

The origin of photochemical anisotropy in SrTiO₃

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Photochemical reactions that deposit insoluble products on catalytic surfaces have been used to probe the anisotropy of the reactivity of SrTiO₃ microcrystals. Both reduced and oxidized products are formed preferentially on {100} surfaces. It is proposed that the anisotropic photochemical reactivity can be explained by the electronic band structure. Because direct optical transitions for charge carriers having momentum vectors in the $\langle 100 \rangle$ direction overlap well with the spectral distribution of the absorbed photons, more photogenerated carriers are moving toward {100} surfaces than other surfaces and, as a result, {100} surfaces are more active. Knowledge of the electronic band structure and the spectral distribution of the light allows predictions to be made about the anisotropic reactivity of photocatalysts with other crystal structures.

KEY WORDS: photochemistry; SrTiO₃; anisotropy; electronic structure.

1. Introduction

Photochemical reactions on metal oxides are anisotropic [1–3]. In other words, they occur at different rates on surfaces with different orientations. Furthermore, it has been observed that some surface orientations can promote the oxidation half of the reaction while another promotes the reduction half reaction [2,4]. While the mechanisms behind this phenomenon are not well understood, it is potentially important for the design of photocatalysts. For example, if the oxidation and reduction halves of a reaction such as water photolysis occur on distinct surfaces (surfaces with different crystallographic orientations) of the same particle, then, because of the spatial separation, the reaction products will be less likely to recombine. Conversely, if the reduction and oxidation products are produced at sites in close proximity, then the reverse reaction to reform water is likely.

Photochemical anisotropies are studied using probe reactions that deposit insoluble products on the surface. For example, the reduction of Ag⁺ from an aqueous AgNO₃ solution leaves silver on the surface. It is important to remember that there is a simultaneous oxidation half reaction (the oxidation of H₂O) that must occur at exactly the same rate. Therefore, while the amount of deposited silver is used to gauge the reactivity and the location of the deposit is used to determine the relative reactivity of specific orientations, there is an invisible oxidation reaction that might actually be the rate limiting step of the reaction and it might occur at a different location. In the past, studies have been carried out using both extended planar samples and three-dimensional microcrystals. The important difference

between these two methods is that when a macroscopically planar specimen is used, the surface contains only a subset of all possible surface sites that occur on a finite three-dimensional microcrystal. If this subset of sites does not include those needed for both half reactions, the planar specimen may exhibit a reduced reactivity with respect to a surface with the same orientation on a microcrystal bounded by several different planes. This difference might contribute to the apparent contradiction between the results of experiments on planar TiO₂ samples and TiO₂ microcrystals [1,2,5].

We have previously reported the results of experiments on macroscopically planar ceramic and single crystal SrTiO₃ specimens [6,7]. The purpose of the present paper is to show that SrTiO₃ microcrystals also exhibit highly anisotropic reactivities and to propose an explanation for the observed anisotropy that is based upon the spectral distribution of the incident light and the electronic band structure of SrTiO₃. Because of the dispersion of the highest occupied and lowest unoccupied states, the lowest energy photons that are able to initiate optical transitions will create charge carriers with wave vectors normal to the most reactive surface. We propose that anisotropic band dispersion provides a general explanation for the observation of anisotropic photochemical reactivities.

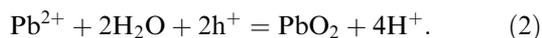
2. Experimental

SrTiO₃ powders were obtained from a commercial source (Alfa Aesar, 99.5% pure). Small, faceted SrTiO₃ crystals were produced using a molten salt flux method. In a typical experiment, equal weights of a Sr–Ti–O source and KCl (Fisher Scientific) were combined by wet grinding in ethanol for several minutes. Either SrTiO₃ or a 1:1.1 mixture of Sr₃Ti₂O₇:TiO₂ was used as the Sr–Ti–O

