



TiO₂ and Nitrogen Doped TiO₂ Prepared by Different Methods; on the (Micro)structure and Photocatalytic Activity in CO₂ Reduction and N₂O Decomposition

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TiO₂ as nanostructured powders were prepared by (1) sol-gel process and (2) hydrothermal method in combination with (A) the processing by pressurized hot water and methanol or (B) calcination. The subsequent synthesis step was the modification of prepared nanostructured TiO₂ with nitrogen using commercial urea. Textural, structural, surface and optical properties of prepared TiO₂ and N/TiO₂ were characterized by nitrogen physisorption, powder X-ray diffraction, X-ray photoelectron spectroscopy and DR UV-vis spectroscopy. It was revealed that TiO₂ and N/TiO₂ processed by pressurized fluids showed the highest surface areas. Furthermore, all prepared materials were the mixtures of major anatase phase and minor brookite phase, which was in nanocrystalline or amorphous (as nuclei) form depending on the applied preparation method. All the N/TiO₂ materials exhibited enhanced crystallinity with a larger anatase crystallite-size than undoped parent TiO₂. The photocatalytic activity of the prepared TiO₂ and N/TiO₂ was tested in the photocatalytic reduction of CO₂ and the photocatalytic decomposition of N_2O . The key parameters influencing the photocatalytic activity was the ratio of anatase-to-brookite and character of brookite. The optimum ratio of anataseto-brookite for the CO₂ photocatalytic reduction was determined to be about 83 wt.% of anatase and 17 wt.% of brookite (amorphous-like) (TiO₂-SG-C). The presence of nitrogen decreased a bit the photocatalytic activity of tested materials. On the other hand, TiO₂-SG-C was the least active in the N₂O photocatalytic decomposition. In the case of N₂O photocatalytic decomposition, the modification of TiO₂ crystallites surface by nitrogen increased the photocatalytic activity of all investigated materials. The maximum N₂O conversion (about 63 % after 18 h of illumination) in inert gas was reached over all N/TiO₂.

Keywords: Titania, Pressurized Hot Fluid, Nitrogen Doped, Photocatalysis, Carbon Dioxide, Nitrous Oxide.

1. INTRODUCTION

Carbon dioxide is regarded to be one of principal contributors to the greenhouse effect and the limitation of its emission is nowadays a key challenge over the world. The photocatalytic reduction of CO_2 using water as the reusable hydrocarbons is of especially interest.¹ The water splitting is the first step of this photocatalytic reaction, which produces hydrogen reacting subsequently with carbon dioxide.²

reductant and a visible light as the source of photon to

All types of photocatalysts, methods and photoreactors used for the CO₂ photoreduction have been reviewed in

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several articles.^{3–15} The most widely used photocatalyst is TiO_2 and generally methane is the product of reaction. The selection of TiO_2 for the CO_2 photocatalytic reduction is not astonishing due to the wide availability of this material, its stability, lack of toxicity, and, in particular, high photocatalytic activity in water splitting. The efficiency of TiO_2 can be increased by doping with metals^{3–5} or non-metallic elements with the creation of oxygen vacancies.^{6–9, 16} The doping improves, in general, an electron trapping capability of modified semiconductor, reduces the recombination of the photogenerated pair of electron and hole (e^-/h^+) and often extends the absorption capability of light until the visible range.

N₂O belongs also to the major greenhouse gases and it plays a significant role in the destruction of the ozone layer. The photocatalytic decomposition of N₂O under UV irradiation on semiconductor materials is one of promising methods for the N₂O removal. Several different photocatalysts are able to decompose N_2O into N_2 and O_2 at ambient temperature.1 In 2000, Sano et al.17 photocatalytically decomposed N₂O over Ag-TiO₂ with methanol vapor. TiO₂ loaded with only 0.16 wt.% of Ag was the most active photocatalyst. Nevertheless, in these experiments, methanol was used as a reducing agent. Kočí et al.¹⁸ described the N₂O photocatalytic reduction by powdered Ag-TiO₂ photocatalysts with Ag loading from 0.7 to 5.2 wt.%. The photocatalysts were prepared by the sol-gel process and calcination. The highest N2O conversion was observed for 3.4 wt.% Ag-TiO₂. On the other hand, Obalová et al.¹⁹ tested Ag-TiO₂ thin films with Ag loading from 0.25 to 1 wt.% of Ag, prepared by the sol-gel method, and did not observ the change in the N2O conversion with increasing Ag amount.

