Title	Study on Nanoscale Electronic Properties of Molecule/SWNT Junction
Author(s)	Hong, Liu
Citation	大阪大学, 2012, 博士論文
Version Type	VoR
URL	https://hdl.handle.net/11094/25959
rights	© 2013 IOP Publishing
Note	

【14】

氏名	洪（ホン）　　流（リウ）　(Liu Hong)
博士の専攻分野の名称	博　士（理学）
学位記番号	第　２５６９２　号
学位授与年月日	平成24年９月25日
学位授与の要件	学位規則第４条第１項該当 理学研究科化学専攻
学位論文名	Study on Nanoscale Electronic Properties of Molecule/SWNT Junction （分子/SWNT接合におけるナノスケール電子物性の研究）
論文審査委員	（主査） 教　授　小川　琢治 （副査） 教　授　久保　孝史　　教　授　松本　卓也

論文内容の要旨

Since its discovery, single-walled carbon nanotube (SWNT) has attracted a lot of research interests due to its excellent electronic, mechanical, thermal and optical properties. As the SWNTs hybridize with molecules, new functionalities may appear which can afford to the development of nanoscale electronics. As one important electronic characteristic, current rectification plays a key role in the electrical applications like transistor, capacitor and diode. Though nanoscale rectification has been already observed at the molecule on SWNTs wiring, effective control of the rectification properties remains as an important research topic. The purpose of this thesis is to control the current rectification properties of the SWNTs complex by the physical adsorption of two different molecules including N,N'-bis(n-alkyl) tetracarbonatenaphthalenediimide (NDI), a planar electron acceptor molecule, along with phosphododecamolybdic acid (PMo_{12}), an inorganic cluster molecule of multi-electron redox capacity.

As-prepared SWNT was purified by hydrochloric acid and rinsed with deionized water. Purified SWNT and particle were sonicated in common organic solvents like dimethylformamide (DMF) or ethanol. After centrifugation, the supernatant was cast onto an insulated substrate (mica or silicon dioxide) and dried under the open air. Topography observation was performed by tapping mode AFM. After that, 30 nm-thick gold was thermally evaporated onto half of the substrate as an electrode. Electrical properties of the complexes were measured in nanoscale using point-contact current imaging atomic force microscopy (PCI-AFM). By using PCI-AFM, topography and *I-V* curve at every pixel of an AFM image can be obtained simultaneously with less damage of sample and cantilever during the scanning. In the measurement, bias was applied to the gold electrode evaporated on the substrate, while platinum-coated cantilever was grounded.

In the case of NDI/SWNT complex, by changing the length of alkyl chain of NDI derivatives, chirality distribution of the SWNT physically adsorbed by NDI differed largely. *I-V* analysis indicated that the majority of SWNTs adsorbed by C3-NDI (NDI derivative of isopropyl chains) was metallic, while semiconducting if C9-NDI (NDI derivative of nonyl chains). This difference in chirality distribution was due to the different packing densities of C3-NDI and C9-NDI on graphitic materials. Plateau width in the *I-V* curve of NDI/SWNT decreased with an increase of C3-NDI particle size, which was considered as the result of a shift in the vacuum level at the interface of NDI/SWNT. On the contrary, rectification ratio of the complex kept constant when the height of C3-NDI particle was below 3 nm, and increased with a further increase in the particle size. It was considered that the conduction mechanism was changed from tunneling conduction to Schottky-like conduction and their boundary was at about 3 nm size. Rectification effect of the SWNTs junction was discussed as well. In a SWNTs junction of which only one SWNT connected with gold electrode while the other did not, C3-NDI nanoparticle was adsorbed on the nanotube unconnected to the electrode. A large rectification was observed on the C3-NDI molecules, and the total rectification effect was considered as a combination of the rectifications induced by Schottky barrier at SWNTs junction and NDI/SWNT interface.

As PMo_{12} was adsorbed on SWNTs, rectification direction of the complex was dependent to the PMo_{12} particle size. The relationship between rectification direction inversion and the height of PMo_{12} nanoparticle was opposite between semiconducting and metallic SWNTs. Kelvin probe force microscopy (KPFM) results further indicated that surface potential of PMo_{12} on semiconducting SWNT was opposite to that on metallic SWNT. Since the protonation of PMo_{12} by the moisture in air and carboxylic acids formed on SWNTs is a must for the conductivity of the complex, the reason to the KPFM results was considered as a different charging efficiency between protonated PMo_{12} and the SWNTs. In the case of semiconducting SWNT, due to a localization of electron in SWNT, protonated PMo_{12} cannot be negatively charged by SWNTs and keeps positive-charged. Oppositely, large sum of free electron of metallic SWNT can charge protonated PMo_{12} negative easily. Density functional theory (DFT) calculation proved this speculation successfully. Based on this speculation, two possible mechanisms for the inversion of rectification direction have been proposed. One is the usual *p-n* junction between PMo_{12} and the SWNTs, in which PMo_{12} and SWNT can be regarded as "*p*-type" and "*n*-type" semiconductors. The other is the *I-V* drifting induced by the charge or dipole moment on the PMo_{12}/SWNT interface, and the direction and intensity of the drifting depend on whether PMo_{12} is charged as positive or negative. Besides, negative differential resistance (NDR) property has been observed in the *I-V* characteristic of PMo_{12} adsorbed on the highly oriented pyrolytic graphite (HOPG) and SWNTs, which was considered as the result of multi-electron stepwise reduction process of PMo_{12} with an increase of the applied bias.