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source material [8]. Particles produced using the Sr₃Ti₂O₇:TiO₂ mixture had more well formed facets than particles produced from the SrTiO₃ source material. The slurry was then transferred to a Pyrex beaker and was mixed by magnetic stirring for 2 h. Following mixing, the excess ethanol was decanted with a pipet and the powders were dried in air at 70 °C. The dried powder was transferred to an Al₂O₃ crucible, heated in air at 5 °C/min, and held at 1200 °C for 10 h. The KCl was then removed by filtering with boiling deionized water and the remaining product was dried in air at 70 °C. The phase identity of the coarsened crystals was confirmed by powder X-ray diffraction. In some preparations, the weight fraction of SrTiO₃ was reduced by 5%, the temperature was increased to 1300 °C, and/or the annealing time was lengthened or shortened by a few hours. However, these variations in processing did not alter the results in any consistent way.

Two photochemical reactions were used to identify reactive facets: the reduction of Ag⁺ by photogenerated electrons and the oxidation of Pb²⁺ by photogenerated holes. These reactions are:



Both reactions leave an insoluble product on the surface (Ag and PbO₂, respectively) that can be observed in a scanning electron microscope. Reaction (1) is completed by the oxidation of H₂O and reaction (2) is completed by the reduction of O₂. These reactions are not directly observed. The photochemical reaction experiments are setup in two different ways, with similar results. In the first, an SEM stub covered by carbon tape was dusted with the powder. After removing the excess powder with forced air, a viton O-ring, 1.7 mm thick, was placed on the sample surface and the interior volume was filled with a solution containing a dissolved metal salt. For the reduction reaction, 0.115 M aqueous AgNO₃ (Fisher Scientific) was used and for the oxidation reaction, 0.0115 M aqueous Pb(C₂H₃O₂)₂ (Fisher Scientific) was used. A 0.2 mm thick quartz cover slip was then placed on top of the O-ring and held in place by the surface tension of the solution. The sample was illuminated using a variable power Hg lamp (Oriel). Exposures of 10–210 s at a lamp power of 300 W were used for the reduction of Ag⁺ and the oxidation of Pb²⁺ on SrTiO₃. After exposure, the sample was rinsed with deionized H₂O and dried with forced air. The second method was to irradiate a suspension of particles in a continuously stirred, 0.0115 M aqueous AgNO₃ solution contained in a Pyrex reaction vessel. A water-cooled quartz inner irradiation cell (450 W high-pressure Hg lamp) was suspended into the bath. The reactor was evacuated and filled with Argon three times and then Ar was bubbled

through the suspension for the remainder of the experiment. The particles were illuminated for 45 min, filtered, rinsed with deionized water, and dried. A number of control experiments described in detail elsewhere confirmed that deposits are formed only when the light source contains photons with an energy greater than the band gap, that reaction products are not formed homogeneously in solution during illumination, and that chemically generated colloidal silver does not attach to the surface [9]. In other words, we are certain that the observed reaction deposits are produced by a photochemical reaction on the crystal surface.

Scanning electron microscopy (SEM, Phillips XL30FEG) was used to examine the surfaces of as-processed and as-reacted particles. Typical imaging conditions were: working distance = 10 mm, spot size = 3 or 4, and accelerating voltage = 5–10 kV. Energy dispersive X-ray (EDX) spectroscopy (Oxford Isis) conducted in a scanning electron microscope (Phillips XL30FEG) was used to analyze the elemental composition of the deposits. It was confirmed that the deposits from the silver reduction reaction contained Ag and that deposits from the lead oxidation reaction contained Pb.

3. Results

Figure 1 shows two SEM images of SrTiO₃ crystals produced in a KCl flux following the reduction of silver. The reduction was carried out using the first reaction method, directly on the SEM sample stub. Note that reactions in the stirred reactor showed similar results. These are well-formed crystals and it is easy to determine the orientations of the facets from their cubic symmetry, which determines the shape and multiplicity of the bounding surfaces. These SrTiO₃ particles are predominately bounded by {100} and {110} type planes and the orientations are labeled in figure 1a. In these images, the white spots correspond to the silver containing reaction products. It is clear from the images that the {100} faces have the most deposited silver. The {110} facets have much less silver. Because {111} surfaces were observed only rarely, their reactivity could not be accurately evaluated. Therefore, the relative activity of the two most prominent facets on SrTiO₃ microcrystals for the reduction of silver is {100} > {110}.

