Layered cesium copper titanate for photocatalytic hydrogen production

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ABSTRACT

Layered cesium copper titanate as well as the unmodified cesium titanate $Cs_{0.68}Ti_{1.83}\square_{0.17}O_4$ ($\square$: vacancy) were synthesized by a solution-based approach. The insertion of small amounts of copper into the vacancies of $Cs_{0.68}Ti_{1.83}\square_{0.17}O_4$ led to a significant red shift of the band gap energy from 3.4 eV to 2.9 eV. During photocatalytic H_2 production experiments, a steady increase in the evolution rate was detected, which can be referred to the *in-situ* reduction of incorporated copper ions to metallic Cu. The reduced copper ions leach out of the lattice to the catalyst surface and act as co-catalyst for H_2 formation, considerably exceeding the activity achieved with $Cs_{0.68}Ti_{1.83}\square_{0.17}O_4$ modified with 0.075 wt.-% of Rh as co-catalyst. The use of diffuse reflectance spectroscopy enabled a direct measurement of the copper nanoparticle formation by following their rising plasmon resonance at operating conditions. Characterization by X-ray diffraction (XRD) revealed a significant change in the crystal structure upon photocatalysis.

1. Introduction

The demand for hydrogen as an alternative fuel has grown steadily in recent decades [1]. Photocatalytic active materials for solar hydrogen production represent one promising solution for this increasing request. Nevertheless, most semiconductor materials suffer from large band gaps and fast electron hole recombination, and therefore of low quantum efficiency [2,3]. Two methods are commonly used to decrease the electron hole recombination: i) utilization of methanol [4], ethanol [5] or triethanolamine [6] as sacrificial agents acting as hole scavengers; and ii) deposition of noble metal particles like Rh [7,8], Au [9,10] and Pt [11,12] to establish Schottky contacts for electron trapping. In general, these two methods are applied together to achieve higher activities. However, these techniques are not cost effective because expensive critical metals as well as valuable chemical compounds are used.

Alternatively to critical noble metals, earth-abundant metals or metal oxides like Cu [13–15] and NiO_x [16,17] are deposited as co-catalysts for hydrogen generation. Investigations by Domen et al. [18] in 1998 initiated a revival of copper species as hydrogen evolution co-catalyst. Different publications characterize the active Cu surface component as Cu_2O or Cu/Cu_2O (core/shell) systems primarily investigated on TiO_2 [13,19,20]. The presence of Cu(I) species is verified by X-ray photoelectron spectroscopy (XPS) measurements [13,19]. Nevertheless, most of the commonly used characterization methods like XPS, X-ray diffraction (XRD), absorption spectroscopy, chemisorption, physisorption, transmission and scanning electron microscopy (TEM, SEM) provide only characterization data of the catalyst or co-catalyst status *ex-situ* before and after the photocatalytic process. In contrast, localized surface plasmon resonance (LSPR) spectroscopy enables an *in-situ* observation of the formation of the plasmon active co-catalyst during photocatalytic H_2 production and gives first insights of the actually operating co-catalyst [21].

The layered cesium titanate $Cs_{0.68}Ti_{1.83}\square_{0.17}O_4$ ($\square$: vacancy) consists of a lepidocrocite γ-FeOOH-type layered structure [22] and represents a good starting material for further modifications with regard to the incorporation of cations [23–25] and anions [26] for band gap reduction, due to its open layered structure and the theoretical amount of 0.17 equivalents of vacancies distributed in the titanium oxide sheets, which are spatially separated by cesium cations. This material enables a simple insertion of, for example, Mg, Fe, Co, Ni, Cu or Zn ions into the vacancies of the titanate sheets. Up to now, the cation modification and the synthesis of the base material have been mainly performed by solid state reaction (SSR) [23,24,27]. However, SSR requires high calcination temperatures [27] and long calcination times [28], resulting in a highly crystalline material but characterized by large particle sizes. A main drawback of the SSR for cation doping can be an inhomogeneous distribution of the inserted metal cation through the catalyst material because of the slow diffusion rate of ions in solids during the calcination period. Already in 2001 Sumida et al. presented