A special attention has been focused on the application of TiO₂ prepared by different methods. TiO₂ processed by pressurized hot fluids (after using the sol–gel process controlled within reverse micelles) gave the highest N₂O conversion.²⁰ The cerium-doped TiO₂ (Ce_{0.05}Ti_{0.95}O₂, Ce_{0.30}Ti_{0.70}O₂ composites), which were prepared by the same procedure, also showed improved photocatalytic activity compared to pure TiO₂. However, the maximum N₂O conversion was reported over the Ce_{0.05}Ti_{0.95}O₂ composite. Such high activity was attributed to two factors:

(i) high disorder within the anatase crystal structure and (ii) the absence of some cerium-containing amorphous phase/s (e.g., CeO_2 or $CeTi_2O_6$), which can partially block the surface active sites on the anatase crystals. Concerning the mechanism, the photocatalytic decomposition of N₂O was accompanied with photolysis of N₂O.²¹

The technique of TiO_2 preparation and the kind of used dopant(s) have been concluded as two main factors crucially affecting the photocatalytic performance of TiO_2 -based materials due to their effects on the material (micro)structure. Therefore, the aim of this work is the synthesis of TiO_2 and nitrogen doped TiO_2 by two different chemical methods as well as by pressurized hot fluids

processing beside the calcination. The prepared materials were tested in both the photocatalytic reduction of CO_2 and the photocatalytic decomposition of N_2O . The photocatalytic activity was correlated with the (micro)structure and optical properties of the developed materials.

2. EXPERIMENTAL DETAILS

2.1. Preparation of TiO₂ and N/TiO₂

In this work two sets of materials were prepared, pure TiO_2 and nitrogen doped TiO_2 (N/TiO₂), where TiO_2 was prepared by three different ways:

(i) sol-gel method combined with calcination (SG-C),

(ii) hydrothermal method combined with calcination (HT-C), and

(iii) sol-gel method combined with pressurized fluid processing (SG-PFE).

Cyclohexane (C_6H_{12} , HPLC grade, Aldrich), nonionic surfactant Triton X-114 ((1,1,3,3-tetramethylbutyl) phenyl-polyethylene glycol, $C_{29}H_{52}O_{8.5}$, Aldrich), titanium (IV) isopropoxide (Ti(OCH(CH₃)₂)₄, 99.999%, Aldrich) and distilled water were used in the sol–gel synthesis. Titanyl sulphate (TiOSO₄, Precheza a.s.), sulphur acid (H₂SO₄, Penta), sodium hydroxide (NaOH, Penta) and distilled water were used in the hydrothermal synthesis. Urea (CO(NH₂)₂ Penta) was used for nitrogen doping. Furthermore, deionized water (electrical conductivity $\sim 0.06+0.08 \ \mu S \pm cm^{-1}$) and methanol (for HPLC) were used as media (solvents) during the pressurized fluids processing.

Sol-gel synthesis of TiO_2 . Titania gel was prepared as follows: In the first step of preparation, cyclohexane was mixed with Triton X-114 and distilled water, and the mixture was kept under vigorous stirring for 20 min at laboratory temperature. In the second step, titanium (IV) isopropoxide was injected into the mixture. The micellar titania sol was stirred for further 20 min. After that the homogeneous transparent sol was poured into Petri's dishes in a thin layer (4 mm) and the dishes were left standing on air for gelation. Generally, the titania sol was prepared keeping the molar ratio of cyclohexane:Triton X-114:H₂O:Ti(OCH(CH₃)₂)₄ to be 11:1:1:1. A gelation period of titania sol was \sim 24 h. After gelation period, the titania gel was grinded to small pieces ($\sim 3 \times 3$ mm) and processed either by calcination at 400 °C for 4 h using 10 °C/min temperature ramp or by pressurized hot fluids (water and methanol) in order to produce TiO₂ nanostructured powders. Processing by pressurized hot water and subsequently by pressurized hot methanol was carried out in a laboratory-made unit equipped with a HPLC BETA10 Plus gradient pump (Ecom s.r.o., Czech Republic), a chromatographic oven operating in the temperature range 25-400 °C, a capillary cooling, and a restrictor operating at ambient temperature. For more details about the setup see Ref. [22] The gel sample placed in 24-ml hightemperature stainless steel cell was processed in a flow

regime at 200 °C and 10 MPa, using 1.5 L of deionized water, 0.25 L of methanol and 0.1 L of deionized water. The solvent flow rate during the processing was kept at $3.5-4.5 \text{ ml} \cdot \text{min}^{-1}$. Both prepared TiO₂ powders (TiO₂-SG-C, TiO₂-SG-PFE) were sieved to <0.160 mm particle-size fraction and divided to two parts: one for the photocatalytic tests and one for the subsequent nitrogen doping.

