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主 論 文 の 要 旨

論文題目 **Photocatalytic application of helium plasma induced nanostructured tungsten oxides in bulk and thin film forms**
(バルクおよび薄膜形態のヘリウムプラズマ誘起ナノ構造酸化タングステンの光触媒応用)

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論 文 内 容 の 要 旨

In this work, starting from the plasma technique, different WO_3 photocatalysts were prepared by helium plasma irradiation using tungsten sheet and tungsten film as a tungsten source, combined with calcination treatments. The photocatalysts were characterized by X-ray powder diffraction (XRD), X-ray photoelectron spectroscopy (XPS), Scanning electron microscopy (SEM), Transmission electron microscopy (TEM), Raman spectroscopy, and the photocatalytic performance and mechanism of photocatalyst were evaluated. Principal results are as follows:

In part one, two photosensitive nanostructured WO_3 photocatalysts were synthesized by helium plasma irradiation combine calcination treatments, and characterized by SEM, XPS. Nanostructured W thin film samples (W_{NTF}) and nanostructured W sheet (W_{Nano}) were synthesized by helium irradiation. The results of SEM reveal that a uniform structure was observed for all W_{NTF} samples but the 100-nm-thick W_{NTF} . The result revealed that the uniform growth of the nanostructure depends on the thickness of the thin film. The results of XPS indicate that after calcination,

the surface of W_{NTF100} (100-nm-thick W_{NTF}) samples was completely oxidized, different from the W_{Nano} cases which still had some W fractions. The low concentration of methylene blue (MB) solution as the target degradation reactant evaluate the degradation performance of prepared samples. The effects of calcination temperature, the surface area, and nonuniformity of nanostructurization on the degradation performance were investigated. The result revealed that the highest photocatalytic activity is observed for W_{Nano} subjected to calcination at 523 K. The difference in the photocatalytic activities between W_{Nano} and W_{NTF100} was possibly caused by the difference in the surface area and the presence of a W/WO_3 interface. The results show that the presence of a W/WO_3 interface is favorable for enhancing efficiency.

Nanostructured 300-nm-thick W thin film samples (W_{NTF300}) were synthesized by helium irradiation. The results of XPS indicate that after calcination, some differences were found in the oxidation degree and oxidation vacancies of W_{Nano} and W_{NTF300} . The low concentration of methylene blue (MB) solution as the target degradation reactant evaluate the degradation performance of prepared samples. Comparison of the degradation per unit of irradiation area showed that W_{NTF300} calcined at 423 K had comparable performance when degrading MB to nanostructured W sheet samples (W_{Nano}) calcined at 523 K. XPS analysis revealed that the optimum calcination temperature is determined by the W/WO_3 interface and the concentration of oxygen vacancies.

In part two, noble metals (Ag, Au, and Pt)/nanostructured WO_3 photocatalysts were synthesized by helium plasma irradiation, calcination treatments, and sputtering technique. The activity of the Pt-loaded samples was higher than that of the other samples; the deposition of Pt and Au on $W_{\text{Nano}}(523)$ had an active effect on photocatalytic activities, while the effect of Ag support was negative. The interpretation was based on the formation of the Schottky barrier as an effective photo-induced electron trap that prevented the recombination of electron holes and prolonged electron life. Additionally, the greatest photocatalytic activity was identified with 10-nm-thick Pt loading. The lower photocatalytic activity of $\text{Pt5}/W_{\text{Nano}}(523)$ compared to $\text{Pt10}/W_{\text{Nano}}(523)$ was the result of the shortfall of the Pt deposit.

The lower photocatalytic performance of Pt15/W_{Nano}(523) was because the layer was so thick that surface activity sites were obscured.

In part three, nanostructured WO₃ photoelectrodes were synthesized by helium plasma irradiation followed by calcination treatments. By controlling the preparation conditions, such as irradiation time and calcination temperature, the surface morphology and crystallinity of nanostructured WO₃ can be adjusted, and the influence of the surface morphology and crystallinity of the material on the PEC performance of nanostructured WO₃ was discussed. The results showed that nanostructured WO₃ photoanodes have higher PEC performance compared to the sample without nanostructures. The 15 min irradiated sample with a 1.2- μ m-thick WO₃ layer exhibited the highest photocurrent density. The calcination temperature dependence (673-973 K) showed that the performance became the best at a calcination temperature of 773 K.