

Electron Hopping Process in SWCNT-Mediated Redox Reaction: An Evidence Observed by DFT Theory

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ABSTRACT

The electron hopping mechanism in SWCNT-mediated redox reaction of anthraquinonyl (AQH₂⁻) and 4-arylhydroxyl amine (4AHA-) groups is systematically studied by DFT for the first time. It was found that electrons from the oxidized AQH₂ group can transfer to the oxidizing 4AHA group at the other end of the nanotube by the hopping process through the mediating SWCNT confirmed by the non-localized distribution of the hopping electrons. The electron density and Hirshfeld partial charges analysis shows that SWCNT can hold 87% of the extra electron density of the hypothetical negative intermediate forming by the oxidation of the AQH₂ process. Chemical attachments of these two redox reagents to the SWCNT also caused new impurity states within the band gap, thereby introducing more metallic characteristics to the system. These findings provide a detailed understanding of the electron hopping process and agree well with the previous experimental study.

Keywords: electron hopping process, SWCNT-mediated redox reaction, generalized gradient approximation (GGA), Perdew-Burke-Ernzerhof (PBE) method, carbon nanotube

1 INTRODUCTION

Among all nanoscale morphologies of carbon, multiwalled carbon nanotubes (MWCNTs) were first observed under transmission electron microscopy (TEM) by Iijima in 1991¹. After that, single-walled carbon nanotubes (SWCNTs) were produced independently by Iijima² and Bethune³ in 1993. Since their discoveries of the low-dimensional carbon nanostructures, carbon nanotubes (CNTs) have attracted much interest in modern nanoscience and nanotechnology due to their novel and structure-dependent properties. Over the years, the physical and chemical properties of CNTs have been well-documented as the results of more sophisticated methods. Novel properties of these CNTs endow their nanoscale applications as nanoelectronic devices⁴, sensors⁵, field emission sources⁶, and composite materials⁷. The CNTs also function as nanowires to transport electrons between the underlying electrode and electroactive protein chemically attached on each end of the tube⁸. The transport distances, controlling the rate of electron transfer, are greater than 150 nm

from the enzymatic active center to the electrode⁹.

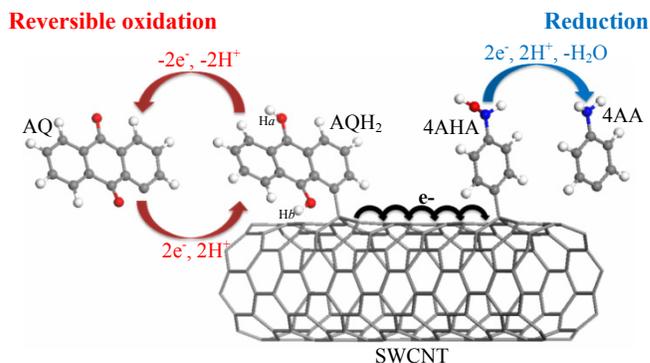
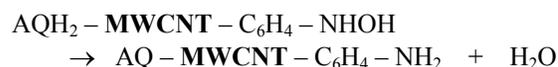


Figure 1: Proposed mechanism for the SWCNT-mediated redox reaction, consisting of the reversible oxidation and the irreversible reduction reactions. The SWCNT accepts electrons from the AQH₂ species and then donates the electrons to the 4-arylhydroxyl amine.

The chemical functionalization reactions for CNTs are categorized into three methods, which are: direct attachment to the graphitic surface, ester linkage, and covalent binding using diazonium reagents with high selectivity. The diazonium media method was also developed by Compton's group to initiate chemisorptions of aryl diazonium salts by direct reduction with hypophosphorous acid in the presence of carbon powder¹⁰⁻¹². The method was further extended to the application on MWCNTs with anthraquinone-1-diazonium chloride and 4-nitrobenzenediazonium tetrafluoroborate, resulting in the synthesis of 1-anthraquinonyl-MWCNTs (AQ-MWCNTs) and 4-nitrophenyl-MWCNTs (NB-MWCNTs)¹³.

