Controllable Growth of Conical and Cylindrical TiO$_2$–Carbon Core–Shell Nanofiber Arrays and Morphologically Dependent Electrochemical Properties

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Abstract: Quasi-aligned cylindrical and conical core–shell nanofibers consisting of carbon shells and TiO$_2$ nanowire cores are produced in situ on Ti foils without using a foreign metallic catalyst and template. A cylindrical nanofiber has a TiO$_2$ nanowire core 30–50 nm in diameter and a 5–10 nm-thick cylindrical carbon shell, while in the conical nanostructure the TiO$_2$ nanowire core has a diameter of 20–40 nm and the thickness of the carbon shell varies from about 200 nm at the bottom to about 5 nm at the tip. Electrochemical analysis reveals well-defined redox peaks of the [Fe(CN)$_6$]$^{3-/4-}$ redox couple and heterogeneous charge-transfer rate constants of 0.010 and 0.062 cm$^2$ s$^{-1}$ for the cylindrical and conical nanofibers, respectively. The coverage of exposed edge planes on the cylindrical and conical carbon shells is estimated to be 2.5 and 15.5% respectively. The more abundant exposed edge planes on the conical nanofiber decrease the overpotential and increase the voltammetric resolution during electrochemical detection of uric acid and ascorbic acid. Our results suggest that the density of edge-plane sites estimated from Raman scattering is not necessarily equal to the density of exposed edge-plane sites, and only carbon electrodes with a large density of exposed edge planes or free graphene sheet ends exhibit better electrochemical performance.

Introduction

Carbon is frequently an electrode material of choice due to its high electrical conductivity, flexible surface chemistry, and wide potential window in aqueous solutions. It is known that graphite and other carbon allotropes, such as carbon nanotubes (CNTs), carbon nanofibers (CNFs), fullerenes, and graphite, are constructed from building blocks consisting of layered graphene.[1] A graphene layer can be defined as a hexagonal network of covalently bonded carbon atoms or a single two-dimensional layer of three-dimensional graphite. The central part of a graphene layer is usually called the graphite basal plane, and the edge is the graphite edge plane.[1] The main characteristic distinguishing CNFs from CNTs is the stacking mode of the graphene sheets.[2] A CNT can be envisioned as a rolled-up seamless graphene tube with graphitic basal planes as the wall and graphitic edge planes as the tube ends. The graphene sheets in CNFs are not parallel to the axis and the edges of different graphene sheets end at the sidewalls, and so CNFs have more exposed edges and unsaturated bonds of graphene planes along the surface. The electron-transfer (ET) rates at edge-plane sites are estimated to be about 10$^7$ times higher than those at basal-plane sites.[3] As a result, CNFs are far more electrochemically active than CNTs.[3] In addition, the more abundant graphitic edge planes on CNFs make modification and immobilization of biomolecules, such as enzymes,[3a–4] antigens,[5] DNA,[6] and even tumor cells[7] easier. Hence, CNFs, especially quasi-aligned CNFs, have attracted increasing attention as electrodes in electrochemical sensors requiring high sensitivity and selectivity.

Carbon nanofibers are usually fabricated by catalytic deposition of hydrocarbons or carbon monoxide on the surface of metal catalysts,[2–8] and most CNFs contain metal nanoparticles inherited from their growth by metal-catalyzed chemical vapor deposition.[28] These metal nanocatalysts are located in the center of the tube channel or sheathed by the graphene multilayers and thus are difficult to remove, even by prolonged contact with strong acids.[8] The remaining metal nanoparticles not only lead to potential misinterpretation of electrochemical signals but also compromise the electrochemical reproducibility and stability.[9] A recent investigation indicated that even 0.01 wt% of metal impurities can
are produced on the TiO₂ nanowire core by simply adjusting the conical shape. In this technique, cylindrical or conical wire cores but variable carbon shell thickness giving rise to aligned CNFs[2a,8b] have been reported, to the best of our knowledge, controllable synthesis of conical and cylindrical CNFs with different exposed graphitic edge planes by a catalyst-free method and their corresponding shape-dependent electrochemical activity have not been systematically investigated more accurately and the materials have more applications.

