Photocatalytic activity enhancement by electron irradiation of fullerene derivative-TiO_2 nanoparticles under visible light illumination

Sung Oh Cho*, Seung Hwa Yoo, Dong Hoon Lee
[a]*Nuclear Department of Nuclear and Quantum Engineering, Korea Advanced Institute of Science and Technology,*

[*]*Corresponding author e-mail: socho@kaist.ac.kr*

1. Introduction

Photocatalytic decomposition of aqueous organic pollutant have attracted many interest due to its simple, low cost, and clean procedure. By only using the sun light and photocatalyst, especially TiO_2 nanoparticles based systems have been extensively studied and commercialized for real life application [1].

However, TiO_2 has a critical disadvantage, which can only absorb the ultra-violet region of the solar spectrum, due to the large band-gap of 3.2 eV. Extensive studies have been preformed to expand the light absorption of TiO_2 to the visible light region of the solar spectrum, by doping metal[2] or non-metal[3] elements on TiO_2 or attaching small band-gap semiconductors on TiO_2 [4].

In this study, a fullerene derivative 1-(3-carboxypropyl)-1-phenyl[6,6]C_{61} (PCBA) was attached on the surface of TiO_2 nanoparticles, and its photocatalytic activity was evaluated by decomposition of methyl orange under visible light. Furthermore, enhancement in the photocatalytic activity of these nanoparticles by electron irradiation is discussed.

2. Methods

In this section, sample preparation methods and conditions of electron irradiation will be described. Experimental conditions of the measurement of photocatalytic activity of as-prepared samples will be described.

2.1. Preparation of PCBA-TiO_2 nanoparticles

2 g of P-25 TiO_2 nanoparticles were dispersed in 200 nL carbon disulfide (CS_2), which 20 or 40 g of PCBA was dissolved in this solution. This dispersion was stirred for 5 h under dark condition. After finishing the stirring, the dispersion was centrifuged and dried, and PCBA-TiO_2 powders were obtained.

2.2. Electron irradiation on PCBA-TiO_2 nanoparticles

The as-prepared PCBA-TiO_2 nanoparticles were subjected to an electron beam. The irradiation was carried out at room temperature and in vacuum lower than 2×10^{-5} Torr. An electron beam was generated from a thermionic electron gun with electron energy of 50 keV and current density of the electron beam was 1.6 μA cm^{-2}. The electron fluence was varied by adjusting the irradiation time. PCBA-TiO_2 nanoparticles were irradiated by 0.5 h, 1 h, 2 h, and 4 h, which corresponds to electron fluence of 1.8×10^{16} cm^{-2}, 3.6×10^{16} cm^{-2}, 7.2×10^{16} cm^{-2}, and 1.44×10^{17} cm^{-2}, respectively.

2.3. Measurement of photocatalytic activity

The photocatalytic activity of PCBA-TiO_2 nanoparticles was measured by the decomposition of methyl orange (MO) molecules dissolved in water under visible light illumination. 80 mg of PCBA-TiO_2 nanoparticles were dispersed in 80 mL of MO aqueous solution, which MO concentration was 10 mg L^{-1}. This dispersion was illuminated by a Xe lamp equipped with an AM1.5 and 420 nm cut-off filters. The estimated light power at the dispersion surface was 100 mW cm^{-2}. During illumination, 2 mL of dispersion was extracted every 40 minutes to measure the residual MO concentration by UV-VIS spectroscopy. Before UV-VIS spectroscopy measurement, all dispersions were centrifuged to eliminate the residual PCBA-TiO_2 nanoparticles. The absorbance of the MO solutions are compared by each samples, which has different visible light illumination time. The ratio of MO concentration C/C_0 could be calculated as follows

$$C/C_0 = A/A_0 \quad (1)$$

where C_0 and C are the concentration of MO at illumination time 0 and t, and A_0 and A are the absorbance values at the wavelength of 464 nm at time of 0 and t, respectively [5].

3. Results and Discussions

Figure 1 shows the photocatalytic activity of TiO_2 and as-prepared PCBA-TiO_2 nanoparticles under visible light irradiation. TiO_2 shows no activity under visible light as expected, due to its large band-gap. After attaching PCBA on TiO_2, visible light response appears, and the photocatalytic activity increases as more amount of PCBA is attached at the synthesis step. As increasing the amount of PCBA from 20 to 40 mg (PCBA-TiO_2 (1) to PCBA-TiO_2 (2)), the photocatalytic activity also enhances two times.

