Evaluation of Highly Functional TiO$_2$ Synthesized by Solution Precursor Spraying in a DC-RF Hybrid Plasma Flow System

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Abstract. Carbon doped TiO$_2$ synthesized in a DC-RF hybrid plasma flow system by the solution precursor spraying method was evaluated. The effects of mass fraction of TTB in solution precursor on contents and photocatalytic activity of carbon doped TiO$_2$ were investigated. Highly functional carbon doped TiO$_2$ at 11 wt% TTB had higher UV-visible absorption characteristics, which showed higher degradation rate of methylene blue solution under visible light irradiation.

1. Introduction
Titanium dioxide (TiO$_2$) is an attractive material for environmental purification commercially used because of its environmentally friendly photocatalytic activity. However, the main drawback of typical undoped TiO$_2$ is low photocatalytic activity activated only under UV light irradiation. Many works have been focused on the preparation of more functional TiO$_2$ doping with metal and non-metal atoms in order to improve photocatalytic activity in UV and visible light irradiation [1-3]. Among distinct papers published within a decade, D. Chen et al prepared highly functional TiO$_2$ doping with carbon element using a sol-gel process [1]. Its higher photocatalytic activity was shown by degradation of methylene blue solution only under visible light irradiation, compared with undoped and nitrogen doped TiO$_2$[1,4]. However, this sol-gel process requires long processing time and needs further toxic chemicals as catalysts. To overcome these difficulties found in the sol-gel process, a solution or suspension plasma spray method was proposed [5-7].

In previous studies, a DC-RF hybrid plasma flow system was optimized for high performance of the alumina spheroidization process even under a small electric power by thermofluid flow controls to increase plasma enthalpy and heat exchange rate [8-11]. Among these studies, water droplet injection into downstream argon plasma flow in the DC-RF hybrid plasma flow system increased effectively plasma enthalpy. Injected droplets are rapidly vaporized and the vapor is transferred along the chamber wall to upstream argon plasma flow by characteristic backflows, which are occurred from the chamber wall to the vicinity of RF coils. The alumina spheroidization rate is increased without increase in a electric power by higher plasma enthalpy induced by mixing with produced hydrogen and argon plasma flow. Hence, a DC-RF hybrid plasma flow system under a small electric power is feasible to synthesize nano-particles with coupling solution precursor spraying and characteristic backflow transportation.
In this study, highly functional TiO$_2$ can be synthesized in a DC-RF hybrid plasma flow system by coupling a solution precursor spraying and characteristic backflow transportation. After vaporization of injected droplets of solution precursor in downstream plasma flow, small particles are transferred to upstream plasma flow by the characteristic backflows near the chamber wall. Then, highly functional carbon doped TiO$_2$ is produced by prolonging the interaction time with plasma flow. Mixing effects of carbon and TiO$_2$ are discussed by using the X-ray diffraction patterns, Raman spectra, and UV-visible absorption spectra. Furthermore, an effect of carbon doped TiO$_2$ on the methylene blue degradation under visible light irradiation is investigated.

2. Experimental setup

2.1. DC-RF hybrid plasma flow system
Figure 1 shows a schematic of DC-RF hybrid plasma flow system with a two-phase atomizer in order to inject droplets of solution precursor into downstream plasma flow. The operating pressure of 33 kPa was kept during the operation. DC power of 1.1 kW and RF power of 6.6 kW (4 MHz) were supplied at constant. The working gas was argon. The flow rates of DC plasma forming gas and swirling sheath gas were 5 and 20 S/$\text{min}$, respectively. A gas-liquid atomizer (YS-03, Yaezaki, Japan) was installed at $r = 95$ mm and $z = 195$ mm. Atomizing gas was kept at 6 S/$\text{min}$ to achieve sufficient atomization. The average gas temperature was $1038.6 \pm 4.8$ °C at $r = 0$ mm and $z = 195$ mm without injections of solution precursor and atomizing gas. Further details of this system are obtained in Refs. 8-11.

2.2. Preparation of solution precursor and undoped TiO$_2$ powders
A solution precursor was prepared to be mixed with titanium tetrabutoxide (TTB, Wako Pure Chemicals Industries, Ltd.) and ethanol (Wako Pure Chemicals Industries, Ltd.). TTB is easily dissolved in ethanol, so that the solution precursor is easily atomized as smaller size of droplets. For complete dispersion the solution precursor was stirred for ten minutes by a magnetic stirrer before implementation of experiments. The solution precursor was sprayed at a mass flow rate of 1.6 g/min on average by the atomizer. The mass fractions of TTB were 11 and 24 %, respectively. Undoped TiO$_2$ powders of anatase and rutile (Wako Pure Chemicals Industries, Ltd.) were used for comparison of physicochemical characteristics with carbon doped TiO$_2$.

