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Limitations of blackbody behavior of vertically aligned multi-walled carbon nanotubes arrays

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ABSTRACT

Reflection spectra for the arrays of vertically aligned multi-walled carbon nanotubes (MWCNTs) in an extremely broadband spectral range (up to half a millimeter) are presented. Using Fourier transform infrared spectroscopy it is shown that in some conditions, the material generally regarded in the literature as a promising candidate for a blackbody, dramatically losses its anti-reflection properties when stepping into infrared range of the electromagnetic spectrum. The experimental results confirm that structural parameters of an array are the key factor responsible for the discussed properties and decide about the spectral extent of a low reflectance level.

1. Introduction

As far as the research on arrays of carbon nanotubes (CNTs) is concerned, a lot of attention has been recently paid to the description on how these systems interact with electromagnetic radiation. The literature delivers both theoretical and experimental analysis of such issues like absorption and reflection spectra [1–3], antenna effect [4,5], or interference effects [6,7], all referring to arrays of vertically aligned CNTs. Among the frequently addressed topics is blackbody behavior of such systems [1,8]. It was experimentally shown [9] that the total reflectance for the vertically aligned MWCNTs film for a wavelength of 633 nm can be as low as 0.045%, what is considered to be the lowest ever reported value for any material. Other authors (e.g. [2]) emphasize the fact of a wide spectral range of a low reflectance level. However, there are practically no works showing how reflective properties of MWCNTs arrays can significantly change when a length of the nanotubes is not of an order of hundreds of microns but several ones instead. The filling of this gap is one the purposes of the letter.

2. Material and methods

In our experiments we used commercially available (NanoLab inc.) samples of vertically aligned MWCNTs grown via chemical vapor deposition method on silicon substrates covered with 1 μm thick chromium layer. Three different samples (A, B, C) of various structural parameters were investigated during the measurements. The samples A and B were random arrays (no specified pattern of tubes placement) with approximate nanotubes diameter of 70 nm (both samples) and length 1.5 μm (A) and 5 μm (B). With the site densities equal to 10^9 /cm^2, these parameters correspond to the filling factor of about 7%. In contrast, the sample C was the array of vertical, mutually supported MWCNTs of length of about 10 μm and diameter of about 20 nm. In this case, the site density of 10^{11} /cm^2 gives rise to the high value of filling factor equal to ~50%. The images of all three samples from a scanning electron microscope are presented in Fig. 1.

The measurements of reflectance (the ratio of reflected and incident radiation intensities) were carried out at room temperature using Bruker 113v vacuum Fourier transform spectrometer with the pyroelectric DTGS (deuterated triglycine sulfate) detectors. As a radiation source Globar and Hg-ARC lamp were used. For the measurements of all three samples the geometrical configuration of the optical paths were the same. Incidence angle was equal to about 8° and no specific polarization state of radiation was provided.

3. Results and discussion

For all investigated samples the reflectance spectra collected for wavelengths from 1.5 μm to about 470 μm are presented in Fig. 2. In the spectral range up to 5 μm the reflection level does not exceed 10%, with the lowest value of about 0.4%, reached for the sample C (mutually supported tubes). Moving into the higher values of the radiation wavelength we observe the drastic increase in reflectance.

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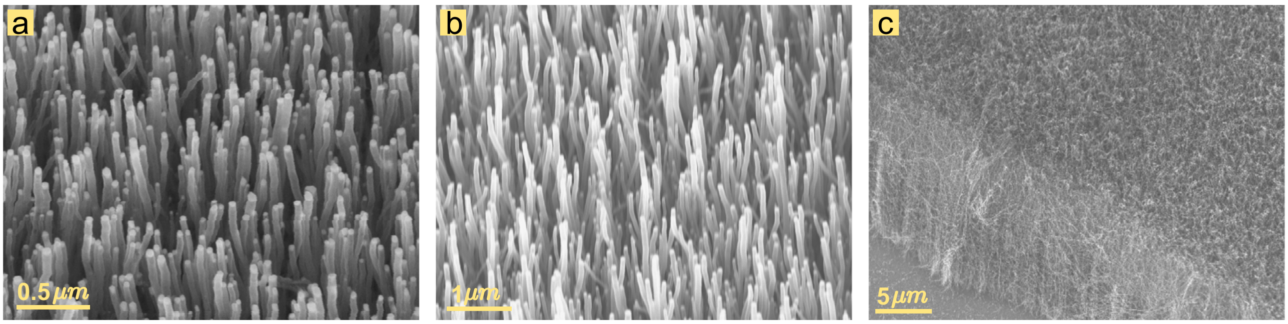

Fig. 1. The images of the investigated samples of vertically aligned MWCNTs from scanning electron microscope. Images a, b, c correspond to the samples A, B and C.