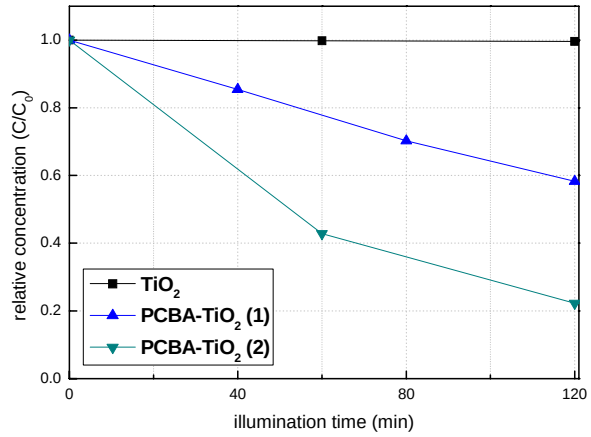

Fig 1. Photocatalytic activity of TiO_2, PCBA-TiO_2 synthesized at different conditions. PCBA-TiO_2 (1) was synthesized with 20 mg of PCBA with 2 g of TiO_2, and PCBA-TiO_2 (2) was synthesized with 40 mg of PCBA with 2 g of TiO_2.

After electron irradiation on PCBA-TiO_2, the photocatalytic activity was further enhanced. Figure 2 and 3 shows the enhancement of photocatalytic activity of electron-irradiated PCBA-TiO_2. The photocatalytic activity gradually increases as the electron fluence increases from 1.8×10^{16} to 3.6×10^{16} cm^{-2}. For PCBA-TiO_2 (1), the activity has been enhanced 1.5 times compared to pristine at 3.6×10^{16} cm^{-2} and for PCBA-TiO_2 (2), the activity has been enhanced 1.07 times compared to pristine at 3.6×10^{16} cm^{-2}. Interestingly, the amount of enhancement by each sample was different at same electron fluence. The enhancement by electron irradiation was inverse-proportional to the attached amount of PCBA on TiO_2. Further analysis are in progress. After electron fluence of 3.6×10^{16} cm^{-2}, the photocatalytic activity begins to deteriorate as the electron fluence increases.

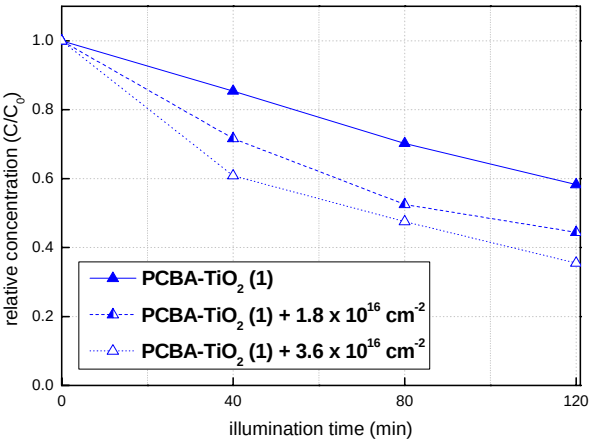

Fig 2. Photocatalytic activity of PCBA-TiO2 (1) at electron fluence of 1.8×10^{16} and 3.6×10^{16} cm^{-2}.

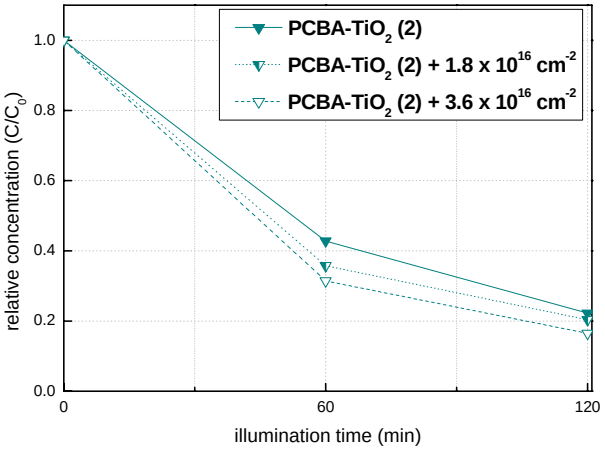

Fig 3. Photocatalytic activity of PCBA-TiO2 (2) at electron fluence of 1.8×10^{16} and 3.6×10^{16} cm^{-2}.

The mechanism of the photocatalytic activity enhancement is unclear up to now. Further measurement of the optical property of the pristine and electron-irradiated PCBA-TiO_2 nanoparticles are required. In addition, the effect of electron-irradiation on PCBA must be clarified.

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