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Photocatalytic Activities of Different Well-defined Single Crystal TiO_2 Surfaces: Anatase versus Rutile

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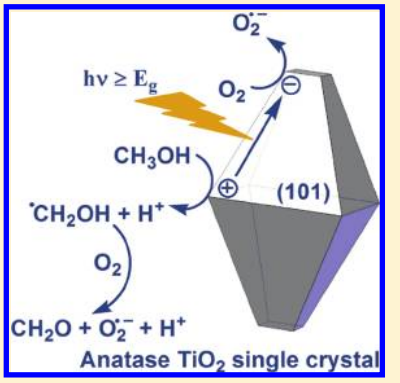
ABSTRACT: The photocatalytic activities of well-defined TiO_2 single-crystal anatase (101) surfaces have been assessed by methanol oxidation and by terephthalic acid hydroxylation evincing the formation of $OH^•$ radicals and have been compared with that of rutile single-crystal (001), (100), and (110) surfaces. The results showed that the anatase (101) surface exhibits a higher photocatalytic activity than all investigated rutile surfaces toward the oxidation of methanol and exhibits a comparable activity to that of the rutile (001) surface with respect of terephthalic acid hydroxylation. The rutile (001) surface shows a higher photocatalytic activity than both the rutile (110) and (100) surfaces for both photocatalytic test reactions. Because anatase (101) and rutile (110) are the thermodynamically most stable surfaces, anatase and rutile nanomaterials possess, thus, a large percentage of (101) and (110) surfaces, respectively. This offers a reasonable explanation why anatase nanoparticles usually exhibit higher photocatalytic activities than the respective rutile powders.



SECTION: Surfaces, Interfaces, Catalysis

Owing to the scientific and technological importance of titanium dioxide (TiO_2) photocatalysts, much effort has been devoted to the understanding of the photocatalytic processes occurring at its surface.[1] Almost all of the studies that have so far been carried out using photoelectrochemical measurements employing the thermodynamically most stable polymorph, that is, the rutile (110) surface mainly due to its commercial availability. In contrast, hardly any photocatalytic experiments on well-defined anatase surfaces have so far been reported.[2] However, technical-grade TiO_2 is very often supplied in the anatase form; most TiO_2 nanomaterials are produced in the anatase form, and in most cases, anatase is reported to be photocatalytically more active than rutile.[3] This lack of experimental data on anatase single-crystal surfaces is mostly due to the limited availability of anatase crystals of sufficiently large size.[4,5] This has motivated several theoretical investigations of anatase,[6−9] but there clearly is lack of experimental data in the literature obtained on well-defined anatase surfaces that could enable verification of these theoretical predictions.

During the past decades, most photocatalytic studies employing TiO_2 nanomaterials indicate that their photocatalytic activity for the decomposition of organic molecules is an extremely complex matter and appears to depend strongly on both the model substrate and the physical properties of TiO_2 particles.[3,10−13] In general, anatase nanomaterials display photocatalytic activities that are higher than those of rutile;[3] however, in some cases, the latter has shown better activities than the former.[14] Research to examine the surprising differences in photocatalytic activity between anatase and rutile has so far focused almost exclusively on the comparison of the powdered forms of these two TiO_2 modifications. These studies are important, but by their nature, the powdered forms of TiO_2 are poorly defined, and it is thus almost impossible to draw any conclusive scientific concepts concerning the photocatalytic activities of TiO_2 photocatalysts from this work.

One of the most serious experimental problems is the difficulty encountered in the preparation of TiO_2 photocatalysts exhibiting the same physical and optical properties, that is, identical surface area, particle size, exposed surface, band gap energy and position, crystallinity, morphology, and light absorption capability, to name but a few. A limited number of studies have suggested a significant role of the exposed surface of TiO_2 polyhedral particles on their photocatalytic activity.[13,15] Thus, there appears to be an urgent need to examine the photocatalytic activities of different well-defined TiO_2 surfaces. In contrast to TiO_2 nanomaterials, where the comparison of the powdered forms of these two modifications has so far not resulted in any reliable database and hence many hypotheses have been proposed, these well-defined surfaces provide a reliable basis for the direct comparison between the photocatalytic activities of anatase and rutile.

