

Synthesis and characterization of carbon-doped titania as a visible-light-sensitive photocatalyst

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Abstract—The synthesis and use of carbon-doped TiO₂ particles in photocatalysis under visible light are demonstrated. The carbon-doped titania with its mesoporous structure was prepared by chemical modification and characterized by several techniques including X-ray diffraction, transmission electron spectroscopy (TEM), X-ray photoelectron spectroscopy (XPS), electron paramagnetic resonance spectra (EPR), and diffuse reflectance UV-Vis. absorption spectra, with emphasis on the effect of carbon as a doping compound to the titania. Based on EPR data, the photocatalytic activity by visible light can be ascribed to the trapping of electrons at interior sites of the carbon-doped titania between the valence and conduction bands in the titania band structure, and is able to be activated by visible light of a wavelength of up to 550 nm. The photocatalytic activity of the carbon-doped TiO₂ nanoparticles was evaluated by examining the decomposition of phenol by irradiation with artificial solar light (>420 nm) and the results were compared with those using Degussa P25, a commercially available titania nanomaterial.

Key words: Carbon, Phenol, Photocatalysis, Titania, Titanium Dioxide, Visible Light

INTRODUCTION

The photodecomposition of various organic pollutants by photocatalysts using wide band-gap semiconductors has been studied extensively [1,2]. In particular, semiconducting titania has been generally considered as an environmentally friendly photocatalyst because it permits the ultimate degradation of stable organic pollutants such as detergents, dyes, and pesticides to the mineralization stage in water [3]. However, some basic problems remain that must be solved to improve the photocatalytic activity of titania. One of the main problems is that titania shows a relatively high reactivity, mainly when irradiated by ultraviolet (UV) light at wavelengths shorter than 387 nm (exceeding the 3.2 eV band gap of the anatase crystalline phase). This constitutes a serious drawback to the use of sunlight or visible light as a source of irradiation in photocatalytic reactions on titania because titania absorbs only a small proportion of solar light in the near-UV region (only 2.7% of the total energy). Therefore, it is highly desirable to develop a photocatalytic system that can be applied under visible light irradiation.

Since the discovery that titania catalyzes the conversion of water to hydrogen and oxygen (Fusishima-Honda effect) by photo-decomposition [4], a number of research groups have attempted to enhance its photo-efficiency. Proposed techniques involve the chemical/physical modification of titania not only to increase its photo-efficiency by enhancing the electron-hole separation and the lifetimes of excited electrons, but also to develop its photo-catalytic activity under visible-light conditions. For activation using visible light, the most commonly used method involves doping with transition metal ions, which enhances absorption in this wavelength range [5]. This creates intra-band-gap states close to the conduction band edges. Another approach involves using a synergic effect with other coupled semi-

conductor photocatalysts, such as WO₃ [6], CdS [7], and In₂O₃ [8], which permits the charge separation in the photocarrier generation process to be enhanced. In order to permit the transfer of photoexcited carriers to reactive sites in a time comparable to their lifetimes, the states in the gap should overlap with the band states of titania. Moon et al. [9] and Abe et al. [10] have shown that dye-sensitized photocatalysis is applicable to the decomposition of organic pollutants under visible light. Anpo and co-workers [11] showed that titania containing implanted V, Mn, Cr, and Fe ions absorbs visible light and functions efficiently as a photocatalyst under visible-light irradiation. Although these materials absorb visible light and show relatively high activity under visible light, the enhancement of photoefficiency is still low and areas of application are restricted due to various limitations: improper hydrogen reduction level, photocorrosion, dye-sensitizer decomposition when pollutant concentration is decreased in aqueous systems, expensive manufacturing costs, etc.

Asahi et al. [12] reported that N-doped titania has photocatalytic activity under visible light at wavelengths longer than 400 nm and also proposed, based on their calculations, that substitutional doping of the anatase crystal with C, F, P, and S for O leads to photo-absorption under visible light. This approach suggests an effective route to visible-light activation because its p states contribute to band-gap narrowing by mixing with the O 2p states. This implies not only that the band state of the dopant overlaps sufficiently with the band states of the titania, but also that the band state of doped titania contains both reduced and oxidized levels of H₂O. Umehayashi et al. [13] and Ohno et al. [14] recently reported that S-doped titania powders show a band gap-narrowing effect when doped with sulphur. Yamaki et al. [15] reported similar results when non-metal atoms such as fluorine were substituted for oxygen. After carbon-modified titania was first reported by Lettman et al. [16], a number of research groups proposed synthetic methods for carbon-doped titania that showed much better photocatalytic activity under irradi-

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ation by artificial solar light [17-19]. However, despite these experimental findings and improvements, the microscopic mechanism of visible-light absorbance in doped titania is still not well established.

