Influence of Morphology and Doping of Titania Nano-porous Materials for Efficient Oxidation of Air Contaminants

F Ghezzo

1 Lulan Technologies, Peking University Science and Technology Park, Guangdong, Shenzhen, 518100, China
2 Nexat Limited, 2107-9 C. C. WU Building, 302-308 Hennessy Road, Wan Chai, Hong Kong, China

*Email: fabriziaghezzo@gmail.com

Abstract. Air pollution is a global concern. Public and governments sensitivity to matters related to air pollution has been constantly increasing since the 1970’s. The urgency to lower greenhouses emissions in order to protect the environment and its wildlife while mitigating the impact of pollution on people’s health reflects into the growing private and government investment on green technologies for renewable energy and sustainable products. Along with CO₂, there are other pollutants that affect the quality of the air we breathe. Among them, nitrogen oxides. To neutralize their effects, the research community has been synthesizing photocatalysts capable to oxidize them. The work focuses on the synthesis of doped titanium dioxide by sol gel method and on the influence of the calcination temperature on the final material photo-oxidation ability.

1. Introduction

If we aim to obtain a better air quality in our cities, we first need to classify pollutants. Strategies to curb them depend on the nature and source of the target substances. If we use a very general classification method, we can divide air pollutants in fine particles, gases and pathogens (bacteria and viruses). The third type of pollutant can be considered such from a human being’s perspective, since not necessarily bacteria and viruses have negative impact on the environment. However, as we are planning to re-conceptualize our urban areas into sustainable living and working spaces for healthier societies, we can include those pathogens which are a threat to people's and animals' life, in a class of organic pollutants. While preventing measures to avoid the spread of epidemic diseases among communities can include aspects that go from the improvement of hygiene standards and adequate food safety regulations, to emergency action plans [1-5], neutralizing and eliminating pathogens from the air and surfaces that surround us can be approached in the same way we target the removal of other air pollutants. Therefore, air cleaning technologies in our urban areas should also include air disinfection solutions. For what concerns the great amount of particulate matter and high concentration of gaseous pollutants such as nitrogen oxides in the air of our urban areas, the problem has been recognized and attributed to the enormous number of vehicles and their emissions [6]. Most airborne NOx gases (x stands for 1 or 2 to indicate NO or NO₂) derive from combustion-related emissions generated by human activities, mainly fossil fuel combustion in electric utilities, high-temperature operations at other industrial sources, and also from the daily use of combustion engines propelled vehicles. As in most part of the world, factories are not present in highly populated metropolis, these
gases are mainly released into the air by road vehicles. Nitrogen oxide emissions are not only present outdoor because fuel-burning appliances, like home heaters and gas stoves, produce considerable amounts of NOx in indoor settings representing a dangerous source of indoor air pollution. Today the concentration of these emissions is so high that NOx come to play a major role in today’s environmental issues and humans’ health. These molecules react with volatile organic compounds (VOCs) in the presence of sunlight to form ozone (O₃), which is well known to be associated with respiratory problems and degradation of the environment [7]. Also, NOx and sulphur derived pollutants in the air react to form chemical compounds that are responsible for acid deposition (acid rain). Deposition of NOx also affects the natural nitrogen cycle. It has been observed that it can contribute to eutrophication with dramatic damage to the ecosystem [8]. Finally, the formation of fine particles is also due to precursors such as sulphur dioxide (SO₂), nitrogen oxides (NOx), volatile organic compounds (VOCs) and ammonia (NH₃). Secondary formation of PM2.5 in fact occurs due to a chemical reaction in the atmosphere, generally at some distance from the original emission source, and the main responsible are NOx. To conclude, NOx plays a role in several other environmental issues, including secondary formation of particulate matter, haze, global climate change, but also in the increase of respiratory diseases which are also connected to other health complications for people living in heavily polluted cities. Recent studies add to these illnesses a serious impairment of the cognitive and learning functions of the brain [9]. Measures to mitigate the effects of these emissions or to remove them from the air have benefits on people’s health and the environment; as a consequence, on the overall economy. This work focuses on the synthesis of titanium dioxide photocatalysts for the removal of nitrogen oxides in the air and specifically on how the calcination temperature in a sol-gel technique influences the visible light photo-oxidation ability of the material. These studies aim to add some results to the already existing literature to confirm and support previous findings.

