Recyclable and High-Sensitivity Electrochemical Biosensing Platform Composed of Carbon-Doped TiO$_2$ Nanotube Arrays

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ABSTRACT: Electrode fouling and passivation are the main reasons for attenuated signals as well as reduced sensitivity and selectivity over time in electrochemical analysis. We report here a refreshable electrode composed of carbon-doped TiO$_2$ nanotube arrays (C-doped TiO$_2$-NTAs), which not only has excellent electrochemical activity for simultaneous determination of 5-hydroxytryptamine and ascorbic acid but also can be easily photocatalytically refreshed to maintain the high selectivity and sensitivity. The C-doped TiO$_2$-NTAs are fabricated by rapid annealing of as-anodized TiO$_2$-NTAs in argon. The residual ethylene glycol absorbed on the nanotube wall acts as the carbon source and no foreign carbon precursor is thus needed. The morphology, structure, and composition of the C-doped TiO$_2$-NTAs are determined, and the corresponding doping mechanism is investigated by thermal analysis and in situ mass spectroscopy. Because of the high photocatalytic activity of the C-doped TiO$_2$-NTAs electrode, the electrode surface can be readily regenerated by ultraviolet or visible light irradiation. This photoassisted regenerating technique does not damage the electrode microstructure while rendering high reproducibility and stability.

Electrochemical biosensors are extremely useful to the detection and monitoring of different analytes in environmental and clinical applications such as neurotransmitters, proteins, nucleic acids, and small molecules because of their simplicity, reliability, high selectivity, and sensitivity. A highly efficient electrode with an interface for the charge transfer process constitutes the core of an electrochemical biosensor and generates potentials and/or currents that are related to the contents in the test solution. Carbon is one of the widely used electrochemical electrode materials due to its high electrical conductivity, chemical inertness, flexible surface chemistry, and a wide potential window in aqueous media. In particular, oriented carbon nanotube and nanofiber arrays are attractive materials for highly sensitive and selective electrochemical biosensors because of their high surface-to-volume ratio, well-defined edge plane structure, and high degree of biologically accessible surface. However, nanostructured carbon electrodes are prone to surface fouling and passivation by radical intermediates or polymerization products generated by the electrochemical reactions between the analytes and electrode surface. This undesirable phenomenon can lead to significant signal attenuation as well as reduced sensitivity and selectivity over time.

Several physical and chemical strategies have been developed to refresh the electrode surface in order to improve the reproducibility and stability. For instance, mechanical polishing has been employed to remove surface contaminants from glassy carbon (GC) and other bulk metal electrodes, but this technique is difficult to implement on nanostructured electrodes. Other processes such as vacuum annealing, laser ablation, flame etching, acid washing, chemical oxidative etching, and electrochemical polarization have also been investigated, but the harsh oxidation procedures easily damage and alter the electrode microstructure and/or surface chemistry. The background current is affected frequently leading to poor reproducibility and stability. Consequently, it is imperative to design a nanostructured electrode having self-cleaning functions or develop a self-refreshable technique to prevent electrode fouling.

In a bioelectrochemical analysis, the fouling substances are primarily organic biomolecules such as serotonin, histamine, amino acids, NADH, aniline, and so on. These organic bio-molecules can be photocatalytically decomposed into inorganic compounds of CO$_2$ and H$_2$O on TiO$_2$ and ZnO photocatalysts by ultraviolet (UV) or visible (Vis) irradiation. This photocatalytic procedure does not alter the morphology and structure of the photocatalyst surface and enables the use of oxide semiconducting nanostructures in self-cleaning and refreshable electrodes. Although one-dimensional Cs$_x$Cu$_{y}$ZnO$_{24-26}$ nanostructures have been proposed as electrodes in electroanalysis, to the best of our knowledge, there has been no investigation on refreshing electrode surface using photocatalytic approaches. Highly ordered TiO$_2$ nanotube arrays (TiO$_2$-NTAs) fabricated by anodic oxidation of titanium in a fluoride-containing...
solution27,28 possess large surface areas, good uniformity and conformability, and high porosity. They are potential electrode materials for electrochemical biosensors because they offer a microenvironment to increase the quantity and bioactivity of immobilized proteins and produce favorable transport pathways for the analytes.24,26,29 However, because of the low conductivity of TiO$_2$, TiO$_2$-NTAs electrodes exhibit worse electrochemical activities$^{29,30}$ than nanostructured carbon electrodes.

