Photocatalytic activity of CaTaO₂N nanocrystals obtained from a hydrothermally synthesized oxide precursor

Florian Oehler[†], Robert Naumann[†], Roberto Köferstein[†], Dietrich Hesse[§], and Stefan G. Ebbinghaus[†],

[†] Institute of Chemistry, Martin-Luther-University Halle-Wittenberg, Kurt-Mothes-Straße 2, D-06120 Halle (Saale), Germany.

[§] Max Planck Institute of Microstructure Physics, Weinberg 2, D-06120 Halle (Saale), Germany.

ABSTRACT. Highly crystalline CaTaO₂N nanoparticles possessing large specific surface areas were investigated as photocatalysts for the decomposition of methyl orange. Two different Ca₂Ta₂O₇ precursors were synthesized by classical solid state synthesis and a hydrothermal soft-chemistry approach, respectively. In both cases, nitridation was carried out by thermal ammonolysis. The obtained CaTaO₂N samples were compared with respect to their optical, thermal and morphological properties as well as their photocatalytic activities. In particular, the influence of ammonolysis temperature on the photocatalytic properties was studied. Using hydrothermally synthesized Ca₂Ta₂O₇, phase pure CaTaO₂N was obtained already at a relatively low ammonolysis temperature of 860 °C. Morphological investigations show that the CaTaO₂N samples from the hydrothermally synthesized precursor consist of single-crystalline particles of 45 to 70 nm diameter with high specific surface areas between 12 and 19 m² g⁻¹, depending on ammonolysis temperature. A considerable photocatalytic activity for methyl orange degradation was found for the nanoscaled CaTaO₂N particles prepared at lower ammonolysis temperatures. Using CoO_x as co-catalyst, a further strong enhancement of the methyl orange decomposition by a factor 5-10 was achieved.

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[§] Max Planck Institute of Microstructure Physics, Weinberg 2, D-06120 Halle (Saale), Germany

E-mail: stefan.ebbinghaus@chemie.uni-halle.de

ABSTRACT. Highly crystalline CaTaO₂N nanoparticles possessing large specific surface areas were investigated as photocatalysts for the decomposition of methyl orange. Two different Ca₂Ta₂O₇ precursors were synthesized by classical solid state synthesis and a hydrothermal soft-chemistry approach, respectively. In both cases, nitridation was carried out by thermal ammonolysis. The obtained CaTaO₂N samples were compared with respect to their optical, thermal and morphological properties as well as their photocatalytic activities. In particular, the influence of ammonolysis temperature on the photocatalytic properties was studied. Using hydrothermally synthesized Ca₂Ta₂O₇, phase pure CaTaO₂N was obtained already at a relatively low ammonolysis temperature of 860 °C. Morphological investigations show that the CaTaO₂N samples from the hydrothermally synthesized precursor consist of single-crystalline particles of 45 to 70 nm diameter with high specific surface areas between 12 and 19 m² g⁻¹, depending on ammonolysis temperature. A considerable photocatalytic activity for methyl orange degradation was found for the nanoscaled CaTaO₂N particles prepared at lower ammonolysis temperatures. Using CoO_x as co-catalyst, a further strong enhancement of the methyl orange decomposition by a factor 5-10 was achieved.

INTRODUCTION

Oxynitrides are promising materials for technical applications, such as pigments^{1,2}, photocatalysts³⁻⁸, phosphors for LED⁹ and dielectrics^{10,11}. Ternary and quaternary oxynitrides containing group 4 and group 5 elements are also promising candidates for photocatalytic water splitting^{3,12,13} as well as wastewater treatment¹⁴⁻¹⁶. Tantalum based oxynitrides have been well studied with respect to their optical properties. Their band gaps increase in the row BaTaO₂N (1.8 eV), SrTaO₂N (2.1 eV) to CaTaO₂N (2.4 eV), correlating with a change in color from brown (BaTaO₂N) to orange (SrTaO₂N) and yellow (CaTaO₂N)¹⁰. These values make tantalum oxynitrides promising candidates as visible light-driven photocatalysts. The photocatalytic properties of oxynitrides can in many cases be improved by combining them with metal- or oxide-based co-catalysts. For example the solid solution of BaTaO₂N and BaZrO₃ shows a considerable photocatalytic activity for water splitting under irradiation with visible light^{4,6}. Loading with co-catalysts like Pt for hydrogen generation or IrO₂ or RuO₂ for oxygen formation is another example for enhancing the photocatalytic reactivity^{8,17,18}. Replacing IrO₂ by the cheaper, more abundant CoO_x leads to a further improvement of the photocatalytic potential of oxynitrides like LaTiO₂N¹⁹. In a recent study, CoO_x-loaded LaTiO₂N was found to show significant higher activities for oxygen generation from water than the unloaded material⁵.

