

Low temperature synthesis, characterization and substrate-dependent photocatalytic activity of nanocrystalline TiO₂ with tailor-made rutile to anatase ratio

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Abstract

TiO₂ photocatalysts with predetermined phase composition (anatase-to-rutile ratio) have been prepared from strongly acidic aqueous HCl/TiCl₄ mixtures with $0.1 \text{ M} \leq [\text{HCl}]_{\text{TOT}} \leq 5 \text{ M}$ and $0.05 \text{ M} \leq [\text{TiCl}_4]_{\text{TOT}} \leq 3 \text{ M}$ (where the subscript TOT denotes total or analytical concentration). During the syntheses, TiCl₄ was added to a cold-HCl solution. The initially precipitate free reaction mixture was boiled, resulting in the formation of large amount of solid, nanocrystalline (particle size 4–12 nm) TiO₂ particles with large specific surface area (up to $\sim 240 \text{ m}^2/\text{g}$). We found from the XRD patterns that at constant $[\text{HCl}]_{\text{TOT}}$, the anatase content of the crystallized solid systematically increases with decreasing $[\text{TiCl}_4]_{\text{TOT}}$, while at constant $[\text{TiCl}_4]_{\text{TOT}}$, the rutile content was found to systematically increase with increasing $[\text{HCl}]_{\text{TOT}}$. Thus the phase composition of the photocatalysts prepared was possible to be fine-tuned with the aid of these two simple initial parameters. The photocatalytic activity of the as-prepared catalysts was found to strongly correlate with the phase composition. In phenol decomposition the samples' photocatalytic performance gradually and significantly increases with their anatase content: photocatalysts containing only anatase as crystalline phase were up to three times more efficient than rutile ones. Interestingly, in salicylic acid decomposition, rutile-only catalysts were found to show no activity at all, but some of our catalysts (both anatase-only and rutile–anatase mixtures) at pH ~ 3 (but not at pH ~ 7) displayed photocatalytic activity commensurable to that of Degussa P25. This can be explained in terms of the efficient surface chemisorption of salicylate ion on large specific surface area TiO₂ particles in acidic solutions.

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1. Introduction

Since the first observation of water splitting with sunlight on irradiated titania coated electrodes [1], the study of TiO₂-based semiconductor photocatalysts is one of the most active areas of materials science, both at fundamental and applied levels [2–4]. The recently attained popularity of titania is mainly due to its environmentally friendly (*i.e.*, non-toxic) nature, low cost, high natural abundance and versatile potential applications. Indeed, the most important use of titania-based photocatalysts is concerned with water- and air-purification, *i.e.*, photocatalytic destruction of hazardous organic pollutant molecules [5].

Of the seven polymorphs of TiO₂, three occur in nature: rutile and anatase (both tetragonal) and brookite (orthorhombic). In photocatalysts studies, anatase and rutile have been studied most widely, as pure brookite is cumbersome to prepare and amorphous TiO₂ has no photocatalytic activity at all. Anatase is known to be the low temperature (300–550 °C) form of titania, and it transforms to rutile upon heating. The transformation takes place (depending on the primary particle size and the way of preparation) from 600 to 1100 °C. For the photocatalytic activity, the band gap between the valence and conducting levels is of key importance. The band gap of rutile is $\sim 3.0 \text{ eV}$ and that of anatase is $\sim 3.2 \text{ eV}$. Rutile is known to have better visible-light response, while anatase is usually of better photocatalytic activity. Phase pure forms of the two common polymorphs are seldom obtained, and the syntheses often yield various mixtures of anatase and rutile. In photocatalysis research, for comparative purposes the

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mass produced Degussa P25 TiO₂ is used (and perhaps considered as the benchmark of photocatalysts), which is composed of rutile and anatase from 1:4 to 1:9 ratio.