Herein, we present a refreshable electrode composed of carbon-doped (C-doped) TiO$_2$-NTAs. It not only exhibits excellent electrochemical activity that is better or comparable to that of existing nanostructured C electrodes in the simultaneous determination of 5-hydroxytryptamine (5-HT) and ascorbic acid (AA) but also can be readily regenerated photocatalytically to recover the high selectivity and sensitivity (see Scheme 1). The C-doped TiO$_2$-NTAs are fabricated by quick annealing of the as-anodized TiO$_2$-NTAs in argon in the absence of foreign carbonaceous precursors. The residual ethylene glycol (EG) absorbed on the nanotube wall during anodization serves as the carbon source, and the C atoms are uniformly distributed along the entire nanotube forming the C-doped TiO$_2$-NTAs. This self-doping approach is different from the conventional process to produce C-doped TiO$_2$ by heating the anatase TiO$_2$ nanotubes under CO$_2$ or acetylene.30,32 In the conventional technique, the C concentration decreases with depth, whereas by using the simpler and easier process described here, a uniform C distribution along the entire nanotube can be accomplished. These highly ordered C-doped TiO$_2$-NTAs have large surface areas, well-defined structures, high conductivity, improved electron transfer (ET) efficiency, and enhanced photocatalytic properties and thus have immense potential in high-sensitivity and selectivity biosensor devices.

**EXPERIMENTAL SECTION**

The highly ordered C-doped TiO$_2$-NTAs electrode was fabricated by rapid annealing of as-anodized TiO$_2$-NTAs in argon. The residual ethylene glycol absorbed on the nanotube wall acts as the carbon source, and no foreign carbon precursor is thus needed. The as-anodized TiO$_2$-NTAs were prepared by electrochemical anodization of a Ti metal foil in an ammonium fluoride (NH$_4$F)–ethylene glycol (EG) solution as described in our previous report.35 A graphite foil and Ti foil (2.0 × 1.0 × 0.1 cm$^3$, 99.6% purity, Advent Materials) served as the cathode and anode, respectively. The electrolyte was EG containing 0.3 wt % NH$_4$F and 3 vol % doubly distilled water (DDW). Anodization was conducted at 60 V for 30 min using a direct current power supply (IT6834, ITECH, Nanjing, China). The anodized samples were rinsed in DDW, dried in air, and then annealed at 350–500 °C in a tube furnace in air (designated as the TiO$_2$-NTAs/air) or Ar (TiO$_2$-NTAs/Ar) at a heating rate of 15 °C/min. The morphology, structure, and composition of the TiO$_2$-NTAs/air and TiO$_2$-NTAs/Ar were characterized by field-emission scanning electron microscopy (FE-SEM, FEI Nova 400 Nano), X-ray diffraction (XRD, Philips X’Pert Pro), X-ray photoelectron spectroscopy (XPS, ESCALB MK-II), transmission electron microscopy (TEM, JEOL 2010 equipped with an X-ray energy dispersive spectrometer (EDS)), and Raman spectroscopy (LabRAM HR). The electrochemical measurements were performed in a conventional three-electrode system. The NTAs were insulated with epoxy resin exposing an area of 81 mm$^2$ as the working electrode. An Ag/AgCl electrode served as the reference electrode, and a Pt foil was the counter electrode.

