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Characterisation, phase-stability and surface chemical properties of photocatalytic active Zr and Y co-doped anatase TiO₂ nanoparticles

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Abstract

We report on the characterization, phase stability, surface chemical and photocatalytic properties of Zr and Y co-doped anatase TiO₂ nanoparticles prepared by homogenous hydrolysis methods using urea as precipitating agent. The materials were analyzed by

scanning electron microscopy, X-ray diffraction, Raman spectroscopy, BET isotherm and BJH pore size distribution measurements. It is shown that Y and Zr ions replace Ti ions in the anatase TiO_2 structures up to a critical total dopant concentration of approximately 13 wt%. The co-doped particles show increased phase stability compared to pure anatase TiO_2 nanoparticles. The anatase to rutile phase transformation is shown to be preceded by cation segregation and dissolution with concomitant precipitation of $\text{Y}_2\text{Ti}_{2-x}\text{Zr}_x\text{O}_7$ and ZrTiO_4 . Co-doping modifies the optical absorption edge with a resulting attenuation of the Urbach tail. The band gap is slightly blue-shifted at high doping concentrations, and red shifted at lower doping concentrations. Formic acid adsorption was used as a probe molecule to investigate surface chemical properties and adsorbate structures. It was found that the relative abundance of monodentate formate compared to bidentate coordinated formate decreases with increasing doping concentration. This is attributed to an increased surface acidity with increasing dopant concentration. Photodegradation of formic acid occurred on all samples. With mode-resolved in situ FTIR spectroscopy it is shown that the rate of photodegradation of monodentate formate species are higher than for bidentate formate species. Thus our results show that the trend of decreasing photo-degradation rate with increasing dopant concentration can be explained by the adsorbate structure, which is controlled by the acidity of the surface.

KEYWORDS: A. nanostructures, B. chemical synthesis, D. catalytic properties, D. phase transactions

1. Introduction

Over the last decades there has been an increasing interest in photocatalytic materials covering a wide range of environmental application areas such as air and water purification, decontamination, self-cleaning, anti-bacterial and anti-fogging surfaces [1, 2]. Although our understanding of the fundamental properties of the simplest photocatalytic systems has increased considerably during the last few decades, in particular TiO_2 photocatalysis [1], the focus today on visible active and improved sustained efficiency has turned the attention to new photo-active materials, and combinations of materials, with largely unknown physicochemical properties.

The need for UVA light ($\lambda < 400$ nm) to drive redox reactions in TiO_2 photo-catalysed systems limits the available energy that can be exploited in the solar spectrum. Moreover, deactivation, for example by means of particle aggregation and growth, with concomitant lowering of active surface area and overall efficiency is a critical issue that limits the applicability of TiO_2 [3]. Several strategies have been employed to achieve visible-active photocatalytic materials. So far the most common strategies have been to modify TiO_2 by metal dopants [4-6] or anion dopant atoms such as sulphur [7-9], carbon [10, 11] and nitrogen [12-14], as well as by mixtures of metal oxides [15-18]. More recently complex heterostructured materials have been reported, such as diode structures made of p- and n-type semiconductors [19]. Studies of tertiary doping of TiO_2 with metal and inorganic elements have suggested that this strategy is potentially beneficial due to synergetic effects of increased lifetime of photo-generated electron-hole pairs following the metal inclusion and improved absorption properties in the visible region by incorporation of inorganic dopants [20-23]. Inclusion of Y in thin TiO_2 films has recently been reported to result in improved visible active photochemical properties with a red-shift of the band gap, which is attributed to the substitution of Ti^{4+} with Y^{3+} in the TiO_2 crystal [24, 25]. On the other hand, inclusion of Zr

into the anatase TiO_2 lattice has been shown to stabilize particle growth and is therefore interesting to avoid loss of active surface area [21, 26, 27]. The reason for this is believed to be the larger radius of Zr^{4+} cation and concomitant relaxation of the anatase structure [27]. An improved activity of Zr-TiO_2 and sintered $\text{ZrO}_2\text{-TiO}_2$ has also been reported for the photo-degradation of methylcyclohexane and ethylene, respectively, which was attributed to an increased surface acidity and larger surface area [4, 17]. The reported optimal metal dopant concentration for anatase TiO_2 in photocatalysis applications generally falls between 1% and 10% [21, 22, 28]. Quite generally the route for cation substitution in TiO_2 appears to be a delicate balance between electronic- and structural modification, which may result in either band gap shifts and phase stabilization or undesirable local band gap states and lattice defects [13, 29]. These defects act as recombination centres for hot electrons and cause collapse of structure and phase segregation (as demonstrated here at high dopant concentrations). Differences in ionic radius and valence charge of possible cation dopant atoms limit the selection of suitable materials combinations and the amount of dopants.

In this study we report on the synthesis, characterization and photocatalytic activity of Zr and Y co-doped anatase TiO_2 nanoparticles. The idea behind this study was two-fold: (i) to investigate whether the reported beneficial photocatalytic properties of Y doping could be combined with the promising structure stabilizing modifications due to Zr doping, and (ii) to use a probe molecule which was sensitive to the surface acid-basic properties to study the effect on the photo-degradation on the surface chemical properties of the catalysts. The photocatalytic activity of the materials is investigated by means of operando diffuse reflectance infrared spectroscopy in order to simultaneously study adsorbate bonding structure and reaction rates under reaction conditions.

