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Density functional theory prediction of pK_a for carboxylated single-wall carbon nanotubes and graphene

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ABSTRACT

Density functional calculations have been performed to investigate the acidities for the carboxylated single-wall carbon nanotubes and graphene. The pK_a values for different COOH-functionalized models with varying lengths, diameters and chirality of nanotubes and with different edges of graphene were predicted using the SMD/M05-2X/6-31G* method combined with two universal thermodynamic cycles. The effects of following factors, such as, the functionalized position of carboxyl group, the Stone-Wales and single vacancy defects, on the acidity of the functionalized nanotube and graphene have also been evaluated. The deprotonated species have undergone decarboxylation when the hybridization mode of the carbon atom at the functionalization site changed from sp^2 to sp^3 both for the tube and graphene. The knowledge of the pK_a values of the carboxylated nanotube and graphene could be of great help for the understanding of the nanocarbon materials in many diverse areas, including environmental protection, catalysis, electrochemistry and biochemistry.

1. Introduction

The functionalization of carbon nanotubes (CNTs) and graphene with simple organic groups, such as —NH$_2$, —OH, —C═O, and —COOH etc., has been the common strategy to improve the properties of the carbon materials [1–8]. Among those, carboxylation is definitely an important structural modification of the nanostructured carbon materials, and has been investigated intensively [9–33]. The functionalization of CNTs and graphene with carboxyl group can not only provide a suitable platform for further derivatizations, but also enhance their dispersibilty, adsorption properties and reactivities, which consequently widen their possible applications in many diverse areas, including industry, environmental protection, energy storage, electrochemistry and biochemistry [1–12]. In addition, carboxyl is an important acidic group, which makes the major contribution to the surface acidity of the activated nanomaterials. And the functionalized nanostructured carbon materials have always been employed in many fields with PH-dependent [34–36]. Therefore, the investigation of the acidic strength of these materials is of great interest to the experimentalist, which can not only provide the key to understand the PH-dependent behavior, but also give the clue to adjust the surface acidity of the materials by varying the synthesis method. To date, different methods have been developed for measuring the surface acidity of various carbon materials and the acid-base titration is still an inexpensive and straightforward one that is commonly used. Very recently, several research groups have carried out the quantitative determination of acidic groups in functionalized graphene and carbon nanotubes [37–43]. However, the complexity of materials and the variety of the group distributions prevent the experimental determination of the individual acidic contribution from the specific group and sites. For example, the oxidized carbon nanomaterials are covered by various oxygen-containing groups, the carboxyl and hydroxyl groups both have acidic properties. Even for the single group (—COOH) functionalized system, the introduced carboxyl moiety can be located on the sidewall (surface) or at the tip (edge) on the CNTs (graphene). It is generally accepted that the acidity of the R—COOH is closely related to the stability of its corresponding conjugate bases (R—COO$^-$). Then when R is graphene or CNTs models, and when COOH is attached to different sites of the materials, what is the acidic difference with the conventional organic carboxylic acid? Among the different forms and sites of functionality, which contributes the most acidity to the nanostructured carbon materials? The present experimental techniques cannot provide the details of the individual acidic contributions of the functionalized groups to the overall acidity, and

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hence, the molecular modeling could be a complementary way to solve such problems.

It is well known that the acidity of a compound in different solvents can be reflected by its acidic constant pK_a value [44–45]. However, although the knowledge of this parameter is of fundamental importance in a wide range of applications and research areas, it is difficult to measure, or uncertain in many cases. Thanks to the rapid development of the computational chemistry, it is convenient to estimate the pK_a values of different compounds employing computational techniques. In the past years, a large number of theoretical studies of pK_a estimation for various compounds including carboxylic acids, phenols, alcohols and amines have been carried out and different strategies have been developed to predict the accurate values compatible with the available experimental results [44–52]. Among the various methods applied in calculating pK_a values, the direct cycle and the proton exchange cycle have been widely used because of their simplicity [44–52]. Therefore, in the present work, we have chosen those two methods to evaluate the effects of various factors on the acidity of carboxylated carbon materials.

Although there are numerous theoretical investigations about the carboxylated CNTs and graphene in the literatures [9–33], most of those researches mainly focus on the investigation in terms of geometric, energetic, and electronic properties induced by the functionalization [14–33]. Kar et al. have estimated the gas-phase acidity of several tip-carboxylated SWCNTs with varying lengths and diameters and the same level different basis set (SLDB) protocol is evaluated [24]. However, the previous literature mainly considered the gas phase acidity, while the acidic materials were always employed in solvents, and the acid dissociation constant (pK_a) could give a direct description of the acidic strength in aqueous phase. Therefore, in the current study, based on the pioneering works [24], the estimation of the aqueous pK_as for the carboxylated nanostructured carbon catalysts has been thoroughly investigated by quantum chemical approaches. The present study was performed to address the following questions: (a) the acidity prediction of -COOH positioned on the sidewall or at the tip of the CNTs with different lengths, diameters and chirality. The impact of two types of defects e.g. the single vacancy (SV) and the classic Stone-Wales (SW) defect, on the acidity of the carboxylated CNTs has also been considered. (b) The acidity of the —COOH positioned on the basal plane or at the (armchair, zigzag or corner) edge of the graphene. Also the acidity of the carboxylated defective graphene has been taken into account.

