International Journal on

"Technical and Physical Problems of Engineering"

(IJTPE)

IJTPE Journal

ISSN 2077-3528

www.iotpe.com

Published by International Organization of IOTPE

ijtpe@iotpe.com

Number 3

September 2023

Issue 56

national Journal on

IJTPE

Journal

Volume 15

Pages 53-58

PHOTOCONDUCTIVITY OF GADOLINIUM-DOPED CARBON NANOTUBES

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Abstract- In this research the photoelectric properties of multiwall carbon nanotubes were studied. The spectral dependencies of photosensitivity for gadolinium-doped multiwall carbon nanotubes (Gd 10%) were investigated. The spectral characteristics for gadolinium-doped multiwall carbon nanotubes have been measured at the wavelength range from 400 nm to 900 nm under the applied voltage from 1 to 9 V. The voltage of 3V leads to the appearance of the highest sensitivity value at a wavelength $\lambda \sim 480$ nm and the most significant photocurrent peak equal to $I_p \sim 0.158 \mu A$. Approximately the same peak value is observed at a wavelength of λ ~540 nm. Using U=5V leads to a decrease and loss of photosensitivity. The widest photosensitivity range is observed at a voltage of U=1 V. Using this voltage value can be effective for detector applications. Experimental data and plotted I-V characteristics are presented for six wavelengths from the 640-880 nm spectral range. Based on I-V curves, the weak photosensitivity for any voltage from 1 to 9 V at λ ~640 nm was registered. The increasing wavelengths λ ~720, 760, 780, and 880 nm lead to an increase in the photocurrent value. The voltage value equal to 7 V leads to the photosensitivity maximum. The results are promising for the accessible and cost-effective fabrication of Gd-doped MWCNTs for detector and optoelectronic devices.

Keywords: Gd-Doped MWCNT, Photocurrent, Spectral Photosensitivity.

1. INTRODUCTION

Carbon nanomaterials attract a lot of attention owing to their unique optical, electronic, and catalytic properties. In [1] the varies optoelectronic applications of carbon nanotubes in single-walled (SWCNT) and multiwalled (MWCNT) forms have been researched. The modern area of research is connected with the investigation of photoelectronic properties in low-dimensional materials such as negative photo-conductivity [2].

A new detector based on fullerene-activated carbon nanotubes was proposed in [3]. This detector shows a high photoresponsivity of up to 10^8 A/W, allows it to register 1.6×10¹¹ Jones, and has an enhancement coefficient of more than 10⁸. Photodetectors based on multiwall carbon nanotubes films in compare with Si have been the advantages for devices as low cost, fast response, high detection, simple fabrication, high reliability, and compatibility with modern technologies [4-5]. Carbon nanomaterials and nanocomposites are perspective due to their unique optical, chemical, mechanical, and electrical properties [6-11]. In our previous articles [12, 13] graphene-based nanomaterials were investigated. In [14-18, 24] structural and electrical properties of graphene oxide were investigated and proposed for future solar cell and optoelectronic applications. In our article [19] the spectral dependencies of photosensitivity for pure carbon nanotubes in the broadband spectral range from UV to NIR (400-900 nm) at values in range from 1 to 9 V of the bias voltage Uapplied to the sample were analyzed.

Therefore, this work aims to investigate of photosensitivity spectrum features for gadolinium-doped MWCNT. The Gd concentration equals 10% (MWCNTs/Gd (10%). We investigated photocurrent features for the wavelength range from UV to NIR (400–900 nm) at different values of the bias voltage applied to the sample (1V, 3V, 5V, 7V and 9V). For this research, the experimental data and approximation approach for I-V curves measured under the different light illumination wavelengths (640 nm, 720 nm, 740 nm, 760 nm, 780 nm, 880 nm) were analyzed.