2. Experimental

2.1 Materials synthesis

Zr^{4+} and Y^{3+} doped TiO_2 was prepared by means of homogenous hydrolysis of TiOSO_4 , ZrOSO_4 and $\text{Y}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ aqueous solution with urea as a precipitation agent using methods described elsewhere [30, 31]. Typically, 100 g TiOSO_4 was dissolved in 100 ml hot distilled water acidified with 98% H_2SO_4 and diluted with 4 l of distilled water. Equal amounts of ZrOSO_4 and $\text{Y}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ were added and mixed with 300 g urea and then heated to 373 K under stirring and kept at this temperature until pH 7.2-7.5 was obtained. The formed precipitates were washed by distilled water with decantation, filtered off and dried at 378 K in a dry oven. By this method five samples, denoted TiZrY1-5, were made using 1, 2, 3, 5 and 10 g of ZrOSO_4 and $\text{Y}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$. As a reference a pure anatase TiO_2 sample was prepared with similar methods, and is denoted TiZrY0.

2.2. Materials characterization

Scanning electron microscopy (SEM) was performed with a Philips XL30CP microscope equipped with energy dispersive X-ray (EDX), Robinson, secondary electron (SE) and back-scattered electron (BSE) detectors.

X-ray diffraction (XRD) was performed with a Siemens D5005 instrument using $\text{Cu K}\alpha$ radiation (operated at 40 kV, 30 mA), and a diffracted beam monochromator. Data were collected in a step-scan mode covering angles $5^\circ < 2\theta < 90^\circ$. Quantitative analysis of XRD diffractograms was done with the ICSD database [32] and Rietveld refinement with the Bruker TOPAS software. Sample TiZrY5 was further studied by in-situ high temperature XRD with a PANalytical XPertPRO diffractometer using Co K radiation (operated at 40 kV, 30 mA) equipped with a multichannel detector (X'Celerator) with an anti-scatter shield and a high temperature chamber (HTK 16, Anton Paar). The measurement started at room

temperature and finished at 1473 K employing temperature steps of 100 K from 373 K to 773 K, and steps of 25 K above 823 K.

The surface areas of the samples were determined from nitrogen adsorption-desorption isotherms at liquid nitrogen temperature using a Coulter SA3100 instrument with outgassing for 15 min at 423 K. The Brunauer-Emmet-Teller (BET) method was used for surface area determination [33], and the pore size distribution (pore diameter, pore volume and micropore surface area of the samples) was determined by the Barrett-Joyner-Halenda (BJH) method [34].

X-ray photoemission spectroscopy (XPS) was carried out with a Kratos Axis Ultra spectrometer equipped with a mono Al- K_{α} X-ray source, operated at 150 W, and a hybrid lens system with a magnetic lens and charge neutralizer. Survey scans were performed with 1 eV resolution, and the binding energy scale was calibrated using the C 1s line of aliphatic carbon at 285.0 eV. High resolution scans of the C 1s, O 1s, Ti 2p, Zr 3d and Y 3d lines were performed with 0.1 eV resolution. Peak deconvolution, background correction and composition determination were performed with Kratos software.

Raman spectra were recorded with a Horiba Jobin-Yvon Labram HR800 confocal Raman microscope equipped with a 785 nm diode laser excitation source operated at 30 W. A grating with 1800 grooves mm^{-1} , yielding a spectral resolution of $\sim 1 \text{ cm}^{-1}$, was used for detailed analysis of the anatase TiO_2 E_g mode at 144 cm^{-1} in order to monitor wavenumber shifts as a function of sample annealing temperature. Large survey measurements between 120 and 1200 cm^{-1} were performed with a 600 grooves mm^{-1} grating and a spectral resolution of $\sim 3.5 \text{ cm}^{-1}$. The gratings were calibrated in such a way that the low wavenumber E_g mode of an anatase single crystal (Commercial Crystal Laboratories) appeared at 144 cm^{-1} [35]. Annealing was done in situ in a Linkam TS 1500 temperature cell. All samples were annealed in the same manner. First, the samples were annealed for 15 minutes at 673 K, then for 120 minutes at

progressively increasing temperatures in steps of 100 K, starting at 873 K. Between annealing the samples were cooled to 298 K prior to Raman measurements.

UV-Vis spectrophotometric measurements were performed with a Perkin-Elmer Lambda900 double beam spectrophotometer equipped with a Spectralon coated integrating sphere. Total reflectance and transmittance as well as diffuse reflectance and transmittance were measured on thin films. The films were made by mixing a small amount of the sample with ethanol and sonicated to obtain slurries with well-dispersed particle aggregates, which was then deposited on quartz substrates. Film thickness was measured by a WYKO NT1100 white light interferometer.

2.3. Formic acid adsorption and photocatalytic degradation experiments

So called operando diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) was employed to study adsorption and photo-degradation under reaction conditions. Formic acid was used as a test molecule to monitor the adsorbate structure, which is related to the surface chemical properties of the materials, and the photo-degradation rate of the TiZrY nanomaterials. The experimental set up for the DRIFTS measurements have been described in detail elsewhere [26]. Briefly, a vacuum pumped Bruker IFS 66v/S FTIR spectrometer equipped with a modified DRIFT reaction cell was employed, which makes simultaneous adsorption, illumination and reaction experiments possible. Repeated DRIFT spectra were acquired every 1 min and consisted of 30 s scan time and 30 s dwell time. Reported spectra were smoothed by a 7 point window Savitzky-Golay algorithm and baseline corrected.

Liquid formic acid (reagent grade, Scharlau) was used as delivered. The liquid was heated to 303 K and introduced into a 100 ml min⁻¹ synthetic air flow through a 5.5 mm diameter diffusion tube via a home-built gas-generator [29]. The formic acid dose rate was determined as 67 µg min⁻¹. Prior to irradiation, formic acid was dosed for 25 min followed by 15 min

purging in 100 ml min⁻¹ flow of synthetic air. Before each experiment all samples were calcinated in the reaction cell at 673 K for 15 min in a flow of synthetic air (100 ml min⁻¹) to remove organic contaminants. After calcination the sample was cooled down to 293 K in a flow of synthetic air.

