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Polarization-dependent optical reflection from vertically aligned multiwalled carbon nanotube arrays

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ABSTRACT

Optical reflection from an array of vertically aligned multiwalled carbon nanotubes (MWCNTs) acting as a black body absorber was investigated. We present the novel results of the experimental analysis of specular reflection involving the different light polarization configurations and wavelengths from visible and near infrared range. It was shown that with the increasing incidence angle, reflectance rises dramatically and is highly dependent upon the polarization state of the incoming light. Our results indicate that popular antenna model commonly used for explaining optical properties of MWCNTs must be applied with care when referenced to nanotube arrays.

The development of manufacturing methods of carbon nanotubes has allowed for creating very complex structures based on this carbon material [1]. One of them are arrays of vertically aligned MWCNTs possessing exceptional optical properties which are strongly dependent on the physical parameters of an array [1,2]. Such structures can be as close to a perfect black body absorber as no other manmade material. This was demonstrated e.g. in [3] where the authors reached the light reflection level of 0.045%. However, in case of MWCNT arrays the analysis of optical reflection available in the literature is mainly limited to diffuse reflectance and concerns only the polarization state of incoming light [3,4]. In this letter, we focus on specular reflectance measurements with the investigation of the polarization state of both incoming and reflected light. In addition, it is demonstrated that the high structural quality of MWCNT array is not the necessary condition for obtaining the reflectance values below 0.1% (for almost normal incidence). This is promising information both from the manufacturing and application point of view.

During the experiments, we used the sample of vertically aligned MWCNT array with the random distribution of nanotubes (site density $\sim 10^9/\mathrm{cm}^2$) with the average diameter $\sim$ 40 nm and the length $\sim$ 1.5 μm. The array was manufactured by plasma enhanced chemical vapor deposition method and the nanotubes were grown on a polished stainless steel substrate covered with a 1 μm thick chromium layer (Fig. 1a). The quality of the structure of tubes and their alignment can be assessed by looking at the integrated intensities ratio

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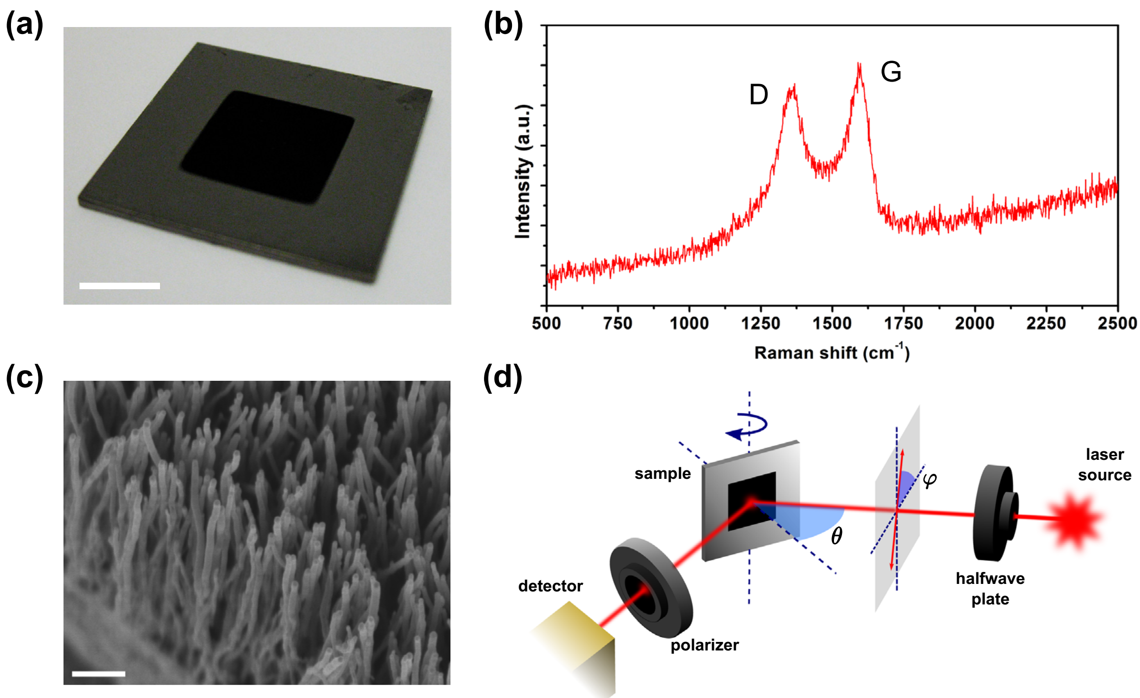