The current research mainly focuses on photocatalytic water splitting using sacrificial agents like methanol and Ag⁺. On the other hand, photocatalytic wastewater treatment is another highly interesting use for oxynitrides²⁰⁻²⁴. Possible applications are treatment of hospital sewerage containing pharmaceutical substances as well as processing of drinking water. In these applications complex mixtures of various organic compounds with varying compositions may occur, while for research purposes simple model substances are usually investigated. These model substances should be representatives for compounds occurring in the real application and should be stable under reaction conditions, i.e. no decomposition should take place without catalyst. Methyl orange was chosen in this

study as it fulfills both requirements. It is a diazo-compound, many of which are known to be carcinogen (like methyl orange itself) and it is stable under irradiation with light having wavelengths ≥ 300 nm, while UV-irradiation causes considerable decomposition even without a photocatalyst. In this article we report on the synthesis of the oxynitride CaTaO_2N from an oxide precursor obtained by a hydrothermal reaction and its optical, thermal and photocatalytic properties. For comparison, CaTaO_2N from $\text{Ca}_2\text{Ta}_2\text{O}_7$ prepared by solid state synthesis was also studied. For both synthesis routes the effect of ammonolysis temperature on crystallite size, BET surface, nitrogen content, optical and photocatalytic properties were systematically studied. It is shown that the hydrothermal route leads to oxynitrides with large surface areas, very high crystallinity, small particle sizes, and enhanced photocatalytic activity. The effect of CoO_x as co-catalysts was also successfully tested. For the sample with the highest activity, a 20 % degradation was achieved already after 3 h of irradiation with light of wavelengths $\lambda \geq 300$ nm.

EXPERIMENTAL METHODS

Solid state synthesis of $\text{Ca}_2\text{Ta}_2\text{O}_7$ powders (samples based on this synthesis route are denoted as S-samples in the following) was carried out by grinding a mixture of CaCO_3 (1.0110 g, 10.1 mmol, Solvay, p. a.) and Ta_2O_5 (2.2095 g, 5.0 mmol, Alfa Aesar, 99%) in a polyamide milling bowl with agate balls under isopropanol (7 mL). To avoid the formation of tantalum-rich by-products, a small excess of 1 mol% CaCO_3 was used. The mixture was calcinated at 1300 °C for 12 hours (heating rate: 10 K/min to 800 °C, 5 K/min to 1300 °C).

The hydrothermal $\text{Ca}_2\text{Ta}_2\text{O}_7$ precursor (H-samples) was prepared based on the procedure described in Ref.²⁵ with some modifications. $\text{Ca}(\text{NO}_3)_2 \cdot 4 \text{H}_2\text{O}$ (0.7776 g, 3.3 mmol, Alfa Aesar, $\geq 99\%$) was dissolved in 20 mL dry ethanol and TaCl_5 (1.0738g, 3.0 mmol, Alfa Aesar, 99.99%) was added to this

solution. An excess of 10 mol% Ca was used to avoid the formation of Ta_3N_5 during ammonolysis. After stirring for 1 minute, the solution was loaded into a Teflon container filled with a solution of KOH (2g) in distilled water (80 mL), which acted as hydrolyzing/precipitation agent. The resulting white suspension was heated in an autoclave at 383 K for 18 h under stirring. The obtained powder was filtered off, washed with water until no chloride ions were detectable and afterwards washed twice with ethanol and acetone and dried overnight. This oxide and its corresponding oxynitride (see below) were tested by SEM/EDX for remaining potassium. As shown in the supporting information, no traces of K were detected.

