Synergetic interplay of Zn and Rh-Cr promoters on Ga_2O_3 based photocatalysts for water splitting reaction

Marta Borges [a], **Atsushi Urakawa** [a, *]

[a] *Institute of Chemical Research of Catalonia (ICIQ), The Barcelona Institute of Science and Technology, 43007 Tarragona, Spain, * aurakawa@iciq.es*

Abstract: Zn and Rh-Cr modified Ga_2O_3 photocatalysts were evaluated for water splitting reaction under UV-light irradiation. Addition of 2 and 4 wt% of Zn and Rh-Cr (0.5-0.75 wt%) on Ga_2O_3 enhanced the efficiency for photocatalytic water dissociation. Synchrotron X-ray spectroscopic methods (XANES and VtC-XES) were used to elucidate the formation of $ZnGa_2O_4/Ga_2O_3$ heterojunction beneficial for the H_2 and O_2 production and to understand the roles of the Rh-Cr co-catalyst in directly boosting the changes in the electronic structure of Zn upon UV-light irradiation, synergetically boosting both red-ox activities.
Keywords: Photocatalysis, X-ray absorption, valance-to-core, modulation excitation spectroscopy.

1. Introduction

Photocatalytic water splitting has been actively studied over the past years for solar energy conversion. Hydrogen and/or oxygen can be generated over semiconductor materials from the reaction using light as activation energy source. Since the first report on TiO_2 from Fujishima and Honda,[1] a variety of photocatalytic metal oxides such as Ga_2O_3, have also been studied and reported to exhibit an excellent water splitting activity under UV-light. Ga_2O_3, particularly Zn-modified Ga_2O_3 reported by Sakata *et al.*,[2] is known to be one of the best performing photocatalysts for pure water splitting.[3] The photocatalytic efficiency can be further improved by loading a co-catalyst which possesses active sites to facilitate redox reactions and at the same time improves electron transfer within the semiconductor. Noble metals like Pt, Ru, and Rh as well as combinations of metal oxides such as NiO, RuO_2 and $Rh_{2-y}Cr_yO_3$ are commonly used as promoters.[4] Although the role of co-catalyst has been extensively studied, there are not many reports focused to elucidate how the electronic properties of a semiconductor are modified after such promoters are added. Since band gap measured by UV-Vis spectroscopy is often not enough to justify the observed photocatalytic activity, element-selective spectroscopic techniques, such the combination of synchrotron X-ray absorption and emission spectroscopies, can be employed to gain deeper insights about the electronic states of the semiconductors materials.[5]

2. Experimental

Photocatalysts (Zn-Ga_2O_3 and Rh-Cr/Zn-Ga_2O_3) were prepared by wet impregnation method of Zn from 0 to 70 wt% followed by calcination treatment at 850 °C for 6 h. After Zn addition, samples were also impregnated with Rh (0.5 wt%) and Cr (0.75 wt%), and further calcined in air at 350 °C for 3 h. Photocatalytic tests were performed at room temperature using a home-made reaction setup. The setup consisted of a slurry reactor made of quartz connected to a gas supply and a water trap. The reaction was followed by an online MS and the product quantification was verified by a microGC. 20 mg of catalyst was dispersed in 35 mL of Milli-Q water. This solution was kept under stirring during the reaction and under the continuous gas flow of N_2 (4.5 mL min^{-1}). A high-pressure Hg lamp (UV-Technik) of 400 W was used as a light source. Several on/off cycles were performed to study the catalyst activity.

X-ray absorption and valance-to-core emission spectroscopy (XAS and VtC-XES) measurements were performed at ID26 at ESRF (Grenoble, France). All the synthesized materials were measured *ex situ* in a pellet form containing 60 mg of material and 60 mg of cellulose with 13 mm diameter. *In situ* irradiation experiments were carried out with 200 mg of pure catalyst and DH-2000 deuterium-halogen light source.

3. Results and discussion

The highest H_2 productivity was achieved for Ga_2O_3 modified with 4 wt% of Zn (1.1 mmol H_2 g_{cat}^{-1} h^{-1}) and Rh-Cr (9 mmol H_2 g_{cat}^{-1} h^{-1}) in pure water under UV-Vis light. The formation of ZnO at high Zn concentrations was reflected on a productivity decrease due to the Zn aggregation and hindrance of light adsorption on Ga_2O_3.

