



Photocatalytic properties of CoO_x -loaded nano-crystalline perovskite oxynitrides ABO_2N ($\text{A} = \text{Ca}, \text{Sr}, \text{Ba}, \text{La}$; $\text{B} = \text{Nb}, \text{Ta}$)



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ABSTRACT

Highly crystalline niobium- and tantalum-based oxynitride perovskite nanoparticles were obtained from hydrothermally synthesized oxide precursors by thermal ammonolysis at different temperatures. The samples were studied with respect to their morphological, optical and thermal properties as well as their photocatalytic activity in the decomposition of methyl orange. Phase pure oxynitrides were obtained at rather low ammonolysis temperatures between 740 °C (CaNbO_2N) and 1000 °C (BaTaO_2N). Particle sizes were found to be in the range 27 nm–146 nm and large specific surface areas up to 37 m² g⁻¹ were observed. High photocatalytic activities were found for CaNbO_2N and SrNbO_2N prepared at low ammonolysis temperatures. CoO_x as co-catalyst was loaded on the oxynitride particles resulting in a strong increase of the photocatalytic activities up to 30% methyl orange degradation within 3 h for $\text{SrNbO}_2\text{N}:\text{CoO}_x$.

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1. Introduction

Quaternary oxynitrides are promising materials for applications such as pigments [1–4], phosphors for LED [4,5], photocatalysts [6,7] and dielectrics [8–10]. Oxynitrides containing e.g. Ti, Nb or Ta possess band gaps in the visible light region and have been studied with respect to their optical and photocatalytic properties in different test reactions including visible-light photocatalytic water splitting [11,12], air purification [13] and wastewater treatment [14]. The photocatalytic properties of oxynitrides can often be improved by using soft chemistry synthesis methods to increase their specific surface or by combining them with metal- or oxide-based co-catalysts. For example the photocatalytic activity at wavelengths $\lambda \geq 600$ nm of the $\text{LaMg}_x\text{Ta}_{1-x}\text{O}_{1+3x}\text{N}_{2-3x}$ series is enhanced by RhCrO_y -loading and titanium oxyhydroxide coating [15].

In a recent study, a hydrothermal synthesis route was established yielding single crystalline nano-particles of CaTaO_2N with high specific surface areas, low strain and enhanced thermal stability. The samples showed improved optical and photocatalytic activities in the methyl orange degradation compared to

reference samples prepared by the conventional mixed-oxide method [16]. CoO_x -loading led to a further pronounced increase of the photocatalytic performance of CaTaO_2N in the decomposition of organic molecules in solution. Such decomposition experiments of organic dyes can act as test reactions for photocatalytic water treatment, e. g. cleaning of drug-contaminated hospital sewerage or purification of drinking water. In our studies methyl orange was chosen as model substance because it is a carcinogenic diazo-compound and stable under the used reaction conditions (irradiation at wavelengths $\lambda \geq 300$ nm) in the absence of a photocatalyst. In this article, the above-mentioned hydrothermal synthesis of CaTaO_2N nanoparticles is expanded to various quaternary niobium and tantalum containing oxynitride perovskites. To avoid particle agglomeration and formation of defects or by-products and in turn to obtain improved photocatalytic properties, the ammonolysis temperature was chosen as low as possible. We report on morphological, optical, thermal and photocatalytic properties of these oxynitrides. It is shown that the hydrothermal synthesis leads to oxide precursors with different reactivities during ammonolysis and finally to oxynitrides with enhanced photocatalytic activities. CoO_x as co-catalyst was also successfully applied. For the sample with the highest activity a 30% degradation after 3 h ($\lambda \geq 300$ nm) and 25% decomposition under visible-light irradiation ($\lambda \geq 420$ nm) was achieved.