The electrochemical experiments were carried out on a CHI660c potentiostat (CH Instruments Inc., Shanghai, China). The redox system used in the evaluation of the ET kinetics consisted of K$_3[Fe(CN)_6]$ (5 mM) dissolved in 1 M KCl. In the electrochemical and biosensing study, the phosphate buffer solution (PBS, 0.1 M) was prepared by dissolving NaH$_2$PO$_4$ and Na$_2$HPO$_4$ in DDW, and the pH value was adjusted to 7.4 by adding H$_3$PO$_4$ and NaOH. 5-HT (99%) and AA (99%) were purchased from Sigma and used without further treatment. Other chemicals were analytical reagent grade purchased from Beijing Chemicals Co., Ltd. The fouled electrode surface was regenerated by exposure to UV light for 30 min or visible light for 120 min in DDW at room temperature. A high-pressure mercury lamp (1000 W, primary wavelength of 365 nm, 12 mW/cm$^2$) and a 500 W xenon lamp (30 mW/cm$^2$) with a 400 nm cutoff filter were used as the UV and visible light sources, respectively. In the XPS spectra, the binding energies were referenced to the Ar 2p peak at 242.4 eV.

**RESULTS AND DISCUSSION**

Figure 1a–c depicts the top-view FE-SEM images of the as-anodized NTAs as well as TiO$_2$-NTAs/air annealed in air and...
TiO₂-NTAs/Ar annealed in Ar at 500 °C for 3 h. The nanotubes have an outer diameter of about 160 nm, and the wall thickness is about 25 nm. The morphology of NTAs does not change significantly after annealing in air or Ar, but the nanotube length is reduced slightly by about 0.3 μm compared to the as-anodized one with a length of 5.4 μm due to partial sintering. The main peaks in the XRD patterns acquired from TiO₂-NTAs/air and TiO₂-NTAs/Ar can be indexed to anatase TiO₂ except those from the substrate (Figure S-1 in the Supporting Information). The elemental map of the TiO₂-NTAs/Ar in Figure 1d shows that Ti, C, and O are homogeneously distributed in the individual nanotube. The formation of the C-doped TiO₂-NTAs is further confirmed by XPS. As shown in Figure 2a, a high C content of about 25 at % is observed on the surface and after sputtering for 2 min (sputtering rate of approximately 21.1 nm/min referenced to SiO₂).

This provides evidence that C is uniformly distributed along the entire length of the nanotube. The high-resolution C 1s spectra obtained at different sputtering times are displayed in Figure 2b. In the near surface, the dominant C 1s component at 284.6 eV and shoulder at a lower binding energy of 281.9 eV are characteristic of sp³ C–C and C–Ti. After sputtering for 4 min, the peak positions are unchanged, but the intensity of the peak at 284.6 eV diminishes dramatically whereas that of the peak at 281.9 eV increases notably. After sputtering for 6 min, the peak at 284.6 eV becomes negligible and there is only one peak at 281.9 eV. This remains the same until the bottom of the NT. The peak at 281.9 eV which is very close to the C 1s peak (281.5 eV) of TiC stems from carbon partially substituting for oxygen in TiO₂ resulting in the formation of Ti–C bonds (TiOₓC₂). The high-resolution Ti 2p spectra obtained at different sputtering times are depicted in Figure 2c. There are four doublet peaks corresponding to four chemical states of Ti, namely, Ti–C (Ti 2p₁/₂, 454.9 eV; Ti 2p₃/₂, 461.0 eV), TiO (Ti 2p₁/₂, 455.5 eV; Ti 2p₃/₂, 461.7 eV), Ti₃⁺/Ti₂O₃ (Ti 2p₁/₂, 457.1 eV; Ti 2p₃/₂, 463.0 eV), and Ti⁴⁺/TiO₂ (Ti 2p₁/₂, 459.0 eV; Ti 2p₃/₂, 464.7 eV). In the near surface, the intensity of the Ti peaks corresponding to TiO₂ is very strong, but with sputtering, the intensity of TiO₂ decreases but that of Ti–C increases. XPS indicates that the top of the TiO₂-NTAs/Ar may be composed of TiO₂ together with a small amount of carbonized graphite and the rest is C-doped TiO₂ nanotube. This is corroborated by Raman spectroscopy (Figure S-2 in the Supporting Information). With regard to TiO₂-NTAs/Ar, besides the peaks at 394, 513, and 635 cm⁻¹ associated with the anatase phase TiO₂, there are two weak peaks at 1365 and 1598 cm⁻¹ corresponding to the D and G bands of carbon. The G band...
shift to 1598 cm\(^{-1}\) indicates that graphite on the outermost surface of the nanotube consists of small sp\(^2\) carbon clusters.\(^{36}\)