Simulated solar light was generated by an arc lamp source equipped with a Xe lamp operated at 300 W and a set of AM1.5 filters (Oriel). A 54 mm long water filter (Oriel) was used to remove the infrared part of the spectrum to avoid excess heating of the sample. The measured photon power was 165 mW cm⁻² in the wavelength region 200 < λ < 800 nm and 19.2 mW cm⁻² for λ < 390 nm (corresponding to the anatase TiO₂ band gap energy [2]) as measured by a thermopile detector (Ophir).

3. Results and Discussion

3.1 Materials characterization

From the SEM micrographs it is evident that the samples exhibit a microstructure consisting of spherical aggregates with a diameter of 2-3 μ m (Fig. 1). Analysis of the XRD data (Fig. 2) shows that these microstructures consist of small crystalline anatase particles with grain sizes in the range 5-8 nm for TiZrY0-TiZrY4, while TiZrY5 contains 4 nm particles with a large fraction of amorphous content. Rietveld refinement analysis of the XRD data shows that the anatase lattice unit cell dimension increases with increasing doping concentration (Table 1). This can clearly be seen by plotting the relative unit cell expansion, $\Delta V/V_0$, versus the cation dopant concentration, where V_0 is the cell volume of the pure anatase TiO₂ (Fig. 3). This is a consequence of substituting the Ti cation with Y and Zr ions; the ionic radius of Y³⁺ and Zr⁴⁺ is 0.89 Å and 0.79 Å, respectively, compared to 0.68 Å for Ti⁴⁺ [36]. A similar expansion of the anatase unit cell has been observed for the Zr-TiO₂ system resulting in a stabilization of the anatase crystal structure [26, 27]. This is also confirmed by XPS and EDX data, which

show an increased amount of Zr and Y and a concomitant decrease of Ti concentration as the concentrations of dopant atoms in the synthesis increase (Table 2). Slight compositional variations in the samples arise due to varying carbon contents. This is particularly evident in the measurements of the as prepared sample TiZrY5, and the same sample annealed at 873 K for 24 h (TiZrY5a). The annealing reduces the carbon content and the relative concentration of the other elements therefore increases. To reduce this effect in the calculated composition, as well as accounting for different amounts of carbon determined from EDX and XPS, the reported elemental concentrations have been corrected for the carbon content. After this procedure, only slight differences in the composition between XPS and EDX remain. XPS measurements reveal a slightly higher metal content for both the dopant atoms and titanium, and consequently a lower oxygen content compared to EDX. The inelastic mean free path for the O 1s and Ti 2p electrons in TiO₂ is of the order of 1 nm [37]. EDX on the other hand is a technique that probes more of the bulk; typically on the order of micrometres [38]. The difference in metal content can therefore be attributed to different correction errors of residual surface carbon, which overestimates the metal concentration in XPS to a larger extent than in EDX. All samples show a Ti 2p binding energy (BE) at ca 459.0 eV characteristic of Ti⁴⁺ ions [39, 40]. For Y 3d we find BE $\approx$ 158.3 eV and for Zr 3d BE $\approx$ 182.6 eV. These BE values are close to those of YOOH and ZrO₂ as reported by Barr[41], and show that Y and Zr are mainly present as +3 and +4 ions, respectively. Three O 1s peaks are apparent at BE $\approx$ 530.4, 531.6, and 532.6 eV, here denoted O 1s(1), O 1s(2), and O 1s(3), respectively. The binding energies for the different samples can be found in Table 3. The different BE of O 1s is attributed to the chemically non-equivalent O atoms: O 1s(1) is due to oxygen bonded to metal atoms; O 1s(2) is due to oxygen in metal-OH bonds; and O 1s(3) is due to oxygen bonded to carbon [42-44]. The O 1s(1) peak (metal-lattice oxygen) broadens with increasing dopant concentration and shows that the amount of Y-O and Zr-O bonded species, whose BE are close to that of Ti-O

[41], increase with dopant concentration and thus further proves that the synthesis results in substitutional Y and Zr doped TiO_2 , where Y and Zr replace Ti in the anatase structure. Sample TiZrY5 exhibits a lower O 1s(1)/metal ratio and a higher O 1s(2) ratio compared to the other samples as a consequence of the amorphous nature of this sample. Moreover, the O 1s(3) concentration (residual carbon) of the as prepared samples is found to decrease at high dopant concentrations. This is in good agreement with our earlier results for Zr doped TiO_2 using the same synthesis method [26]. The raw and fitted XP data for the different O 1s peaks are found in the supplementary information, S1.

Fig. 4 shows Raman spectra of the TiZrY samples as well as pure TiO_2 anatase. The results agree with previous studies of TiO_2 in the anatase modification [27, 35]. Minor shifts of a few cm^{-1} are observed for the bands at $\sim 150, 200, 399, 519$ and 639 cm^{-1} in the Yr and Zr doped samples. In particular, there is a trend of a blue-shift of the E_g mode at $\approx 150 \text{ cm}^{-1}$ with increasing dopant concentration. These variations are not consistent with phonon confinement and surface stress effects [27, 45], which are apparent at particle sizes $< 10 \text{ nm}$, and cause an up-shift of the E_g mode with decreasing particle size since in our case the particle size increases slightly with increasing dopant concentration (see Table 1). Thus we attribute these minor shifts to dopant induced effects. Further studies are, however, required to fully understand the nature of these frequency up-shifts. Much weaker bands are observed at 297, 360, 577, 650 (only as a shoulder on TiZrY5) and 900 cm^{-1} , in addition to the anatase peaks. For intermediate doping concentrations (TiZrY2, 3 and 4) a band at 250 cm^{-1} is also present. Except for the shoulder at 650 cm^{-1} , these bands disappear after annealing (see below). The Raman spectrum of sample TiZrY5 exhibits a broad background and less distinct bands, again signalling an amorphous content with a characteristic Bose–Einstein background [27, 46], in good agreement with the XRD observations.

