Research Article

Electrochemical Oxidations of *p*-Doped Semiconducting Single-Walled Carbon Nanotubes

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Two oxidation peaks at 0.99, 1.48 V versus Fc/Fc^+ appear in the cyclic voltammograms of a series of defect-site functionalized SWNTs in methylene chloride solution in the presence of ferrocenes. These two peaks are demonstrated to be the electrochemical responses to the independent oxidation of v_1 and v_2 valence bands of *p*-doped semiconducting SWNTs.

1. Introduction

The electrochemistry of fullerenes and their derivatives has been well documented since first report in 1990 [1]. So far, six one-electron reductions [2] and three one-electron oxidations [3] were reported for C_{60} in scrupulously experimental conditions such as dry solvent and adoptable supporting electrolyte. These established redox potentials for C_{60} have played a pivotal role in understanding its electronic and chemical behaviors [4, 5]. As the extended member of fullerene family, single-walled carbon nanotubes (SWNTs) have been extensively investigated for their unique electronic and chemical properties [6]. For examples, the side-wall addition reactions onto SWNTs have been correlated to the charge-transfer precursors [7–9] occurring from carbon nanotubes to chemical reactants. In addition, the photoinduced charge-transfers from carbon nanotubes to chromophores have been proposed in several systems [10–19]. Unlike C_{60}, these theoretical remarks are based on the density of electronic states (DOS) of SWNTs instead of their redox potentials. Such an awkward situation could be considerably ascribed to the lack of the redox potential data for SWNTs. Though a great deal of efforts have been made to investigate the electrochemical properties of SWNTs, most results demonstrated the fast electron transfer and catalytic properties of SWNTs [20–31]. A direct electrochemical measurement on Prato-type side-wall functionalized SWNTs with cyclic voltammetry was recently reported; however, no apparent redox potential was

observed experimentally [32]. On the other hand, like C_{60}, the chemical doped SWNTs with either the electron donors (K, Cs) or the electron acceptors (I_2, Br_2) have been characterized in their corresponding optical absorption spectra of band gap energies [33, 34]. Moreover, these characteristic optical absorption spectra of chemical doped SWNTs were observed when tuning the electron potential of SWNTs films at 1.4 and 1.8 V (versus Ag), respectively [35, 36]. The facile oxidation of the semiconducting SWNTs dispersed in aqueous solution with small molecule reagents like oxygen was also reported [37–39]. These literatures [33–39] strongly suggest that the oxidation potentials of SWNTs should be comparable to those of fullerenes.