This may arise from carbonization of the absorbed EG on the outer surface during annealing in Ar. However, because of the nanoscale space confinement effect, the gas pressure in the nanotube is larger than that on the surface.\(^{37}\) The nanotubular space provides a favorable nanoscale local environment with high pressure for enhancing the reaction of gaseous carbon species from the decomposition of EG with TiO\(_2\) to form C-doping TiO\(_2\) as the anodized NTAs are annealed in argon, resulting in the formation of C-doped TiO\(_2\)-NTAs. However, during annealing in air, carbon is oxidized to form CO\(_2\) and so the XPS elemental depth profile acquired from TiO\(_2\)-NTAs/air indicates the presence of Ti and O but not C (Figure S-3 in the Supporting Information).

Figure 3a,b exhibits the thermogravimetric differential thermal analysis (TG-DTA) results and corresponding in situ mass spectra (MS) of the as-anodized TiO\(_2\)-NTAs annealed in Ar. A weight loss of about 0.45% resulting from water desorption is observed from room temperature to about 100 °C. Two clear exothermal peaks emerge at approximately 295 and 360 °C in the DTA curve, accompanied by 1.02% and 4.86% weight losses in the TG analysis. The weight loss of 1.02% and corresponding small exothermal peaks arise from dehydration and the small degree of crystallization from anodized hydrated titania to anatase TiO\(_2\)\(^{37}\) as well as partial decomposition of EG. The weight loss of 4.86% and corresponding larger exothermal peaks can be contributed to total EG decomposition and C doping reactions forming the Ti–C bonds. This is corroborated by the MS results. As shown in Figure 3b, at 295 and 360 °C, the in situ mass spectra disclose the presence of H\(_2\) (2 amu), CH\(_4\) (16 amu), H\(_2\)O (18 amu), CO (28 amu), and CH\(_2\)CHO (44 amu). All these species are principle products of the decomposition reaction of EG.\(^{38}\) The exothermic crystallization reactions on the anodized TiO\(_2\)-NTAs at 295 °C and C-doping reaction at 360 °C offer local nanoscale space with high energy and temperature to aid the decomposition of EG and the carbothermal reaction, although the normal decomposing temperature of EG is about 500 °C.\(^{38}\) The nanotubular space provides a high pressure for in situ generation of CH\(_4\), CO, CH\(_2\)CHO, and consequently the reaction with TiO\(_2\) to form the C-doped TiO\(_2\). The TG-DTA-MS results indicate that the annealing temperature of about 360 °C is a significant transition point for the C doping reaction, and so the states of carbon in the TiO\(_2\)-NTAs/Ar samples annealed at 350 and 400 °C are also evaluated by XPS (Figure S-4 in the Supporting Information). At 350 °C, there is no signal of Ti–C bonding while the chemical states of Ti–C can be easily identified from the sample annealed at 400 °C. These results verify that C-doped TiO\(_2\)-NTAs can be readily fabricated by annealing as-anodized NTAs prepared in EG in Ar at a temperature higher than 400 °C.

The electrochemical activity of C-doped TiO\(_2\)-NTAs and TiO\(_2\)-NTAs associated with the ET reactions between the electrode and electrolyte containing the Fe(CN)\(_6\)\(^{3−/4−}\) redox couple has been evaluated. Figure 4a shows the cyclic voltammetry (CV) profiles acquired from the surface of the TiO\(_2\)-NTAs and C-doped TiO\(_2\)-NTAs in 1 M KCl with 5 mM K\(_3\)[Fe(CN)\(_6\)] at a scanning rate of 100 mV/s. The C-doped TiO\(_2\)-NTAs show a pair of well-defined oxidation and reduction peaks at 0.308 and 0.235 V indicative of negligible reactions is observed from the TiO\(_2\)-NTAs. The peak-to-peak potential separation (Δ\(E_p\)) on the C-doped TiO\(_2\)-NTAs electrode is approximately 68 mV. A small Δ\(E_p\) (close to the ideal value of 59 mV\(^{39}\)) indicates a fast ET kinetics for a single-electron redox process.