Recently, Wong *et al.*¹⁴ reported a redox reaction on the same nanovessel MWCNT for the first time. This MWCNT is functionalized from two redox-active species directly attached by the diazonium salt method. The 4-arylhydroxyl amine (4AHA) and AQH₂ species are generated in the first oxidation cycle from NO₂-C₆H₄-MWCNT and AQ-MWCNT, respectively. This redox reaction consists of a reversible oxidation and an irreversible reduction studied by the cyclic voltammetry technique. They proposed the redox reaction mechanism, where AQH₂ is an oxidizing agent while NHOH-C₆H₄ is a reducing group.



Structure	Hirshfeld charge			Total	Energy gap / eV	Relative energy / kcal mol ⁻¹
	Partial charge					
pristine SWCNT	-	-	-	-	0.62 D	-
substrate	AQH ₂ = 0.05	SWCNT = -0.07	4AHA = 0.03	0.01	0.00	-
intermediate-1-a	AQH = -0.06	SWCNT = -0.91	4AHA = -0.02	-0.99	0.04 D	0.00
intermediate-1-b	AQH = -0.16	SWCNT = -0.81	4AHA = -0.02	-0.99	0.04 I	-0.95
intermediate-2	AQ = -0.19	SWCNT = -1.73	4AHA = -0.07	-1.99	0.10 I	-
intermediate-3	AQ = -0.07	SWCNT = -0.77	Ph-NH = -0.16	-1.00	0.16 I	-
product	AQ = -0.01	SWCNT = -0.03	4AA = 0.05	0.01	0.00	-

Table 1: Hirshfeld partial charge, energy gap (eV), and relative energy (kcal mol⁻¹) calculated with the PBE method and DNP basis set for pristine SWCNT, substrate, intermediate, and product states. (D = direct, I = indirect energy gap)

The mechanistic pathway of electron transfer from AQH₂ to the 4-arylhydroxyl amine group is also investigated, to determine whether it is intermolecular electron tunneling between reagents or by electron hopping via the CNT. Nevertheless, the hopping was proposed to be more favorable because of the shorter distance in the electron transfer. Such phenomenon is unique for both oxidizing and reducing groups confined on the same CNT.

Herein, we report the theoretical study on the possibility and the process of the electron hopping between two redox reagents that are functionalized on the same CNT. Even mediating MWCNT in the real system is simplified to the semiconducting SWCNT for computational efficiency; the periodic calculations are performed improve the electronic results so that they are more reasonable. In addition, we focus only on the redox reaction instead of the chemical attachment and the preparation steps. Thus, this redox reaction from AQH₂-SWCNT-4AHA terminated at AQ-SWCNT-4AA is proposed in the reversible oxidation and the irreversible reduction, where 4AA (4-arylamine) is noted.

Total reaction:



Oxidation:



Reduction:

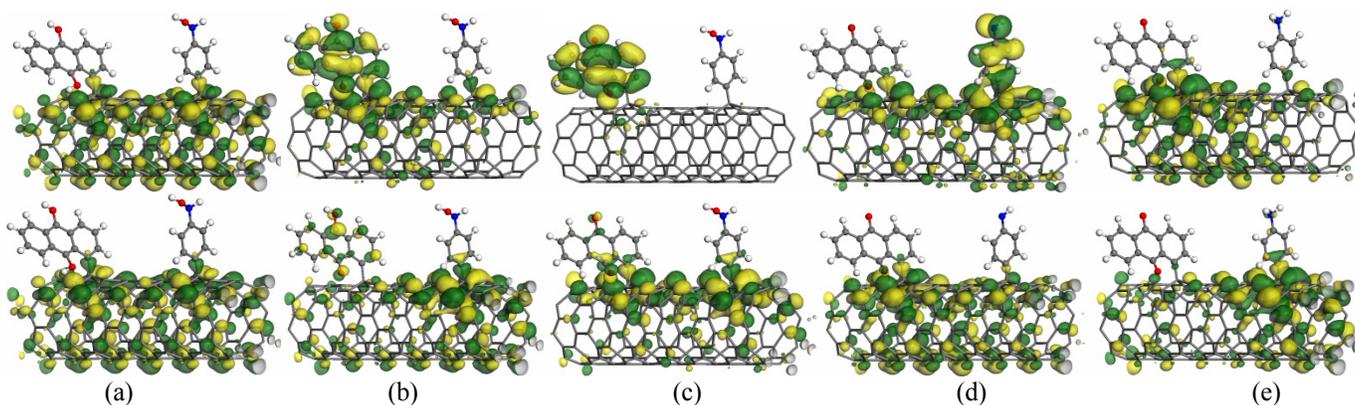


Figure 2: LUMO (top) and HOMO (bottom) plots of *subs* (a), *int-1-b* (b), *int-2* (c), *int-3* (d), and *prod* (e).

2 MODELS AND METHODOLOGY

The periodic calculations were carried out using the density functional theory (DFT) method as implemented in the DMol3 package^{15,16}. The generalized gradient approximation (GGA) in the various methods and an all-electron double numerical basis set with polarized function (DNP) were chosen for the spin-unrestricted DFT computation. The real space global cutoff radius was set to be 3.70 Å. For geometrical optimization, the forces on all atoms were optimized to be less than 0.05 eV.Å⁻¹. The Brillouin zone was sampled using the Monkhorst-Pack scheme¹⁷.

2.1 Diameter calibration of SWCNTs

Zigzag SWCNTs are calibrated in different diameters from (6,0) to (12,0). Each initial structure is generated in a supercell periodic box with 20 × 20 × 8.52 Å³ composed of two unit cells of SWCNT. The nearest distance between two neighboring SWCNTs is greater than 10 Å for ignoring an intertube interaction. The calibrations are performed by the GGA in the Perdew-Burke-Ernzerhof (PBE)¹⁸, Becke's exchange and Lee, Yang, and Parr's correlation functional (BLYP)^{19,20}, and non-local exchange-correlation functional (PW91)²¹ with *k* point 1 × 1 × 40.

2.2 Redox system

An (8,0) SWCNT, the smallest semiconducting zigzag providing an acceptable energy gap, was chosen to be functionalized by two redox groups which were more than 12 Å

distant from each other to neglect an intermolecular interaction of these two species. A supercell with $40 \times 40 \times 24.15 \text{ \AA}^3$ comprised of six periodic lengths for the zigzag SWCNT was adopted in the calculation with the PBE function. Each supercell consists of two redox groups, which are covalently bonded to the sidewall of the SWCNT. The nearest distance between two neighboring SWCNTs is greater than 30 \AA . Only Γ point was considered in the Brillouin zone for the geometric optimization and orbital analysis but k points $1 \times 1 \times 10$ was sampled to calculate electronic properties of the redox system. Even though the individual processes in the overall redox reaction take place concurrently, we simplify the problem by dividing the redox pathway into five hypothetical states, which are AQH₂-SWCNT-4AHA (substrate: *subs*), [AQH-SWCNT-4AHA]¹ (intermediate-1), [AQ-SWCNT-4AHA]² (intermediate-2: *int-2*), [AQ-SWCNT-Ph-NH]¹ (intermediate-3: *int-3*) and AQ-SWCNT-4AA (product: *prod*) (AQ = anthraquinonyl, 4AHA = 4-arylhydroxyl amine, 4AA = 4-arylamine, SWCNT = (8,0) zigzag SWCNT). The intermediate-1 state can be considered in two configurations, which are intermediate-1-a (*int-1-a*) and intermediate-1-b (*int-1-b*) for Ha and Hb removal, respectively.