Fig. 1 – (a) Real photograph of the sample, the scale bar equal to 5 mm. (b) Raman spectrum of MWCNTs forming the array (laser line 514 nm). (c) SEM image of the array, the scale bar equal to 300 nm. (d) Experimental setup for the reflectance measurements.

of D to G bands (positioned respectively at 1360 cm^{-1} and 1588 cm^{-1}) on the Raman spectrum (Fig. 1b) and the SEM image (Fig. 1c). The mentioned ratio is equal to about 2 what suggests the presence of a significant amount of structural defects or amorphous carbon [5]. The deviations from the model of an ideal array are also seen on the SEM image as the tubes are not perfectly aligned with respect to each other and some of them are of irregular shapes. The influence of such kind of misalignment on optical properties of MWCNT arrays can be also studied in a more qualitative way [6].

Reflectance, defined as the ratio of the reflected and incoming light intensities (I_R/I_0), was calculated based on the measurements carried out with the use of the setup presented in Fig. 1d. The polarization of the incoming light is linear and its state (described by the φ angle) was changed from p-type ($\varphi = 0°$) to s-type ($\varphi = 90°$). The light is directed at the array at an incidence angle θ which was controlled by means of a rotational holder that the sample was placed in. For the investigated array, specular reflection was the dominant process as the specularly reflected light was much more intense than the total diffusely scattered light. In consequence, intensity of almost all reflected light was measured by a photodetector placed at the angle equal to the incidence one. It should be emphasized that whether specular or diffuse reflection is observed depends on the structural parameters characterizing an array and the nature of this dependence can be quite complex. The polarizer shown in Fig. 1d was used for analyzing the polarization components of the reflected light what is discussed later.

Fig. 2 presents specular reflectance of investigated MWCNT array for θ angles from 10° to 80° (the consequence of the optical setup architecture) for visible radiation wavelengths ($\lambda = 514$ nm, 633 nm) and near infrared one ($\lambda = 1064$ nm). The obtained patterns for both p and s configuration demonstrate the behavior similar to an exponential increase, especially for the range of larger θ values. This leads to the difference between reflectance for extreme incidence angles reaching two orders of magnitude (e.g. 0.07% and 17% for $\lambda = 514$ nm). As the wavelength increases the reflectance also shows the growing tendency for both types of polarization. Higher reflectance for p polarization, observed for larger θ, can be understood as the consequence of high anisotropy of nanotubes. The same behavior was reported in case of inelastic scattering of light for a single MWCNT [7] .

From the insets in Fig. 2, it is clearly visible that s-polarized light (polarization perpendicular to a single tube axis) gives the higher reflectance for the lower values of the incidence angle. This is the unexpected result in the view of the popular antenna theory which states that a nanotube should reflect more effectively the light polarized along its axis [8]. What is more, there exists a particular incidence angle θ_0 for which the reflectance is the same regardless of the polarization of incoming radiation. This value might be understood as the characteristic feature of an array, possibly being a function of the wavelength and the structural parameters. The presented results are in qualitative agreement with the theoretical calculations (based on finite difference time domain method) [9] predicting the patterns of $I_R(\theta)$ for arrays of tubes of 1 μm length. In particular, it concerns the similar θ_0 values and lower reflectance in case of s-polarized light for angles lower than θ_0. It should be also noted that results obtained in [9] using Maxwell–Garnett model demonstrate different, more typical behavior of $I_R(\theta)$. This confirms the assumption that various structural features of an array, neglected by the

