe core of the QDs[20]. It is well known that PL decay time changes reflect a change of the ratio between radiative and nonradiative rates in luminophores:

$$\tau = \frac{1}{k_r + k_{nr}}$$

(3)

where k_r is the radiative rate constant, and k_{nr} is the non-radiative rate constant.

There are no physical reasons of changing the radiative rate in QDs under a low power external irradiation. Therefore, we believe that photoinduced changes of PL properties of CdSe/ZnS QDs are accompanied by change of their non-radiative rate (k_r) that reflects the change of the number of trap states on the QD surface.

An investigation of photoelectric properties of the QD/graphene structures revealed that photoinduced increasing of QD PL decay time is accompanied by significant growth of the structure photoconductivity. Figure 4 demonstrates that after two hours of structure irradiation by 365 nm-lines mercury lamp their photoelectric properties are undergoing significant qualitative and quantitative changes.
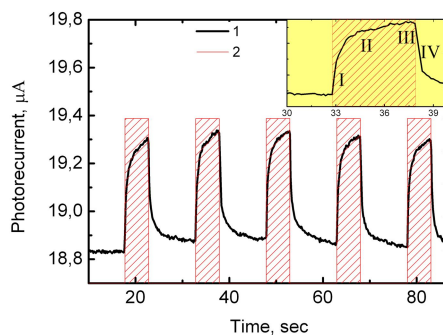

Figure 4. Electric properties of the QD/graphene structures on Ti-electrodes under voltage of 10 mV after two-hour irradiation by 365 nm-lines of mercury lamp (1); the crosshatched area (2) shows the periods of sample photoirradiation. Inset is an enlarged graph of the photoresponse. Four components of different current behavior indicate: I is the fast increase of the photoresponse, II is the slow increase of the photoresponse, III is the photocurrent saturation, IV is the current drops.

Analysis of the photoresponse of the structures presented in Fig.4 has shown a presence of two components, a fast component with the 0.1 µA·s^{-1} rate and a slow component that is characterized by 0.01 µA·s^{-1} rate (regions I and II on insert in Figure 4, respectively). It should be noted that the fast component in photoresponse of the structures appears after external light irradiation only (see Figure 3). The presence of two components in the photoresponse of the structures characterized by different rates indicates to existence of two mechanisms of QD sensibilization of the graphene conductivity[21]. The presence of the slow component can be attributed to the presence of trap states in graphene. To determine the exact mechanisms of these processes, further research is needed.

As expected the shortening of the QD decay time in the structures, which was observed after last session of mercury lamp irradiation, (see Table 2) is accompanied by decrease of their photocurrent. All estimated photoelectric parameters of the QD/graphene structure are presented in the Table 3.

Table 3. Estimated photoelectric parameters of the QD/graphene structures.

Dose, J	Fast component rate, µA/s	Slow component rate, µA/s	Photoresponse $\Delta I/I$, %
0	-	0.013±0.005	0.2±0.025
14.4	0.10±0.05	0.010 ±0.005	1.4±0.05
28.8	0.77±0.1	0.104±0.005	2.6±0.07
43.2	0.64±0.1	0.034±0.005	1.3±0.05

Correlation between the QD PL decay time and photoconductivity of the QD/graphene structures is demonstrated in Figure 5.
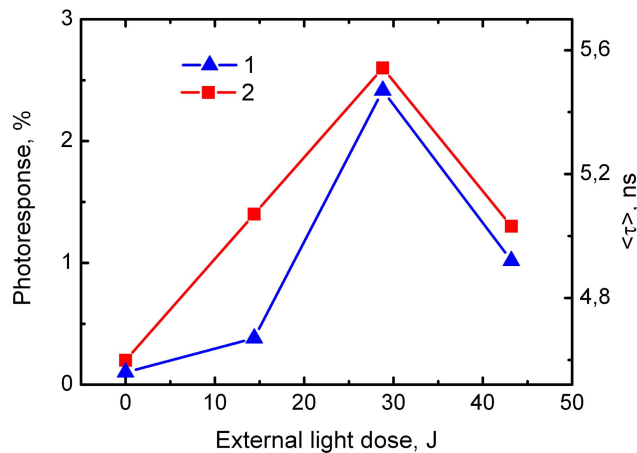

Figure 5. Dependence of average QD PL decay time in the QD/graphene structures (1) and photoresponse of this structures (2) on the irradiation dose.

The data presented in Fig.5 clearly shows that the photocurrent in the structures depends on the QD non-radiative rate constant i.e. of the number of non-radiative channels in QDs.

CONCLUSION

The influence of external irradiation on luminescent and photoelectrical properties of the hybrid structures based on multilayered graphene nanobelts covered by colloidal CdSe/ZnS quantum dots were investigated. Photoinduced changes in the QD PL quantum yield were provided by the irradiation of the structures with 365 nm-lines mercury lamp with total dose in 43.2 J. An analysis of dependences of the photoluminescent and photoelectric properties of the QD/graphene structures on light doses showed a good correlation of their photoresponse with the photoinduced changes in the QD PL quantum yield. Our data clearly demonstrate an opportunity to regulate the photoelectric properties of the QD/graphene structures by photoinduced changing of QD photoluminescence quantum yield.

ACKNOWLEDGMENTS

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