The results from the XRD and Raman analysis are consistent with Y and Zr replacement of Ti atoms in the anatase lattice up to a total doping concentration of about 3 at% Zr and 3 at% Y as determined by XPS. Above this concentration the anatase structure becomes unstable and an amorphous phase is formed in the synthesis. This corresponds to approximately 13 wt% of dopant atoms and is similar to the concentration (solubility) limit we previously have observed with the same synthesis procedure using only Zr [26, 27]. This limit is most likely due to the larger radius of Zr^{4+} and Y^{3+} compared to Ti^{4+} . Using the lattice parameters deduced from the XRD analysis (Table 1) we infer that the anatase structure becomes unstable when the unit cell expansion exceeds $\Delta V/V_0 > 0.7\%$ (Fig 3). In comparison, annealing the partly amorphous sample at 873 K for 24 h (sample denoted TiZrY5a) results in well-crystallized particles with anatase structure with an apparent total dopant concentration of approximately 7 at% (Table 1). The unit cell dimensions determined from the Rietveld analysis are, however, in this case smaller than for sample TiZrY4 and suggest that XPS picks up signals from Y and Zr ions, which are not incorporated in the anatase structure, and hence that Y and Zr appears as precipitated compounds not present in the anatase structure. This is consistent with previous findings [27] and is discussed further below.

3.2 Phase stability

Rutile is the thermodynamically most stable phase in bulk TiO_2 although the difference between the naturally occurring polymorphs is small [47]. The thermodynamics is, however, reversed when nanoparticles are considered and depending on crystallite size, either anatase ($d < 5$ nm), brookite ($5 < d < 30$ nm) or rutile ($d > 30$ nm) has been reported to be the most stable phase [47]. The anatase to rutile phase transformation is readily monitored in Raman spectroscopy by the appearance of rutile Raman active phonons at 143, ~ 235 , 447, 612, and 826 cm^{-1} and the concurrent reduction of the anatase modes [35, 48]. Typically the anatase to

rutile transition starts around 900 K when TiO₂ is annealed in air [47]. We estimate the relative amounts of rutile and anatase according to:

$$\frac{\sigma_A(144)}{\sigma_R(447) + \sigma_R(612)} \approx 1 \quad (1)$$

where $\sigma_R(447)$, $\sigma_R(612)$ and $\sigma_A(144)$ are the Raman cross sections of the modes at 144 cm⁻¹ (anatase), 447 cm⁻¹ (rutile) and 612 cm⁻¹ (rutile), respectively [49]. The composition can thus be calculated from eq. (1) using the measured Raman intensity of each respective mode. In Fig. 5 the amount of rutile as a function of annealing temperature is shown. In general, the anatase content as a function of annealing temperature is similar in all samples with a trend of increasing anatase phase stability with increasing doping concentration. There are however some exceptions to this trend, as is evident in Fig 5. The particle growth rate and hence the phase transformation temperature are also affected by sample properties such as particle packaging and morphology. A lower density (higher BET area) causes a more rapid grain growth and hence promotes a lower phase transition temperature than a similar denser sample [50]. The much higher BET area seen in sample TiZrY2 compared to sample TiZrY1 can thus be the reason for the lower phase transition temperature, despite the higher doping concentration in this sample. It has also been reported that the faces of the anatase TiO₂ nanocrystals affect the kinetics of the phase transformation, where crystals with a dominant fraction of {101} faces display a higher thermal stability[51]. Examination of the XRD patterns for the samples show that the <004>/<101> ratio is similar for all samples, which indicates that oriented facet growth cannot explain the observed phase stability. The exception is sample TiZrY3, which has a larger fraction of <101> planes. This can explain the slightly higher phase transition temperature of this sample compared to TiZrY4, which has a slightly higher dopant concentration.

Figure 6 shows results from in situ XRD annealing experiments. It is clear that the in situ and Raman measurements agree well with each other. The rutile starts to form at temperatures above 1273 K and is completed at 1473 K. The variations between the in situ Raman and in situ XRD results are due to different annealing set-ups and shorter dwell times (approximately 17 min) in the in situ XRD measurements compared to the Raman measurements (120 min). Interestingly, precipitation of ZrTiO_4 occurs at temperatures below the anatase to rutile phase transition (approximately 1123 K) in proportion to the loss of anatase phase. This suggests a mechanism where cations are dissolved from the anatase structure to form a co-existing ZrTiO_4 , followed by the anatase to rutile transformation to finally yield co-existing rutile and ZrTiO_4 . These experiments explain the results from the Raman measurement above and suggest that the Zr, Y doped anatase TiO_2 are meta-stable at the highest dopant concentrations (> 7 at% as determined by XPS).

We have previously shown that Zr doped anatase nanoparticles exhibit a delayed anatase to rutile phase transformation up to $\Delta T \sim 150$ K, and that at 13 wt% Zr the transformation is completed at 1473 K after similar annealing procedures as employed here [26, 27]. In these studies the Raman line profiles were modelled to follow the grain growth upon annealing. Because of phonon confinement effects in the nanocrystals the full width at half maximum (FWHM) increases and the $E_g(\nu_6)$ peak, which for bulk TiO_2 is at $\sim 144 \text{ cm}^{-1}$, shifts to higher wavenumbers when the crystal size decreases (this is typically significant in anatase for $d < 10$ nm) [27]. Since these spectral modifications are suppressed in Zr doped anatase as a function of annealing temperature it is conjectured that the grain growth is also slowed down [26, 27]. Here the FWHM and anatase E_g peak position as a function of annealing temperature follow a similar functional form for TiO_2 and doped TiO_2 , indicating similar grain growth kinetics (Fig. 7). Hence, in contrast to Zr doped TiO_2 , co-doping Y and Zr do not appear to significantly modify the grain growth kinetics. Qualitatively, this agrees with the much lower

temperature for the observed anatase to rutile phase transition for Zr, Y co-doped samples, compared to Zr doping alone. We attribute this to the much larger ionic size of Y^{3+} compared to Zr^{4+} , which destabilizes the material structure.