Hydrothermal synthesis of TiO₂. Titanyl sulphate solution (160 ml, concentration of 100 g $TiO_2/l TiOSO_4$) was mixed with sulphuric acid (840 ml, 0.5 mol $\cdot 1^{-1}$ H₂SO₄). The solution was under constant mixing heated up to $80\pm$ 1 °C. After this temperature was reached the 20 wt.% NaOH solution was added dropwise until the pH was neutral (the pH was checked by universal pH paper indicator). The formed suspension was left to cool down. Then, the suspension was filtered. The filter cake was washed with 5 l of deionized water to remove the sulphate anions, the presence of sulphate anions was tested with 10 wt.% BaCl₂ solution. The filter cake was dried in a Petri's dish on air at 40 °C overnight. The prepared powder was crushed and sieved to 0.160-0.315 mm particle-size fraction, which was calcined at 400 °C for 1 h using 10 °C/min temperature ramp (TiO₂-HT-C). After calcination TiO₂ was repeatedly sieved to 0.160-0.315 mm particle-size fraction and divided to two parts: one for the photocatalytic tests and one for the subsequent nitrogen doping.

Nitrogen doping. The prepared TiO_2 powders $(\text{TiO}_2\text{-SG-C}, \text{TiO}_2\text{-HT-C}, \text{TiO}_2\text{-SG-PFE})$ were modified by nitrogen using commercial urea. The nitrogen amount in TiO₂ was selected to be 10 wt. % of N. The mechanical mixtures of proper amounts of TiO₂ and urea were dried at 100 °C for 2 h in an oven and then calcined at 400 °C for 2 h using the temperature increase of 2 °C/min. After that, the mixtures were sieved to <0.160 mm particle-size fraction. This particle-size fraction was used for all the characterizations as well as the photocatalytic investigations. The nitrogen doped TiO₂ were denoted as N/TiO₂-SG-C, N/TiO₂-HT-C and N/TiO₂-SG-PFE.

2.2. Characterization of Prepared Materials

Nitrogen physisorption, X-ray powder diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and UV-vis diffuse reflectance spectroscopy were carried out to determine the textural, structural, surface and optical properties of the investigated materials.

Nitrogen physisorption was performed at 77 K on an automated volumetric apparatus NOVA2000e (Quantachrome Instruments, USA) after degassing of materials at 110 °C overnight under vacuum less than 1 Torr. The specific surface area, $S_{\rm BET}$, was calculated according to the classical Brunauer–Emmett–Teller (BET) theory for the p/p_0 range = 0.05–0.30.^{23,24} Additionally, the mesopore surface area, $S_{\rm meso}$, and the micropore volume, $V_{\rm micro}$, were also evaluated based on the *t*-plot method.^{25–27} The net pore volume, $V_{\rm net}$, was determined from the nitrogen adsorption isotherm at maximum $p/p_0(\sim 0.993)$. The pore-size distribution was evaluated from the adsorption branch of the nitrogen adsorption–desorption isotherm by the Barrett–Joyner–Halenda (BJH) method.²⁸

XRD patterns were measured in the Bragg-Brentano geometry using a Bruker D8 Advance diffractometer equipped with a LYNXEYE position sensitive detector and using Ni-filtered CuK α radiation. The measurements were carried out in the reflection mode with sample spinning. Powder samples were dispersed in acetone on a low background Si-substrate. The XRD patterns were recorded in the 2 Θ range of 10–80° with the data step of 0.015°. The phase composition, crystallite-size and lattice parameters were evaluated from Rietveld refinement of XRD data using MStruct software.^{29, 30} The method was described in more detail in Refs. [29, 31]. A special attention was paid on the treatment of higher scattering background at positions of brookite reflections in some samples, as it can be assumed^{32, 33} the effect is related to presence of amorphous TiO₂. The amorphous phase was modelled by very small (0.6 nm) particles of brookite structure.³³

