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Influence of gadolinium doping on structural properties of carbon nanotubes

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The paper presents an analysis of SEM, EDX, Raman scattering, and FTIR of Gadolinium-doped multi-walled carbon nanotubes obtained by hydrothermal method. The morphological characteristics of the materials were studied and their compositions were analyzed. Hydrothermal doping of MWCNs with Gd causes the formation of 3D network architecture and sharply increases the content of oxygen surface functionality. An unidentified intense broad peak for Gd-doped material at 2940 cm^{-1} was observed. The defect state of Gd-doped MWCNTs was studied by Raman spectroscopy.

Keywords: carbon nanotube, gadolinium, SEM, EDX, Raman analysis, FTIR.

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Introduction

Gadolinium-doped multi-walled carbon nanotubes (MWCNTs) are a type of nanomaterial that has attracted significant interest due to their potential applications in various fields. The doping of gadolinium ions onto the surface of MWCNTs has been studied for potential use in biomedical applications. The incorporation of gadolinium ions onto the surface of MWCNTs has been shown to enhance the magnetic resonance imaging (MRI) contrast of the nanotubes, making them useful for biomedical imaging [1] and drug delivery [2]. Additionally, gadolinium-doped MWCNTs have also been studied for their potential in cancer therapy [3]. Gd-doped multi-walled carbon nanotubes also have shown potential as a sensor material due to their unique properties, including high surface area, chemical stability, and sensitivity to to various gases, including hydrogen, ammonia, and nitrogen dioxide [4]. The sensitivity of the material can be tuned by adjusting the concentration of Gd dopant amounts and the surface functionalization of the nanotubes. By functionalizing the nanotubes with biomolecules such as antibodies or enzymes, the material can detect specific biomarkers or pathogens in biological samples [5].

Overall, the unique properties of gadolinium-doped MWCNTs make them a promising candidate for various applications. However, further research is needed to optimize the material properties depending on the synthesis method. There are several approaches for synthesizing gadolinium-doped MWCNTs, such as co-precipitation, hydrothermal method, chemical vapor deposition (CVD), arc discharge, laser ablation, and chemical functionalization.

The «common synthesis» methods (co-precipitation, chemical vapor deposition) involves the precipitation of gadolinium ions on the carbon nanotubes during the high-temperature catalyst-supported decomposition of carbon source in a pressurized vessel at high temperatures and pressures. Another approach of Gd-doped MWCNTs

obtaining by hydrothermal route allow using the commercial or previously synthesized MWCNTs [6]. The advantage of hydrothermal approach is the simply control of the amount of Gd dopant by adjusting the concentration of gadolinium precursors in the reaction chamber. The doping of MWCNTs with Gd can be realized at respectively low temperatures [7] using previously tested methods for doping graphene materials [8].

This article presents the results of gadolinium-doped MWCNTs obtained using hydrothermal method. A feature of the presented research is the use of a reaction temperature of 220 °C (close to the temperature of Teflon decomposition). The resulting materials were characterized using various techniques, including scanning electron microscopy (SEM), FTIR, and Raman spectroscopy.

I. Experimental details

Multi-walled carbon nanotubes were prepared accordingly to the next protocol. Ferrocene (0.3 g) and thiophene (0.6 ml) were dissolved in 15 ml of xylene to prepare the catalyst precursor solution. The solution was added to a flask and heat it at 100 °C for 1 h under stirring to evaporate the solvent and obtain a dry catalyst precursor. The catalyst precursor was loaded into a quartz vessel and transferred to the center of a quartz tube furnace preheated to 900 °C under an argon gas flow. Once the furnace reaches the desired temperature ethanol was introduced into the furnace using a syringe pump at a flow rate of 0.5 ml/min for 20 min. After the furnace cooled down to room temperature under argon flow the quartz vessel was removed from the furnace and MWCNTs were treated with a mixture of HCl and HNO_3 to remove any residual catalyst. The MWCNTs were rinsed with deionized water several times to remove any residual acids. At the final stage obtained product was washed with ethanol and dried at room temperature for 12 h.

Gadolinium-doped multi-walled carbon nanotubes (Gd-MWCNTs) was obtained using a hydrothermal approach.

