



Understanding the redox reactions of adjacent carboxyl groups and anhydride groups following citric acid treatment of defect-containing multiwalled carbon nanotubes

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ABSTRACT

Although carbon materials have been widely used in battery applications, the origin of the redox reaction appearing in the important potential region is not well understood. Moreover, typical functionalization treatments that use diluted strong acids are limited by strong oxidation and the properties of water-based solutions. Thus, most treatments cannot precisely control the nature of functional groups. The present work investigates a citric acid treatment that selectively fixes carboxyl and anhydride groups onto multiwalled carbon nanotubes at low temperatures. The results show that the edges of the defect structures of multiwalled carbon nanotubes provide suitable positions at which redox-active adjacent carboxyl groups and anhydride groups can form during citric acid treatment.

1. Introduction

Because of their flexible structure and modifiable surface, carbon nanotubes (CNTs) are widely used as a base material for batteries and capacitors [1]. For these applications, the redox reaction is very important because it relates directly to the faradaic process [2]. However, untreated CNTs do not meet the demand for high redox activity [3]. Thus, oxidation treatments that use nitric acid, sulfuric acid, or hydrochloric acid have been studied as methods to functionalize CNTs by introducing oxygen-containing functional groups (OFGs) [4].

Although a better understanding of the redox reaction and OFGs is highly desirable, investigations have heretofore only considered redox reactions between quinone and multiwalled carbon nanotubes (MWCNTs) [5]. However, most studies that use traditional strong-acid treatments introduce large amounts of compounds with different types of functional groups, which usually results in a broad redox feature [6,7]. Moreover, such acid treatments are limited by the uncontrollable oxidation properties of strong acids and the properties of water-based solutions and therefore cannot be used for selective and precise introduction of electrochemical properties that are conferred by specific types of OFGs [8].

There have been comparatively few investigations of the redox properties of OFGs at low temperatures. We noticed that adjacent carboxyl groups (ACIGs) on the surface of MWCNTs can transform into anhydrides, which are thought to show redox activity. Thus, an

investigation of the influence of ACIGs and anhydride groups by selective introduction of these groups may provide critical information for understanding CNT-based catalysts. In this study, we therefore introduce OFGs at low temperature by applying a solid citric acid treatment to different types of MWCNTs. Citric acid is a weak tricarboxylic acid that contains three carboxyl groups, as indicated by a strong carboxyl peak around 130 °C in temperature-programmed desorption. In addition, it is not stable at high temperatures and starts to decompose at around 200 °C [9]. The results suggest that citric acid treatment allows redox-active OFGs to form on the edges provided by hole-defect structures.

2. Material and methods

2.1. Citric acid properties

The dehydration products of citric acid are trans-propene-1,2,3-tricarboxylic acid and cis-propene-1,2,3-tricarboxylic acid [10]. Because these two acids also contain three carboxyl groups and because the decomposition temperature of citric acid is relatively low (< 200 °C), citric acid can be used to introduce ACIGs [11].

2.2. Preparation of multiwalled carbon nanotubes

In this study, three different types of MWCNTs [i.e., untreated

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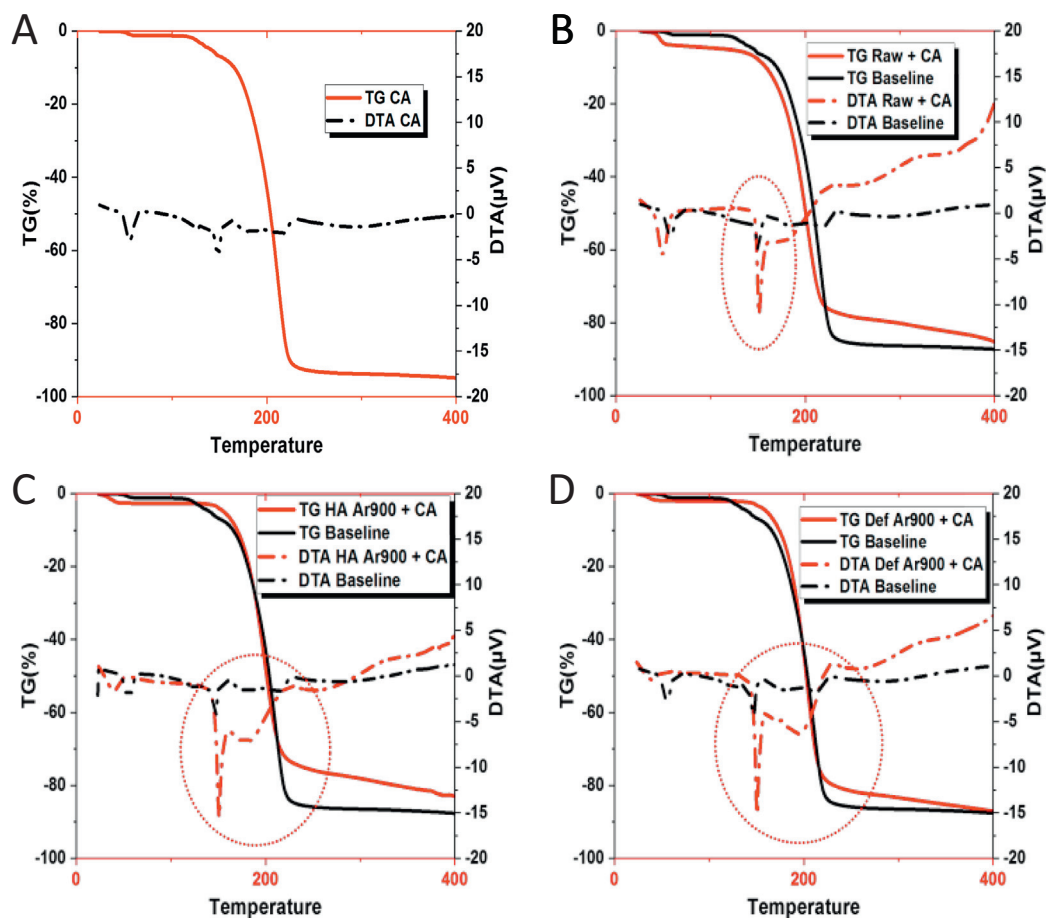


