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Effect of Calcination Temperature in The Synthesis of Carbon Doped TiO₂ Without External Carbon Source

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Abstract. Carbon doped TiO₂ have been successfully synthesized in this study using sol-gel method and followed by carbonization in hypoxic condition. Titanium (IV) isopropoxide and isopropanol were used as starting material without addition of external carbon precursor. The carbon doped TiO₂ were synthesized with different calcination temperature at 200, 300, 400 and 500°C under hypoxic condition. The physical properties of carbon doped TiO₂ were characterized by Fourier Transformation Infrared Spectroscopy (FTIR), X-Ray Diffraction (XRD) and Diffuse reflectance UV-Vis Spectroscopy (DRUVS). The synthesized material shows carbon related peak at 1540 and 1400 cm⁻¹ that can be ascribed as carboxylic (COO⁻) and carbonyl (CO₃²⁻) vibration respectively from FTIR spectra. Based on XRD result, it can be inferred that TiO₂ with anatase phase were initially formed at calcination temperature 200°C showed by amorphous phase with single peak at 25,30° and crystal growth along with increasement of temperature. Rutile phase as impurities was formed at calcination temperature 500°C. The DRUVS result shows significant red shift in spectra that indicate decrease bandgap of synthesized carbon doped TiO₂ compared to conventional anatase TiO₂. The carbon doped TiO₂ in this study show ability to absorb at visible light radiation as suggested by DRUVS spectra. It is hoped that our work could be applied as visible light photocatalyst in industrial and environmental application and provided valuable information in synthesis of non-metal doped TiO₂.

Keyword : Carbon doped, Sol-gel method, TiO₂, Visible light

1. INTRODUCTION

Titanium dioxide (TiO₂) has been extensively studied the field of catalyst and environment due to its attractive optical and electronic properties, chemical stability, inexpensiveness and non-toxicity (1) (2). Much work has already done with increasing and expanding utility of TiO₂ in catalyst and environmental application such as water splitting, water purification, air cleaning, self-cleaning coating, anti-corrosion coating, solar cell, sensor and batteries (3). However, due to interistic properties, such as wide band-gap (3,2 eV) and fast recombination rate of photo-generated electron-hole pair, limiting the activity of TiO₂ only on ultraviolet (UV) light region and hardly decrease its effectivity. Hence, many effort has been carried out in order to extend the utilization of TiO₂ into visible light region and enhance its photoactivity (4) (5).

On of the promising strategies to solve this problem was modified by surface anchoring of organic dyes molecule, and incorporation of either noble metal, transition metal or non-metal doping on structure of TiO₂ (6). Among of them, modification of TiO₂ with non-metal doping (such as F, N, C, etc) has been proven to be effective strategies for extending the photoactivity of TiO₂ from UV light region into visible light region (7).

Carbon as non-metal doping has been studied because the optical and electrical properties of carbon. Doping of TiO₂ using carbon has many advantage that carbon act as electron acceptor of the photo-generated electrons, reduce the electron-hole pair recombination rate and carbon has wide absorption range from 400-800 nm that facilitate charge transfer from bulk into surface of TiO₂ (5). Unique oxidation state that can form +4 (as cation) and -4 (as anion) causing carbon can form Ti-C (Carbide) bond via substitution of oxygen site (C_{S-O}) or form C-O (carbonate) bond via substitution of titanium site (C_{S-Ti}) in TiO₂ lattice. Formation of those bond in lattice lead to narrowing band gap of TiO₂ or creating localized mid-gap state between forbidden energy level (8).

In this study, we reported synthesis of carbon doped TiO₂ through sol-gel method without addition external carbon source. Carbon on titanium precursor were used as carbon source for synthesis with suitable calcination temperature in hypoxic condition for obtaining a degree of carbon as doping on TiO₂. Non-hydrolytic sol-gel method was used in this study because its low-cost, versatility, environmental-friendly and more homogenous crystal size and distribution of materials. The composite photocatalysts were systematically characterized using X-ray diffractometer (XRD), Fourier Transformation Infrared Spectroscopy (FTIR) and Diffuse Reflectance UV-visible Spectroscopy (DRUVS) to evaluate the effect of temperature and C atom on structural and optical properties of Carbon doped TiO₂.