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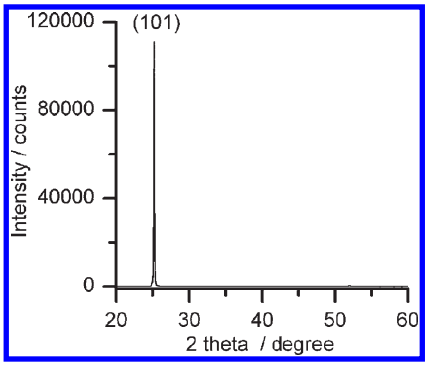

Figure 1. XRD diffraction pattern of the anatase TiO_2 single-crystal surface.

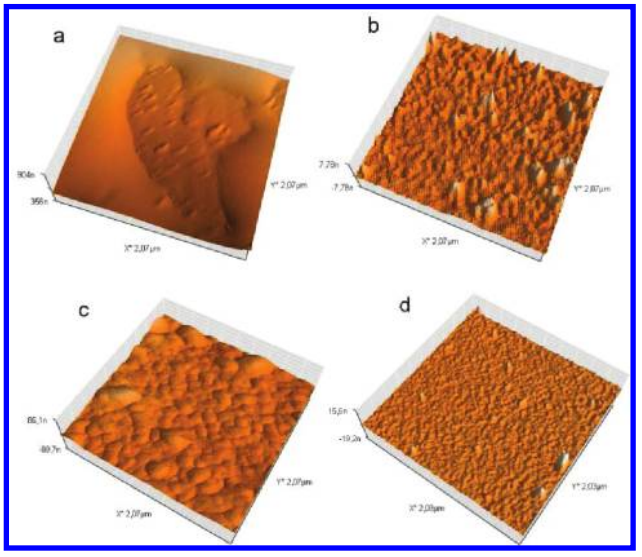

Figure 2. Three-dimensional AFM images of (a) the anatase TiO_2 single-crystal (101) surface and (b–d) the rutile TiO_2 single-crystal (001), (100), and (110) surfaces, respectively.

Because it is usually rather difficult to prepare anatase single crystals in the laboratory, the anatase (101) surfaces employed in the present study have been obtained from a natural mineral single crystal that has been oriented, cleaved, and polished. The resulting surface was $3 \times 3 \times 0.5$ mm^3 in size. It was initially clear with an orange shade and turned gray after exposure to a stream of hydrogen gas at 600 °C for 2 h to achieve n-type doping by oxygen vacancies. Rutile TiO_2 single-crystal surfaces with a size of $10 \times 10 \times 0.5$ mm^3 exhibiting a polished (110), (001), or (001) surface, respectively, on one side were purchased from K & R Creation Co., Japan, and cut into pieces of $5 \times 5 \times 0.5$ mm^3. To achieve n-type doping by oxygen vacancies, the wafers were also exposed to a stream of hydrogen gas, employing the same experimental conditions as in the case of the anatase (101) surface.

The anatase (101) surface and the rutile (001), (100), and (110) surfaces have been characterized by X-ray diffraction (XRD) and by atomic force microscopy (AFM). Figure 1 shows the XRD pattern of TiO_2 anatase (101). It is obvious from the high intensity of the XRD pattern that the anatase single crystal is of high quality, exhibiting a perfect (101) surface. No other reflections have been observed, revealing the perfect

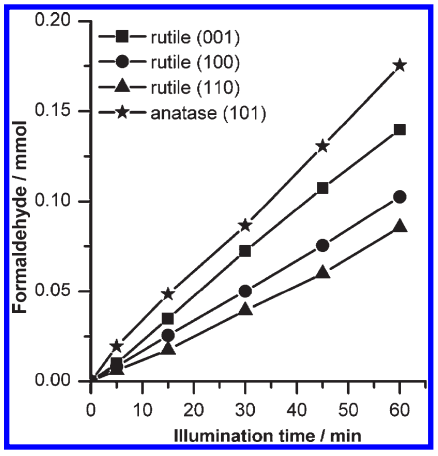

Figure 3. Photocatalytic methanol oxidation to formaldehyde on different TiO_2 single-crystal surfaces under 35 mW/cm^2 UV(A) illumination as a function of time; the illuminated area of rutile and anatase surfaces are 0.25 and 0.09 cm^2, respectively. Note: the amount of formaldehyde formed on the anatase surface has been normalized to 0.25 cm^2.

cutting parallel to the (101) direction. Figure 2 shows the three-dimensional AFM images for the TiO_2 anatase (101) and the rutile (001), (100), and (110) surfaces. It can clearly be seen that all surfaces exhibit a relatively rough texture.