In Fig. 8 Raman spectra of the amorphous TiZrY5 sample annealed at different temperatures are shown. The heat-treated sample (TiZrY5a) is also included in Fig. 8. After the phase transformation to rutile (bottom trace in Fig. 8.) an additional peak is observed at 315 cm^{-1} in the Raman spectrum. This peak is also apparent for TiZrY4 after the phase transformation, but it is not clearly distinguishable for lower doping concentrations (not shown). Based on previous studies we attribute the 315 cm^{-1} Raman band to precipitation of $Y_2Ti_2O_7$, which is reported to form under these conditions and produce intense Raman bands in this region [52, 53]. In contrast to the in-situ XRD measurements, no Raman bands can unambiguously be associated with $ZrTiO_4$ in Fig. 8, which can be explained by the different measurement protocols, where XRD were performed at elevated temperatures and Raman at room temperature (after annealing and subsequent cooling). For $TiZrO_4$ there is a strong dependence of the position of the Raman bands on the cooling rate. Very slow cooling rates, of the order of $\sim 10\text{ K h}^{-1}$, result in distinct Raman bands at 815 cm^{-1} , which become weaker with increasing cooling rate. With the cooling rates employed in the Raman measurements (3000 K h^{-1}), the spectra appear less distinct with the largest features at approximately 400 and 640 cm^{-1} [54], which overlap with the positions of the TiO_2 rutile bands.

3.3 Optical absorption coefficient

Fig. 9 shows the absorption coefficient deduced from spectrophotometry measurements. The absorption coefficient for the films was calculated according to the equation $\alpha(\lambda)d = \ln((1-R_{\text{corr}}(\lambda))/T_{\text{corr}}(\lambda))$, where d is the film thickness, and R_{corr} and T_{corr} are the corrected values of the total reflectance and transmittance, respectively [55]. The position of the band

gap shown in Table 1 is determined using the procedure described by Panda and co-workers [56]. A slight decrease of the band gap is seen for low and intermediate concentrations whereas at the highest doping concentrations an up-shift of the band gap of approximately 0.1 eV occurs (Fig. 10). Recent theoretical calculations have shown that band gap narrowing and broadening in TiO_2 can be obtained by applying external pressure or lattice deformation [57]. Applying these results to the measured lattice deformation that occurs in our samples (Fig. 3), a blue shift of the band gap of up to 0.04 eV is inferred (Fig 10). This indicates that lattice deformation contributes to an increase of the band gap. For low and intermediate doping concentrations a red shift of the band gap is observed, contrary to the blue shift predicted by the lattice deformation effect. We attribute this to colour centres created in the material as a consequence of the inclusion of Y and Zr in the lattice, rather than an actual band gap narrowing, in agreement with previous studies (See Ref. [58] and references therein). Recent calculations of the electronic and optical properties in Y doped TiO_2 have shown that Y doping does not introduce any states in the band gap but instead shifts the valence and conduction band maximum closer to each other[59], which can be interpreted as colour centres in the band gap. With increasing doping concentration the lowest lying levels in the conduction band will start to fill up and thus shift the absorption edge towards higher energies which is the Burstein-Moss effect [60, 61]. Thus we interpret the findings in Fig. 10 as a result of two opposing effects. At low and intermediate doping concentrations colour centres or local band gap narrowing occurs due to Y doping, which results in a red shift of the absorption edge. At higher concentrations the Burstein-Moss effect and the lattice deformation are dominant and thus create a blue shift of the absorption edge. Interestingly, the low-energy absorption tail, which is generally seen in semiconductors and described by the Urbach rule [62], is suppressed in the doped samples. This suggests that excitonic coupling to the TiO_2 optical phonons is modified by even small amounts of cation doping. The results

resemble the result obtained after Zr doping alone [63]. We conclude that co-doped Y and Zr do not result in visible light absorption, as suggested by the results for Y doping alone [24, 25], and that the absorption edge instead resembles that of Zr doped anatase TiO₂.

3.3 Formic acid adsorption

Carboxylate coordination can be used to probe the chemical properties of metal oxide surfaces [64]. In particular carboxylate coordination on TiO₂ has been extensively studied in the past (see Refs. [64, 65] and references therein). Ester bond formation and splitting of the surface-coordinated $\nu_{as}(\text{OCO})$ and $\nu_s(\text{OCO})$ vibrational modes have been used to classify the carboxylate bonding and adsorption sites. Fig. 11 shows DRIFT spectra of formic acid pre-adsorbed on different co-doped samples (solid, thick curves). By comparisons with previous reports [65-68] it is evident from Fig. 11 that formic acid dissociates on all samples to form bidentate and monodentate coordinated formate molecules on the surface of the particles with their typical vibrational $\nu_{as}(\text{OCO})$ and $\nu(\text{C=O})$ bands occurring at $\sim 1560\text{ cm}^{-1}$ and $\sim 1670\text{ cm}^{-1}$, respectively. Additionally, an absorption band at $\sim 1580\text{ cm}^{-1}$ contributes to the broad absorption band in the $1550\text{-}1600\text{ cm}^{-1}$ region as suggested from the asymmetric shape of the broad absorption band, and deduced from peak deconvolution (not shown). This absorption band can be attributed to un-coordinated formate ions (aqueous-like) [66, 67]. This is further supported by the strong absorbance of this band seen on the amorphous TiZrY5 sample, which contains more adsorbed OH/H₂O as shown by XPS (Section 3.1). Overall the vibrational frequencies and their relative intensities for the doped samples are similar to those reported for small pure anatase particles [65, 67]. The important difference to be noted in Fig. 11 is that a higher Zr and Y doping concentration results in relatively larger fraction of formate ions ($\sim 1580\text{ cm}^{-1}$) compared to bidentate formate ($\sim 1560\text{ cm}^{-1}$), and that the concentration of monodentate species ($\sim 1670\text{ cm}^{-1}$) decreases monotonously with increasing

