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# Structure Sensitivity and Photocatalytic Reactions of Semiconductors. Effect of the Last Layer Atomic Arrangement

Jarod N. Wilson and Hicham Idriss*

*Department of Chemistry, The University of Auckland, 23 Symonds Street, Private Bag 92019,*
*Auckland 1020, New Zealand*

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Understanding the relationships between the surface structure of solid materials and their reactivity has wide interest and applications because the majority of chemical and biological processes are directly affected by the atomic arrangement of the last layer. These reactions extend from evolution theories[1] (where mineral surfaces may have acted as catalysts for making simple biological molecules) to biomaterials[2] and catalysis.[3] We report in this work the first evidence of the effect of changing the last layer surface structure of a semiconductor on its photocatalytic activity. Although structure sensitivity is a well-known concept in surface science and catalysis, most of the related studies are conducted for dark catalytic reactions, while few are conducted for the photocatalytic reactions.[4,5] There is one major conceptual difference between dark and photocatalytic reactions: the former is relatively insensitive to the bulk structure, while the latter can be dramatically affected. All photocatalytic works reported so far have failed to recognize this subtle difference because they relied on changing the crystallographic structure of the bulk materials for changing the surface structure. This is fundamentally different from the work reported here where the bulk of the structure is totally maintained and only the surface is allowed to reconstruct. The decoupling of both structures (surface and bulk) is of major importance if one wants to study the effect of the upper layer on the photocatalytic process because a large number of physical parameters affecting the reaction will be kept constant. These include bulk electron−hole recombination, electron and hole diffusion, and the bulk dielectric constant.

Figure 1 shows a model of the two surface structures obtained by annealing a rutile $TiO_2(001)$ single crystal at 750 (A) and 950 K (B), respectively. These surfaces have been thoroughly studied in the past by several spectroscopic techniques.[6] The main difference between the two surfaces is in the coordination number of Ti atoms. On the {011}-facetted surface (A), all Ti atoms are five-fold coordinated, while they are four-, five-, and six-fold coordinated on the {114}-facetted surface (B). The difference in coordination number of Ti cations to oxygen anions will change the electronic charge distribution and the position of the conduction band[7] and may then affect the rate of charge transfer. More important, the rate of surface electron hole recombination is expected to be considerably affected by changing the atomic arrangement and coordination number.

We have investigated the reaction of acetic acid, as a prototype molecule, on these two surfaces in an ultrahigh vacuum environment in steady-state conditions. Under UV irradiation, the following two reactions (called Photo−Kolbe reactions) occur:

$$CH_3COOH_{(ads)} \rightarrow CO_{2(g)} + CH_{4(g)}$$

$$2CH_3COOH_{(ads)} + \mathbf{O}_{(lattice)} \rightarrow 2CO_{2(g)} + CH_3CH_{3(g)} + H_2\mathbf{O}_{(g)}$$

The surface was cleaned by $Ar^+$-sputtering and annealing cycles. Dark experiments of acetic acid were checked for before photoreactions, and the results perfectly matched those previously reported.[6] The quantum yield was calculated for both surfaces after dividing the reaction rate of acetic acid per unit surface area by that of the photon flux of the UV lamp ($5 \times 10^{15}\ h\nu\ cm^{-2}\ s^{-1}$, for the 365 nm line − the excitation source). Analyses were conducted with a quadrupole mass spectrometer at ~1 mm from the crystal surface. The {011}-faceted surface was found far more active than the {114}-faceted surface. The large difference in the reactivity between the two surfaces can be tracked to surface effect. Surface electron−hole recombination is most likely the main difference between the two structures because all other parameters are kept the same. The quantum yield ($\phi$) of a photocatalytic process is directly proportional to the ratio of the rate constant of charge transfer ($k_{CT}$) to that of both $k_{CT}$ and the rate constant of hole−electron recombination ($k_R$) (recombination occurs at the surface and in the bulk):

$$\phi \propto \frac{k_{CT}}{k_{CT} + k_R} \qquad (1)$$

From eq 1 we obtain the following equation relating $\phi$ to $k_R$ (bulk and surface), neglecting variations of $k_{CT}$ for both surfaces:

$$\frac{k_{R\{011\}}}{k_{R\{114\}}} = \frac{\phi_{\{114\}}(1 - \phi_{\{011\}})}{\phi_{\{011\}}(1 - \phi_{\{114\}})} \approx 0.40 \qquad (2)$$

