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# Cloaking by π-electrons in the infrared

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Hybrid materials composed of single walled carbon nanotubes (SWCNTs) as hollow containers and small molecules as fillers possess intriguing physical and chemical properties. Infrared spectroscopy is a useful method in most cases to characterize hybrid systems; however, regardless of the type of small molecule encapsulated in the SWCNT, the IR spectrum of the hybrid system remains silent. The possible explanation involves the highly polarizable π-electron system of the SWCNTs. Image charges induced in the SWCNT walls cancel out the transition dipole moment of the molecular vibrations resulting in the cloaking of the material inside the nanotube. To confirm the role of the delocalized π-electron system in this process, insulating boron nitride nanotubes filled with $C_{60}$ were also investigated and found to be transparent to infrared radiation. We have also demonstrated the cloaking effect in two dimensions using a thin film of $C_{60}$ covered by single layer graphene. The significance of our results lies in the fact that the cloaking layer is a real material, not a metamaterial.

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**1 Introduction** "Cloaking," or hiding objects from incoming light, has been attempted with increasing success lately, extending our knowledge of fundamental optics and predicting useful real-world applications. Most efforts are centered on metamaterials with ingeniously designed dispersive properties, guiding the rays around the objects [1, 2]. A different kind of cloaking was found in carbon nanotubes.

In an earlier paper[3], we observed that in $C_{60}$ peapods the IR signal of $C_{60}$ disappeared on removing the adsorbed fullerene molecules, while all other methods proved their presence inside the tubes. The effect was reported by other groups as well [4, 5]. We tentatively explained this observation by the interaction of the extended π-electron system and the molecular vibrations, suggested previously by Setyowati et al. [6]. Here, we present additional control experiments on boron nitride-based peapods, where the delocalized π-electron system is missing. As expected from the model, the IR activity of the encapsulated molecules is preserved in this case. In contrast, the two-dimensional analogue,

graphene, shows a similar attenuation of vibrational modes as carbon nanotubes.

**2 Experimental** $C_{60}$@SWCNT peapods were prepared from arc-discharge nanotubes (P2 by Carbon Solutions, Inc.) by nanoextraction from supercritical carbon dioxide [3]. For the graphene experiment, $C_{60}$ was evaporated on a silicon substrate coated by 100 μm of gold and CVD graphene was transferred on top of the $C_{60}$ layer. Infrared measurements on peapods were conducted by a Bruker Tensor 37 interferometer equipped with a Helios ATR unit using a single-bounce Ge crystal in attenuated total reflectance (ATR) mode.

High resolution transmission electron microscopy (HRTEM) was done at the Nottingham Nanotechnology and Nanoscience Centre (NNNC–University of Nottingham).

Few walled boron nitride nanotubes were purchased from BNNT LLC (Newport News, VA, USA). Infrared mapping experiments on the graphene samples were performed at the SMIS beamline in Synchrotron Soleil. Raman mapping was
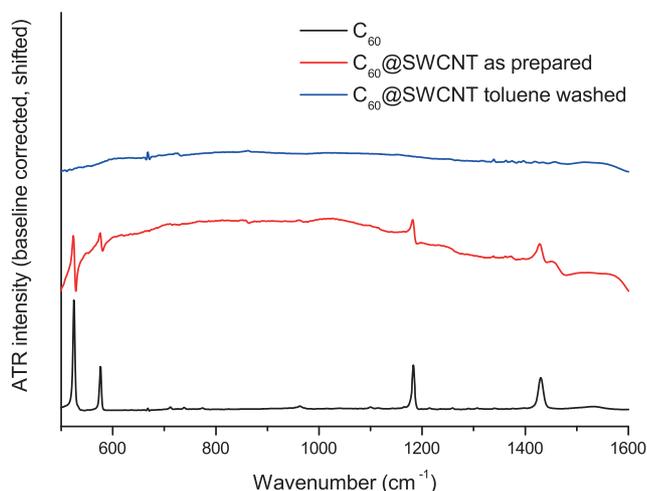
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**Figure 1** ATR-IR spectra of $C_{60}$ and $C_{60}$@SWCNT before (as-prepared) and after washing with toluene. After removing the adsorbed molecules, the spectrum shows no vibrational peaks of $C_{60}$.

also performed at Synchrotron Soleil using 532 nm laser excitation.

## 3 Results and discussion

**3.1 $C_{60}$@SWCNT** Figure 1 shows the infrared spectra of an as-prepared and a toluene-washed peapod sample, compared to that of $C_{60}$. The $C_{60}$ vibrational bands disappear when the adsorbed molecules are removed from the surface of the nanotubes; HRTEM (Fig. 2), Raman and UV spectra still prove the presence of encapsulated molecules [3].