dopant concentration. The different adsorption modes for formate on TiO₂ are schematically given in Fig. 12.

The origin of this dopant dependent coordination trend may be due to both dopant-induced physical and surface chemical modifications of the samples. The physical properties reported in Table 1 do not show obvious trends that support the former, that is that formate ion formation correlates with decreasing surface area and pore-size distribution (the opposite is found), or that bidentate coordination correlates with decreasing grain size (and possibly number of low-coordinated surface sites; the opposite is found). Instead, we attribute the formate speciation to be primarily a consequence of modifications of the surface chemical properties, where doping results in an increasing concentration of Brønsted acid sites and metal-OH groups, which promotes formation of formate ions. According to the XPS measurements the number of metal-OH groups increases with increasing dopant concentration. This trend correlates with a larger concentration of formate ions ($\sim 1580\text{ cm}^{-1}$) observed in DRIFTS (Table 4). The reason for the larger number of metal-OH groups with increasing doping concentration can be found in the surface acidity. Incorporation of dopant cations creates a charge imbalance resulting in Brønsted or Lewis acid sites depending on the coordination geometry and valence of the dopant [17, 69]. Utilising the model of mixed oxides by Tanabe *et al.*[69], which states that the dopant cation enters the host oxide while maintaining its coordination number, it can be predicted whether Brønsted or Lewis acid sites are formed. TiO₂, ZrO₂ and Y₂O₃ have 6-fold, 8-fold, and 6-fold coordination, respectively [69], and the oxidation states of the metals, as determined by XPS, are Ti⁴⁺, Zr⁴⁺, Y³⁺. It follows that incorporation of Zr and Y oxides into the TiO₂ lattice creates a negative charge imbalance, -4/3 and -1 respectively, and that Brønsted acid sites are expected, which becomes protonated to maintain charge neutrality. Thus within this simplified model the observed trend of increasing OH concentration observed in XPS and DRIFTS as a function of dopant

concentration, can qualitatively be understood. The protonated surfaces promote formation of formate ions as schematically depicted in Fig 12. For the sample doped only with Zr, TiZr₂, the same trend is expected, since both Zr and Y will create a negative charge imbalance, with Zr being even more electronegative than Y, according to the model by Tanabe. Hence more formate ions and less monodentate species is expected to be formed on this sample compared to the pure TiO₂ sample. This is also observed experimentally and evaluation of the peak intensities shows that the amplitude ratio between the η -coordinated formate and formate ion ratio is slightly lower for sample TiZr₂ than for sample TiZrY₄, Table 4. This is expected because of the higher doping concentration in the sample made with only Zr compared to TiZrY₄. For the high temperature annealed sample TiZrY_{5a}, where precipitation occurs, the model fails, as expected, to predict observed acid-base properties as is evident by examining the DRIFTS and XPS data. The $\nu_a(\text{OCO})$ band appears similar to that at low dopant concentrations with smaller concentration of formate ions. This is concerted by smaller numbers of displaced OH-groups (in the 3600-3750 cm⁻¹ region; not shown) upon HCOOH adsorption compared to the other samples, which indicates fewer surface OH groups. Moreover, XPS shows a smaller concentration of O 1s(2), i.e. metal-OH bonds (Table 2). These results are expected since dissolution and phase-segregation occur as well as O-deficiency and dehydroxylation as a result of the thermal treatment in sample TiZrY_{5a}. Considering the low overall dopant concentration in TiZrY₅ these results also support the argument that cation dissolution to the surface regions precedes precipitation.

3.4 Photo-degradation of formic acid

Fig. 11 shows operando DRIFT spectra acquired after different times of simulated solar light irradiation (0 to 60 min). The formic acid absorption bands decrease as a function of solar light irradiation on all samples except the amorphous sample TiZrY₅. However, mode

resolved analysis of the individual bands show that the monodentate species ($\sim 1670\text{ cm}^{-1}$) decrease faster than the $\nu_{\text{as}}(\text{OCO})$ bands at $\sim 1560\text{ cm}^{-1}$ and $\sim 1580\text{ cm}^{-1}$ (Fig. 13). An initial increase of the $\nu_{\text{as}}(\text{OCO})$ and $\nu_{\text{s}}(\text{OCO})$ bands indicates that monodentate formate initially is partly transformed into bidentate formate and formate ions. No new absorbance bands appear in DRIFTS during irradiation, implying complete oxidation of adsorbed formic acid.

