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Influence of Organic Functional Groups on the Electrical Properties of Carbon Black - A Theoretical Study

A. Chutia[1], Z. Zhu [1], R. Sahnoun[1], H. Tsuboi [1], M. Koyama [1], N. Hatekeyama[1], A. Endou[1], H. Takaba[1], M. Kubo [1], C. A. Del Carpio[1], A. Miyamoto[1, 2]

[1]Department of Applied Chemistry, Graduate School of Engineering, Tohoku University, 6-6-11-1302 Aoba, Aramaki, Aoba-ku, Sendai 980-8579, Japan
[2]New Industry Creation Hatchery Center, Tohoku University, 6-6-10 Aoba, Aramaki, Aoba-ku, Sendai 980-8579, Japan
*Phone: +81-22-795-7237 Fax: +81-22-795-7235 E-mail: miyamoto@aki.che.tohoku.ac.jp

1. Introduction

With the miniaturization of silicone based electronic devices there has been a massive hunt for new and novel compounds that can meet with future needs. The search for organic compounds for their application in future miniaturized electronic devices is no exception.

In the present investigation a theoretical investigation on the electrical properties of carbon black is carried out which has wide range of application e.g., in video and audiotapes where it adds pigmentation, electrical conductivity and other functionalities. The basic structural units (BSUs) in carbon black constitutes of graphene sheets that are concentrically arranged as aggregates. To these BSUs different kinds of organic functional groups like –COOH, –CHO, –OH and some other sulfur containing groups, are attached and these functional groups along with other in plane defects results in their unique electrical properties. This work presents a study on the dependence of conformational arrangements of these BSUs on the electrical properties of carbon black. For this study the models were constructed by considering graphene clusters with 17 fused phenyl rings each saturated with Hs at the edges and two organic functional groups i.e., –OH and –CHO.

2. Computational Details

Colors program, based on tight-binding approximation, was used for studying the electronic and the electrical properties of carbon black. In this program the total energy term is given by:

$$E=\sum_{i=1}^{N}\tfrac{1}{2}m_i v_i^2+\sum_{k=1}^{OCC}n_k\varepsilon_k+\sum_{i=1}^{N}\sum_{j>1}^{N}\frac{Z_i Z_j e^2}{r_{ij}}+\sum_{1=1}^{N}\sum_{j>1}^{N}E_{rep}(r_{ij}) \quad (1)$$

Where, the first, second, third and fourth terms in the right hand side of equation represents kinetic energies, eigenvalues, electrostatic interactions, and short-range exchange repulsions respectively. The electrical conductivity of the systems under investigation was estimated using the following equation; $\sigma = n\ e\ \mu$, where σ, n, e and μ represents electrical conductivity, number of carriers, elementary electrical charge, and mobility respectively. The details of the present methodology can be found elsewhere [1]. DMol^3 program was also employed for studying the electronic properties of the models under investigation. All the calculations by DMol^3 were performed using DNP basis set and GGA/PW91 exchange and correlation functional.

3. Results and Discussion:

Near-near conformations

First, investigations were carried out by placing the carbon black BSUs near to each other (See Fig. 1). For these investigations four different models were constructed. In the first model there are no organic functional groups on the edge of the graphene sheets and are fully saturated by hydrogen (Cln-Cln) (Fig. 1(a)), in the second, the functional groups namely –OH and –CHO are far away (Fr-Fr) (Fig. 1(b)), in the third the functional groups of one are near to the hydrogen terminated surface of the other (Fr-Nr) and in the fourth both the functional groups are near to each other (Nr-Nr).

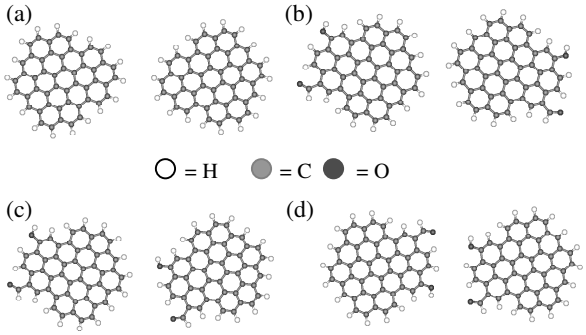

Fig. 1 Carbon black models (a) Cln-Cln, (b) Fr-Fr, (c) Fr-Nr and (d) Nr-Nr

Table I. Energy gap and electrical conductivity of carbon black models

Systems	Energy gap (eV)		Electrical conductivity (S cm^{-1})	
	Colors	DMol^3	Calc.	Exp.
Cln-Cln	1.909	1.897	0.2	0.2-10^2
Fr-Fr	1.777	1.692	17	
Fr-Nr	1.758	1.639	37	
Nr-Nr	1.765	1.676	28	

* Cln = clean, Fr = far and Nr = Near

In this investigation first, the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energy gap of all the models was considered. It was seen that with the inclusion of –OH and –CHO groups in the models the energy gap decreased in general. This decrease in energy is understood to have been due to the extra states of O 2p orbital appearing in the HOMO with the inclusion of the –OH and –CHO groups.

