Electronic Supplementary Information (ESI)

Electronic Properties of TiO_2-Based Materials Characterized by High Ti^{3+} Self-Doping and Low Recombination Rate of Electron-Hole Pairs

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FTIR spectroscopy

The FTIR spectrum of HSGT (Fig. S1) displays the characteristic splitting (Δ) between the asymmetric ($\nu_{asyC=O}$) and symmetric ($\nu_{symC=O}$) stretching of C=O bonds of the carboxylate groups ($\Delta = 145$ cm^{-1}), attesting the existence of a bidentate interaction between the acetylacetonate (acac) ligand and Ti^{4+} in the Ti-acac complexes.

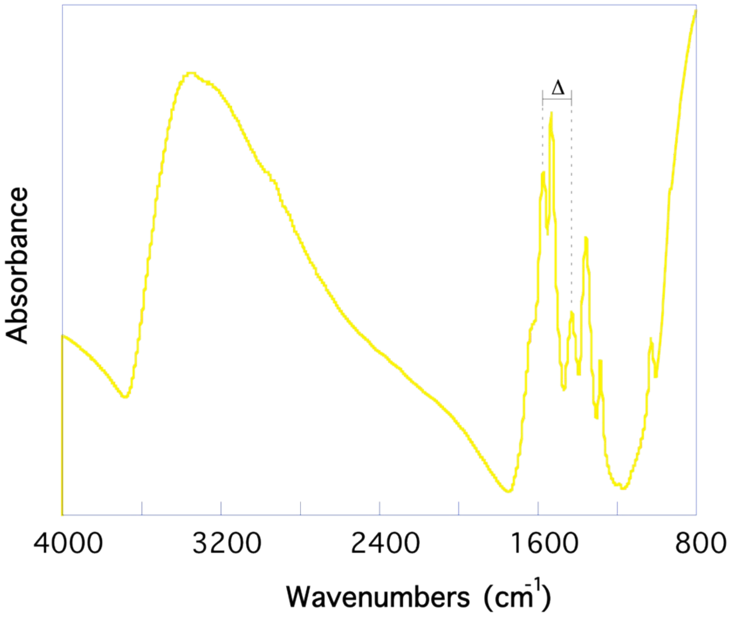


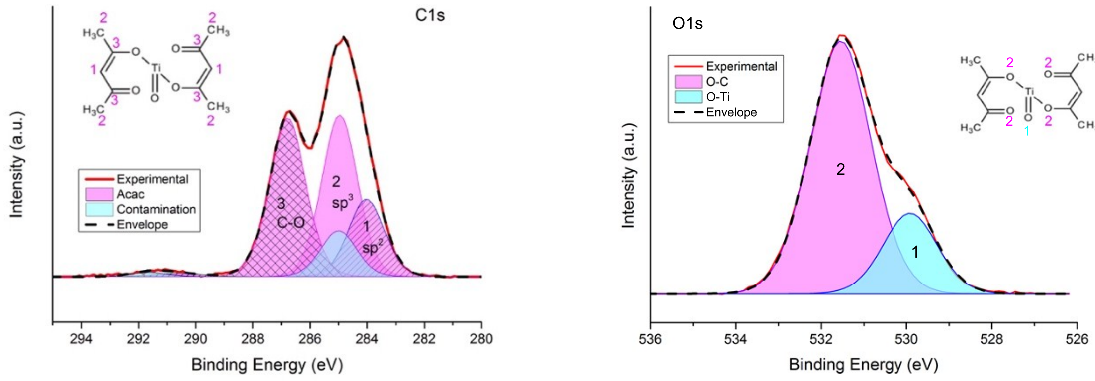
Figure S1. FTIR spectrum of HSGT sample recorded at room temperature.