an alternative synthesis of $Cs_{0.68}Ti_{1.83}\square_{0.17}O_4$ by employing the polymerized complex (PC) method applying citrate ions and ethylene glycol as complexing agent [28]. Cation modification of materials prepared *via* solution-based routes can minimize the inhomogeneity issue because of the improved dispersion of the metal ions. Additionally, a solution-based method like the PC-route allows the synthesis of mixed metal oxides at lower calcination temperatures in shorter reaction times, as shown in this work.

In this paper, the properties of layered cesium copper titanate for photocatalytic H_2 generation are presented and discussed. The *in-situ* formation of metallic Cu as co-catalyst on the photocatalyst surface is followed by Cu LSPR, and an explicit effect on the long-term hydrogen evolution is observed. Structural changes after H_2 production are investigated in detail, leading to new insights into the tested photocatalyst.

2. Experimental

2.1. Catalyst preparation

Cesium copper titanates were synthesized by a complex-based process similar to the PC method [29–31]. The photocatalysts were synthesized by an aqueous citrate-based method [30–32]. The used quantities of the metal compounds correspond to the stoichiometric composition of $Cs_{0.68}Ti_{1.83}O_4$. Basing on this formula relative to cesium a 3 at.-% excess of Ti was used in the synthesis in order to obtain complete phase purity. In the synthesis of Cu containing cesium titanates, Copper ions were added to the synthesis batches in Cu: Cs atomic ratios of 1:7 and 1:14, respectively.These amounts were chosen in order to tune the amount of structural vacancies. Citric acid monohydrate and ethylene diamine tetra acetic acid (EDTA) were utilized as complexing reagents. 8.23 g (28.16 mmol) EDTA and 8.51 g (40.49 mmol) citric acid were dissolved in a mixture of 580 mL deionized water and 18.5 mL of 33% ammonium hydroxide solution. After adjusting the pH value at pH = 5 with 65% nitric acid (HNO_3), 1.36 g cesium nitrate ($CsNO_3$ Sigma Aldrich 99.99%) and 0.12 g or 0.24 g copper nitrate trihydrate ($Cu(NO_3)_2 \cdot 3H_2O$, Sigma-Aldrich, 99.99%), each dissolved in 25 mL deionized water, were inserted into the complexing reagent solution. Pre-diluted 6.53 mL titanium(IV)-*n*-butoxide (Sigma-Aldrich, > 97%) in 240 mL absolute ethanol were added to the mixture. After evaporation to approximately 25 mL at 373 K, the produced gel was transferred to a ceramic bowl and heated at 723 K. The so obtained powder precursor was calcined in air at 873 K for 10 h.

2.2. Characterization

XRD measurements were carried out to characterize the phase composition of the calcined samples. Diffraction patterns were recorded in reflection geometry with a PANalytical Empyrean Theta-Theta diffractometer equipped with a copper tube (K_α = 0.154 nm), 0.25° divergent slit, 0.5° anti scatter slit (incident beam), 7.5 mm high anti scatter slit (diffracted beam), incident and diffracted beam 0.04 rad soller slits, and position sensitive PIXcel-1d detector. The Cu-K_β emission line is suppressed by a nickel filter. For qualitative phase analysis the specimen were scanned in the 5–50° 2θ range with a step width of 0.0131° and 200 s collection time per step at an ambient temperature of 300 K.

UV–vis diffuse reflectance spectra were measured on a Varian Cary 4000 UV–vis spectrophotometer equipped with an integrating sphere. Spectra were collected in the range of 200–800 nm. MgO was used as a white standard material. Band gap energies were determined by constructing Tauc plots for an indirect semiconductor from the calculated Kubelka-Munk functions of the respective diffuse reflectance spectra. The band gap energies were estimated by extrapolation of the absorption edge to the energy axis of the Tauc plot. Investigation of the LSPR was performed on the above mentioned UV–vis spectrophotometer

under the same conditions. For the LSPR measurement 3 mL of the catalyst suspension were taken out of the reactor and transferred into a full quartz cuvette. The cuvette was placed in front of the integrating sphere. The MgO reference was placed on the back side of the cuvette to ensure all scattered light being reflected back to the detector.