The electrochemical reaction pertinent to electrochemical biosensing is an interfacial process between the outer surface of the electrode and electrolyte and, in this regard, only sites on the exposed edge plane contribute to the electrochemical transfer reaction on carbon electrodes. CNFs have a cylindrical or conical morphology according to the different arrangements of graphene sheets. In comparison with cylindrical CNFs, conical CNFs may have more abundant exposed edge-plane sites and better mechanical stability. If conical and cylindrical CNFs with different edge-plane densities and edge-plane exposure sites could be produced in a controllable fashion, the shape-dependent electrochemical properties and the fundamental mechanism could be studied accurately. Better knowledge of the electrochemical behavior of carbon electrodes enables proper design and construction of highly sensitive and selective biosensors. Although the fabrication and electrochemical biosensing properties of aligned CNFs[2a,8b] have been reported, to the best of our knowledge, controllable synthesis of conical and cylindrical CNFs with different exposed graphitic edge planes by a catalyst-free method and their corresponding shape-dependent electrochemical activity have not been systematically investigated.

Here we report a simple method to grow in situ conical and cylindrical core–shell TiO₂–C nanofibers on titanium foils by a thermal reaction under acetone vapor without using any template or catalyst. The cylindrical nanofiber arrays have uniform TiO₂ nanowire cores and carbon shells, while the TiO₂–C nancone arrays have uniform TiO₂ nanowire cores but variable carbon shell thickness giving rise to the conical shape. In this technique, cylindrical or conical carbon shells with different exposed graphitic edge planes are produced on the TiO₂ nanowire core by simply adjusting the reaction temperature and acetone content. The two different microstructures permit investigation of the electrochemical behavior of carbon nanostructures. The ET rate in the [Fe(CN)₆]³⁻/⁴⁻ redox system on the conical CNFs was measured to be much larger than that on the cylindrical CNFs. The coverage of exposed edge planes on the cylindrical and conical CNFs is estimated to be 2.5 and 15.5%, respectively, and this indicates the possibility to control the density of exposed edge-plane sites by using this catalyst-free method. The oxidation overpotentials of uric acid (UA) determined for the conical aligned CNFs are lower than those measured for the cylindrical CNFs, and the voltammetric resolution for direct determination of UA in the presence of ascorbic acid (AA) is larger on the conical aligned CNFs. Cylindrical and conical CNFs can be depicted as “kaleidoscope” and “Christmas tree”, respectively, to visualize the differences in exposed edge-plane sites and electrochemical behavior. The quasi-aligned conical TiO₂/C nanoelectrodes have large specific surface area and controllable exposed edge-plane sites that can be easily accessed by molecules in the solution and thus have immense potential in electrophysiological studies and biosensing applications.

**Results and Discussion**

**Characterization of cylindrical and conical aligned CNFs:** Figure 1a and b depict the field-emission scanning electron microscopy (FE-SEM) images of products fabricated at 800 and 850°C and reveal that uniform cylindrical and conical nanofibers were synthesized directly on Ti foils. Transmission electron microscopy (TEM) images show that the cylindrical nanofiber consists of a nanowire core 30–50 nm in diameter and a shell 5–10 nm in thickness (inset in Figure 1a). The conical nanofiber has an inner core 20–40 nm in diameter and a shell with thickness diminishing from about 200 nm at the base to 5 nm at the tip (inset in Figure 1b). The main diffractions peaks of both the cylindrical and conical nanofibers in the XRD pattern in Figure 1c correspond to tetragonal rutile TiO₂, except for those from Ti substrate. The XPS survey scan spectrum (Figure 1d) shows a strong Cls peak at 284.5 eV, a small O 1s peak at 532 eV, and a weak O KLL Auger band at 973 eV, suggesting the presence of only carbon in the shell with the exception of some absorbed oxygen on the surface. The synthesized nanofiber consists of a rutile TiO₂ nanowire core and a carbon nanofiber shell, and the shape of the shell gives rise to the final morphology.

