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Fluorine Ions in Photocatalysts' Synthesis: an Obstacle or an Ally? The Investigation of Photocatalysts in Ti-O-F System †

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Abstract: Recently, fluorine-mediated synthesis of the TiO_2 photocatalysts has gather increased attention as a potential agent to obtain highly photoactive materials. However, depending on the synthesis conditions, a different effect of F^- ions might occur, including (i) stabilization of the specific crystal facets, (ii) surface fluorination, (iii) creation of non-stoichiometry, and (iv) incorporation of fluorine into the anatase lattice. Based on our findings, the possible effects of F^- introduced with different alcohols during synthesis, as well as different capping agents in the water-based systems, were discussed. The Ti-O-F photocatalysts and obtained structures were studied in photocatalytic degradation of organic pollutants.

Keywords: fluorine; TiO_2; photocatalysts; crystal facet engineering

1. Introduction

Titanium(IV) oxide is one of the most promising photocatalysts, especially considering its application in the photocatalytic degradation of xenobiotics. Due to the high quantum efficiency and chemical stability in various environments, TiO_2 is the most described photocatalyst in the literature [1–3] (more than 13,000 document results on Scopus in the topic of TiO_2 and photocatalysts). However, due to the low bandgap, which allows to absorb only UV light, much effort has been paid to enhance the photocatalytic activity of TiO_2-based photocatalysts in UV-vis light by modifying its bulk and surface structure.

Recently, fluorines have been used both to control the TiO_2 photocatalysts' surface structure and modify TiO_2 activity towards ·OH generation. Moreover, due to the extremely strong Ti-F interactions, the formation of the intrinsic defects inside the crystal lattice of TiO_2 is also considered. Particularly, fluorine atoms can stabilize thermodynamically unfavored, highly energetic {0 0 1} facets [4,5]. Including the formation of highly energetic facets and surface fluorination, Ti-O-F based photocatalysts are supposed to be highly photoactive. For example, Xiang *et al.* have reported surface-fluorinated anatase nanosheets, which exhibited nine times higher photocatalytic activity than commercial TiO_2 P25 (Evonik) in photocatalytic degradation of acetone in the air [6]. However, our previous studies showed that fluoride ions in the reaction system are not always beneficial for enhancing photocatalytic activity. Inspired by this, the present study summarizes different attitudes to F^- ions in the preparation of TiO_2 nanostructures.

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2. Fluorine ions in anatase nanosheets with exposed {0 0 1} facets

At present, thermodynamic stabilization of the high-energy {0 0 1} facets is one of the most crucial applications of fluorine in the preparation of TiO_2-based photocatalysts.

Pristine anatase crystals are mostly enclosed with the {1 0 1} facets, with a surface energy of 0.44 $J \cdot m^{-2}$. However, as presented by Yang *et al.* in the fluorine-rich system, the surface energy of the {0 0 1} structure is not only minimized, but it also became more stable than the {1 0 1} [7]. In this regard, the design and morphological control of crystal facets of anatase using fluorine ions is a prospective research area and needs further investigation. Both surfaces are visualized in Figure 1 using the VESTA program.

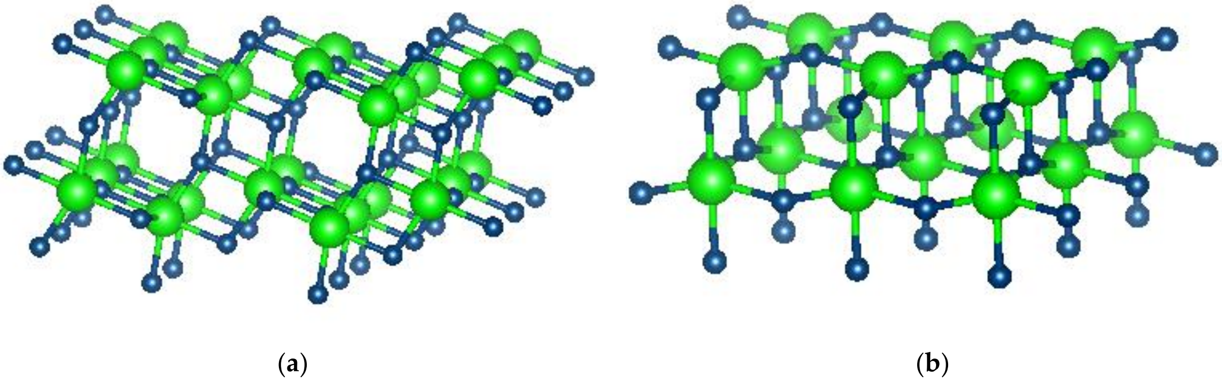

(**a**) (**b**)

Figure 1. Visualization of anatase crystal facets (**a**) {1 0 1}; (**b**) {0 0 1}.

