Photocatalysts for Air Pollution Control and Abatement

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Abstract. Titanium dioxide (TiO$_2$) has been largely studied in the past decades for its photocatalytic properties [1]. The material is a n-type of superconductor whose photocatalytic property is due to the absorption of photons ($h\nu$) with energy higher than the energy of the valence band. The electrons in the valence band use such energy to jump into the conduction band. This process, originally studied for the photolysis of water [2], has revealed itself of great use for the efficient removal of hazardous molecules and micro-organisms in water and in the air [3]. The high energy required by the electrons in the valence band to jump in the conduction band, which is 3.2eV for anatase TiO$_2$, has limited the use of the material to the very narrow wavelength bandwidth of the ultraviolet (UV) radiation. In order to make use of the material under a much larger spectrum of light frequencies, especially under visible light, modifications of the TiO$_2$ lattice by adding extra elements have been made and they still represent today a challenge for the research community. The change of the lattice can be done by doping TiO$_2$ with different elements, this includes non-metal elements like carbon and nitrogen [4]. The importance of these studies stands on the fact that the resulting material, simply exposed to sun light or LED light, is able to sterilize the air from harmful bacteria and neutralize other well-known indoor volatile organic pollutants such as formaldehyde. This work presents some experimental observations on visible light photocatalytic carbon doped titanium dioxide, C-TiO$_2$, obtained by a sol gel method. The study focuses on the crystal structure of the synthesized material. The aim is to evaluate the consistency of the method in reproducing the desired crystal structure and therefore the desired photo-catalytic properties of this material.

1. Introduction

Photocatalysis induced by anatase titanium dioxide (TiO$_2$) under UV light is today largely studied for applications in water disinfection and air sterilization. High photo-activity, chemical and biological inertness, along with low price makes TiO$_2$ a good candidate for these commercial purposes. Numerous studies have shown the effectiveness of TiO$_2$ photocatalysts to remove bacteria both in water and in air. The photo-chemical sterilization of Escherichia coli using Platinum doped TiO$_2$ was in fact first reported in [5]. Since then TiO$_2$ photocatalysts and TiO$_2$ coated materials have also been utilized to remove a large variety of other micro-organisms [6-8]. The aim of removing bacteria, led to the main use of UV activated TiO$_2$ filters today present in indoor air purifier units. In recent years, in view of the increasing concerns on environmental pollution, TiO$_2$ is being also considered for neutralizing hazardous volatile molecules. Since the class of air pollutants include different types of
organic and inorganic substances, the research community has been highly productive in the attempt of modifying the TiO\textsubscript{2} crystal structure and enhance its photocatalytic performance. By changing the crystal structure and the material composition, the material can remove more efficiently a series of air pollutants, including formaldehyde and nitrogen oxides. TiO\textsubscript{2} anatase crystal structure absorbs photons (hv) only with energy equal to or higher than its band gap energy (3.2eV) resulting in the jump of electrons from the valence band (VB) into the conduction band (CB), generating “holes” and electrons. The hole-electrons pair oxidizes molecules of water (OH groups) in the surface of the TiO\textsubscript{2} lattice and these radicals have been proven very effective to un-harm several organic compounds. The photocatalytic activity of TiO\textsubscript{2} is very limited though by the large energy required by the photons to excite the electrons in the valence band. Therefore, in the past decade numerous attempts to shift the band gap to visible light have been made. There are several studies and still quite a lot of research on the doped versions of TiO\textsubscript{2} and the effect of the different doping on the material properties. Still, these materials are not commercially popular since, in terms of cost and scalability to mass production, their synthesis represents a challenge [9]. Several methods have been proposed and tested, among them co-precipitation, mechnochemical, hydrothermal and sol-gel [10,11]. The most popular among these methods is probably the sol-gel technique due to the full control on the process and a higher understanding of the key factors that influence the properties of the final product. Good reproducibility of the results can also be obtained. There are disadvantages though, which include the expensive precursors and the limited size of the samples that can be synthesized which is the main challenge to face for the effective industrialization of these materials. This work presents some of the experimental results on carbon-doped TiO\textsubscript{2} obtained by a non-hydrolytic sol gel method. Since the synthesis can largely impact the final material’s photocatalytic performance and many are still the variables to investigate, this work focuses on the observation of the material’s crystal structure. Proving the consistency of the results is in fact the first step for choosing the possible pioneer route towards the industrial scalability of the manufacture and large commercialization of these materials.

