



One-pot titration methodology for the characterization of surface acidic groups on functionalized carbon nanotubes



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ARTICLE INFO

Article history:

Received 8 April 2015

Received in revised form

3 August 2015

Accepted 23 August 2015

Available online 28 August 2015

Keywords:

Carbon nanotube

Surface acidic group

Surface characterization

One-pot titration

direct titration

indirect titration

ABSTRACT

Functionalization is one of the key procedures for real applications of carbon nanotubes (CNTs) as it involves the generation of the acidic functional groups on their surfaces. In these procedures, precise elucidation of these surface acidic groups is significant for the proper utilization of the functionalized CNTs. For easy characterization of the practical acidic groups on CNTs, one-pot titration methodology is developed, breaking the boundary between the conventional indirect and direct titration methods. The practical acidic functional groups including carboxylic, lactonic, and phenolic groups were successfully computed from the acid ionization constant (pK_a) distribution from the direct titration of nitric acid-oxidized multi-walled CNTs by means of a one-pot titration methodology. These results were fairly identical to the results of the popular indirect titration method, showing that the developed methodology is essentially applicable for the surface characterization of acidic groups on CNTs and potentially extended to the other carbon nanomaterials.

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1. Introduction

Carbon nanotube (CNT) has been recognized as one of the most fascinating materials which are potentially utilized into next-generation electrical and energy/environmental applications because of its unique and outstanding mechanical, electrical, optical, and thermal properties [1–4]. Functionalization by oxidation is one of the key procedures leading to viable applications of CNT as this process generates desired functional groups on the surfaces [3]. These functional groups adjust the surface properties of CNT to enhance their dispersibility, adsorption properties, and reactivity levels, thereby potentially broadening the areas in which it may be applied.

Among the variety of these functional groups, the surface acidic groups including carboxylic or phenolic groups are in particular importance in the various utilization of CNT due to their capability of generating surface charges and ion exchange capability by easy deprotonation [5,6]. Specifically, the repulsion forces due to the generated surface charge make CNT more readily dispersible in the aqueous/organic solvents or matrix by overcoming the strong van

der Waals interactions for processing and preparation of high-performance composites [3]. Additionally, the ion exchange capability induced from the acidic sites adjusts the adsorption properties of CNT, which makes it applicable to metal/organic adsorbents for the energy and environmental devices including secondary batteries/supercapacitors [7], pollutants filters [8], and catalyst supports [9]. The acidic functional groups can be utilized with the crosslinking agents between the CNT strands for their high-performance self-assembled structures [10].

For proper utilization of the functionalized CNT, precise elucidation of the surface functional groups including the acidic moieties is significant to correlate the surface properties of CNT and the desired performances. For this purpose, various chemical investigation techniques such as Fourier-transform infrared spectroscopy (FT-IR), temperature-programmed desorption (TPD), and X-ray photoelectron spectroscopy (XPS) have been widely adopted for the surface characterization of functionalized CNT or other carbon material.

Specifically, FT-IR detects the vibration energies which originate from the stretching, bending, scissoring, wagging, twisting, or rocking of chemical bonds which absorb infrared light [7,11]. Though FT-IR technique is powerful tool for qualitative classification of various functional groups, the sensitivity of the infrared absorbance is lower than that of other techniques as the carbon

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usually absorbs the entire infrared range, making the quantification of these groups unlikely.

TPD utilize the different thermal stability levels of surface functional groups or physically attached moieties on the graphene layers of CNT [12]. For oxygen-containing groups, less thermally stable functional groups than graphene layers generally evolve into volatile gases such as carbon dioxide (CO₂) or carbon monoxide (CO) with a thermal treatments at an elevated temperature [12,13]. Generally, TPD equipment is coupled with mass-spectrometer to differentiate the evolved gas for the further quantification of functional groups such as carboxylic acids/anhydrous, lactones, phenols, and/or quinones [12].

XPS is one of the most widely utilized and well-established techniques for the surface characterization of various materials, including metals, ceramics, polymers, and carbon materials. In an XPS analysis, the binding energies (BE) of photoelectrons emitted as a result of X-ray irradiation to the core electrons of the samples are measured. This technique is useful for the quantitative elucidation of atomic compositions of functionalized CNT and of the chemical compositions of desired atoms [14]. For example, the bonding states (including carbon single/double bonds) of carbon atoms with heteroatoms can be estimated by deconvoluting the C1s spectra, which are generally located around a BE value of 284.5 eV [8]. Though quantitative analysis of the functional groups is possible with TPD and XPS measurements, the interpretation of the spectra might be ambiguous when the deconvolution temperature (TPD) or binding energy (XPS) ranges of functional groups are similar [15].