To date, a number of studies have been conducted on the origin of the response of doped titania to visible light, but no effective synthetic method and no clear experimental evidence for this has been reported. In this study, we propose a novel method for the synthesis of titania modified by carbon and show that the absorption edge is shifted to a lower energy, thus increasing overall photoreactivity in the visible-light region. The structural properties of the product were examined by XPS, UV-DRS, TEM, BET, EPR, and elemental analysis. The superiority of the photocatalytic reaction under visible light conditions was verified in a photodegradation experiment using an organic pollutant.

EXPERIMENTAL

Titaniumtetrakisopropoxide (TTIP, Dupont) was used as the titania precursor and acac (2,4-pentadion, Aldrich) was used as the carbon precursor and structuring agent. All other chemical reagents were used as received without further purification.

After dissolving TTIP (10 g) in 100 ml of solvent (EtOH or PrOH) with stirring, the temperature was increased to 60 °C. Acac (3.45 ml) was then added to the above solution and the stirring was continued for 20 min. The hydrolysis and condensation reactions were initiated by adding deionized water (50 ml, 60 °C) followed by stirring for one hour, during which time the temperature was increased to ca. 80 °C. The solution was initially light brown and became darker as the condensation reaction progressed. The resulting dark-beige solution was transferred to a Teflon-lined autoclave and aged at 200 °C for 12 hr. The product was centrifuged (3,000 rpm, 10 min) and washed several times with ethanol to remove undesired by-products. The particles were dispersed in ethanol to prevent particle aggregation and dried at 80 °C. Finally, calcination was performed at 200 °C for 3 hr under aerobic conditions.

The pore size and size distribution of the particles were evaluated by transmission electron microscopy (TEM; JEM-200CX, JEOL). The surface area was determined by the Brunauer-Emmett-Teller (BET) method (ASAP 2010, Micromeritics), and the pore size distribution was calculated from the desorption branch of the isotherm. Changes in the crystalline structures of the synthesized particles under a variety of operating conditions were investigated by XRD (D/Max-3C, Rigaku) analysis. XPS measurements (ARIE-SARSC 10MCD 150, Vacuum Science Workshop) were carried out for surface characterization. In order to estimate the photocatalytic activity of the synthesized particles, the photooxidation of phenol was performed with a Xe arc lamp (300 W, Oriel). A 420-nm cut-off filter was used for irradiation with visible light. A 30 ppm solution of phenol and 0.08 g of titania were mixed in a total of 40 ml of water, and the progress of the reaction was followed by UV-Vis analysis (HP 8453, Hewlett Packard). The concentration of phenol was monitored by measuring the absorbance at 270 nm with a UV-Vis spectrophotometer at room temperature. The total organic carbon concentration of the remained phenol solution was evaluated by 5310 C Laboratory TOC Analyzer (GE Analytical Instruments, USA) at room temperature.

RESULTS AND DISCUSSION

When titania powders are synthesized by the sol-gel method, it is well known that they show weak crystallinity, resulting in low photocatalytic activity. In this study, the reaction temperature for the synthesis of carbon doped titania was increased to 200 °C in order to increase the crystallinity of the powders instead of increasing the pressure to simplify the preparation conditions.

Fig. 1 shows a transmission electron microscopy (TEM) image of carbon-doped titania and a high resolution (HR) TEM image. The TEM images show that the particles have mesoscaled pores with a relatively uniform pore size gradient (the pore size distribution will be explained below). The primary particles were ca. 10 nm in size and they aggregated during the condensation reaction.

