Journal of Sustainable Energy & Environment 2 (2011) 27-29

Optical Studies of the Microwave-Treated TiO_2 Photocatalyst by MIR-FEL

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Absract: Recently, several strategies to produce the visible-light-active TiO_2 by doping of TiO_2 with transition metal and nonmetal dopants such as C, N and S were proposed. Among them, carbon doping was reported to be effective to improve the photocatalytic activity. In this study, we applied a microwave heating to produce the carbon-modified TiO_2 photocatalyst. This technique is very simple and rapidly produces the visible-light-active carbon-modified TiO_2 due to the nature of microwave heating. In addition, we have investigated optical properties of the microwave-treated TiO_2, and proposed a several new approaches to evaluate its optical properties by uses Mid-Infrared Free Electron Laser (MIR-FEL).

1. Introduction

Photocatalyst of titanium dioxide (TiO_2) has been widely applied for environment purification and defogging due to its low-cost, non-toxicity, and high efficiency [1-5]. It is also one of the most promising photoanode materials for splitting of water to produce hydrogen fuel [1-3]. However, due to the wide bandgap of 3.2 eV, its photocatalytic activity is available only under ultraviolet (UV) light at the wavelength of shorter than 400 nm which is a small fraction of total solar spectra on the earth. Therefore, it is necessary to develop the visible-light-active titanium dioxide in order to expand the benefit of sunlight for photocatalytic activity and give rise to its wider practical application for environmental purification.

It has been discovered that elemental substitution of oxygen with nitrogen in TiO_2 enabled to achieve the photcatalytic activity under visible light irradiation [6-7]. At present, the reason for visible light photcatalytic activity is usually considered to be due to the decrease of bandgap, which is attributed to either mixing the nitrogen 2p states with O 2p states or creation of a N-induced mid-gap bands [6-7]. The narrowing of bandgap as well as creation of new mid-gap bands into original bandgap by chemical doping are most promising to develop the visible-light-active photocatalyst.

Recently, several strategies to produce the visible-light-active TiO_2 by doping with transition metal and nonmetal dopants such as C, N and S have been proposed. Among them, carbon doping was reported to be effective to improve the photocatalytic activity [8-9]. In this study, microwave irradiation was applied to produce the carbon-modified TiO_2 photocatalyst [10], and a new approach to evaluate the optical properties caused by their mid-gap bands using a Mid Infrared Free Electron Laser (MIR - FEL) was proposed.

2. Experimental

2.1 Materials

The paste precursor of TiO_2 and ethanol were heated by microwave to obtain the carbon-modified TiO_2. Commercially available TiO_2 powder, Ishihara ST-01 (Ishihara Co., Ltd), and ethanol were used as starting materials. The TiO_2 powder of 100 mg and 0.25 ml of ethanol were mixed, and its paste was placed on the alumina board with graphite susceptor and heated in the commercial microwave oven (2.45 GHz, 600W, multimode) for 3 minutes (referred to as samples (MW3-CM)) and 6 minutes (referred to as samples (MW6-CM)) under atmosphere to obtain the carbon-modified TiO_2 [10].

2.2 Characterization and photocatalytic activities

The UV-Vis diffuse reflectance spectra were obtained with a powder UV-Vis spectrophotometer. X-ray diffraction (XRD) analyses were performed on a powder diffractometer. ATR-FTIR spectra were collected by using FT-IR spectrometer ranged from 1000 to 3000 cm^{-1} in wavelength. The photocatalytic activity was evaluated through the formation of I_3^- in KI aqueous solution. The sample powder of 50 mg was dispersed into 30 ml of aqueous solution with a concentration of 0.2 mol/l in a cylindrical Pyrex vessel. The suspension was mixed with a magnetic stirrer and irradiated by a 300 W xenon lamp with the long-wave-pass edge filter with the cut-off wavelength of 420 nm. The concentration of I_3^- was monitored by UV-Vis spectrophotometer.