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2. Experimental methods

Hydrothermal synthesis of the ABO_y oxide precursors was carried out based on previously reported procedures [16,17]. The Ca- and La- containing oxide precursors were prepared by dissolving $Ca(NO_3)_2 \cdot 4 H_2O$ (0.7776 g, 3.3 mmol, Alfa Aesar, $\geq 99\%$) or $La(NO_3)_3 \cdot 6 H_2O$ (1.3250 g, 3.06 mmol, Alfa Aesar, 99.9%) in dry ethanol (20 mL). Afterwards $TaCl_5$ (1.0738 g, 3.0 mmol, Alfa Aesar, 99.99%) or $NbCl_5$ (0.8105 g, 3.0 mmol, Alfa Aesar, 99%) was added to these solutions. An excess of 10 mol% Ca or 2 mol% La, respectively, was used to avoid the formation of tantalum-rich by-products like Ta_3N_5 . After stirring for 1 min, the solutions were transferred into Teflon containers filled with a solution of KOH (2–3 g) in distilled water (80 mL). The resulting white suspensions were heated in an autoclave under stirring at 383 K for 18 h.

The synthesis of Sr- and Ba-containing oxide precursors was carried out in a similar way by dissolving $Sr(NO_3)_2$ (0.6984 g, 3.3 mmol; Alfa Aesar, 99%) or $Ba(NO_3)_2$ (0.8624 g, 3.3 mmol; Alfa Aesar, 99%) and KOH (4–6 g) in distilled water (50 mL). To these solutions, $TaCl_5$ (1.0738 g, 3.0 mmol) or $NbCl_5$ (0.8105 g, 3.0 mmol) in 50 mL dry ethanol was added. An excess of about 10 mol% Sr or Ba was used. The resulting white suspensions were heated in an autoclave under stirring at 383 K for 18 h.

The obtained powders were collected, washed with water until no chloride ions were detectable, afterwards washed twice with ethanol and acetone and dried overnight at room temperature.

About 100 mg of each precursor was placed on an alumina boat in a tube furnace (Carbolite STF-15-180) which was flushed with ammonia before heating. Depending on their chemical composition, the oxide precursors were heated in flowing ammonia (Linde 99.998%, gas flow 5 L/h), at temperatures between 740 °C and 1000 °C for 10 h (heating rate: 5 K/min). The samples were cooled to room temperature in NH_3 -atmosphere.

To remove traces of carbonates, the sample $BaNbO_2N$ was additionally washed after ammonolysis with diluted acetic acid, water and dried overnight.

Powder X-ray diffraction (XRD) patterns of the oxynitrides were collected on a Bruker D8 Advance diffractometer ($Cu-K_\alpha$ radiation) equipped with a LynXEye detector in the range 10° – $120^\circ 2\theta$ with a step size of 0.0053° and a counting time of 2 s per data point. To determine the size and strain parameters Rietveld refinements were carried out using the FullProf software suite [18]. A Thompson-Cox-Hastings pseudo-Voigt function was used to determine the crystallite size and strain parameters from peak broadening.

SEM images were recorded on a Philips ESEM XL 30 FEG electron microscope using the backscattering electron detection mode.

Five-point BET measurements were carried out in the p/p_0 range between 0.05 and 0.25 with a Quantachrome NOVA 100. Particle sizes were estimated from the specific surface area assuming spherical particle shapes.

To determine the thermal stability of the oxynitrides, thermogravimetric analysis was carried out using a Netzsch STA 449C thermo balance applying a gas flow of 20 mL/min synthetic air and a heating rate of 10 K/min up to 1200 °C. The samples were placed in Al_2O_3 crucibles.

Diffuse reflectance UV–Vis spectra were measured with a Perkin Elmer Lambda 19 spectrometer in the wavelength range 300 nm–800 nm. $BaSO_4$ was used as white standard. The bandgap was determined applying the Kubelka–Munk function and assuming an indirect allowed band gap transition. Additionally, the Shapiro interpolation method of the linear parts of the absorbance spectra was adopted [19].