The charge transfer resistance of the Fe(CN)\(_6\)\(^{3−/4−}\) redox system is near 100 kΩ on the TiO\(_2\)-NTAs, while the resistance on the C-doped TiO\(_2\)-NTAs drops by 4 orders of magnitude to about 30 Ω. We also investigate the CV curve (Figure S-5 in the Supporting Information) acquired from the TiO\(_2\)-NTAs after coating with a layer of carbon nanotubes. The results reveal no change except a
small shift in the reduction peak corresponding to the Fe-
(CN)$_6^{3-/4-}$ redox system in comparison with TiO$_2$-NTAs. It
can thus be concluded that the fast ET kinetics in the Fe-
(CN)$_6^{3-/4-}$ redox system mainly stems from the highly
conductive C-doped TiO$_2$-NTAs. The electrochemical properties
of the C-doped TiO$_2$-NTAs annealed at different temperatures
(350−500 °C) (Figure S-6 in the Supporting Information) show
that a higher temperature leads to a smaller Δ$E_p$ value and larger
peak current in the Fe(CN)$_6^{3-/4-}$ redox system. However, if the
annealing temperature is higher than 600 °C, the C-doped TiO$_2$-
NTAs layer delaminates from the Ti substrate (Figure S-7 in the
Supporting Information). Hence, the C-doped TiO$_2$-NTAs
electrode annealed at 500 °C at a heating rate of 15 °C/min is
selected for subsequent evaluation of the biosensing properties.
5-HT, also known as serotonin, is an important biogenic amine
present in many food products and acts as a chemical messenger
in the biological system. In conventional electrochemical anal-
ysis, 5-HT and AA in the body
overlapping voltammetric responses on metal and unmodi-
fied nanostructured carbon electrodes,40 thus making quantitative
evaluation of the bioactive species difficult.35 The C-doped TiO$_2$-
NTAs produced in this work without any pretreatment or modifica-
tion can be directly used as an electrode to distinguish 5-HT from AA with high sensitivity and selectivity. Figure 5a
depicts the CV response of 0.2 mM 5-HT at the electrodes of
TiO$_2$-NTAs and C-doped TiO$_2$-NTAs in a 0.1 M pH = 7.4 PBS.
No oxidation peak is observed from the TiO$_2$-NTAs electrode
at 500 °C. The C-doped TiO$_2$-NTAs electrode is contaminated and the current diminishes. How-
ever, if the electrode surface is cleaned photocatalytically and renewed by UV or vis light
irradiation. Figure 6a shows the CV results of 20 cycles at the original C-doped TiO$_2$-NTAs electrode and the first cycle of the
photocatalytically refreshed C-doped TiO$_2$-NTAs electrode,
respectively, in a 0.1 M pH 7.4 PBS containing 0.2 mM 5-HT
at a scanning rate of 100 mV/s. It can be observed that the
electrochemical signal vanishes almost completely after 20 cycles
on the C-doped TiO$_2$-NTAs, but after UV light irradiation with an intensity of 12 mW/cm$^2$ for 30 min, the sensitivity is restored
with a relative standard deviation (RSD) of 2.2% (n = 10, Figure 6b). Hence, excellent reproducibility is demonstrated.
To confirm the self-renewable capacity of the electrode made
of C-doped TiO$_2$-NTAs, a GC electrode (Figure S-9 in the
Supporting Information) is also studied for comparison. The
results suggest that a fouled GC electrode cannot be refreshed
by UV light exposure. Figure 6c shows the typical amperometric response on the C-doped TiO$_2$-NTAs by successive introduction
of different concentrations of 5-HT (5−210 μM) into the
stirred PBS at 380 mV with and without UV irradiation. The
current response increases with 5-HT concentrations. The calibration plot without UV irradiation (black) in Figure 6d illustrates a linear response from 5 to 85 μM with a correlation coefficient of 0.9938. At higher concentrations of 5-HT, the electrode is contaminated and the current diminishes. How-
ever, under UV irradiation, the calibration plot (red) shows a wider linear response from 5 to 150 μM with a correlation coefficient of 0.9939. The linear range increases significantly under UV irradiation, and it can be attributed to photoassisted cleaning of the C-doped TiO$_2$-NTAs electrode surface. The detection limit of 5-HT is calculated to be about 4.1×10$^{-8}$ M
(S/N = 3), which is lower than or comparable to values in the
literature.15,42 Meanwhile, the enhanced photocurrent measured
from the C-doped TiO$_2$-NTAs (red curve in Figure 6c)
under UV irradiation further confirms the high photocatalytic
activity.