Both types of oxide precursors (S- and H-) were heated in flowing ammonia (Linde 99.998%, gas flow 5 L/h). About 200-300 mg of each precursor was filled in an alumina boat, placed in a tube furnace, which was flushed with ammonia gas before heating, and reacted at temperatures between 860 °C and 950 °C for 10 h (heating rate 10 K/min).

Powder X-ray diffraction (XRD) patterns were recorded on a Bruker D8 Advance diffractometer with LynXEye detector in the angular range $10^\circ - 120^\circ 2\theta$ with a step size of 0.0053° and a counting time of 1 s per data point. For Rietveld refinements, the FullProf software suite was applied²⁶. A Thompson-Cox-Hastings pseudo-Voigt function was used and the crystallite size and relative strain was determined from peak broadening. For quantification of the oxynitride content of oxide/oxynitride mixtures the ratio of peak areas between $2\theta = 27.92^\circ - 30.90^\circ$ (oxide) and $2\theta = 31.34^\circ - 32.75^\circ$ (oxynitride) was used (see supporting information). The values were calibrated with oxide/oxynitride mixtures of known composition.

Five-point BET measurements were carried out with a Quantachrome Corporation NOVA 1000 in the p/p_0 range between 0.05 and 0.25 to determine the specific surface area. Additional BET-isotherms

were collected in the range $0.06 \leq p/p_0 \leq 0.99$ with a step size of 0.05. Particle sizes were estimated from the specific surface area assuming spherical or cubic particles.

UV-Vis-spectra were measured in diffuse reflectance modus with a Perkin Elmer Lambda 19 spectrometer in the range of 300 – 800 nm using BaSO₄ as white standard. The bandgap was determined applying the Kubelka-Munk-equation assuming an indirect allowed band gap transition. For comparison the Shapiro method of interpolation the linear parts of the absorbance spectra was additionally applied²⁷.

To determine the nitrogen contents of the samples, thermogravimetric analysis was carried out using a Netzsch STA 449C thermo balance applying a heating rate of 10 K/min up to 1200 °C and a gas flow of 20 ml/min synthetic air. Samples were placed in Al₂O₃ crucibles.

Infrared spectra were collected on a Bruker Alpha FT-IR spectrometer with ATR-module in the spectral range of 4000 - 400 cm⁻¹ with a resolution of 4 cm⁻¹ in absorbance mode on a diamond crystal. For semi-quantitative analysis, the spectra were normalized in the wavelength region between 2000 cm⁻¹ and 400 cm⁻¹.

SEM-images were recorded on a Philips ESEM XL 30 FEG microscope using a backscattering electron detector. TEM investigations were carried out on a Philips CM 20T electron microscope with an acceleration voltage of 200 kV.

Photocatalytic activities were determined by suspending the sample powders in a solution of methyl orange (50 µM, Feinchemie K.-H. Kallies KG, p.a.) in distilled water. The used concentration of the oxynitride catalyst was 200 mg/L. 3.3 mL of the suspension was irradiated under stirring for 3 hours in a closed vessel with a 150 W Xenon arc lamp (LOT-Oriel). Different wavelength filters were used (300 nm, 420 nm) according to irradiation with UV/Vis-light or purely visible light. After irradiation,

the catalyst was centrifuged and the concentration of methyl orange was determined at $\lambda = 467$ nm using a spectrophotometer (UV-3100 PC, VWR).

CoO_x-loading of the oxynitride samples was carried out as described in literature^{5,19}. For the impregnation, Co(NO₃)₂ · 6 H₂O (Merck, p.a.) was dissolved in dematerialized water (3 mL) and about 100 mg of the oxynitride was suspended. The amount of Co(NO₃)₂ · 6 H₂O corresponds to 2 wt% Co ions with respect to the oxynitride. The suspension was treated for 5 min in an ultrasound bath and afterwards slowly evaporated under heating. The resulting powders were heated in ammonia atmosphere at 700 °C for 1 h and subsequently in air at 200 °C for 60 minutes.