Figure 2 shows SEM images of SrTiO₃ crystals after the oxidation of lead. This reaction was carried out directly on the SEM sample stub. The crystals used for these experiments were not as well formed as those used for the silver reduction, but it is still possible to confidently index the orientations of the facets for some of the crystals. For crystals where the indexing was clear, we found that the {100} orientation consistently had the highest activity for the oxidation reaction; these are the

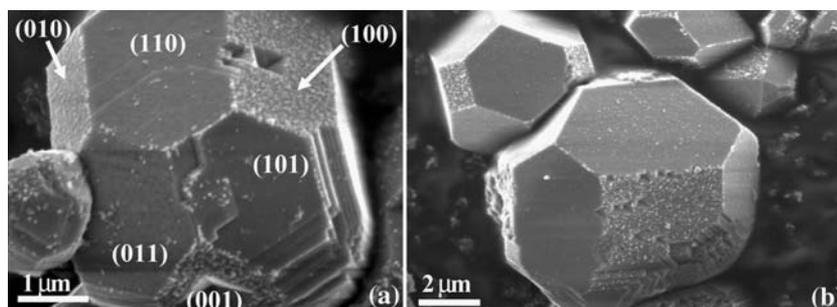


Figure 1. SEM images of faceted SrTiO₃ crystals after exposure to UV light in an aqueous AgNO₃ solution. The white contrast on the crystal facets corresponds to silver containing deposits produced by the photochemical reduction reaction.

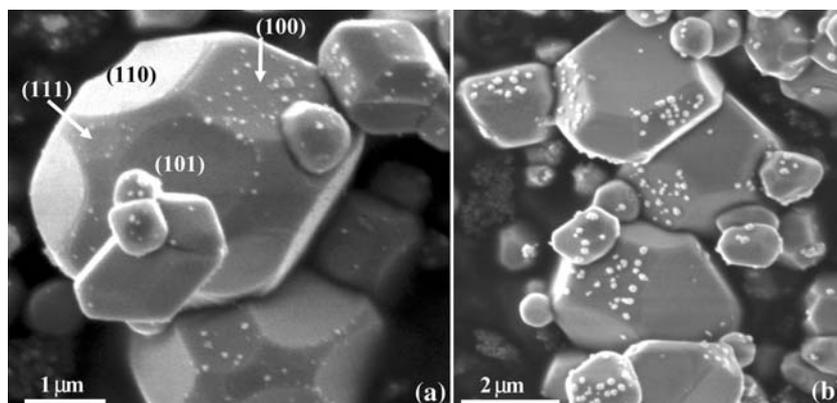


Figure 2. SEM images of faceted SrTiO₃ crystals after exposure to UV light in an aqueous lead acetate solution. The white contrast on the crystal facets corresponds to lead containing deposits.

facets covered with reaction product (white spots) in figure 2. The {111} and {110} surfaces had similar and very low reactivities for the oxidation reactions. Therefore, the relative reactivity of the bounding facets for the oxidation of lead can be ranked as $\{100\} > \{110\} \approx \{111\}$.

4. Discussion

The relative reactivities of the SrTiO₃ surfaces bounding the faceted particles are consistent with earlier experiments on extended planar substrates: the {100} surfaces are the most reactive [7]. In the experiments on planar substrates, a uniform coverage of silver was observed on the (100) oriented surfaces while oxidized lead was found in irregularly spaced clusters. This is consistent with what is observed on the three-dimensional microcrystals in figures 1 and 2. Therefore, for SrTiO₃, macroscopically planar crystals and faceted microcrystals display a consistent anisotropy. In the remainder of the discussion, we will consider a possible explanation for this anisotropy.