XPS spectra were recorded on a Prevac photoelectron spectrometer equipped with a hemispherical VG SCIENTA R3000 analyzer. The photoelectron spectra were recorded with constant pass energy of 100 eV for the survey and for high resolution spectra using a monochromatized aluminum source Al K α (E = 1486.6 eV) and a low energy electron flood gun (FS40A-PS) to compensate the charge on the surface of nonconductive samples. The base pressure in the analytical chamber was 5×10^{-9} mbar. The binding energies were referenced to the C 1s core level ($E_b = 285.0$ eV). The composition and chemical surrounding of the sample surface were investigated on the basis of the areas and binding energies of Ti 2p, N 1s, O 1s and C 1s photoelectron peaks. The fitting of high resolution spectra was provided through the Casa XPS software.

UV–Vis diffuse reflectance spectra of materials (<0.160 mm) were measured in quartz cuvettes (thickness 5 mm) by using a GBS CINTRA 303 spectrometer (GBC Scientific Equipment, Australia) equipped with an integrating sphere covered by a $BaSO_4$ layer. The spectra were recorded against a spectralon reference material in the wavelength range of 200–900 nm (lamps switched at 350 nm). The scan rate was 100 nm/min. The scan step was 1 nm and the width of monochromator slit was 2 nm. The reflectances were recalculated to the absorption using the Kubelka–Munk equation:

$$F(R_{\infty}) = (1 - R_{\infty})^2 / 2 \cdot R_{\infty} \tag{1}$$

where R_{∞} is the diffuse reflectance from a semi-infinite layer. The obtained spectra were transformed to the dependencies $(F(R_{\infty}) \cdot h\nu)^2$ against $h\nu$ in order to obtain the values of the energy of absorption edge.³⁴

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2.3. Photocatalytic Reduction of CO₂

The CO₂ photocatalytic reduction was performed in a stirred batch photoreactor with a suspended photocatalyst (0.12 g) illuminated by a UV 8 W Hg lamp ($\lambda = 254$ nm) situated on the top of photoreactor; the shell tube was made from stainless steel. Supercritical fluid-grade CO₂ was used as a reactant and 0.2 M NaOH solution (120 mL) was a reduction medium. The analysis of gaseous reaction products was performed in GC/BID. The details about the experiment setup and analytical methods were depicted in our previous work.³⁵

The accuracy of measuring was verified by repeated measurements and the relative error of products yields of 10% was determined. Blank tests were also carried out to ensure that the hydrocarbon production was due to the photoreduction of CO_2 .³⁵ CH₄, CO and H₂ were not detected in any blank tests.

2.4. Photocatalytic Decomposition of N₂O

The N₂O photocatalytic decomposition was performed in a batch annular photoreactor with or without a photocatalyst (photocatalysis and photolysis, respectively). The powdery photocatalyst was spread on the bottom of the photoreactor (of 660 mL volume). The photoreactor was filled with the N₂O/N₂ mixture (968 ppm). The reaction was initiated by switching on a 8 W Hg lamp ($\lambda = 254$ nm) situated in the center of the quartz tube; the shell tube was made of stainless steel. The pressure and the temperature inside the photoreactor were monitored constantly. A gas chromatograph with barrier ionization discharge detector (GC/BID) was used for the analysis of N₂O concentration at the start of reaction and during the reaction. The reproducibility of photocatalytic experiments was verified by repeated measurements.

3. RESULTS AND DISCUSSION 3.1. Photocatalysts Characterization

The prepared materials were characterized by using several complementary techniques in order to reveal their physicochemical and optical properties, which could explain their performance in both photocatalytic reactions.

Surface chemical composition of the N-doped TiO₂ materials was measured by XPS. Table I gives the content of Ti and N. All N-doped TiO₂ samples exhibit the emission of Ti $2p_{1/2}$ and Ti $2p_{3/2}$ spin-orbital splitting photoelectrons at binding energies of 464.1–464.3 eV and 458.3–458.5 eV, respectively, which are characteristic of Ti⁴⁺. Furthermore, the separation of peak 5.8 eV to the Ti $2p_{1/2}$ and Ti $2p_{3/2}$ signals corresponds to the values reported for TiO₂ (NIST, 2012). Surface oxygen is present in three chemical states–as O²⁻ lattice ions ($E_b = 529.6-529.8 \text{ eV}$), hydroxyls ($E_b = 530.8-531.2 \text{ eV}$), and strongly adsorbed water ($E_b = 535.0 \text{ eV}$).³⁶ For the N/TiO₂-SG-PFE and N/TiO₂-SG-C, the traces of nitrogen appear on the surface as it is identified by very weak N 1*s* peak at

