Synthesis of Carbon-doped TiO$_2$ Nanotube Arrays and Their Application for Photocatalysis

Xiaoyi Wang $^{1,*,}$, Yulong Liao $^{1,a}$, Michile Johnson $^{2,b}$

$^1$ State Key Laboratory of Electronic Thin Film and Integrated Devices, University of Electronic Science and Technology of China, Chengdu, China
$^2$ Materials Science & Engineering Department, University of Delaware, Delaware, USA

*$\text{Corresponding author e-mail: uxy}_\text{wang}@\text{std.uestc.edu.cn}$
$a\text{yulong.liao}@\text{uestc.edu.cn}$, $b\text{hessii0424}@\text{gmail.com}$

Abstract. Carbon-doped TiO$_2$ Nanotube Arrays (CDTNAs) are synthesized via a facile method consists of electrochemical anodization and annealing in Ar atmosphere. Since the existence of residual ethylene glycol (EG) adhering to the walls of as-anodized TNAs, the EG can serve as carbon sources and subsequently avoids the employment of extrinsic carbon precursors. The properties of CDTNAs are investigated by X-ray diffraction (XRD), energy dispersive spectrometer (EDS), scanning electron microscope (SEM). Further, the photocatalytic performance of CDTNAs is significantly enhanced owing to the introduction of carbon. It is expected that the CDTNAs could be a promising candidate acting as an effective photocatalyst.

Keywords: TiO$_2$ nanotubes, photocatalysis, oxidation.

1. Introduction
Over the past few years, semiconductor photocatalysts have been widely investigated to solve the problem of organic pollutants in water [1, 2]. Among the various photocatalysts, TiO$_2$ is considered to be a promising candidate due to the advantages of low-cost, non-toxicity and high photosensitivity [3, 4]. Particularly, TiO$_2$ Nanotube Arrays (TNAs) have attracted much attention because they possess two outstanding features: high specific surface area and favorable carrier transport pathway [4, 5]. However, TiO$_2$ can only be activated in the range of ultraviolet spectrum owing to wide bandgap energies (3.2 eV for anatase and 3.0 eV for rutile phases), which will hinder the photocatalytic performance [6, 7].

In this context, much effort has been made to improve the photosensitivity of TNAs, and carbon doping is proved to be an effective approach [8, 9]. For example, Jong et al. used CO as carbon source to fabricate carbon-doped TiO$_2$ Nanotube Arrays (CDTNAs), and the modified products exhibited better performance [8]. Those approaches use extrinsic carbon sources for doping, resulting in a drawback that the carbon concentration is not uniform within the TNAs. Since TNAs are usually synthesized via an anodization method, the residual electrolyte which contains ethylene glycol (EG) could serve as carbon source [10, 11]. Specifically, the residual EG absorbed on the TNAs walls will decompose in the process of annealing, and the CDTNAs with uniformly distributed carbon atoms can be obtained.
Herein, a self-doping approach was employed to prepare the carbon-doped TiO$_2$ nanotube arrays by using the residual EG as carbon source. Methyl orange was used to investigate the photocatalytic performance, and the results showed that the CDTNAs products were suitable for photocatalysis.

2. Experiment
Firstly, amorphous TiO$_2$ nanotube arrays were prepared by the electrochemical anodization method [12, 13]. Ti sheets (length: 5 cm, width: 1.5 cm, thickness: 0.2 mm) were rinsed with acetone, and then they were treated with sonication in ethyl alcohol. Those Ti sheets were used as anodes, and the electrolyte was composed of ethylene glycol (97 % volume), deionized water (3 % volume) and NH$_4$F (0.3 % mass ratio). A constant voltage of 60 V was applied and the distance of the two electrodes was 2 cm. In the anodization process, a magnetic rotor was continuing stirring to keep the electrolyte homogeneous. After 2 h, the anodic sheet was taken out and a film was obtained on the Ti substrate. Different from the traditional method, the amorphous TiO$_2$ nanotube arrays were not rinsed with ethyl alcohol or deionized water. In this work, the as-anodized products were directly annealed in Ar atmosphere under 500 °C for 3h (heating rate: 5 °C/min).

The crystalline structure of CDTNAs was investigated by X-ray diffraction (XRD; D/max 2400 X Series X-ray diffractometer) in the range of 10 – 70 °. The morphology and structure of CDTNAs were studied by a scanning electron microscope (SEM, JSM-7000F, Japan). Energy dispersive spectrometry (EDS) technique was used to analyze the elemental distribution of the microscopic region qualitatively. The photocatalytic performance of TNAs and CDTNAs were evaluated by degrading the methyl orange solution (concentration: 0.00005 mol/L). Before the degradation experiment, the as-prepared CDTNAs were treated with sonication.

3. Discussion
Figure 1 shows a schematic illustration of the preparation process. After anodization, the inside of the nanotube is full of electrolyte. As for the traditional method, the as-anodized TNAs will be soaked and rinsed by ethyl alcohol. Then the TNAs without electrolyte are sintered in air atmosphere, resulting in the formation of anatase TNAs. In contrast, the as-anodized TNAs are directly sintered in Ar atmosphere in our study, leading to the formation of black CDTNAs.

