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Analysis of photocatalytic performance of nanostructured pyrogenic titanium dioxide powders in view of their polydispersity and phase transition: Critical anatase particle size as a factor for suppression of charge recombination

Anna Moiseev [a], Marina Krichevskaya [b,*], Fei Qi [c], Alfred P. Weber [c], Joachim Deubener [a]

[a] Institute of Non-Metallic Materials, TU Clausthal, Zehntnerstrasse 2a, 38678 Clausthal-Zellerfeld, Germany
[b] Department of Chemical Engineering, Tallinn University of Technology, Ehitajate tee 5, 19086 Tallinn, Estonia
[c] Institute of Particle Technology, TU Clausthal, Leibnizstrasse 19, 38678 Clausthal-Zellerfeld, Germany

HIGHLIGHTS

- Flame synthesis of homologous TiO_2 materials closed to benchmark P25.
- Correlation of photocatalytic activity with polydispersity of pyrogenic titania.
- Ascertainment of the particles with the highest surface density of reactive sites.

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ABSTRACT

Series of TiO_2 nanopowders from flame aerosol synthesis with average particle size from 7.1 to 21 nm with increased rutile content were studied for particle size distribution (PSD) and anatase-to-rutile transition to be correlated with their photocatalytic performance. The certain particles' growth regime favours the formation of defect-rich anatase nanoparticles which were found to condition the overall reactivity of polydispersed nanostructured powders. Two crucial roles of oxygen vacancies as key characteristics of nanoparticles are discussed: (a) they are responsible for anatase-to-rutile transition and (b) are vital for the adsorption of oxygen as electron acceptor, i.e. for the photoelectrochemical efficiency. The linear dependence of the photocatalytic oxidation reaction rate constant on the content of the specific anatase particles fraction amenable to phase transition was revealed by the regression analysis.

1. Introduction

Photocatalysis, where semiconductor, usually titanium dioxide, activated by light energy initiates electrochemical reactions, has a wide range of functions involving conversion of solar energy, treatment of polluted water and air, modification of surface properties [1] and implementation of water and/or organic matter splitting for the light-assisted production of hydrogen [2,3]. Environmental applications of photocatalysis are of extremely high potential, therefore, because of process low efficiency, the synthesis of basic catalytic materials of considerably higher intrinsic performance is of top priority.

The technological significance of TiO_2 in optoelectronic applications is related to its defects; the presence of defects is also crucial for titania surface reactivity [4–7]. In photocatalysis the interfacial charge transfer between TiO_2 nanoparticle surface and adsorbate molecules is in competition with the electron–hole pair recombination. Also, in order the photocatalytic process to be efficient, electron–hole pair recombination must be suppressed before the trapping reactions occur at the surface [8]. It has been observed that the photocatalytic activity of TiO_2 is completely obstructed in the absence of an electron scavenger such as molecular oxygen [8]. Besides it is recognised now that surface defects of single TiO_2 crystal, oxygen vacancies, play an essential role in governing the oxygen adsorption producing superoxide species [9].

Anatase polymorph of TiO_2 shows higher activity than rutile [10,11], but more striking phenomena is higher photoelectrochemical performance of mixed titania phases exceeding the activity of one-polymorph crystallites [12–18]. The better performance of

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* Corresponding author. Tel.: +372 6202851; fax: +372 6202856.
E-mail addresses: anna.moiseev@tu-clausthal.de (A. Moiseev), marina.kritsevskaja@ttu.ee (M. Krichevskaya), fei.qi@mvt.tu-clausthal.de (F. Qi), weber@mvt.tu-clausthal.de (A.P. Weber), joachim.deubener@tu-clausthal.de (J. Deubener).

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mixed-phase titania is seen only in thermally as-prepared or treated materials; no such effect could be observed for physically mixed anatase and rutile powders [16]. This phenomenon is explained by the synergetic effect, where photoexcited charge migration through the direct phase junction between individual particles of rutile and anatase occurs, i.e. throughout the defined boundary between two phases. There are still debatable questions on the synergetic effect as no rutile distribution in randomly dispersed anatase nanoparticles was studied with any effective sizes of rutile particles found and discussed. The way of electron transfer in hypothesis of synergetic effect is not definite: authors describe electron transfers from the rutile conduction band to anatase trapping sites [14] and vice versa [18]. Though, there have been no reports showing direct evidence of such inter-particle charge migrations [19]. Moreover, the positive impact of high-temperature treatment step on the photocatalytic activity of anatase in absence of rutile is also well-known and this do not embed the phase junction hypothesis [20–22] and electrical conductivity of anatase is defined largely by its defect chemistry [23].

This hypothesis does not also take into consideration the mechanism of phase transition, where the driving force for anatase-to-rutile phase transition is the formation of defects, oxygen vacancies, on anatase surface [24]. Anatase-to-rutile transformation is initiated in an individual anatase grain followed by rapid conversion through the entire crystallite; the individual crystallites were found to be either entirely anatase or entirely rutile, and no partially reacted crystals were detected [25,26]. The formation of oxygen vacancies controls the sintering and phase transition rate [27]. The reactivity of defective surface is supposed to be interrelated with the photocatalytic performance of real nanomaterials.