The photocatalytic activities of the different TiO_2 single-crystal surfaces have been assessed by the photocatalytic oxidation of methanol. Methanol has been chosen as a model compound because it has been shown to be a suitable molecular probe to explore surface properties through different experimental techniques.[16,17] Moreover, methanol has been frequently used as a hole scavenger to achieve enhanced photocatalytic hydrogen production rates.[18,19] The photocatalytic experiments have been carried out employing 3.5 mL standard rectangular quartz cuvettes. For easier handling of the single-crystal surfaces, they have been fixed by connecting copper wires to the surfaces opposite to the polished surfaces of these single-crystal surfaces using conductive epoxy resin. The copper wires were covered with glass tubes, and the connections between the glass tubes and the wafers, except for the polished surfaces, were sealed with nonconductive epoxy resin (Araldite Rapid, Ciby Geigy). Afterward, the single-crystal surfaces were immersed in 3 mL of 1 vol % aerated methanol aqueous solutions and illuminated by UV(A) light filtered through a 320 nm long-pass cutoff filter (LOT-Oriel, Germany, light intensity 35 mW cm^{-2}) for different times using a high-pressure Xe lamp (OSRAM HBO 450 W). Methanol was photocatalytically oxidized to formaldehyde. The produced formaldehyde was analyzed by employing HPLC using the Nash reagent.[20] Figure 3 shows the time course of formaldehyde formation on the different TiO_2 single-crystal surfaces. It is obvious from the results shown in Figure 3 that the anatase (101) surface exhibits a higher photocatalytic activity than any of the investigated rutile surfaces.

Because the photocatalytic tests have been carried out by employing aqueous methanol solutions, there will be a competition between the direct photo-oxidation of methanol and that of water on the TiO_2 surfaces. It remains unclear whether the methanol photo-oxidation proceeds via the direct interfacial transfer of photogenerated holes or involves the reaction with photogenerated hydroxyl radicals ($OH^{\bullet}$) as an intermediate step.[21,22] It is a frequently employed concept that hydroxyl

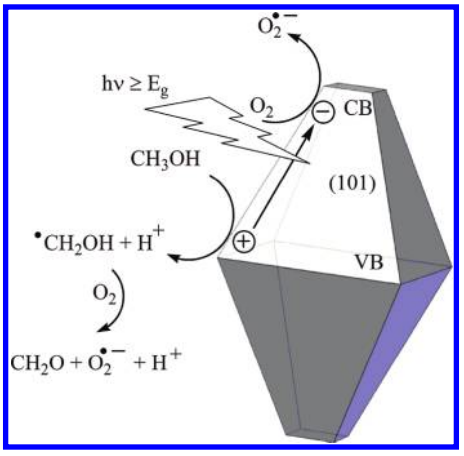

Figure 4. Scheme representing the photocatalytic steps of methanol photo-oxidation on the anatase TiO_2 single-crystal (101) surface. Note: for simplicity, the formation of hydroxymethyl radicals ($^{\bullet}CH_2OH$) by $OH^{\bullet}$ radicals is represented by the hole oxidation step.

radical species are responsible for the oxidation pathways of chemical compounds initiated by heterogeneous photocatalytic processes. For instance, methanol has been employed as a $OH^{\bullet}$ radical scavenger in order to determine the quantum yield and photonic efficiency of $OH^{\bullet}$ radical generation from photogenerated holes at the TiO_2 surface.[22−24] Methanol reacts with $OH^{\bullet}$ radicals and/or with surface-trapped holes, leading to the formation of $^{\bullet}CH_2OH$ radicals. The latter is further oxidized by reacting with molecular oxygen, leading to the formation of formaldehyde. The possible reaction steps are illustrated in Figure 4.

