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Synthesis of short graphene oxide nanoribbons for improved biomarker detection of Parkinson's disease

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ABSTRACT

We demonstrate the microwave-assisted synthesis of short graphene oxide nanoribbons (GONRs) through unzipping cut multiwalled carbon nanotubes (MWCNTs). Transmission electron microscopy and dynamic light scattering spectroscopy were used to examine the length, size, and morphology, i. e. unzipping level, of our various products. The nanotube core and nanoribbon shell can be observed from short GONRs via a modified unzipping recipe. Then the short GONRs were adopted to modify the glassy carbon electrode for the electrochemical detection of ascorbic acid (AA), uric acid (UA), and dopamine (DA). Compared to other nanomaterials, cyclic voltammograms of short GONRs show higher anodic oxidation currents for AA, UA, and DA. The detection limits of three analytes are 26, 98, and 24 nM, respectively, in amperometric current–time measurements. Especially, the sensitivity for DA is improved to be 40.86 $\mu A\ \mu M^{-1}\ cm^{-2}$. The improved detection signals are due to the increased active sites of the open ends of short GONRs. Moreover, the width side of short GONRs could be more active than their length side. All above-mentioned results reveal that the short GONRs can provide a novel platform for electrochemically biomarker detection of Parkinson's disease.

1. Introduction

Carbon is one of the most abundant elements in nature, and novel crystalline nanocarbons have been predicted and synthesized over the past few decades (Campos-Delgado et al., 2008; Iijima 1991; Kroto et al., 1985; Novoselov et al., 2005, 2004; Tapaszto et al., 2008). Since the discovery of graphene, it has attracted lots of attention in electrochemical biosensing (Kuila et al., 2011; Liu et al., 2012; Pumera 2011; Pumera et al., 2010; Yang et al., 2010). There is a bright future for graphene as a sensing material because of its biocompatibility, lack of metallic impurities, high conductivity and abundance of inexpensive source material. The large surface area and excellent electrical conductivity of graphene allow it to connect between the redox centers of an enzyme or protein and an electrode surface. Rapid electron transfer facilitates accurate and selective detection of biomolecules. The applications of graphene for the detection of glucose, cytochrome c (Cyt-c), nicotinamide adenine dinucleotide (NADH), hemoglobin (Hb), cholesterol, ascorbic acid (AA), uric acid (UA), dopamine (DA), and hydrogen peroxide (H_2O_2) have been discussed (Kuila et al., 2011). Among all analytes, UA and DA are reported to be the biomarkers of Parkinson's disease (Cheemalapati et al., 2013; Cheng Xiang Lim et al., 2010; Ezhil Vilian et al., 2014; Hong Yan Yue et al., 2014; Ming Zhou and Dong, 2009; Palanisamy et al., 2013; Rajkumar et al., 2014; Shang et al., 2008; Sheng et al., 2012; Sun et al., 2011a, 2011b).

Because of its superior electronic properties, graphene is broadly considered to be the most promising candidate to replace Si in future electronic devices (Ma et al., 2013). However, the zero bandgap of graphene normally gives its field effect transistors (FET) a low on/off ratio. Great efforts have been dedicated to opening a bandgap in graphene. Among the most used techniques, making graphene into narrow nanoribbons to open the bandgap through the lateral quantum confinement effect is one of the most promising approaches (Son et al., 2006; Verónica Barone and Scuseria, 2006). There are many ways to synthesize graphitic nanoribbons. In 1990, graphitic nanoribbons were first produced using a chemical vapor deposition (CVD) process involving the disproportionation of carbon monoxide at 400–700 °C, which was catalyzed by $Fe(CO)_5$ particles in flowing CO/H_2 gas (Murayama and Maeda, 1990; Terrones et al., 2012). These graphitic nanoribbons consisted of filaments of 10 μm in length and 0.1–0.7 μm in width while a metal catalyst particle was always located at one of their ends. An alternative CVD production method for obtaining graphitic nanoribbons was reported by Campos-Delgado et al. (2009). On the other hand, pure organic chemical routes have been

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used to synthesize graphene nanoribbons (GNRs) by linking tetra- and hexa-phenylbenzenes via the Suzuki–Miyaura reaction (Xiaoyin Yang et al., 2008). GNRs have also been produced by sonochemically cutting graphene sheets (Wu et al., 2010) or by using nanowire etch masks (Bai et al., 2009). In addition, carbon nanotubes (CNTs) have been more recently utilized as the starting material to obtain GNRs (Terrones 2009, 2010). For example, (Jiao et al., 2009) have described the chemical synthesis of GNRs by plasma etching of nanotubes partially embedded in polymer or by heating expanded graphite to 1000 °C in 3% H_2 in Argon. In 2011, we demonstrated that GNRs can be used to detect AA, DA, and UA, respectively (Sun et al., 2011a). Graphene nanoribbons and their composites were utilized to detect the brevetoxin B, interleukin-6, matrix metallopeptidase-9, H_2O_2, dobutamine, uric acid, ascorbic acid, dopamine, NADH and DNA bases, namely guanine and adenine (Asadian et al., 2014; Hernández-Ferrer et al., 2014; Lim et al., 2014; Shi et al., 2014; Tang et al., 2012). However, little is known about how the length of GNRs will affect their properties and applications. Therefore, it is of interest to investigate the length effects of GNRs on the electrochemical biosensing.