RESULTS AND DISCUSSION

The properties of the CaTaO₂N powders were found to be strongly influenced by both the synthesis route of the Ca₂Ta₂O₇ precursor and the ammonolysis temperature. The oxide from the hydrothermal synthesis (H-oxide) showed very broad diffraction peaks in the XRD-pattern as shown in Figure 1.

The reaction temperature of 110 °C was chosen to avoid the formation of K₂Ta₂O₆, which crystallizes at higher synthesis temperatures²⁵. After calcination of the H-oxides at 1000 °C for 2 hours no K-containing compounds were detectable in the XRD pattern. Furthermore, no Ca-rich phase was found although an excess of 10 mol% Ca was used in hydrothermal synthesis. Instead, all peaks could be assigned to Ca₂Ta₂O₇ (PDF-card 44-1008). This can be explained either by the presence of an amorphous Ca-rich phase or more like by a fraction of Ca-ions remaining dissolved in the reaction mixture or being leached out during washing. From solid state synthesis (S-oxide), also phase pure Ca₂Ta₂O₇ was obtained but with a much higher crystallinity as reflected by the smaller peaks width (Fig. 1). While the S-oxide has only a low specific BET surface area of 2.7 m² g⁻¹, hydrothermal synthesis leads to a much larger BET area of 183 m² g⁻¹ (Tab. 1). The full BET-isotherm of the H-oxide

shows a hysteresis at high p/p_0 values as shown in Fig. 2a, indicating mesoporosity of the material.

TEM images of the H-oxide show strong agglomerated particles well below 10 nm diameter (Fig. 3a).

Both oxide precursors were ammonolyzed at four different temperatures, namely 860 °C, 890 °C, 920 °C and 950 °C. While the ammonolysis of the H-oxide resulted in phase-pure CaTaO_2N (PDF-card 50-1174) for all temperatures, ammonolysis of the S-oxide at 860 °C led to an oxide/oxy-nitride mixture (Fig. 4). From the XRD pattern, the composition of the phase mixture oxide/oxy-nitride = 0.84/0.16 (w/w) was estimated (see supporting information). Upon ammonolysis at higher temperatures, i.e. ≥ 890 °C, phase-pure CaTaO_2N was obtained.

Rietveld analysis of the oxy-nitride powders was carried out to determine the crystallite sizes and relative strains of the different samples. With increasing ammonolysis temperature, the crystallite sizes of both the S- and H-samples increase (Tab. 2). The crystallite sizes of the H-oxy-nitrides range from approximately 40 to 70 nm and are significantly smaller than those of the S-samples ammonolysed at the same temperatures (50-110 nm). The strain of the oxy-nitride samples also strongly depends on the synthesis method. The H-oxy-nitrides exhibit lower relative strains (in the range 10-20), than the S-oxy-nitrides (20-30) indicating higher crystallinity, i.e. fewer crystal defects. In addition, the H-oxy-nitrides have larger specific BET surface areas ($12\text{-}19\text{ m}^2\text{ g}^{-1}$), which corresponds to smaller particle sizes (45-70 nm; see Table 1) than the ammonolyzed S-precursors, which have in most cases specific BET areas between 7 and $10\text{ m}^2\text{ g}^{-1}$ (corresponding to 85-120 nm particle size). With increasing nitridation temperature, the BET surface area of the ammonolyzed H-samples becomes smaller (Fig. 2b). The TEM image of the H-oxy-nitride ammonolyzed at 950 °C illustrates the small particle size and high crystallinity of the samples obtained from the hydrothermal synthesis route (Fig. 3b). In figure 3d the electron diffraction pattern of one isolated particle is shown. The sharp diffraction spots evidence a very high crystallinity. Furthermore, the diffraction pattern can conclusively be indexed revealing that each particle basically consists of one single crystal.

This finding is corroborated by the fact that the crystallite sizes (determined from XRD) and the particle sizes (from BET) of the H-oxynitrides are nearly identical as shown in Figure 2b. In contrast, the S-sample ammonolyzed at 950 °C consists of strongly agglomerated particles of roughly 500 nm diameter, while the dimension of the agglomerates is in the micrometer range as can be seen from Fig. 3c.