The photonic efficiencies (ζ) of the methanol photo-oxidation on the different TiO_2 single-crystal surfaces have been calculated by dividing the rate of formaldehyde formation (r) by the incident photon flux (I_0) according to the following equation[25]

$$\zeta = r \times 100/I_0$$

The incident photon flux per 0.25 cm^2 of illuminated surface has been calculated to be 1.54 μEinstein min^{-1} based on the UV(A) light meter measurements and assuming an average illumination wavelength of λ = 350 nm. The rates of formaldehyde formation (μmol min^{-1} per 0.25 cm^2 of electrode surface area) have been calculated from the slope of the time course of formaldehyde formation presented in Figure 3. The photonic efficiency of the anatase (101) surface has been calculated to be ζ = 0.190%, while the photonic efficiencies of the rutile (001), (100), and (110) surfaces have been calculated to be ζ = 0.153, 0.110, and 0.089%, respectively. The photonic efficiency values of all well-defined TiO_2 surfaces investigated here are higher than the reported value (ζ = 0.036)[26] for methanol photo-oxidation on nanocrystalline TiO_2 layers and also higher than the reported values for methylene blue photodegradation on anatase and on Pilkington active films,[27] evincing that the tuning of the exposed surface should be able to further enhance the photocatalytic activity of TiO_2 coatings.

The photocatalytic activities of the anatase and the different rutile single-crystal surfaces have also been evaluated by the photocatalytic hydroxylation of terephthalic acid, which is usually regarded as an indirect detection of $OH^{\bullet}$ radicals. Therefore, the $OH^{\bullet}$ radical formation at the TiO_2 surfaces has been detected by

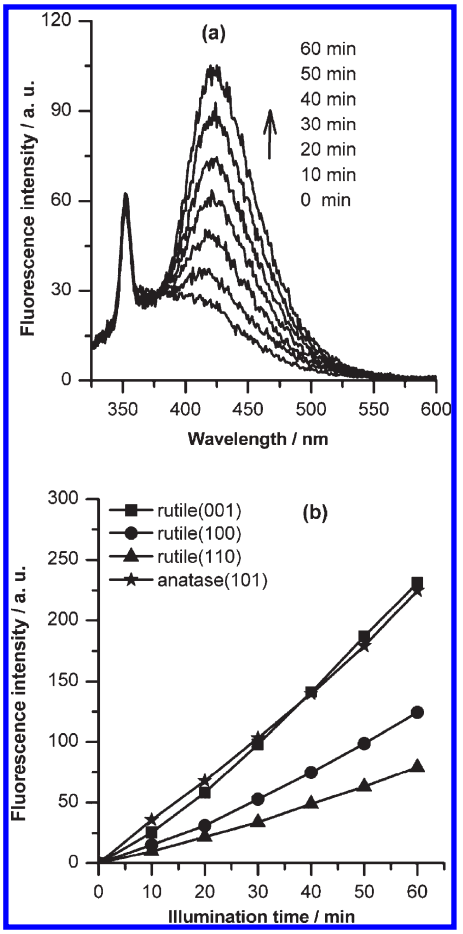

Figure 5. (a) Fluorescence spectra of a 4 × 10^{-4} M basic solution of terephthalic acid excited at 315 nm as a function of illumination time; the illuminated area of anatase surface is 0.09 cm^2. (b) Fluorescence intensity at 425 nm as a function of illumination time; the illuminated areas of the rutile and anatase surfaces are 0.25 and 0.09 cm^2, respectively. Note: the fluorescence intensity on the anatase surface has been normalized to 0.25 cm^2.