2. EXPERIMENTAL

2.1. Materials

Carbon doped TiO₂ were prepared using Titanium(IV)Isopropoxide (97%, Sigma-Aldrich) and 2-propanol (99%, Merck) without further purification. Aqua DI were collected from Millipore Milli-Q system used within one week. TiO₂ (80%, Evonik) were used as reference materials.

2.2. Synthesis

The synthesis procedure of this work follow the previous literature as described elsewhere (9). The typical preparation of Carbon doped TiO₂ was as follows: 5 mL of Titanium(IV) Isopropoxide were dissolved in 10 mL of 2-propanol. The solution then vigorously stirred until solution turn into white colloidal. The solution then transferred into petridish and left in room temperature overnight for drying process. The dried powder then transferred into quartz boat crucible and calcined for 3 hours under nitrogen flow. The calcination temperature were varied from 200 to 500°C. The resulted sample were named as CT-X with X indicating calcination temperature.

2.3. Characterization

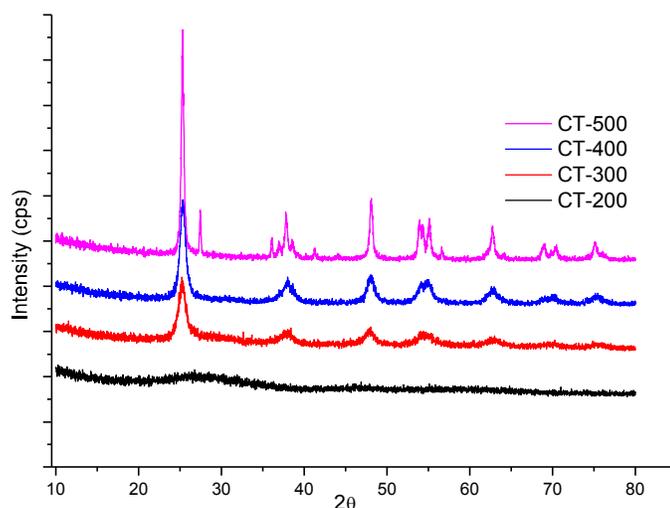
X-ray diffractometer (PANalytical, USA) was used to analyze phase and crystallinity of the materials. Cu-K α irradiation was used at 2θ 10-80° with scan step of 0,017° under 40 kV accelerating voltage and 20 mA of applied current. The FTIR spectra of material were measured using Spectrometer FTIR-8400S (Shimadzu, Japan) with KBr pellet method to identify the functional group. The spectra of materials were measured from wave number 4000-400 cm⁻¹. Diffuse Reflectance UV-Visible Spectroscopy (DRUVS) were recorded on Lambda-35 Spectrophotometer (Perkin-Elmer, USA) with an integrating sphere to analyze light absorption ability and energy band gap of materials. The spectra of material were measured in the wavelength range 200–800 nm.

3. RESULTS AND DISCUSSIONS

3.1. X-Ray Diffraction Analysis

X-Ray Diffraction (XRD) analysis were carried out to investigate the change of carbon doped TiO₂ phase with different calcination temperature. **FIGURE 1** show the diffractogram of carbon doped TiO₂ with different calcination temperature from 200 to 500°C. Based on those results, sample with calcination temperature 200°C for 3 hours only show one broad peak with no specific pattern on 2θ : 26,79° that indicate material were still in amorphous phase. This indicate that low temperature calcination with hypoxic condition (N₂ flow) was not enough

to transform titanium precursor (titanium isopropoxide) into TiO₂ crystal (10). Hence, resulting amorphous phase that



come from precursor rather than crystalline phase of TiO₂.

FIGURE 1. Diffractogram of carbon doped TiO₂ with calcination temperature 200, 300, 400 and 500°C.

