Novel nanostructurization method using helium plasmas : vanadium and niobium oxides for photocatalysis

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Abstract: Fabrication of highly efficient photocatalytic material is a high priority issue; nanostructurization of material can increase the performance due to large surface area. In this study, we show the morphology changes of vanadium and niobium by He plasma irradiation; the He plasma irradiation lead to formation of fiberform fuzzy nanostructures accompanied by the growth of He bubbles. Using the oxidized nanostructured sample, photocatalytic reactivity was investigated. It was found that hydrogen production and methylene blue decomposition efficiency was improved by the nanostructuriziation.
Keywords: helium plasma (ion), nanostructure, vanadium oxide, niobium oxide.

1. Introduction

Vanadium (V) and niobium (Nb) oxides have various applications including chemical catalysts and photocatalysts. Because nano and micro-structures can improve the performance in devices due to larger surface area, various methods have been utilized to fabricate mesoporous oxide material. In mid 2000's, it was found that fiberform nanostructures called fuzz was grown on tungsten surface by helium (He) plasma irradiation [1]. The interactions of helium (He) atoms and metals are special; after He atoms are implanted by He plasma irradiation at low energy, typically <100 eV, the He atoms form clusters and He bubbles are formed while diffusing in metal matrix, and, consequently, significant morphology changes occur. As the plasma irradiation has an advantage that the bottom up approach requires only one step dry process, the fabricated materials are anticipated to be used for industrial application. Performance as photocatalytic material has been investigated on oxidized helium irradiated tungsten and titanium. It was found that partially oxidized fuzzy tungsten has a visible light response to decompose methylene blue [2] and enhanced performance to split water [3]. On oxidized nanostructured Ti, it was also identified that the efficiency of H_2 production from aqueous methanol solution was enhanced by the formation of nanostructures [4]. In this study, we show various morphology changes occurred on V and Nb surfaces including fibber-form nanostructures by He plasma irradiation. Using the fabricated V and Nb oxides, we conducted photocatalytic experiments. It is demonstrated that nanostructurization by He irradiation enhanced the photocatalytic reactivity of vanadium oxide and niobium oxide.

2. Experimental

Helium plasma irradiation was conducted in the linear plasma device NAGDIS-II. V or Nb plate with the thickness of 0.1 mm was installed on a water cooling stage to control the irradiation temperature especially when the surface temperature was below 1000 K. The incident ion energy was controlled by biasing the sample negatively. The surface temperature was measured with a radiation pyrometer.

The amount of the produced H_2 from 20 vol% aqueous methanol solution was measured using a gas chromatograph (Shimadzu, GC-8A). A xenon lamp was used for the light source, and cold ultra violet (UV) mirror and a short-pass optical filter of 430 nm was utilized to use UV light mainly; the UV power measured was 2.0 mW/cm^2. A sample and 10 ml aqueous methanol solution was installed to a quartz cylindrical shaped reactor and the size of the sample used for the photocatalytic experiments was 10×10 mm^2 and 0.1 mm in thick.

3. Results and discussion

Figure 1(a,b) shows TEM micrographs of V sample exposed to the He plasma. To observe by TEM directly, semi-circular 3 mm in diameter sample was used for the He plasma irradiation. The incident ion energy was 110 eV, and the surface temperature was 1090 K, and the ion fluence was 8.9×10^{25} m^{-2}. We can see that fine fibers less than 50 nm in diameter are entangled together; the feature is quite similar to W fuzz [5], and we can see many He bubbles inside the structure. The shape of He bubbles was not ideal spherical or hexagonal. The irregular shape indicated that the pressure was lower than the one determined by the balance with the surface tension. The size of the He bubbles are mostly less than 10 nm in diameter; some bubbles are larger than 20 nm. In the similar manner, fuzzy structures were formed on Nb surfaces.

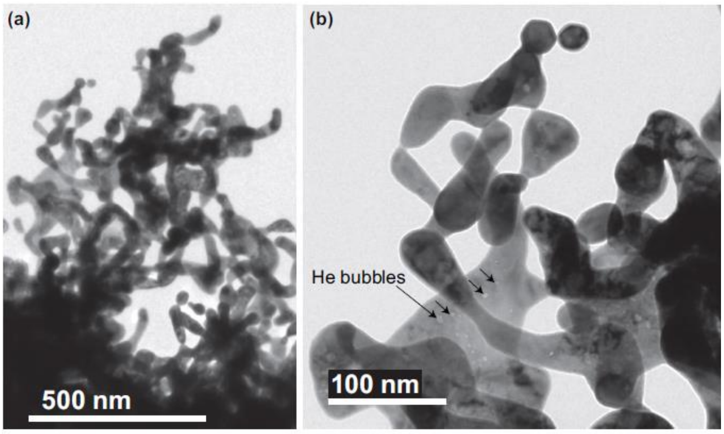

Figure 1. TEM micrographs of He plasma irradiated nanostructured vanadium sample.

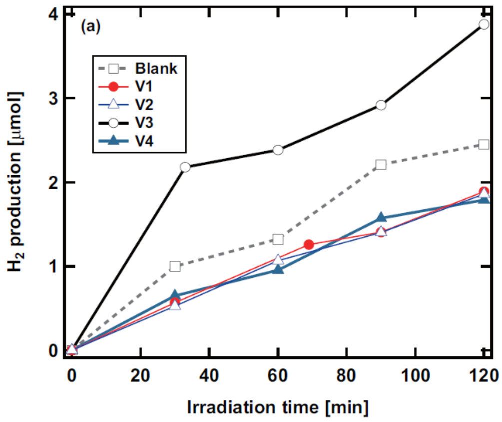

Figure 2. Time course of produced H_2 from 20 vol.% aqueous methanol solution during UV light irradiation.

Hydrogen production experiments using V samples were conducted using 20 vol.% aqueous methanol by UV light irradiation. We used four samples: a pristine V sample, an oxidized V sample at 773 K, a nanostructured V sample, and an oxidized nanostructured V sample. From XPS analysis, it was confirmed that all of the samples were sufficiently oxidized. Figure 2 shows the time course of the produced H_2 from 20 vol.% aqueous methanol solution by UV light irradiation. The produced hydrogen increased with time from all the cases including a blank case (control experiment), where no photocatalyst was introduced. Except for V fuzz sample, the produced hydrogen was less than the blank level, indicating that no clear photocatalytic reaction occurred on the pristine and oxidized samples. It was found that only the nanostructured V sample oxidized in the air atmosphere had a capability to produce hydrogen and other three samples were photocatalytically inactive. It was suggested that nanostructurization by the plasma irradiation has an effect to enhance the photocatalytic activity similar to highly dispersed photocatalysts. Because vanadium oxides are used in various fields of research, it is of interest to investigate the applicability to other usages including batteries and sensors in addition to photocatalysts in future.

References

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