3. Results and Discussion

3.1 Material Characterization

The ATR-FTIR spectra of the samples are presented in Fig. 1. The large peak at around 1630 cm^{-1} is attributed to the intrinsically absorbed water on the surface of TiO_2 [8-9]. After 3 min treatment, new absorption bands are created in a region of 1350-1480 cm^{-1}, which are attributed to CO band (1440 cm^{-1}) and $-CH_3$ band (1378 cm^{-1}), respectively [9]. There is also an absorption bands at around 1550-1610 cm^{-1}, which is possibly ascribed to acetate on the surface [9-10]. Within the irradiation time studied, these newly appeared bands are decreased after 6 min microwave treatment probably due to their thermal decomposition. The XRD patterns of untreated TiO_2 (ST01), and carbon-modified TiO_2 of MW3-CM and MW6-CM are shown in Fig. 2. The carbon-modified TiO_2 shows the same XRD pattern and peak width at (101) with untreated TiO_2 (anatase). It is therefore interpreted that an absorbed ethanol on TiO_2 are carbonized during microwave treatment for 3 min and formed some carbonaceous

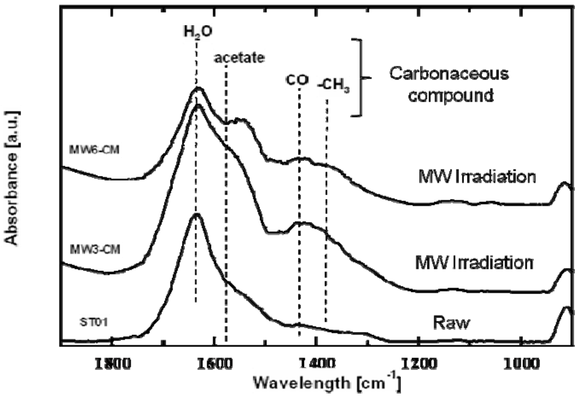

Figure 1. ATR-FTIR spectra of untreated TiO2 (ST01), and microwave treated TiO2 for 3 min (MW3-CM) and 6 min (MW6-CM).

compounds only on the surface of TiO_2 without changing the crystal structure and crystal size of the sample.

Fig. 3 shows UV-Vis absorption coefficients obtained from diffuse reflectance spectra with Kubelka-Munk relation for TiO_2 (ST01), and microwave carbon-modified TiO_2 of MW3-CM and MW6-CM. The pure TiO_2 barely show absorption at the wavelength of 400 nm. On the other hand, the carbon-modified TiO_2 prepared by microwave heating for 3 minutes (MW3-CM) shows a remarkable absorption even at the wavelength of around 800 nm, while MW6-CM mildly shows at the wavelength up to 600 nm.

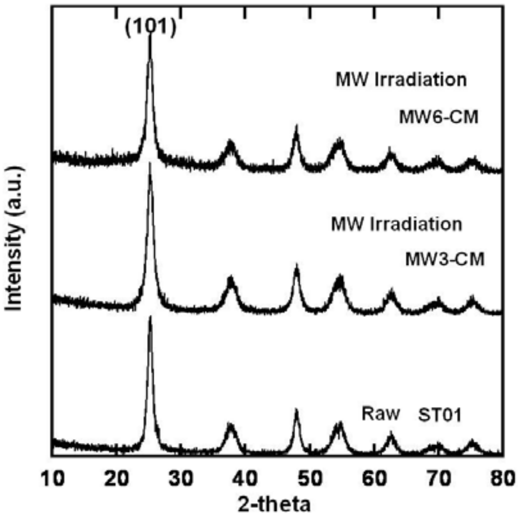

Figure 2. XRD patterns of untreated TiO_2 (ST01), and microwave treated TiO_2 for 3 (MW3-CM) and 6 min (MW6-CM).

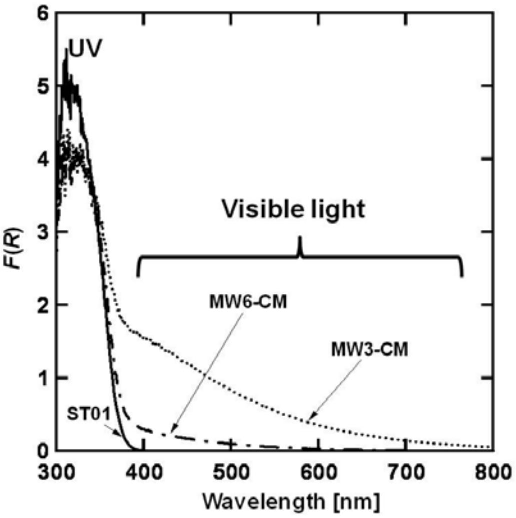

Figure 3. UV-Vis absorption coefficients [10].

