Mechanistic study on the interfacial variation of carbon electrode under electrochemical oxidation

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ABSTRACT

Previously, we have reported that different procedures employed for electrochemical oxidation of glassy carbon (GC) can lead to remarkably different interfaces for the redox reactions of copper species in the presence of Cl$^-$ anion. In this article, we further investigated the interfacial variation mechanism of other carbon electrodes employing both cyclic and potentiostatic oxidation methods in H_2SO_4 solution. The electrochemical studies were limited to the end-edge planes of vertically aligned multi-walled carbon nanotubes (eVAMWCNTs) and the edge planes of highly oriented pyrolytic graphite (eHOPG). Differences in the pristine surfaces and bulk structures of these two sp^2 carbon electrodes were merely resulted from the arrangements of graphene multilayers by rolling seamlessly or parallel alignment. Experimental results showed that cyclic oxidation favored the generation of oxygen-containing groups at eVAMWCNTs, due to that rigid MWCNT surface and bulk structures were unfavorable for the intercalation reaction of SO_4^{2-} anion. On the other hand, potentiostatic oxidation was found to cause the oxidation of eVAMWCNTs via a different reaction route. By contrast, the oxidation of the soft eHOPG predominantly involved the intercalation of SO_4^{2-} anion into the gaps between graphene layers, which might restrain the increase of oxygen-containing groups at eHOPG. As probed by Raman spectroscopy and the redox reactions of copper species, significant differences in the interfacial variation with two oxidation methods were observed for eVAMWCNTs. As indicated by an abnormal behavior of metallic copper deposition/dissolution, only the cyclic oxidation could quickly generate a very high ratio of oxygen-containing groups to other electron transfer sites (edge steps and defect sites) at the eVAMWCNT interfaces, similar to the previous observations for GC. Due to limitation in the increase of oxygen-containing groups at the eHOPG interfaces, two oxidation methods would not cause significant differences in the electrode responses for the redox reactions of copper species.

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1. Introduction

As one of the most important electrode materials, sp^2 carbon continues to attract massive interest from many different perspectives. This type of carbon material shows very different electrochemical interfaces due to diverse bulk phases. Usually, different carbon electrodes display different electrochemical characteristics [1–9]. Great efforts have been made to explore the carbon electrode interfaces in the past several decades. A large portion of fundamental research, mainly focusing on highly oriented pyrolytic graphite (HOPG) and multi-walled carbon nanotubes (MWCNTs), has indicated that three types of electron transfer sites exist at carbon electrode interfaces, including discrete defects on basal planes, edge steps, and oxygen-containing groups [10–24]. Substantially, the variation in interfacial structures is attributable to the ratio and the structure of these different electron transfer

sites [10–24]. On the other hand, carbon electrodes often undergo various pretreatments before use [25–41]. The resulting electrode interfaces have been found to be closely related to their histories of pretreatment [37–41]. Nevertheless, the variation in interfacial structures of various carbon electrodes resulted from different pretreatment procedures has not yet been fully understood so far.

In comparison with other methods, electrochemical oxidation is a simple, controllable and reproducible means to pretreat carbon electrode [3,37–51]. Most of relevant pretreatment methods usually involve the application of a relatively high anodization potential in an acidic or neutral aqueous electrolyte employing different electrochemistry procedures. In summary of findings from various researches, electrochemical oxidation of carbon electrodes always involves complicated processes, in which many different reactions may occur simultaneously [3,37–51]. Related reactions can be roughly classified as: 1) the generation of oxygen-containing groups;2) the removal of carbon material, which can create defect sites and/or edge steps;3) the formation of graphite intercalation, which is caused by the intercalation of electrolyte

anion into the gaps between graphene layers. Obviously, each of the different reactions will cause a distinct influence on the electrode interfaces. Theoretically, the combined effects, presumably including the pretreatment procedure, the electrolyte solution, the pristine surface and bulk structure, would likely facilitate or inhibit a certain reaction occurring in the whole pretreatment process. For example, it has been reported that glassy carbon (GC) is unfavorable for the graphite intercalation reaction in the anodic polarization process, due to its rigid bulk structure originated from the interwoven sp^2 carbon nanoribbons [1–3,45–47]. Our previous studies further indicated that different procedures employed for electrochemical oxidation of GC would lead to remarkably different interfaces [46,47]. Concretely speaking, cyclic oxidation conducted in sulfuric acid solution would preferably lead to a low distribution density of active sites at the GC interfaces for the early nucleation of metallic copper in the presence of Cl^- anion, being remarkably different from potentiostatic oxidation [47]. These findings intrigued us to explore whether such an interfacial variation mechanism is suitable to other carbon electrodes or not, when their pristine surface and bulk structure have very different rigidity features.

Besides GC, MWCNTs also have the rigid pristine surface and bulk structure constituted by rolling graphene multilayers seamlessly. It has been reported that MWCNTs were resistive to the intercalation of electrolyte anion in the anodic polarization process [53]. By contrast, HOPG has a typically soft pristine surface and bulk structure, due to the parallel alignment of graphene multilayers, which may allow the formation of graphite intercalation [52]. In this article, HOPG and vertically aligned MWCNT electrodes were prepared in the same way for comparison [54–56]. Electrochemical studies were limited to the edge planes of HOPG (eHOPG) and the end-edge planes of vertically aligned MWCNTs (eVAMWCNTs) exclusively. The interfacial variations of eVAMWCNTs and eHOPG resulted from both cyclic and potentiostatic oxidation approaches were investigated in H_2SO_4 electrolyte solutions. The electrochemical interfaces of eVAMWCNTs and eHOPG were examined by utilizing the redox reactions of copper species occurring at high Cl^- anion concentration, which have been shown to be very sensitive to the carbon electrode interfaces, especially to the electron transfer sites for the early nucleation of metallic copper [47,57].