The degradation rates were quantified by comparing the integrated absorbance in the $3050\text{--}2600\text{ cm}^{-1}$ region due to the $\nu(\text{C-H})$ stretching modes in formate, the absorbance due to monodentate formate at 1670 cm^{-1} , formate ions at 1580 cm^{-1} and bidentate formate at 1560 cm^{-1} , respectively. We stress that with DRIFTS differences in sample morphology (particle size, surface area and porosity) are effectively handled, since the sample signal is deduced by internal reference of the reflectivity of each sample (background measurement). Assuming first-order kinetics, the initial degradation rates were calculated from spectra acquired between 0 and 10 min. Due to partly conversion of monodentate formate into bidentate formate and formate ions the two latter species initially increase (Fig 13). Thus the rate coefficient for these two species is determined after this initial increase, which settles at different times for the different samples depending on the decomposition rate of the monodentate species. The rate constants are shown in Table 4. Corresponding data obtained on pure anatase TiO_2 and 6.8 wt% Zr doped TiO_2 prepared by the same methods as the TiZrY samples [26] are also included in Table 4. The Zr doped sample exhibited the highest formate degradation rate of the studied Zr doped TiO_2 samples [26]. It is evident that the best Zr doped sample degrades formate slightly faster, 0.009 min^{-1} (0.008 min^{-1}) compared to the best Y and Zr co-doped sample, TiZrY1 0.006 min^{-1} (0.008 min^{-1}), during the first 10 min. In contrast, after extended illumination times ($> 60\text{ min}$) the removal rates become similar (values in parenthesis above determined between 60 and 70 minutes of illumination assuming first order kinetics).

As seen in Table 4 the sample with only Zr-doping exhibit a decomposition rate that is higher than the co-doped samples. Since both types of samples create Brønsted acid sites that favour formate ions, the reason for this discrepancy cannot be found in different surface properties, which favours differently coordinated formate species (*vide infra*). Instead an increased recombination rate in the co-doped samples is likely. With inclusion of the much larger Y atom in the TiO₂ lattice, it is reasonable to assume that more discrepancies and defects are found in the crystals that can act as charge trapping and recombination centres, and thereby reduce the number of charge carriers available for the redox processes occurring on the photocatalyst surface.

The photo-degradation rates calculated from the $\nu(\text{C-H})$ bands disguise the fact that the observed total removal rates is due to different photo-reactivity of the different coordinated formate species. It has previously been shown that the degradation rate on TiO₂ is different for differently coordinated formate species and highest for monodentate coordinate species [65, 67, 70]. In Table 4 the mode-resolved degradation rates for monodentate, bidentate and formate ions are shown. Monodentate coordinated species exhibit the highest degradation rate, and thus samples with the highest fraction of monodentate species accordingly have the highest total degradation rates. As noted in the previous section, the fraction of monodentate species correlates inversely with the dopant concentration and explains the trend deduced by analyzing the $\nu(\text{C-H})$ bands. This trend has also been reported for rutile nanoparticles exposing different crystal faces [70]. Finally, comparisons of the photo-degradation rates of bidentate formate and formate ions show that their decomposition rates are similar. Accordingly, we are able to group the relative photo-degradation rates of the samples to their relative concentration of monodentate species, and indirectly to the surface acidity of the samples. The more acidic samples have a higher concentration of metal-OH groups, with less complexing ability for formate, and favour instead formation of hydrogen bonded formate

ions. These results show that the observed trend of the photo-degradation rate of cation doped TiO_2 is largely governed by the coordination of the adsorbed species. Since, carboxylate species are common intermediates in photo-oxidation reactions, these results point to an additional important property to control for optimum photocatalytic activity.

4. Conclusions

Co-doped anatase TiO_2 with Zr and Y was synthesized by means of homogenous hydrolysis using urea as precipitating agent. XRD, EDX, XPS and Raman spectroscopy analyses confirm substitutional doping of Ti^{4+} with Zr^{4+} and Y^{3+} in the anatase structure up to a critical concentration (approximately 3 at% Zr + 3 at%Y, or ~13 wt% total dopant concentration) with improved thermal stability compared to pure anatase TiO_2 nanoparticles. However, co-addition of Y ions in the anatase structure result in poorer phase stability compared with Zr doping alone using similar dopant concentrations. Cation segregation and dissolution with concomitant precipitation of $\text{Y}_2\text{Ti}_{2-x}\text{Zr}_x\text{O}_7$ and ZrTiO_4 precede the anatase to rutile phase transformation. Y and Zr co-doping modifies the optical absorption edge with a resulting attenuation of the Urbach tail and a slight red shift of the absorption edge for low and intermediate doping concentrations and a minor blue-shift for high doping concentrations. The blue-shift of the band gap at the highest dopant concentration is attributed to the Burstein-Moss effect and also the expansion of the anatase unit cell.

Formic acid dissociates on all samples and results in differently coordinated surface species: bidentate formate > formate ions > monodentate formate, in order of their relative abundance. Re-distribution of surface formate species occurs with increasing Zr and Y dopant concentrations. An increasing concentration of bidentate formate ions is observed relative to monodentate coordinated formate species with increasing Y and Zr loadings, and is attributed to an increasing surface acidity. The total photo-degradation of formate is highest at the very lowest dopant concentrations, and similar to pure anatase and the best Zr doped TiO_2

photocatalyst, while it deteriorates with increasing Y and Zr concentrations. This reactivity trend is directly related to the relative concentration of monodentate species compared to bidentate and ionic formate species, respectively, since the photo-degradation rate of monodentate coordinated formate is highest. The extended (> 60 min) photo-degradation rate for the best Zr, Y co-doped TiO₂ samples is, however, similar to the best Zr doped TiO₂ sample prepared by a similar method. Our analysis suggests that adsorption and photo-degradation of formic acid on Y, Zr co-doped TiO₂ can be explained in terms of dopant-induced charge imbalance and surface chemical modification models, which favours differently coordinated formate species.

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Table 1. Physical properties of the samples.