Figure 1 shows the combination of XAS and VtC-XES measurements for Zn and Ga K-edge where at first two opposite trends can be observed from the absorption edges. The results confirmed the formation of $ZnGa_2O_4$ at small Zn concentrations (Figure 1a), while by increasing Zn wt% the coordination environment and zinc electronic state appeared to be like those of ZnO presenting a shorter valance-conduction band gaps (distance between the maximum of the emission spectra and the absorption edge). On the other hand, unoccupied states of Ga are shifted to higher energies with increasing the loading of Zn; meanwhile, occupied states remained unchanged with Zn addition (Figure 1b). The perturbation of the Ga_2O_3 conduction band could be explained by the formation of an interphase between Ga_2O_3 and $ZnGa_2O_4$ (known as heterojunction) at 2-4 wt% loading of Zn,[6] thus this would explain the enhanced photocatalytic efficiency due to the electron donation from $ZnGa_2O_4$ (CB at higher adsorption energies) to Ga_2O_3 (CB at lower adsorption energies).

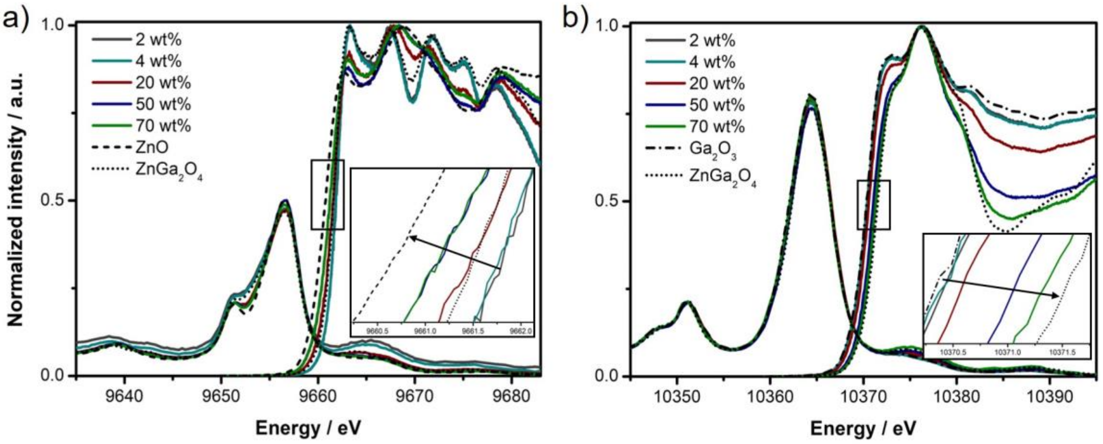

Figure 1. Combined XAS and VtC-XES for a) Zn K-edge and b) Ga K-edge. $ZnGa_2O_4$ (dotted line), ZnO (dashed line), and Ga_2O_3 (dot-dashed line) are also included. Spectral intensity was normalized to the maximum using PyMca software.

H_2 and O_2 production under UV light was promoted by the addition of Rh-Cr to Zn-Ga_2O_3 because of the main role of Rh-Cr co-catalysts as electron sink. In addition, absorption spectra of Zn (unoccupied-state electronic structure) in the presence of Rh-Cr and under *in situ* illumination manifested stronger electronic perturbations compared to those without Rh-Cr, clarified by sensitivity boosting enabled by modulation excitation spectroscopy. These results show that the presence of Rh-Cr co-catalyst modifies the degree of electronic structure changes of the Zn element by enhancing the charge separation and consequently boosting both water reduction and oxidation activity.

4. Conclusions

Great photocatalytic activity was achieved when small concentrations of Zn were added to Ga_2O_3 indicating the formation of a heterojunction between $ZnGa_2O_4$ and Ga_2O_3 that favors the electron transfer. The appearance of ZnO was detrimental for the overall photocatalytic activity due to the light absorption hindrance of Ga_2O_3. Rh-Cr promoters together with $ZnGa_2O_4$ boosted the photocatalytic activity of Ga_2O_3, which could be studied through deeper analysis of Ga and Zn electronic states.

References

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