Thermogravimetry was carried out for determination of the thermal stability and to estimate the nitrogen contents of the oxynitrides. Fig. 5 shows as an example the thermal behavior of the H- and S-samples ammonolyzed at 950 °C. The reoxidation of the oxynitride samples in synthetic air can be divided into four regions. The very low mass decrease below roughly 400 °C corresponds to the release of physisorbed water and possibly the decomposition of carbonates. The following strong mass increase in the temperature range 400-650 °C is explained by formation a reoxidation intermediate containing chemically bonded di-nitrogen^{28,29}. The final weight loss is due to release of N₂, leading to the fully reoxidized product. The mass difference between the end of step 1 and the beginning of step 4 corresponds to the released nitrogen, which is replaced by oxygen according to $2 \text{N}^{3-} + 3/2 \text{O}_2 \rightarrow 3 \text{O}^{2-} + \text{N}_2$. A different thermal stability was found for the two synthesis routes. While the reoxidation of the S-sample already starts at 420 °C, the reoxidation of the H-sample begins at a clearly higher temperature of 550 °C. Remarkably, although the H-samples have smaller particle sizes and higher surface areas, their thermal stability is higher than the one of the S-samples. This can be explained by the better crystallinity and fewer defects of these compounds. From the weight gain (Δm) the nitrogen content was estimated according to a previously reported formula²⁰. The obtained values are listed in Table 2. Apart from the S-sample ammonolyzed at 860 °C, which consists of a mixture of the unreacted oxide and the oxynitride all samples exhibit similar nitrogen contents in the range of 0.9. It should be noted, though, that thermogravimetrically determined nitrogen stoichiometries are often dependent on the thermal history and in many cases are too small. For example, phase pure samples of

LaTiO₂N show an apparently too low nitrogen content^{24,30}. The values reported here should therefore be considered as a lower limit only.

In an alternative approach, the nitrogen incorporation was also investigated by IR-spectroscopy. In comparison to Ca₂Ta₂O₇, after ammonolysis two additional broad peaks appear at 952 cm⁻¹ and 904 cm⁻¹ as depicted in Fig. 6a,b. The peak at 952 cm⁻¹ allows a semi-quantitative analysis of the nitrogen content. For the S-sample ammonolyzed at 860 °C a lower intensity of this peak was observed in accordance with its incomplete reaction, while the other samples show basically identical intensities supporting the TG results. Using Lambert-Beer's law and assuming complete nitridation for the other samples, an oxide/oxynitride ratio of 0.85/0.15 was calculated for the sample S-860 °C, which is in good agreement with the XRD and TG-results (16% and 21 %, respectively).

The oxynitrides obtained from the hydrothermal and solid state synthesis also show deviating optical properties. For the H-oxynitrides the slopes of the band edges are steeper and the reflectivities above 600 nm of are higher compared to the corresponding S-samples as shown in Figure 7 (The S-sample ammonolyzed at 860 °C is not shown because of its incomplete reaction). Visually, the yellow colors of the H-oxynitride are brighter, which is advantageous for a possible application as pigments.

These findings again reflect the better crystallinity of the H-oxynitrides. On the other hand, the band gaps of the H-oxynitrides are not significantly different from the ones of the S-oxynitrides. For all samples, values in the range 2.4 eV – 2.5 eV were found (Tab. 2), in accordance with earlier reports¹⁰. An indirect band gap transition was assumed according to a McLean-analysis^{31,32}. For both S- and H-samples the band gaps decrease slightly with increasing ammonolysis temperature as depicted in Figure 8 but the changes are only slightly above the estimated standard deviation of the method.

The IR-spectra of the CoO_x-loaded samples prove the complete decomposition of Co(NO₃)₂ · 6 H₂O during ammonolysis, because no NO₃-vibration modes were detected. The CoO_x-loaded samples show

a slightly higher absorbance at high wavenumbers and the yellow color of the CaTaO_2N samples turns to green after CoO_x -loading. The corresponding UV-Vis spectra are shown in the supporting information.