measuring the fluorescence intensity at 425 nm of 2-hydroxyterephthalic acid excited by 315 nm. The single-crystal surfaces have been immersed in standard rectangular quartz cuvettes containing 2 mL of a 4 × 10^{-4} M basic solution of terephthalic acid and have been illuminated by UV(A) light filtered through a 320 nm long-pass cutoff filter (LOT-Oriel, Germany, light intensity 15 mW cm^{-2}) for different times using a high-pressure Xe lamp (OSRAM HBO 450 W). Terephthalic acid reacts with the $OH^{\bullet}$ radicals, leading to formation of 2-hydroxyterephthalic acid.[28] Figure 5a shows the change in the fluorescence spectra recorded for the terephthalic acid solution under UV illumination in the presence of the anatase (101) surface (shown as an example). Figure 5b shows the change in fluorescence intensity recorded for the basic terephthalic acid solution under UV(A) illumination as a function of irradiation time for the anatase (101) surface and for the rutile (001), (100), and (110) surfaces, respectively. The linear relationship between the fluorescence intensity and irradiation time indicates that the amount of $OH^{\bullet}$ generated on the TiO_2 surface is proportional to the irradiation time during the photocatalytic process. Figure 5b clearly shows that the rate of $OH^{\bullet}$ radical formation on the anatase (101) surface is comparable to that on the rutile (001) surface and higher than that on the

rutile (100) and (110) surfaces. This trend is the same as that observed for the photocatalytic oxidation of methanol, except that anatase (101) and rutile (001) exhibit more or less the same photocatalytic activities toward $OH^{\bullet}$ generation. The higher activity of the photocatalytic methanol oxidation on the anatase (101) surface as compared with that on the rutile (001) surface, despite the fact that both of them show the same $OH^{\bullet}$ radical generation activity, can be explained either by direct interfacial transfer of photogenerated holes leading to the photocatalytic oxidation of methanol or by the fact that the photogenerated $OH^{\bullet}$ radicals on the anatase (101) surface are more reactive than those on the rutile (001) surface at least toward methanol photo-oxidation.

The reduced reactivity of $OH^{\bullet}$ radical generation on the rutile (110) surface in comparison to that on the anatase (101) surface is in agreement with the behavior observed on rutile and anatase powders reported by Hirakawa et al.[29] For example, comparing two of the investigated TiO_2 materials by Hirakawa et al., that is, ST-21 (Ishihara, 100% anatase, BET surface area 56.1 $m^2\ g^{-1}$)[30] and PT101 (Ishihara, 100% rutile, BET surface area 25 $m^2\ g^{-1}$),[30] one can clearly see that the formation rate of $OH^{\bullet}$ radicals on ST-21, normalized to the BET surface area, is approximately 3 times higher than that on PT101. In our reported data, the formation rate of $OH^{\bullet}$ radicals on the anatase (101) surface, normalized to the surface area, is ~2.8 times higher than that on the rutile (110) surface. This good agreement between the ratio of the formation rates of $OH^{\bullet}$ radicals on anatase and rutile powders and the ratio of the formation rates of $OH^{\bullet}$ radicals on anatase (101) and rutile (110) surfaces can be explained by the fact that anatase (101) and rutile (110) are the thermodynamically most stable surfaces, and hence, anatase and rutile powders possess a large percentage of (101) and (110) surfaces, respectively. This might support the importance of the exposed surface on the photocatalytic activity and highlight the importance of investigating different well-defined surfaces and comparing the results with a nanomaterial exhibiting the corresponding exposed surface.

In conclusion, for the first time, the photocatalytic activities of a well-defined anatase TiO_2 single-crystal (101) surface have experimentally been assessed by measuring the photocatalytic activity of methanol oxidation and by measuring the photocatalytic activity of $OH^{\bullet}$ radical generation. Comparison of its photocatalytic activity with that of rutile TiO_2 single-crystal (001), (100) and (110) surfaces indicates that the anatase (101) surface exhibits a higher activity than all investigated rutile surfaces toward methanol photo-oxidation and comparable $OH^{\bullet}$ radical generation activity to that on the rutile (001) surface. The rutile (001) surface exhibits the highest photocatalytic activity among the three investigated rutile surfaces, while rutile (110) shows the lowest activity regardless of the employed test. Because the (101) and the (110) are the thermodynamically most stable surfaces for anatase and rutile, respectively,[31−33] it is expected that most synthesized anatase and rutile nanomaterials possess a large percentage of these surfaces. This explains why anatase usually exhibits a higher photocatalytic activity than rutile. The preparation of rutile nanomaterials with a large percentage of the (001) surface is expected to notably increase the photocatalytic activity of rutile nanomaterials.

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