Gadolinium nitrate hexahydrate (0.1 g) was dissolved in 50 ml of deionized water and stirred for 30 min to prepare the solution. 1 g of previously obtained MWCNTs was added to the $Gd(NO_3)_3 \cdot 6H_2O$ solution and sonicated for 1 h to obtain a homogeneous mixture. NaOH (2.5 g) was added to the MWCNTs / $Gd(NO_3)_3 \cdot 6H_2O$ mixture and stirred for 1 h to adjust the pH to about 12. The obtained colloidal solution was transferred to a Teflon-lined stainless steel autoclave and heat it at 220 °C for 12 h. After autoclave cool down to room temperature precipitate was filtered and a black solid product was collected. The product was rinsed with deionized water and ethanol several times to remove residual impurities. The product was dried at 60-70 °C for 12 h.

The resulting MWCNTs and Gd-MWCNTs were characterized using various techniques, such as scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS), and Raman spectroscopy. Raman spectra were measured on a confocal Raman spectrometer Nanfinder 30 (Tokyo Inst., Japan) with a 532 nm Nd:YAG laser (resolution about 0.5 cm^{-1}). The laser irradiation power was less than 1 mW/sm^2, which made it possible to avoid local overheating of the samples. SEM and EDX analysis was carried out using a Scanning Electron Microscope by JEOL (Oxford Instruments,15 kV SEI, WD equals 4,5mm). Fourier-IR absorption spectra of carbon nanotube samples were obtained in the range of 4000-1000 cm^{-1} on a Varian-640IR IR spectrometer. The mixture of MWCNTs or Gd-MWCNTs and KBr (1:300 mass ratio) after vibrating milling was pressed into pellets (50÷100 μm) and measured in the transmission mode.

II. Results and discussion

SEM investigations provide valuable information about the morphology as well as structure of MWCNTs, which is useful for understanding their physical and chemical properties and verifying the synthesis results. Figure 1, a-b shows the SEM of MWCNTs and Gd-MWCNTs samples, respectively. Both doped and non-doped MWCNTs show a foam-like morphology. The nanotube diameters in a range of 15-20 nm while the length could reach tens of micrometers were observed. The decrease of average diameter to 12-15 nm for Gd-doped MWCNTs is observed with simultaneous growth it tortuous compared to the non-doped sample. Gd-MWCNTs are wavy, entangled, interconnected with each other, and assembled into 3D net-work architecture. Similar morphology was analyzed in [9].

Table 1.
EDX data of elemental composition of MWCNTs and Gd-MWCNTs samples

No.	Sample	C Weight %	O Weight %	Gd Weight %
1.	MWCNTs	100	0	0
2.	Gd-MWCNTs	90	9,5	0,5

EDX analysis of pure MWCNTs shows the presence of carbon only with the trace Si (Fig. 1a, Tab.1). As well as the elemental analysis of the Gd-doped MWCNTs demonstrates the presence of C, O, and Gd which is an indication of surface functionalization with an oxygen-contained species as a side effect of the decoration with Gd (Fig. 1b, Tab.1). The presence of Si is a result of thermal treatment in a ceramic vessel. The additional possible reason for oxygen present is the presence of Gd_2O_3 clusters on the surface of the MWCNTs but it's only a minor factor taking into account the mass ratio of oxygen and gadolinium (9.5 and 0.5 mass %, respectively).

FTIR analysis was used to probe the surface functional group's presence for MWCNTs and Gd-MWCNTs samples (Fig.2). The broad peaks observed around 3400 and 1610 cm^{-1} correspond to the O-H stretching and bending vibration of hydroxyl groups [10]. At the same time, these peaks are completely missing for Gd-MWCNTs which indicates the absence of surface hydroxyl functionalities. The sharp band at 1350 cm^{-1} also is attributed to the presence of hydroxyl groups (-OH) on the MWCNT surface (the presence of carboxylate groups –COOH is also possible) [11].