In this work, the cyclic voltammetry (CV) of a series of defect-site functionalized SWNTs, **THPP·SWNTs**, **THPP-HMP-SWNTs**, **THPP-HHP-SWNTs**, and **C_{20}-SWNTs** (Scheme 1), was measured in the absence and presence of ferrocenes in CH_2Cl_2 solutions with $[(t\text{-}Butyl)_4N^+]\cdot[PF_6^-]$ as supporting electrolyte. In the cyclic voltammograms of these studied SWNTs, weak and broad oxidation peaks at 1.33 V (versus Ag^+/Ag) appear with reducing current trend of **C_{20}-SWNTs** < **THPP-HHP-SWNTs** < **THPP-HMP-SWNTs** < **THPP·SWNTs** in the absence of ferrocenes, while by adding ferrocenes a consistently strong oxidation peak at 1.48 V (versus Fc/Fc^+) emerges with the similarly inclined weak and broad oxidation peak at 0.99 V (versus Fc/Fc^+) following **C_{20}-SWNTs** < **THPP-HHP-SWNTs** < **THPP-HMP-SWNTs** < **THPP·SWNTs**. However, the expected redox waves of
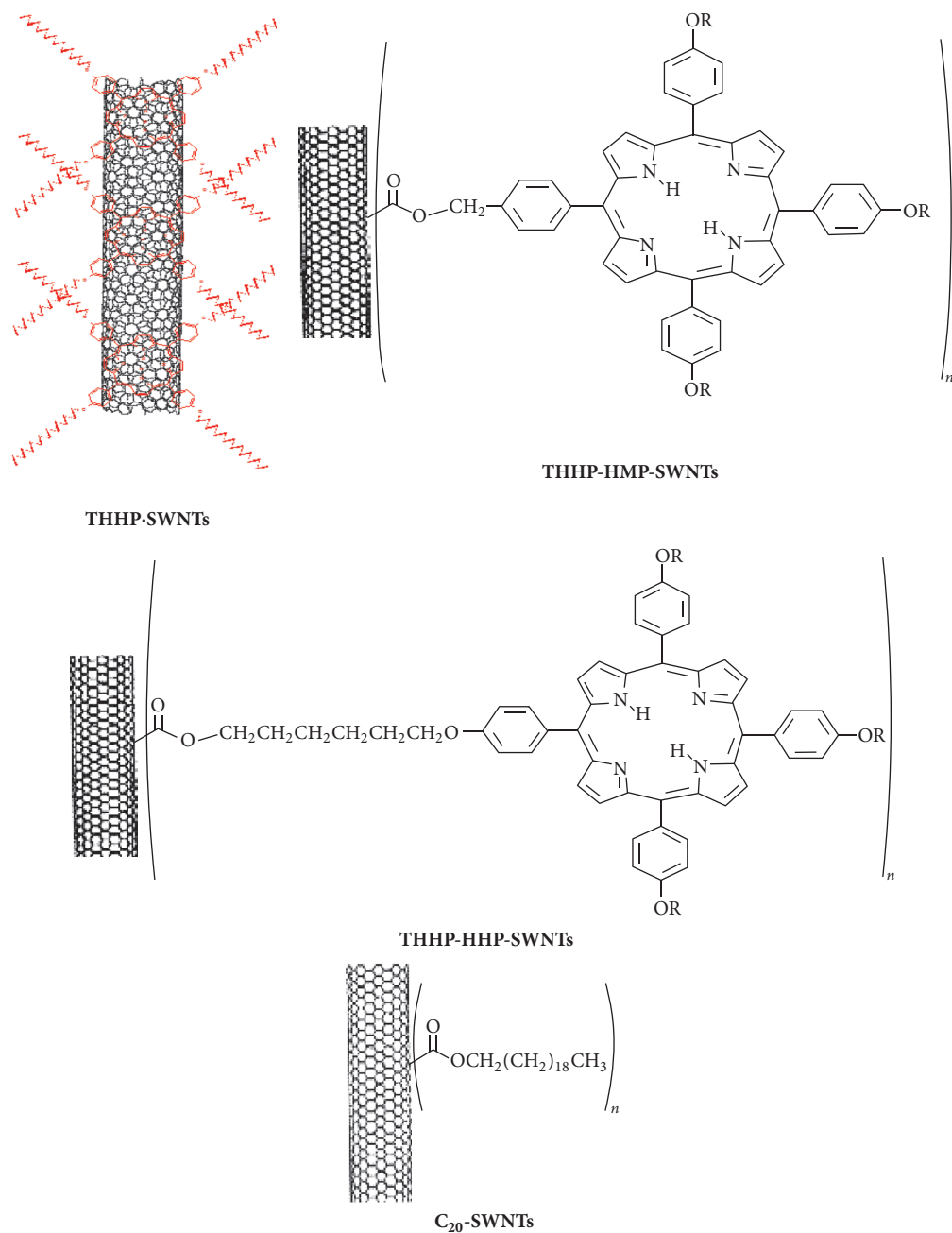
SCHEME 1: The structures of **THHP·SWNTs**, **THHP-HMP-SWNTs**, **THHP-HHP-SWNTs**, and **C$_{20}$-SWNTs**.

porphyrin derivatives do not appear in these CVs of these porphyrin derived SWNTs. These observed peaks are rationalized and assigned to the independent oxidations of v$_1$ and v$_2$ valence bands of SWNTs, respectively. And the effects of π-network SWNTs could account for the missing redox responses of porphyrin derivatives.