Table I. Surface and textural properties of investigated TiO_2 and $\mathrm{N}/\mathrm{TiO}_2.$

	XPS		Nitrogen physisorption				
Material	Ti (at.%)	N (at.%)	$\frac{S_{\rm BET}}{({\rm m}^2/{\rm g})}$	S_{meso} (m ² /g)	$V_{ m micro} \ (m mmmmmmmmmmmmmmmmmmmmmmmmmmmmmmmmm$	V_{net} $(\text{mm}_{\text{liq}}^3/\text{g})$	
TiO ₂ -SG-C	n.d.	n.d.	105	88	26	140	
N/TiO ₂ -SG-C	24.97	0.76	103	65	23	159	
TiO ₂ -HT-C	n.d.	n.d.	115	71	26	190	
N/TiO ₂ -HT-C	20.48	0.00	101	60	24	208	
TiO ₂ -SG-PFE N/TiO ₂ -SG-PFE	n.d. 23.37	n.d. 0.49	180 120	133 88	31 21	301 288	

Note: n.d. not determined.

about 400 eV. The position of this peak corresponds very well to the E_b value described in the literature as typical of nitrogen in O–Ti–N linkages.³⁷ So high E_b value suggests the reduction of electron density in nitrogen atoms by their introduction into the TiO₂ lattice together with highly electronegative oxygen atoms.

The results of nitrogen physisorption measurements are shown in Figures 1(a-c) and summarized in Table I. All investigated materials possess mesoporous structure with small amounts of micropores. Each set of TiO₂ and N/TiO₂ materials (i.e., SG-C, HT-C and SG-PFE) show very similar microporous-mesoporous structure. With respect to the different preparations, TiO₂ and N/TiO₂ materials processed by pressurized fluids (TiO2-SG-PFE, N/TiO2-SG-PFE) exhibit the highest surface areas (S_{BET} of 180 m²/g and 120 m²/g). These values are markedly higher than that of both calcined sets (Table I). It is also evident that in N/TiO₂-SG-C undergoing re-calcination after doping of TiO₂-SG-C by nitrogen any significant sintering did not occur, since TiO₂-SG-C and N/TiO₂-SG-C have very similar surface areas (S_{BET} of 105 m²/g and 103 m²/g, respectively). This effect was, however, more significant in the HT-C and SG-PFE sets.

The XRD patterns (Fig. 2(a)) confirm the existence of major anatase phase in all investigated materials. Besides the major anatase phase, the presence of brookite phase is also identified in all sets of materials, which is evident from the whole powder pattern fitting of XRD data (Figs. 2(b and c)). Quantitative analysis gives a fraction of nanocrystalline brookite around 25 wt.% in TiO₂-SG-PFE and N/TiO₂-SG-PFE (Table II). Such intermixture of nanocrystalline anatase and brookite is not surprising.^{38, 39} Increased background between first two anatase lines in TiO₂-HT-C and N/TiO₂-HT-C may indicate some amounts of brookite-like TiO₂ present rather in amorphous form (Table II, Fig. 2). Small amounts of amorphous brookite are also observed in TiO2-SG-C (17 wt.%) and N/TiO2-SG-C (6 wt.%). For all N/TiO₂, the peak intensities increased compared to corresponding undoped TiO₂. This indicates that nitrogen doped TiO₂ show enhanced crystallinity with larger anatase crystallite-size (by ~ 1 nm) than undoped TiO₂. Anatase lattice parameters and cell



Figure 1. Measured nitrogen adsorption-desorption isotherms and evaluated pore-size distributions (in insets) of investigated TiO₂ and N/TiO₂.

volumes (136.27–136.41 Å³) of all TiO₂ do not change markedly and are very similar to values reported in Ref. [40]. Moreover, it can also be seen that the anatase cell volume of N/TiO₂-SG-C and N/TiO₂-SG-PFE are comparable slightly to parent TiO₂-SG-C and TiO₂-SG-PFE. These facts reveal that low nitrogen doping did not affect the microstructure of parent TiO₂ and the anatase crystallite-size in N/TiO₂ increased in a consequence of the re-calcination during preparation.