The explanation we offer for the absence of the infrared signal on encapsulation was suggested earlier for adsorbed molecules on nanotube surfaces by Setyowati et al. [6] and supported by experiments and calculations on encapsulated molecules by Kazachkin et al. [4]. The main idea is the presence of induced mirror dipoles in the polarizable $\pi$-electron system of the nanotube, canceling the transition dipole moment during vibration [7]. On metal surfaces, this effect leads to the well-known surface selection rules enhancing the vibrational modes with normal coordinates perpendicular to the
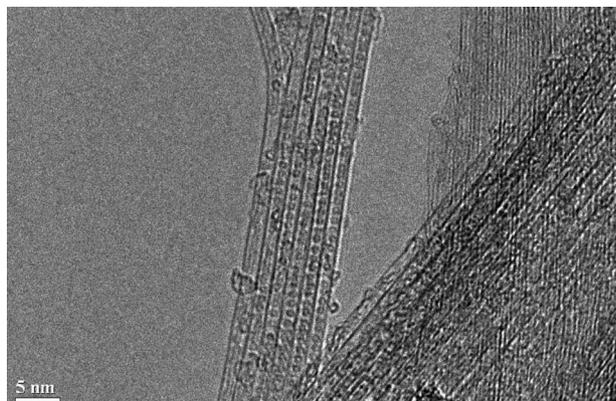


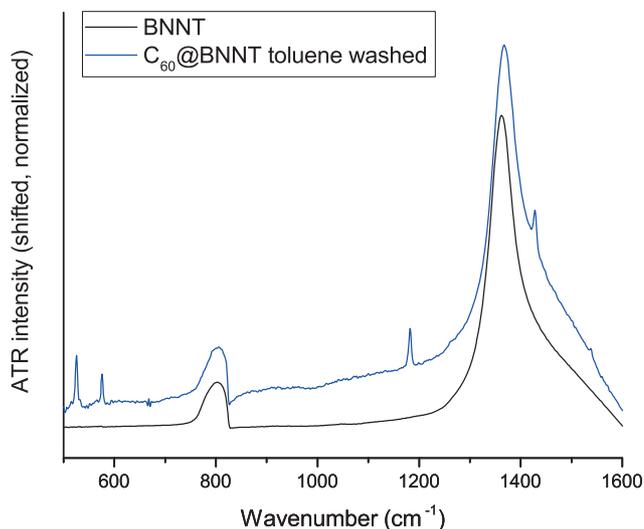**Figure 2** HRTEM image of $C_{60}$@SWCNT after toluene washing.



**Figure 3** ATR-IR spectra of boron nitride nanotubes (BNNT) and $C_{60}$@BNNT powder. $C_{60}$ vibrational modes are clearly discernible in the washed sample.

surface and attenuating the ones parallel to it; in the case of the cylindrical nanotube surface, however, each vibrational dipole can induce a mirror dipole and this mechanism leads to the disappearance of all molecular modes.

**3.2 $C_{60}$@BNNT** IR spectra of BNNT and $C_{60}$@BNNT are shown in Fig. 3. The encapsulated sample was washed with toluene and the HRTEM image (Fig. 4) does not show adsorbed molecules, but the four $C_{60}$ vibrational modes appear in the spectra. As the $\pi$-electrons in BNNT are much more localized on the N atoms than the $\pi$-electrons on the curved graphene-like sheet in carbon nanotubes, their polarizability is much less and the mirror charges do not appear on the surface. This leads to transparency in the infrared of the boron nitride tube walls.

**3.3 Graphene** The two-dimensional analogue of the above experiment is to study the infrared spectrum of a $C_{60}$ layer coated by graphene (Fig. 5).

Due to the poor adhesion of the graphene to the $C_{60}$ layer the maximum size of the graphene flakes that could be deposited was around 10 $\mu$m. To be able to characterize such a small sample with infrared microscopy we had to perform the measurements at a syncrhrotron facility.
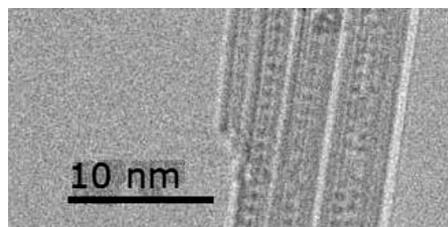


**Figure 4** HRTEM image of $C_{60}$@BNNT after washing with toluene. The surface of the tubes is free of adsorbed molecules.

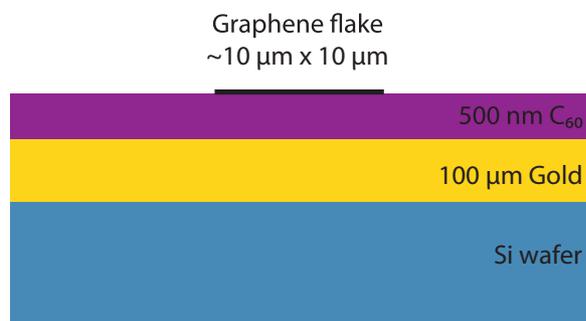Phys. Status Solidi B 253, No. 12 (2016)

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**Figure 5** Structure of the graphene-coated $C_{60}$ sample.



The sample was placed under the objective of an infrared microscope and the spectrum was measured in reflectance mode. The incident light passes through the graphene-coated $C_{60}$ layer, is then reflected from the gold surface and passes again through the layer to the detector. The patch-like structure of the graphene transferred to the $C_{60}$-coated sample enables reference measurements on the non-coated part.