Photocatalytic methyl orange degradation was performed by suspending the sample powders in a 50 μM aqueous solution of

methyl orange (Feinchemie K.-H. Kallies KG, p.a.). The used catalyst concentration was adjusted at 200 mg/L. 3.3 mL of the suspensions were irradiated for 3 h with a 150 W Xenon arc lamp (LOT-Oriel) in a closed vessel under stirring. For irradiation with UV/Vis light or solely visible light, different wavelength filters were used (300 nm, 420 nm). After the photocatalytic reactions, the suspensions were centrifuged and the methyl orange concentrations were determined by UV/Vis-spectroscopy (UV-3100 PC, VWR) at the wavelength $\lambda = 467$ nm.

CoO_x -loading of the photocatalyst was done as described in literature [20,21]. For the impregnation $Co(NO_3)_2 \cdot 6 H_2O$ (Merck, p.a.) was dissolved in demineralized water (3 mL) and about 30 mg of the oxynitride powder was suspended. The amount of $Co(NO_3)_2 \cdot 6 H_2O$ was adjusted to 2 wt% Co ions with respect to the oxynitride powders. The suspensions were treated for 5 min in an ultrasound bath and afterwards the solvent was slowly evaporated under heating. The resulting powders were heated first in flowing ammonia atmosphere at 700 °C ($CaNbO_2N$: 650 °C) for 1 h, leading to metallic Co-nanoparticles. The active CoO_x co-catalyst was obtained by mild oxidation in air at 200 °C for 60 min.

3. Results and discussion

The optical and photocatalytic properties of the obtained oxynitrides were found to be strongly influenced by the reactivities of the oxide precursors during ammonolysis, which depend on their chemical composition and their specific surface areas. In all cases, phase pure oxynitrides were obtained (Fig. 1) after 10 h ammonolysis at rather low temperatures in the range 740 °C ($CaNbO_2N$) to 1000 °C ($BaTaO_2N$). Remarkably, $CaNbO_2N$ can be synthesized as a phase pure compound from the hydrothermal oxide precursor at the low ammonolysis temperature of 740 °C. In contrast, the synthesis of phase pure $CaNbO_2N$ from $Ca_2Nb_2O_7$ or $CaCO_3/Nb_2O_5$ mixtures is not possible due to the necessarily higher ammonolysis temperatures, which cause the formation of different niobium(oxy-)nitrides NbO_xN_y [8,22,23]. As a general trend, the niobium containing oxide precursors are more reactive than the corresponding tantalum compounds, resulting in smaller crystallite sizes of the obtained oxynitrides. Rietveld refinements of the XRD patterns were carried out to determine the crystallite sizes and relative strain parameters of the different compounds. While the Ca-, Sr- and La- containing oxynitrides have relatively low crystallite sizes of approximately 20–40 nm, the samples $BaNbO_2N$ and $BaTaO_2N$ show significantly higher crystallite sizes of about 100 nm and 76 nm, respectively. Possible reasons are the higher ammonolysis temperatures of 1000 °C ($BaTaO_2N$) and 950 °C ($BaNbO_2N$), respectively, which were necessary to obtain phase pure products, and the lower specific surface areas of the Ba-containing oxide precursors (Table 1). The calculated strain parameters also depend on ammonolysis temperature and chemical composition. It was found that $BaNbO_2N$ and $BaTaO_2N$ exhibit higher strain parameters (18–22) than the other samples, for which values between 5 and 15 were found. These small strains indicate comparatively few crystal defects in the Ca-, Sr- and La-containing oxynitrides (Table 1). Fig. 1b illustrates the peak broadening of the various samples depending on crystallite size, strain and space group.

The Ca- and Sr-containing oxynitrides possess large specific surface areas up to 37 $m^2 g^{-1}$ in the case of $CaNbO_2N$ (Table 1). $SrTaO_2N$ and $SrNbO_2N$ also exhibit surface areas above 20 $m^2 g^{-1}$ which are comparatively high values for oxynitrides. With increasing ammonolysis temperatures and decreasing specific surfaces of the oxide precursors, also the BET surfaces of the final oxynitrides become smaller and in turn the calculated particle sizes increase. The comparison of the crystallite sizes (XRD) and the particle sizes (BET) leads to nearly identical values as shown in

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