The UV-vis reflectance spectra of all the investigated materials from which the absorption edges were determined are shown in Figure 3. Plotting $((F(R_{\infty})h\nu)^2 \text{ versus } h\nu \text{ provides the extrapolated intercept corresponding to the band gap energy (<math>E_g$) values (Table II). The absorption edge energies of TiO₂ were shifted to lower values in the order: TiO₂-HT-C (3.36 eV) > TiO₂-SG-PFE

 $(3.24 \text{ eV}) > \text{TiO}_2\text{-SG-C}$ (3.21 eV). Nitrogen loading did not lead to any significant changes in the band gap energies. In correlation with structural and microstructural results it can be said that the different band gap energies of individual TiO₂ may be caused by different phase composition (i.e., ratio of anatase-to-brookite) and crystallinity (i.e., character of brookite, anatase crystallitessize) of individual TiO₂. Negligible changes in TiO₂ band gap energies after nitrogen doping can be explained by the trace contents of nitrogen being incorporated into the TiO₂ lattice.

3.2. Photocatalytic Reduction of CO₂

The different types of TiO_2 and N/TiO₂ were investigated for the photoreduction of CO_2 over a period of 0–24 h. Figure 4 shows the progression of all reaction products as

Figure 2. (a) XRD patterns of all prepared TiO_2 and N/TiO₂, (b) the background fit of TiO_2 -HT-C with amorphous-like brookite and (c) the fit of small brookite peaks in TiO_2 -SG-PFE. Three full black lines at the bottom of the (a) sub-plot represent simulated nanocrystalline diffraction patterns for anatase, amorphous-like brookite and naocrystalline brookite with typical parameters used in the fits.

functions of the irradiation time for TiO₂-SG-C. Two main products were determined, methane and carbon monoxide in a gas phase. Hydrogen was also detected. The appearance of other products such as formic acid, methanol and formaldehyde was not noticed. The observed yields $(\mu \text{mol/g}_{cat})$ order was: CO > H₂ > CH₄.

Comparisons of CO, CH_4 and H_2 yields over all investigated materials are shown in Figures 5(a–c), respectively. The highest yields from all detected products were observed for carbon monoxide (Fig. 5(a)). The yields of carbon monoxide increased evenly during the reaction. The CO yields were comparable for all materials with the exception of TiO₂-SG-C.

The yields of methane were two orders of magnitude lower than the yields of carbon monoxide (Fig. 5(b)).

The yields of methane over calcined materials (TiO_2 -SG-C, N/TiO_2-SG-C) were significantly higher in comparison with other ones. 1:31:07

So The yield of hydrogen (Fig. 5(c)) increased evenly during the reaction. The formation of hydrogen in presence of all N/TiO₂ was significantly lower in comparison with all undoped TiO_2 . The substantially higher activity was proved over TiO_2 -SG-C.

The highest yields of all reaction products were observed for TiO_2 -SG-C. The presence of nitrogen in N/TiO_2-SG-C caused the decline of all products.

3.3. Photocatalytic Decomposition of N₂O

The N_2O photocatalytic decomposition over all prepared materials was investigated over a period of 0–18 h. The

Table II. Structural, microstructural and optical properties of investigated TiO₂ and N/TiO₂.

Material	Phase composition		VPD above		Anatase lattice parameters			
	X_a (wt.%)	X_b (wt.%)	character of brookite	$\langle D_a \rangle_V (\mathrm{nm})$	a (Å)	c (Å)	V_{cell} (Å ³)	Absorption edge (eV
TiO ₂ -SG-C	83	17	Amorphous (n.d.)	9.2	3.787	9.503	136.30	3.21
N/TiO ₂ -SG-C	94	6	Amorphous (n.d.)	10.1	3.786	9.506	136.27	3.20
TiO ₂ -HT-C	51	49	Amorphous (~0.6 nm nuclei)	10.7	3.789	9.502	136.41	3.36
N/TiO ₂ -HT-C	53	47	Amorphous (~0.6 nm nuclei)	11.5	3.789	9.503	136.41	3.35
TiO ₂ -SG-PFE	75	25	Nanocrystalline (~2.5 nm)	8.8	3.791	9.489	136.38	3.24
N/TiO ₂ -SG-PFE	77	23	Nanocrystalline (~2.5 nm)	10.3	3.790	9.492	136.34	3.22

Notes: X_a —weight fraction of anatase. X_b —weight fraction of brookite. $\langle D_a \rangle_V$ —volume-weighted anatase crystallite-size.