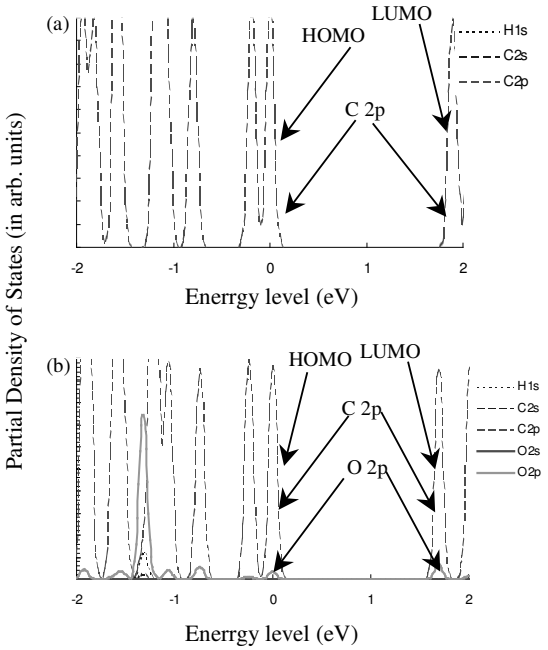

Fig. 2 PDOS for (a) Cln-Cln and (b) Fr-Nr models

For comparison the partial density of states for Cln-Cln model and Fr-Nr models have been shown in Fig. 2. But, though the chemical constituents of models b, c and d (in Fig. 1) are same they have different energy gap based on their conformations. The energy gap for model in which the functional groups of one carbon black BSU was near to the hydrogen terminated surface (Fr-Nr) was found to be least. The electrical conductivity of these models was then estimated theoretically (see Table I). From the estimated values for electrical conductivity it was seen that the electrical conductivity for all the models were in the experimental range [2] and the electrical conductivity for the model in which the organic functional groups were near the hydrogen terminated surface (Fr-Nr) was found to be highest. The lower energy gap and the higher electrical conductivity of this model can be associated with the slightly higher 2p orbital contribution of oxygen atoms in the Fermi level as compared to the other two models with –OH and –CHO groups.

Parallel Conformations

In various literatures it has been cited that the BSUs in the carbon black aggregates are also stacked over each other [3]. To investigate the influence of arrangements of functional groups on the stacked BSUs on the electrical conductivity three different models were investigated as shown in Fig. 3. Fig. 3(a) shows the first model in which one BSU is stacked over the other and has no functional groups. In this model the BSUs are only saturated with hydrogen. The second model is similar to the first but the BSUs are arranged in such a fashion that the distances between the –OH and –CHO groups are farthest (see Fig. 3 (b)) and in the third model the BSUs are arranged to have these groups near to each other (see Fig. 3 (c)).

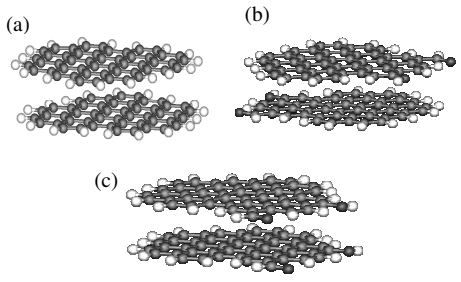

Fig. 3 Carbon black models (a) Cln-Cln, (b) Fr-Fr and (c) Nr-Nr

Table II. Energy gap and electrical conductivity of carbon black models

Systems	Energy gap (eV)		Electrical conductivity (S cm^{-1})	
	Colors	DMol^3	Calc.	Exp.
Cln-Cln	1.757	1.647	$\sigma_{\parallel} = 4.75$ $\sigma_{\perp} = 0.20$	$0.2\text{-}10^2$
Fr-Fr	1.687	1.539	$\sigma_{\parallel} = 4.99$ $\sigma_{\perp} = 0.39$	
Nr-Nr	1.645	1.493	$\sigma_{\parallel} = 5.08$ $\sigma_{\perp} = 0.56$	

From Table II it can be seen that the energy gap of the systems in general decreased with the modification of the carbon black models with –CHO and –OH groups and in particular the energy gap for the system in which the organic functional was nearest (Nr-Nr) is having the least energy gap. This least energy gap in this system too could be attributed to the higher contribution of O 2p orbital at the Fermi level.

The electrical conductivity was then estimated. The calculated values have been shown in Table II. In this study the electrical conductivity was estimated to the plane parallel ($\sigma_{\parallel}$) to the BSUs and plane perpendicular ($\sigma_{\perp}$) to the BSUs of the models. It was found that $\sigma_{\parallel}$ of the BSUs was higher than the $\sigma_{\perp}$. This can be attributed to the fact that in the planes the C-C atoms are strongly bonded by covalent bonds making it easier for the electrons to move while in the plane perpendicular to the BSUs the BSUs are weakly held by van der Waals forces with a distance of ~3.8 Å (calc.).

4. Summary and Future Direction:

In the present investigation the dependence of electrical properties of carbon black on the conformational arrangements of the BSUs was investigated. It was revealed that the electrical conductivity was dependent on the arrangements of the organic functional groups in the BSUs. A similar study is also carried out with sulfur-modified carbon black. A detailed discussion on this study will be presented in the conference.

References:

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