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XAFS Study of Different Size Au Nanoparticles-doped TiO_2 Nanocomposite Photocatalytic Films Prepared by Sol-Gel Method

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Introduction

Au nanoparticles (AuNPs) are known to enhance a photocatalytic activity with suppressing recombination of photo-generated electron-holes in a photocatalyst [1]. On the other hand, we have found that AuNPs affect morphology of a host material like TiO_2 during heattreatment of a sol-gel process, resulting in an improvement in the activity [2]. In this paper, we report a size effect of AuNPs on morphology and structure of TiO_2 studied by XAFS measurements.

Experimental section

AuNPs were synthesized by a chemical reduction of Au^{3+} aqueous solution with ethanol solution of $NaBH_4$ and stabilized with polyvinylpyrrolidone. Different reducing rates produced AuNPs of 2.0±0.7 and 7.9±3.2 nm in diameter. These AuNPs were dispersed in a TiO_2 sol solution followed by coating on a quartz substrate, and annealed at 500 °C [3]. Finally, we obtained three types of films: TiO_2, smaller AuNPs-doped TiO_2 ($sAuTiO_2$), and lager AuNPs-doped TiO_2 ($LAuTiO_2$).

Photocatalytic and adsorption abilities were evaluated using methylene blue aqueous solution. XAFS measurements were carried out at a BL-12C beamline of Photon Factory, Japan, for Ti-*K* in FY mode and at a SGM beamline of Canadian Light Source for Ti-$L_{3,2}$ and O-*K* [4].

Results and discussion

Ti *K*-edge XANES spectra in the pre-edge region are shown in Figure 1. All spectra had four bands: A_1 band (quadrupolar $1s\rightarrow3d$ (t_{2g}) transitions), A_3 band (dipolar transitions of $1s\rightarrow3d$ (t_{2g})-$4p$ hybridized states in nature plus a little $1s\rightarrow3d$ (e_g) quadrupolar component), B band (pure dipolar transitions of $1s\rightarrow3d$ (e_g)-$4p$ hybridized states), and A_2 band (five-coordinated Ti atom). A_2 was shown to relate to the mean particle diameter of TiO_2, that is, the A_2/A_3 integrated intensity ratio was increased with decreasing particle size [5]. The A_2/A_3 ratio in the present study is also shown in Figure 1 and $sAuTiO_2$ (A_2/A_3 = 0.794) had the highest value, followed by $LAuTiO_2$ (0.646) and TiO_2 (0.554), indicating the smaller AuNPs doping into TiO_2 film increased the ratio of five-coordinated Ti sites.

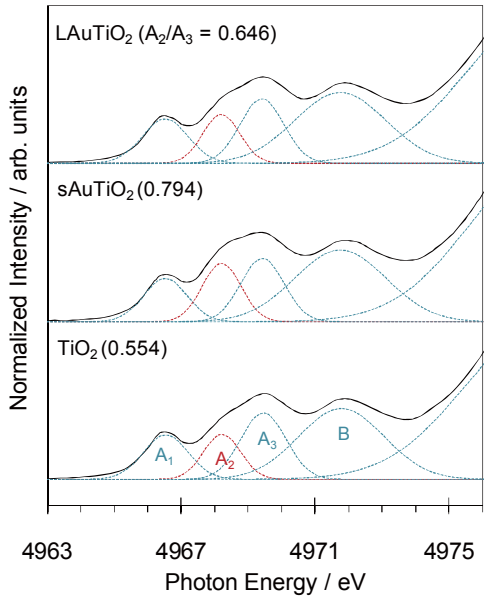

Figure 1. Ti-*K* edge XANES spectra of the films (pre-edge region) and their deconvolution.

The amount of MB in the dark (adsorption ability) and MB degradation rate under 365-nm UV irradiation (photocatalytic activity) of the films were evaluated. The results showed that both the adsorption and photocatalytic abilities were enhanced with increasing the A_2/A_3 ratio and the amount of adsorbed MB was proportional to the A_2/A_3 ratio, indicating the five-coordinated Ti site works as an adsorption site in these series of the films, leading to the improvement in the photocatalytic activity. As for Ti-$L_{3,2}$ and O-*K* edge XANES spectra, there were little difference in those spectra detected by surface-sensitive total electron yield and bulk-sensitive FY mode.

References

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