Fig. 1. Thermogravimetric analysis and differential thermal analysis: (a) Citric acid, (b) Raw-CNT with citric acid, (c) HA-Ar900 with citric acid, and (d) Def-Ar900 with citric acid. Ovals show increase in citric-acid decomposition peak.

MWCNTs (Raw-CNTs), heat- and acid-purified MWCNTs (HA-CNTs), and defect-containing MWCNTs (Def-CNTs)] were used to study the introduction of OFGs. We used untreated hollow MWCNTs from Showa Denko KK, Japan (VGFX-X 250001, 15 nm diameter, approximately 3 mm long, < 1 wt% Fe impurities). Heat and acid pretreatments were applied to remove the amorphous carbon and metal impurities. Defects in the MWCNTs were introduced by chemical drilling [12].

2.3. Citric acid treatment

The citric acid used in this research was obtained from Sigma-Aldrich (citric acid monohydrate, ACS reagent $\geq 99.0\%$). Considering that the original OFGs may cause unexpected effects, we begin by annealing the HA-CNTs and Def-CNTs at $900\text{ }^{\circ}\text{C}$ in an Ar atmosphere (Def-Ar900) to remove all OFGs. The Raw-CNTs did not require this step because they contain even fewer functional groups than HA-Ar900 or Def-Ar900. Next, we mixed the MWCNTs with citric acid monohydrate at a 1:1 mol ratio and heated the mixed powder to $250\text{ }^{\circ}\text{C}$ for 10 min in the ambient air. The citric acid treatment was carried out at $250\text{ }^{\circ}\text{C}$ for two reasons: (i) citric acid decomposes above $250\text{ }^{\circ}\text{C}$ [13], and (ii) the reaction at $250\text{ }^{\circ}\text{C}$ has the highest carboxyl peak and forms an anhydride functional group [14]. Finally, the samples were washed by ultrapure water and dried overnight in a vacuum oven.

2.4. Electrochemical characterization

A glassy carbon disk electrode was prepared by the dropping method. A 10 mg/ml dispersion of CNTs in a water-ethanol solution was prepared by 2 h of ultrasonication. The modified glassy carbon electrode was prepared by dropping $10\text{ }\mu\text{l}$ of the dispersion onto glassy carbon and drying overnight at $70\text{ }^{\circ}\text{C}$. All electrodes were cleaned using aluminum polish and washed with distilled water prior to use.

Cyclic voltammetry (CV) measurements were recorded from 0.059 to 1.059 V vs RHE (-0.2 to 0.8 V vs Ag/AgCl) in Ar-saturated 0.1 M HClO_4 solution at room temperature at a scan rate of 5 mV/s by using a Metrohm Autolab (PGSTAT30) instrument.

3. Results and discussion

3.1. Citric acid treatment and molecular change

We used thermogravimetric analysis and differential thermal analysis (Rigaku, Thermo plus EVO TG-DTA 8120ST) to study the reaction between the citric acid and the CNT mixture (Fig. 1). The baseline is given by a linear combination of the thermogravimetric spectra of CNTs and citric acid. The differences between the measured line and the baseline are caused by the reaction. After mixing with the MWCNTs, the magnitude of the citric acid decomposition peak increases [see ovals in Fig. 1(b) and (d)]. The comparison shows that the mass of the Def-Ar900 + CA sample decreases rapidly with a high heat-absorption peak

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