2. Computational details

2.1. pK_a calculations

The thermodynamic cycles (Cycle A and Cycle B) for the generally employed direct method and relative method to calculate the pK_a are illustrated in Scheme 1 [44–52].

In the direct thermodynamic cycle A, the free energy of the acid dissociation in water and subsequently the pK_a can be calculated as

$$\Delta G_{(aq)} = \Delta G_{(g)} + \Delta G_{solv}(A^-) + \Delta G_{solv}(H^+) - \Delta G_{solv}(HA) \tag{1}$$

$$\Delta G_{(g)} = G_{(g)}(A^-) + G_{(g)}(H^+) - G_{(g)}(HA) \tag{2}$$

$$pKa = \frac{\Delta G_{(aq)}}{RT\ln(10)} \tag{3}$$

Because of its simplicity, this method has been extensively used previously. However, the free energy of the solvated proton ($\Delta G_{solv}(H^+)$) is difficult to model theoretically, and thus we use the generally accepted value e.g. −265.9 kcal mol^{-1} in the present work [47], which is consistent with the parameterization of the SMD (solvation model based on density) model [53]. Since Ho has pointed out that the direct cycle is less accurate than the proton exchange method for most of the pK_a calculations [45], the proton exchange cycle, which based on an isodesmic reaction, is also evaluated. In this cycle, the reference acid is introduced and the uncertainties related to the free energy of the solvated proton are eliminated. Another advantage of this cycle is related to the cancelation of the errors in the solvation free energies since the involved charged species is conserved on both sides of the equation [44–51]. Therefore, more reliable acidic constant is expected to be obtained by this method. In the present paper, we choose benzoic acid as the reference acid and the experimental pK_a values for it is 4.20, respectively. According to the thermodynamic cycle in Scheme 1 (cycle B), the exchange free energy in water and the pK_a are calculated using Eqs. (4)(6).

Cycle A

$$\begin{tikzcd}
HA_{(aq)} \arrow[r, "\Delta G_{(aq)}"] \arrow[d, "-\Delta G_{solv}(HA)"'] & H^+_{(aq)} & +\ A^-_{(aq)} \\
HA_{(g)} \arrow[r, "\Delta G_g"] & H^+_{(g)} \arrow[u, "\Delta G_{solv}(H^+)"] & +\ A^-(g) \arrow[u, "\Delta G_{solv}(A^-)"']
\end{tikzcd}$$

Cycle B

$$\begin{tikzcd}
HA_{(aq)} \arrow[d, "-\Delta G_{solv}(HA)"'] & + & Ref^-_{(aq)} \arrow[r, "\Delta G_{(aq,\ PX)}"] \arrow[d, "-G_{solv}(Ref)"'] & HRef_{(aq)} & + & A^-_{(aq)} \\
HA_{(g)} & + & Ref^-_{(g)} \arrow[r, "\Delta G_{(g,\ PX)}"] & HRef_{(g)} \arrow[u, "\Delta G_{solv}(HRef)"'] & + & A^-(g) \arrow[u, "\Delta G_{solv}(A^-)"']
\end{tikzcd}$$

Scheme 1. Direct (Cycle A) and Proton exchange (Cycle B) thermodynamic cycles used in this study.

$$\Delta G_{(aq,PX)} = \Delta G_{(g,PX)} + \Delta G_{solv}(HRef) + \Delta G_{solv}(A^-) - \Delta G_{solv}(HA) - \Delta G_{solv}(Ref^-) \tag{4}$$

$$\Delta G_{(g,PX)} = G_{(g)}(HRef) + G_{(g)}(A^-) - G_{(g)}(HA) - G_g(Ref^-) \tag{5}$$

$$pKa = \frac{\Delta G_{(aq,PX)}}{RT\ln(10)} + pKa(HRef) \tag{6}$$

2.2. Computational methods

Based on the previous work reported by Kar et al. [24], the molecular models of the carboxylated SWCNT were constructed with the single —COOH group attached at the tip or on the sidewall of the tubes and terminated with hydrogen atoms. Different types of SWCNTs have been considered in the work, which include armchair ((5,5), (6,6), and (7,7)) and zigzag ((8,0), (9,0), and (10,0)) CNTs. To account for the effect of the tube lengths on the acidity, we selected (5,5) tube with six different lengths having the molecular formulas as $C_{40}H_{20}$, $C_{60}H_{20}$, $C_{80}H_{20}$, $C_{100}H_{20}$, $C_{120}H_{20}$, $C_{140}H_{20}$. For the comparison purpose, the carboxylated graphene sheets were also taken into account. Three configurations including the armchair and zigzag sheets were built with the carboxyl group attached at the basal plane or at the edge (armchair, zigzag and corner) for better understanding the configuration and the site