The use and performance of TiO₂ for a given application almost always depend not only on the phase composition but also on the morphology, the size and porosity of the particles, their specific surface area, hydrophilicity, concentration of surface hydroxyl groups, *etc.* Accordingly, it is of importance to develop synthetic methods by which these properties (or at least some of them) can simultaneously be controlled (for a recent review see Ref. [6]). Plenty of synthetic methods are already published in the literature. The most common routes include the sol–gel process using titanium alkoxides [7,8], hydrolysis of inorganic salts such as titanium-sulphate [9], titanium trichloride [10] or titanium tetrachloride [11–15], combustion synthesis [16] and reverse micelle method [17]. The hydrolytic syntheses are often coupled with hydrothermal treatment for transforming the amorphous titania to various crystalline products [8–10,18,19]. The majority of these syntheses require very strict control of the experimental parameters to achieve the desired titania properties. Furthermore, they are usually too costly for mass-producing TiO₂, due to the special instrumental requirements or processing conditions. Recently, an inexpensive and simple synthesis has been described by Chu et al. [15]. The method is based on the very good solubility of Ti(IV) in ice-cold concentrated aqueous HCl solutions, which rapidly decreases with the increasing temperature, resulting in the precipitation of crystalline TiO₂ upon heating. According to Chu et al. [15], from solutions of $[\text{HCl}]_{\text{TOT}} \geq 0.1 \text{ M}$ and $[\text{TiCl}_4]_{\text{TOT}} \geq 0.1 \text{ M}$ phase pure rutile was obtained and the particle size was found to systematically increase with increasing $[\text{HCl}]_{\text{TOT}}$. Given, that the photocatalytic activity of the nanocrystals thus prepared has not been characterized in Ref. [15], and rutile is known to behave as reasonably good photocatalyst in certain conditions [19], we repeated these syntheses in our laboratories with the aim of establishing correlation between the photocatalytic activity and the structural properties (phase composition, particle size, morphology, specific surface area) of the photocatalysts thus prepared. The composition of the reaction mixture was significantly broader than was in Ref. [15] and covered $0.1 \text{ M} \leq [\text{HCl}]_{\text{TOT}} \leq 5 \text{ M}$ and $0.05 \text{ M} \leq [\text{TiCl}_4]_{\text{TOT}} \leq 3 \text{ M}$. Somewhat surprisingly, in this concentration range not only rutile, but also anatase and rutile anatase mixtures were isolated and we found that with the composition of the reaction mixture it is possible to manipulate the anatase-to-rutile ratio of the photocatalysts. This made it possible to use this inexpensive preparative method for producing phase-mixtures with pre-determined composition and thus to systematically investigate the relationship between the phase composition and the photocatalytic activity of titania specimens. In the current study, two model compounds, *i.e.*, phenol and salicylic acid were used as substrates. Phenol was chosen, because it is indeed the most frequently studied model compound for such studies, and it possesses several chemical properties of anthropogenic organic pollutants in our environment. Salicylic acid, a substrate with adsorption properties superior to phenol, was

also investigated. This made possible to compare photocatalytic performances of our photocatalysts against ligands with different sorption properties.

2. Experimental

2.1. Syntheses

For the syntheses, analytical grade HCl_{cc} (*ca.* 37 wt.%, Merck) was used. TiCl₄ (>99%) precursor was supplied by Sigma–Aldrich and was stored at $-15 \text{ }^\circ\text{C}$ in a refrigerator, to minimize fuming, which is observed when TiCl₄ reacts with airborne moisture. Titanium dioxide powders (anatase and rutile, 99.9%, Sigma–Aldrich) were used as XRD calibration standards, and Degussa P25 (90 wt.% anatase and 10 wt.% rutile) was employed as photocatalytic standard, all of them as received. For the experiments Millipore Milli-Q water was used throughout.

During the preparation, 200 mL of HCl solution with the desired concentration was placed in a three-necked bottle. The TiCl₄ was kept in a dropping funnel equipped with a CaCl₂ pipe to exclude moisture. All the quickfit connections were lubricated with H₂SO_{4cc}. The reaction mixture was kept in an ice-water bath, and was vigorously stirred during the drop wise (*ca.* 0.5 mL min⁻¹) addition of the calculated amount of TiCl₄. At the place of dropping, a yellowish precipitate was formed, which then instantaneously dissolved. At this point of the preparation, all the systems in the concentration range investigated were transparent and free of any precipitate. The solution was stirred for 15 min. The dropping funnel was changed to a condenser and the mixture was heated to 95–100 °C and then refluxed for 3 h. By the end of the heating a white suspension was formed which was then allowed to cool. From this point the synthesis resolves to four slightly different sub-routes (Scheme 1) Synthesis 1 involved ageing of the reaction mixture under vigorous stirring for 24 h at room temperature (unless otherwise stated), followed by evaporation. In the other methods, after decantation, washing with 0.1 M HCl and centrifugation, the suspension was exhaustively dialyzed in a 12,000 Da cut-off limit dialysis sack (Medicell International Ltd., London) against distilled water (until the pH of the dialyzing solution reached ~5.5) and either evaporated (Synthesis 2, which is practically identical to that described in Ref. [15] or freeze-dried at $-52 \text{ }^\circ\text{C}$ and 60 Pa (Synthesis 3). Synthesis 4. is identical to Synthesis 3, except that aging of the suspension was carried out in a Teflon lined, closed autoclave, at 110 °C and for 24 h.

The solid photocatalysts thus obtained were milled in an agate mortar and kept in closed screw top containers.

2.2. Photocatalyst characterization

X-ray diffraction (XRD) measurements were performed on a Philips PW 1820/1830 diffractometer (Cu K α = 0.15406 nm, 40 kV, and 30 mA, in the $20^\circ \leq 2\theta \leq 40^\circ$ regime for solid powder samples). The average diameters of the particles, (d) were obtained by means of the Scherrer equation [20] [$d = k\lambda$

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