2. Results and Discussion

The syntheses of 5,10,15,20-Tetrakis(hexadecyloxyphenyl)-*21H,23H*-porphyrin (**THPP**), 5-hydroxymethylphenyl-10,15,

20-tris(hexadecyloxyphenyl)-*21H,23H*-porphyrin (**HMP-THPP**), and 5-hydroxyhexyloxyphenyl-10,15,20-tris(hexadecyloxyphenyl)-*21H,23H*-porphyrin (**HHP-THPP**) were reported in literatures [40, 41]. **THPP** was sonicated with purified SWNTs in chloroform to give rise to noncovalently functionalized SWNTs (**THHP·SWNTs**), which are soluble in THF, CH$_2$Cl$_2$, and others [40]. **THPP-HMP-SWNTs** and **THPP-HHP-SWNTs** soluble in most common organic solvents were synthesized by reacting **HMP-THPP** and **HHP-THPP** with SOCl$_2$ treated SWNTs at 105°C under the atmosphere of N$_2$ [41]. **THPP· SWNTs**, **THPP-HMP-SWNTs**, and **THPP-HHP-SWNTs** were well characterized with NMR, IR,

NIR, and Raman spectroscopies and electron microscopy [40, 41]. **C$_{20}$-SWNTs** was synthesized using eicosanol (**C$_{20}$**) in similar procedures to **THPP-HMP-SWNTs** and **THPP-HHP-SWNTs** [41]. The electrochemical experiments were conducted on a CHI-660 electrochemical workstation.

SWNTs produced via different methods (including arc discharge SWNTs studied herein) are composed of both metallic and semiconducting parts with statistical ratio of one to two [42]. The electrochemical and conducting investigations on pristine SWNTs showed that the semiconducting SWNTs dominate the electric properties of mixed SWNTs [43, 44]. And SWNTs purified with routine procedures [45, 46] usually display *p*-type doping properties. For one example, Day et al. [43] demonstrated that the oxidization current intensity was higher than reduction current intensity on purified SWNTs network. More recently, *p*-doping effect was reported to be further enhanced on SWNTs by SOCl$_2$ treatment [47]. Though the semiconducting components of SWNTs were enriched in **THPP·SWNTs** [40], the similar electrochemical responses of *p*-doped SWNTs are expected for these studied SWNTs. As evident in their CV curves (Figures 1 and 2), the oxidation current intensities are obviously stronger than the reduced current intensities.

Anodic Electrode. Fullerenes undergo facile reduction with stepwise, reversible electron accumulations [2]. The electrochemically reduced fullerides are stable enough to be exploited for fullerene separation [48]. Unlike fullerenes, the anodic current response of all studied SWNTs is very weak in proximity to the background (Figures 1 and 2). These silent anodic responses of SWNTs can be correlated to *p*-doping electronic features. In *p*-doped semiconducting materials, the Fermi level is usually beneath the first valence band. And the Fermi level of *p*-doped SWNTs can only shift to a level possessing maximum intensity of band gap absorption and minimum electronic conductivity by electrochemical tuning of negative potential [36]. This implies that the external anodic potential (up to −1.8 V) can not reduce SWNTs to a negatively charged specie, but only adjust preexisting electrons and orbitals in their original electronic states. Though the optical absorption of the metallo-SWNTs (CCs$_{0.10}$) was reported at 1.3 eV [33], such a characteristic absorbance was not observed for *p*-doped SWNT films charged with negative potential up to −1.4 V versus Ag [35]. In our experiments, no peak corresponding to the reduction reaction from SWNT to SWNT$^-$ appears in these CV curves with a spectral window to −2.2 V versus Ag$^+$/Ag. The lack of reduced species for SWNTs is possibly because the supporting potentials in these experimental conditions are insufficient to overcome the intrinsic Coulomb blockade effect [49] in quantized *p*-type semiconducting SWNTs.