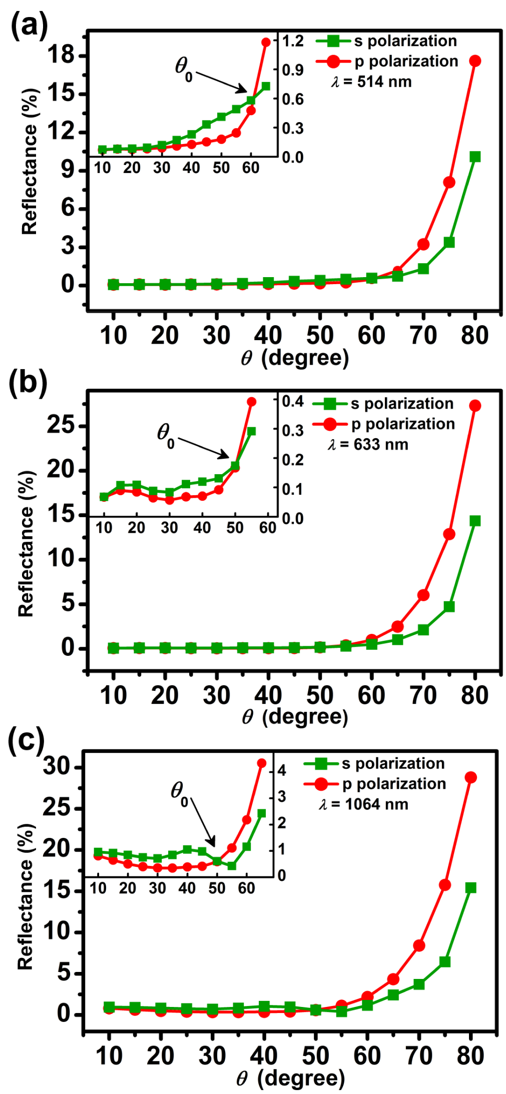

Fig. 2 – Specular reflectance for different incidence angles for s- and p-polarized incoming light with three radiation wavelengths: 514 nm (a), 633 nm (b) and 1064 nm (c). Insets show the range of low θ angles with θ_0 indicated for each wavelength.

Maxwell–Garnett model, play a key role in determining a value of θ_0. Because the mentioned calculations were performed only for one specific set of array parameters then formulating further conclusions about this quantity would require more detailed studies. Interestingly, also the experimental results achieved for singlewalled nanotube arrays demonstrate the reflectance dependencies similar to presented in Fig. 2 [10].

Now we turn our attention to the polarization of the light reflected from nanotubes forming the array. In order to determine its state, the full experimental setup (including the polarizer) shown in Fig. 1d was used. After repeating the same procedures as for the specular reflectance measurements, it turned out that the reflected light is polarized in practically the same way as the incoming light. This observation (the same for different places on the sample) was valid for the whole θ range and also for all used wavelengths. Quantitatively, we estimated that when the array is illuminated with the light of a given polarization (s or p) then over 99% of the reflected light exhibits that specific polarization. Thus, expecting that light reflected from MWCNTs forming the array should be polarized only along tubes axis is unjustified. This is one of the subtle aspect of antenna theory applied to MWCNT arrays. It is worth mentioning that above result stands in opposition to the results presented in [9]. However, one has to note that the experimental conditions and structural parameters of the samples are not the same in both cases and this accounts for differences in the results.

In conclusion, the polarization-dependent optical reflection from the random array of MWCNTs was investigated experimentally. Both for the visible and the near infrared range, the obtained reflectance patterns exhibit some peculiarities which at first sight may seem to be contradictory to antenna theory. We also confirmed that the reflectance values below 0.1% can be reached even for MWCNT array with different structural defects. Our results are in qualitative agreement with the theoretical calculations and bring the new insight into the issue of optical properties of MWCNT arrays.

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