Sample	Crystal Structure	Lattice parameters		Crystal size (nm)	Specific surface area (m ² g ⁻¹)	Pore volume (ml g ⁻¹)	Band gap (eV)
		<i>a</i> (Å)	<i>c</i> (Å)				
TiZrY0	Anatase	3.806	9.470	4.9	291	0.24	3.18
TiZrY1	Anatase	3.798	9.514	6.6	280	0.23	3.17
TiZrY2	Anatase	3.804	9.528	6.6	488	0.41	3.15
TiZrY3	Anatase	3.804	9.532	7.4	418	0.54	3.14
TiZrY4	Anatase	3.806	9.533	7.5	477	0.50	3.26
TiZrY5	Amorphous	3.807	9.567	4.2	564	0.73	3.25
TiZrY5a	Anatase	3.795	9.541	13.0	101	0.35	

Table 2. Chemical composition of TiZrY samples as determined by XPS and EDX after subtraction of the carbon content. Three chemically non-equivalent O atoms with different BE are apparent in XPS.

Sample	XPS (at. %)						XPS Oxygen to metal ratio			EDX (at. %)		
	O 1s(1)	O 1s(2)	O 1s(3)	Ti	Zr	Y	O1s(1)	O1s(2)	O1s(3)	Ti	Zr	Y
TiZrY1	55.8	8.6	5.5	29.3	0.5	0.5	1.85	0.28	0.18	25.2	0.3	0.2
TiZrY2	55.6	10.8	3.8	28.8	0.9	0.9	1.81	0.33	0.12	26.7	0.6	0.6
TiZrY3	55.9	10.6	3.0	28.0	1.2	1.4	1.82	0.34	0.10	25.4	0.8	0.8
TiZrY4	55.9	10.4	3.1	26.1	1.9	2.6	1.83	0.34	0.10	26.6	1.3	1.3
TiZrY5	51.2	13.0	4.5	24.4	3.4	3.5	1.64	0.42	0.14	23.4	2.1	2.1
TiZrY5a	59.8	6.1	1.6	25.2	3.5	3.9	1.83	0.19	0.05	n.a.	n.a.	n.a.

Table 3. Binding energy for the elements detected in XPS measurement.

Sample	XPS binding energy (eV)					
	O 1s(1)	O 1s(2)	O 1s(3)	Ti	Zr	Y
TiZrY1	530,2	531,2	532,3	458,9	182,4	158,2
TiZrY2	530,2	531,3	532,4	458,8	182,3	158,1
TiZrY3	530,4	531,6	532,7	459,1	182,6	158,4
TiZrY4	530,5	531,9	532,9	459,1	182,7	158,4
TiZrY5	530,5	531,6	532,7	459,0	182,7	158,2
TiZrY5a	530,4	531,8	532,6	459,0	182,6	158,1

Table 4. Mode-resolved, first-order rate constants, k_{dec} , for photocatalytic decomposition of differently coordinated format species determined for the first 10 minutes of illumination compared with the corresponding result for the integrated area of the C-H band. Also the relative amounts of monodentate and formate ions are shown.

Sample	$\int \nu(\text{C-H})$	Monodentate (η) (1670 cm^{-1})	Formate ions (1580 cm^{-1})	Bidentate (1560 cm^{-1})	Amplitude ratio η - coord / ions
TiZrY0	0.012	0.052	0.011	0.009	0.552
TiZrY1	0.006	0.067	0.008	0.007	0.421
TiZrY2	0.003	0.052	0.004	0.003	0.416
TiZrY3	0.003	0.056	0.005	0.004	0.429
TiZrY4	0.003	0.032	0.002	0.002	0.422
TiZrY5	0.003	0.029	0.002	0.002	0.310
TiZrY5a	0.002	0.023	0.001	0.001	0.320
TiZr2	0,009	0.063	0.007	0.007	0.385

Figure captions

Fig. 1 SEM images of samples a) TiZrY1, b) TiZrY2, c) TiZrY3, d) TiZrY4 and e) the partly amorphous TiZrY5.

Fig. 2 XRD spectra of as prepared samples TiZrY0-TiZrY5.

Fig. 3 Relative unit cell expansion for the doped samples compared to the pure TiO₂ sample. Data for a linear relationship is given in the figure.

Fig. 4 Raman spectra of the as prepared samples.

Fig. 5 Anatase to rutile phase transformation of all samples as function of annealing.

Fig. 6 Concentrations of anatase, rutile and ZrTiO₄ crystals (amorphous content in the sample excluded) during heat treatment of sample TiZrY5 as determined from in situ XRD measurements.

Fig. 7 Peak position (a) and FWHM (b) of the anatase E_g(v₆) mode as function of annealing.

Fig. 8 Raman spectra of sample TiZrY5 annealed at different temperatures. The major anatase and rutile Raman bands are indicated with "A" and "R", respectively. A new band due to Y₂Ti₂O₇ occurs at 315 cm⁻¹ after high temperature annealing.

Fig. 9 Absorption coefficient as a function of wavelength for the different Zr, Y doped TiO₂ samples as deduced from spectrophotometry measurements.

Fig. 10 Measured band gap for the different samples as a function of dopant concentration. Also shown is the bandgap change caused by lattice deformation.

Fig. 11 In situ DRIFT spectra of formic acid on samples a) TiZrY0 (pure TiO₂), b) TiZrY1, c) TiZrY3, d) TiZrY4, e) TiZrY5 and f) TiZrY5a, respectively, as a function of simulated solar light illumination (0 to 60 min).

Fig. 12 Schematic diagram for adsorption of different coordinated formate species on TiO_2 . Left to right monodentate (η -coordinated), bridge bonded (μ -coordinated) and formate ion via a hydroxyl group on the surface.

Fig. 13 Normalized peak intensity for a) the bidentate formate specie at $\sim 1560\text{ cm}^{-1}$, b) the formate ions specie at $\sim 1585\text{ cm}^{-1}$ and c) the monodentate formate specie at $\sim 1670\text{ cm}^{-1}$.