Among the numerous characterization methods assessed thus far, the titration method is a powerful tool for elucidating populations of functional groups with acid or base characteristics on CNT surfaces. More importantly, since the titration methods provide the absolute equivalence of the acidic groups on carbon surfaces, this technique has been applied to quantitative analysis of the adsorption properties [16] or reactivity [17,18] of these acidic functional groups.

For example, Carrasco-Marin et al. demonstrated the effects of acidic or basic groups on activated carbons on the adsorption properties of water [16]. In this work, the numbers of water-adsorbable sites and acidic or basic functional groups determined by titration method were correlated to investigate the number of water molecules interacting with each functional group. The results showed that *ca.* 3 molecules interacted with the carboxylic and lactonic groups, while *ca.* 1.5 molecules interacted with the phenolic and basic groups.

Titration methods were also used to determine the reactivity of the acidic functional groups of CNT. Worsley et al. covalently attached octadecylamine (ODA) to carboxylic groups on single-walled CNT to make them dispersible in tetrahydrofuran [17]. The degree of ODA loading was determined from the difference between the numbers of carboxylic groups before and after the DCC (1,3-dicyclohexylcarbodiimide) coupling amidation reaction. A similar investigation was reported for the covalent bonding of *n*-butylamine to carboxylic groups on multi-walled CNT (MWCNT) by means of EDAC (1-ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride) coupling amidation [18]. The covalent reactivity of carboxylated MWCNT was determined to range from 58 to 78% depending on the oxidation degree of the MWCNT.

Titration methods for elucidation of these useful surface acidic groups of carbonaceous materials are largely categorized into the indirect and direct methods. The indirect titration method, also known as Boehm titration [19], is commonly used due to its simple principles for the identification of the practical information on the surface of various carbonaceous materials including activated carbons, carbon fibers, carbon nanotubes, and graphene oxides [17,20–28]. With this method, three major types of functional

groups (carboxylic, lactonic, phenolic groups) are determined. These are responsible for the surface properties and for the numerous applications of the carbon materials. For the classification and quantification of these functional groups, Boehm suggested three bases with different basicities (NaOH, Na₂CO₃, and NaHCO₃) which are selectively neutralized with functional groups. Particularly it is generally assumed that NaOH reacts with all three functional groups, while Na₂CO₃ reacts with the carboxylic and lactonic groups, and NaHCO₃ reacts only with the carboxylic group [19].

Though indirect titration provides practical information about the acidic groups of carbonaceous materials for their appropriate utilization, several limitations prevent the simple adoption of the indirect titration method. For example, experimental procedures such as reaction, filtration and titration are fairly complicated and time-consuming comparing to other surface characterization methods [23,26,27]. Specifically, a carbon sample is mixed with a reaction base for a sufficient period, followed by filtration, after which the filtrate is titrated with an acid titrant. Additionally, the filtrates are acidified to remove dissolved carbon dioxide and are then titrated with the base solution (known as the inverse or back titration method) [23]. In our previous works on indirect titration, the acidification step appeared to be completely unnecessary in a systematic study of the effects of carbon dioxide (CO₂) on the titration of Boehm's reaction bases [20,21]. Nevertheless, complex experimental procedures remain and must be repeated for each reaction base, which is time-consuming and also make the indirect titration method inaccessible. Moreover, filtration steps for highly oxidized CNT individually dispersed in a reaction base [17,29] or GO with two-dimensional nanostructures [30,31] are hardly feasible or even impossible. These carbon nanomaterials can act as secondary filters and inhibit the filtration of the reaction mixture, which is an essential process in the indirect titration method. In such cases, surface characterization of carbon nanomaterials with indirect titration becomes difficult.

In contrast, when using the direct titration method [32–37], the sample is simply mixed with the titrand solution and is directly titrated for the identification of the acidic or basic characteristics of carbon materials. This method is widely used for the characterization of carbons and polymers with acidic (or basic) properties under the assumption that the acid constant (*pK_a*) values of numerous acids (or bases) are not discrete but are instead continuously distributed in a wide *pK_a* range expressed as the “*pK_a* distribution function.” While the direct titration method can effectively determine the population of the strong or weak acidic groups, the practical functions of these groups for the efficient utilization of carbon materials are not commonly provided, in contrast to indirect titration.

Therefore in this work, we develop a one-pot titration methodology penetrating the principles of direct and indirect titration for the simple elucidation of the surface properties of carbon nanomaterials especially for CNT. With this methodology, the *pK_a* distribution function of the direct titration of carbon nanomaterials is converted into practical indirect titration results based on the previously developed modified Henderson–Hasselbalch equation [20,21]. The validity of the developed methodology is verified with oxidized MWCNT (MWCNT).

2. Experimental

2.1. Chemicals and materials

All of the chemicals used as the titrants or titrands for the titration process, including NaOH, Na₂CO₃, NaHCO₃, and HCl, were provided by Daejung Chemicals, Korea, and the MWCNT was purchased from Hanwha Chemicals (CM250). For the functionalization

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