Application of Nanostructured Tungsten Fabricated by Helium Plasma Irradiation for Photoinduced Decolorization of Methylene Blue*

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The dendritic nanostructure was fabricated on a surface of tungsten plate by helium plasma irradiation. The nanostructure consisting of W metal was partially oxidized to form WO3 on exposure to air, and the resulting surface exhibited a broad photoabsorption in the range from 1 to 5 eV. We examined photoinduced reaction of methylene blue (MB) on the material. It was found that the partially and fully oxidized surface nanostructures were able to promote a decolorization of MB under photoirradiation even with the near-infrared light (<1.55 eV), whose energy is lower than the band gap of WO3. The reaction rate was varied with the fraction of W and WO3 on the surface layers, that is, the partially oxidized sample promoted the reaction at a higher rate than the fully oxidized one. It is also found that the reaction rate decreased with time, which would be caused by the products accumulation on the surface and the surface oxidation. [DOI: 10.1380/ejssnt.2014.343]

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I. INTRODUCTION

Various kinds of organic pollutants spreading over our environment have become serious problem. As one of the methods for environmental cleanup, photocatalytic degradation of organic compounds has been attracted much attention because it can utilize abundant solar energy and it can mineralize the organic compounds. It is explained that photoexcited electron and hole pairs generated in a semiconductor photocatalyst have high potentials enough to cause reductive and oxidative reactions with adsorbed molecules, respectively. Since the Honda-Fujishima effect reported in 1972 [1], photocatalysis has been widely studied and then its environmental application was extensively carried out over the world [2], where most of photocatalysts such as titanium oxide (TiO2) only can function with UV light. However, since the main part in the wavelength distribution of sunlight and interior illuminations are visible light, photocatalysts that can utilize visible light has been desired for more efficient use. Tungsten oxide (WO3) has been reported as such photocatalyst that can utilize visible light [3–5].

Generally the nanosized semiconductor photocatalyst is expected to have higher activity due to the variation of band structure while the higher energy of the light is required for the photoexcitation [6, 7]. Recently, it has been noticed that surface plasmon resonance (SPR) of metal nanoparticles deposited on a semiconductor material promotes some photocatalytic reactions with visible light irradiation [8–14], because electrons excited by SPR transfer from the metal nanoparticles into the conduction band of the attached semiconductor.

In the field of nuclear fusion, it has been reported that the dendritic nanostructure is fabricated on a tungsten (W) plate by helium (He) plasma irradiation in certain conditions [15, 16]. Helium plasma generates thermal vacancies and He bubbles, conclusively the dendritic nanostructure on the W surface. In this study, we examined to fabricate a nanostructured photoactive material with the metal-semiconductor interface prepared by the He plasma technique followed by gentle oxidation, which is expected to consist of both nanosized W and nanosized WO3, and

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the nanosized WO₃ might show photoactivity by the aid of the SPR of neighboring tungsten metal nanostructure under less energy light irradiation than band gap of WO₃.

II. EXPERIMENTAL

A. Sample Preparation

The dendritic nanostructured surface was fabricated by the He plasma irradiation to a monocystal W plate (The Nilaco Corporation, 0.1 × 8 × 8 mm³, 99.95% purity) in the linear type diverter plasma simulation test device NAGDIS [17, 18]. The incident energy, ion fluence and flux of the helium plasma were 50-60 eV, \(5 \times 10^{25}\) m⁻² and \(2 \times 10^{22}\) m⁻²s⁻¹, respectively. The surface temperature of the sample in steady state was measured as 1500 K with a radiation pyrometer. After the plasma irradiation, the surface of the sample was partially oxidized on exposure to air at room temperature. This oxidation process took a long time: we prepared three samples in this manner through the oxidation for 12, 97 and 200 days, and the surface oxidation ratios \((x)\) of these samples estimated by XPS measurements were 20, 35 and 60%, respectively. Another sample with the surface oxidation ratio of \(x = 100\%\) was prepared by further heat-treated at 773 K for 2 h in air. These samples are referred to as WO₃\((x)\)/W.