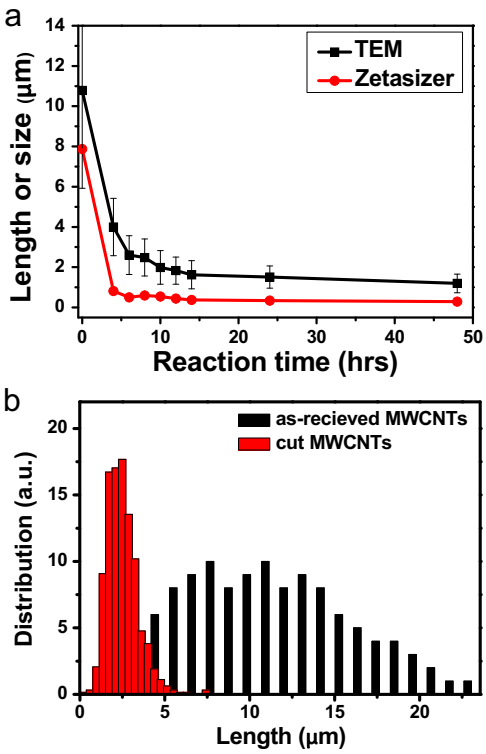

Fig. 1. (a) Reaction-time-dependent length or size for as-received and cut MWCNTs using TEM or Zetasizer observation, respectively. (b) Length distribution plot of as-received and cut MWCNTs at the reaction time of 8 h from TEM observation.

In 1998, Liu et al., used H_2SO_4/HNO_3 and sonication to cut single-wall carbon nanotubes (SWCNTs) (Liu et al., 1998). Zhao et al. (2011) utilized the silicon carbide particles adhered on the abrasive papers to cut long and entangled MWCNTs. Wang et al. (2011) cut MWCNTs through selective etching in molten nitrate. For Li-ion batteries, short CNTs as anode have a lower electrical resistance and Warburg prefactor, resulting in better rate performance at high current densities (Wang et al., 2007). In terms of double layer capacitance and surface area, the sample of short MWNTs have larger capacitance and higher surface area than those of long MWCNTs (Y. Wang et al., 2009; Yuan et al., 2010). On the other hand, short CNTs also showed much better electrochemical performance as catalyst supports in fuel cells (X.X. Wang et al., 2009). Compared to short CNTs, there has been little research performed on the electrochemistry of short GNRs. Although PEGylated short GONRs were used as drug nanocarriers to develop an efficient cancer therapy strategy, it was difficult to mass produce short GONRs using our early reported recipe (Lu et al., 2014). Herein, we not only prepare short GONRs derived from short MWCNTs in a scale-up process but also present their simultaneous electrochemical detection of three analytes. The

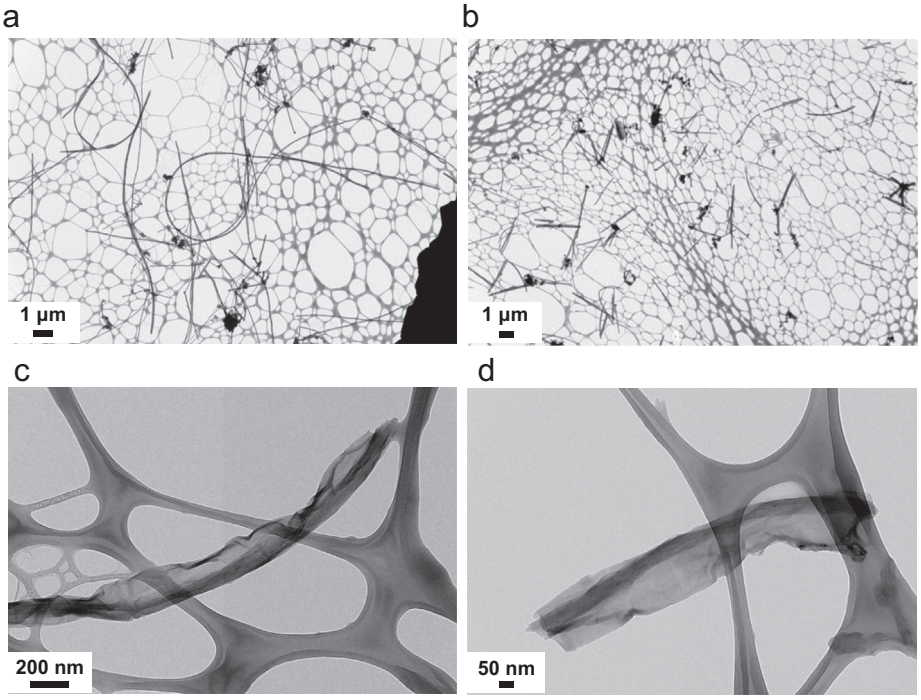

Fig. 2. Transmission electron microscope images of (a) as-received MWCNTs, (b) cut MWCNTs, (c) an individual long GONR, and (d) an individual short GONR derived from the cut MWCNTs in (b). The reaction time for cut MWCNTs in (b) in acidic solutions is 8 h. The short GONRs in all the following figures are prepared using the cut MWCNTs in (b).

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