As a single layer of carbon atom with 2D honeycomb structure, graphene has been widely researched and utilized in many applications. In this study, graphene nanoribbon (GNR) was synthesized by the unzipping of double-walled carbon nanotube (DWNT), and physically adsorbed by PMo_{12}. Large rectification could be observed on the PMo_{12} particle on GNRs. The preliminary results indicated that the rectification ratio of PMo_{12}/GNR complex was mainly tuned by GNR width rather than PMo_{12} particle size, and plateau width decreased as the height of PMo_{12} particle increased.

In conclusion, the rectification properties of the SWNTs complex have been controlled successfully by the molecular adsorption. Plateau width and rectification ratio of NDI/SWNT complex was dependent to NDI particle size, while the rectification direction of PMo_{12}/SWNT complex was reversed by the variation of PMo_{12} particle size or the "chirality" of the SWNTs. These experiment results are expected to be helpful in improving the quality of nanoscale electronic device in the near future.

論文審査の結果の要旨

カーボンナノチューブや、グラフェンナノリボンのような、炭素ナノ材料はシリコンに比べ遙かに大きなキャリア移動度を持つ、安価、軽量であるなどのメリットがあり、電子材料として大きな期待が持たれている。

洪流君は、これらの炭素ナノ材料が、表面分子によりどのように電子的な摂動を受けるかを、ナノスケールの空間分解能を持つ電気特性計測を行う事で明らかにしていった。

以前の研究で、半導体性の単層カーボンナノチューブ(SWNT)の表面に、比較的電子供与性の高いポルフィリン分子が吸着した場合には、ポルフィリンを通して電気特性を計測すると正側の電流が抑制される整流効果が見られることを見いだしていた。この整流の方向や、整流比を異なる分子を用いる事で制御できるかを検討した。

最初に用いた分子は、ナフタレンジイミド(NDI)という電子吸引性の分子である。この場合にも、ポルフィリンの場合と同様に、NDI 上で電気特性を計測すると正側の電流が抑制される整流効果が見られた。また、その整流比は、NDI 分子の粒子径に比例していることと、粒子径が 3nm を下回ると整流比が変化しなくなることを見いだした。

次に、ホスホドデカモリブデン酸 (PMo_{12})という、NDI よりも更に電子吸引性の高い分子を用いて実験を行った。この分子を用いると整流作用は、非常に不思議な振る舞いをする。まず、SWNT が半導体性の場合には、PMo_{12} の粒子径が小さい場合には正側の電流が抑制されるが、粒子径が大きくなると次第に整流性が逆転して負側の電流が抑制されるようになる。ところが、SWNT が金属性の場合には、振る舞いが逆転して、粒子径が小さい場合には、負側の電流が抑制されるが、粒子径が大きくなるに従い正側の電流が抑制されるようになる。SWNT/PMo_{12} の表面電荷を調べるために、ケルビン力顕微鏡(KFM)の測定を行った。その結果、SWNT が半導体性の時には、PMo_{12} の粒子径が大きくなるに従い、表面電位が小さくなる（正側に動く）が、SWNT が金属性の場合には、逆に粒子径が大きくなるに従い、表面電位が大きくなる(負側に動く)ことが分かった。これらの結果は、たいへん予想外のものであり、これまでに類似の現象さえ報告された例が無いものである。これらの現象を、分子軌道計算の助けを借りて、いくつかの仮説を立てることで説明することに成功した。

次に、SWNT を熱処理と超音波処理により開いて作る、グラフェンナノリボン(GNR)を用いた整流性の実験も行った。GNR は、幅が 18～28nm で長さが数百 nm 程度のものであり、その電子特性は半金属的である。これに、PMo_{12} 粒子を吸着させると、正側の電流が抑制される整流性がみられた。その整流比は、粒子径が大きいと大きくなることがわかったが、粒子径に対する依存度はあまり大きくなかった。興味深い事に、整流比が GNR の幅に大きく依存し、18nm の幅の GNR の場合には整流比がおよそ 20 であるのに対して、28nm の幅の GNR においては 1.7 と10倍以上の差があることがわかった。

以上のように、炭素ナノ材料の電気特性が表面分子の構造や粒子径により制御可能であることを明らかにしてきたが、これらの発見はこれまでに報告も予想もされていない新規で興味深い現象である。これらの結果は、既

報１報、投稿中２報、投稿準備中１報の論文として、まとめられている。

よって、本論文は博士(理学)の学位論文として充分価値あるものと認める。