Influence of Zn and Rh-Cr Promotion on the Electronic Structure of Ga_2O_3 Photocatalysts for Water Splitting Reaction

Experimental conditions

Experiments were performed with incoming energy selected by the (111) reflection of a pair of cryogenically cooled Si crystals and the beam footprint on the sample was 1.0 x 0.2 mm^2. Higher harmonics were suppressed by three Si mirrors working at 2.5 mrad. An emission spectrometer with four spherically bent (r = 50 mm, R = 1000 mm) analyser crystals in vertical Johann geometry was employed to select the Kβ fluorescence lines of Cr, Zn and Ga using the reflections Ge (333), Si (555) and Ge (555), respectively, and a diode IF3 with Cu+Ni filter was used for Rh detection. HERFD-XANES were recorded on the maximum of the $K\beta_{1,3}$ line (9572.6 eV for Zn and 10265.37 eV for Ga) and by varying the incident energy from 10.36 to 10.46 keV (Ga), and 9.65 to 9.75 keV (Zn), in continuous scan mode. The spectra were not corrected for incident beam self-absorption (over-absorption) effects. Linear combination fitting was performed by using additional fitting parameters that account for the spectral distortion arising from self-absorption.
XES was measured for Ga, Zn and Cr K-edges at a fixed incident energy of 10.50, 9.80, and 6.10 keV, respectively. VtC-XES were acquired from 10.28 to 10.4 keV (Ga), 9.59 to 9.70 keV (Zn), and 5.96 to 6.02 keV (Cr) with a step size of 0.30 eV. All samples and reference materials were measured *ex situ* in the form of pellet (13 mm diameter), containing 60 mg of material and 60 mg of cellulose. For *in situ* irradiation experiments, pellets (13 mm diameter) containing 200 mg of pure material were transiently irradiated with DH-2000 (Ocean Optics) UV-vis-NIR deuterium-halogen light source while measuring 10 spectra under dark and then another 10 under light conditions. The light on-off cycles were repeated several times (120 s for each spectral acquisition), and the subtle differences of the spectral features were studied by modulation excitation methodology.

Results

Element selective X-ray absorption and emission spectroscopies (XAS and XES) were employed to learn about the structures of unoccupied (related to conduction band) and occupied (related to valance band) electronic states of Zn and Ga within the photocatalysts materials, respectively. The information from XAS-XES uniquely showed how the electronic structures of atoms in a material are altered and, together with additional structural insights gained by electron microscopy and X-ray diffraction, the exact functions of Zn-Ga heterojunction favourable for charge separation could be elucidated. The direct involvement of Rh-Cr component on the charge separation in Zn element was evidenced by means of XAS combined with a modulation excitation technique, explaining the electronic interactions of the two promoters and their concerted synergistic functions.

The data we obtained during the beamtime was analysed and the results were successfully published as M. Borges Ordoño, S. Yasumura, P. Glatzel, and A. Urakawa. *Phys. Chem. Chem. Phys*., 20 (2018) 23515.