Catalysis Today 249 (2015) 23–29

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Characterization of functional groups on oxidized multi-wall carbon nanotubes by potentiometric titration

Zhiteng Zhang, Lisa Pfefferle, Gary L. Haller*

Department of Chemical and Environmental Engineering, School of Engineering and Applied Science Yale University, New Haven, CT 06520-8286, USA

ARTICLE INFO

Article history:
Received 26 August 2014
Received in revised form 4 December 2014
Accepted 5 December 2014
Available online 31 January 2015

Keywords:
Carbon nanotubes
Functionalization
Potentiometric titration
Principle component analysis
Characterization

ABSTRACT

Since the discovery of carbon nanotubes (CNT), this material has been recognized as an attractive material because of its exceptional physical and chemical properties. CNT must be functionalized for most applications. However, the functional groups on the CNT are very complex. Here a simple acid–base titration is introduced to characterize the functionalized multi-wall carbon nanotubes (MWCNT). By using the principle component analysis (PCA) of a titration data set of 21 independent curves, we can calculate the density of Brønsted acid functional groups for each differently functionalized MWCNT.

© 2015 Published by Elsevier B.V.

1. Introduction

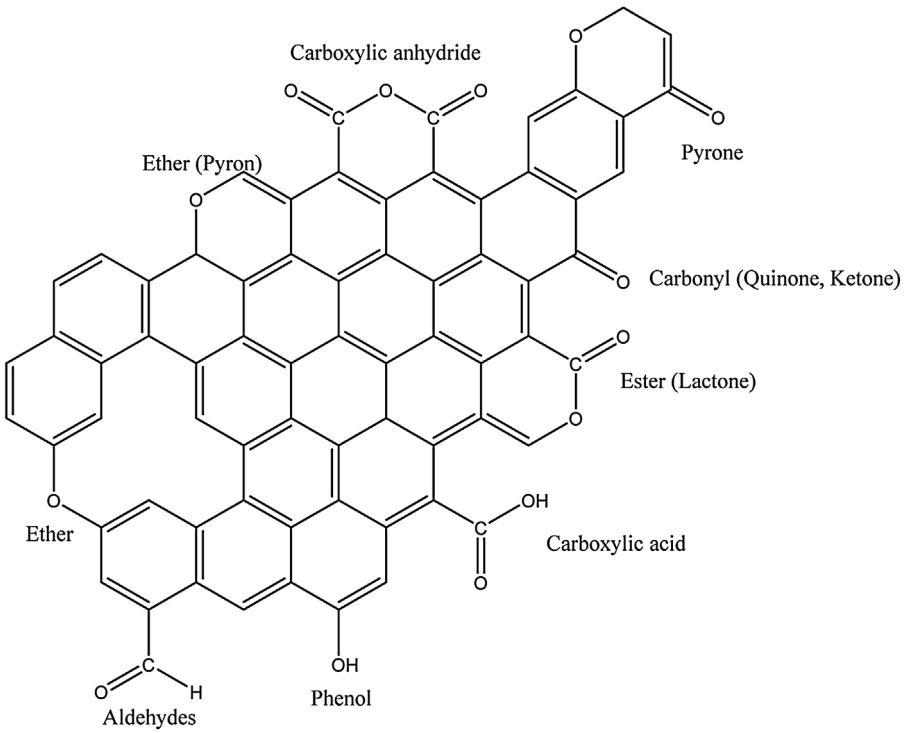
Carbon nanotubes (CNT), an array of graphene sheets rolled up into a hollow cylinder, were discovered by the Japanese researcher Sumio Iijima in 1991 [1]. The molecular structural understanding of CNT has been actively pursued by various researchers over the past couple of decades due to their small dimensions and mechanical, electrical, thermal and chemical properties [2]. These properties suggest enormous potential applications for CNT in many fields including nano-composite materials [3], nanosensors [4], as catalysts [5] and catalyst supports [6], optical devices [7], hydrogen storage [8,9] and nanoelectronic devices [10]. Despite the many desirable properties, the hydrophobicity and chemical inertness of CNT frequently hinders their commercial utilization. To overcome these limitations, CNT surfaces are often tailored using covalent or non-covalent modification methods. One of the most promising and widely utilized methods of surface modification is to oxidize the surface of CNT by some reagent such as nitric acid, sulfuric acid, hydrogen peroxide or potassium permanganate [11–13].

After oxidation, the surface of CNT has hydrophilic properties, which enhances the wettability for polar solvents. Moreover, the oxygen functional groups can be used as anchoring sites for metal particles and large molecules [14]. Therefore, it is of practical interest to understand the details of the nature and concentration of oxygen functional groups on the CNT surfaces, especially for using CNT as catalyst support. Scheme 1 shows some possible functional groups on CNT surfaces after nitric acid treatment.