Graphene is highly transparent in the infrared and does not show considerable reflectivity [8], therefore, the absorbance of the graphene and $C_{60}$ is additive. We can treat the graphene contribution as a background in the narrow region of the vibrational peak of $C_{60}$ and remove it. After correction, if there is no interaction between the two materials we do not expect to observe weakening of the $C_{60}$ absorption lines in the coated areas.

We chose a graphene flake of about $10 \times 10$ μm size and examined it with Raman mapping, shown in Fig. 6. The area proved to be sufficiently homogeneous.

Figure 7a shows the optical microscope image of the region containing the graphene flake. We have performed a series of infrared spectroscopy measurements along the line indicated on the image. The raw data were baseline corrected and fitted with a Lorentzian to extract peak height information (Fig. 7b).

Figure 7c shows the baseline corrected absorption at the $T_{1u}(4)$ IR mode of $C_{60}$ at 1429 cm$^{-1}$ along the cross-sectional
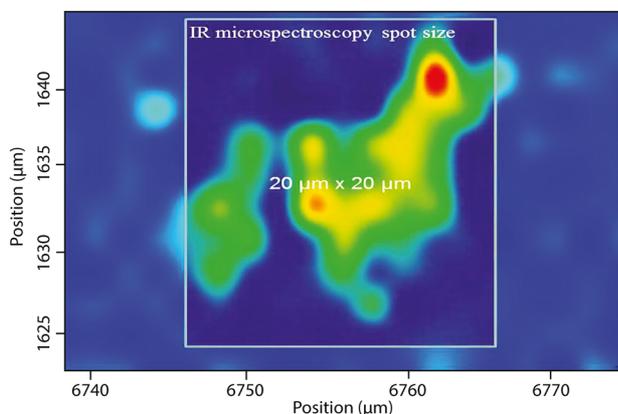


**Figure 6** Raman map of the graphene flake region, at the graphene 2D mode (2700 cm$^{-1}$).
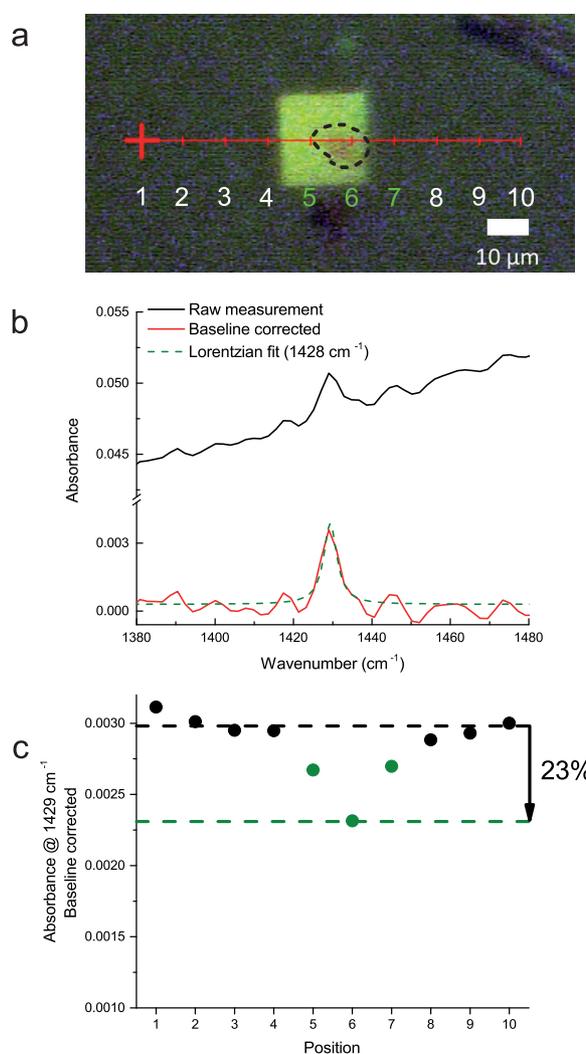
**Figure 7** (a) Optical microscope image of the sample indicating the measured positions along a line. The bright rectangle is the spot size of the IR measurement ($20 \times 20$ μm). The dashed black line highlights the single layer graphene area. (b) A single spectrum showing one of the $C_{60}$ vibrational peaks. The data was first baseline corrected then fitted with a single lorentzian. (c) The intensity of the lorantzians fitted to the IR absorption feature at 1429 cm$^{-1}$ along the line indicated on the map (a).

line indicated on the graphene flake image. A 23% decrease in absorption in the central position is found, although the conditions are in no way optimized: the light spot is larger than the graphene flake. We regard this result as proof of principle that graphene can indeed act as a cloak in the infrared region. In this two-dimensional case, carefully designed polarization-dependent experiments can help to clarify the situation further.

**4 Conclusions** We found a cloaking mechanism based on the interaction of dipoles with a polarizable $\pi$-electron system in graphene sheets both cylindrical (nanotubes) and

planar (graphene flakes). $C_{60}$ molecules can be effectively hidden either inside carbon nanotubes or behind a graphene sheet; this is different from metamaterials where the light is diverted from the object. The effect clearly deserves more attention and can lead to interesting applications on the nanoscale.

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