3 RESULTS AND DISCUSSION

The diameter of carbon nanotubes and the periodic calculation

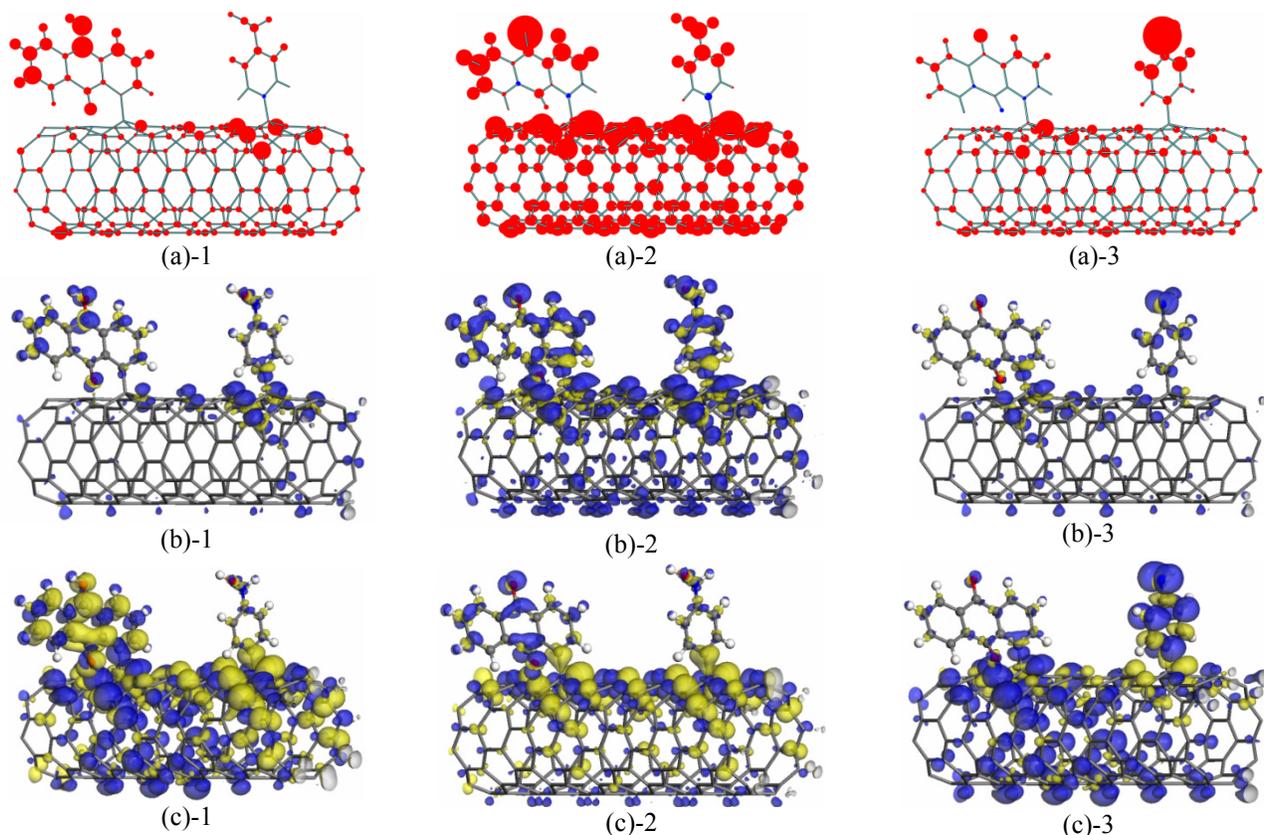


Figure 3: **Hirshfeld charge difference** of *int-1-b* (a)-1, *int-2* (a)-2, and *int-3* (a)-3 where the red color is a negative charge and the blue color is a positive charge. **Electron density difference** of *int-1-b* (b)-1, *int-2* (b)-2, and *int-3* (b)-3 is plotted for an isovalue of $\pm 0.004 e/\text{\AA}^3$, where the blue and yellow color is represented for the electron accumulation and electron depression zones, respectively. **Nucleophilic Fukui function plot** of *int-1-b* (c)-1, *int-2* (c)-2, and *int-3* (c)-3.

with three functionals (PBE, BLYP, and PW91) was calibrated for searching a zigzag SWCNT suited to our models. Although all methods of investigating (n,0) zigzag SWCNTs give the same energy gap results, the PBE functional is chosen in our calculations following the previous theoretical studies. Moreover, it was found that the (6,0), (9,0), and (12,0) SWCNTs obey the $n - m = 3i$ metallic rule with $E_{\text{gap}} = 0.00, 0.17,$ and 0.14 eV , respectively. The (7,0) SWCNT presents as a semi-metallic character with a 0.15 eV energy gap. Fortunately, the (8,0) SWCNT is the first smallest zigzag carbon nanotube that provides semiconducting behavior with an acceptable 0.62 eV energy gap. Therefore, the SWCNT-mediated redox models in this paper are generated from the (8,0) SWCNT and calculated by periodic calculations with PBE method.