One thing that distinguishes the (100) surface from the (110) and (111) surfaces of SrTiO₃ is that it is nonpolar. The (100) surface can be terminated by an SrO layer or a TiO₂ layer and both of these compo-

sitions are charge neutral. The (111) surface can be terminated by a positively charged Ti layer or a negatively charged SrO₃ layer and the (110) surface can be terminated by a positively charged SrTiO layer or by a negatively charged oxygen layer containing two oxide ions per formula unit. Studies of extended crystal surfaces with the (110) and (111) orientations indicate the existence of domains with different polar terminations. The dipolar fields created by these charged domains lead to the spatial localization of reaction products in such a way that oxidation and reduction products form only on specific domains. Note that the sizes of the domains on the extended surfaces are comparable to the sizes of the facets on the microcrystals. The SEM images of the product distribution on the microcrystals provide no evidence for such domains, so we assume that a single termination occurs on each facet. If so, crystals terminated by charged surfaces that strongly promote the reduction of silver or the oxidation of lead (as observed on the planar substrates) have not been found. It is also possible that because the reaction occurred so readily on the (100) surfaces, not enough material deposited on the less reactive polar surfaces to expose the domains.

The nonpolar characteristics of the SrTiO₃(100) surface are likely to be one of the factors contributing to its

high reactivity. However, polar surfaces with the appropriate charge have also been shown to strongly promote certain half reactions [4,7]. This suggests that there are other factors that might contribute to the observed anisotropic reactivity. We propose that a factor contributing to the high reactivity of the (100) surface is the electronic band structure of the crystal, which favors the creation of photogenerated carriers with wave vectors perpendicular to the (100) surfaces. This explanation departs from the typical “flat band” picture, in which it is assumed that the difference between the highest occupied and lowest unoccupied states is the same for charge carriers moving in all directions. The bands closest to the band gap are sketched in figure 3. While schematic, the bands are based upon and consistent with those calculated by Mattheiss [10] and van Benthema *et al.* [11]. The main difference between the sketch in figure 3 and the calculated results is that the band gap has been adjusted to the experimentally observed value of 3.25 eV for indirect transitions and 3.75 eV for a direct transition at the origin of the Brillouin zone (referred to as the Γ -point) [11].

The high pressure Hg lamp used for these reactions produces a broad spectrum of UV and visible light that is relatively constant between 800 and 300 nm [12]. However, below 300 nm, a wavelength that corresponds to a photon energy of about 4.1 eV, the intensity falls off by more than two orders of magnitude. There is a sharp peak at 240 nm before the intensity goes to zero. However, the number of photons arising from this narrow feature is much smaller than from the main part of the spectrum and, because of their higher energy, they are attenuated more strongly by the intervening air and fluid during the experiment. Therefore, we conclude that the majority of the electron-hole pairs used for the photochemical reactions are created by photons with energies greater than the band gap but less than 4.1 eV. The wave vector states where vertical transitions are

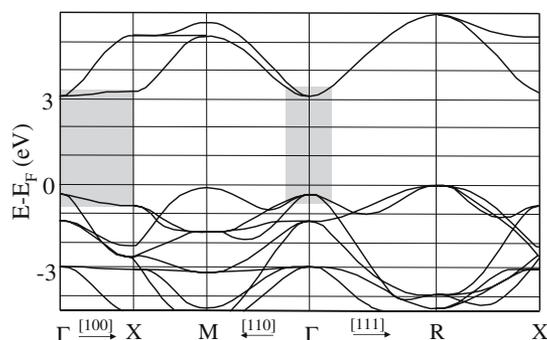


Figure 3. Schematic representation of the structure of the bands closest to the Fermi level for SrTiO₃. The bands were drawn based on the results in references [9] and [10], but they have been rigidly translated by a small amount to match the experimentally observed band gap. The Fermi level is set to the highest occupied level. The shaded regions indicate momentum states where vertical transitions are possible when the photon energy is 4 eV.