Figure 3. UV-Vis DRS spectra of investigated TiO_2 and N/TiO₂ and the determination of absorption edges.

time dependences of N_2O conversion over all investigated materials are shown in Figure 6(a). The progressive increase in N_2O conversion with the growing irradiation time was observed. The N_2O conversions reached over all investigated materials were higher than in the case of photolysis (reaction without photocatalyst).

For TiO₂, the N₂O conversion decreased in the order: TiO₂-HT-C > TiO₂-SG-PFE > TiO₂-SG-C (Fig. 6(b)). In contrast, the conversion of N₂O for all N/TiO₂ was comparable and it was comparable to TiO_{2} -HT-C₂ which was Fri 63% after 18 h (Fig. 5(c)).

3.4. Aspects Influencing the Photocatalytic Reduction of CO₂ and the Photocatalytic Decomposition of N₂O Over Different TiO₂ and N/TiO₂

Different photocatalytic behaviour of TiO_2 and N/TiO₂ revealed an important role of structure and nitrogen doping in both reactions. In the CO₂ photocatalytic reduction,

Figure 4. The time dependences of the product yields over TiO_2 -SG-C.

the activity decreased in order: TiO_2 -SG-C > N/TiO₂- $SG-C > TiO_2-HT-C \sim N/TiO_2-HT-C \sim TiO_2-SG-PFE \sim$ N/TiO₂-SG-PFE. Since all investigated materials were the mixtures of anatase and brookite, however, with different crystallographic composition and character of the brookite phase, it is evident that these features are more decisive parameters influencing the photoactivity than the nitrogen doping or the surface area. In agreement to some reports,⁴¹⁻⁴³ the anatase–brookite mixture is more effective than the pure anatase, brookite or anatase-rutile for the photocatalytic reactions. However, only few reports have been focused on the bicrystalline anatase-brookite mixture for the CO₂ photoreduction.⁴⁴⁻⁴⁶ Liu et al.⁴⁶ tested the crystal phase of TiO₂, i.e., pure anatase (A), an anataserich anatase/brookite mixture (AB), or a brookite-rich anatase/brookite mixture (BA) and found out that the most active photocatalyst was anatase-rich anatase/brookite mixture. Zhao et al.⁴⁶ reported that the bicrystalline anatasebrookite was generally more active than the single-phase anatase or brookite in the photocatalytic reduction of CO₂. Kočí et al.⁴⁴ showed that the feature responsible for better photocatalytic activity in the CO₂ photoreduction was the surface heterojunction of bicrystalline anatase-brookite. It is necessary to point out that any of these works did not discuss the effect of character of brookite in the mixture with anatase.

1 In our work, the different mixtures of anatase and brookite were prepared due to the application of different preparation approaches (Table II). In the case of TiO₂-SG-C and N/TiO₂-SG-C, the anatase phase with minimum of brookite-like phase in rather amorphous form, 17 wt.% and 6 wt.%, respectively, was obtained. Very similar were TiO₂-HT-C and N/TiO₂-HT-C, however, with higher content of brookite-like phase (47 wt.% and 49 wt.%, respectively). The only nanocrystalline anatase-brookite mixtures were TiO₂-SG-PFE and N/TiO₂-SG-PFE. Considering the highest surface areas of bicrystalline TiO₂-SG-PFE and N/TiO₂-SG-PFE, which showed low photoactivity in the CO₂ photoreduction, and practically very similar anatase crystallite-sizes of all investigated materials, it is evident that the surface area and the anatase crystallitesize, which are usually very important parameters, are not crucial ones in this case.

The enhanced photoactivity of anatase-brookite mixture can be explained by three reasons:

(i) the excited electrons on brookite conduction band (CB) can transfer to anatase conduction band (CB) due to a slightly higher CB edge of brookite (about $0.14 \text{ eV})^{42, 43, 46}$ than anatase, thus enhancing charge separation;

(ii) the facilitated formation of the intrinsic defect sites in brookite may enhance electron trapping;^{46,47} and

(iii) the distorted interfaces between anatase and brookite crystals may facilitate interfacial electron transport and prevent the recombination of electron–hole pairs.^{46, 48}

Figure 5. The time dependence of (a) carbon monoxide yields (b) methane yields and (c) hydrogen yields over individual investigated materials in the CO_2 photocatalytic reduction.