The electronic properties of the redox system are reported in Table 1. The results show the difference of relative energy of *int-1*, resulting in the *int-1-b* being more favorable than *int-1-a* due to the less steric effect between the hydrogen atom of AQH group and the nanotube media. Thus, the proposed mechanism pathway of the redox reaction starts with the *subs* configuration and forwards to *int-1-b*, *int-2*, *int-3*, and *prod*, respectively. Chemical attachments of these two redox reagents to the SWCNT cause new impurity states within the band gap, thereby introducing more metallic characteristics to the system. These properties lead to the ease of electron delocalization among the modified system.

The electron density difference and Hirshfeld partial charges analyses show that SWCNT can hold 87% of the extra electron density of the hypothetical negative intermediate forming that forms by the oxidation of the AQH₂ process.

The explanation of how an electron transfers from AQH₂ to 4AHA via SWCNT is illustrated in Figure 2. First, an electron ionization and reception occurs at SWCNT, which can be clearly observed at both the HOMO and LUMO for the substrate. At the intermediate steps, an electronic connection between the AQ and the 4AHA molecules on the SWCNT is shown clearly at the HOMO levels. An electron in the *int-1-b* and *int-2* that strongly remained at the AQ part can reversely reduce the AQ to AQH₂. Electrons move to the 4AHA side result in a reduction reaction, and the HOMO of the product shows that the electrons distribute mostly at 4AA and no longer occupy the AQ side. The opposite trend is observed for the LUMO of the product.

Hirshfeld charge density difference plots are presented in Figure 3(a). An electron in the intermediate states has a high occupation at the AQH, leading to the reverse reduction of AQH to AQH₂. Two electrons in the *int-2* step have a high occupation at the AQ, 4AHA, and the bridge in the nanotube media as shown in Figure 3(a)-2. Therefore, the AQ and 4AHA groups can be reduced to AQH₂ and 4AA, respectively. In Figure 3(b), the calculations are performed from the difference of the electron density between the negative-charge structure and its neutralized geometry, resulting in the density of only the negative charge. It is clearly presented about the negative charge from the reducing group connecting to the oxidizing group. The electron density obviously occupies only the redox molecules and their junction in the SWCNT media. The nucleophilic Fukui function plots as demonstrated in Figure 3(c) strongly confirmed the electron hopping process of the redox reaction via nanotube. The mechanism starts with high nucleophilic character at AQ and the connection. Then, the reducing negative behavior at AQ leads to the increase at 4AHA. Therefore, the electron transfer between two redox groups can occur apparently by electron hopping via the SWCNT.

4 CONCLUSIONS

The the PBE functional using the DFT calculation is used to investigate the reaction mechanism of electron hopping in the SWCNT-mediated redox reaction of anthraquinonyl (AQH₂-) and 4-arylhydroxyl amine (4AHA-) groups. Our findings can be summarized into three main points. First, the electron density and Hirshfeld partial charges analysis shows that SWCNT can hold 87% of the extra electron density of the hypothetical negative intermediate forming by the oxidation of AQH₂ process. Second, chemical attachments of these two redox reagents to the SWCNT also caused new impurity states within the band gap, thereby introducing more metallic characteristics to the system. Third, the electrons from the oxidized AQH₂ group can transfer to the oxidizing 4AHA group at the other end of the nanotube by the hopping process through the mediating SWCNT. The mechanism is confirmed by the non-localized distribution of the hopping electrons. These findings provide a

detailed understanding of the electron hopping process and agree well with the previous experimental study. This work is not only complementing experimental study by giving a fundamental interpretation but also demonstrating one other promising application of the CNT materials in the nanotechnology field.

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