Among others, Zheng *et al.* have further shown differences in the growth of {0 0 1} enclosed nanosheets in relation to alcohol type (methanol, ethanol, propanol, butanol) [8]. However, the amount of solvent was not under consideration. In this regard, we demonstrated the series of {0 0 1} exposed anatase nanosheets from HF-assisted solvothermal synthesis, including the detailed effect of the alcohol environment on the growth of the TiO_2 nanostructures. Obtained materials were thoroughly studied towards their application in photocatalytic phenol degradation. Detailed characteristics are described in [9].

The presented series of 2D TiO_2 with exposed {0 0 1} facets consist of anatase nanosheets, which vary from solvent type (methanol, ethanol, n-butanol, n-hexanol), and amount as well as the solvothermal reaction time. Although the major samples are TiO_2 nanosheets with the high exposition of {0 0 1} facets, they vary in size distribution and thickness. SEM images of selected two-dimensional TiO_2 photocatalysts were presented in Figure 2.

Different synthesis conditions influence fluorine adsorption at photocatalysts' surfaces, which impacts the photocatalytic properties. In this study, some samples of anatase nanosheets are much more photoactive under UV-Vis irradiation towards phenol degradation than the other one. Based on *k*-constant rates and total organic carbon (TOC) measurements, presented samples were grouped into two series: A and B. The photocatalytic performance of described photocatalysts was presented in Figure 3. The series A was denoted as well-defined 2D nanoparticles, which allow efficient phenol photocatalytic degradation (series A), and the obtained rate constants are comparable or higher than presented in the literature. In the case of series B, a significant decrease in the phenol degradation rate was noticed. This declined was caused by two main factors: the low amount of surface fluorine observed for these samples and the possible surface defects associated with the presence of Ti^{3+} states. Therefore, it can be assumed that fluorine ions have a positive impact on phenol photocatalytic degradation and mineralization to carbon(IV) oxide using the {0 0 1} enclosed TiO_2 nanosheets, as long as their surface remain defect-free. However, Han *et al.* observed an increase in photocatalytic methyl orange removal after subsequent cycles compared to the first cycle of the process. This abnormal performance of the 2D TiO_2 in the first cycle can be explained by the presence of surface fluorine ions on TiO_2 nanosheets. After the first cycle, these F^- were desorbed from the surface, resulting in the accelerating degradation rate in the other degradation cycles. This hypothesis was confirmed when photocatalysts' surfaces were cleaned from fluorines with sodium hydroxide. After this procedure, the degradation efficiency of the anatase nanosheets in alkaline solution was remarkably improved [10].