2. Methods
To decrease the concentration of NOx gases in urban areas, we can approach the problem in three ways. The first consists on preventing their emission at the source, which implies changing the energy sources of our transportation means to sources that are not based on fuel combustion engines. The second consists on minimizing their emission while still using current vehicles, which implies that we remove most of the emissions right before the fumes are discharged into the air. In these first two cases regulatory standards and government incentives for green technology and renewable energy are going to be key promoters for progress. We can think for instance of the progressive shift toward the use of electric and hybrid electric vehicles that we have witnessed in recent years. Finally, for those gases that are already present in the air because they were previously emitted, we need to find ways to absorb or filter them in order to remove them permanently from the air and avoid their accumulation. A lot is being reported about technologies to absorb CO₂. However, given the rise of serious health complications, we have good reasons to worry about living in areas with high concentration of nitrogen oxides and therefore we should promote and dedicate research efforts to promising technologies that can effectively remove them. This approach includes the research on the optimization of the oxidative power of photocatalytic materials towards organic pollutants (including pathogens) and nitrogen oxides.

3. Titanium Dioxide Photocatalysts
Photocatalysis induced by UV light on TiO₂ is a well-known phenomenon [10]. A lot of studies have shown the effectiveness of TiO₂ photocatalysts and TiO₂ coated materials to remove bacteria both in water and in air and therefore they have been utilized to remove a large variety of micro-organisms [11]. In view of the increasing concerns on environmental pollution, TiO₂ is being considered also for neutralizing hazardous volatile molecules, such as formaldehyde (CH₂O) and nitrogen oxides. Since the natural occurring material is a photocatalyst only under UV light, the idea of changing its lattice in order to shift the activation of its oxidative-reductive power under visible light started to be explored. By changing the lattice of TiO₂ and its composition through doping, the final material can efficiently
remove a series of air pollutants under visible light. There are several studies and still quite a lot of research on the doped versions of TiO$_2$ and the effect of different doping elements on the material photocatalytic properties under visible light [12]. One of these doped versions of TiO$_2$ is carbon doped TiO$_2$ (C-TiO$_2$) which is still a very attracting photocatalytic material. In past studies, C-doped TiO$_2$ was shown to be five times more active than N-doped TiO$_2$ for the light degradation of 4-chlorophenol [13]. The higher activity of Carbon doped TiO$_2$ was attributed to its capability of absorbing visible light in a wider range of wavelengths (400–800nm).

3.1. Synthesis Methods
There exist several methods to synthesize TiO$_2$ photocatalytic materials [14], and these methods have also been used to obtain doped Titania nanomaterials. The sol gel technique [15] seems to have few advantages in the synthesis of doped titanium dioxide, such as the possibility to synthesize these materials at low temperature (key variable for a change towards a low carbon emissions industry), control over the key variables in the process, and good reproducibility of the results. There are several variables that can influence the resulting material properties. One is certainly the choice of the starting materials which is determinant for the successful doping, and another consists on the calcination process that, depending on the temperature, transforms the amorphous sol into one of the typical TiO$_2$ polymorphs (anatase, rutile, or brookite). This step seems to influence the material photocatalytic efficiency and therefore its light absorption ability. The calcination temperature in earlier works was chosen in order to obtain a material preferably with anatase crystal phase [16] but in later studies, the positive effect of a mixed anatase-rutile crystalline structure on the photocatalytic properties of the doped Titania was also observed [17]. Notwithstanding the fact that the main choice of the synthesis method depends in part on the target application [18], a material that demonstrates high efficiency in the oxidation of air pollutants and effective degradation of bacteria and other pathogens under a larger spectrum of light wavelengths is today of great interest. The amount of successful efforts spent by the research community up to date, indicate that this objective can be reached by narrowing the band gap of the material through doping and increasing the material specific surface area. In the sol gel technique, the doping depends on the starting materials, and the final morphology depends also on the calcination temperature. In this work the interest is posed on observing how the visible light absorption properties of carbon doped Titania change when the calcination temperature varies. The main reason for the change is also qualitatively identified in one case. The observations are made on the material obtained through the specific sol gel method described in the following sections.

4. Calcination Temperature and Light Absorption Properties of C-TiO$_2$

4.1. Chemicals
Titanium chloride (TiCl$_4$) and Ethanol ACS reagent grade were purchased from Macklin Shanghai. Anatase TiO$_2$ nano-powder was also purchased and used as a reference for the comparison of results.

4.2. Method
The synthesis of the carbon doped TiO$_2$ nanoparticles followed one of the sol gel methods present in the literature where Titanium chloride (TiCl$_4$) is used as a precursor [19]. In a previous work the method was used keeping the calcination temperature constant and equal to 400°C for all batches of material that were synthesized [20]. In this work, different samples were prepared in order to investigate the influence of the calcination temperature on the final material light absorption properties. TiCl$_4$ was slowly added to ethanol and stirred for more than 12 hours at room temperature. The obtained yellowish sol was dried in an oven at 100°C for about 10 hours. In this process about 10g of nanopowder was obtained. The material was then placed in a ceramic crucible which was closed and positioned at the centre of a muffle furnace. At this point, samples of a few grams from the same batch of material were calcinated at different temperatures. One sample was calcinated at 250°C. A second sample was calcinated at 400°C and afterwards, part of this same sample was re-calcinated at 500°C.
In this specific case the light absorption properties of the material before and after the second temperature treatment was observed. After the calcination, the material was slowly cooled to room temperature and then grinded by hand in an agate stone mortar. All test results are compared with the commercial anatase TiO$_2$.