3.2 Photocatalytic Activity

The time-dependent formation profiles of I_3^- under visible light irradiation ($\lambda > 420$ nm) in the suspension of samples are shown in Fig. 2. The I_3^- formation rate of pure TiO_2, and carbon-modified TiO_2 (MW3-CM and MW6-CM) per unit mass are calculated as 9.09×10^{-6} mol/g h and 2.25×10^{-4} $molg^{-1}h^{-1}$, 1.25×10^{-4} $molg^{-1}h^{-1}$, respectively. It can be clearly seen that the visible light photocatalytic activity of carbon-modified TiO_2 prepared by microwave heating are drastically higher than that of pure TiO_2, where the I_3^- formation rate of carbon-modified TiO_2 are almost 25 times higher for MW3-CM and 14 times higher for MW6-CM than that of pure TiO_2. This high photocatalytic activity under visible light region is attributed to the high visible light response due to the surface modification by organic functional groups after microwave heating.

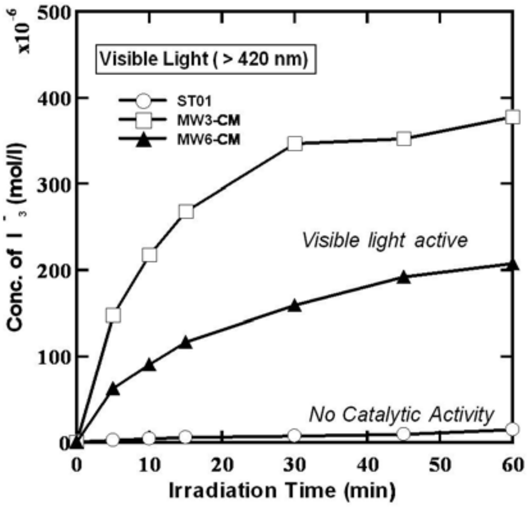

Figure 4. Formation profile of I^3- as a function of visible light ($\lambda > 420$nm) irradiation [10].

3.3 Development of materials evaluation by MIR-FEL

It is well known that MIR region light has a good resonance with phonon in some solid compounds. Owing to the special features of FEL such as tunable wavelength (13–14 μm), short pulse, and high power, it is possibly considered that the irradiation of MIR-FEL gives rise to the change in optical properties by exciting a particular phonon mode as well as the electrons at mid-gap bands. To measure the electronic state during FEL irradiation on the materials, PL system with FEL transport line has been installed.

PL measurement system is consist of He-Cd laser excitation (wavelength: 325 nm, power: 10 mW, beam diameter: 1.0 mm: Kimmon IK5451R-E) and a monochromator (Zolix Omni-λ, 300), and a CCD detector (INTEVAC Mosir 350). To measure the temperature dependence of the PL spectrum, controllable temperatures down to 10K achieved by using a closed cycle He refrigerator. Trigger is used for simultaneous irradiation between FEL and He-Cd laser. Data from CCD detector are collected in PC.

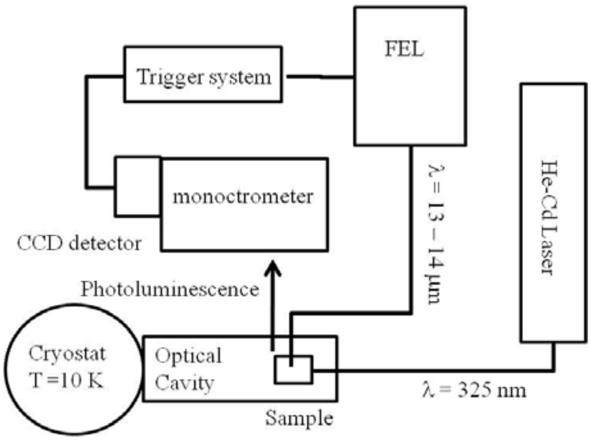

Figure 5. View of optical measurement system by FEL.

4. Conclusion

The modified TiO_2 was simply synthesized through microwave carbonization of ethanol by using a domestic microwave oven. This process enabled to form the carbonaceous compounds on the surface of TiO_2. The carbon-modified TiO_2 showed remarkable visible-light absorption and photocatalystic activity compared with pure TiO_2. A new approach for measuring optical properties of the carbon-modified TiO_2 by KU-FEL has been also developing.

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