![Figure 1. Schematic of DC-RF hybrid plasma flow system with a two-phase atomizer in order to inject droplets of solution precursor into downstream plasma flow.](image-url)
2.3. Analysis of carbon doped TiO$_2$

Carbon doped TiO$_2$ powders were collected at the chamber wall of $z = 200$ mm to 400 mm. The production rates of carbon doped TiO$_2$ powders were 0.4 and 0.56 g/h at 11 and 24 wt%, respectively. After annealing at 300 °C to remove all contaminants, analyses of the powders were carried out. However, a part of powders was additionally annealed at 500 °C for the further accurate analysis of X-ray diffraction (XRD; RINT-V, Rigaku Co., Japan) patterns. The morphological analysis was carried out by a transmission electron microscopy (TEM; HF-2000, Hitachi Co., Japan). Successful incorporation of carbon in TiO$_2$ was analyzed by a Raman spectrometer (NRS-5100, JASCO Co., Japan) at the laser excitation of 532 nm. The UV-visible absorption characteristic was measured by an UV-visible spectrometer (V-7200, JASCO Co., Japan). Additionally, highly functional carbon doped TiO$_2$ for photocatalytic activity was assessed by degradation of methylene blue solution under visible light irradiation.

3. Experimental results and discussion

3.1. Mechanism of carbon doped TiO$_2$ synthesis by solution precursor spraying

Figure 2 shows optical spectra with and without solution precursor injection measured at $z = 70$ mm. A sauter mean size of solution precursor droplets is estimated to be 48 μm from the model proposed by A. Aliseda et al., which shows a good agreement for a liquid mixture [12]. The characteristic time of droplet vaporization is also estimated to be 45 and 16 ms at the temperatures of 1000 and 1500 K. When injecting the solution precursor into downstream plasma flow at $z = 195$ mm, droplets of the solution precursor are completely vaporized before arriving at the chamber wall, because the maximum power for complete vaporization is estimated to be 0.024 kW. The vapor is transported to upstream plasma flow in the DC-RF hybrid torch by characteristic backflows [11] and successfully dissociated into titanium and carbon in the plasma flow, as shown in Fig. 2. Synthesis of carbon doped TiO$_2$ is favored under high concentration of carbon and low concentration of oxygen [13]. Excited carbon is clearly observed at wavelengths of 193 and 247 nm. Excited titanium is also observed at wavelengths of 368 and 373-376 nm. Furthermore, the presence of OH band at wavelengths of 306-309 nm indicates the presence of species of oxygen and hydrogen in the plasma flow, because OH band is produced by the chemical reaction with oxygen and hydrogen. However, the amount of
oxygen for the chemical bond with titanium can be decreased to form different chemical species such as OH, H$_2$O, and CO$_x$. Then, oxygen vacancy in TiO$_2$ structure is occurred and carbon is substituted in oxygen vacancy under high concentration of carbon [4,13].

### 3.2. Analysis of XRD pattern

Figure 3 shows XRD patterns of carbon doped TiO$_2$ powders. The results of the contents and the average crystallite size are tabulated in Table 1. The XRD patterns indicate that crystal structure of carbon doped TiO$_2$ is mixed with anatase and rutile, because the phase transformation of quasi-stable anatase phase is preferred in the thermal plasma flow [14]. The contents of anatase and carbon in carbon doped TiO$_2$ at 11 wt% TTB have 1.66 and 1.21 times larger than that of carbon doped TiO$_2$ at 24 wt% TTB, respectively. The average crystallite size ($L$) is estimated by the Scherrer formula [14]:

$$ L = \frac{K \cdot \lambda}{B \cdot \cos \theta} \quad (1) $$

where $K$ denotes the shape factor of 0.89, $\lambda$ is the wavelength of X-ray (Cu K$\alpha$), $B$ is the full width half maximum, and $\theta$ is the Bragg angle. The crystallite sizes of both phases are similarly estimated in both powders. From the result of the XRD analysis, it is found out that the mass fraction of TTB in solution precursor plays a dominant role for the contents of anatase and carbon in carbon doped TiO$_2$.

### 3.3. Morphological characteristics

Figures 4 (a) and (b) show TEM micrographs of carbon doped TiO$_2$ at 11 and 24 wt% TTB. The crystalline carbon doped TiO$_2$ and amorphous activated carbon are observed. The crystalline size of carbon doped TiO$_2$ is mainly several ten nm in both Figs. 4 (a) and (b), which shows a good agreement with the average crystallite sizes in Table 1. However, the average particle sizes of carbon doped TiO$_2$ are $123.2 \pm 40$ and $104.2 \pm 36$ nm at 11 and 24 wt% TTB, respectively, which are measured by a particle size analyzer (UPA EX250, Microtrac Inc.). It can be explained that nano-crystalline TiO$_2$

### Table 1. Contents and crystallite size of carbon doped TiO$_2$ powders

| Mass fraction of TTB | Contents (%) | Crystallite size (nm) |
|----------------------|-------------|-----------------------|
|                      | Anatase | Rutile | Carbon | Anatase (101) | Rutile (110) |
| 11 wt%               | 25.9    | 20.3   | 53.8   | 11.0          | 19.3         |
| 24 wt%               | 15.6    | 40.0   | 44.4   | 13.6          | 15.2         |

![XRD pattern](image)

**Figure 3.** XRD patterns of carbon doped TiO$_2$ powders.
particles are preferred to be agglomerated in plasma flow, as shown in Fig. 4. In Fig. 4 (a), carbon doped TiO$_2$ with a lattice spacing of 0.35 nm crystallized in anatase TiO$_2$ is observed. In Fig. 4 (b), carbon doped TiO$_2$ with a lattice spacing of 0.32 nm crystallized in rutile TiO$_2$ is observed.

