

Effect of Sn surface states on the photocatalytic activity of anatase TiO₂

Freddy E. Oropeza, Bastian Mei, Ilia Sinev, Ahmet E. Becerikli, Martin Muhler, Jennifer Strunk*

Laboratory of Industrial Chemistry, Ruhr-University Bochum, Universitätsstrasse 150, 44801 Bochum, Germany

ARTICLE INFO

Article history:

Received 12 November 2012
Received in revised form 22 March 2013
Accepted 27 March 2013
Available online 2 April 2013

Keywords:

Photocatalysis
TiO₂
SnO₂
Dye degradation
Grafting
Surface doping
Temperature-programmed reduction
X-ray absorption spectroscopy
X-ray photoelectron spectroscopy
Surface charge trapping

ABSTRACT

The influence of surface Sn-doping on the photocatalytic properties of anatase TiO₂ has been investigated in samples prepared by a grafting route using Sn(IV) *tert*-butoxide as Sn precursor. The grafting procedure leads to the formation of isolated Sn(IV) sites on the surface of anatase TiO₂ powders as gauged by structural characterisation based on XRD, Raman spectroscopy and XAS. Studies of the surface reduction based on TPR experiments and XPS provide the conditions for a selective reduction of surface Sn(IV) to the divalent oxidation state. Electronic structure characterisation based on valence band XPS and DRS shows that there is a slight widening of the band gap upon Sn(IV)-grafting, but Sn(II) related states emerge at the top of the main valence band upon reduction at temperatures up to 350 °C, and this induces visible light absorption. Grafting of TiO₂ with Sn(IV) increases the formation rate of •OH radicals on the surface of the material. Reduction of the Sn(IV)-grafted TiO₂ to form surface Sn(II) brings about substantial increase of the photocatalytic efficiency for the methylene blue degradation under irradiation with $\lambda \geq 320$ nm compared with Sn(IV)-grafted and pure anatase TiO₂. This observation is explained based on a surface hole trapping by the Sn(II)-related surface states which lie above the top of the main valence band and can therefore act as trapping sites for holes produced under photoexcitation.

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1. Introduction

There is a growing interest in the use of wide band-gap oxide semiconductors as photocatalysts with the ability to use sunlight to bring about reactions such as the degradation of organic pollutants or the production of hydrogen from water or hydrocarbons. TiO₂ and SnO₂ are both well characterised semiconductors that have been shown to act as photocatalysts for some of those important reactions. Furthermore, being of great abundance and low price, these materials are very attractive for industrial application. However, the use of these solids in solar energy technologies is limited because they are *only active under UV irradiation*, which represent less than 5% of the solar spectrum. A second factor that limits the activity of photocatalysts, and therefore their applied use, is *the quick recombination of the electrons and holes generated under irradiation*.

Visible light photocatalytic activity has been previously achieved by cationic and anionic doping of TiO₂ with coloured transition metals [1] and with nitrogen [2,3], respectively. Nonetheless, this method often decreases the catalytic efficiency of TiO₂ by inhibiting charge migration through the metal oxide [1,4] because

of carrier localisation produced by the breaking of translational symmetry upon the positionally disordered introduction of dopant species [5]. However, it has been reported that low level doping of TiO₂ with Sn(IV) enhances its photocatalytic activity towards the oxidation of organic compounds under visible light [6,7] as well as in UV light [8–10].

SnO₂ has the rutile TiO₂ structure and it is possible to prepare rutile solid solutions in the whole range of concentrations [11,12]. Anatase TiO₂ with up to 10% Sn doping has been also successfully synthesised [13]. Regardless of the polymorph, Sn-doping in TiO₂ leads to an enhanced photocatalytic activity, especially in the range 0–10% of Sn cation contents [13,14]. Based on electronic structure studies of rutile Sn_xTi_{1-x}O₂ solid solutions, the improved photocatalytic activity upon Sn doping has been partially attributed to surface states associated with segregated Sn ions in the divalent state. Free post-transitional metal ions in the *N* – 2 oxidation state such as Sn²⁺ and Sb³⁺ have a configuration 5s²5p⁰. In solid state oxides, the 5s electrons hybridise strongly with O 2p states to give antibonding states of mixed metal 5s–O 2p character at the top of the valence band. These states can further interact with nominally empty metal 5p states to give a directional electron lone pair as long as the cation occupies a site which lacks inversion symmetry [15–17]. Bulk sites within the rutile structure are centrosymmetric, but the lowered coordination at surface sites removes the inversion symmetry, which allows the 5s–5p hybridisation and a lowering

* Corresponding author. Tel.: +49 2343223566.

