Preparation and Photo-electrochemical Properties of Quaternary Ti-O-C-N Materials

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1. Introduction

Doping of carbon and nitrogen into TiO_2 has been investigated for the development of photo-electro chemical properties such as photocatalysis excited by visible light [1]. In the present study, we have tried to prepare quaternary Ti-O-C-N materials by a chemical reaction of $TiCl_4$ with organic materials such as CH_3CN or bamboo. Photo-electrochemical properties of the materials have been investigated.

2. Experimental

Ti-C-N materials were prepared by a chemical vapor deposition (CVD) reaction of titanium tetrachloride ($TiCl_4$) with acetonitrile (CH_3CN) at 1270K (mole ratio = 1:1-1:5). Ti-C-N-O materials were prepared by a reaction of $TiCl_4$ with bamboo stick at temperature 1270K under N_2 atmosphere. Obtained products were analysed by XRD and ESCA.

Photo-electrochemical properties were measured by cyclic voltammetry in 20wt% methanol aqueous solution or 0.5M-H_2SO_4 aqueous solution. A platinum plate and saturated calomel electrode (SCE) were used as counter and reference electrode, respectively. 500W halogen lamp was used as a light source.

3. Results and Discussion

A silver film was obtained as the Ti-C-N material by the CVD reaction with the mole ratio 1:3. Figure 2(a) shows a powder XRD pattern of the product. Sharp diffraction peaks could be assigned as TiC/TiN solid solution (indicated as "Ti/C/N" in Fig.2), while a broad diffraction around 26º in 2θ could be an amorphous carbon. ESCA measurement suggested that Ti-O bonds mainly exist on the surface of the film. The Ti-O bonds on the surface could be made after Ti-C-N material was exposed to air.

White film was formed on the product (bulk: black in color) prepared by the reaction of $TiCl_4$ with bamboo stick. Figure 2(b) shows a powder XRD pattern of the product. Strong broad diffraction around 24º in 2θ could be assigned as non-crystalline carbon. Several diffractions are due to TiC/TiN solid solution. Although no diffraction owing to TiO_2 was observed, Ti-O chemical bond was detected by ESCA particularly on the surface of the product.

Figure 3 shows photo current-voltage curves for the bamboo-based Ti-O-C-N material in the methanol aqueous solution. Photo-electrochemical current increased by the irradiation of halogen lamp. Increasing in both oxidation and reduction current suggested that both electrons and holes could make photo-electrochemical reaction. The maximum current density did not change during 10 cycles. The Ti-C-N material prepared by CVD method did not clearly show such photo-catalytic behavior. The photo-catalytic behavior observed for the bamboo-based Ti-O-C-N material could be explained by the fine structure of the Ti-O-C-N material, which is composed of carbon as an electro-conductive bulk with Ti-O-C-N hybridized surface having a photo-catalytic role.

References

[1] For example: S. Sakthivel, and H. Kisch, *Angew. Chem. Int. Ed.*, **42**, 4908(2003).

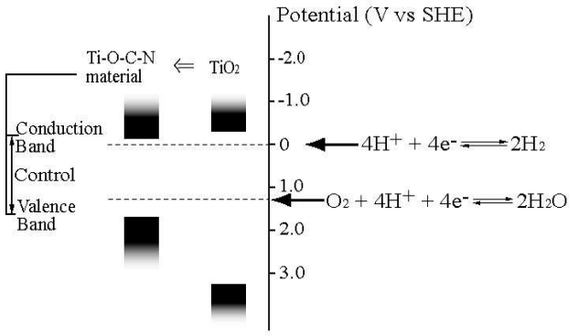

Figure 1 Modification of electronic structure by doping of carbon and nitrogen into TiO_2.

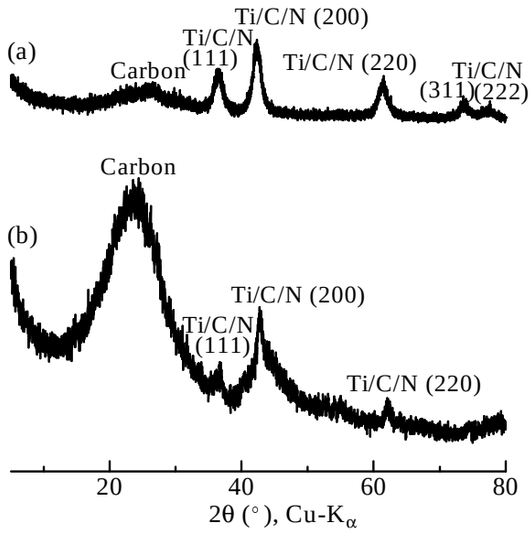

Figure 2 XRD pattern of quaternary Ti-O-C-N compound prepared by reactions of (a) $TiCl_4$ with CH_3CN, and (b) $TiCl_4$ with bamboo.

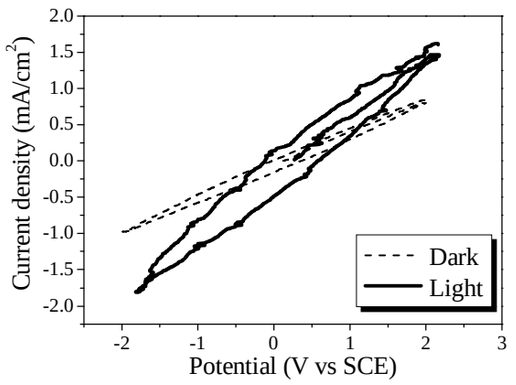

Figure 3 Photo current-voltage curves for quaternary Ti-O-C-N compound prepared by the reaction of $TiCl_4$ with bamboo. Reference: SCE. Electrolyte: 20wt% methanol aqueous solution. Light source: 500W halogen lamp.