As pointed out in the introduction, the photocatalytic methyl orange decomposition can be used as a test reaction for the purification of water from (potentially) carcinogen diazo-compounds. Therefore, the influence of synthesis method, ammonolysis temperature, irradiation wavelength and CoO_x -loading on the photocatalytic activity was studied in detail. It should be stressed that the test reactions were carefully controlled and repeated several times. The reproducibility can be estimated to be within 10 % relative error. XRD analysis of the used photocatalyst proves the stability of the catalyst during photocatalysis. After irradiation for three hours, all CaTaO_2N samples show considerable photocatalytic activities when illuminated with UV/Vis-light ($\lambda \geq 300 \text{ nm}$) as listed in Table 3.

Oxynitrides obtained from the hydrothermal oxide exhibited higher activities but the absolute values were rather low ($< 2\%$). In contrast, no methyl orange decomposition was detected after irradiation with visible light ($\lambda \geq 420 \text{ nm}$). The measured decomposition rates clearly depend both on the synthesis method and the ammonolysis temperature. For the oxynitrides from the solid state synthesis the activity under UV/Vis-irradiation shows a maximum at the intermediate ammonolysis temperature of 920°C and decreases with higher ammonolysis temperature as depicted in Fig. 9b. The same trends were observed both for the pure oxynitrides and the samples loaded with CoO_x co-catalyst. Similar results were already reported for LaTiO_2N -samples in the photocatalytic acetone decomposition²⁴ as well as for the photocatalytic hydrogen evolution from water-methanol mixtures with nitridated $\text{Sr}_2\text{Nb}_2\text{O}_7$ photocatalysts³³. It was argued that surface area, nitrogen content, band gap and crystallinity of the samples have an influence on the photocatalytic activity. Because the band gap is very similar for all samples used in this study, the influence of specific surface area and crystallinity can be studied in detail here. The H-oxynitrides are the most promising candidates for photocatalysis, because they have

large specific surface areas and steeper band edges than the S-samples. Additionally, the H-samples consist of small single crystals with comparably low strain, which may also be advantageous for photocatalysis. Loading of the samples with CoO_x led to a considerable increase of the photocatalytic activity, even under irradiation with visible light. The activity of the CoO_x -loaded S-samples for $\lambda \geq 420$ nm increases with increasing ammonolysis temperature. A remarkable exception is the (incompletely reacted) sample ammonolysed at 860 °C, which shows no activity even with CoO_x as co-catalyst. This leads to the important conclusion that CoO_x -loading of inactive compounds does not induce photocatalytic activity and proves that CoO_x itself does not act as a catalyst but only as a co-catalyst.

A strong enhancement of the photocatalytic activity by CoO_x -loading was found for the H-oxynitrides. As shown in Fig. 9a, even under illumination with visible light ($\lambda > 420$ nm) more than 4 % decomposition of methyl orange was observed for the samples ammonolyzed at 860 °C and 890 °C. When a cut-off filter of 300 nm is used the activity further increases to a maximum value of 18 %. The CoO_x -loaded H-samples show clearly higher photocatalytic activities than the corresponding S-samples both in the UV/Vis and the Vis-region. On the other hand, a different dependence on the ammonolysis temperature was found for the two sets of samples. As a general trend the activity increases with ammonolysis temperature for the S-samples. In contrast, with increasing ammonolysis temperature, the activities of loaded and unloaded H-samples generally decrease but the highest photocatalytic activity was measured for the sample ammonolyzed at 890 °C, which also has the highest specific surface area. For the H-oxynitrides complete ammonolysis was already obtained at 860 °C. Lower reaction temperatures result in fewer defects in the crystal lattice, which is reflected by the smaller value of the strain parameter for these samples. Defects act as potential recombination centers for electron-hole pairs. Our photocatalytic data show that good crystallinity and high specific surface area are key parameters to enhance the photocatalytic activity of CaTaO_2N . Therefore, oxynitrides obtained from

hydrothermally synthesized oxide precursors, which possess large surfaces and few crystal defects are promising candidates for photocatalytic wastewater treatment or even water splitting.