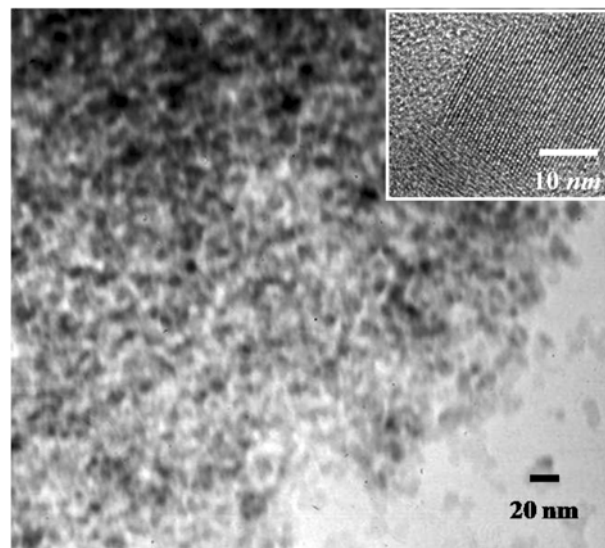


Fig. 1. TEM image of as-synthesized carbon-doped titania.

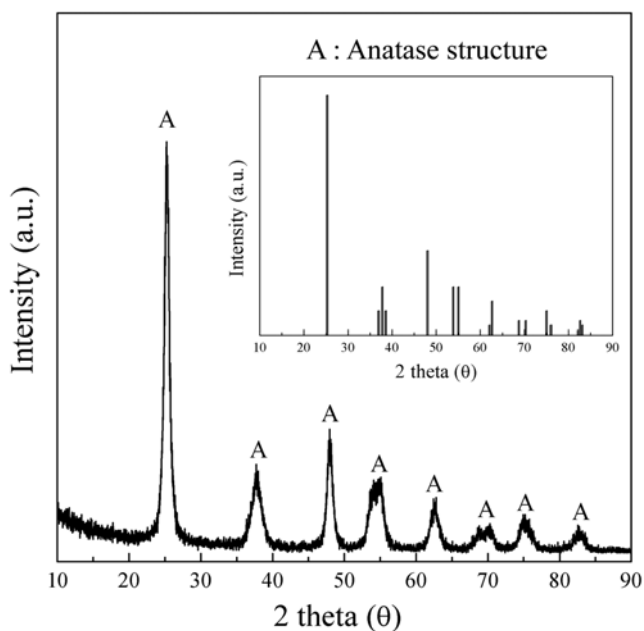


Fig. 2. XRD pattern of as-synthesized carbon-doped titania.

HR TEM images indicated that the primary particles had a high degree of crystallinity. In addition, all of the resulting materials had a highly ordered anatase crystalline structure, which was confirmed by X-ray diffraction (XRD) analysis as shown in Fig. 2.

The average meso-scaled pore-window diameter can be controlled within the range of 5 nm to 17 nm by changing the synthetic conditions. The concentrations of acac and H₂O and the ramping rate of the reaction temperature were key factors in controlling the condensation speed, which leads to the pore size distribution. However, the concentration of acac was not a controllable factor because acac is also used as the carbon precursor. Generally, a large amount of added H₂O (ex. 50 ml) and fast ramping rate of the reaction temperature (e.g., 5.0 °C/min) cause large pore sizes because of a rapid condensation reaction; a small amount of added H₂O (e.g., 30 ml) and a slow ramping rate of the reaction temperature (e.g., 0.5 °C/

min) cause small pore sizes because of a slow condensation reaction. In addition, the solvent had little effect on pore size distribution. However, the pore sizes were larger when PrOH was used as a solvent versus EtOH.

Fig. 3(a) shows N₂ adsorption-desorption isotherms for the synthesized photocatalyst. The hysteresis loop clearly observed at a relatively high pressure is related to capillary condensation associated with mesoscaled pore channels in the product. The pore size distribution curves obtained from the desorption branch of isotherms of titania modified by carbon exhibit a maximum in the region from 5 to 17 nm, depending on the synthetic conditions used (Fig. 3(b)). The Barrett-Joyner-Halenda (BJH) method was used for a maximum pore size of less than 10 nm, and the Broekhoff-de Boer (BDB) method was used for a pore size larger than 10 nm to estimate the pore size distribution. In each case, the Brunauer-Emmett-Teller (BET) surface areas of the powders ranged from 146 to 212 m²g⁻¹. This value is 3-4 times higher than the commercial titania nanomaterial, Degussa P25 (ca. 50 m²g⁻¹). A mesoscaled pore system should efficiently transport guest species to the framework binding sites. These results satisfy the basic requirements for a photoactive material for enhancing photoefficiency.