Conditions: 23 h of irradiation time, 8 W Hg lamp, CO_2 pressure at carbonation of 110 kPa, 120 mL of H_2O , photocatalyst concentration of 1 g/L, pH 7.

Thus, the key property affecting the photocatalytic activity of anatase-brookite mixtures in the CO_2 photoreduction is the character of brookite, which influences the interface arrangement of both crystal phases and thus the photoactivity as mentioned in points (ii) and (iii). It can be concluded that the presence of amorphous brookite in the anatase-rich anatase-brookite mixture enhances the material photoactivity in the CO_2 photoreduction.

The surface states play a crucial role in photocatalytic reactions. The oxygen defects on the surface of photocatalyst are a sort of trapped site for photoexcited electrons, which can separate electrons from holes, which is very significant for photocatalysis. However, too many oxygen defects can act as recombination centers and reduce the by nitrogen can increase the number of oxygen defects considerably.^{49,50} The nitrogen doping in TiO₂ decreased a bit its photocatalytic activity in the CO₂ photocatalytic reduction. According to the anatase lattice parameters determined by WPPM analysis (Table II), which are similar for all investigated TiO₂ and N/TiO₂ it is obvious that the nitrogen doping did not influence any significantly the anatase crystal structure. However, it can be assumed that due to the number of valence electrons and the atomic diameters of N and O which are various, the amount of nitrogen doped leads to the appearance of defect sites and non-stoichiometry in the material. The doped nitrogen ions and oxygen defects, which can acts as

lifetime of photoexcited electrons and holes. The doping

Figure 6. The time dependences of N_2O conversion over (a) all investigated materials, (b) all TiO₂ and (c) all N/TiO₂.

recombination centers and limit the lifetime of photoexcited electrons and holes, thereby come down photocatalytic activity of materials under UV irradiation in the CO₂ photoreduction, particularly water splitting and hydrogen radicals formation which are necessary for CO₂ photoreduction. It is obvious that the production of hydrogen in presence of all N/TiO₂ is significantly lower compared to all pure TiO₂. On the other hand, an opposite effect is evidenced in the N₂O photocatalytic decomposition. The best photoactivity was proved for all N/TiO₂ and TiO₂-HT-C. As was reported, oxygen vacancies enhance the N₂O decomposition, and the lifetime of the N₂O-vacancy interaction may play the key role in this reaction.⁵¹ In our case the nitrogen doping obviously led to creation of more defect sites and non-stoichiometry on the TiO₂ surface. This feature could explain the comparable and higher photoactivity of all N/TiO₂ in the N₂O photocatalytic decomposition.

4. CONCLUSIONS

TiO₂ as nanostructured powders were prepared by sol–gel process or hydrothermal method in combination with (1) the processing by pressurized hot water and methanol or (2) calcination. The prepared TiO₂ were modified with nitrogen using commercial urea. The developed photocatalysts showed significantly different textural properties (specific surface area) and phase composition (different ratio of anatase-to-brookite and character of brookite). In addition, the photocatalysts also showed different behaviour in the CO₂ photocatalytic reduction and the N₂O photocatalytic decomposition.

The modification of TiO_2 by nitrogen was shown to be beneficial in the N₂O decomposition. In this case, the nitrogen doping significantly increased the N₂O decomposition over N/TiO₂ prepared by sol–gel method combined with calcination (SG-C) and by sol–gel method combined with pressurized fluid processing (SG-PFE). It was suggested that the nitrogen doping led to the formation of

more defect sites and non-stoichiometry on the TiO₂ surface that increased the N₂O decomposition in the case of these nitrogen-doped TiO2. In contrast, the effect of nitrogen loading was not observed in TiO₂ prepared by hydrothermal method combined with calcination (HT-C), as hydrothermal synthesis itself represents the process leading to a significant amount of defect sites and nonstoichiometry on the TiO₂ surface.

On the other hand, the CO_2 photocatalytic reduction is a reaction, in which defect sites do not play so dramatic role as in the case of N₂O decomposition and, thus, the nitrogen loading did not result in any increase of CO₂ reduction. In the case of the CO₂ photocatalytic reduction, the key role plays the structure of surface phase junction within bicrystalline mixture of anatase and brookite, where the recombination of electrons and holes is reduced more effectively. The optimum ratio of anatase-to-brookite for the CO₂ photocatalytic reduction was determined to be about 83 wt.% of anatase and 17 wt.% of brookite (being amorphous-like) (TiO₂-SG-C).

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