Cathodic Electrode. In contrast to their reduction, the oxidation of fullerenes is difficult. However, it has been reported that higher fullerenes (C$_{70}$, C$_{76}$, C$_{78}$, and C$_{80}$) are easier to oxidize than C$_{60}$, despite being in the irreversible fashion [50]. Structurally analogous to fullerenes, SWNTs are expected to oxidize easily, at least comparable to these higher fullerenes. As seen in Figures 1 and 2, the cathodic responses of these
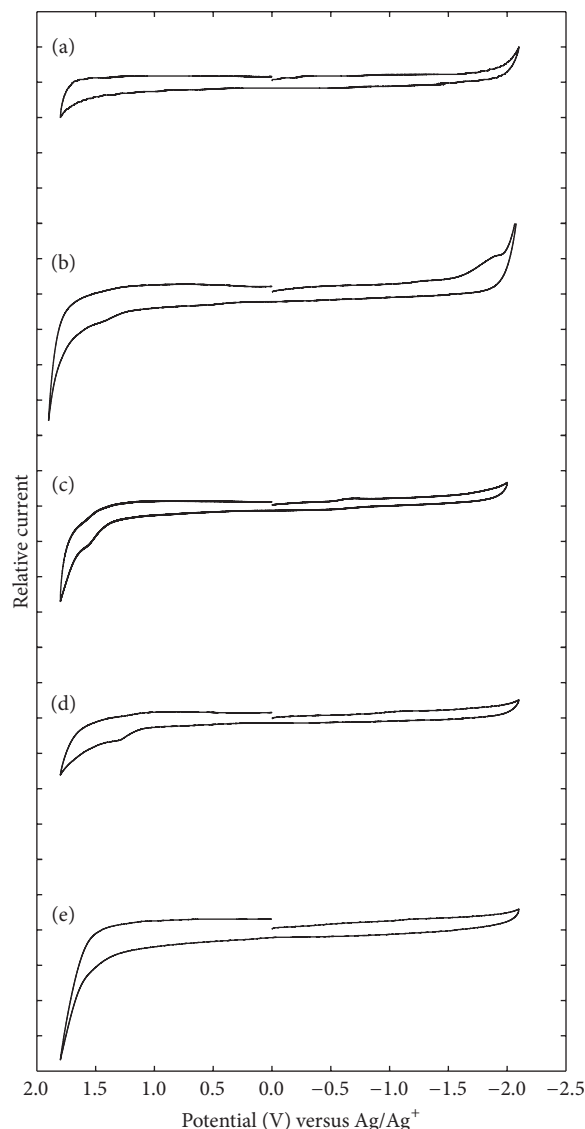

FIGURE 1: The cyclic voltammograms of porphyrin derived SWNTs and **C$_{20}$-SWNTs** in the absence of ferrocenes in CH$_2$Cl$_2$ solution using $[(t\text{-Butyl})_4\text{N}]^+[\text{PF}_6]^-$ as supporting electrolyte. (a) Background, (b) **THHP-HHP-SWNTs**, (c) **THHP-HMP-SWNTs**, (d) **THHP·SWNTs**, and (e) **C$_{20}$-SWNTs**.

studied SWNTs are more informative than their anodic responses. In the absence of ferrocenes (commonly used as the reference of potential), the irreversibly weak and broad oxidation peaks (E^0 = 1.3 V versus Ag/Ag$^+$) appear in Figure 1 superimposing the conductive curves. The visibility of this oxidation peak follows the trend: THPP.SWNTs > THPP-HMP-SWNTs > THPP-HHP-SWNTs > C20-SWNTs. When adding ferrocenes, the well-defined steady-state CV curves with two irreversible half-wave oxidation peaks (E^0 = 0.99, 1.48 V versus Fc/Fc$^+$) overlap the conductive curves (Figure 2). The oxidation peaks at 0.99 V are weak and broad, similar to the ones measured in the absence of ferrocenes. The oxidation peaks at 1.48 V are strong and consistent for all studied samples. The CVs of studied SWNTs were conducted
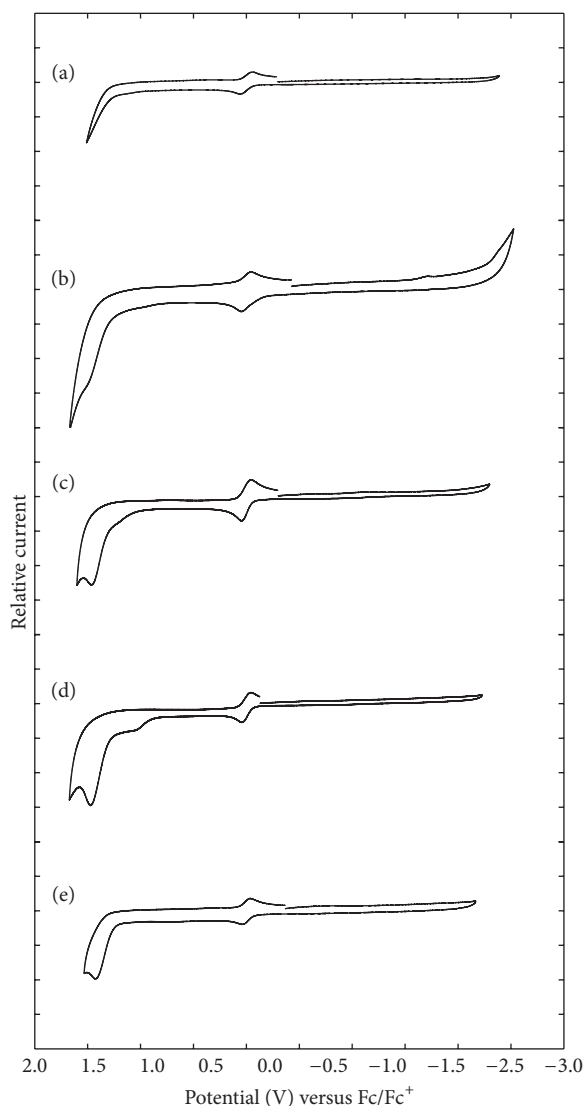
FIGURE 2: The cyclic voltammograms of porphyrin derived SWNTs and C_{20}-SWNTs in the presence of ferrocenes in CH_2Cl_2 solution using $[(t\text{-Butyl})_4N]^+$ $[PF_6]^-$ as supporting electrolyte. (a) Background, (b) **THHP-HHP-SWNTs**, (c) **THHP-HMP-SWNTs**, (d) **THHP·SWNTs**, and (e) C_{20}-**SWNTs**.