Figure 2 (a) shows the XRD patterns of the prepared CDTNAs. Four main diffraction peaks locating at 25.3, 36.8, 37.8, 53.9 ° could be attributed to (101), (103), (004), and (105) lattice planes. Obviously the CDTNAs exhibited an anatase phase, which was consistent with the samples sintered under air
atmosphere [14, 15]. It is noted that there is no other peak could be detected of the XRD patterns, indicating that the obtained CDTNAs are pure anatase phase. Since the sintering temperature was only 500 °C, only the amorphous carbon could be formed and there is no carbon peak could be observed. EDS spectrum is displayed in Figure 2 (b), peaks of Ti, C and O elements are obvious and the results match well with the literature [3, 16]. In order to intuitively see the difference of the traditional method sample and CDTNAs, a photograph is displayed in Figure 2 (c). It can be seen that the normally fabricated TNAs show a blue color (left one) while the CDTNAs show an obvious black color (right one). Because the experimental parameters were same for the two sample, the dramatically color difference was attributed to the electrolyte decomposition. In a word, the prepared CDTNAs were quite different from the normal TNAs while the anatase phase was well maintained.

![Figure 2](image-url)

**Figure 2.** (a, b) XRD and EDS patterns of CDTNAs. (c) Photographs of TNAs and CDTNAs.

SEM images of different samples are presented in Figure 3. Figure 3 (a) shows the morphology of the traditionally prepared TNAs, it can be seen that the tubular structure is clearly visible. The diameter of the nanotube is about 80 nm and the thickness of tube wall is about 15 nm, which is quite close to the literature [17, 18]. Figure 3 (b) displays the SEM image of the prepared CDTNAs, the nanotubular structure is well maintained and the tube size is nearly equal to that of the TNAs sintered in air atmosphere. Furthermore, side of the nanotube can also be observed, proving the existence of nanotube architecture. The tube wall is smooth and no obvious crack phenomenon can be detected, indicating the CDTNAs are robust. However, there are some aggregated contents covering part of the top areas, which may be resulted from the decomposition of residual electrolyte. It is no doubt that those contents will hinder the contact between nanotubes and organic pollutants, deteriorating the photocatalytic performance. In contrast, Figure 3 (c) shows the SEM image of the after-sonication CDTNAs sample. It is distinct that the top of the nanotube is clear and no huge shelter is observed, meanwhile, the tubular structure is not destroyed. The open nanotubes will facilitate the solution flow into the tubes and subsequently improve the degradation efficiency. Figure 3 (d) shows the section-view image of the CDTNAs, the length of the nanotube is about 17 μm and a compact architecture is observed. Although there are some broken parts, most of the nanotubes are intact.
The photocatalytic performance of the prepared CDTNAs for degrading organic pollutants was investigated by degrading the methyl orange solution. The CDTNAs were immersed into the solution for degradation, and some amount of solution was sampled every 30 min. The concentration of the solution was measured and labeled as C (the initial concentration was labeled as C0). Therefore the degradation rate could be defined as C/C0. As shown in Figure 4 (a), the methyl orange was not degraded when there was no catalyst in the solution (green line). When the normal TNAs were immersed in the solution (blue line), the value of C decreased with the increase of time and a degradation rate of 0.6 was obtained after 210 min reaction. Remarkably the degradation performance of the CDTNAs was significantly higher than TNAs, indicating that the carbon-doped TNAs can dramatically enhance the photocatalytic performance (red line).

**Figure 3.** SEM images of (a) TNAs, (b) CDTNAs, (c) CDTNAs after sonication treatment, and (d) section view of CDTNAs.

**Figure 4.** (a) Degradation performances of different samples. (b) Proposed mechanism of CDTNAs acting as photocatalyst.
Figure 4 (b) shows a schematically illustration of the proposed mechanism to explain the enhanced photocatalytic performance of CDTNAs. It is known that electrons (e\textsuperscript{-}) and holes (h\textsuperscript{+}) will be excited when anatase TNAs are under illumination, however, the excited e\textsuperscript{-} and h\textsuperscript{+} will recombine quickly. Therefore the formation of hydroxyl radical will be hindered, resulting in a reduced degradation performance because the hydroxyl radical plays a crucial role in degrading organic pollutants. As for the CDTNAs, some of the excited e\textsuperscript{-} can be transferred to carbon as shown in Figure 4 (b). Correspondingly the recombination is restrained, more excited e\textsuperscript{-} can take part in producing hydroxyl radical and finally improve the photocatalytic performance.

4. Conclusion
Black CDTNAs were successfully synthesized by using the residual EG as carbon source. The nanotubular structure was well maintained after introducing carbon and the CDTNAs were still anatase phase. After sonication treatment, the top of nanotube is clear and the original architecture was not destroyed. The black CDTNAs showed excellent photocatalytic performance when serving as catalyst to degrade organic pollutants. The enhanced performance could be attributed to the introduction of carbon, and CDTNAs are considered to be a kind of promising candidate for photocatalyst.

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