possible with photon energies as large as 4.1 eV are shown by the shaded areas of figure 3. Note that transitions to all wave vector states in the lowest occupied band with momentum vectors in the [100] direction can be excited by photons with an energy of 4.1 eV. This is because the bands are weakly dispersive (flat) in this direction. Photons with energies of 4.1 eV can also excite transitions near the Γ -point. Some of these states are in the [110] and [111] directions, but the number of these states is much lower than the excited states in the [100] direction. To excite all of the states in the [110] direction (Γ to M), light with an energy greater than 5 eV is required. To excite all of the states in the [111] direction (Γ to R), light with an energy of about 6 eV is required. Therefore, it is easier to excite carriers with momentum in the [100] direction. Note that this same lamp excited enough charge carriers to initiate reactions on macroscopically planar samples with the (110) and (111) orientations, but the amount of reaction product was much less than on the (100) oriented crystals [7].

It is recognized that just because more carriers are created traveling toward the (100) surface, this does not by itself mean that this will be the most reactive surface. The carriers must reach the surface without recombining, they must be trapped on the surface prior to reacting, and reactant species must be adsorbed on the surface with a sufficient density. Furthermore, carriers will be excited throughout the volume of the crystal and traveling in a $\langle 100 \rangle$ direction does not guarantee that they will intersect a $\{100\}$ surface. Therefore, we must also consider why charge carriers with momentum in a $\langle 100 \rangle$ direction do not react after reaching other surfaces. The surface states where the charge carriers are trapped prior to reaction are believed to be just above the highest occupied states in the valence band and just below the lowest unoccupied states in the conduction band. Calculations of the surface electronic structure of the SrTiO₃ (100) surface indicate that the bands at the surface are very similar to the bulk bands [13]. Therefore, the trap states on the (110) and (111) surface are expected to be proportionally higher (for electrons) and lower (for holes) than the trap states on the (100) surface. If this is so, then charge carriers in the bands with wave vectors in the $\langle 100 \rangle$ direction may be at too low an energy (for electrons in the conduction band) or too high an energy (for holes in the valence band) to access traps on the (110) or (111) surface. This confines the reaction to the one surface where these charge carriers can access the surface states that mediate the reaction.

If the rationale described above is correct for SrTiO₃, it should also apply to other photocatalysts. At the current time, the limited available data make it difficult to make comparisons. The published band structure of rutile structured TiO₂ shows the band dispersion in the [110], [100] and [001] directions [14]. Based on this, we would say that the (110) and (100) surfaces are expected to be more reactive than the (001) surface. Ohno *et al.*

[3] found that Pt deposits preferentially on {110} surfaces and this is consistent with our predictions. However, experiments on planar substrates suggest higher reactivity for the reduction of Ag on {101} surfaces [1,4]. At the current time it is not clear how to interpret this result, because we do not know the band dispersion in the $\langle 101 \rangle$ direction nor the source of discrepancy between the microcrystal and planar substrate results. Nevertheless, the same rationale can be used to can predict that the most reactive orientation for transition metal oxides with the rock salt structure is (100) [15] and the most reactive orientation for III–V and II–VI materials with the zinc blende structure is (111) [16]. We plan to experimentally test these predictions in the future so that we can determine if it is a general phenomenon. There are many factors that influence photochemical reactions. However, if reactions can be systematically controlled through the overlap of the incident light's spectral distribution and the band structure, this will be an important factor in the design of catalysts that promote reactions with less energy. This is especially important for the development of water photolysis catalysts that can be activated by solar light.

5. Conclusions

Photochemical reactions that deposit insoluble products on the surfaces of SrTiO₃ microcrystals were used to examine the anisotropy of the reactivity. The observations indicate that the {100} type surfaces are the most reactive. We propose that this anisotropic reactivity is because electron hole pairs with momentum in the $\langle 100 \rangle$ direction are excited by lower energy light

than charge carriers with momentum in other directions. This argument can be applied to predict the anisotropic reactivity of crystals with other structures.

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