FIGURE 3: The comparison of DPV spectrum to UV-near infrared absorption of SWNTs. Up: DPV curve of **THHP·SWNTs**; bottom: UV-near infrared absorption spectrum of **THHP·SWNTs**.

at different conditions such as various scanning rate, different temperatures, and solvents (see Supplementary Material available online at http://dx.doi.org/10.1155/2016/8073593), and the similar CV curves were obtained. These results prove that the observed oxidation peaks are real, not false responses. The next is the assignment of these two oxidation peaks. These two oxidation peaks seem not to be from the functionalities or from the charge-transfer complex between functionalities and SWNTs. The strong argument is that the same oxidation peaks at 1.48 V appear in these CVs for both porphyrin derived SWNTs and eicosanol derived SWNTs. The skepticism on the impurities associated with SWNTs, such as fullerenes and carbonaceous nanoparticles, is unsupportive. Although the oxidation peaks of fullerenes resemble the observed ones, their reduction peaks could
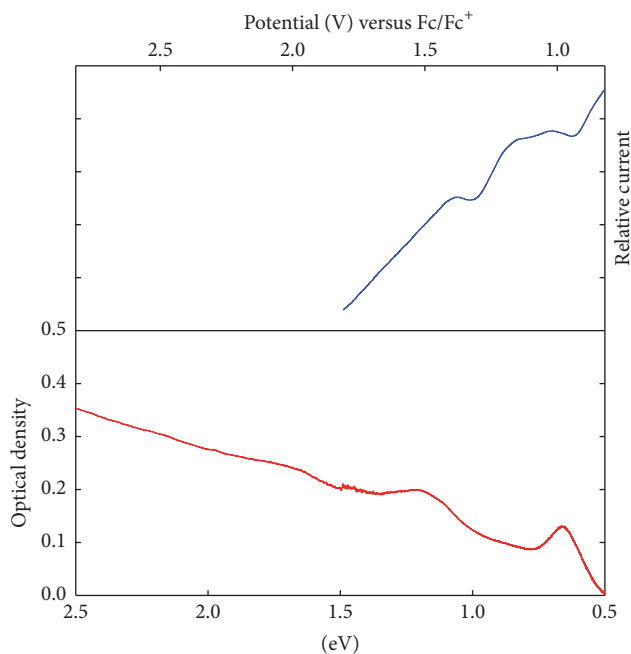
not be identified in these CV curves. As for carbonaceous nanoparticles, our previous spectroscopic investigations [41] on these studied SWNTs are lack of the reported fluorescence emissions, characteristic of carbonaceous nanoparticles [51, 52]. The left possibility for these two oxidation peaks is from SWNTs. The oxidation of SWNTs can be rationalized. First of all, the oxidation potentials of 0.99, 1.48 V versus Fc/Fc$^+$ are surprisingly close to those of C_{78} C_{2v}-isomer fullerene (0.95, 1.43 V vs Fc/Fc$^+$) [50]. This means that the two potentials of 0.99, 1.48 V versus Fc/Fc$^+$ are rational to oxidize SWNTs. Secondly, like the near IR absorption of C_{60}^+ ($E_{1/2}(C_{60}/C_{60}^+)$ = 1.26 V versus Fc/Fc$^+$ [53]) at 1.26 eV [54], the first oxidation potential of 0.99 V versus Fc/Fc$^+$ is proximately corresponding to the near IR absorption of Br_2-doped SWNTs ($CBr_{0.15}$) [33, 34] at 1.07 eV. Thirdly, two near IR absorption peaks were observed at 1.15 eV and 1.24 eV when the p-doped SWNTs film electrochemically tuned at 1.4, 1.8 V versus Ag, respectively [35]. The oxidation potential of 1.33 V versus Ag/Ag$^+$ in Figure 1 and the oxidation potentials of 0.99, 1.48 V versus Fc/Fc$^+$ in Figure 2 are consistent with these electrochemical tuning results. Finally, the DPV (differential pulse voltage) spectrum of **THPP·SWNTs** was measured in the presence of ferrocenes. As seen in Figure 3, two clear oxidation peaks were obtained at 0.99 and 1.48 V versus Fc/Fc$^+$. Interestingly, the potential differences of these two oxidation peaks and their wave shapes are similar to those of two band gap energy transitions (S_{11} and S_{22}) of semiconducting SWTNs (seen in Figure 3). This implies that these two oxidation peaks are closely related to the band gap energy absorption of SWNTs. Therefore, the oxidation reactions of SWNTs can be expressed as $E_1^{ox} = E_{11}^S + E'$ and $E_2^{ox} = E_{22}^S + E'$, where E' represents