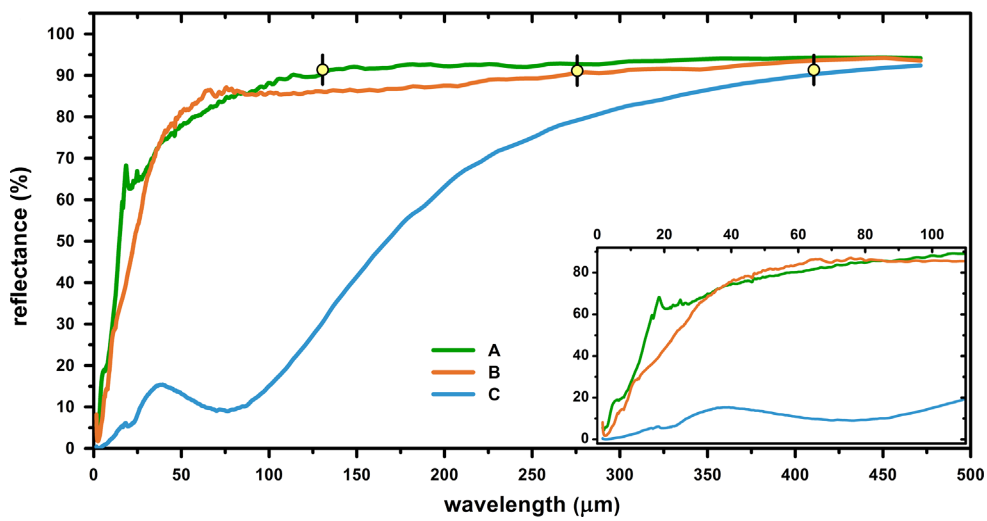

Fig. 2. The reflection spectra of the MWCNTs arrays of different heights in a broadband spectral range. The markers indicate the saturation wavelengths. The inset shows a range of the wavelength from near and mid infrared.

These changes are the more dynamic the longer are the tubes forming the sample. In order to demonstrate it more quantitatively one can introduce a term of the saturation wavelength, defined as the wavelength which corresponds to the reflectance level of 90%. For arrays A, B and C, the trend in tubes length is clearly seen in their saturation wavelengths which are respectively equal to about 115, 265 and 405 μm (see markers on spectra in Fig. 2). Approaching the terahertz region, all the spectra show the little growing tendency and the difference between three curves is slowly decreased.

The presented results, to the best of our knowledge, are the first experimental demonstration of the limitations which are imposed on MWCNTs arrays if they are supposed to be considered as a blackbody material in the wide spectral range. Some authors suggest that the crucial factor for obtaining the extremely low reflectance of nanotubes arrays is a low density of such systems (e.g. [10]). Meanwhile, the samples A and B are the typical examples of low density nanotubes forests and the fulfillment of this condition is not translated to low reflectance in the broadband range. Taking into account the complex nature of interactions between electromagnetic radiation and a MWCNTs array, it becomes obvious that discussion about the one major structural parameter responsible for the optical properties of such systems is still open. Nevertheless, it seems that one of the most important issues, suggested in [10] is a length of the tubes constituting the array.

The requirements as to the length are connected with the fact that the radiation entering the array undergoes multiple reflection and absorption acts. The number of such processes strongly depends on the length of the tubes what explains the tendency shown in Fig. 2. When the height of an array is not long enough then the radiation reaches a substrate (see [11]) and after being successfully reflected is reemitted, giving rise to the significant reflectance. For the confirmation of the above reasoning, one can compare the reflectance spectra of the samples A and C with the spectra of the respective substrates which the arrays were grown on (Fig. 3). It is easily seen that in case of the sample A, some features on the substrate spectrum are transferred on the array spectrum (e.g. the local maxima around 17 μm). Therefore, the total optical response is highly determined by the properties of the substrate. For the sample C (the thickest and the densest array) the influence of substrate on the reflectance signal is practically negligible but it does not change the fact that the reflectance quickly reaches considerable values in the mid- and far-infrared.

It seems then, that the key factor for observing blackbody behavior in the wide spectral range is above all the complex internal structure of arrays which allows for trapping the radiation inside a nanotubes forest. The detailed analysis of single parameters affecting the optical response of nanotubes arrays is beyond the scope of this letter however it opens the space for further research in this area.

4. Conclusions

To sum up, we showed for the first time that reflectance spectra of vertically aligned MWCNTs can significantly evolve its form, mainly depending on a length of the nanotubes. By performing the measurements in the ultra broadband spectral range it was found that the reflection level drastically increases in the range of

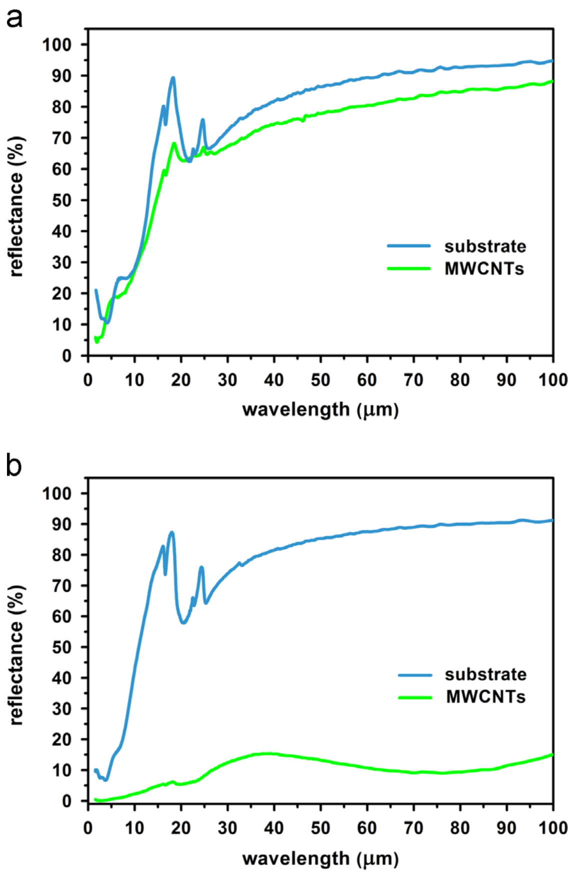

Fig. 3. The comparison between the reflectance spectra of MWCNTs arrays and their substrates for the samples A (a) and C (b).

mid-infrared and the rate of these changes is strictly related to the structural parameters describing the arrays. In the terahertz region the reflectance spectra become saturated and the samples reflect practically all the incoming radiation. Thus, the general statements concerning blackbody behavior of MWCNTs arrays must be formulated with care and should always emphasize the crucial role of structural parameters, especially a length of nanotubes.

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