2. Materials and Method

2.1. Chemicals and Method

Titanium chloride (TiCl\textsubscript{4}) analytical grade, Ethanol ACS reagent grade, Tetrahydrofuran (THF) reagent grade, were purchased from Macklin reagent Shanghai. Commercial TiO\textsubscript{2} nano-powder Degussa P25 for the results comparison, was a gift sample from a Shanghai cement industry (BeiMo).

2.2. Method

The synthesis of the TiO\textsubscript{2} nanoparticles followed the non-hydrolytic sol gel route previously described in [12], using Titanium chloride (TiCl\textsubscript{4}) as a precursor. Several batches of material were prepared in order to investigate the reproducibility of the results and consistency of the method while varying some of the key variables in the process, such as the solution stirring time, drying time of the sol and calcination temperature. TiCl\textsubscript{4} was slowly added and stirred over-night in ethanol at room temperature. The final solution was dried in a muffle furnace at 100°C for about 10 hours. The final compound was a solid light brown powder. It was placed in a ceramic crucible which was then closed. Afterwards, the material was calcinated at different temperatures. After the calcination, the material was slowly cooled to room temperature and then ground by hand in an agate stone mortar in order to smash large particles agglomerates. In this work only the results on batches of material calcinated at 400°C are presented.

2.3. Experiments

Scanning electron microscopy, SEM, investigations on the synthesized carbon-doped TiO\textsubscript{2} (C-TiO\textsubscript{2}) were performed to assess the size and morphology of the nanoparticles obtained with the specific sol gel method chosen for this work. SEM were performed by using a TESCAN electron microscope. The X-ray diffraction, XRD, was used to investigate the crystalline phases in the material. A Bruker XRD
diffractometer and X-ray Cu-Kα radiation with 0.15418nm wavelength was used. The purpose of the test was to confirm previous research results reporting that anatase phase was the only phase present in the material. The X-ray Photoelectron Spectroscopy technique, XPS, was instead used to determine how and if the carbon atoms were successfully integrated in the TiO₂ lattice. A Thermo Fisher ESCALAB 250 was used for these analyses. If the doping occurred correctly, the method would be able to detect carbon element in 1s electronic state levels that indicate the different bonding with the atoms in the TiO₂ lattice. This method was therefore essential to detect the presence of carbon in the lattice and to further investigate its bonds to oxygen and titanium atoms.

3. Results

The first step of the experimental investigation consisted on observing the morphology of the material which was achieved by scanning electron microscopy (SEM) imaging. Figure 1a shows the typical SEM image of P25 Degussa commercial nanopowder. It presents agglomerates of highly packed well distinct nanoparticles. The agglomerates, in this case, indicate that the nanoparticles are very small. The smaller the nanoparticle, in fact, the higher the surface energy the higher the tendency to aggregate. Depending on the use of the material, the separation of the particles can be done in solution using particles dispersants. Figure 1b, instead, shows the image of the carbon doped TiO₂ as obtained from the chosen sol gel method and after calcination at 400°C. A mass of crystallized mesoporous material is clearly seen. From the P25 TiO₂ images, the size of a single particle was estimated to be less than 150nm while for an evaluation of the single crystal size, the XRD data was used. For the C-TiO₂ samples, a distinct measurement of the nanoparticles’ size was instead not possible, nevertheless the XRD measurements were conducted on all samples. A comparison of the XRD patterns of C-TiO₂, and P25 TiO₂ is given in Figure 2.

