Adsorption and photocatalytic activity of electron-irradiated polystyrene nanosphere multi-layer film

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1. Introduction

Photocatalytic decomposition of aqueous organic pollutant on semiconductor materials has been widely studied as a simple and clean process for organic pollutant removal. The reaction mechanism have been revealed and some fundamental requirements should be satisfied for high photocatalytic activity, such as high chemical, thermal stability in water, intense light absorption, efficient charge separation, large surface area, high pollutant adsorption ability, etc. However, until now on, no single material fulfills all these requirements. Therefore, lots of efforts have been made to enhance the activity of photocatalysts by several approaches. By controlling the band-gap of photocatalyst or combining with narrow band-gap semiconductor, the light absorption can expand to the visible-light spectrum region that increases the charge-carrier generation. By adopting nanostructured morphologies, large surface area can provide huge amount of surface reaction sites and reduce the charge-carrier recombination before it reaches these sites. Also, several reports have shown that, by increasing the adsorption of pollutant on the photocatalyst surface, synergistic enhancement can occur in the photocatalytic activity.

Along with these fundamental requirements, photocatalysts should be non-toxic, abundant, and easily synthesizable for economical and eco-friendly applications. During a few decades, various inorganic semiconductors, especially, metal oxides (TiO_2, ZnO_2, WO_3, etc) [1,2], metal sulfides (CdS, PbS, etc) [3,4], and dye molecules with a metal core (Ru-, Ir- based single-molecules) [5] have been widely studied as a photocatalyst. However, even though lots of studies have been made, issues related to the potential threat against human health by using these kinds of metal-containing inorganic semiconductors are still under dispute. Recently, metal-free organic photocatalyst (g-C_3N_4, $C_3N_3S_3$) [6,7] have been synthesized, and showed outstanding photocatalytic activities for H_2 production from water, after the first report of poly(p-phenylene) (PPP) in 1990 [8]. Both of these work shows enhanced activity by incorporating a co-catalyst. However, to date, there is no reported literature about single material organic photocatalyst for removal of organic pollutant from water. In this paper, we present a novel low-cost, metal-free organic photocatalyst that consists of only carbon and hydrogen fabricated by electron-beam irradiation on polymer nanospheres. Characterization results and adsorption-photocatalytic activities are shown of electron-irradiated polystyrene (PS) nanospheres.

2. Methods and Results

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 PS multi-layer film

2 drops of PS aqueous dispersion were deposited on a silicon substrate. Prior to deposition, the silicon substrate was cut in dimensions of 0.8 cm × 3.5 cm and treated in a piranha solution for hydrophilic surface. After drying overnight, PS multi-layer film was formed on the silicon substrate. The film consists of PS nanospheres with 100 nm size as shown in Fig. 1a.

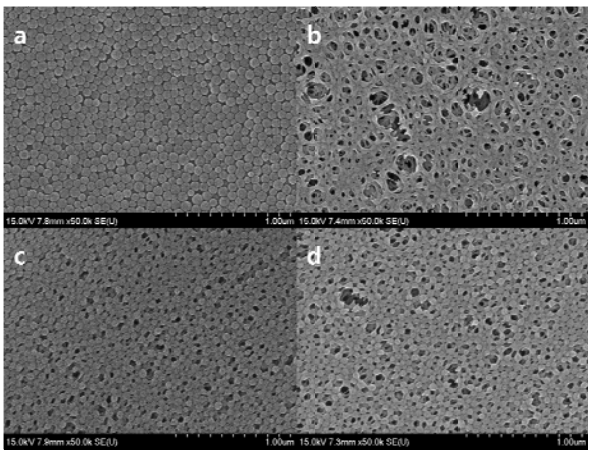

Fig 1. FESEM images of (a) PS multi-layer film, (b) electron irradiated at fluence 7.5×10^{17} cm^{-2} and heat treated at 360 ℃ for 1h, (c) electron irradiated at fluence 10^{18} cm^{-2} and heat treated at 360 ℃ for 1h and (d) electron irradiated at fluence 3×10^{18} cm^{-2} and heat treated at 360 ℃ for 1h

2.2 Electron irradiation on PS multi-layer film and post heat treatment

The as-prepared PS multi-layer films 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 10 μA cm^{-2}. The electron fluence was varied from 7.6×10^{16} to 3×10^{18} cm^{-2} by adjusting the irradiation time. The irradiated samples were heated at 360 ℃ for 1h to remove the residual polymeric materials. The change in morphologies are shown in Fig. 1.

2.3 Measurement of adsorption and photocatalytic activity

The adsorption and photocatalytic activity of electron-irradiated PS nanosphere multi-layer films were measured by the removal of methyl orange (MO) molecules dissolved in water. Adsorption properties were measured under dark for 3 h and the photocatalytic activities were measured under simulated sun-light illumination. The estimated light power was 100 mW cm^{-2}. The samples were vertically immersed in a qualtz cell which contains 10 mg L^{-1} of MO aqueous solution. During certain time intervals, the absorbance of the MO solutions were measured by UV-VIS spectroscopy. The absorbance of the MO solutions are compared by each time intervals, which has different 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

Fig 2. shows the adsorption and photocatalytic activities of electron-irradiated and heat treated samples at different electron fluences. The adsorption property and photocatalytic activity gradually increases as electron fluence increases up to 10^{18} cm^{-2}. However, the adsorption and photocatalytic activities starts to decrease for further electron irradiation.

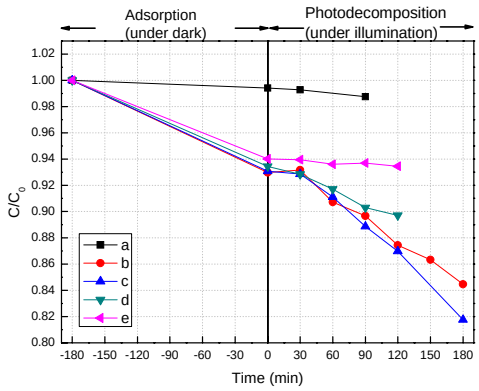

Fig 2. Adsorption and photocatalytic activity of electron-irrdiated PS film at electron fluence of (a) $7.6 \times 10^{16} cm^{-2}$, (b) $7.5 \times 10^{17} cm^{-2}$, (c) $10^{18} cm^{-2}$, (d) $1.25 \times 10^{17} cm^{-2}$7and (e) $3 \times 10^{18} cm^{-2}$.

3. Conclusions

Electron-irradiated PS nanospheres show weak but certain adsorption and photocatalytic activity at different fluences. Further improvements are expected at optimal sample preparation procedure and measurement conditions. Also investigation of the operation mechanism of electron-irradiated PS nanospheres are challenging.

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