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Supporting Information

Oxidative photo-deposition of chromia: Tuning the activity for overall water splitting of the Rh/CrO_x co-catalyst system

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Experimental Procedure

 Ga_2O_3 was synthesized by a chemical precipitation route from $Ga(NO_3)_3$ (≥ 99.9 %. Chempur) and Na_2CO_3 (≥ 99.9 %, VWR Chemicals) at pH 6 according to the method described by Behrens and co-workers.¹ After aging for 24 h at 55 °C and drying overnight, precipitated GaOOH was calcined in synthetic flowing air for 2 h at 750 °C to obtain pure β -Ga₂O₃. Photodeposition and water-splitting experiments were performed in a home-made quartz reactor (Scheme SI1) using an Hg lamp (Peschel) operated at 500 W with an intensity of 59 mW/cm² from 250-700 nm. For the detection of the evolved gases an on-line 3channel analyzer (Emerson) equipped with detectors for determination of the concentration of H₂ (thermal conductivity detector, detection limit 100 ppm), O₂ (paramagnetic detector, detection limit 100 ppm) and CO₂ (IR detector, detection limit 10 ppm) was used. Reductive photodeposition of Rh and CrO_x was performed using Na₃RhCl₆ · 2 H₂O and K₂CrO₄ as precursors in 50 ml methanol/500 ml H₂O and oxidative photodeposition of CrO_x using CrCl₂ precursor in 5 mmol NalO₃/550 ml H₂O, both at pH 7. All catalysts were filtrated, washed three times with H₂O and dried overnight at 100 °C. Overall water splitting experiments in the liquid phase were performed using 300 mg catalyst dispersed in 550 ml H₂O with a N₂ carrier gas flow of 50 sccm. X-ray diffraction measurement was performed with a PANalytical MPD diffractometer with Cu K_{α} radiation in a 20 range from 5° to 80°. Diffuse reflectance UV-Vis spectra were measured using a PerkinElmer Lambda 650 spectrophotometer and a Harrick Praying Mantis diffuse reflectance accessory. Spectra were recorded at ambient conditions from 800 nm to 220 nm with a resolution of 1 nm and 0.4 s integration time. BaSO₄ was used as internal 100 % reflectance standard. The band gap was determined from Tauc plots assuming a direct band gap transition for Ga₂O₃ based on the Kubelka-Munk function calculated from the reflectance spectra. DLS measurements where performed using a Malvern Zetasizer Nano ZS90 with a dispersion of 100 mg/L β-Ga₂O₃. Highresolution STEM studies were carried out on a Jeol JEM 2200fs microscope equipped with a probe-side Cs-corrector operated at 200kV acceleration voltage. Elemental analysis was carried out on a Perkin Elmer AAS Model AAnalyst 200. XPS measurements were performed in an ultrahigh vacuum (7x10⁻¹⁰ mbar) setup equipped with a monochromatic Al K_{α} X-ray source (1486.6 eV, anode operating at 14.5 kV and 30.5 mA) and a high-resolution Gammadata-Scienta SES 2002 analyzer. The spectra were recorded in a fixed transmission mode with 200 eV pass energy. Charging effects were compensated applying a flood gun, and binding energies were calibrated based on the aliphatic carbon species at a binding energy of 284.8 eV. Analysis and fitting of the recorded spectra were performed with a minimum number of peaks using the CasaXPS software.

[1] L. Li, W. Wei, M. Behrens, Solid State Sci. 2012, 14, 971-981.

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700 nm.

Optimization of co-catalyst loadings

CrO_x loading

Oxidative photodeposition of CrO_x

The optimized CrO_x loading for oxidatively photodeposited CrO_x was determined in three individual steps. First, different amounts of CrO_x were deposited, second, the optimized loading Rh was reductively deposited and, at last, the OWS activity was tested. Usually one should assume that the O_2 evolution in NaIO₃ solution directly correlate with the activity in oxygen evolution reaction (OER) during water splitting (Fig. SI5). However, under the conditions used in this study NaIO₃ decomposes and O_2 is evolved (under irradiation, without catalyst).

Photodeposition of CrO_x from water

The optimization of the CrO_x loading in water (Fig. SI5) was carried out in the same way, but without methanol as sacrificial agent. Therefore, evolved H₂ and O₂ were monitored.

Reductive photodeposition of CrO_x

The optimization of reductively deposited CrO_x (Fig. SI5) was performed in a 10 vol% methanol solution with 300 mg dispersed β -Ga₂O₃ in the photoreactor. 50 sccm N₂ was used in order to remove air and to transport produced gases to the analyzer. After complete degassing, aqueous solution of the K₂CrO₄ precursor equivalent to a loading of 0.02 wt% was added and the lamp was turned on. The concentration of evolved H₂ was measured. Subsequently, the light was turned off, K₂CrO₄ precursor was added and the evolved H₂ was measured. This procedure was carried out until the H₂ amount did not increase further.

Rh loading

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The optimization of the reductively deposited Rh loading was performed in the same way as the deposition of CrO_x from the K_2CrO_4 precursor solution. For the deposition of Rh an aqueous solution of Na_3RhCl_6 was used.



Additional Figures



Figure SI1. X-ray diffraction pattern of precipitated Ga_2O_3 calcined at 750 °C.



Figure SI2. SEM image of precipitated ${\rm Ga_2O_3}$ calcined at 750 °C.



Figure SI3. Particle size distribution of precipitated β -Ga₂O₃ calcined at 750 °C for 2 h determined by dynamic light scattering.



Figure SI4. Stepwise photodeposition of Rh on precipitated β -Ga₂O₃ (300 mg catalyst) to determine the optimum co-catalyst loading for hydrogen evolution.



Figure SI5. Optimization of CrO_x loading: a) Water splitting results of different amounts of photo-oxidatively deposited CrO_x and 0.04 wt.% Rh on β -Ga₂O₃. b) Stepwise reductive photodeposition of CrO_x in 10 vol% methanol on precipitated β -Ga₂O₃ to determine the optimum CrO_x loading. The peaks in the O₂ signal result from opening the reactor to add K₂CrO₄ solution. The optimum loading by reductive photodeposition was determined to be 0.1 wt%. c) Stepwise photodeposition of CrO_x in water on precipitated β -Ga₂O₃ to determine the optimum CrO_x loading. The peaks in the O₂ signal result from opening the reactor to add K₂CrO₄ solution. The optimum loading by reductive photodeposition was determined to be 0.1 wt%. c) Stepwise photodeposition. The optimum loading by photodeposition in water was determined to be 0.1 wt%.



Figure SI6. H₂ and O₂ evolution during the first 2 h of OWS of Ga₂O₃ with only one co-catalyst deposited. 0.1 wt% CrO_x was photo-deposited reductively, oxidatively and in water without sacrificial agent. 0.04 wt% Rh was photo-deposited reductively.





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Figure SI8. XPS survey spectra (left) and diffuse reflection UV-Vis spectra (right) of all three Rh/CrOx optimized Ga2O3 catalysts and pure Ga2O3.



Figure SI9. Electron energy loss spectrum of a Rh nanoparticle showing the characteristic peaks at 307 eV of the Rh-M₄ and Rh-M₅ edge and the characteristic peak at 496 eV of the Rh-M₃ edge. Due to carbon deposition around the Rh nanoparticle during the measurement the spectrum shows a high signal-to-noise ratio. For further comparison, please see the EELS spectrum of Rh₂O₃ in the EELS Atlas (C.C. Ahn, O.L. Krivanek).