![Figure 1](image1.png)

**Figure 1.** a) SEM image of pure TiO₂ particles, b) SEM image of the synthesised carbon-doped TiO₂ calcinated at 400°C

Based on the characteristic anatase (101) diffraction line and using an X-ray radiation Cu-Kα with 0.15418nm wavelength, for the P25 TiO₂ sample the Scherrer equation with shape factor k kept constant (0.9) gave a crystalline size equal to 53.19nm. If the shape factor is corrected with 0.3, the crystal size according to the authors in [13] is estimated more precisely and results of 17.73nm. For the four C-TiO₂ samples instead, the crystal size resulted of 13.6-16nm from the standard Scherrer equation, and if corrected in k, the average crystal size is of 5nm. Contrary to [14], the sol gel method used in this research and with a calcination temperature of 400°C did not lead to a completely amorphous material, but a clear dominance of anatase phase was shown in the XRD data. The XRD patterns show that a good level of crystallinity was obtained, while the broadening of the peaks can be
due both to the misalignment of the sample in the test setup and the very low size of the crystal, which seems to be the case. For achieving a full phase transformation and complete crystallization of the material, higher calcination temperature could be used; 500°C is suggested in [14,15], however, in these previous works a different synthesis method or doping element (N) was used, therefore the predicted results should be verified.

The second step of the experimental investigation consisted in further analyzing the crystal structure of the C-TiO₂ material. Although there is still a debate on whether a mixed crystal phases or mainly anatase phase has the best effects on the photocatalytic performance of TiO₂, in this study the presence of a sole anatase crystal phase was observed. A comparison of the XRD patterns of a pure anatase C-TiO₂, TiO₂ P25 is given in Figure 2.

The results show that the anatase reflections are dominating in the XRD patterns. A 100% anatase phase was detected by the XRD instrument. The diffraction lines for the (101) anatase peak were detected at a slightly different angle than those for P25 TiO₂. Four different C-TiO₂ samples and one P25 TiO₂ sample (two points analyses per sample) were tested. In all experiments the un-doped TiO₂ showed the (101) peak for 2θ between 25.49 and 25.5 degree while all the C-TiO₂ samples presented a (101) characteristic peak at 2θ between 25.1 and 25.3 degree. This shift could imply changes of the lattice such as the change of the crystal size [16], but in confirming such point a great uncertainty remains since a small angle shift is often due to a sample misalignment during the test setup. Additionally, the observed shift was towards lower values of 2θ angles. A shift towards lower diffraction angles, generally means the lattice increased in size. Looking at the possible combinations, this would imply that C substituted Oxygen atoms. At this point, to further clarify the elements arrangement in the crystal structure, the XPS technique was used. Figure 3 shows a typical result obtained for carbon doped Titania. The XPS survey in Figure 3 (a) indicated that the sample presents binding energies for the elements Ti, O and C, which are the only elements that were found in the material. In one of the samples, a Cl impurity was detected, this sample was not considered for further analysis, however, it introduced the doubt that this specific sol gel method and the calcination temperature may not lead to a doped material completely free of impurities, and Cl element from the precursor can then be found still trapped in the final material forming additional oxides. The carbon state in the material is given by the C1s electronic level displayed in Figure 3 (b). Two peaks can be

![Figure 2](image-url)
seen, at 284.8eV and at around 288.8eV. It is now well acknowledged in the literature that the 284.8eV peak implies that C only exist on the outer surface of the lattice, it corresponds to C–C bond (amorphous carbon) that is due to contamination induced by the experiment [17] and that the 288.8eV peak also represents a C element present on the surface of TiO₂ lattice but in a C-O bond [18]. At this point it can be said that Carbon could substitute either Oxygen or Titanium in the TiO₂ lattice. Differently from [12] the C1s peak at 279.9eV was not observed. But the deconvolution of curves for C1s indicates a peak around 280.9eV which seems to be a typical Ti-C bond reported in several publications [18].