Optical absorption in the visible-light region is an essential requirement for visible-light activation. To evaluate optical absorption ability, the optical absorption spectra (UV-DRS) of the samples are shown in Fig. 4. As shown, compared to commercial titania (P25, Degussa Corp.), the absorption edge was shifted to a higher wavelength region in carbon-doped titania. This indicates that carbon-doped titania can absorb more visible light than P25. Accordingly, this data suggests that the photocatalyst can be activated by visible light.

Electron paramagnetic resonance has been used as an investigative tool in the study of radicals formed in solid materials, since the radical typically produces an unpaired spin on the molecule from which an electron is removed. In the process of photocatalysis, photogenerated electrons and holes are trapped on the surface, result-

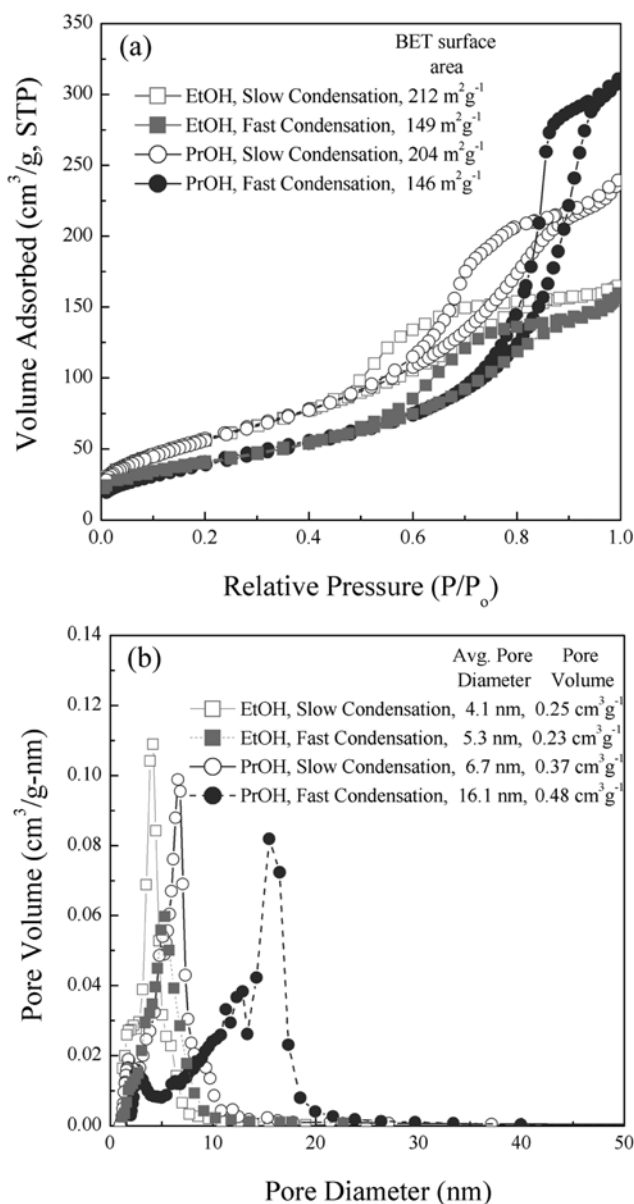


Fig. 3. (a) Nitrogen adsorption and desorption isotherms and (b) pore-size distribution curves for carbon-doped titania.

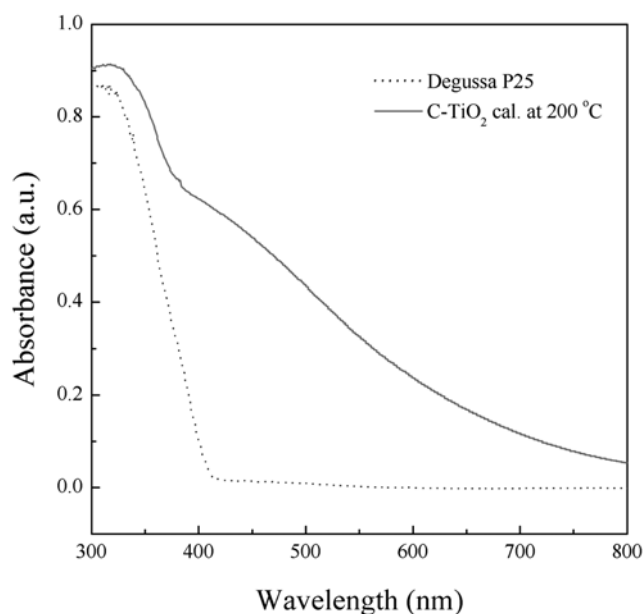


Fig. 4. Diffuse reflectance UV-Vis. absorption spectra of carbon-doped titania treated at 200 °C.