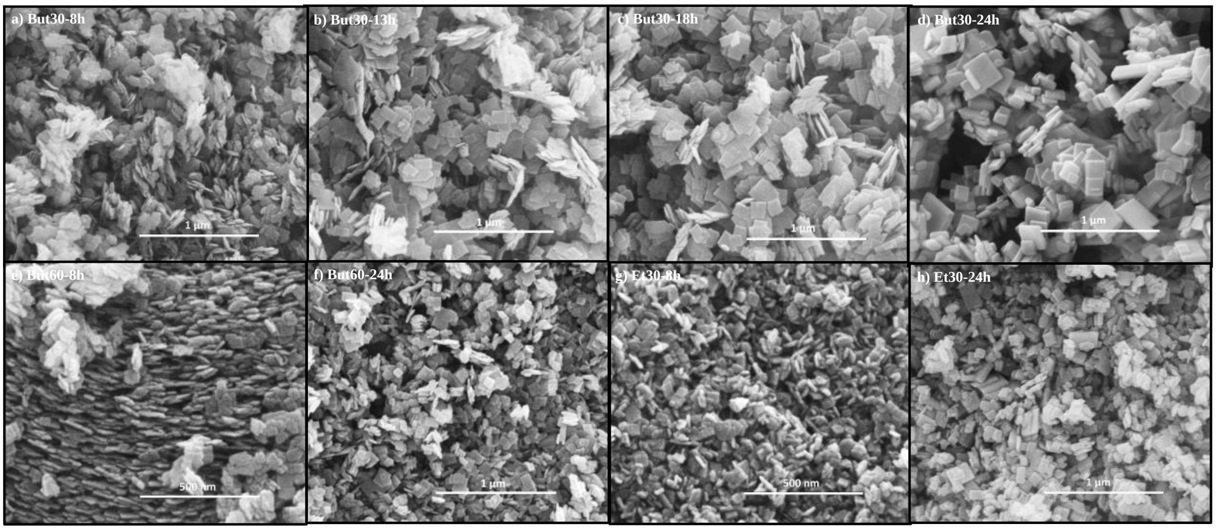


Figure 2. SEM images of selected anatase nanosheets obtained with different synthesis times and alcohols content [9].

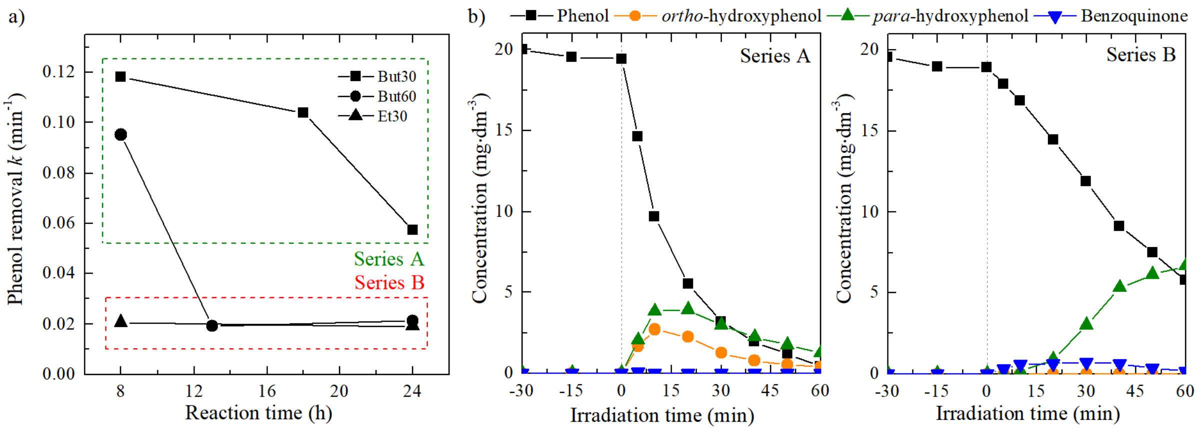
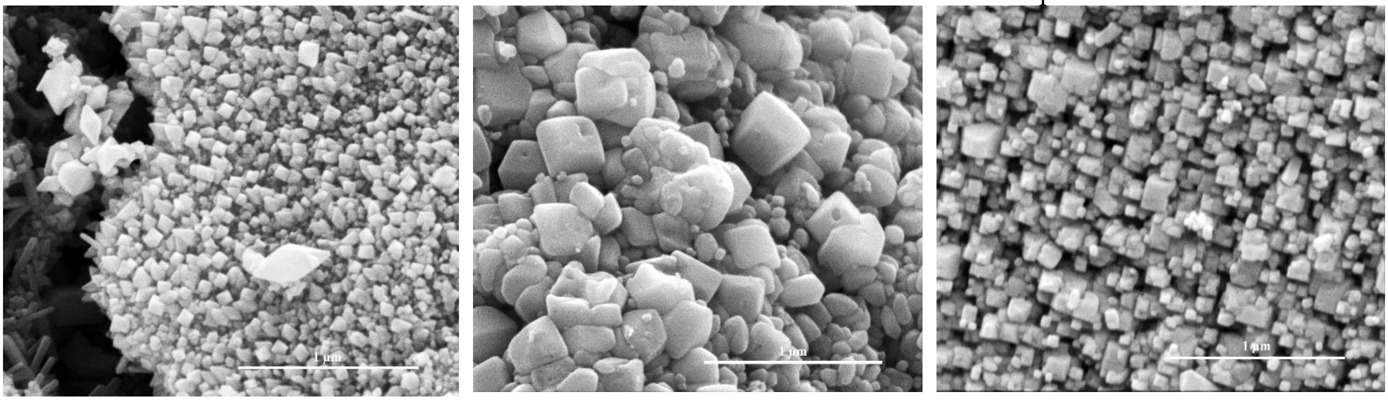


Figure 3. Photocatalytic performance of 2D TiO_2: (**a**) *k*-constant vs. reaction time, **(b)** changes in phenol concentration during the photocatalytic process for series A and B [9].