B. Reaction Experiment under Photoirradiation of NIR

Photoinduced reactions of methylene blue (MB, C₁₆H₁₈N₃SCl), an organic dye compound, were conducted to evaluate the activities of the samples in the reported manner [18]. A typical reaction experiment consisted of placing the dendritic sample and 2 ml of MB aqueous solution (10 \(\mu\)mol/L) into a quartz cell, subsequently exposing the sample to near infrared light using a 300 W extra high pressure Xe lamp (USHIOPAX R300-3J) with a cut-off filter permitting \(\lambda > 800\) nm. The light absorbance of the MB aqueous solution at \(\lambda = 664\) nm was measured by transmission method in UV-vis spectroscopy with a spectrometer JASCO V-670. The MB concentration in each reaction time was estimated from the absorbance of the MB aqueous solution at 773 K for 2 h in air. These samples are referred to as WO₃(60)/W.

C. Characterization of the Samples

X-ray photoelectron spectroscopy (XPS) measurements were carried out for the samples before and after the MB decomposition reactions with a ESCA-3300 (SHIMADZU) spectrometer with 10 mA -12 V Al Kα emission as the X-ray source. The atomic ratios for carbon, oxygen and tungsten in each sample’s surface were estimated from the peak areas of C1s, O1s and W4f regions. Energy correction of the spectra was performed using C1s peak (284.6 eV) originated in the contaminants.

III. RESULTS AND DISCUSSION

Figure 1(a) shows a SEM image of the dendritic WO₃(60)/W sample. The surface of the sample was covered with a submicrometer fine structure, corresponding to the dendritic nanostructure. In a TEM image of the piece of the sample shown as Fig. 1(b), the He bubbles were clearly observed in the dendritic structure, and it was observed that the dendritic surface was not fully but
Fig. 3: UV-visible-NIR diffuse reflectance spectra of (a) the WO$_3$(100)/W sample, (b) the WO$_3$(60)/W sample and (c) a W plate before the He plasma irradiation.

Fig. 4: Time courses of the MB concentration in aqueous solution with the samples under the photoirradiation of NIR light (> 800 nm in wavelength).

Fig. 5: Time courses of the MB concentration in aqueous solution with (a) the WO$_3$(60)/W sample and (b) the WO$_3$(100)/W sample under the NIR light irradiation and in the dark.

Fig. 6: Time courses of the MB concentration in aqueous solution with the WO$_3$(60)/W sample or the WO$_3$(100)/W sample in the first and second runs.

Table 1: Nonlinear least-square curve-fitting results of the dendritic W (the WO$_3$(60)/W sample) and a W foil.

| Sample      | Shell | Coordination number | Average distance (Å) |
|-------------|-------|---------------------|----------------------|
| dendritic W | W–W   | 8.0                 | 2.75                 |
|             | W–W   | 6.4                 | 3.18                 |
| W foil      | W–W   | 8.0                 | 2.74                 |
|             | W–W   | 6.0                 | 3.17                 |

partly covered with oxidized moiety, where the WO$_3$/W interface existed on the surface. The WO$_3$ film thickness was estimated to be less than 5 nm.

Figure 2 shows the Fourier transforms (FT) of the W L$_3$-edge EXAFS of the WO$_3$(60)/W sample and a tungsten foil. The spectrum of the WO$_3$(60)/W sample was similar to that of a W foil. The large peaks observed at ~ 2.7 Å and ~ 3.2 Å correspond to the first- and second-shells, respectively, which are assignable to the W atoms. We also performed nonlinear least-square curve-fitting to the Fourier-filtered EXAFS including the first and the second coordination shells. In the dendritic WO$_3$(60)/W sample, the average distances and coordination numbers of first neighboring W shell were estimated to be 2.75 Å and 8.0, respectively, while those of second neighboring W shell were estimated to be 3.18 Å and 6.4, respectively. As shown in Table 1, these values are approximately same to those of a W foil, indicating that the local structure of a tungsten atom is fundamentally maintained after the He plasma irradiation. In this analysis, no oxidized phase was found, which means that the oxidized moiety is limited to only a part of the surface, supporting the TEM observation (Fig. 1(b)).