ing in the formation of paramagnetic species. Photocatalytic reactions arise from the reaction of these radicals with reactant molecules on the titania surface. Electron paramagnetic resonance spectroscopy has thus been used to detect photogenerated radicals on titania [20]. Fig. 5 shows the EPR spectra of the synthesized titania catalyst in air at room temperature. As shown in the figure, the EPR signal was enhanced after light irradiation. In addition, the EPR signal was not enhanced in air at room temperature for titania catalyst that did not contain carbon. The EPR signal at $g=1.997$ shows that electron trapping occurs at interior sites of the carbon-doped titania [21]. The increase in EPR signal intensity indicates that more radicals are formed. This can be attributed to an increase in photocatalytic activity due to the doping materials. The signal intensities were enhanced with increasing wavelengths of light up to 550 nm (2.25 eV), and then decreased with a further increase in wavelength. This suggests that the synthesized titania effectively undergoes activation by visible light at 550 nm. These results are in agreement with the UV-DRS results.

The characteristics of the bonds between titanium and carbon were investigated by using XPS. Ti 2p, O 1s and C 1s XPS spectra

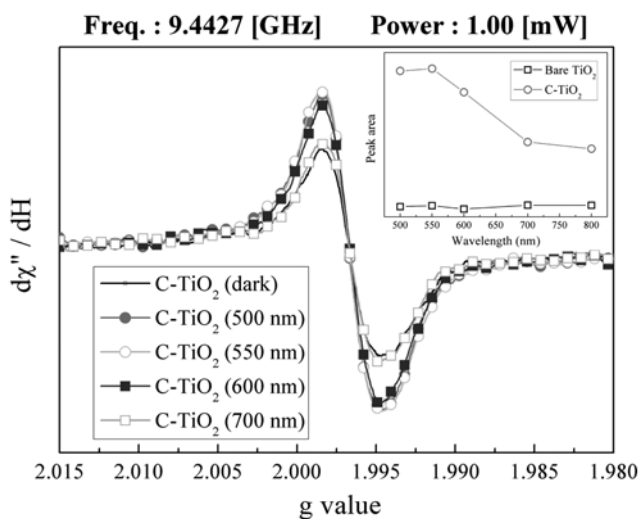


Fig. 5. EPR spectra of carbon-doped titania irradiated with different wavelengths of light.

of the photocatalyst are shown in Fig. 6. The Ti 2p spectrum (Fig. 6(a)) could be deconvoluted into two spin-orbit components at binding energies of 464.2 and 462.6 eV and are assigned to the Ti(III) and Ti(IV) fractions, respectively, on the surface of the particles [22]. The spectra were decomposed assuming Gaussian line profiles. The decomposition of the O 1s spectrum is shown in Fig. 6(b). The O 1s spectrum could be deconvoluted into three spin-orbit components for the best fit. The binding energies of the Ti-O, Ti-OH and Ti-OH₂ components are 530.2, 531.8 and 532.8 [22,23]. Fig. 6(c) shows the C 1s spectrum core level photoelectron spectrum of the particles. This spectrum can be deconvoluted into two spin-orbit components. The binding energies of the Ti-C and C-H components are 281.0 and 285.8. It should be noted that the intensity of the Ti-C binding peak is not strong. Instead, the peak related to the carbonate group was revealed, and it played an important part in the photocatalytic activity [24-26].