Titanyl acetylacetonate

In order to obtain an experimental evidence of the formation of the Ti-acac complex and to identify the contributions to the C1s signal of the sample HSGT, the commercial titanyl acetylacetonate

(Merk KGaA, Darmstadt, Germany) was analyzed by XPS as reference compound. In Figure S2 the C1s and O1s peaks are shown together with the scheme of the molecule. The carbon atoms and the oxygen atoms are numbered with the aim of showing the peak assignment. For curve fitting, CASA XPS software (Version 2.3.17PR1.1, CASA Software Ltd, UK CASA Software Ltd, UK) was used. The C1s experimental line was modeled using four Gaussian – Lorentzian product functions (Table S1). The lower BE signal was ascribed to sp^2 carbon (C labeled 1 in the inset). This peak has a small shake-up satellite at + 6.6 eV. The area ratio between the satellite and the main peak was constrained to 0.06 in agreement with literature.[1] The area ratio of C_{sp3}/C_{sp2} and $C_{C\text{-}O}/C_{sp2}$ was set equal to 2 in agreement with the stoichiometry of the acetylacetonate ligand.

Some C contamination (285 eV light blue curve) was also taken into account: this is due to the exposure to the atmosphere. Its contribution originates a small peak at about 285.0 eV.



A

B

Figure S2. High-resolution C1s (A) and O1s (B) spectra of titanyl acetylacetonate, used as reference compound for the subsequent curve fitting of the signals of HSGT sample.

To check the reliability of the fit the quantitative analysis has been performed neglecting the contribution of the contamination and the results are in very good agreement with the expected stoichiometry as reported in Table S1.

Table S1. Peak fitting parameters used for the XPS-spectra of C1s and O1s signals of the titanyl acetylacetonate. The quantitative composition of the compound is also reported. The binding energy values are the mean calculated using three measurements. The standard deviation is given in parentheses. The accuracy of the quantitative analysis is estimated to be ± 10 %.

	Line Shape	**FWHM (eV)**	**Binding Energy (eV)**
C1s: C-sp^2	GL (30)	1.6 (0.1)	284.3 (0.2)
C1s: C-sp^3	GL (30)	1.6 (0.1)	285.0
C1s: C-O	GL (30)	1.6 (0.1)	287.1 (0.2)
C1s: C contamination	GL (30)	1.6 (0.1)	285.0 (0.1)
O1s: O - Ti	GL (30)	1.5 (0.1)	529.9 (0.2)
O1s: O - C	GL (30)	1.7 (0.1)	531.5 (0.2)
Quantitative analysis (at. %)			
	Ti	C	O
Stoichiometry	6.2	62.5	31.3
Experimental XPS	6.7	62.2	31.1

Survey spectra of the analyzed TiO_2 samples

The survey spectra (Fig. S3) of the all the investigated samples were acquired to ascertain their purity: for the samples SGT, SGT-400 and HSGT-400 only the signals of Ti and O were detected together with very small amounts of carbon which is always present when a sample has been in contact with the atmosphere.

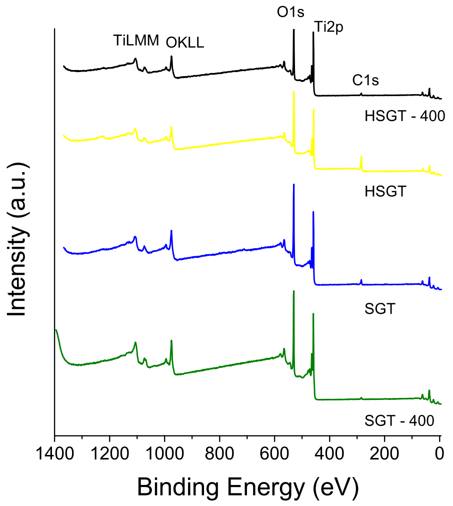


Figure S3. Survey spectra of the investigated titania samples. X-ray source: Al Kα.