Figure 3 shows the diffuse reflectance UV-visible-NIR spectra of the WO$_3$(100)/W sample, the WO$_3$(60)/W samples and the pristine W plate before the He plasma irradiation. The plasma-irradiated samples exhibited higher absorption at the entire range (Fig. 3(a) and (b)), which is consistent with the black color of these samples. Such broad absorption bands would originate from the nanostructured metal W, which is expected to absorb visible and/or near infrared light by SPR on the W nanostructured surface. The WO$_3$(100)/W sample showed partly less absorbance in the energy range of 2-4 eV. Although the reason was unclarified, it should be due to the structural variation with heating at 773 K in air. The aggregation of the dendritic structure by heating might reduce the absorbance due to the SPR by nanostructured W, or, the further oxidation might change the surface chemical states from W to WO$_3$ to reduce the absorbance around 2-4 eV.

The results of photoinduced reactions for each sample under near infrared light irradiation are shown in Fig. 4. In the separate experiments, we have also con-
TABLE II: Atomic ratios of the surfaces of the WO₃(60)/W sample and the WO₃(100)/W.

| Sample       | MB decomposition | W(0) (%) | W(6⁺) (%) | C (%) | O (%) |
|--------------|-----------------|----------|-----------|-------|-------|
| WO₃(60)/W    | before          | 4        | 9         | 63    | 24    |
|              | after           | 0        | 7         | 73    | 20    |
| WO₃(100)/W   | before          | 0        | 14        | 46    | 40    |
|              | after           | 0        | 19        | 35    | 46    |

Fig. 7: XPS spectra of the W 4f region for the WO₃(60)/W sample (a) and the WO₃(100)/W sample (b). XPS spectra were recorded for these samples before and after the reaction.

confirmed that the samples show photoinduced reaction activity under photoirradiation of both UV light and visible light simultaneously. As shown in Fig. 4, the photoinduced reaction rate over the WO₃(100)/W sample is higher than that without any sample. The WO₃ species on the WO₃(100)/W sample would be one of the active sites, which consisted with literature [19, 20]. The reaction rates of the partially oxidized samples depended on the surface oxide ratio, i.e., it increased in the order 20, 35 and 60% to the maximum, followed by decreasing in 100%. Since the WO₃(60)/W sample would have more WO₃/W interface sites than the other samples, it is suggested that the WO₃/W interface on the nanostructured surface should be more active sites for the photoinduced reaction than the fully oxidized surface of the WO₃(100)/W sample.

Note that the energy of the irradiation light (<1.6 eV) was less than the bandgap of WO₃ (>2.7 eV). Thus, this photoinduced reaction should take place with definitely different mechanism from that on the semiconductor photocatalyst as mentioned above. The photoinduced reaction mechanism in the dendritic WO₃/W sample is speculated as the following process; (i) light absorption due to SPR on the nanosized W would occur under the near infrared light irradiation, (ii) the plasmon excitation would make electrons inject into the conduction band of the surface nanosized WO₃ moiety at the WO₃/W interface, and finally (iii) the electrons at the WO₃ surface would react with the adsorbed MB molecules. The electrons closed to the interface would contribute to the reaction more readily, because the long traveling might cause deactivation of the excited electrons. Thus, it is suggested that the WO₃/W interface would be the most important active sites for the photoinduced reaction.

Figure 5 shows the time courses of the concentration of MB under the light and in the dark with the WO₃(60)/W sample and the WO₃(100)/W sample. In the dark, the

Fig. 8: SEM images of the WO₃(60)/W sample (a) before and (b) after the photoinduced reaction, and those of the WO₃(100)/W sample (c) before and (d) after the photoinduced reaction.
MB concentration very slowly decreased with time in the presence of the dendritic \( \text{WO}_3(60)/\text{W} \) sample, where the MB molecules would be gradually adsorbed and the adsorption density would increase on the nanostructural surface of the \( \text{WO}_3(60)/\text{W} \) sample. On the other hand, the \( \text{WO}_3(100)/\text{W} \) sample was adsorbed by only small amount of the MB molecules, suggesting that the oxidation treatment on the dendritic sample would reduce the specific surface area or the adsorption ability. Upon light irradiation, both samples reduced the MB concentration at higher rate, confirming that photoinduced reaction would occur on the samples. Since the separate experiments elucidated that the commercially obtained \( \text{WO}_3 \) powder and the \( \text{WO}_3 \) thin film on the tungsten plate showed no light-responsiveness, it is notable that the photoinduced activity would be unique property for the partially or fully oxidized \( \text{WO}_3 \) nanostructure on the dendritic nanostructure of tungsten.

