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Shape-controlled agglomeration of TiO_2 nanoparticles. New insights on polycrystallinity vs. single crystals in photocatalysis

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Abstract

The photocatalytic activity of TiO_2 photocatalysts depends mainly on its crystal phase composition, primary particle size and specific surface area. Shape manipulation is an interesting way to increase the photocatalytic efficiency. The shape-tuning can be carried out at different levels, both at single crystal and polycrystalline agglomeration levels. The aim of our present study was to compare the structural and photocatalytic performances of two type/level of crystal organization of TiO_2, namely single crystal shaping vs. polycrystalline/shape tailored agglomeration. The morphological analysis was achieved by XRD, SEM, TEM, Raman spectroscopy, DRS. The photocatalytic performance of the materials was evaluated by the degradation of a model pollutant (phenol). It was found, that both shape manipulating approaches bear the necessary potential which can be exploited in future development of efficient photocatalysts' synthesis procedures.

Keywords: Titania; Crystal growth; Polycrystalline system; Single crystals; Surface normalized photocatalytic activity

1. Introduction

Nowadays several papers are focused on heterogeneous photocatalysis due to the increase of environmental problems, including water and air pollution. It is known that the photoactivated semiconductor oxides are able to decompose various kinds of organic pollutants from water (dyes, phenol and phenolic compounds) and also from air (e.g. VOCs) which are toxic and non-biodegradable under normal conditions [1–3].

One of the widely studied, promising semiconductor photocatalyst is titanium-dioxide (TiO_2) [4]. The reasons why this material is so popular are: the biological and chemical inertness, cost effectiveness and long-term stability against photo- and chemical corrosion, and its high quantum yield. Additionally, there are many other possible applications of the nano-sized TiO_2 such as dye-sensitized solar cells (DSSC), chemical sensors [5,6] and photocatalytic H_2 production [7,8]. Furthermore, high number of studies revealed that a large spectrum of harmful organic contaminants can be degraded by TiO_2 nanoparticles [9–13]. The photocatalytic performance depends on many structural/morphological and optical parameters of the chosen semiconductor, shape, size, crystallinity, the crystal structure (crystal phases) and the reactive crystal facets. In the case of titania three crystal phases are well-known: rutile, anatase and brookite [14]. Anatase usually possess higher photocatalytic activity than other crystal phases thanks to its better charge (e^-/h^+ pairs) separation efficiency and higher electron mobility [15,16]. The photocatalytic performance can be influenced by modifying other parameters, such as crystallite size, surface area, etc. Furthermore, the

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tuning of the structural properties of TiO_2 can be easily carried out applying simple crystallization methods, such as the calcination [17,18].

Unfortunately the bare TiO_2 has lower activity under visible light, thus it is necessary to include them in composite materials with other semiconductors or/and doping with metals [19]. Useful semiconductor oxides for this purpose can be SnO_2, SiO_2, WO_3 [20], etc. Another possible solution is the deposition of noble metal nanoparticles (Au, Pt, etc.) on the titania surface [21].

Recently researchers combined TiO_2 with different type of carbons and nanocarbons to increase the lifetime of the charge carriers: activated carbon, carbon nanotubes (CNTs) and graphene [22–24]. Carbon–TiO_2 composites are so-called "rising star"-type of materials applied successfully in the degradation of various pollutants [25], while some of them were proven to be also biocompatible [26].

As it is known, the photocatalytic efficiency in the case of TiO_2 is influenced by the particle size, crystal phase, the main reactive crystal facets and the partner materials' nature in the case of composite materials (noble metals, semiconductors or carbon materials) [27–30]. The (001) crystal facets have higher photocatalytic activity (oxidative power) compared to the (100) or (101) crystallographic surfaces, especially at nanometer scale [31–34]. The (001) planes can be grown in the presence of F^-, which are very efficient species in the shape tailoring of TiO_2 nanoparticles [35–37]. There are some papers regarding the improvement of rutile's photocatalytic activity by the formation of (111) facet dominated pyramid-shaped nanoparticles [38]. "Shape-reforming" is indeed a powerful tool for the increase of the photocatalytic efficiency as shown above. However, shape manipulation can be executed at different levels. The "classical way" is the morphology control at crystallite level (single crystals), while a more difficult challenging modality of shape tuning is the hierarchical shape build-up.