Figure 2a and b display the high-resolution TEM (HRTEM) images of a cylindrical and conical nanofiber,
which reveal that the TiO$_2$ nanowire core of both the cylindrical and conical nanofibers is single-crystalline with tetragonal rutile structure. The lattice spacing between adjacent lattice planes of the nanowire core of about 0.25 nm corresponds to the distance between two (101) planes of rutile TiO$_2$. The graphene sheets in both the cylindrical and conical structures are not parallel to the axis of the nanowire core but rather intersect the sidewalls at a small angle. In addition, the carbon shell is not well graphitized, and thus a large number of graphitic edge-plane sites inevitably exist at the edge due to the discontinuity of graphite planes. The free graphene-sheet ends can be clearly observed in the HRTEM images, as indicated by arrows in Figure 2b. In comparison with the cylindrical carbon shell, the conical shell has more abundant free graphene-sheet ends. This leads to better electrochemical properties (see below).

The above characterization results confirm direct growth of cylindrical and conical core–shell TiO$_2$–C nanofibers on Ti foils by simply adjusting the reaction temperature and acetone precursor content without the need for a template or foreign catalyst. The mechanism of this catalyst-free growth process is described below. At the high temperature of 800°C, acetone is decomposed into CH$_3$ radicals and CO,[12] and the CO generated in situ reacts with the Ti surface to form TiO$_2$. The Ti atoms in the Ti foil continuously diffuse upwards through the grain boundary of the formed TiO$_2$ and react with CO to form more TiO$_2$ species, and finally grow epitaxially into TiO$_2$ nanowires. At the same time, carbon atoms produced by the reaction Ti+2CO→TiO$_2$+2C and decomposition of CH$_3$ radicals precipitate on the surface of the TiO$_2$ to form the carbon shell. The carbon shell prevents TiO$_2$ from growing randomly and leads to quasi-aligned growth and formation of aligned TiO$_2$ nanowires. Consequently, cylindrical nanofibers consisting of a TiO$_2$ nanowire core and C shell are produced at 800°C. When the reaction temperature is raised to 850–900°C and more acetone precursors are introduced, deposition of C from CH$_3$ radicals is faster. On the substrate, more carbon atoms precipitate onto the base of the TiO$_2$ nanowires due to the relatively local high temperature, but at the tip the precipitation rate of C from CH$_3$ radicals is smaller due to the lower temperature.[13] At the same time, H atoms produced by pyrolytic decomposition of CH$_3$ can move upwards and etch the deposited carbon layer at the top (tip).

Finally, a conical CNF shell is formed on the surface of the TiO$_2$ nanowire at 850°C. The conical TiO$_2$–C nanofiber has a nanowire core and conical carbon shell, and the morphology is different from that of common nanocones with a conical core and uniform shell.[14] More importantly, this fabrication technique is simpler and more economical due to the one-step in situ synthesis of the core–shell structures on a conducting metal substrate without using any catalyst or template.

**Electrochemical performance:** The heterogeneous charge-transfer kinetics on the cylindrical and conical carbon shells were studied by monitoring the [Fe(CN)$_6$]$^{3-}/^4-$ redox couple, which is sensitive to carbon surface microstructure and the density of electronic states near the Fermi potential. The voltammetric experiments were carried out without any pretreatment on as-synthesized cylindrical and conical CNFs in a 1.0 mm K$_3$[Fe(CN)$_6$] and 1.0 m KCl solution over a potential range of −0.1 to 0.6 V (vs. Ag/AgCl) at different scanning rates from 10 to 500 mV s$^{-1}$. Figure 3a shows a reversi-
ble voltammetric response to the $[\text{Fe(CN)}_6]^{3-/4-}$ redox couple with a peak-to-peak potential separation ($\Delta E_p$) of 69–101 mV and a peak current ratio $i_p/i_n$ of 0.97–1.02 for the cylindrical CNFs. For the conical CNFs measured under the same conditions, $\Delta E_p$ is in the range of 63–68 mV, which is very close to the ideal value of 59 mV for a single ET process$^{[3]}$ and $i_p/i_n$ is between 0.97 and 1.03 (Figure 3b). The anodic and cathodic peak currents for cylindrical and conical nanofibers are directly proportional to the square root of the scanning rate of 10–500 mV s$^{-1}$ (insets in Figure 3a and b), which implies that the ET kinetics of the $[\text{Fe(CN)}_6]^{3-/4-}$ redox couple on the aligned CNFs surface is predominantly diffusion controlled.

