Facile Preparation of Tungsten Oxide doped TiO_2 Photocatalysts using Liquid Phase Plasma Process for Enhancing Degradation of Diethyl Phthalate

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Highlights

- Tungsten oxide were doped on the surface of TiO_2 powder by liquid phase plasma process.
- The band gap energy of tungsten oxide doped TiO_2 powder was lower than that of bare TiO_2.
- The photocatalytic activity of modified TiO_2 was improved under blue light source.

1. Introduction

Phthalate esters (PAEs) are used in various applications such as cosmetics, adhesives, and plasticizers for resins. However, there are known to be harmful to human body due to the release of environmental hormones. Although biological process using microorganisms is known as a treatment process for removal PAEs, it has some disadvantages such as requirement long time and low removal efficiency. The titanium dioxide (TiO_2) photocatalyst has been in the spotlight due to advantages such as low cost, non-toxicity, and powerful redox properties. On the other hand, its intrinsic band gap energy as high as 3.2 eV allowed its surface to be activated only under ultraviolet (UV) irradiation. The transition metals introduced as dopants are famous for improving the photocatalytic activity of various advanced materials, including the TiO_2 photocatalyst. In particulary, tungsten oxide has the small band gap energy extending from 2.4 to 2.8 eV, which corresponds to the visible light region. In addition, liquid phase plasma (LPP) method has recently received great attention due to its ability to generate transition metals or metal oxides directly from aqueous precursor solution in the absence of any reducing agents. The aim of this study was to reduce the intrinsic band gap energy of TiO_2 by doping tungsten oxide onto the photocatalyst surface using LPP method. Also, the photocatalytic activity of modified TiO_2 photocatalysts was compared with bare TiO_2 under both ultraviolet (UV) and visible light sources.

2. Experimentals

Tungsten oxide doped TiO_2 photocatalysts (TOTPs) were prepared by the following method using LPP process. Tungsten hexachloride was completely dissolved in the mixture of ethanol and deionized water. Sodium dodecyl sulfate was added into the solution and stirred to ensure complete dissolution. TiO_2 powders (P-25) was inserted into the mixture and vigorously stirred to establish uniform dispersion. After a reactant solution was injected into the LPP reactor, TOTPs was prepared by depositing tungsten oxide on the surface TiO_2 using LPP process. The photocatalytic degradation experiments for diethyl phthalate (DEP) were carried out in a quartz reactor that was equipped with a circulation pump with a light-emitting diode (LED) light. The LED light was provided by installing 100 pcs of a blue LED (NSPB510BS, Nichia) or UV LED (NSPU510CS, Nichia) in a cylindrical pipe. The photocatalytic activity through DEP degradation was evaluated by measuring concentration of DEP in aqueous solution under UV and blue light conditions. The concentration of DEP was determined by absorbance using UV spectrometer (UV-1280, Shimadzu Co. Ltd.).

3. Results and discussion

The chemical active species such as excited hydrogen, oxygen, and hydroxyl radical generated from LPP reaction converted the tungsten ions to tungsten oxide in aqueous solution. The tungsten oxide was successfully deposited on the surface of bare TiO_2. The amount of tungsten in the TOTPs were increased

with increasing the initial concentration of precursor in the reactant solution. In the TOTPs, the tungsten element was uniformly dispersed on the surface of TiO_2 and confirmed to exist in the form of WO_3 by XPS analysis. The specific surface area for the bare TiO_2 powders and modified photocatalyst TOTP – 5 mM was 50.32 m^2/g and 44.57 m^2/g, respectively. The tungsten oxide which was incorporated in the lattice on the bare TiO_2 surface were probably responsible for lowering the specific surface area in TOTP – 5 mM. The light absorption between bare TiO_2 powders and TOTP was compared using UV-DRS with the Kubelka-Munk function that calculated band gap energy. Fig. 1 displays light absorption behaviour as a function of wavelength for bare TiO_2 and TOTPs. As shown in the figure, the absorption edge of bare TiO_2 photocatalyst was confirmed at 397 nm. Contrarily, those edges in the modified TiO_2 photocatalysts were slightly shifted toward visible light region such as 402 nm (for TOTP - 3 mM) and 408 nm (for TOTP – 5 mM). The band gap energy for bare TiO_2 was estimated to be 3.13 eV, which agreed well with values reported for anatase TiO_2 (3.0-3.2 eV). And, the calculated band gap energies for TOTP – 3 mM and TOTP – 5 mM were 3.08 eV and 3.04 eV, respectively, which were lower than that of bare TiO_2. These results revealed that tungsten oxide deposited on the surface of bare TiO_2 using LPP process reduced its intrinsic band gap energy. The photocatalytic degradation rate of DEP using TOTPs was slightly lower than that of bare TiO_2 photocatalysts under UV irradiation. Otherwise, the photocatalytic activity of TOTPs was improved than that of bare TiO_2 photocatalyst under blue light source. It is attributed to decrease the band gap energy of TOTPs due to the doping of tungsten oxide on the surface of TiO_2 powder.

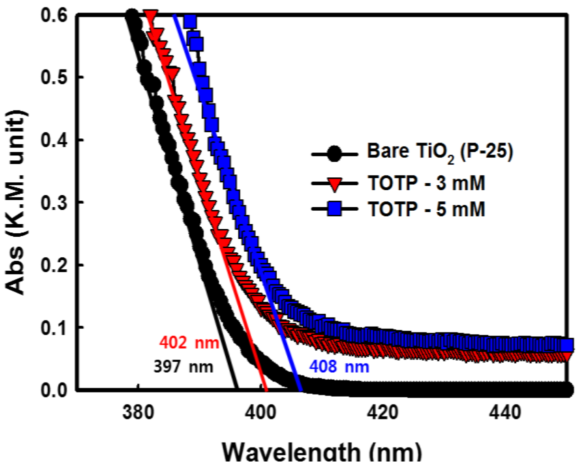

Figure 1. Comparison of the light absorption between bare TiO_2 powders and TOTPs.

4. Conclusions

Tungsten oxide doped TiO_2 photocatalysts were prepared by facile process as liquid phase plasma process. The precursor concentrations loaded in the reactant determined the amount of tungsten oxide formed in the TOTPs. The band gap of TOTPs were decreased with increasing the initial concentration of precursor. The photocatalytic activity of TOTP was improved than that of bare TiO_2 photocatalysts under blue light source.

References

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Keywords
Tungsten oxide, TiO_2 photocatalyst, Liquid phase plasma, Band gap energy.