E-mail address: jennifer@techem.rub.de (J. Strunk).

of the internal electronic energy of the dopant ion. Thus segregation and reduction of bulk ions in the N oxidation state to give surface ions in the $N - 2$ oxidation state lowers the surface energy and provides a thermodynamic driving force for segregation. Since Sn(II)-derived electronic states lie above the top of the main valence band of TiO_2 , they induce visible light absorption and act as trapping sites for holes produced under photoexcitation [18,19].

The effect of bulk Sn(II)-doping in TiO_2 has been recently studied by Boppana and Lobo [20]. Although no clear evidence of tin incorporation into the TiO_2 lattice was provided, it was found that Sn(II)-doped samples were active towards the photocatalytic oxidation of organic compounds under visible light irradiation ($\lambda > 420 \text{ nm}$). However, photocatalytic tests using the full range of a Xe lamp (UV–vis light) showed that pure TiO_2 was more active than doped samples. Moreover, within the range of concentrations studied, higher concentrations of tin led to a further decrease of the photocatalytic efficiency of the solid.

Here, we report a study of the effect of Sn(II)-doping of TiO_2 restricted to the surface. Surface Sn(II)-doped TiO_2 samples were prepared by a controlled reduction of Sn(IV)-grafted anatase TiO_2 , based on combined analysis of temperature programmed reduction (TPR) profiles and X-ray photoelectron spectra (XPS). Photocatalytic characterisation based on methylene blue degradation and terephthalic acid hydroxylation shows that surface Sn(II)-doping greatly enhances the activity and overall efficiency of TiO_2 in degradation of organics. Enhanced photocatalytic efficiency can be attributed to the larger concentration of oxidising agents at the surface of the material as Sn(II) surface states act as hole trapper sites.

2. Experimental

2.1. Preparation of samples

The procedure used for grafting tin onto commercial anatase TiO_2 was based on the deposition of TiO_x on MCM-48 as previously reported [21]. With the help of a glove box and a vacuum line the procedure here described was carried out under inert atmosphere. Approximately 2 g of TiO_2 (pure anatase with $100 \text{ m}^2/\text{g}$ supplied by Sachtleben) were dried over night at 120°C under dynamic vacuum. The Sn precursor, tin (IV) *tert*-butoxide (Aldrich, 99.99%) was dissolved in about 50 ml of dry toluene. The amount was chosen according to the desired surface coverage, with maximum of $1.5 \text{ Sn}/\text{nm}^2$. The precursor solution was brought in contact with the dry support at room temperature and stirred for at least 4 h. The support was separated from the solution by means of sedimentation. The Sn-grafted TiO_2 was then washed three times with dry toluene ($\sim 30 \text{ ml}$), separating sample and solution each time by sedimentation, and dried under dynamic vacuum. The calcination was performed by heating the sample with $2^\circ\text{C}/\text{min}$ under a flow of $100 \text{ ml}/\text{min}$ N_2 to 300°C holding the temperature for 1 h. During the time at 300°C , the gas flow was switched to synthetic air, before the temperature was ramped at $2^\circ\text{C}/\text{min}$ to 450°C and kept for 4 h. Grafted samples were labelled as $\text{Sn}(x)/\text{TiO}_2$, where x is the nominal Sn loading in atoms of tin per nm^2 .

2.2. Physicochemical characterisation

Powder X-ray diffraction (XRD) and Raman spectroscopy were used to check crystalline phase of the samples. XRD was carried out on a Panalytical X'Pert Pro instrument using monochromated $\text{Cu K}\alpha_1$ radiation, whereas Raman spectra were recorded at room temperature using a Thermo Fisher Scientific FT-Raman spectrometer with excitation by a Nd:YAG laser ($\lambda = 1064 \text{ nm}$).