2. Experimental section

2.1. Chemicals

Copper(II) chloride, sodium chloride and 3.4-dihydroxybenzaldehyde (DHB) were purchased from Aldrich. Reagent solutions were freshly prepared and degassed for at least 10 min before use. Deionized water was obtained by purification through a Millipore system. All chemicals were of reagent grade and were used as received.

2.2. Electrode preparation

An ultra-long VAMWCNT film (of 4 mm in thickness, 20 nm in diameter and a surface area of about 1 cm^2) on a silicon wafer was synthesized by a chemical vapor deposition method. For the preparation of eVAMWCNT electrode, highly permeable epoxy resin (SPI-Pon-812, SPI) was pipetted onto the vertical MWCNT forest circulated by a Teflon ring mold (2 mm in diameter) and was allowed to be solidified at 60 °C under vacuum for 48 h. After taking off from the Teflon mold, both sides of the VAMWCNT/epoxy disk were polished with finer paper to expose all the nanotube end-edge planes. One side of the disk was deposited with gold and then attached to the end of a steel cylinder by conductive silver glue, while another side was open for electrolyte contact.

The same procedure was employed for the preparation of eHOPG (ZYH grade, Advanced Ceramics) and the basal planes of HOPG (bHOPG) electrodes with one side of either edges planes or basal planes for electrochemical study.

According to the method reported in the literature [58,59], another MWCNT paste was prepared by mixing epoxy resin with MWCNTs (with a diameter of 20– 40 nm and a length < 5 μm; obtained from Shenzhen Nanotech Port Co., Ltd.). The MWCNT paste electrode was fabricated by the same procedure described above.

Prior to use, eVAMWCNT, eHOPG, GC (CHI104, CHI) and MWCNT paste electrodes were polished progressively with finer emery-paper and Al_2O_3 powder (0.3 μm) on a polishing cloth. Then the electrodes were cleaned by deionized water in an ultrasonic bath for 1 min. The newly resurfaced bHOPG electrode was obtained by using stripping means with adhesive tape.

2.3. Apparatus and measurements

Voltammetric measurements were recorded with a CHI-660A Voltammetric Analyzer (CH Instruments, Inc.). A three-electrode cell was employed, incorporating a working electrode (eVAMWCNTs, eHOPG, bHOPG, GC, and MWCNT paste), a saturated calomel reference electrode (SCE) and a platinum foil counter electrode. All potentials were quoted versus the SCE reference.

Two different voltammetric oxidation methods were employed in 0.5 M H_2SO_4. For potentiostatic oxidation, the working electrodes were anodized at +2.0 V for a short period of time (from 0.5 to 3.0 min) and then polarized at −1.0 V for 1 min. Cyclic polarization was employed by cycling the electrodes between −0.3 and +2.0 V at 0.1 V/s for the desired number of cycles.

The images of scanning electron microscopy (SEM) were obtained by an S-4800 (Hitachi, JP) electron microscope. The images of scanning tunneling microscopy (STM) were captured using a Nanoscope III AFM instrument (Digital Instrument, CA, USA) with Pt/Ir tips mechanically shaped by scissors. The tip current was 1 nA and the bias voltage was in the range between 0.1 and 0.5 V.

Raman spectroscopy was conducted with a Renishaw 2000 equipment (532 nm). Raman signal was averaged with the measurements from six different spots for each sample. Raman shifts were calibrated with the silicon reference peak at 521 cm^{-1}.

3. Results and discussion

3.1. Electrochemical oxidation of eVAMWCNT and eHOPG electrodes

Fig. 1A shows the cyclic voltammograms (CV) for the oxidation of the polished eVAMWCNT electrode. Potential was continuously cycled between −0.3 to +2.0 V at a scan rate of 0.1 V/s in degassed 0.5 M H_2SO_4 solution. The electrode surface was oxidized at the potential higher than +1.1 V. The highest anodic current was observed at +2.0 V as a consequence of water electrolysis. On the reverse scan, a cathodic peak was built up gradually at around −0.01 V. The electrode responses became stable after 10 cycles. However, if the upper-potential was set at lower than +1.0 V, the polished eVAMWCNT electrode would not give any cathodic peak. These observations revealed that the cathodic peak was due to the continuous increase of oxygen-containing groups caused by the over-oxidation of eVAMWCNTs, being similar to the findings for the electrochemical oxidation of polished GC electrodes [45].

As a control experiment, the oxidation of the polished eHOPG electrode was carried out in the same way (Fig. 1B). The oxidation was observed at the potential higher than +1.4 V. On the reverse cycles, a broad cathodic peak appeared at around +1.5 V, which is due to the reduction reaction of graphite intercalation resulted from the intercalation of SO_4^{2-} anion into the gaps between the graphene layers [52]. Nevertheless, no obvious cathodic peak involving the reduction of oxygen-containing groups was observed in the whole cyclic voltammetric measurements.

Two kinds of edge planes of two different sp^2 carbon electrodes offered different responses to the identical CV procedure, confirming