Several researchers have developed different ways to characterize the functional groups qualitatively or quantitatively. The most common techniques include: transmission electron microscopy (TEM), Raman spectroscopy, infrared spectroscopy (IR), thermogravimetric analysis (TGA), temperature programmed desorption (TPD), Boehm titration, near-edge X-ray absorption fine structure (NEXAFS), X-ray photoelectron spectroscopy (XPS) and chemical derivatization (CD) [15]. However, all these methods have their own drawbacks and are either time consuming or sample consuming. TEM is capable of imaging the structure of CNT, including the presence of side wall damage. However, the electrons used for imaging can themselves damage the sidewalls. Also, TEM is a localized characterization, which makes it an unreliable method to do quantitative characterization [16]. Raman spectroscopy of the CNT typically consists of a graphitic G-band and a D-band representing the disorder in the sidewalls [17]. Theoretically, the ratio of the intensity of D–G bands characterizes the defect density on the sidewall of CNT. Unfortunately, many CNT may have amorphous carbon adsorbed on the sidewalls, which also contributes to the D-band intensity. IR spectroscopy does not provide a quantitative measurement of functional group concentrations, and peaks are often hard to distinguish from background features [18]. TGA and TPD can give some indirect information on the functional groups by oxidation or dissociation that occur at different temperatures. One limitation of this method is that it requires a significant amount

* Corresponding author. Tel.: +1 203 432 4378; fax: +1 203 432 4387.
E-mail address: gary.haller@yale.edu (G.L. Haller).

http://dx.doi.org/10.1016/j.cattod.2014.12.013
0920-5861/© 2015 Published by Elsevier B.V.



Scheme 1. Possible functional groups on CNT surface after nitric acid treatment.

of sample. Another disadvantage is that interpreting the data is quite arbitrary due to the close proximity of different peaks whose characterization temperature is affected by catalyst impurities. Xia and coworkers [19] have determined the concentration of surface carboxyl groups on multiwalled carbon nanotubes (MWCNT) by measuring the concentration of CO_2 produced during COOH decarboxlyation at ~400 °C. Boehm titration is a classical way to determine quantities of protic functional groups. The analysis is carried out by neutralizing different protic groups with bases of various basicities (e.g., $NaHCO_3$, Na_2CO_3, NaOH, $NaOC_2H_5$) [20–22]. The limitation of this analysis is that it cannot be applied to aprotic groups. Furthermore, it is a very time and sample consuming process also. NEXAFS has also been used to elucidate the oxygen functional groups. The oxygen concentration is quantified based on π^*(C=O) and σ^*(C—O) resonances in the carbon K-edge. Both carbonyl and ether groups have been identified. Upon heating to 500 K, the carbonyl group concentration decreased. At 1073 K all the carbonyl and ether groups were removed [23]. However the use of NEXAFS for routine analysis is limited by the need for a synchrotron. Also, NEXAFS edge spectra can only be reliably interpreted when a few chemical states of an element are present. When a complex system is involved, like the oxidized CNT, the unambiguous fitting becomes extremely difficult. XPS analysis is a powerful way to do the quantitative analysis. Many researchers have used both the O (1s) and C (1s) spectral windows to identify different groups (e.g., C—H, C—O, C=O, COOH) [19,21,24]. However, deconvolution of XPS spectral envelopes may also be ambiguous. Wepasnick and coworkers compared the analysis of two different sets of literature values for the peaks of oxygen-containing groups, although both fits give low levels of error, the deconvolution results have significant differences [25]. Another powerful method is chemical derivatization. In three separate reactions, hydroxyl, carbonyl and carboxyl groups are labeled, by reaction with trifluoroacetic anhydride, trifluoroethyl hydrazine and trifluoro ethanol and carbodiimide, respectively [25]. Using chemical derivatization-X-ray photoelectron spectroscopy (CD-XPS), they found that $KMnO_4$ and HNO_3 treated MWCNT exhibit greater fractions of COOH groups compared with the O_3 treated MWCNT. The limitation of this analysis is similar to the Boehm titration, which means it is a time and sample consuming process.

In our previous study, we characterized functionalized MWCNT by the point of zero charge (PZC) [26]. It is well known that the PZC is affected by the functionalities, but an analytical relationship is not known. Gorgulho et al. [27] have used potentiometric titration to characterize oxygen containing groups on carbon material. In order to quantitatively compare the pH curves, a nonlinear program was used to calculate the pK_a distribution and the acid site concentrations. Data fitting was started by assuming the presence of all three functional groups (carboxylic acid, lactone, and phenol). After the preliminary results, more sites were added to the model until no statistically significant improvement was observed. However, this method ignored the existence of different carboxylic, lactone and phenol groups. Although the fitting result is good, there is no objective way of choosing the number and pK_a's of the functional groups.

Here we have developed a conventional auto titration method, coupled with principle component analysis (PCA), to characterize the Brønsted acidity functional groups. The PCA does provide an objective method of determination the number of the major proton titratable functional groups and their pK_a, but there is still a degree of subjectivity in identifying the structure of the functional groups associated with a given pK_a.

2. Experiment

The MWCNT (20–30 nm outer diameter, 10–30 μm in length, and >95% purity, as provided by the vendor) used in this research, synthesized by the chemical vapor deposition (CVD) method, were purchased from Cheap Tubes Inc., and labeled as-received-MWCNT. Combustion of the MWCNT produces a residual mass of non-volatiles of 2.3 wt%. All other reagents, unless stated otherwise, were used as received and were supplied by Aldrich.

Download English Version:

https://daneshyari.com/en/article/53704

Download Persian Version:

https://daneshyari.com/article/53704

Daneshyari.com