



Activity versus selectivity in photocatalysis: Morphological or electronic properties tipping the scale



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ABSTRACT

In this paper a structure-activity and structure-selectivity relation is established for three commercial TiO₂ sources (P25, P90, and PC500). Morphological and electronic parameters of the photocatalysts are determined using widely applicable and inexpensive characterization procedures. More specifically, the electronic properties are rigorously characterized using an electron titration method yielding quantitative information on the amount of defect sites present in the catalyst. Surface photovoltage measurements on the other hand provide complementary information on the charge carrier recombination process. As model reaction, the degradation of a solid layer of stearic acid is studied using an in situ FTIR reaction cell that enables to investigate the catalyst surface and possible formation of reaction intermediates while the reactions are ongoing. We show that the order of photocatalytic conversion is PC500 > P90 > P25, matching the order of favorable morphological properties. In terms of selectivity to CO₂ formation (complete mineralization), however, this trend is reversed: P25 > P90 > PC500, now matching the order of advantageous electronic properties, i.e. low charge carrier recombination and high charge carrier generation. With this we intend to provide new mechanistic insights using a wide variety of physical, (wet) chemical and operando analysis methods that aid the development of performant (self-cleaning) photocatalytic materials.

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1. Introduction

Photocatalysis is a well-established technology for pollution abatement in both the gas phase and aqueous phase [1–4]. More recently, photocatalytic self-cleaning materials have become an important application field as well [5]. In the selection of the most suitable catalyst, not only high activity but also pricing and safety play important roles. In this regard titanium dioxide (TiO₂) is an ideal candidate since it is relatively inexpensive, non-toxic, (photo-)stable and easily activated under UV light illumination [6]. In addition, it is already used in a number of everyday applications such as the food industry, sunscreen, paint and cosmetics, that could facilitate rapid transition of self-cleaning TiO₂ applications from the laboratory scale to commercial applications [5]. One of the major drawbacks of TiO₂ based photocatalysis is its low efficiency, which is mainly due to charge carrier recombina-

tion. This problem can be circumvented by improving the photo-electronic properties or by modifying the photocatalyst on the morphological level [7]. The former involves the formation of composite semiconductors, doping or modification with (noble) metal nanoparticles [8]. The latter is mainly based on maximizing the exposure of the catalyst surface to pollutants by increasing the surface area using different (nanosized) geometries [9]. An additional advantage is that charge carriers are formed closer to the surface thus reducing charge carrier recombination [7,10]. It is evident that different factors play an important role and understanding the interplay between these phenomena is essential for further optimizing the photocatalytic efficiency. One should also keep in mind the final application. It is shown that the material properties that dominate the overall photocatalytic activity in aqueous phase differ from those in gas phase [11–13]. On the other hand, very limited information is available on the driving properties for self-cleaning applications taking place at the solid (catalyst) - solid (pollutant) - gas (ambient) interface.

In this study both morphological and electronic properties of three commercially available photocatalysts are rigorously characterized in order to adequately evaluate the photocatalytic

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self-cleaning activity and thus establish a full structure-activity relation. A valuable correlation between photocatalytic activity and structural and physical properties of commercial TiO₂ has been established by Ohtani's group using statistical multivariable analysis [13]. They used five different representative reactions and their relative rates were linked to six different material properties. Since all reactions were conducted in aqueous or gas phase, no conclusions can be made on the driving factors of self-cleaning photocatalytic materials. The electronic properties of photocatalysts can be studied using different (fundamental) spectroscopic techniques like electron paramagnetic spectroscopy (EPR) [14–16], time resolved microwave conductivity (TRMC) measurements [17], photoacoustic spectroscopy (PAS) [18,19] and other ultrafast spectroscopic techniques [20–22]. While these techniques yield insightful information, they require dedicated expensive equipment and often tedious and complex sample preparation steps. In this work it is our intent to use simple, widely applicable and inexpensive characterization procedures that yield all the information required. In particular, we used a facile and fast characterization technique based on an adapted electron titration method using a thiazine dye (thionine) yielding information on the electronic properties of powder TiO₂ samples. This electron titration method is based on the generation and storage (trapping) of electrons of irradiated TiO₂ colloids in de-aerated conditions in the presence of a hole scavenger. UV excitation of TiO₂ in de-aerated ethanol renders the suspension blue, which is attributed to trapping of electrons at Ti⁴⁺ sites. This electron excess can be titrated using a suitable acceptor molecule like thionine. Because of the charging effect and the possibility to titrate the excess charge, it is possible to quantify the number of electrons stored on the TiO₂ particles [23–30]. The abovementioned electron titration method is thus used to evaluate the electronic properties of different commercially available TiO₂ photocatalysts. These results are complemented by direct surface photovoltage (SPV) measurements and morphological characterization data. Further linking the electronic and morphological characteristics of the samples to their ability to degrade a solid layer of stearic acid (SA), enables us to interpret the photocatalytic self-cleaning behavior of the investigated catalysts.

2. Experimental

2.1. Chemical reagents

All products were used as received from the manufacturers without any modification or purification unless stated otherwise. Three commercially available TiO₂ sources were used: Aeroxide P25 (Evonik), Aeroxide P90 (Evonik) and PC500 (CristalACTiV). All other chemicals were purchased from Emplura or Sigma-Aldrich.

