Preparation of high-concentration substitutional carbon-doped TiO₂ film via a two-step method for high-performance photocatalysis

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In this paper, we present a facile two-step method for preparing a high-concentration substitutional carbon-doped TiO₂ (TiO₂₋ₓCₓ) film. First, the titanium substrate undergoes gas carburizing, followed by micro-arc oxidation (MAO) to form a carbon-doped TiO₂ film on the surface. The process can be described as direct oxidation of titanium carbide (O→TiCₓ). The experimental results reveal that compared with traditional thermal annealing, this process could increase the carbon doping concentration to 6.07 at% and x to 0.24 in TiO₂₋ₓCₓ. The TiO₂₋ₓCₓ film exhibits a significant red-shift in the band-gap transition, a narrow band gap of 2.77 eV, and excellent photocatalytic performance, more than two times higher than that of undoped TiO₂ film. This method is simple, efficient, economical, environmentally friendly, and adapts to mass production. This experimental strategy can also be used in preparing other doped elements.

1. Introduction

In recent years, degradation of organic compounds by photocatalysis has become a very attractive research subject in the field of environmental pollution treatment. Different metal oxide semiconductors have been studied. Among various metal oxide photocatalysts, TiO₂ is indicated to be an ideal photocatalyst, especially with a large band gap of 3.20 eV. metallic TiO₂ (anatase TiO₂) is not activated by sunlight, whereas doped TiO₂ can be activated by visible light, much superior to P25 and N-TiO₂. Rasoulnezhad et al. synthesized carbon-doped TiO₂ thin films on glass substrate by a combination of chemical vapor deposition and ultrasonic methods. It was found that carbon doping in the TiO₂ structure greatly improved the optical properties for visible light absorption.

adsorption spectra through direct thermal oxidation of TiC. It was found that carbon atoms were located at oxygen sites and the C/C0 ratio increased from 0.32% to 0.24 in TiO₂₋ₓCₓ. The TiO₂₋ₓCₓ film exhibits a significant red-shift in the band-gap transition, a narrow band gap of 2.77 eV, and excellent photocatalytic performance, more than two times higher than that of undoped TiO₂ film.

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In general, the doping content of nonmetal-doped TiO$_2$ films produced using the regular doping method is low, found mostly as interstitial doping, and has poor thermal stability. In our previous work, various TiO$_2$ composite films, such as TiO$_2$/YAG:Ce$^{3+}$ and TiO$_2$/Eu$_2$O$_3$ composites, have been prepared in situ by using micro-arc oxidation (MAO) technique on the titanium or titanium alloy substrate for high photocatalytic performance.\textsuperscript{18,19} In particular, we reported a new process which combined the technique of plasma nitriding and MAO to simply prepare a high-concentration substitutional N-doped TiO$_2$ photocatalytic film.\textsuperscript{20} The principle is that the rapid oxidation process of MAO can restrict the nitrogen atoms’ escape from the substrate and maximally keep the nitrogen atoms in the TiO$_2$ film. Moreover, due to the direct oxidation reaction of TiN, the Ti–N bond is retained to the maximum extent, and more substitutional N-doped TiO$_2$ is obtained.

In this paper, a facile two-step method is applied to prepare substitutional carbon-doped TiO$_2$ film with high doping content. That is, as an important thermochemical treatment, gas carburizing is firstly used to form a carburized layer with rich TiC compound upon the titanium (Ti) surface, and then MAO treatment is used to directly oxidize the TiC compound into carbon-doped TiO$_2$ film. Because of the fast, high-temperature, and in situ MAO treatment, the resulting carbon doping is of high content and in the form of substitutional doping in the TiO$_2$ crystal lattice as the TiO$_2$–xC$_x$ film. Compared to plasma nitriding, gas carburizing has the advantages of simpler operation, higher carburizing concentration, large area, and more potential industrial application, among others.

## 2. Experimental

The two-step process for preparing the TiO$_2$–xC$_x$ film is as follows: (1) preparation of the TiC$_x$ compound on the Ti substrate via gas carburizing in a self-made tubular furnace, i.e., the Ti substrate was placed in a quartz tube reactor, heated to 600 °C, kept in 30 sccm C$_2$H$_2$ for 20 h, then kept in closed C$_2$H$_2$ for 10 h, and finally cooled to room temperature, while 200 sccm Ar gas was continuously introduced into the quartz tube. (2) Preparation of the TiO$_2$–xC$_x$ film via MAO, i.e., the carburized Ti substrate was used as anode in 5 L electrolyte (Na$_3$PO$_4$·12H$_2$O 10 g L$^{-1}$), and 400 V constant pressure mode was adopted. As a comparison, a pure TiO$_2$ film was also prepared via MAO under the same experimental conditions on the Ti substrate. The detailed experimental conditions are listed in Table 1.