4.3. Experiments

Scanning electron microscopy imaging, SEM, on the synthesized carbon-doped TiO$_2$ (C-TiO$_2$) was performed to assess the size and morphology of the obtained powder by using a TESCAN electron microscope. A Bruker XRD diffractometer and X-ray Cu-K$_\alpha$ radiation with 0.15418nm wavelength was used for investigating the crystal phases. The X-ray Photoelectron Spectroscopy technique, XPS, was instead used to determine the presence of carbon atoms in the TiO$_2$ lattice. For these analyses a Thermo Fisher ESCALAB 250 was used. Finally, the ultraviolet visible light diffusive reflectance absorption spectra were obtained by using a PerkinElmer Lambda 750 spectrophotometer.

5. Results

The morphology of the material is shown in the images obtained by scanning electron microscopy. Figure 1a shows the typical SEM images of the purchased TiO$_2$, while Figure 1b and 1c is the as synthesized C-TiO$_2$ nanopowder calcinated at 400°C. We can notice the different morphology and the size difference of the nano particles. Although commercial TiO$_2$ nanoparticles are probably a result of a ball mill process, while here the material is as it resulted after calcination and the grinding by hand, the image shows clearly a highly porous material with a good degree of crystallization.

![Figure 1](image.jpg)

**Figure 1.** a) commercial anatase TiO$_2$; b) and c) C-TiO$_2$ calcinated at 400°C at different magnifications.

It is possible to distinguish very small nanoparticles, all highly packed in large agglomerates. In a previous work [20] it was shown by the XRD analyses that the material presents almost entirely an anatase crystal phase (it can have still very small residue of the amorphous state) with crystallites of a typical 7nm size. The results were reconfirmed for these samples. Based on the characteristic anatase (101) diffraction line and using an X-ray radiation Cu-K$_\alpha$ with 0.15418nm wavelength, for the commercial undoped TiO$_2$ nanopowder the Scherrer equation with shape factor k kept constant (0.9) gave a crystalline size of 53.19nm. If the shape factor is corrected with 0.3, the crystal size according to the authors in [21] is estimated more precisely and results of 17nm. For the C-TiO$_2$ samples instead, the standard Scherrer equation gave a crystallite of 13-16nm, and if corrected in k, the average crystal size is of 6nm. With or without correction in k, it is undoubtful that the doping with C element reduces considerably (>30%) the crystallite size and, as a consequence, we should expect a noticeable increase of the specific surface area; characteristic that requires further quantification. The sol gel method used in this research with a calcination temperature of 400°C led to a clear dominance of anatase phase as shown in the XRD data, Figure 2. The broadening of the peaks for the doped TiO$_2$ compared to the typical sharp peaks observed in anatase undoped TiO$_2$ confirms the very low size of the crystals. The sample calcinated at 500°C showed a large presence of the rutile phase. In fact, rutile diffraction peaks were detected. This means that a calcination temperature higher than 400°C leads to a progressive
phase transformation into rutile with a decrease of the visible light photocatalytic properties and that 400°C may be the borderline for the phase transformation. This observation confirms what previously was reported on the results that C-doping decreases the typical temperature needed for the different phase transformations [22].

Figure 2. XRD data comparison, C-TiO₂ calcinated at 400°C in red and C-TiO₂ calcinated at 500°C in green. In blue the XRD results on commercial anatase TiO₂.

The change of colour from the bright white of non-doped titanium dioxide to the light brown of the carbon doped samples was a qualitative indication of the change of the material light absorption properties. The surface composition and the electronic arrangement of these doped samples can be investigated through XPS analyses. The presence of carbon as a possible substitutional element, replacing oxygen, and as an interstitial element in TiO₂ lattice was shown in a previous work [20]. In this work, it can be added that carbon is not only present in the lattice, but it may also present on the surface of the material in the form of carbonaceous species (C-C) and in carbonate species (C-O) linked to carbon residues on the surface, as suggested in [23]. Following the reasoning in [22], we can take a closer look to the XPS results and add some considerations for the specific sol gel synthesis of carbon modified TiO₂ chosen for this work. The detected binding energies for the electronic state C1s with the relative atomic percentages for the samples calcinated at 250°C and 500°C are given in Table 1. Since C-TiO₂ is amorphous at 250°C and fully crystallized at 500°C, we can observe if these species are formed during the synthesis. In fact, if these species are present on the surface, they may decrease while the temperature increases. If they are not on the surface and just part of the TiO₂ lattice, then the chosen increase of the calcination temperature will not influence the results.

