



## Short communication

## Electrochemistry of partially unzipped carbon nanotubes

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## ABSTRACT

Despite several pioneering work, the fundamental study of partially unzipped carbon nanotubes (PUCNTs) as an electrode material has hardly been done. In this work, we synthesized PUCNTs by solution-based longitudinal unzipping of carbon nanotubes (CNTs) and rigorously studied their electrochemical characteristics by using three representative redox probes. Electrochemical measurements reveal the superior electrochemical response of PUCNTs in comparison with CNTs, which can be attributed to the unique CNT–graphene complex structure of PUCNTs. Besides, for the three redox probes involved, the electron transfer kinetics of PUCNTs behave variously, indicating that the extent to which structural features affect electron transfer rates depends on the analytes. Our work suggests the great potential of PUCNTs as a sort of new electrode material for future electrochemical applications.

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## 1. Introduction

Carbon-based electrode materials have attracted much attention owing to their well-defined nanostructure, excellent electrical conductivity and chemical stability [1–8]. The electrochemical behaviors of graphitic carbon are significantly affected by its edge configuration, structural defects, and oxygen-containing groups, which act as active sites for electrochemical reactions. Much of the catalytic activity, electron transfer (ET), and chemical reactivity occurs at surface defect sites, in particular edge-plane-like sites/defects [1,9–13].

As a well known carbon allotrope, carbon nanotubes (CNTs) have been intensively and extensively studied. Recently, it has been found that CNTs can be longitudinally cut to give partially unzipped carbon nanotubes (PUCNTs) by controlling the oxidative opening degree [14]. PUCNTs possess unique unzipping-degree-dependent electronic and magnetic properties [15,16]. They can be seen as CNT–graphene junctions, which develop a graphene-like structure on the outer walls with abundant edges and defect sites responsible for electrochemical and other activities, while partially inherit the tube structure from CNTs on the inner walls maintaining high electrical conductivity needed to sustain efficient charge transport during electrochemical processes [17]. We assumed that, by combining these two factors, PUCNTs can be expected to behave electrochemically superior to CNTs and graphene. However, despite several pioneering work about the theoretical researches and applications of PUCNTs [17–20], the systematic study of

PUCNTs as an electrode material in fundamental electrochemistry has hardly been done.

In this work, we synthesized PUCNTs by solution-based longitudinal unzipping of CNTs [14]. We used three representative outer- and inner-sphere redox probes to study the electrochemical characteristics of the as-prepared PUCNTs and compared that with their parent CNTs. Our work gives further insights into the electrochemistry of PUCNTs and sheds light on the potential usefulness of them in various electrochemical applications.

## 2. Experimental

Multiwalled carbon nanotubes (purity >97%, ca. 20 nm in diameter and 5–15 μm in length) were used as received from Shenzhen Nanotech Port Co. Ltd., China. Ru(NH<sub>3</sub>)<sub>6</sub>Cl<sub>3</sub> (stored at 2–8 °C) was purchased from Sigma-Aldrich Co., LLC, USA. Other reagents were obtained from Sinopharm Chemical Reagent Co., Ltd., China, and of analytical grade. All solutions were prepared with ultrapure water of resistivity not less than 18.25 MΩ cm<sup>−1</sup>. PUCNTs were prepared according to the method proposed by Tour et al. [14], except that the addition of KMnO<sub>4</sub> was 300 wt.%.

Transmission electron microscopy (TEM) images were obtained with a Tecnai G2F20 S-TWIN field emission transmission electron microscope. Raman spectroscopy (inVia + Reflex, Renishaw) and X-ray photoelectron spectroscopy (XPS, ESCALAB 250) were used to analyze the composition of the as-prepared materials. Electrochemical experiments were performed with a CHI 660E electrochemical workstation (Shanghai Chenhua Instrument Co. Ltd., China). All the experiments were carried out with a three-electrode system with a glassy carbon electrode (GCE, Φ = 3 mm) as the working electrode, a platinum wire

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as the auxiliary electrode, and a saturated calomel electrode (SCE) as the reference electrode. Prior to modification, GCE was carefully polished to a mirror-like surface with alumina slurries and rinsed thoroughly. PUCNT or CNT dispersion was coated onto the GCE surface and dried in air to fabricate a PUCNT/GCE or CNT/GCE.

### 3. Results and discussion

PUCNTs were first examined using TEM. As shown in Fig. 1A, CNTs have been partially cut to give PUCNTs consisting of a few layers with widths of 30–50 nm. The PUCNTs are randomly oriented and entangled with each other as a result of strong molecular interactions. The outer walls of the CNTs have been cut to form some graphene pieces of different sizes, while the inner walls possess the hollow core of the nanotubes visible within. Fig. 1B further shows that the edges are partly destroyed and become rough, but the inner walls still retain the layer graphitic structure of CNTs.

Raman and XPS spectra were undertaken to study the effect of oxidative-unzipping on the defect density and oxygen content of the samples. Raman spectra (Fig. 1C) indicate that, from CNTs to PUCNTs, the ratio of the D to G band intensities ( $I_D/I_G$ ) increases (Table 1), reflecting the increase of their defect density, which is caused by the reduction in size of the  $sp^2$  domains due to the strong oxidation. The complex structure of CNTs and graphene makes PUCNTs heterogeneous in nature, giving rise to the larger amount of defects. Besides, the 2D

band becomes broader and weaker, suggesting the gradual destruction of the multilayer graphitic structure within the CNTs [21]. XPS (Fig. 1D) reveals that after oxidative unzipping, for PUCNTs, the carbon contents (81.36%) comprise of 48.75 atomic% at 284.6 eV, which is characteristic of graphitic groups, and 23.44 and 9.17 atomic% at 286.3 and 288.6 eV, which correspond to hydroxyl/carbonyl and carboxyl groups, respectively. The O/C ratio is 0.23, much larger than that for CNTs. Detailed data are listed in Table 1.