CONCLUSIONS

CaTaO₂N nano crystals were obtained for the first time by thermal ammonolysis of a semi-amorphous Ca₂Ta₂O₇ precursor obtained from hydrothermal synthesis. For comparison Ca₂Ta₂O₇ was additionally synthesized by solid state synthesis. The starting oxide precursors vary in their specific surface area of 2.7 m² g⁻¹ for the solid state reaction compared to 183 m² g⁻¹ for the hydrothermal approach.

Ammonolysis at temperatures above 860 °C (hydrothermal precursor; H-samples) and 890 °C (solid state precursor; S-samples) leads to phase pure polycrystalline CaTaO₂N powders with different morphologies and specific surface areas. The S-oxynitrides consist of highly agglomerated particles with diameters in the micrometer range while ammonolysis of the hydrothermal precursor results in single crystalline nanoparticles with roughly 45-67 nm size. These CaTaO₂N nanocrystals show interesting physical characteristics like high specific surface area in the range of 12-19 m² g⁻¹, good crystallinity, low strain and enhanced optical properties reflected by a steeper band edge and brighter colors. Thermal analysis shows that the H-CaTaO₂N samples have a better thermal stability, which makes them interesting for applications at elevated temperatures. CaTaO₂N samples from the hydrothermal soft-chemistry synthesis show enhanced photocatalytic activity for methyl orange degradation, which can be further strongly increased using CoO_x as a co-catalyst. The main parameters for the enhanced photocatalytic activities of the H-CaTaO₂N samples are large surfaces and a low defect concentration. With a BET area up to 19 m² g⁻¹, CoO_x-loaded hydrothermal synthesized CaTaO₂N decomposes more than 5% of the methyl orange solution under irradiation with visible light and 18% under UV-irradiation for the experimental parameters chosen here (150 W Xe-lamp, 10 mg catalyst in 50 ml solution, 3 h reaction time). In conclusion, CaTaO₂N obtained from a hydrothermally

synthesized oxide precursor is a promising candidate for photocatalytic wastewater treatment and very likely also for gas-phase decomposition of organic molecules. The corresponding experiments are currently carried out and results will be presented elsewhere.

SUPPORTING INFORMATION

Additional XRD, EDX, IR and UV/Vis investigations are available free of charge via the internet.

ACKNOWLEDGMENTS

The authors thank Dr. Frank Syrowatka for his help during the SEM investigations.

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Table 1. Specific surface areas, crystallite sizes and particle sizes of the hydrothermal oxide precursor and the corresponding oxynitrides.

precursor synthesis method	Ammonolysis temperature / °C	crystalite size^{a)} nm	BET surface area / m² g⁻¹	particle size^{b)} / nm
H	uncalcined precursor	7 ^{c)}	183	5
H	860	44	16.7	50
H	890	39	18.7	45
H	920	52	16.4	51
H	950	69	12.4	67

a) from Rietveld-analysis

b) from the BET surface area assuming spherical or cubic particles

c) from the peak at $2\theta = 34^\circ$

Table 2. Crystallite size, relative strain, nitrogen stoichiometry and band gaps of CaTaO₂N samples prepared via the solid state (S) and hydrothermal (H) route.

precursor synthesis method	ammonolysis temperature / °C	crystallite size^{a)} / nm	relative strain^{a)}	nitrogen stoichiometry^{b)}	E_g (Shapiro) / eV^{c)}	E_g (Kubelka- Munk) / eV
S	860	-	-	0.21	2.46	2.50
S	890	49	22	0.80	2.42	2.51
S	920	72	27	0.79	2.43	2.50
S	950	108	29	0.92	2.41	2.47
H	860	44	12	0.88	2.41	2.49
H	890	39	9	0.86	2.40	2.48
H	920	52	14	0.85	2.39	2.46
H	950	69	18	0.88	2.40	2.44
a) from Rietveld-analysis		b) from TG results		c) see supporting information		

Table 3. Methyl orange degradation of pure and CoO_x-loaded oxynitride samples.