2. EXPERIMENT AND DISCUSSION

2.1. The Photosensitivity Spectra for MWCNT/Gd Nanotubes

For measurement of photocurrent, the home-build setup consists of a white light source, monochromator and digital registration electronics was used at room temperature [19]. The Gd-doped MWCNT powder was pressed into a special shape holder for deposition of metal contacts. Technology aspects of manufacturing Gd-doped MWCNT and morphology, structural, optical properties investigations were described in [20-22]. Figure 1 shows the photosensitivity spectra for MWCNT/Gd (10%) in the spectral range from UV to NIR (400-900 nm) at bias voltages equal to 1V and 3V applied to the sample.



Figure 1. The photosensitivity spectra of MWCNTs/Gd at bias voltage 1V and 3V applied to the sample

The seven photocurrent peaks λ =440, 500, 580, 740, 780, 840 and 900 nm were registered for voltage U=1V. Some symmetry in this characteristic (around λ =660 nm) and peaks periodicity were observed. At an illumination wavelength equal to 740 nm the highest photosensitivity value 0.115 μ A is measured. The other peaks have a photocurrent value of the order of I_p ~0.04-0.1 μ A. In the spectral range from 600 to 720 nm zero photosensitivity is registered.

Peaks λ_{p1} ~415 nm, λ_{p2} ~480 nm, λ_{p3} ~540 nm, λ_{p4} ~645 nm, λ_{p5} ~700 nm, λ_{p6} ~820 nm were registered at U=3 V. Two maximum amplitude peaks at λ_{p2} ~480 nm and λ_{p3} ~540 nm were registered. But their equivalent values increased and amounted to I_{p2} ~0.158 µA and I_{p3} ~0.155 µA. The peaks with highest value of photocurrent shifted to the low-wavelength range. Zero photosensitivity for wavelength ranges $\lambda=560$ -620 nm and $\lambda=720$ -800 nm was observed. The zero-photosensitivity total range has expanded up to 140 nm. The photosensitivity spectral dependencies for a CNT/Gd (10%) in the spectral range from UV to NIR (400-900 nm) at the bias voltages 5 V, 7 V, and 9 V U which were applied to the sample are shown in Figure 2.

Using of voltage value equal to 5 V generated following photocurrent peaks: 415 nm, 480 nm, 640 nm, 700 nm, 740 nm, 815 nm, 880 nm. The highest photocurrent peak value for wavelength equal to 480 nm has decreased up to $0.085 \,\mu$ A.

Zero photosensitivity is observed in the spectral range from 500 to 615 nm. However, for spectral range from UV to NIR (400-900 nm) at U=5V registered very weak photosensitivity.



Figure 2. The photosensitivity spectra of MWCNTs/Gd at bias voltages 5V, 7V, and 9V which applied to the sample

Using of U=7 V generated the photocurrent peaks at λ_{p1} ~480 nm, λ_{p2} ~540 nm, λ_{p3} ~640 nm, λ_{p4} ~720 nm, λ_{p5} ~780 nm, λ_{p6} ~840 nm, λ_{p7} ~880 nm. The peaks at λ_{p2} ~540 nm and λ_{p6} ~840 nm is very small. The weak photosensitivity spectral range expanded from 500 to 700 nm. The maximum photocurrent value at wavelength 880 nm is 0.15 μ A. The six photocurrent peaks at voltage equal to 9V, were registered. In this case, the peaks at wavelengths 660 nm and 740 nm are very insignificant. The weak photosensitivity spectral range from 620 to 800 nm narrowed slightly. In this case, in the specified range, there are two weak peaks at λ_{p4} ~660 nm, λ_{p5} ~740 nm. The maximum peak is observed at λ_{p3} ~560 nm and is I_{p3} ~0.148 μ A.