Table 1. C1s atomic percentage and binding energies (BE) in eV for two samples S4 and S4T.

|       | S4 (250°C), the sample is mainly amorphous | S4T (500°C) anatase and rutile |
|-------|-------------------------------------------|-------------------------------|
|       | Start BE | Peak BE | End BE | Atomic % | Start BE | Peak BE | End BE | Atomic % |
| C1s   | 298.68   | 284.81 | 279.78 | 16.78    | 298.78   | 284.8   | 279.88 | 15.47    |
| C1s Scan A | 298.68   | 286.13 | 279.78 | 2.33     | 298.78   | 286.33  | 279.88 | 2.11     |
| C1s Scan B | 298.68   | 289.23 | 279.78 | 1.84     | 298.78   | 289.03  | 279.88 | 1.37     |
Figure 3. UV-vis Absorption spectra of commercial anatase TiO$_2$ (S0); C-TiO$_2$ calcinated at 250°C (S4); C-TiO$_2$ calcinated at 400°C (S9) and (S4) re-calcinated at 500°C (S4T).

Binding energies peaks for the carbon electronic state 1s can be found in elemental carbon C-C bonds (C1s) in both samples. The characteristic peak at 284.6eV was in fact mainly attributed to carbon contamination due to the experiment, however the atomic percentage is quite high to be neglected. The decrease of its atomic percentage at higher calcination temperatures could suggest that C-C structures could indeed be present on the surface of the lattice. The C1s dominant peak at 284 eV has a shoulder at higher binding energies, which is attributed to the presence of carbonate species associated to C-O bonds, where the carbon can also be present as interstitial carbon in the new Ti-O-C structure. The question is, are all these C-O species connected to an interstitial presence of carbon in the lattice or we also have species associated to residues of carbon on the surface? The additional XPS C1s scans in this region detect peaks at around 286 eV and 289 eV. These peaks energy shifts if the calcination temperatures change, as shown in Table 1. This means that not only the calcination temperature influences the morphology of the material but also the atomic percentages of carbon in these states (both in C-C and C-O bonds), and more precisely, it decreases. It was previously reported that if carbon is only present as interstitial carbon, the C1s peaks would not change [22], which differs from the findings in this work. It is also interesting that the formation of these carbon species according to previous works cause a long-tailed absorption in the visible light region [24] and this was indeed observed in UV-vis spectra result where the amorphous C-TiO$_2$ sample S4 present a surprisingly high and broad visible light absorption, not only a pronounced UV absorption, as also reported in [24]. The light absorption properties were verified by conducting UV-visible diffuse reflectance absorption spectra analyses. Figure 3 reports the results comparison of C-TiO$_2$ calcinated at 250°C, 400°C and 500°C. A plot of the results in the 400-800nm wavelengths window and a picture of the samples are also presented. The darker color of the sample S9 (C-TiO$_2$-400°C) and S4 (C-TiO$_2$-250°C) is clearly visible. The best light absorption characteristics are presented by sample S9 followed by the amorphous sample S4, which confirms that the presence of carbon species on the surface is an aid to the higher absorption of light in the visible spectrum. A calcination temperature that goes beyond 400°C has instead a negative effect on the final absorption properties of the material which seems to have completely lost its broad visible light absorption ability, results in agreement with other works [23].

6. Discussion and Conclusions
In the sol gel synthesis of carbon modified titanium dioxide for visible light photocatalysis the calcination temperature and the carbon content influence the final material light absorption properties. The sol gel method chosen in this work produces TiO$_2$ with an interstitial presence of carbon in the lattice and with carbonaceous species on the surface. The increase of the calcination temperature for
this specific synthesis method leads to the appearance of a rutile phase for a calcination temperature lower than 500°C which decreases considerably the presence of residual carbon on the surface. The combination of these two synthesis variables affects the light absorption properties of the material. High photocatalytic activity is associated with a calcination temperature of 400°C. Lower calcination temperatures show an interesting widening of the absorption spectra even if the material is amorphous. In this case, the shift of the absorption ability to visible light can be attributed to the presence of carbon on the surface. Although further analyses could lead to better characterization of these carbon species, we can certainly confirm that they have an important role in the photo-oxidation ability of the material as reported also in the literature. To conclude, the light absorption properties of carbon doped Titania is highly influenced by the chosen sol gel method, which should carefully consider the combination of doping and calcination temperatures.

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