On other hand, the materials that synthesized with 300, 400 and 500°C for 3 hours under N₂ flow shows specific peak pattern that perfectly indexed as anatase phase of TiO₂ [JCPDS no. 21-1272]. However, intensity of sample are greatly affected with calcination temperature, materials with calcination temperature 300°C has the lowest crystallinity and sample with calcination temperature 500°C has the highest crystallinity compared to the other. This results indicate that calcination temperature can affect crystallinity, when increasing the calcination temperature can also increase the relative crystallinity of product (10) (11).

What surprising is that the sample with calcination temperature 500°C has distinct peak pattern from anatase pattern that can be ascribed from rutile phase. This phenomenon are not observed under air flow since anatase to rutile transformation only occur when calcination temperature above 800°C. This can be explained that calcination under hypoxic condition can form larger crystal size that accelerate transformation of anatase phase to rutile phase rather than in oxygenated condition (10).

3.2. FTIR Analysis

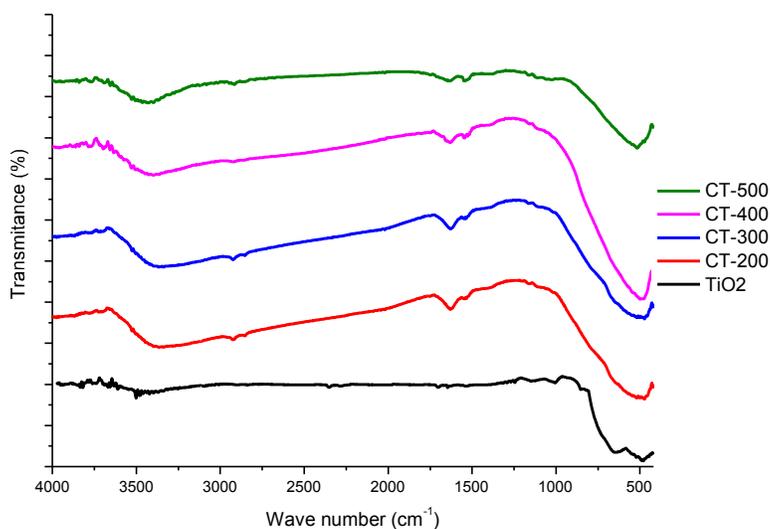


FIGURE 2. FTIR Spectra of commercial TiO₂ and carbon doped TiO₂ with calcination temperature 200, 300, 400 and 500°C.

FTIR analysis were carried out to determine the functional group in resulted materials under different calcination temperature. FTIR spectra also employed to identify carbon species in TiO_2 lattice.

Spectra of synthesized materials can be seen at **FIGURE 2**. Broad peak at wave number $3500\text{-}3000\text{ cm}^{-1}$ and 1645 cm^{-1} can be assigned as vibration of hydroxyl group (-OH) from surface hydroxyl group and absorbed water. The presence of hydroxyl groups play important role on inhibition of the recombination of photogeneration of electrons and holes. The broad band in the range of $400\text{-}800\text{ cm}^{-1}$ is attributed to the stretching of the Ti-O and Ti-O-Ti group, this broad band is shown in all synthesized carbon-doped titanium dioxide (12).

The prepared sample with variation of calcination temperature shows different peak from standard TiO_2 . On all sample, weak peak at 2900 and 2800 cm^{-1} belong to asymmetric and symmetric vibration of -CH group that arise from incomplete combustion (unburned) organic materials. The bands of 1540 and 1440 cm^{-1} are indexed to be carbon related group stretching vibrations of the carboxylic group (COO^-) and carbonate (CO_3^{2-}) species, respectively (11). Hence, in this synthesis, carbon atom are embedded in TiO_2 lattice in cationic form that substituting of titanium site ($\text{C}_{\text{S-Ti}}$) in TiO_6 complex and forming C-O bond with its neighboring oxygen atom.