One good example is the TiO_2 hierarchical nanorod-spheres which were found to be quite efficient in photocatalytic applications, due to their enhanced light absorption capability, enlarged specific surface area and enhanced charge transfer rate of photogenerated electrons [39]. These TiO_2 crystals can be built also in nano- and micro particle size range possessing two morphology types at two levels: three dimensional (3D) TiO_2 nanostructures made up of one dimensional (1D) TiO_2 nanorods. The shape-controlled synthesis of the above mentioned materials were carried out applying several synthesis routes, such as: hydrothermal crystallization [40–43], anodic oxidation [44,45] and template assisted synthesis [46–48].

As it was presented above, two morphology control strategies can be found in the literature: one of them focuses on the individual shape-tailoring of single crystals, while the other one is centered on the importance of the agglomeration of the single crystals in secondary geometries. Consequently, it would be crucial to see the influence of the different shape tailoring approaches (hierarchical vs. single crystal) on the photocatalytic activity of TiO_2, while keeping in focus the different structural peculiarities of the specific titania morphology.

2. Experimental section[2]

2.1. Materials

Titanium tetrachloride ($TiCl_4$; 99.9%, Aldrich); sodium dodecyl sulfate (SDS, $CH_3(CH_2)_{11}OSO_3$ 99% Aldrich), thiourea (H_2NCSNH_2; 98%, Aldrich), HCl 37% (Sigma-Aldrich, Germany), HF 40% (Sigma-Aldrich, Germany), 2-propanol (anhydrous, 99.5%; Sigma-Aldrich, Germany), 69% (Reanal NORMAPUR), $Ti(OBu)_4$ 97% (Aldrich, USA), commercially available TiO_2 powder (Aeroxide P25, Evonik Industries) and phenol (ReAnal NORMAPUR) were used as received.

2.2. Hydrothermal synthesis of the egg-shaped TiO_2

SDS (5.3 g) was dissolved in distilled water and mixed with 7 g of thiourea. After complete solubilization, the titanium precursor ($TiCl_4$) was added drop-wise to this aqueous solution under vigorous stirring. During the addition of the precursor caution should be taken on the quick release of HCl as $TiCl_4$ it is extremely sensitive to moisture. This mixture was stirred at 50 °C for 1 h to yield a transparent solution. Into the previous mixture 1 mL of HCl (37%) was added three times in the last 15 minutes (1 mL of HCl/5 min). The final molar ratios applied during the synthesis were: $TiCl_4$: SDS: thiourea: HCl: H_2O = 1:2:10:11:300. The solution was immediately transferred into a sealed, Teflon-coated autoclave and was further heated to 180 °C for 36 h. The obtained white precipitate was washed several times with distilled water until no H_2S was noticed and the organic impurities were completely removed. After this, the product was dried in an oven at 80 °C for 24 h, under air flow. The titania nanocrystallites were calcined at four different temperatures (500, 650, 800 and 1000 °C), at a heating rate of 4 °C min^{-1} for 3 h in a muffle furnace. These samples were coded as follows: ME-X – **m**icro-**e**ggs-X (the value of the calcination temperature).

2.3. Hydrothermal synthesis of the single crystal anatase TiO_2

In a typical synthesis of the TiO_2 microcrystals: 8 mL tetrabutil titanante $Ti(OBu)_4$ was added into 104 mL, HCl solution (5 mol L^{-1}), under magnetic stirring for 30 min at room temperature. After that 2.475 mL HF (47%) was added to the mixture. Following a 5 min long vigorous stirring, the resulting solution was transferred into a Teflon-lined stainless steel autoclave. Additionally 40 mL of HCl (5 mol L^{-1}) was also added to the autoclave. The device was maintained at 180 °C for 1, 5, and 24 h. Afterwards, the autoclave was cooled down using a continuous water jet for 30 min. The product was washed several times with 2:1 (v/v) mixture of 2-propanol and distilled water. This

[2]Please note that the formation mechanism of the obtained nanomaterials it is not discussed, as the main subject is on the photocatalytic activity of these materials in the frame of the polycrystallinity (crystal geometries formed by crystallization/agglomeration) vs. single crystals (with exposed facets).