The morphology and chemical compositions of the samples were characterized using a scanning electron microscope (Sirion SEM; FEI, Eindhoven, The Netherlands) with an energy-dispersive X-ray spectrometer (EDS). The phase analysis proceeded using an X-ray diffractometer (XRD) (D8 Advanced XRD; Bruker AXS, Karlsruhe, Germany) with Cu Kα source. The quantitative elemental compositions were analyzed by X-ray photoelectron spectroscopy (XPS) (VG Multilab 2000, Thermo Scientific, UK). UV-Vis diffuse reflectance spectra (DRS) of the samples were measured by using a diffuse reflectance accessory of the UV-Vis spectrophotometer (UV-2550; Shimadzu, Kyoto, Japan).

The photocatalytic performance was tested according to the following process: a 450 W high-pressure mercury lamp was used as light source, and 1 × 1 cm$^2$ samples were placed in

### Table 1 Experimental conditions of MAO

| Samples       | Anode      | Voltage (V) | Frequency (kHz) | Duty cycle (%) | Time (min) | Electrolyte                |
|---------------|------------|-------------|-----------------|----------------|------------|----------------------------|
| TiO$_2$       | Ti         | 400         | 0               | 1              | 20         | 3                          | Na$_3$PO$_4$·12H$_2$O (g L$^{-1}$) |
| TiO$_2$–xC$_x$| TiC$_x$    | 400         | 0               | 1              | 20         | 3                          | 10                          |

![Fig. 1](image-url)  
**Fig. 1**  
Surface characteristics of the carburized layer: (a) SEM morphology, (b) EDS profile.
a quartz colorimetric dish containing 2 mL terephthalic acid (TA) solution (10 mM NaOH and 3 mM C₈H₆O₄). Changes in the 2-hydroxy-terephthalic acid (TAOH) concentration were measured by UV-Vis spectrophotometer (UV-2550; Shimadzu) every 60 min.

3. Results and discussion

Fig. 1 shows the SEM morphology and EDS profile of the gas carburized Ti substrate. It could be seen that the surface is loose, and there are many submicron grain sizes. EDS analysis revealed that besides Ti element, carbon (C) peaks also appeared obviously, which indicated that C atoms were infiltrated into the Ti substrate. From the cross-section of the gas carburized Ti substrate, as shown in Fig. 2, the carburized layer was about 1 µm in thickness, and the Ti and C content changed with an opposite variation from the outside surface into the interior substrate. Fig. 3 shows the XRD pattern of the gas carburized Ti substrate; evidently, TiC phase existed in the carburized layer.

Fig. 4 and 5 show the SEM morphologies of pure TiO₂ film and the TiO₂₋ₓCₓ film after MAO treatment, respectively. Both films showed no obvious difference; that is, all of the mesopores were separated well and distributed homogeneously over the film’s surfaces with a diameter around 0.2–1 µm and thickness about 3–4 µm. It could be seen from Fig. 2 that the carburized layer was about 1 µm in thickness after gas carburizing. However, the coating thickness after MAO treatment was about 3–4 µm, which indicated a complete reaction in the carburized layer. Fig. 6 illustrates the XRD patterns of pure TiO₂ film and the TiO₂₋ₓCₓ film after MAO treatment, respectively. Both films were mainly composed of anatase phase, and no new phase was produced during doping. A small amount of TiC phase in the TiO₂₋ₓCₓ film indicated that TiC was not completely oxidized to TiO₂₋ₓ during MAO treatment.

XPS is an effective technique for verifying the concentration of elements on the surface of materials. In order to confirm the carbon atom site and content in the TiO₂₋ₓCₓ film, XPS analysis was conducted, as shown in Fig. 7. Besides the element phosphorous (P) from the electrolyte, the existence of C element was clearly observed. In general, the doped C has two existing modes in the TiO₂ lattice: (1) C replaces the position of oxygen (O) to form an O–Ti–C structure; (2) C is stabilized at an interstitial position. The multiplex high-resolution scans over the C 1s spectral region revealed two peaks at 284.8 and 282.3 eV, respectively. According to the commonly recognized C–C (285.3 eV) and Ti–C (281.9 eV) bonds, we believe that these two peaks belong to the C–C and Ti–C bonds, respectively. The C–C peak at 284.8 eV was the C peak for XPS calibration, not the peak of C in the sample, so its content was very high. Only the Ti–C peak at 282.3 eV was the peak of C in the TiO₂₋ₓCₓ film. According to these XPS results, the O concentration was about 44.94 at%, compared with 44.10 at% of C. According to the area ratio of the C–C and Ti–C peaks, the concentration of Ti–C could...
be calculated as 6.07 at%. Then, \( x = 0.24 \) could be calculated from the generic formula of TiO\(_{2-x}\)C\(_x\). Compared with the other methods, the present two-step process provided a possibility for both substitutional carbon-doping and high doping content. Table 2 lists the carbon doping data for various methods.

Fig. 5  SEM morphologies of the TiO\(_{2-x}\)C\(_x\) film after MAO treatment: (a) surface, (b) cross-section.