Figure 5. (a) CV profiles of 0.2 mM 5-HT in 0.1 M PBS (pH = 7.4) at TiO$_2$-NTAs and C-doped TiO$_2$-NTAs electrodes. (b) CV curves at C-doped TiO$_2$-NTAs electrode in PBS with 1 mM AA, 0.1 mM 5-HT, and their mixture. Scan rate: 100 mV/s.
renewed electrode after UV photocleaning. In comparison with that of the original C-doped TiO$_2$-NTAs electrode, the XPS spectrum of the fouled electrode shows an obvious peak at 400.3 eV attributable to the N signals in amide or amine (N–C) that originates from absorbed and/or electrochemically oxidized products of 5-HT. These intermediate species reduce the electrochemical activity of the C-doped TiO$_2$-NTAs electrode, and so decreased sensitivity and selectivity are observed over time during the detection of 5-HT. In contrast, after UV light irradiation for 30 min, the N signals in the XPS spectrum disappear and the sensitivity of the electrode after 10 fouling/refreshing runs is still about the same as that in the first experiments. During UV light irradiation, the absorbed intermediate species of 5-HT can be decomposed completely into H$_2$O, CO$_2$, and NO$_x$ without damaging the surface microstructure. Hence, the electrode surface can be refreshed to recover the sensing ability. The high photocatalytic activity of the C-doped TiO$_2$-NTAs is also reflected by photodecomposition of rhodamine B (RB) in a solution (Figure S-8 in Supporting Information). These results verify that the C-doped TiO$_2$-NTAs electrode is a recyclable platform for a high-sensitivity biosensor.

Figure 6. (a) CV profiles of 0.2 mM 5-HT in a 0.1 M pH = 7.4 PBS obtained from the original (black) and renewed (red) C-doped TiO$_2$-NTAs electrodes. Scan rate: 100 mV/s. (b) The peak current of different scan number and renew times. (c) Typical current–time response curves at the C-doped TiO$_2$-NTAs electrode through successive addition of different concentrations of 5-HT (5–210 μM) into a stirred 0.1 M PBS (pH = 7.4) at an applied potential of 380 mV with and without UV irradiation, respectively. The electrodes are not removed between measurements at different concentrations without UV irradiation. (d) The calibration curve of the response currents versus concentrations of 5-HT with and without UV irradiation. The error bars represent the response current of three independent experiments.

Figure 7. (a) XPS survey spectra and (b) high-resolution N 1s spectrum acquired from the fresh, fouled, and renewed C-doped TiO$_2$-NTAs electrodes. The XPS spectrum of the fouled electrode shows a large peak at 400.3 eV attributable to N in amide or amine (N–C) that originates from absorbed and/or electrochemically oxidized products of 5-HT. The small peak at about 400.8 eV may come from adsorbed nitrogen on the electrodes.
CONCLUSIONS

