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XAFS study on local structure of Cr-containing mesoporous silica thin film having superhydrophilic property

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Introduction

The silica materials having nano-scale pore structure, such as zeolite and mesoporous silica, are attractive for using the adsorption materials, catalyst supports, and separation materials. The materials containing the TiO_2 moiety in a highly dispersed state within the porous silica matrix are called single-site photocatalyst and show the unique photocatalytic properties. In particular, the thin film materials have an ideal morphology for promising applications because of the inherent features of thin films. By the addition of chromium ions within the mesoporous silica thin film, it becomes possible to form unique surface active sites and develop of new optical functionalized materials can be expected.

In this report, Cr-containing mesoporous silica thin film having superhydrophilic property was synthesized by using spin-coating method and the local structure of chromium oxide species within the mesoporous silica framework was investigated by X-ray absorption fine structure (XAFS).

Experimental

The Cr-containing mesoporous silica thin film (Cr-MSTF) was prepared by spin-coating method. TEOS as silica source, $Cr(NO_3)_6 \cdot 9H_2O$ as chromium oxide source , Brij®30 as structure directing agents (SDA), HCl, ethanol, and H_2O were mixed, stirred, dropped on the quartz plate and spun-coated at 4000rpm for 1 min. Finally, this film/plate sample was calcined in air at 525 K for 5 h to remove the SDA. Cr K-edge XAFS spectra were recorded at room temperature in the fluorescence mode. The EXAFS data were examined by Rigaku EXAFS.

Results and discussions

The Cr-MSTF was colourless transparent and well fixed on the quartz substrate. The thickness of the Cr-MSTF was approximately 500–700 nm. Low-angle XRD pattern show the sharp peak at 2-3 degree associated with the existence of the mesoporous structure. No other peaks are observed at the higher angle, suggesting that the chromium oxide moieties are highly dispersed in the silica framework.

Figure 1 shows the results of Cr K-edge XAFS measurement of K_2CrO_4 as reference sample of tetrahedrally-coordinated chromium species and synthesized Cr-MSTF, which ratio of Cr to Si was 0.05. In the XANES spectra of K_2CrO_4 and Cr-MSTF (Figure 1-a), single sharp pre-edge peak observed at around 5992

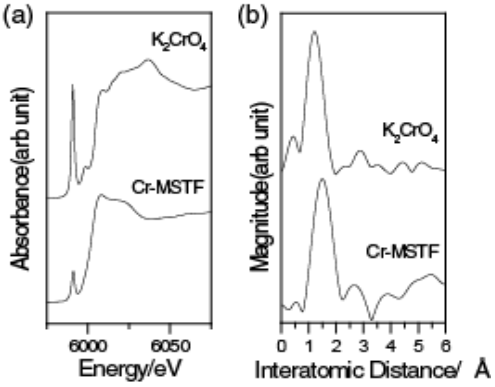

Figure 1 Cr K-edge XANES (a) and FT-EXAFS (b) spectra of K_2CrO_4 and Cr-MSTF

eV assigned to the so-called 1s–3d transition, indicating the presence of tetrahedrally-coordinated chromium oxide species surrounded in the mesoporous silica matrix. The Fourier transforms (FT) of k^3-weighted EXAFS data of these samples are showed in Figure 1-b. The only peak at around 1-2 Å attributed to the Cr=O bond was observed Analysis of XAFS spectra of the Cr-MSTF suggested that tetrahedrally-coordinated chromium oxide moieties involving two terminal Cr=O bonds existed as in an isolated state.

Surface hydrophilic property on Cr-MSTF before and after UV-light irradiation was appraised by water contact angle measurement. Before UV-light irradiation, contact angle of Cr-MSTF was much smaller than that of the MSTF without chromium ions and after UV-light irradiation, Cr-MSTF showed the photoinduced superhydrophilicity.

Conclusions

Synthesized transparent Cr-containing mesoporous silica thin film was well fixed on the quartz plate and showed hydrophilic property even before UV-light irradiation. Under UV-light irradiation on this film, appearance of photoinduced superhydrophilicity was confirmed. The local structure of the chromium species in the Cr-containing mesoporous silica thin film was investigated by XAFS analysis, which suggests that chromium oxide moieties were embedded in mesoporous silica matrix in the highly dispersed tetrahedrally-coordinated state.

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