3. Fluorine ions in the formation of other anatase nanocrystals with defined morphology

The earlier studies were focused only on anatase nanosheets. Meanwhile, if suitable precursors and environments are applied, other shapes of the nanocrystals with defined facets exposition can be obtained. One of the appropriate precursors and sources of both titania and fluorine atoms is titanium oxyfluoride ($TiOF_2$). Titanium oxyfluoride is a metastable phase in the Ti-O-F reaction system, easily transforming into titanium(IV) oxide. Most of the previous reports concerned simple calcination [11] or anatase fluorination [12] for the transformation of $TiOF_2$ to TiO_2. Meanwhile, using $TiOF_2$ and simple growth-controlling agents like hydrazine, ammonia hydroxide, hydrofluoric acid, and hydrochloric acid results in the preparation of anatase nanocrystals with different well-defined morphology [13].

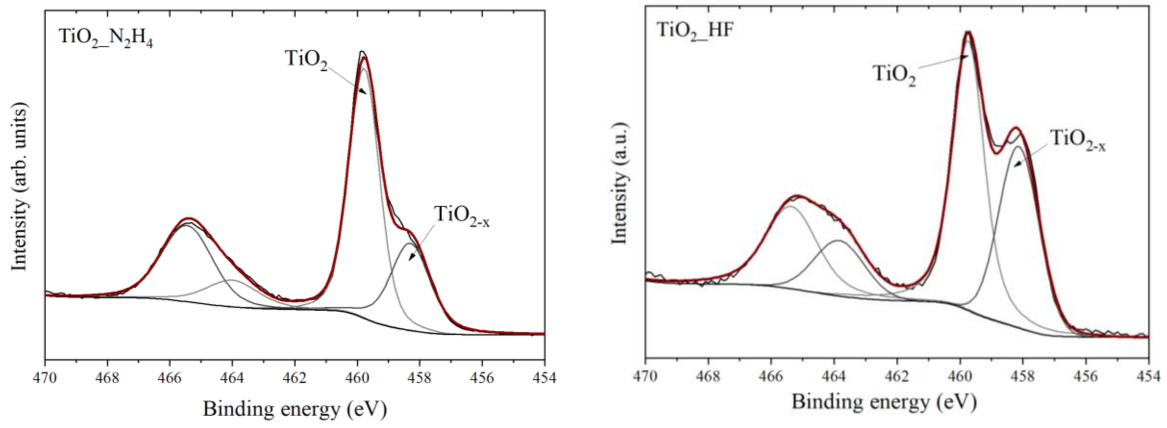
The presented series of TiO_2 nanostructures synthesized using $TiOF_2$ were systematically characterized. The SEM images of selected samples are presented in Figure 4. It was proven that different environments of reactions with titanium oxyfluoride and capping agents allow to obtain TiO_2 nanostructures with various morphologies (decahedral, octahedral, rectangular prisms). The morphology results from the formation and stabilization of different crystal facets {0 0 1}, {1 0 1} and {1 0 0} of TiO_2. Moreover, the performed two-step synthesis from TIF_4 to $TiOF_2$ and subsequently to TiO_2 caused a significant size reduction than during the one-step solvothermal process. The large anatase nanocrystals from direct TiF_4 transformation to TiO_2 were described earlier [5]. However, this approach does not solve the problem of low surface exposure rate, so the transformation of $TiOF_2$ to TiO_2 is more sufficient from this point of view.



(a) (b) (c)