Reduction of the samples was studied by temperature-programmed reduction (TPR). All TPR profiles were taken in a flow setup using 4.54% H_2 in argon at a rate of $84.1 \text{ ml}/\text{min}$. The reactor was heated from room temperature to 850°C at a rate of $5^\circ\text{C}/\text{min}$ and held for 60 min. The H_2 concentration in the gas flow was analysed by thermal conductivity detector.

Electronic characterisation was based on valence band photoemission spectroscopy and UV/vis diffuse reflectance spectroscopy. X-ray photoemission spectra (XPS) were recorded on a UHV system equipped with a Gammadata-Scienta SES 2002 analyzer. The base pressure in the measurement chamber was $5 \times 10^{-10} \text{ mbar}$. Monochromatic Al $\text{K}\alpha$ (1486.6 eV ; 13.5 kV ; 37 mA) was used as incident radiation and the analyzer pass energy was set to 200 eV , resulting in an energy resolution better than 0.6 eV . For all samples it was necessary to use an electron flood gun to stabilise the surface charge. Use of a flood gun shifts all spectral features to high kinetic energy. Photoelectron spectra were therefore charge calibrated using the weak C 1s contaminant peak which was assigned a binding energy of 285.0 eV . The spectrometer is calibrated regularly to set the Fermi edge of a silver reference sample at zero binding energy. Diffuse reflectance (DR) spectra were measured in the visible and near-ultraviolet (UV) region using a Perkin-Elmer Lambda 650 instrument equipped with a Praying-Mantis mirror construction.

X-ray absorption fine structure (XAFS) measurements were carried out at HASYLAB (DESY in Hamburg, Germany) on the beamlines C and X1 (SnK edge 29200 eV) using a double-crystal Si(311) monochromator, which was detuned to 50% of maximum intensity to exclude higher harmonics in the X-ray beam. The spectra were recorded in the transmission mode at liquid nitrogen temperature. For the measurements the appropriate amount of each sample was pressed into self supporting pellets (13 mm diameter) and wrapped with Kapton tape. All the spectra were measured simultaneously with the reference spectrum of Sn foil placed between second and third ionisation chambers, so that the absolute energy calibration is performed. The spectra of Sn(II) and Sn(IV) oxides, which were used as references, were collected at the same conditions. All spectra were measured twice to ensure their reproducibility.

Analysis of the EXAFS spectra was performed with the software VIPER for Windows [22]. In the spectra of the absorption coefficient μ , a Victoreen polynomial was fitted to the pre-edge region for background subtraction. A smooth atomic background μ_0 was evaluated using a smoothing cubic spline. The Fourier analysis of the k^2 -weighted experimental function $\chi = (\mu - \mu_0)/\mu_0$ was performed with a Kaiser window. The required scattering amplitudes and phase shifts were calculated by the ab initio FEFF8.10 code [23] for SnO_2 rutile-type tetragonal structure. The fitting was done in the k - and r -spaces. The shell radius r , coordination number N , Debye–Waller factor σ^2 and adjustable “muffin-tin zero” ΔE were determined as fitting parameters. The errors of the fitting parameters were found by decomposition of the statistical χ^2 function near its minimum, taking into account maximal pair correlations.

2.3. Photocatalytic characterisation

The photocatalytic activity was evaluated by monitoring the photodecomposition of an aqueous solution of methylene blue (MB) with a concentration of 10 ppm. TiO_2 -based photocatalysts under UV irradiation have been shown to oxidise MB, with an almost complete mineralisation of carbon and of nitrogen and sulfur heteroatoms into CO_2 , NH_4^+ , NO_3^- and SO_4^{2-} respectively [24]. This method of assessing photocatalytic activity is a popular one for screening catalysts despite the possibility of direct photolytic degradation of the dye. To take account of this possibility the activity of all catalysts was always compared with that of pure anatase

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