2.2. Photocatalyst characterization

X-ray powder diffraction (XRD) measurements were conducted using a STOE StadiP apparatus with Cu K α radiation and an image plate detector. The Brunauer-Emmett-Teller (BET) specific surface area was determined via N₂ adsorption with a Micromeritics Tristar Surface Area and Porosity Analyzer. The samples were first degassed overnight at 573 K. A filler rod and isothermal jacket were used during the measurements.

The amount of electrons stored on TiO₂ was determined quantitatively using thionine acetate salt (Sigma-Aldrich) as electron acceptor. 0.625 mg TiO₂ powder was suspended in 5 mL absolute ethanol (Emplura, 99.5%) in an airtight reaction vessel and de-aerated with N₂. The weight before and after the de-aeration step was measured to account for volume losses. The reaction vessel

was subsequently illuminated with a low-intensity UVA lamp ($\lambda_{\text{max}} = 352 \text{ nm}$, $5.3 \pm 0.3 \text{ mW cm}^{-2}$ at sample distance) for one hour while stirring. The holes are readily scavenged by the organic solvent and the suspension turns grayish-blue, which indicates the formation of electron-rich TiO₂. Afterward, 1 mL of a de-aerated aqueous solution of thionine (0.1 mM) was added to the reduced TiO₂ suspension causing the stored electrons to reduce the thionine dye (blue) to its colorless *leuco*-thionine form. The resulting suspension was centrifuged for 20 min at 6000 rpm to eliminate the photocatalyst, after which the supernatant was loaded in a sealable quartz cell (optical path length 10 mm) and the UV-VIS absorption at 602.5 nm was measured using a Shimadzu UV-VIS 2501PC double beam spectrophotometer. To exclude the adverse effect of oxygen, all experiments were entirely conducted under N₂ atmosphere (two-hand Atmosbag with zipper lock, Sigma-Aldrich). Blanc samples were measured to correct for dye adsorption on the TiO₂ catalyst. These samples underwent the same experimental procedure but were shielded from UV light illumination using aluminum foil.

Surface photovoltage measurements were conducted as described by Verbruggen et al. [12] using a custom made apparatus where the catalyst powder is sandwiched between two ITO electrodes (Sigma-Aldrich, $d = 1.2 \text{ mm}$, resistivity: $8\text{--}12 \Omega \text{ cm}^{-2}$), connected to an amplifier (1×10^6 voltage amplification). No external bias was applied. For all samples, $4.0 \pm 0.1 \text{ mg TiO}_2$ powder was used in such a way that a controlled area of 5 mm by 5 mm was illuminated with UVA light ($\lambda_{\text{max}} = 352 \text{ nm}$, 1.8 mW cm^{-2} at sample distance).

2.3. Photocatalytic self-cleaning activity measurement

The photocatalytic self-cleaning test was conducted by means of an in situ stearic acid (SA) degradation experiment, based on the method proposed by Paz et al. [31]. Silicon wafers ($1.5 \text{ cm} \times 1.5 \text{ cm}$) were ultrasonically cleaned in ethanol and dried with compressed air. Afterward, a 2 wt% TiO₂ suspension in absolute ethanol was prepared of which 25 μL was drop casted on the silicon wafer. The coated wafers were subsequently dried overnight at 363 K. A layer of stearic acid (Sigma-Aldrich, 98.5%) was applied by spin coating 50 μL of a 0.25 wt% stearic acid solution in chloroform (Sigma-Aldrich, 99.8%) for 1 min at 1000 rpm after which the samples were dried for 15 min at 363 K. The photocatalytic degradation of stearic acid was monitored by means of FTIR spectroscopy using a patented in situ reaction cell developed in our research group [32]. This cell enables the in situ observation of volatile and non-volatile reagents, intermediates and products on the surface while the reactions are ongoing. The samples were placed at the center of the reactor at an angle of 9° with the IR beam to minimize internal reflection effects. During the experiments, IR spectra were recorded from 4000 to 400 cm^{-1} at a resolution of 1 cm^{-1} by a Thermo Nicolet 6700 spectrometer (Thermo Fisher Scientific). The reactor was first flushed with air after which it was sealed airtight and the sample was allowed to equilibrate for one hour. An average of eight spectra was logged every three minutes using an automated protocol (MacrosBasic, Thermo Fisher) and the built-in UV LEDs ($\lambda_{\text{max}} = 377 \text{ nm}$, 1.8 mW cm^{-2} at sample distance) were switched on. The disappearance of stearic acid was followed by monitoring the integrated area in the wavenumber range 3000–2800 cm^{-1} , corresponding to the asymmetric $\nu_{\text{as}}(\text{CH}_3)$ in-plane C–H stretch at 2958 cm^{-1} , an asymmetric $\nu_{\text{as}}(\text{CH}_2)$ in-plane C–H stretch at 2923 cm^{-1} and a symmetric $\nu_{\text{s}}(\text{CH}_2)$ in-plane C–H stretch at 2853 cm^{-1} [33]. The concomitant formation of CO₂ and CO was monitored following the peak height of the asymmetric stretch $\nu_{\text{as}}(\text{CO}_2)$ at 2360 cm^{-1} and the stretch $\nu(\text{CO})$ at 2179 cm^{-1} respectively.

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