When the photoinduced reaction test was repeated on the same sample (Fig. 6), the remarkable decrease of the reaction rate in the second run was observed for the \( \text{WO}_3(60)/\text{W} \) sample and less deactivation was observed for the \( \text{WO}_3(100)/\text{W} \) sample. Thus, it is considered that the active sites at the \( \text{WO}_3/\text{W} \) interface on the \( \text{WO}_3(60)/\text{W} \) sample would be much deactivated and the active sites on the \( \text{WO}_3(100)/\text{W} \) sample would be less deactivated. Table II summarizes the atomic ratios of carbon, oxygen and tungsten on the surfaces of the two samples before and after the reaction, which were determined by XPS measurements. The carbon before the reaction would be the surface contamination while that after the reaction might include the adsorbed organic or carbonaceous species. The ratio of carbon on the \( \text{WO}_3(100)/\text{W} \) sample did not vary remarkably before and after the reaction. On the other hand, the ratio of carbon on the \( \text{WO}_3(60)/\text{W} \) sample increased after the reaction, suggesting the presence of the adsorbed products originating from the MB molecules on the surface.

Figure 7(a) shows the XPS spectra of the \( \text{WO}_3(60)/\text{W} \) sample before and after the reaction. Before the reaction, the \( W\,4f_{7/2} \) and \( 4f_{5/2} \) peaks at 31.6 and 33.6 eV and those at 35.5 and 37.6 eV originated from \( W(0) \) and \( W^{6+} \), respectively, are recorded, suggesting that \( W(0) \) and \( W^{6+} \) species coexist on the surface of the \( \text{WO}_3(60)/\text{W} \) sample. However, after the reaction, \( W(0) \) peaks at 31.6 and 33.6 eV disappear and only \( W^{6+} \) peaks at 35.5 and 37.6 eV are observed. On the other hand, XPS spectra of \( \text{WO}_3(100)/\text{W} \) sample show only \( W^{6+} \) species on the surface before and after the reaction (Fig. 7(b)). As shown in Table II, almost all of the \( W(0) \) species on the surface of the \( \text{WO}_3(60)/\text{W} \) sample change to \( W^{6+} \) species after the reaction, which means the amount of \( \text{WO}_3/\text{W} \) interface decreased on the \( \text{WO}_3(60)/\text{W} \) sample. As shown in the SEM images, the dendritic nanostructure thickened on the \( \text{WO}_3(60)/\text{W} \) sample after the reaction (Fig. 8(a) and 8(b)), while those on the \( \text{WO}_3(100)/\text{W} \) sample exhibited no significant change (Fig. 8(c) and 8(d)). From these results, it is proposed that the obvious deterioration of the \( \text{WO}_3(60)/\text{W} \) sample would be caused by the following reasons: (i) the oxidation of the surface during the reaction would reduce the active sites at the \( \text{WO}_3/\text{W} \) interface, and (ii) the accumulation of the reaction products on the active sites.

**IV. CONCLUSIONS**

We prepared the \( \text{WO}_3 \) nanolayers partially covering the surface of the unique dendritic W nanostructure by the He plasma irradiation technique followed by gentle oxidation on exposure to air for a long period, and confirmed the activity for the photoinduced reaction of methylene blue (MB) as an organic dye. The photoinduced reaction was conducted under irradiation of near infrared light whose energy is lower than band gap of \( \text{WO}_3 \). Moreover, we found that both the \( \text{WO}_3/\text{W} \) interface and \( \text{WO}_3 \) surface would be the active sites for the photoinduced reaction and the former was more active than the latter. The mechanism of the photoinduced reaction is proposed as follows: (i) the initial photocexcitation due to SPR on the nanosized \( W \) would occur under the near infrared light irradiation, (ii) the plasmon excitation would make electrons inject into the conduction band of the surface nanosized \( \text{WO}_3 \) moiety at the \( \text{WO}_3/\text{W} \) interface, and (iii) the electrons at the \( \text{WO}_3 \) surface would react with the adsorbed MB molecules. At present, the active species at the \( \text{WO}_3/\text{W} \) interface could be unfortunately deactivated by adsorption of the reaction products and the surface oxidation during the reaction.

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