When anatase titania powders are synthesized by the sol-gel method, the particles contain a certain fraction of oxygen vacancies in

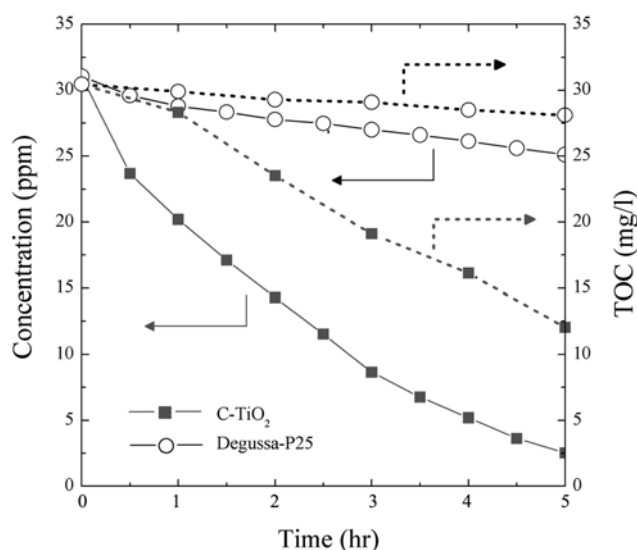


Fig. 7. Photooxidation of phenol under visible light (>420 nm) and TOC concentrations using Degussa-P25 (\circ) and carbon-doped titania (\blacksquare) calcined at 200 °C.

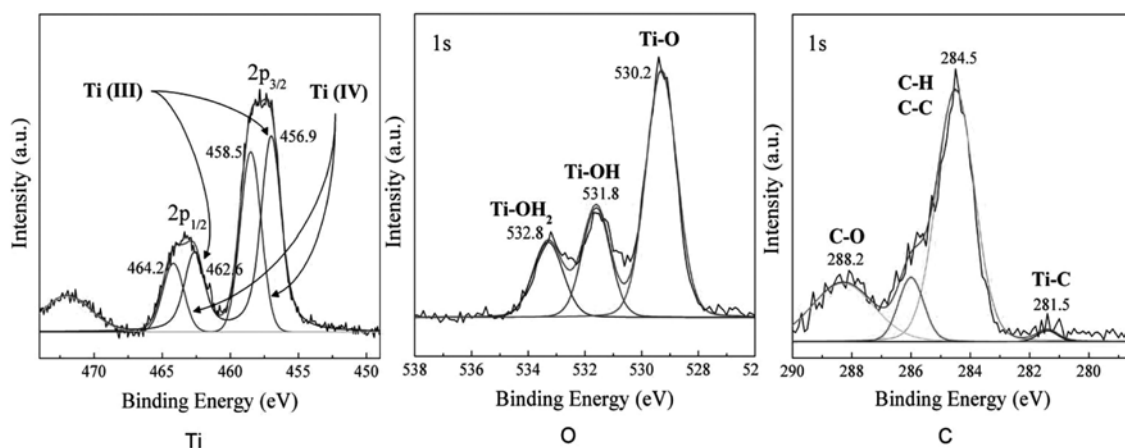


Fig. 6. XPS spectra of carbon-doped titania: (a) Ti(2p); (b) O(1s); (c) C(1s).

the anatase structure as evidenced by XPS results. Interestingly, the Ti(III) sites created as a partial vacancy for oxygen substitution improve the photocatalytic activity of photocatalysts by narrowing the energy band gap [27,28]. Importantly, the existence of carbonate species stabilizes Ti(III) and oxygen vacancy sites in the modified TiO₂ structure [29].

In order to investigate the photooxidation of carbon-doped titania, phenol was examined as a substrate. Changes in the phenol concentration and TOC during the decomposition of an aqueous solution of phenol are shown in Fig. 7. The phenol was effectively oxidized under visible light. However, the TOC concentration remained at a relatively high level even after the phenol had been decomposed. This can be attributed to the presence of intermediate products, such as hydroquinone and fumaric, maleic, and formic acids. These products can also be mineralized by further irradiation with light under aerobic conditions.

CONCLUSIONS

In conclusion, carbon-doped titania materials with a mesoscaled pore structure were synthesized in a simple, one-step chemical synthesis. The pore characteristics could be controlled from 5 nm to 17 nm by changing the synthetic conditions. The high photocatalytic activity of carbon-doped titania under visible light at a wavelength of less than 550 nm can be explained by the band gap narrowing effect by vacancy states in the anatase structure stabilized by carbon doping. Doping shifted the absorption edge to a lower energy, thus effectively increasing the photocatalytic activity in the visible-light region.

Based on these results, a possible geometrical structure is proposed for titania modified by carbon. The synthesized carbon-doped titania showed high photooxidation activity for the decomposition of an aqueous solution of phenol under visible light.

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