3.4. Raman spectrum analysis

Figures 5 (a) and (b) show Raman spectra for comparison of carbon doped TiO$_2$ with undoped TiO$_2$. In Fig. 5 (a), undoped anatase TiO$_2$ shows three Raman peaks with high intensities at 379.2, 504.2, and 626.2 cm$^{-1}$. On the other hand, the Raman spectrum of carbon doped TiO$_2$ at 11 wt% TTB is observed for shifted three Raman peaks of anatase TiO$_2$ for 386.5, 506.5, and 630.5 cm$^{-1}$ and three Raman peaks of graphite at 1351.5, 1597.5, and 2668.2 cm$^{-1}$. From this result, carbon doped TiO$_2$ at 11 wt% TTB is inferred to mainly form anatase TiO$_2$ and small shifts of Raman peaks are caused by rutile presence and carbon incorporation. In Fig. 5 (b), undoped rutile TiO$_2$ shows two Raman peaks with high intensities at 436.2 and 600.2 cm$^{-1}$. On the other hand, the Raman spectrum of carbon doped TiO$_2$ at 24 wt% TTB is observed for shifted two Raman peaks of rutile TiO$_2$ at 398.3 and 586.3 cm$^{-1}$ and three Raman peaks of graphite at 1327.2, 1567.3, and 2672.3 cm$^{-1}$. Carbon doped TiO$_2$ at 24 wt% TTB is inferred to form mainly rutile TiO$_2$ and large shifts of Raman peaks are caused by anatase presence and carbon incorporation [15].

Figure 4. TEM micrographs of carbon doped TiO$_2$ at (a) 11 and (b) 24 wt% TTB.

Figure 5. Raman spectra for comparison of carbon doped TiO$_2$ at (a) 11 and (b) 24 wt% TTB with undoped TiO$_2$. 
3.5. UV-visible absorption characteristics
Figure 6 shows the effect of carbon doped TiO$_2$ on UV-visible absorption. Compared with undoped anatase TiO$_2$, carbon doped TiO$_2$ at 24 wt% TTB, in spite of being carbon and a larger content of rutile, slightly increases in UV-visible absorption by a cut-off wavelength of around 380 nm [16]. On the other hand, carbon doped TiO$_2$ at 11 wt% TTB shows higher UV-visible absorption by a cut-off wavelength of around 630 nm. It can be explained by that larger contents of carbon and carbon incorporation with TiO$_2$ increase UV-visible absorption more [17]. Then, UV-visible absorption of carbon doped TiO$_2$ is sensitively dependent on the contents of carbon doped TiO$_2$.

3.6. Degradation of methylene blue solution
Figure 7 shows the effect of carbon doped TiO$_2$ on degradation of methylene blue solution under visible light irradiation using a light-emitting diode (LED) of 0.6 W. Methylene blue solution with 0.3 mg/L is degraded by the reactive oxygen radicals produced by photocatalytic activity of TiO$_2$ under visible light irradiation. Carbon doped TiO$_2$ at 11 wt% TTB completely degrades the methylene blue solution even under visible light irradiation due to increase in visible light absorption, as shown in Fig. 6. However, degradation of carbon doped TiO$_2$ at 24 wt% TTB remains to be 35 %. Photocatalytic

![Figure 6. Effect of carbon doped TiO$_2$ on UV-visible absorption.](image)

![Figure 7. Effect of carbon doped TiO$_2$ on degradation of methylene blue solution under visible light irradiation.](image)
activity of undoped anatase TiO$_2$ shows the worst degradation of methylene blue solution under visible light irradiation due to low visible light absorption, as shown in Fig. 6. Therefore, highly functional carbon doped TiO$_2$ at 11 wt% TTB improves degradation rate of methylene blue solution even under visible light irradiation due to larger contents of anatase TiO$_2$ and carbon.

4. Conclusions
In the present paper, highly functional carbon doped TiO$_2$ powders were successfully synthesized by solution precursor spraying in a DC-RF hybrid plasma flow system. The results are summarized as follows;

(1) Solution precursor droplets are vaporized and dissociated sufficiently in the upstream plasma flow by the backflow transportation. This is verified from the presence of titanium and carbon by the optical emission spectroscopy.

(2) The contents of carbon doped TiO$_2$ are dependent on the mass fraction of TTB in the solution precursor. Larger contents of anatase TiO$_2$ and carbon are obtained at 11 wt% TTB than at 24 wt% TTB.

(3) Highly functional carbon doped TiO$_2$ at 11 wt% TTB is validated from higher degradation of methylene blue solution that of carbon doped TiO$_2$ at 24 wt% TTB even under visible light irradiation.

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