The search for new photocatalytic materials by the trial and error method could hardly explain the mechanisms responsible for the performance improvements. So far the progress in the development of photocatalysts is evaluated by the industrial nanopowder P25 (Evonik) staying unfortunately still a black box in terms of explanation of the phenomenon of its comparatively high unselective activity towards wide spectra of single model pollutants as well as wastewater matrix [28–32]. Namely in contrast to classic catalysis the complex nature and often unknown composition of polluted air and water requires unselective activity of photocatalytic materials as a main process design criterion. Moreover, this feature should be directly linked to the reactivity of oxidizing species in photocatalytic system [33–35]. In contrast to catalytic application of metal nanoparticles [36] no conformity in activity and optimal particle size of TiO_2 photocatalyst was found, as intrinsic properties of materials synthesized by different methods and within different ranges of sizes fluctuate; i.e. the quantity/generation rate of oxidizing species could not be deduced from simple materials' characteristics like nanoparticle size.

Synthesis ultimately determines the morphology of nanomaterials [37–39]. And one of the prospects to solve the fundamental question on crucial factors responsible for photocatalytic activity is to synthesize and specify the homologous sequence of materials with gradually changing crystalline composition closed to that of P25. Flame aerosol synthesis is a single step process which combines chemical reaction, nucleation and particle growth, where the unique characteristics of final pyrogenic particles could be formed within a short residence time (ms) and at high process temperature [40–44].

In our previous studies on photocatalytic activity of flame synthesized nanoparticles there was no beneficial effect of rutile in mixed-phase titania observed [45,46]. Instead of that the activity of nanopowders in the photocatalytic oxidation of heteroatomic aliphatic dichloroacetic acid (DCA) and aromatic 4-chlorophenol (4-CP) in aqueous phase was increased strongly with decreasing average particle size larger than critical in terms of anatase transition crystallite size, d_c, but was not positively correlated with particle sizes lower than d_c. The continuation of this study was thought to be essential as it could be stated from the facts mentioned above that a correlation between phase transition and photocatalytic activity in titania exists. However, series of catalysts synthesized and tested in [45] did not include pure anatase and industrial flame synthesized P25 and P90 samples and the d_c point was obtained graphically only as the number of samples analysed was not enough for detailed analyses and calculations. Because of the pyrogenic titania polydispersity the relation between photocatalytic activity of polycrystalline titania and primary particle size distribution (PSD) not considered before should have been studied.

Thus, observations that pure anatase powders are inferior to more photoactive nanopowders containing small amount of rutile [12] encouraged us to supplement the series and analysis of aerosol flame titania and search for hypothesis explaining this phenomenon. The objective of present paper was to find mechanistic insights that correlate the solid state properties of semiconducting nanoparticles with their photocatalytic activity by means of phase transition mechanisms.

2. Experimental

2.1. Materials

Nine titanium dioxide nanopowders L1–L3, F1–F6 with average particle size, d_{TEM}, increased with small steps from 7.1 to 20.6 nm accompanied under studied process conditions with steady and continuous growth of the rutile phase content [45,46], W_R, from 0 to 13.5 wt.% were synthesized, analysed and tested as photocatalysts; two industrial pyrogenic titania, P25 and P90 (Evonik), were used in this study [47–49]. The model compounds, two organic molecules: well-adsorbed aliphatic DCA and poorly adsorbed aromatic 4-CP, widely used in photocatalysis activity screening and thoroughly studied for reaction intermediates and kinetics [50–54], were selected due to difference in photocatalytic reaction mechanisms, their high toxicity and resistance to conventional treatment methods [55–59]. Three additional TiO_2 samples with d_{TEM} of 7.2, 11.6 and 13.4 nm were synthesized in small quantities to be analysed only for rutile content.

2.2. Synthesis

The experimental setup and procedure for flame aerosol synthesis of six F1–F6 titania samples are described in detail elsewhere [45]. The series was extended by pure anatase samples labelled L1, L2 and sample L3 with 1.4 wt.% of rutile synthesized correspondingly at Ar/$TiCl_4$ flow rates of 2.5, 3 and 3.5 $l\,h^{-1}$. The vapour of the catalyst precursor titanium tetrachloride was formed by passing dry argon gas through a bubbler submerged to the $TiCl_4$-liquid at room temperature. Methane, oxygen and nitrogen were premixed with Ar/$TiCl_4$ and the mixture was introduced into the burner. The TiO_2 particles were collected on a glass fibre filter placed about 50 cm above the flame. The overall synthesis reaction is given by the following equation:

$$TiCl_4(g) + 4O_2(g) + 2CH_4(g) \rightarrow TiO_2(s) + 4HCl(g) + 2CO_2(g) + 2H_2O(g) \quad (1)$$

Residence time in the flame, i.e. the total gas mixture flow rate adjusted by appropriate nitrogen flow rate, and process temperature (ca. 900 °C) were kept nearly constant for all the syntheses.