The surface compositions of the prepared compounds, the chemical environment, oxidation states of the species of interest were investigated by XPS. Spectra were run on a Perkin-Elmer Φ 5600ci spectrometer using standard Mg radiation (1253.6 eV) working at 250 W, to avoid signal overlaps occurring by using the Al source. The working pressure was $< 5*10^{-8}$ Pa. The spectrometer was calibrated by assuming the binding energy of the $Au4f_{7/2}$ line at 83.9 eV with respect to the Fermi level. The standard deviation for the binding energy values was 0.15 eV. The reported binding energies were corrected for the charging effects by assigning the C1s line to a binding energy of 284.6 eV. Survey scans (187.85 pass energy, 0.4 eV/step, 25 ms per step) were obtained in the 0–1200 eV range. Detailed scans (29.35 eV pass energy, 0.1 eV/step, 100–150 ms per step) were recorded for the C1s, O1s, N1s, Ti2p, Ti_{LMM}, Cu2p, Cu_{LMM}, Cs3d regions. The atomic composition was evaluated, after a Shirley type background subtraction, using sensitivity factors supplied by Perkin Elmer. The assignment of the signals was carried out by using values reported in the reference handbook, in the NIST XPS database.

HR-TEM measurements were performed on a JEOL JEM2100F transmission electron microscope. Au sample grids with 200 meshes were used for HR-TEM measurements.

X-ray fluorescence spectroscopy (XFS) measurements for element analysis were performed on a Philips PW 2400 wavelength dispersive X-ray fluorescence spectrometer.

All energy dispersive X-ray spectroscopic measurements were performed on a Helios NanoLab 600i scanning electron microscope from FEI.

2.3. Photocatalytic hydrogen production

Photocatalytic H_2 production was performed in a double-walled semi-batch glass reactor. The reactor was cooled down to 283 K by a cryostat (Lauda) to prevent any thermal influence on the tested photocatalyst. The reaction medium consists of 550 mL water, 50 mL of methanol as a sacrificial agent, and 500 mg of the investigated photocatalyst. Before irradiation, the reactor was degassed in an Argon flow of 200 NmL. The catalyst suspension was irradiated with UV–vis light by a 500 W Hg mid pressure immersion lamp (Peschl Ultraviolet) without optic filters. During irradiation a carrier gas flow of argon (Ar 6.0) was set to 50 NmL/min by a mass flow controller for the transport of the produced gases to the detection unit. The evolved H_2 was detected by a thermal conductivity detector in a multi gas analyzer from Emerson.

3. Results and discussion

During incorporation of additional elements into the crystal structure of a metal oxide, the overall charge neutrality of the host material has to be kept. For the compensation of the Cu substitution, in principle a decrease in the titanium and cesium content or an increase in the vacancy amount may occur. X-ray fluorescence analysis for element determination was performed in order to clarify the accurate stoichiometric composition of the cesium copper titanates. According to the stoichiometry of $Cs_{0.63}Ti_{1.82}Cu_{0.05}O_4$ and $Cs_{0.64}Ti_{1.79}Cu_{0.1}O_4$ calculated from X-ray fluorescence measurements (table S1, S2 Supporting Information SI) for the obtained cesium copper titanates, the lowered cesium and titanium contents in comparison to $Cs_{0.68}Ti_{1.83}\square_{0.17}O_4$ lead to the conclusion of a dual A and B-site occupation by Cu ions or rather to a dual incorporation of Cu^+ ions into the titanate sheets and the interlayers.

Fig. 1 shows the XRD patterns and the Tauc plots of