Charge properties and fractal aggregation of carbon nanotubes

Dmitry A. Zhukalin, Andrey V. Tuchin, Sviatoslav V. Avilov, Larisa A. Bityutskaya, Evgeniy N. Bormontov

Abstract—A theoretical and experimental investigation of the influence of internal electric fields on the fractal aggregation of short and long carbon nanotubes was made. Results show that the electric field occurred in the interface of C60–SWNT, and the nanotube length determined the presence of either a point charge (for short nanotubes) or a distributed charge (for long nanotubes).

Keywords—carbon nanotubes, interface, aggregation, electric charge, electric field.

I. INTRODUCTION

The aggregation process is one of the most important in nanotechnology. During aggregation a big number of interparticle interactions which are significant for composite and hybrid material synthesis take place. Generally, Van-der-Waals interactions, hydrogen and covalent bonds are characteristic for carbon nanotubes (CNT) [1,2]. Electrostatic interactions are of great interest at synthesis of self-organised structures based on CNT [3]. In a number of papers [4-6] the nanotubes' sensitivity to an external electrical field was discovered and studied. In the 500 Hz - 50 MHz frequency range at 10 V an orientation of CNT occurs in accordance with the field in different liquids. The current work is dedicated to theoretical and experimental studies on the influence of CNT's electrical activity [7] on their fractal aggregation[8].

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II. MODELING

Often armchair single-walled carbon nanotubes seem as a defect free cylindrical conductors with low resistance and without local charges. This approach is applicable for defect free, non functionalized infinite nanotubes. A capped SWCNTs have two general defects – tube caps. A calculation of the electronic structure of the capped SWCNTs were carried out by a semiempirical AM1 method in the Gaussian software

Let us consider the capped SWCNTs (5,5). Nanotube caps are two hemispheres of a fullerene C60 dissected perpendicular to a C5v axis. The interface boundary between a SWCNTs body and the cap includes two rings, where each of them consist of ten carbon atoms. The first ring is formed by hexagon sides of the nanotube body. The second ring is formed by pentagon sides of the cap (fig 1).

Fig. 1. Structural images of capped SWCNTs (5,5) and (0,9) (a). The mutual orientation of two C60 hemisphere of the capped SWCNTs (5,5) D5h and D5d symmetries (b) and SWCNTs (0, 9) D3h/D3d and D3 symmetries (c).

The charge distribution at the SWCNTs (5,5) interface cap/body is local. Atoms of the cap ring pull back the electron density from atoms of the nanotube body ring. The dependence of a module of the maximum effective charge is the non monotonic and rapidly converges to the constant value Qmax=0.017 (fig.2).
Caps of the SWCNTs (0,9) are hemispheres of the fullerene C60 dissected perpendicular to a C3v axis. The boundary between the cap and the nanotube body is formed by both hexagon and pentagon sides that lead to a less localized charge distribution than in the case of the SWCNTs (5,5). The module of the maximum effective charge increases with the length of the nanotube (fig.3).

Thus we have concluded, that the dependence of module of the maximum effective charge rapidly saturates with the length independently to the type and symmetry of nanotubes. The region of the charge that opens up strong electric fields (~108-109 V/m) can be considered as localized. Hence, the induced electric field affects the fractal aggregation of nanotubes.

III. EXPERIMENT

The CNT's fractal aggregation was studied in the point and distributed charge approximations. We used purified CNTs obtained by the CVD technique.

The CNTs were separated by length by sedimentation. A dispersion of CNTs in distilled water was dispersed in an ultrasonic bath (Bandelin SONOREX RK512H) at 45 °C for 10 minutes. Then the obtained dispersion was sedimenting for 5 days at 20 °C. The samples were probed from 3 levels (fig. 4): h; h/2; h/4. The solution was separated into fractions with the subsequent extraction of isotropic and anisotropic fractal aggregates of carbon nanotubes (A, B, C). Optic microscopy (NU-2E) and electron microscopy (JEOL JSM-6380) techniques were applied in order to study the topology of these fractal aggregates. An object-plate was used as substrate for optical microscopy studies. A flat conductive substrate was used for electronic microscopy.

Fig. 4. Sedimentation of the CNT conglomerate in distilled water. A: sampling level h; B: h/2; C: h/4.

Depending on the sampling level a hierarchy of clusters was observed, differing in morphology and size. Large anisotropic clusters were found at the h/4 level, isotropic and anisotropic clusters at the h/2 level and isotropic clusters at the h level.

The fractal dimension D and Anisotropy coefficient A were estimated from the microphotographs. The anisotropy coefficient was calculated as a ratio between the greatest cluster diameter to the greatest orthogonal axicon. The fractal dimension was calculated using the grid method.

It was found that with the increase of the CNT concentration in the dispersion, defined by the level h, the
fractal dimension is decreasing with the increase of the anisotropic aggregate percentage and the anisotropy coefficient (table 1).

Table 1. Fractal dimension versus sample probing level and anisotropy coefficient.

<table>
<thead>
<tr>
<th>level (h)</th>
<th>Fractal Dimension D</th>
<th>Anisotropy coefficient A</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>1.55</td>
<td>1, 1.4</td>
</tr>
<tr>
<td>h/2</td>
<td>1.5</td>
<td>1, 1.4</td>
</tr>
<tr>
<td>h/4</td>
<td>1.45</td>
<td>1, 2.1</td>
</tr>
</tbody>
</table>

The scale invariance of the studied fractal clusters was observed using SEM of light CNT dispersions from the pre-surface level (Fig. 5a). With further magnification (Fig. 5b) the morphology of the primary fractal CNT cluster is observed.

Fig. 5. SEM image (JEOL JSM-6380) of the CNT fractal clusters. A: fractal clusters (50-200 µm) X90. B: fractal clusters (0.5-2 µm) X33000

By characteristic lengths it was determined that the fractal clusters consist of solitary CNTs and their conglomerates.

IV. CONCLUSION

In isolated length-restricted closed SWNT the reorganization of charge occurs at the interface C60 - SWNT. The localization of the induced charge at the interface is determined by the location of the cap’s pentagons in relation to the tube’s hexagons at a very short distance in two layers. These charges create powerful electric fields (~ $10^8-10^9$ V/m). The dependence of the maximum effective charge module from the CNT’s length quickly reaches saturation, irrespective of tube’s symmetry. Therefore, similar mass quantities of short and long SWNT will cause a different charge reorganization in the surrounding medium. We can view short nanotubes as structures with a point charge, and long nanotubes as structures with a distributed charge and electrical fields at each end. Based on this difference in charge distribution, we propose a new interpretation of experimental results for CNT self-organization from water dispersion. With the increase of the CNT’s length their ability to aggregate reduces.

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REFERENCES