

Effect of C Content and Calcination Temperatures on the Characteristics of C-doped TiO₂ Photocatalyst

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ABSTRACT

In this work, glucose was applied as C source, the ratio of glucose to TBT was 0.02 to 3.00. The range of calcination temperatures is from 400°C to 600°C. XRD pattern shows that anatase phase is dominant. Anatase decreases with increasing in glucose/TBT ratio under the same calcination temperature. Band gap was narrowed down from 3.2 to 2.9 eV. Base on the identification of soft X-ray, results of C K edge absorption spectrum revealed that photon energy at 282.9 eV assigned to Ti-C structure. Result shows that oxygen sites were substituted by carbon atoms and C-Ti-O formed.

Keywords: C-doped TiO₂, C Content, Calcination Temperatures, Vis-responsible photocatalyst

1 INTRODUCTION

Photocatalytic process of TiO₂ is novel technology for gas sensors [1], pigment [2], solar-energy conversion [3]. Nevertheless, pure TiO₂ only adsorbs UV light which is less than 5 % in the solar light spectrum because of its wide band gap of 3.2 or 3.0 eV in anatase or rutile crystalline phase, respectively. In order to utilize wider range of solar energy, studies had an attention on modifying the characteristics of TiO₂ by doping with nonmetal atoms such as N [4, 5], C [6-9] or transition metals such as Cr [10], and Fe [11]. However, the photoactivity of doping with transition metals is poor due to the thermal instability, or the growth of carrier trapping [12]. Therefore, doping TiO₂ with non-metal elements has received much attention.

Janus et al. (2006) improved the photoactivity by doping TiO₂ with C due to reduction of the recombination rate of photogenerated electron-hole pairs by the electron scavenger, C, doped into TiO₂ structure. Beside, C-doped TiO₂ was capable of lowering the band gap, shifting the optical response to the visible light region and decreasing the recombination rate of photogenerated electron-hole pairs [7].

In this study, we had focused on the sol gel synthesis of C-doped TiO₂ at various reaction temperatures. All samples were characterized using XRD, and UV-Vis. Eventually, soft X-ray spectroscopy were used to demonstrate the electronic structure of C-doped TiO₂.

2 EXPERIMENT

In this work, the characteristics of C-doped TiO₂ at various C contents and calcination temperatures were studied. The molar ratio of glucose to TBT was 0.02 to 3.0. Samples were calcinated from 400 to 600°C. C-doped TiO₂ was prepared by sol-gel method. Chemicals include 0.05 mole of titanium n-butoxide (TBT), glucose and ethanol. TBT is the catalyst precursor while glucose is the carbon source. C-doped TiO₂ powder was obtained after drying. The desired calcination temperatures was in the range from 400 to 600°C. The molar ratio of glucose to TBT is from 0.02 to 3.0.

The crystalline structure of prepared C-doped TiO₂ photocatalyst was indentified using X-ray diffraction with Cu-K radiation at a scan rate of 0.05° s⁻¹ (PANalytical X'Pert Pro MRD, USA). Soft x-ray absorption spectroscopy was used to identify the electronic and crystal structure. Ti L edge (2p), O K edge (1s), and C K edge (1s) were investigated. The experiments were performed at National Synchrotron Radiation Research Center (NSRRC) in Taiwan.

3 RESULTS

3.1 Effect of Calcination Temperature

Samples calcinated at 400, 500, and 600°C were investigated. The effect of calcination temperature on the structure and optical properties of C-doped TiO₂ was listed at the Table 1. Based on the results of XRD analysis, it is seen that anatase content decreases while the calcination temperature increases from 400 to 600°C. Anatase content was about 83 ~ 100 % at 400°C. However, it drops to 30 ~ 73 % as the calcination temperature rises to 600°C.

Particle size was investigated via XRD and DLS analysis. Based on XRD, anatase which is more active phase than rutile was the dominant component for samples from 400 to 600°C. Nevertheless, the phase transformation from anatase to rutile took place at 600°C. Based on the Scherrer equation, the results showed that particle size increases as the reaction temperature increases due to the vapor molecule accumulation and the development of rutile phase which has larger particle size than anatase. Crystal size was in the range from 9 to 38 nm while size was 175 ~

954 nm by DLS analysis. The difference was due to the aggregation of prepared particles during the process of DLS measurement. Result suggests that size grows as calcination temperature increases.