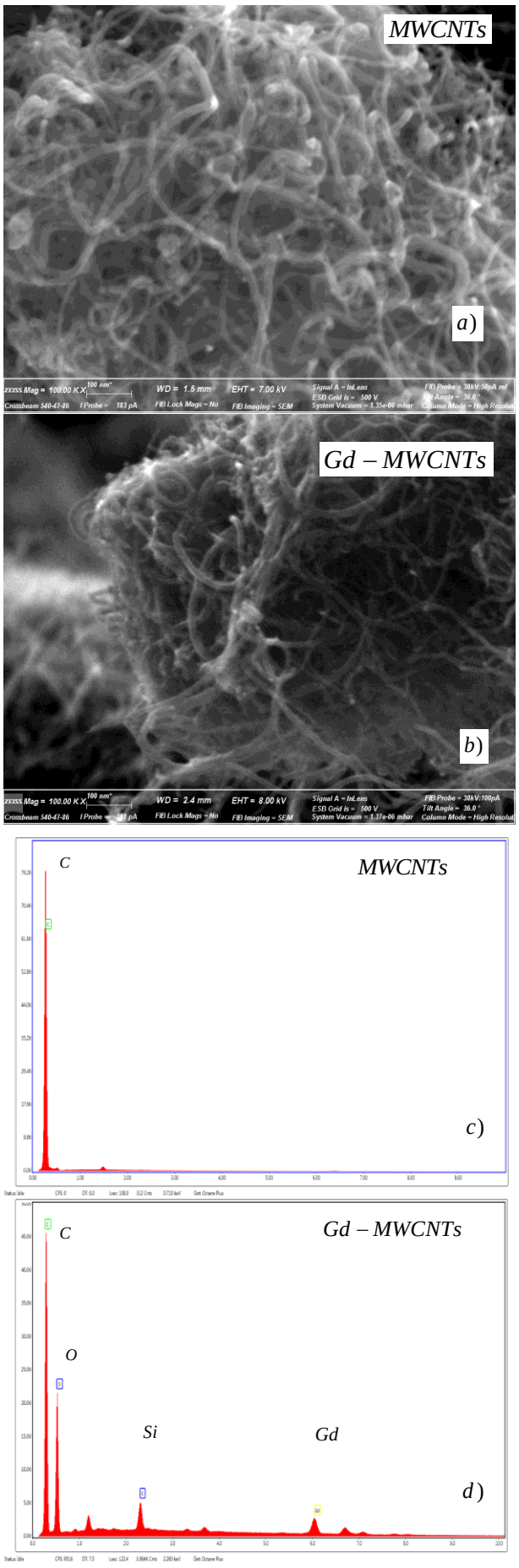

Fig. 1. SEM images (a-b) and EDX spectra (c-d) of MWCNTs and Gd-MWCNTs samples.

The peak at 1350 cm^{-1} is only traced for Gd-MWCNTs. Two intense broad peaks for this Gd-doped material are observed around 2940 and around 1900 cm^{-1} (Fig. 2). The first one can correspond to the overlapped peaks due to the presence of $C(sp^3)$-H bonds [12]. The other characteristic is not typical for MWCNT and can be attributed to the structural changes induced by the Gd-doping process.

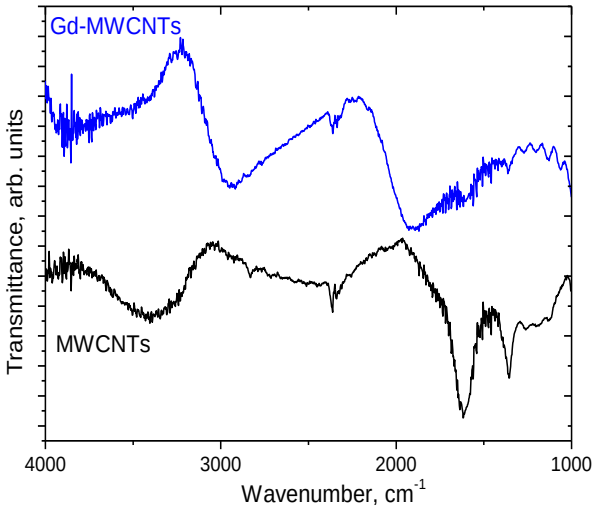

Fig.2. FTIR spectra of MWCNTs and Gd-MWCNTs samples.