The relationship between $\Delta E_p$ and scanning rate is illustrated in Figure 3c. The $\Delta E_p$ value measured for the conical CNFs is much lower than that of the cylindrical CNFs for all scanning rates, and indicates much larger ET rates on the conical CNFs. The heterogeneous charge transfer rate constants $k^0$ can be estimated by Nicholson’s method$^{[15]}$ [Eq. (1)]:

$$k^0 = \psi \left( \frac{nFV}{RT} \right) \frac{D_R}{D_0} \frac{n}{nF}$$

in which $\psi$ is the kinetic parameter, $n$ is the number of electrons transferred in the electrochemical process, $F$ is the Faraday constant, $v$ is the scanning rate, $R$ is the gas constant, $D$ is the diffusion coefficient of ferricyanide ($D_0 = 7.6 \times 10^{-4}$ cm$^2$s$^{-1}$ and $D_R = 6.3 \times 10^{-4}$ cm$^2$s$^{-1}$)$^{[16]}$ and $\alpha$ is the transfer coefficient (0.5). According to the $\Delta E_p$ values measured at a scanning rate of 500 mV s$^{-1}$, $k^0$ is 0.010 and 0.062 cm s$^{-1}$ for $[\text{Fe(CN)}_6]^{3-/4-}$ on the cylindrical and conical CNFs, respectively, that is, ET rates on the conical nanofibers are higher. The exposed edge-plane sites on the electrode surface can be approximated by Equation (2):$^{[17]}

$$k^0_{\text{obs}} = k^0_{\text{edge}} \theta_{\text{edge}}$$

in which $\theta_{\text{edge}}$ is the global coverage of the edge-plane sites, $k^0_{\text{obs}}$ is the observed ET rate constant at the electrode surface, and $k^0_{\text{edge}}$ is the ET rate constant on the edge planes of the redox probe with a value of 0.4 cm s$^{-1}$. Equation (2) gives estimated global coverages of the edge-plane sites $\theta_{\text{edge}}$ on the cylindrical and conical CNFs of 2.5 and 15.5%, respectively. The results suggest that the morphology of the carbon electrodes is an important factor affecting the exposed edge-plane sites that account for the electrochemical activity. The density of the exposed edge-plane sites on the conical CNFs is much larger than that of the cylindrical CNFs. Consequently, larger ET rates and electrochemical activity are expected from the conical CNFs due to the more abundant exposed edge-plane sites.

Selectivity in determination of uric acid and ascorbic acid: Uric acid (UA), the final oxidation product of purine metabolism in the human body, is excreted in urine.$^{[18]}$ UA concentrations outside the normal range are symptoms of some diseases, such as gout, Lesch–Nyhan syndrome, cardiovascular problems, and multiple sclerosis.$^{[19]}$ Monitoring of the UA concentrations under biological conditions is of great importance to early diagnosis of many diseases. Although voltammetry is a simple and effective approach, voltammetric detection of UA is often interfered with by coexisting ascorbic acid (AA) in biological fluids such as blood and urine. To demonstrate the different electrocatalytic activities of the conical and cylindrical TiO$_2$–C nanofibers, we investigated electrocatalytic oxidation of AA and UA. Figure 4a and b show the cyclic voltammograms (CV) obtained from 0.1 mM UA, 1.0 mM AA, and a mixture of 0.1 mM UA and 1.0 mM AA in 0.1 M phosphate buffer (pH 7.4). a) Cylindrical CNFs and b) Conical CNFs at a scan rate of 5 mV s$^{-1}$.