Table 1. Effect of Calcination temperatures

Sample	Calcination Temp. (°C)	Phase composition A % / B %	C content (%)	Size (nm)		Band gap (eV)
				XRD	DLS	
P25	-	81 / 19	-	22	-	3.20
G002T4	400	100 / 0	0.1	16	740	3.13
G002T5	500	100 / 0	0.2	20	463	2.97
G002T6	600	73 / 27	0.2	38	560	2.94
G02T4	400	100 / 0	0.2	13	669	2.95
G02T5	500	86 / 14	0.3	19	514	2.94
G02T6	600	61 / 39	0.2	34	502	2.94
G05T4	400	87 / 13	0.1	12	954	2.95
G05T5	500	81 / 19	0.2	20	318	2.92
G05T6	600	47 / 53	0.2	34	260	2.94
G10T4	400	100 / 0	0.5	10	397	2.94
G10T5	500	78 / 22	0.3	16	197	2.96
G10T6	600	47 / 53	0.2	27	175	2.94
G20T4	400	83 / 17	0.3	9	228	2.96
G20T5	500	74 / 26	0.2	17	162	2.99
G20T6	600	30 / 70	0.2	28	191	2.93
G30T4	400	84 / 16	0.3	9	221	3.03
G30T5	500	39 / 69	0.1	31	185	2.93
G30T6	600	76 / 24	0.4	19	164	2.97

3.2 Effect of Carbon Content

The effect of carbon content on the characteristics of C-doped TiO₂ was summarized in Table 2. Samples were synthesized at various amounts of glucose. Based on results of XRD analysis, two phases including anatase and rutile were dominant for C-doped TiO₂ samples. The anatase content decreases with increase in the molar ratio of glucose to TBT precursor under the same calcination temperature. In the other words, the rutile phase shows gradually as the amount of glucose increases. With respect to particle size, insignificant influence was observed by the molar ratio of glucose to TBT under the same calcination temperature.

The band gap narrows from 3.20 to 2.92 eV. Band gap of samples calcinated at 600⁰ C was smallest among all samples calcinated at 400 and 500⁰ C. Substitutional carbon atoms introduce new states (C 2p) close to the valence band edge of TiO₂ (i.e. O 2p states). As a result the valence band edge shifts to higher energy compared with the reference TiO₂ and the band gap narrows. The energy shift of the valence band depends on the overlap of carbon states and O 2p states. A higher doping concentration of carbon results in higher energy shift due to significant overlap of carbon and oxygen states and this leads to narrower band gap in the compound [13]. Band gap of G05T5 is 2.92 eV which is the smallest.

Table 1. Effect of C content

Sample name	Calcination Temp. (°C)	Phase composition A % / B %	C content (%)	Size (nm)		Band gap (eV)
				XRD	DLS	
P25	-	81 / 19	-	22	-	3.20
G002T4	400	100 / 0	0.1	16	740	3.13
G02T4		100 / 0	0.2	13	669	2.95
G05T4		87 / 13	0.1	12	954	2.95
G10T4		100 / 0	0.5	10	397	2.94
G20T4		83 / 17	0.3	9	228	2.96
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G02T6		61 / 39	0.2	34	502	2.94
G05T6		47 / 53	0.2	34	260	2.94
G10T6		47 / 53	0.2	27	175	2.94
G20T6		30 / 70	0.2	28	191	2.93
G30T6		39 / 69	0.1	31	185	2.93

G:GTY. X means the molar ratio of glucose to TBT. Y means the calcination temperature.

3.3 X-ray absorption

C K edge absorption spectra are showed in Figure 1. The C 1s spectrum revealed two components at 285.9 and 288.8 eV. The smaller component at photon energy of 285.9 eV could be attributed to C 1s electrons. Ren et al. (2007) observed only one kind of carbonate species with binding energies of 288.6 eV and revealed that carbon may substitute for some of the lattice titanium atoms and form a Ti - O - C structure [14]. The results indicated that the C 1s XPS peak (288.8 eV) could be assigned to Ti-O-C structure in carbon-doped TiO₂ by substituting some of the lattice titanium atoms by carbon.

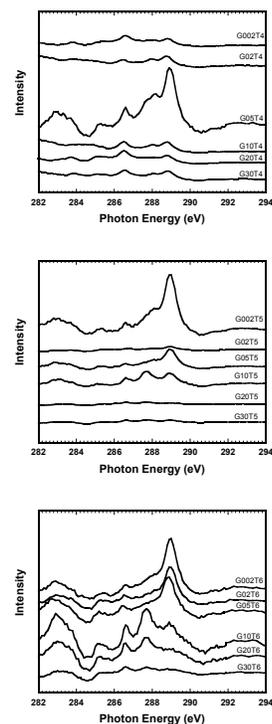


Figure 1. X-ray absorption spectra of the C K edge

4 CONCLUSION

1. The rutile content increases as the temperature rises up. The phase transformation temperature is 600⁰ C.
2. Band gap narrows because the substitutional carbon atoms that introduce new states (C2p) close to the valence band edge of TiO₂ (i.e. O2p states).
3. Carbon may substitute for some of the lattice titanium atoms and form a Ti - O - C structure.

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