the required energy to remove one electron from conduct bands, E_{11}^{S} and E_{22}^{S} are band gap energies of S_{11} and S_{22} absorptions, respectively, and E_1^{ox} and E_2^{ox} represent the required energies to remove one electron from v_1 and v_2 valence bands, respectively. From these two expressions, the oxidation peaks can be considered as the electrochemical responses to the independent removal of one electron from v_1 and v_2 valence bands. This unambiguously explains why the oxidation peak at 1.48 V appears even without the oxidation peak at 0.99 V in the CV of **C_{20}-SWNTs**.

The oxidation peaks of SWNTs at 1.48 V appear only in Figure 2. The different condition in Figure 2 from Figure 1 is the addition of ferrocenes. Though Barazzouk et al. [55] recently reported that the electrochemical activities of C_{60} cluster film were efficiently improved by the electrocatalysis of encapsulated ferrocenes, the electrochemistry of ferrocene derived SWNTs did not display any electrocatalytic effect of ferrocenes on the redox properties of SWNTs [56]. Therefore, the observed oxidation peaks of these studied SWNTs at 1.48 V need an alternative explanation. In an electrolyte gated carbon nanotube field emission transistor (NFET), the ionic cloud of the electrolyte was reported to behave like a near-lying gate electrode to compensate the excess charge drawn onto SWNTs when applying an external potential [57, 58]. As long as the ionic cloud of the electrolyte immediately responds to the external potential, the redox reactions of SWNTs cannot occur. Commonly, *p*-doped SWNTs are so conductive when applying a positive potential that the real voltages on SWNTs keep below their oxidation potentials. When adding ferrocenes, the ferrocenium cations electrochemically produced from the surface of the electrode eliminated the compensating effect of surrounding electrolyte ionic cloud on SWNTs and lifted up their real voltages for the oxidation reactions.