**Figure 4.** Cyclic voltammograms of 0.1 mM UA, 1.0 mM AA, and a mixture of 0.1 mM UA and 1.0 mM AA in 0.1 M phosphate buffer (pH 7.4). a) Cylindrical CNFs and b) Conical CNFs at a scan rate of 5 mV s$^{-1}$.
Raman scattering and microstructural analysis: Raman scattering is a useful tool to discern ordered and disordered crystalline structures of carbon. In electrochemical analyses, Raman scattering is also widely used to evaluate the density of edge-plane sites by monitoring the D band/G band ratio \( I_D/I_G \). It is generally accepted that a larger \( I_D/I_G \) value represents more disorder and defects and better electrochemical activity. \(^{[20]}\) The Raman spectra acquired from the cylindrical and conical CNFs are depicted in Figure 6. The two principal peaks corresponding to the D and G bands are observed at about 1344 and 1588 cm\(^{-1}\), respectively. Shifting of the G band to 1588 cm\(^{-1}\) indicates that the carbon shells are made of nanocrystalline graphite or sp\(^2\) clusters. \(^{[21]}\) The band locations for both of the cylindrical and conical CNFs are similar, but the \( I_D/I_G \) ratios are different (1.68 and 1.21, respectively). The Raman results imply a higher density of edge-plane sites on the cylindrical CNFs compared to the conical CNFs. However, the density of exposed edge planes derived from electrochemical characterization of the cylindrical CNFs is much lower than that of the conical CNFs. Evidently, the density of the edge-plane sites is not necessarily identical to the density of exposed edge plane sites on the carbon electrode. In other words, a bigger \( I_D/I_G \) ratio does not necessarily translate into a higher electrochemical electron-transfer rate. The optical penetration depth in graphite is about 20 layers, \(^{[22]}\) as determined by Raman analysis at an excitation wavelength of 514 nm. The electrochemical behavior associated with electrochemical biosensing is dictated by an interfacial reaction between the outer surface of the electrode and the electrolyte. Therefore, only the exposed edge-plane sites on the surface contribute to the electrochemical transfer reactions. The edge-plane sites in the bulk are not involved in the electrochemical reaction, because they are covered by the outer graphene layers and not in contact with the electrolyte. Thus, the efficacy of the electrochemical activity of a carbon electrode cannot be judged by the \( I_D/I_G \) ratio alone, since the density of the edge-plane sites determined by Raman scattering is not necessarily equal to the density of the exposed edge-plane sites. Faster ET and better electrochemical properties are attributed to more abundant free graphene-sheet ends but not to the density of total edge-plane sites. Only a carbon nanoelectrode with high density of exposed edge-plane sites on the surface has better electrochemical transfer and electrocatalytic activity. Our results reveal that Raman scattering data must be examined in the proper context.

The microstructure of the cylindrical and conical CNFs synthesized directly on Ti foils can be depicted as “kaleidoscope” and “Christmas tree”, respectively (Figure 7) to distinguish the difference in the exposed edge-plane sites. The cylindrical TiO\(_2\)–C nanofiber has a nanotubular shell with a large amount of defects and smaller sp\(^2\) domains. Graphitic edge-plane sites that inevitably exist at the edge are attributed to discontinuity of the graphite planes. The conical nanofibers have a shell with decreasing thickness from the bottom (200 nm) to the tip (5 nm). The gradually changing...
diameter is the result of a quantum process in which the graphitic layers are reduced one by one and the edges of different graphene sheets end at the sidewalls. Hence, the density of exposed graphitic edge-plane sites on the conical CNFs is higher than that on the cylindrical CNFs, and the conical CNFs have better electrochemical activity than the cylindrical CNFs.