Electrochemical impedance spectroscopy (EIS) is used to investigate the ability of the electrode to transfer and exchange charges with the analyte solution. Such ability is strongly influenced by the structural conformation and surface chemistry of the electrode material [22]. In our case (Fig. 2A), the charge-transfer resistance ( $R_{CT}$ ) of PUCNT/GCE ( $\sim 100 \Omega$ ) is smaller than that of CNT/GCE ( $\sim 240 \Omega$ ), corresponding to the favorable charge transport kinetics. This is because for the PUCNTs, the outer graphene-like structure and the inner tube-like structure behave as completely transparent contacts for each other. Besides, the former can act at certain energy ranges as perfect valley filters for the latter. Both lead to the maximum possible conductance of the complex system [15].

We further studied the electrochemical behaviors of PUCNT/GCE using cyclic voltammetry (CV), with three redox probes,  $[\text{Ru}(\text{NH}_3)_6]^{3+}$ ,  $[\text{Fe}(\text{CN})_6]^{4-}$ , and  $\text{Fe}^{3+}$ . CVs of CNT/GCE were also performed as control experiments. The obtained CV curves are shown in Fig. 2 and the CV data (including peak-to-peak separation  $\Delta E_p$  and ET rate constant  $k^0$ )

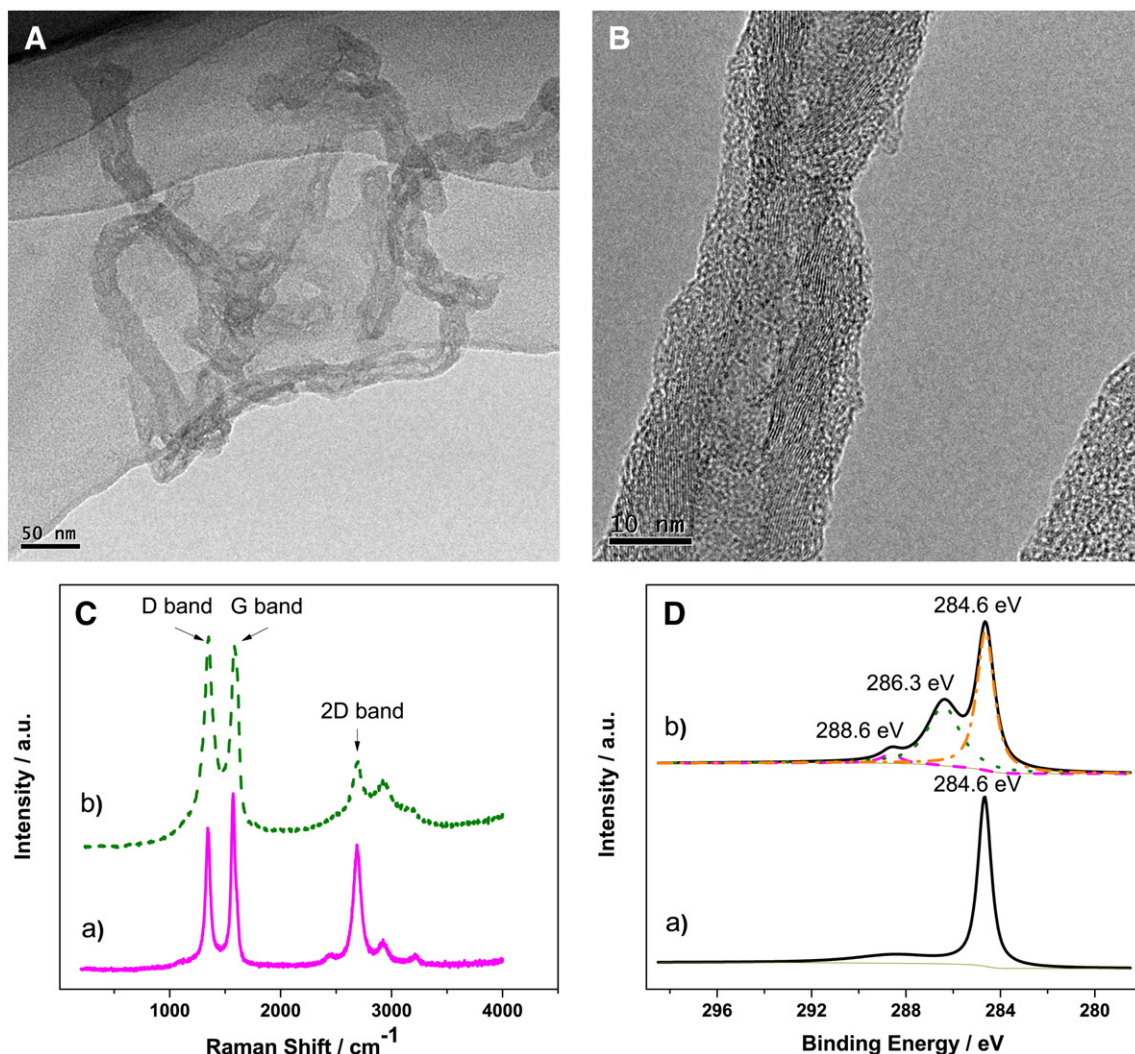


Fig. 1. (A) Typical and (B) high-resolution TEM images of PUCNTs; (C) Raman and (D) XPS C1s spectra of (a) CNTs, (b) PUCNTs.

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