3.3. DRUVS Analysis

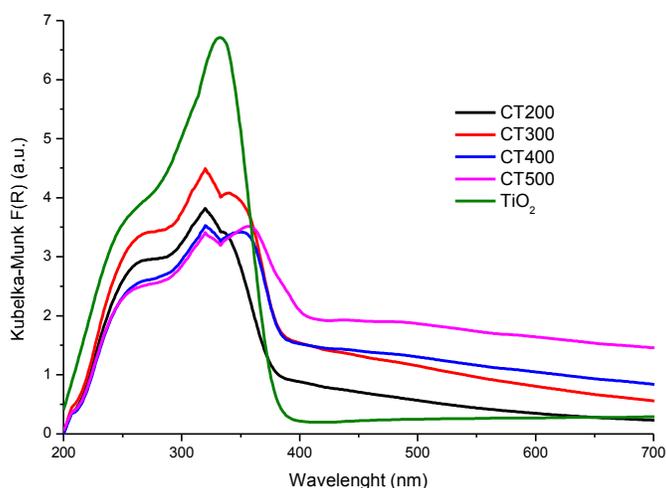


FIGURE 3. Kubelka-Munk Plot of commercial TiO_2 and synthesized carbon doped TiO_2 with different calcination temperature

DRUVS analysis were carried out to determine optical properties of commercial TiO_2 and synthesized carbon doped TiO_2 with different calcination temperature. The Kubelka-Munk plots of corresponding materials are illustrated in **FIGURE 3**.

Based on the Kubelka-Munk plot, it clearly show that the Carbon doped TiO_2 prepared exhibit a significant shift of the absorption edge of where carbon doped TiO_2 with calcination temperature 200 , 300 , 400 and 500°C has absorption edge at 390 , 400 , 410 and 450 nm in which the absorption are slightly shifted towards the visible region as compared to the commercial TiO_2 on 385 nm . This phenomenon is called red shift in which the absorption edge is at higher wavelength then reference material. It can be suggested that the Carbon doped TiO_2 with higher calcination temperature up 500°C exhibit a significant absorption at higher wavelength.

Particularly, the long tail up to about 700 nm in the DRUVS spectra for all synthesized materials was clearly observed. Many researchers suggested that a band tailing extension might be resulted from coke formation on surface of TiO_2 , or inclusion of the carbonaceous species as photosensitizer on TiO_2 bulk and surface, while others argued that a long tail was probably caused by the lattice defects, such as oxygen vacancies (13). Although there is still many argument for role of carbon as dopant in TiO_2 lattice, but the band tail extension can further confirming photo-absorption and photo-activity of carbon doped TiO_2 in visible light region.

4. CONCLUSION

In this research, carbon doped TiO_2 have been successfully synthesized by non-hydrolytic sol gel method without external carbon source addition. The synthesized carbon doped TiO_2 then characterized by XRD, FTIR and DRUVS.

The results show that controlled calcination in hypoxic condition can effectively inhibiting oxidation and gasification process of carbon in organic matter and playing role in inclusion of carbon atom in TiO₂ lattice. The synthesized material shows carbon related peak at 1540 and 1400 cm⁻¹ that can be ascribed as carboxylic (COO⁻) and carbonyl (CO₃²⁻) vibration respectively from FTIR spectra. The carbon species embedded in TiO₂ lattice with forming C-O bond with its neighboring oxygen atom that resulting in surface and bulk carbonaceous group. Based on XRD result, it can be inferred calcination temperature influences formation of crystal phase and the degree of crystallinity, which pure anatase phase was observed with calcination temperature under 500°C and readily converted to Rutile phase with calcination temperature above 500°C. The DRUVS result shows that carbon related species in TiO₂ lattice can cause red shift in absorption edge that indicate decrease band gap of synthesized carbon doped TiO₂ from conventional anatase TiO₂. The formation of carbon related carbonate species or coke-like structure on surface of TiO₂ could cause a long-tail absorption in the visible-light region, which took role on photoactivity in visible light region. Thus, carbon doped TiO₂ is an effective photocatalyst that is responsive to visible light and can be used for future industrial and environmental application.

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