Obviously, the weak and broad oxidation peaks in Figure 1 were not significantly changed in Figure 2 by adding ferrocenes. This hints that the oxidation of v_1 band of SWNTs is determined by their *p*-doping electronic properties relative to S_{11} absorption. Different from **THPP·SWNTs**, the preparations of **THPP-HMP-SWNTs**, **THPP-HHP-SWNTs**, and **C_{20}-SWNTs** were via thionyl method [59] which was reported [47] to enhance *p*-doping effects. Therefore, the v_1 oxidation peak is much more visible for **THPP·SWNTs**. Even though the *p*-doping effects are determining, the v_1 oxidation peaks could still be traced for **THPP-HMP-SWNTs and THPP-HHP-SWNTs**, but not for **C_{20}-SWNTs**. This indicates that the porphyrin moieties have some impacts on the v_1 oxidation of SWNTs. In addition, the v_1 oxidation peak of **THPP-HMP-SWNTs** is a little bit more visible than that of **THPP-HHP-SWNTs** which has a longer linker onto the surfaces of SWNTs than **THPP-HMP-SWNTs**. This means that the impacts of porphyrin moieties on the v_1 oxidation of SWNTs are relative to their linking lengths.

Porphyrin Moieties on SWNTs. Porphyrin and its analogy have been investigated for their conjugation with C_{60} [60–63], nanoparticles [64–66], and electrodes [67–69] due to their diversity of tunable functionalities. The redox properties of porphyrins in these conjugates [60–69] are strongly influenced by the molecular proximity/orientation to the substrates. The conjugations between porphyrin derivatives and SWNTs were reported for their photophysical properties [10–17]. The electrochemistry of porphyrin moieties on SWNTs is scarce, though the outstanding electrocatalytic properties of hemin (containing a porphyrin ring) were demonstrated on MWNT electrodes [70]. The electrochemical responses of porphyrin moieties with varied orientation and proximity to a SWNT surface are presented in this work. For **THPP·SWNTs**, porphyrin cores are directly in contact with the π-network of SWNTs, while porphyrin cores are 1- and 6-CH_2- far away from defect sites of the SWNT surface in **THPP-HMP-SWNTs** and **THPP-HPP-SWNTs**, respectively. As shown in Figures 1 and 2, the redox waves of porphyrin moieties in these porphyrin derived SWNTs are invisible except the two weak and broad irreversible reduction peaks at −1.7, −2.35 V versus Fc/Fc$^+$ emerge in the CV for **THPP-HPP-SWNTs**, comparable to those of **HPP-THPP** with $E_{1/2}$ of −1.74, −2.14 V versus Fc/Fc$^+$ (seen in Supplementary Material). These results are sharply in contrast to the redox behaviors of porphyrin derivatives/analogy on other substrates [60–69], which indicates that the effects of SWNTs on the electrochemistry of porphyrin derivatives are different from those of C_{60}, nanoparticles, and electrodes. These different effects are possibly due to the π-network electron screening and/or strong π-π interactions of SWNTs with porphyrin moieties. The electron screening usually escapes porphyrin moieties from the direct charging from the electrode. The π-π interaction can merge the frontier molecular orbits of porphyrin rings into the electronic states of SWNTs. With these two effects, porphyrin moieties on the surface of SWNTs are hardly to be electrochemically active. The weak and broad irreversible reduction peaks for porphyrin derivatives shown in the CV curve possibly came from the lucky molecules tethered with the 6-CH_2 flexible chain in **THHP-HHP-SWNTs**, which escaped out of the above-described effects of SWNTs.

3. Conclusion

In summary, the CV measurements of **THPP·SWNTs**, **THPP-HHP-SWNTs**, **THPP-HMP-SWNTs**, and **C_{20}-SWNTs** methylene chloride solutions were conducted in the absence and presence of ferrocenes. The CV results in the presence of ferrocenes display two oxidation peaks at 0.99, 1.48 V versus Fc/Fc$^+$, consistent with the electrochemical results of *p*-doped SWNT films in literatures [35, 36]. By comparison of these two oxidation peaks in the DPV spectrum of **THPP·SWNTs** to its band gap energy absorption, these two peaks can be assigned to the independent oxidization of v_1 and v_2 valence bands, respectively. On the other hand, the redox behaviors of porphyrin moieties on these porphyrin derived SWNTs are invisible in their CV curves, except for **THHP-HHP-SWNTs** with two weak irreversible broad reduction waves. This could be due to the strong electronic effects of π-network SWNTs on the porphyrin molecules.

Competing Interests

The authors declare that they have no competing interests.

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