In summary, an electrode composed of C-doped TiO2-NTAs fabricated by rapid annealing of anodized nanotubes exhibits excellent electrochemical performance in the simultaneous determination of S-HIT and AA that would produce interfering and overlapping voltammetric responses in conventional electrodes. The residual EG resulting from the anodization process provides the carbon source, and the nanotube provides the favorable nanoscale space to enhance the carbon-doping reaction. The high photocatalytic activity of the C-doped TiO2-NTAs enables regeneration of the fouled surface simply by UV or vis light irradiation without damaging the microstructure, and the surface can recover the high selectivity and sensitivity. These outstanding and promising electrochemical properties demonstrate that the C-doped TiO2-NTAs have immense potential in high-sensitivity and high-selectivity biosensor devices.

ASSOCIATED CONTENT

* Supporting Information. Additional information as noted in text. This material is available free of charge via the Internet at http://pubs.acs.org.

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REFERENCES

Supporting Information

A Recyclable and High-Sensitivity Electrochemical Biosensing Platform Composed of Carbon-Doped TiO₂ Nanotube Arrays

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Figure S-1. XRD patterns of as-anodized TiO$_2$-NTAs, TiO$_2$-NTAs/air and TiO$_2$-NTAs/Ar.
Figure S-2. Raman scattering spectra acquired from TiO$_2$-NTAs/air and TiO$_2$-NTAs/Ar.
Figure S-3. XPS depth profile of TiO$_2$-NTAs/air (sputtering rate of approximately 21.1 nm/min referenced to SiO$_2$).
Figure S-4. High-resolution C 1s spectra of TiO$_2$-NTAs/Ar: (a) Annealed at 350 °C and (b) annealed at 400 °C. Four peaks at 283.3, 284.3, 286.4 and 287.8 eV on the surface and three peaks at 283.3, 284.3, and 286.4 eV in a deeper region can be identified from TiO$_2$-NTAs/Ar after annealing at 350 °C. The peaks at 283.3, 284.3, 286.4, and 287.8 eV are attributed to carbide, graphitic carbon, C=O bonds$^{[s1]}$, and C-C=O bonds. $^{[s2]}$ For TiO$_2$-NTAs/Ar annealed at 400 °C, the carbide peak is located at 282.2 eV which can be attributed to O-Ti-C.
**Figure S-5.** CV profiles of 5 mM K$_3$[Fe(CN)$_6$] in 1 M KCl solution obtained from the electrodes made of TiO$_2$-NTAs and TiO$_2$-NTAs/CNTs at a scanning rate of 100 mV/s.
Figure S-6. CV profiles of 5 mM K$_3$[Fe(CN)$_6$] in 1 M KCl solution acquired from the electrodes made of TiO$_2$-NTAs/Ar with different annealing temperature at a scanning rate of 100 mV/s.
Figure S-7. Optical image of TiO$_2$-NTAs/Ar annealed at 600 °C. If the annealing temperature is higher than 600 °C, the TiO$_2$-NTAs will delaminate due to the large interface stress between the nanotube arrays and underlying substrate during rapid heating.
Figure S-8. Concentration versus time for Rhodamine B (RB) under (a) UV and (b) visible light irradiation in the presence of C-doped TiO$_2$-NTAs and TiO$_2$-NTAs.

The photocatalytic activity of the TiO$_2$-NTAs and C-doped TiO$_2$-NTAs were examined in an RB aqueous solution as a model organic pollutant. The samples with a size of 1.5 cm$^2$ were immersed in 20 ml of RB aqueous solution with an initial concentration of 25 µM. The solution was stirred in the dark for 3 hrs to saturate the photocatalyst with RB and the photodegradation experiments were performed at the natural pH of the RB dye. The solution was aspirated continuously with air during the photocatalytic reaction.
**Figure S9.** CV profiles of 0.2 mM 5-HT in a 0.1 M pH = 7.4 PBS obtained from original (curve A) and fouled GC electrode. The fouled GC electrode is irradiated for 30 min with UV light (curve B). The scanning rate is 100 mV/s and the results suggest that the fouled GC electrode cannot be refreshed by light exposure.

**References**