Thus, the data analysis shows that an increase in the value of bias voltage (up to U=5V) applied to the MWCNT/Gd sample leads to a decrease in photosensitivity. In this case, the sample loses photosensitivity in the wavelength range $\lambda = 400-900$ nm. The widest range of photosensitivity is observed at U=1V. The most amplitude peak, equal to $I_p \sim 0.158 \mu A$, is registered for 480 nm illumination wavelength. Approximately the same peak value is observed at a wavelength equal to 540 nm. The experimental data of photocurrent can be plotted in I-V curves format for different wavelengths of illuminated light. The dependencies of photo-current and applied bias voltage are presented in Figure 3a-3c. Dependencies allow us to evaluate the parameters of the photosensitivity of the MWCNTs/Gd sample.

2.2. Analysis and Modeling of the I-V Characteristics for MWCNT/Gd Nanotubes

I-V characteristics for MWCNT/Gd with illumination wavelengths equal to 640 nm and 720 nm are shown in Figure 3a. These characteristics can be approximated by:

$$I = 0.00151 \cdot U^{4} - 0.002354 \cdot U^{3} + + 0.0008052 \cdot U^{2} + 0.009854 \cdot U - 0.0157$$
(1)

 $I = -0.0007109 \cdot U^4 + 0.01275 \cdot U^3 -$ (2)

$$-0.07314 \cdot U^2 + 0.1538 \cdot U - 0.08965$$

The range from 4.2 to 7.2 V under light with the wavelength λ ~640 nm can be characterized as a negative differential resistance. The range from 1 to 4 V can be characterized as positive differential resistance. The range from 7 to 9 V can correspond to a zero-photoconductivity region. As can be seen from Figure 3a the current-voltage characteristic at wavelength λ ~640 nm has a rather low photocurrent.

The *I-V* curves at wavelength λ ~720 nm from 3 to 5 V regions have zero photocurrent. At wavelength λ ~720 nm, from 5 to 7.7 V regions can be characterized as positive, and from 7 to 9 V region is characterized by negative differential resistance. The voltage of 7.7 V corresponds to the photocurrent peak I_p ~0.08 µA. I-V curves with a very low photocurrent values are registered for the 1-5 V voltage range. The *I-V* curves of MWCNT/Gd at illumination with wavelengths equal to 740 nm and 760 nm are shown in Figure 3b. These dependencies can be approximated by:

$$I = 0.0009167 \cdot U^4 - 0.0199 \cdot U^3 +$$
(3)

$$+0.147 \cdot U^{2} - 0.4231 \cdot U + 0.4091$$

$$I = -0.000651 \cdot U^{4} + 0.0115 \cdot U^{3} -$$
(4)

 $-0.06474 \cdot U^2 + 0.1355 \cdot U - 0.08161$

The region 3-5 V at wavelength $\lambda \sim 740$ nm is characterized by positive, and region 1-2.2 V, and 5.8-8.2 V are characterized as negative differential resistance. Zero photocurrent is typical for the 2.2-3 V region. As can be seen from Figure 3b, the photocurrent peaks $I_{p1} \sim 0.115 \ \mu A$ and $I_{p2} \sim 0.058 \ \mu A$ of the current-voltage characteristic curves are detected at voltages of 1 V and 5.4 V. The *I-V* at wavelength $\lambda \sim 760$ nm in the 1-5 V region has a very low photocurrent. At wavelength λ ~760 nm, the 4.7-7.4 V region is characterized as positive, and the 7.8-9 V region is characterized as negative differential resistance. A voltage of 7.6 V corresponds to a photocurrent peak of 0.084 µA. For I-V characteristics in Figure 3b the curves presented are identical trend. The I-V characteristics for MWCNT/Gd at illumination with wavelengths equal to 780 nm and 880 nm are shown in Figure 3c. These dependences are approximated by:

$$I = -0.0007422 \cdot U^4 + 0.01213 \cdot U^3 -$$
(5)

$$-0.05745 \cdot U^2 + 0.07238 \cdot U + 0.0327$$

$$I = -0.00113 \cdot U^4 + 0.01944 \cdot U^3 -$$
(6)