For the characterization of the defect structure of MWCNTs and investigation of the influence of Gd doping the Raman spectroscopy was used [13]. Raman scattering spectra for MWCNTs and Gd-MWCNTs samples and also the Lorentz functions deconvolution results are presented in Fig.3.

The spectra consist of two intensive G and D peaks. The G-peak is a first-order high-frequency mode E_{2g}. Its feature for MWCNTs is splitting into two bands: G and its small high-frequency shoulder D'. The last line is associated with disorientation in carbon nanotubes [14]. Disordering and defects in nanotubes are also observed in bands I, D, and D". The I band is observed for nanotubes with a highly disordered structure and is recorded as a low-frequency shoulder of the D band [15]. Despite the D and D" bands being associated with the presence of structural defects, they have different origins. The D" band takes place when the packaging of a regular layer of graphite is broken by the defects (breaks of graphene sheets in nanotubes and graphene flakes). The D band is associated with lattice disorder or finite-size effects [16]. The analysis of Raman spectra shows that the ratio of intensities of the G and D peaks (I_G/I_D) increases after Gd doping, which indicates a decrease in defects [17] in MWCNT. The 2D and D+G lines were determined as second-order overtones, the presence of which is characteristic of such structures.

The peak intensity ratio I_G/I_D can indicate the level of disorder in graphite structure. Based on a unique opportunity from 2D peak for the characterization of graphene layers number the increasing ratio I_{2D}/I_D for Gd-doped MWCNT can indicate a decrease in the number of graphene sheets.

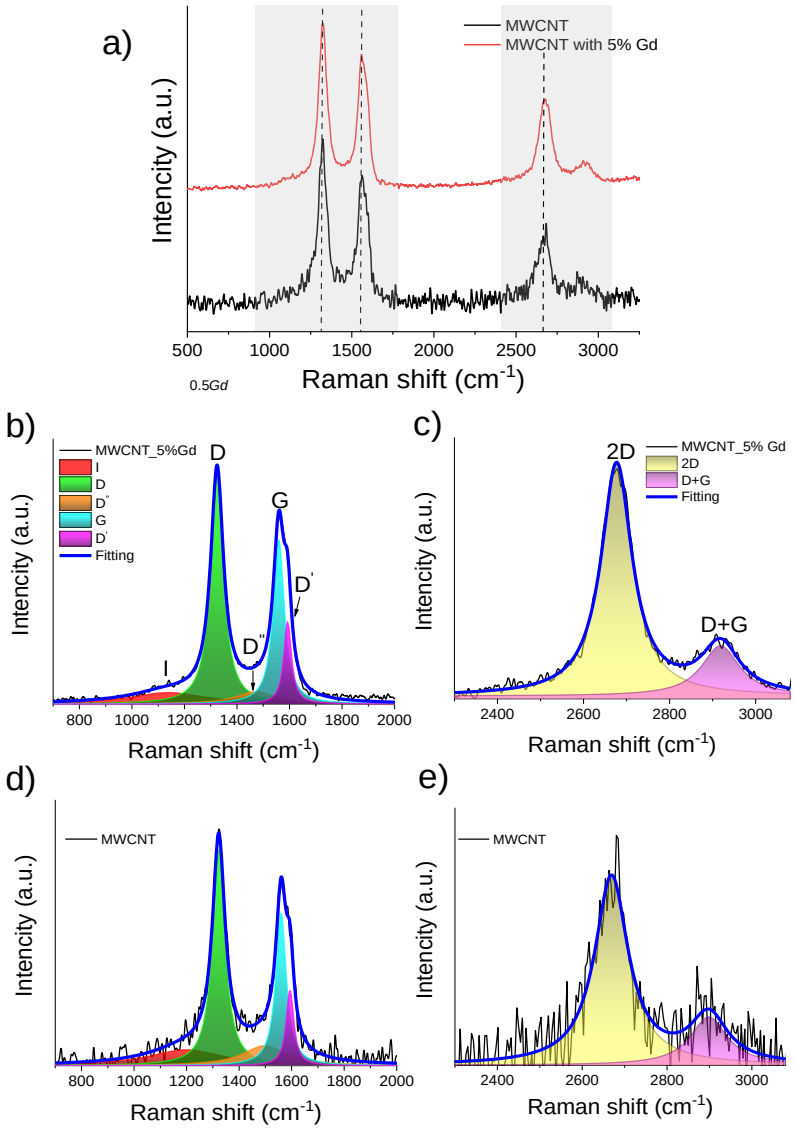

Fig.3. Raman spectra (a) and corresponding results of spectra deconvolution (c-e) for MWCNTs and Gd-MWCNTs samples.