precursor synthesis method	ammonolysis temperature / °C	$\Delta c / c_0$ after 3 hours / % $\lambda \geq 300$ nm unloaded samples	$\Delta c / c_0$ after 3 hours / % $\lambda \geq 300$ nm CoO _x -loaded samples	$\Delta c / c_0$ after 3 hours / % $\lambda \geq 420$ nm CoO _x -loaded samples
S	860	0.33	5.17	0.17
S	890	0.04	4.41	0.91
S	920	0.58	14.70	3.53
S	950	0.50	6.60	3.79
H	860	1.77	13.05	4.52
H	890	1.64	17.47	5.13
H	920	0.42	6.49	1.44
H	950	0.96	3.65	1.29

Irradiation conditions: 150 W Xe-lamp, 3h, 200 mg/L catalyst, 50 μ M methyl orange.

Figure 1. XRD-pattern of uncalcined H-precursor after synthesis (bottom), calcined H-precursor (1000°C , 2h, middle) and S- $\text{Ca}_2\text{Ta}_2\text{O}_7$ (top). Reference: $\text{Ca}_2\text{Ta}_2\text{O}_7$ (red lines, PDF-card: 44-1008).

Figure 2. a) Adsorption-desorption isotherm of the uncalcined H-precursor. b) Specific BET surface area (left axis), particle size assuming spherical or cubic particles (right axis) and crystallite size (from Rietveld-refinement; open data points) depending on ammonolysis temperature of the H-oxynitrides.

Figure 3. SEM-image (backscattering mode) of the ammonolyzed S-precursor (a) (ammonolysis conditions: 5 L/h NH_3 , 10h, 950 $^{\circ}\text{C}$); TEM images of the uncalcined H-precursor (b), ammonolyzed H-precursor (c) (ammonolysis conditions: 5 L/h NH_3 , 10h, 950 $^{\circ}\text{C}$) and electron diffraction of a CaTaO_2N nano crystal viewed along the [100]-axis (d).

Figure 4. XRD-pattern of ammonolyzed H-samples (a) and ammonolyzed S-samples (b). The inset shows a detailed view of the peak width depending on ammonolysis temperature of the H-oxynitrides.

Figure 5. Weight change of the H-sample (solid lines) and the S-sample (dashed lines) both ammonolyzed at 950 °C.

Figure 6. IR-spectra of the oxynitride samples obtained from hydrothermal synthesis (a) and from solid state synthesis (b).

Figure 7. Diffuse reflectance spectra of ammonolyzed H-samples (a) and ammonolyzed S-samples (b) together with the corresponding Kubelka-Munk plots (insets) assuming an indirect allowed band gap transition.

Figure 8. Band gap of ammonolyzed H-samples (close squares) and S-samples (open circles) determined from the Kubelka-Munk function (black, left axis) and the Shapiro-method (red, right axis).

Figure 9. Photocatalytic activities for methyl orange decomposition of ammonolyzed H-samples (a) and ammonolyzed S-samples (b).

Determination of the peak areas O (oxide peak, orange) and N (oxynitride peak, brown) for quantitative phase analysis for the S-sample ammonolyzed at 860 °C.

Calibration for quantitative analysis of oxide/oxynitride content. Points represent oxide/oxynitride mixtures of known composition. N is defined as the area of the oxynitride peak and O symbolizes the area of the oxide peak.

IR-spectrum of the uncalcined oxide precursor obtained from hydrothermal synthesis.

Band gap determination from the absorbance-UV/Vis-Spectrum according to the Shapiro-method for the sample H-860.

XRD patterns of the sample H-950 recorded before and after photocatalysis showing the stability of the catalyst.

Light emission profile of the used 150 W Xe arc lamp (from LOT Quantum Design; http://www.lot-qd.de/files/downloads/lightsources/en/LQ_Lamp_spectra_and_irradiance_en.pdf)

Diffuse reflectance UV-Vis spectra of the sample H-890 with and without CoO_x -loading (left) and the sample S-920 with and without CoO_x -loading (right).

EDX-map of the H-oxide as received (a, black) and the sample H-950 (a, red), SEM-image of the sample H-950 (b) and SEM-image of the H-oxide precursor (c).