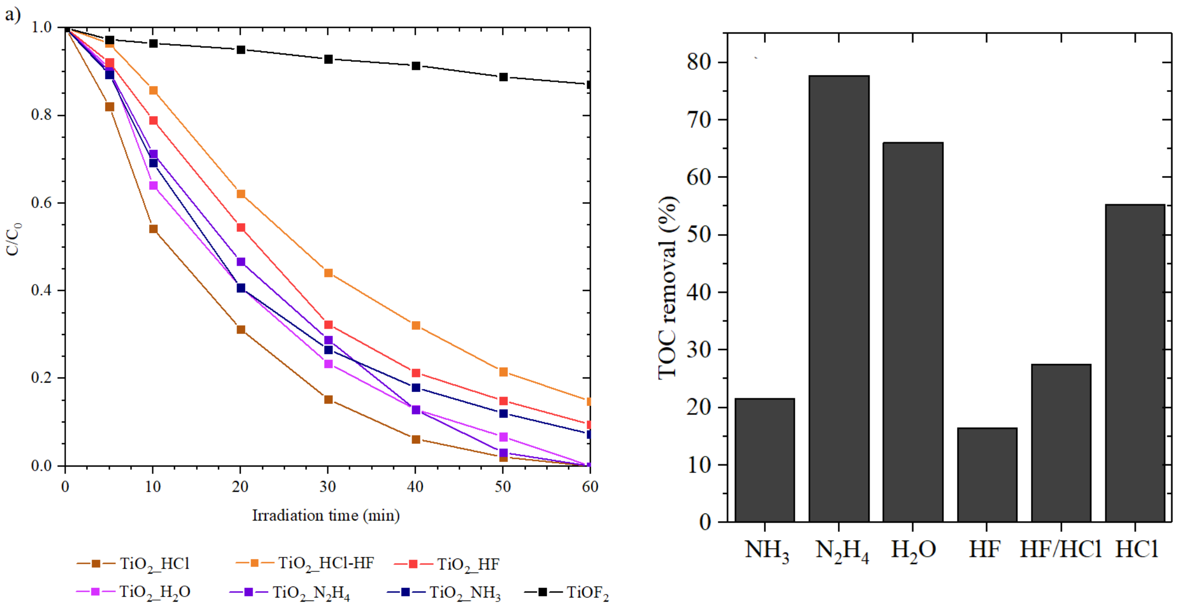
Figure 4. SEM images of the (**a**) octahedral, **(b)** decahedral, **(c)** rectangular prisms shaped TiO_2 obtained from the $TiOF_2$ [13].

What is worth highlighting, it was found that the morphology of presented photocatalysts influences the photocatalytic activity, mineralization efficiency, and the pathway of phenol degradation. From the demonstrated series, the octahedral TiO_2 with exposed {1 0 1} facets exhibited the highest phenol degradation together with the highest mineralization rate under UV–Vis light irradiation. Next to the facet dependence, the surface composition is crucial concerning the photodegradation process efficiency. X-ray-induced photoelectron spectroscopy (XPS) measurements were performed to study the surface composition of the samples (Figure 5 (a) and (b)). In this series, low content of F^- ions (less than 1%) was detected, so the effect of fluorine ions adsorbed on the surface of the photocatalysts was negligible. However, for all titania-based photocatalysts formation of a non-stoichiometric TiO_{2-x} next to the pure form was detected. The overall tendency was that the amount of stoichiometric TiO_2 on the surface decreased at acidic conditions, especially for samples synthesized using HF as a capping agent. It is concluded that the formation of the oxygen-deficient surface structure originates from HF-induced surface etching [4]. Without the HF addition, the total amount of F^- ions was limited only to the dissociating $TiOF_2$ structure, and therefore such process was limited. Our studies showed that fluorine ions introduced to the reaction system had a negative impact on photocatalytic activity because they favored the growth of {0 0 1} facets present in decahedral nanostructures, which were found to be less active than the {1 0 1} ones in octahedral TiO_2. These {0 0 1} facets had an increased formation of the TiO_{2-x}, which is supposed to be unfavorable for photocatalytic performance. The photocatalytic activity towards phenol degradation is presented in Figures 6 (a) and (b).



(**a**) (**b**)

Figure 5. XPS spectra of samples showing Ti2p signals of **(a)** octahedral and (**b**) decahedral TiO_2 [13].



(**a**) (**b**)

Figure 6. (a) Phenol photocatalytic degradation for obtained samples and (**b**) their mineralization efficiency [13].

4. Conclusions

Herein, the comparative study of titania-based photocatalysts in the Ti-O-F system was presented. Based on that, we summarized the advantages and disadvantages of using fluorine ions in photocatalysts' preparation towards the degradation of organic pollutants. According to our experimental results, it can be assumed that fluorine ions are beneficial for the photocatalytic performance of titanium(IV) oxide, but only when they are adsorbed on pure photocatalysts' surfaces. When hydrofluoric acid is used as a fluorine source during the synthesis, it can initiate surface etching and enable to create non-stoichiometric phase TiO_{2-x}. This process has a negative impact on the photocatalytic performance of TiO_2 nanostructures.

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