Table 2.

The Raman Spectra Parameters of MWCNTs and Gd-MWCNTs samples

Raman mode parameters, cm^{-1}	MWCNT	5% Gd doped MWCNT
I (peak position)	1198	1138.2
FWHM	343.8	349
D (peak position)	1322.4	1324.1
FWHM	57.9	58.9
D''(peak position)	1496.9	1472.9
FWHM	203.5	185.9
G (peak position)	1559	1559.3
FWHM	48.5	51.2
D' (peak position)	1594.1	1593
FWHM	35.2	35.5
2D (peak position)	2668.9	2676.9
FWHM	95.9	87.5
D+G (peak position)	2898.5	2918.3
FWHM	106.5	107.5
I_G/I_D	0.59	0.63
$I_G/I_{D'}$	2.77	2.87
I_{2D}/I_G	1.18	1.26

The properties of Raman scattering analyzes of the studied samples$_{0.5Gd}$ were analyzed and, as can be seen from the results of the studies, changes in the intensities in the scattering spectra and displacement of the peaks at higher frequencies are observed. The change of the peaks in the Raman scattering spectrum is related to the change in the concentration of defects.

The fitting procedure of D and G bands with Lorentzians peaks using OriginPro software allow to calculate the ratio of I_D and I_G integral intensities. These data were used for the average size of graphitic fragments along the basal plane (002) estimate [18]: $L(nm) = (2.4 \times 10^{-10})\lambda_{0.5Gd}^4 \left(\frac{I_D}{I_G}\right)^{-1}$, where λ is the laser excitation wavelength. In all cases, the average lateral size of graphitic fragments for both samples are close to 20.0±0.3 nm so the doping procedure probably doesn't affect dramatically on the structural properties of the materials

Conclusion

Gd-doped multiwall carbon nanotubes (average Gd content of 0.5 mass %) were obtained by hydrothermal approach (220 °C for 12 h) on the base of previously synthesized MWCNTs (catalytic ethanol decomposition at 900 °C in argon gas flow was used for CNT synthesis). Hydrothermal doping of MWCNs with Gd causes the formation of 3D network architecture and the presence of oxygen-contained surface functionality (oxygen content of about 9 mass %). Simultaneously the hydroxyl group content for doped material is insignificant compared to the origin MWCNs. The unidentified intense broad peak for Gd-doped material observed around 2940 cm-1 can be the result of both doping- and hydrothermal treatment-induced structural changes. The growth of defect concentration for Gd-doped MWCNTs was observed by Raman spectroscopy, but the changes in average lateral sizes of graphene crystallites (along (002) basal plane) were not observed.

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Вплив допування гадолінієм на структурні властивості вуглецевих нанотрубок

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В роботі здійснено систематичне вивчення методами SEM, EDX, комбінаційного розсіювання та FTIR багатошарових вуглецевих нанотрубок легованих гадолінієм, отриманих з використанням гідротермального методу. Досліджено морфологічні характеристики матеріалів та проаналізовано їх склад. Гідротермальний варіант легування багатошарових вуглецевих нанотрубок гадолінієм викликає формування тримірної архітектури матеріалу та різко підвищує вміст поверхневих функціональних груп. Спостерігався неідентифікований інтенсивний широкий пік для матеріалу, легованого Gd при 2940 $см^{-1}$. Методом комбінаційної спектроскопії досліджено дефектний стан багатошарових вуглецевих нанотрубок легованих гадолінієм.

Ключові слова: вуглецеві нанотрубки, допування гадолінієм, CEM, EDX, Раманівська спектроскопія, FTIR.