Modelling of removal kinetics of 2,4-DCP

The experimental curves in Figure 7 could not be satisfactorily described neither by a pseudo first-order kinetic model nor by a pseudo second-order kinetic model as both these models yielded low values correlation coefficient r^2.[2] The concentration-time profiles could be successfully described by double-exponential curves as described in the model (S1).

$$C_{sol}(t)=Ae^{-\lambda_1 t}+Be^{-\lambda_2 t} \tag{S1}$$

where C_{sol} is the 2,4-DCP concentration in the liquid phase (mmol dm^{-3}), and t the time (min).

The model (S1), previously developed to describe the removal kinetics of different herbicides,[3] is compatible with a physico-chemical model, based on the hypothesis that a reversible, first-order adsorption on HSGT surface is followed by a subsequent reaction of the pollutant according to the scheme:

$$C_{sol} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} C_{ads} \xrightarrow{k_2} P \tag{S2}$$

where C_{ads} is the concentration of adsorbed pollutant, P indicates the degradation products, k_1 and k_{-1} are the direct and inverse first-order kinetic constants of the pollutant sorption, and k_2 is the first-order kinetic constants of the pollutant degradation.

The estimates of parameters of the mathematic model (S1), based on the experimental curves in Figure 7 (Table S2) confirm that the characteristic times of both the pollutant sorption and degradation, corresponding to $1/\lambda_1$ and $1/\lambda_2$ respectively, are much shorter when using smaller particles of HSGT.

Table S2. Estimates of parameters of the mathematic model (S1).

Granulometry	**A (mmol dm^{-3})**	**B (mmol dm^{-3})**	**λ_1 (min^{-1})**	**λ_2 (min^{-1})**
uncontrolled	0.17	0.13	$6.07\cdot10^{-2}$	$1.28\cdot10^{-3}$
D < 90 μm	0.17	0.13	$3.37\cdot10^{-1}$	$9.67\cdot10^{-2}$

Effect of the intraparticle diffusion.

In order to establish whether the overall 2,4-DCP removal kinetics is limited by the intraparticle diffusion or by the adsorption/reaction mechanism, we carried out an approximate evaluation of the Thiele modulus (φ^2), adopting the follow definition:[4]

$$\varphi^2 = \frac{R^2 \lambda_2}{D} \qquad \text{(S3)}$$

In the present context, R is the average size of titania particles, D is the diffusion coefficient of 2,4DCP in free water, λ_2 is the kinetic constant in the mathematical model (S1).

The Thiele modulus can be thought of as the ratio of a diffusion time to a characteristic chemico-physical time. The diffusion time is the time needed for a free molecule to diffuse within a titania particle (R^2/D), whereas the chemical-physical time (i.e. a characteristic time of the adsorption/reaction process) can be obtained adopting the inverse of the parameter λ_2. For large values of the Thiele modulus ($\varphi >> 1$), the rate of adsorption/reaction is much greater than the rate of diffusion. In this case the effectiveness factor (η) of the catalyst is significantly less than unity and $\eta \approx 1/\varphi$ (*diffusion limited process)*. On the contrary, at small values of the Thiele modulus ($\varphi << 1$), the diffusion rate is much larger than the reaction rate, and the effectiveness factor is near unity (*reaction limited process)*[4].

We adopted the following values for the parameters in equation (S3):

from the experimental results in the Table S2: $\lambda_2 \approx 10^{-3}$ min$^{-1} \approx 1.6\ 10^{-5}$ s^{-1};

assuming the 2,4-DCP as model pollutant, the diffusion coefficient in free water is:[5]

$D \approx 7.8\ 10^{-10}$ m^2 s^{-1};

the average size of titania particles is: $R \approx 100$ mm $\approx 10^{-4}$ m.

Using these data we obtained $\varphi^2 = 2.1\ 10^{-4}$ and $\varphi = 1.4\ 10^{-2}$. Consequently, it can be assumed that the overall kinetics of the herbicide removal is not affected by the intraparticle diffusion.

References

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