![Figure 3](image)

**Figure 3.** Intensity unit (Counts/s) versus Binding Energy (eV). XPS results: a) survey spectrum on C-TiO₂ nanopowder; b) C₁s spectrum; c) Ti₂p spectrum; d) O₁s spectrum.

Following the discussion of the results in [18] The Ti₂p spectrum shows two peaks at 458.7 and 464.6± 0.2eV that represents Ti⁴⁺ 2p₃/₂ and Ti⁴⁺ 2p₁/₂ respectively, in agreement with pure TiO₂. From the Ti₂p spectra it was not possible to identify the peaks of Ti²⁺ 2p₃/₂ and Ti²⁺ 2p₁/₂ at around 455eV and 460eV even if the convolution curves on the raw data in Figure 3 do peak around these values. Further tests are necessary. If such a case is confirmed, given the presence of C1s at 280.9eV, the Ti²⁺ peak at 455eV would confirm the presence of Ti-C bond. Finally, the spectrum curve for O₁s shows a peak at around 530eV assigned to the lattice of doped TiO₂, and a second at around 532eV which according to [19] corresponds to C-O bonds. As characteristic peaks values for O₁s in the case of undoped TiO₂ are slightly lower, the results once again seem to indicate lattice distortion upon doping. Data from the experiment also confirms presence of the following elements in percentages Ti 2p 27.36%, O₁s 56.44% and C₁s 16.2%. As the presence of C₁s is not negligible, along with the above analysis we can assume C is present in the lattice both as a surface element (replacing O) and as a replacement of Ti atoms.
4. Discussion and Conclusions
In the process of synthesising a novel material it is indispensable to prove that the desired properties are achieved, and the results are consistent. The challenge to face, in fact, stands on the industrial scalability of the process used in the laboratory while attaining the best material performance and maintaining the simplicity of the methodology. According to an evaluation of cost and performance and having in mind a specific application for the material, sol gel methods seem to be a possible viable route for a large industrial fabrication and commercialization of doped Titania. The nature of the carbon-induced modifications of the TiO$_2$ electronic band structure has been studied for decades and it still seems to need further research. Band gap narrowing or the formation of localized mid-gap states have been alternatively proposed in past. These doped version of TiO$_2$ are certainly sensitive to the method used, the calcination temperature, and several other variables. The results in this work confirm the presence of C element in the TiO$_2$ lattice both in a substitutional Ti and O elements’ place. Some discrepancies from previous studies have been found regarding the influence of the calcination temperature on the complete crystallization of the material and as the literature presents different results on different methods, the author feels that additional research work on the way impurities are incorporated or simply bonded to the surface of the TiO$_2$ lattice is still needed. In order to move further and propose such a method for an industrial fabrication of the material, the effects of the main variables on the synthesis process and the final crystal size and nanoparticle size, should be understood in full. As for the material itself, the visible light photocatalytic property implies almost automatically the self-cleaning, antifungal, antibacterial properties since these are inherent with the nature of the photo-oxidation process induced by TiO$_2$ nanoparticles under UV and/or visible light. TiO$_2$ and all its doped versions are also widely used to photo-decompose formaldehyde, which is at date a well-established technology. These properties though, require specific tests to further prove they were indeed achieved by the synthesis.

Acknowledgments
The author acknowledges the financial support obtained from Shenzhen and Bao’An District Government, Science and Technology Committee, “The 2018 Shenzhen City and Bao’An District Women Entrepreneur Award” and the “10th China Shenzhen innovation competition and the 5th Bao’An district innovation competition award for novel materials industries”. The SEM tests were performed at the materials testing centre of Tsing Hua University in Shenzhen and XRD tests were conducted at the materials department of Shenzhen University.

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