Conclusion

Conical and cylindrical core–shell TiO₂–carbon nanofiber arrays could be controllably synthesized directly on Ti foils by catalyst-free thermal reactions, and their electrochemical activities were evaluated. Electrochemical analysis reveals well-defined redox peaks of the [Fe(CN)₆]³⁻/⁴⁻ redox couple and heterogeneous charge-transfer rate constants of 0.010 and 0.062 cm s⁻¹ for the cylindrical and conical nanofibers, respectively. The coverage of exposed edge planes on the cylindrical and conical CNFs is estimated to be 2.5 and 15.5%, respectively. “Kaleidoscope” and “Christmas tree” models are proposed to explain the different microstructures and electrochemical behavior. Our results show that the density of exposed edge-plane sites cannot be inferred simply from the I_p/I_c ratio determined by Raman scattering alone, but rather other characterization techniques such as electrochemical measurements and HRTEM must also be employed. The high density of exposed edge-plane sites decreases the overpotentials and increases the voltammetric resolution. The gradually decreasing thickness of the conical shell from bottom to top of the conical carbon shell allows more effective exposure of graphitic edge-plane sites, and consequently a higher electron-transfer rate and higher electrocatalytic activity are expected. Concentrations of 2.0–15.0 mM of UA in the presence of 1.0 mM AA can be detected by the conical aligned CNFs without pretreatment, and the voltammetric detection limit of UA is as low as 0.22 μM. The fabrication method and unique core–shell structures have great potential in electrochemical biosensors requiring high sensitivity and selectivity.

Experimental Section

Preparation and characterization of quasi-aligned CNFs: Quasi-aligned CNFs were fabricated directly on a Ti metal substrate by a thermochemical reaction under acetone vapor. Titanium foils (10 × 10 × 1 mm², Advent, 99.5%) were degreased by ultrasonication in acetone and then ethanol, followed by polishing in a solution containing H₂O, HF, and HNO₃ with a volume ratio of 5:1:4 for 5 min to remove the surface native oxide. After rinsing with double-distilled water (DDW) and drying under a nitrogen flow, the Ti foil was loaded onto a ceramic substrate placed at the center of an alumina tube in a horizontal tube furnace. The reactor was purged with pure argon several times to remove residual oxygen and moisture before heating to 800–900°C under Ar. Acetone was then introduced into the chamber together with argon at a flow rate of 50 sccm (standard cm³ min⁻¹ for cylindrical CNFs) or 150 sccm (for conical CNFs). After 1.5 h, the tube was cooled to RT under flowing argon. The black products on the Ti foil were characterized by XRD (Philips XPert Pro), FE-SEM (FEI Nova 400 Nano), TEM, (Philips CM20), HRTEM (JEOL JEM-2010), Raman scattering (Renishaw 2000), and X-ray photoelectron spectroscopy (XPS, Physical Electronics PHI 5802).

Electrochemical measurements: The electrochemical experiments were conducted on a CHI 660b potentiostat (CH Instruments, Shanghai, China). The aligned CNFs produced on the Ti foil were insulated with epoxy resin to leave an open area of 9.9 mm² as working electrode, an Ag/AgCl electrode as the reference electrode, and a Pt wire as counter-electrode. Uric acid (UA) and ascorbic acid (AA) were of reagent grade and purchased from Sigma. Potassium ferricyanide and other chemicals were of analytical grade. DDW was used to prepare the solutions and clean the electrodes. The ET kinetics was determined by CV in 1.0 M KCl containing 1.0 mM K₃[Fe(CN)₆]⁻. Determination of UA and AA was accomplished by CV and differential pulse voltammetry in 0.1 M phosphate buffer solution at a pH of 7.4.

Acknowledgements

This work was jointly supported by the National Natural Science Foundation of China (50902104 and 21105077) and a City University of Hong Kong Strategic Research Grant (SRG) #7008089.


Received: July 20, 2011
Published online: November 22, 2011