$$-0.1055 \cdot U^2 + 0.2126 \cdot U - 0.1214$$

I-V characteristics for the wavelengths λ ~780 nm and 760 nm indicate very similar trend. Zero photocurrent is typical for the 2.5-5 V region. As before, the voltage of 7.6 V corresponds to the photocurrent peak, which is now slightly increased and is equal to 0.11 μ A. At wavelength λ ~880 nm, the 4.3-7.4 V region is characterized as positive, and the 7.7-9 V region is characterized as negative differential resistance. As before, the voltage of 7.6 V corresponds to the photocurrent peak, which has now increased even more and is equal to 0.164 μ A. The *I-V* curves are identified a very low photocurrent range for 1-4.5 V. The following dependence is observed at wavelengths λ ~720, 760, 780, and 880 nm, the voltage value of 7.6 V, which is characterized by photocurrent peaks, is constant, and the magnitude of the peaks increases.

2.3. Discussion and Prospects of Using MWCNT/Gd Nanotubes in Optoelectronics

In this research, in comparison with data for pure MWCNT [19] shows the same trend with [23] with and remarkable increase in the photogenerated current signal from the metal (Gd) nanoparticles onto MWCNTs composite and the effect was detected for spectral range from visible and near-infrared illumination light. The metal nanoparticles greatly enhance the intrinsic ability of MWCNTs to behave as an efficient low-dimensional media for generating e-h carriers [23]. When light interacts with carbon, nanomaterial light is absorbed and, generated electron-hole pairs. The electron-hole pairs can be separated and controlled using the bias voltage. For this mechanism the carrier concentration, conductivity and current are increased.



Figure 3. The *I-V* characteristics for MWCNT/Gd under light illumination with different wavelengths

Samples of pure MWCNT [19] lose photosensitivity in almost the entire studied wavelength range λ =400-900 nm at U=9V, while samples of gadolinium-doped carbon nanotubes lose photosensitivity at U=5V. The widest ranges of photosensitivity for CNTs and CNT/Gd nanotubes are observed at the same voltage U=1V. For MWCNTs nanotubes at voltage 1 V under illumination with wavelength equal to 715 nm, the maximum sensitivity value is observed. Moreover, at voltage 3V and illumination with wavelength equals 480 nm corresponded to the highest value. The doping led to a shift in the photosensitivity peak towards higher voltage values and a decrease in the wavelength.

The *I-V* curves for MWCNTs/Gd for wavelength equal to 640 and 720 nm showed weak photosensitivity for all investigated voltage ranges (1-9 V). For optoelectronic applications, the data about photoelectrical properties of carbon nanomaterials in the spectral ranges 800-900 nm and 550-900 nm is important. Mostly, these ranges can be overlapped and correspond to laser lines for different types of solid-state lasers. Also, the laser such as argon, krypton, helium-neon, and ruby with emission wavelengths 490 nm, 630 nm, and 690 nm motivated to investigate the photosensitivity of carbon nanomaterials

3. CONCLUSION

In this work, we reported the possibility of MWCNTs/Gd (10% gadolinium) for photocurrent generation for visible to near-infrared spectral ranges (400–900 nm) at bias voltages from 1 to 9 V which applied to the sample. The ability of Gd nanoparticles light absorption in broadband spectral range makes MWCNT/Gd nanocomposite more perspective for light-energy conversion in comparison with functionalized carbon nanotubes due to higher resistance to continuous optical excitation [23]. Our result can be perspective for photovoltaic and detector applications.

For wavelengths $\lambda \sim 720$, 760, 780 and 880 nm, the characteristics of the *I-V* curves at a voltage of 7.6 V show the maximum photocurrent value for the corresponding wavelengths. The maximum photocurrent value increases with increasing wavelength from 720 to 880 nm. The maximum value equals $I_p \sim 0.158 \,\mu$ A, which was also obtained for voltage 3 V and wavelength $\lambda \sim 480$ nm. A voltage value equals 1V leads to photocurrent generation in a wide spectral range. Approximation expressions for the *I-V* characteristics of gadolinium-doped multiwall carbon nanotubes (Gd 10%) were obtained using of MATLAB software.

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