Fig. 6  XRD patterns of pure TiO\(_2\) film and TiO\(_{2-x}\)C\(_x\) film after MAO treatment.

wavelength response range to visible light; i.e., the absorption edge of TiO\(_{2-x}\)C\(_x\) film was shifted from the wavelength of 400 nm to 410 nm and exhibited a higher absorption. Using the Kubelka-Munk equations,\(^{12}\) the relationship between \((ahv)^2\) and the photo energy of the films can be determined. As shown in Fig. 9, the bandwidths of pure TiO\(_2\) film and TiO\(_{2-x}\)C\(_x\) film were 3.02 eV and 2.77 eV, respectively, which demonstrates that the energy band-gap of TiO\(_2\) had been narrowed by C doping.

Further, we measured the content of \(·\)OH to reflect the photocatalytic properties of the samples. Because TA can be combined with \(·\)OH, the generated TAOH has a strong fluorescence emission peak at 426 nm, so it is used as a reagent for fluorescence detection. Fig. 10 shows the fluorescence intensity of TA solutions containing pure TiO\(_2\) film and TiO\(_{2-x}\)C\(_x\) film at different illumination times. The experimental results indicated that the content of \(·\)OH from the TiO\(_{2-x}\)C\(_x\) film was about two times more than that of pure TiO\(_2\) film, and it exhibited a high photocatalytic performance.

In general, there are two kinds of strategies to prepare the C-doped TiO\(_2\), i.e., incorporating carbon atoms into the TiO\(_2\) lattice (C\(\rightarrow\)TiO\(_2\)) and oxidizing the titanium carbide (O\(\rightarrow\)TiC\(_x\)). However, for preparation of the substitutional C-doped TiO\(_2\), the most used methods include direct thermal oxidation of TiC powders, pulsed laser deposition, chemical-vapor deposition, hydrothermal method, and annealing. Direct thermal oxidation of TiC powder is a simple one-step process, but the C doping concentration is low, and it is difficult to be recycled and can
easily cause secondary pollution during photocatalytic degradation. Pulsed laser deposition and chemical-vapor deposition can also be a one-step process for producing the C-doped TiO\(_2\), but they usually require high energy under more stringent experimental conditions. Hydrothermal reaction and annealing are undoubtedly the most commonly used two-step method to prepare C-doped TiO\(_2\). However, some special reagents used in hydrothermal processes may pollute the environment, and the problem of low C concentration still exists.

For the present work, although the experiment is a two-step process, both gas carburizing and MAO are commonly used techniques in industry for surface modification of workpieces. Significantly, it can produce the substitutional C-doped TiO\(_2\) film with high concentration. Thus, it possesses the advantages of being simple, economical, and efficient, and the processes of gas carburizing and MAO causes no environmental problems. In addition, it adapts to mass production for the preparation of high-concentration substitutional C-doped TiO\(_2\) film, particularly with a large surface area.

### 4. Conclusions

A high-concentration substitutional carbon-doped TiO\(_2\) (TiO\(_2\)-\(\_C\)) film is prepared via a novel two-step process, i.e., combining gas carburizing thermochemical treatment and MAO techniques. The concentration of the Ti–C band reaches 6.07 at\%, and the carbon doping amount is as high as \(x = 0.24\). Therefore, the TiO\(_2\)-\(\_C\) film exhibits a significant red-shift in the band-gap transition, a narrow band gap of 2.77 eV, and excellent photocatalytic performance. This method is simple, efficient, economical, environmentally friendly, and adapts to mass production. According to this principle, doping with other materials, such as metal element doping, nonmetal element doping, metal and non-metal element co-doping, etc., can be performed in the future.

### Table 2 Carbon content of the substitutional carbon-doped TiO\(_2\) produced by various methods

| Catalyst                     | Method                  | Carbon content | Ref. |
|------------------------------|-------------------------|----------------|------|
| Carbon-doped TiO\(_2\) powders | Thermal oxidation       | 0.32%          | 12   |
| TiO\(_2\)-C1a/TiO\(_2\)-C1b/TiO\(_2\)-C2 | Hydrolysis and calcination | 2.98/0.42/0.03% | 25   |
| C-TiO\(_2\) film              | Pulsed laser deposition | 0.3%           | 26   |
| C-TiO\(_2\)/C-TiO\(_2\)-200  | Hydrothermal and annealing | 0.19/0.28 at%  | 15   |
| CT-BE/CE-BE-265               | Calcination assisted solvothermal | 0.6/0.42 at%  | 16   |
| TiO\(_2\)-1/TiO\(_2\)-2/TiO\(_2\)-3 | CVD, hydrothermal, and annealing | 2.3/2.8/3.9% | 27   |
| Carbon-doped TiO\(_2\) film   | Gas carburizing and MAO | 6.07 at%       | Our work |
Conflicts of interest

There are no conflicts to declare.

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