From the ratio of the experimental quantum yield, the ratio of $k_R$ for both surfaces can be deduced. Because $k_R$ is a contribution from both bulk and surface rates and because the bulk rate is expected to be the same (along the (001) direction), then the difference in the rate of recombination values can be tracked to the effect of surface atomic charge and arrangement.

Knowing the quantum yield of the reaction ($\phi$) allows the calculation of the width of the depletion layer, $W$. $W$ directly affects the rate of electron−hole recombination and was computed following eq 3 and found equal to 18.2 and 6.6 nm for the {011}- and {114}-reconstructed surfaces, respectively.

$$W = \frac{\phi}{\alpha} + L(\phi - 1) \qquad (3)$$

where α the reciprocal absorption length is $2.6 \times 10^4\ cm^{-1}$ at 320 nm, $L$ the minority carrier diffusion length is $\sqrt{D\tau}$, $D$ is the

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* To whom correspondence should be addressed. E-mail: h.idriss@auckland.ac.nz.

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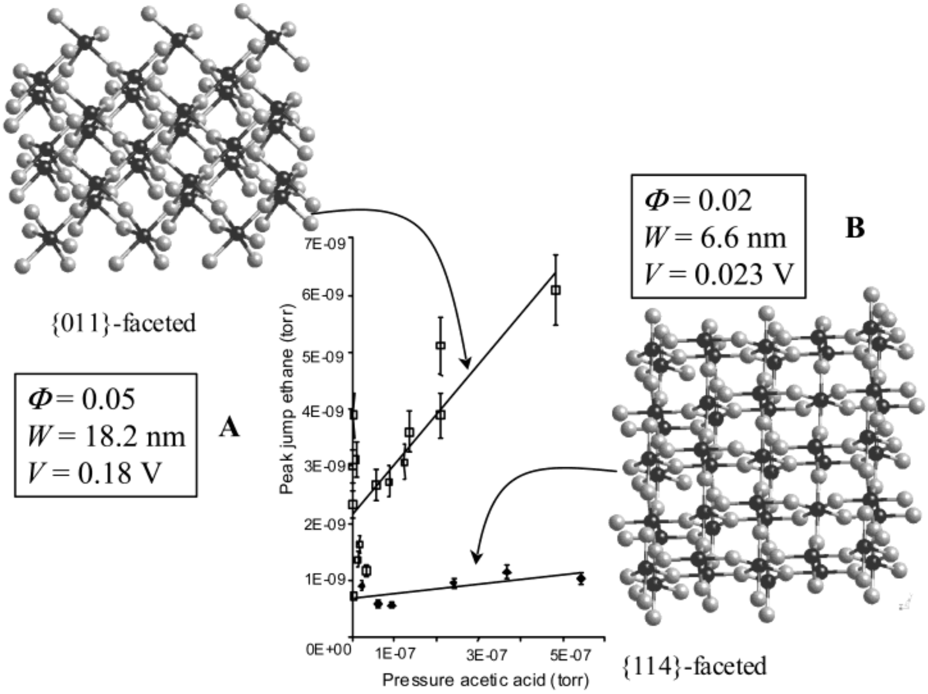

***Figure 1.*** The two stable surfaces reconstruction of a $TiO_2(001)$ single crystal. Black balls, Ti atoms; gray balls, O atoms. The plot (center) shows the formation of the main reaction product (ethane) as a function of acetic acid pressure in steady-state conditions in an ultrahigh vacuum. Also shown are the estimated width of the depletion layer ($W$) and barrier height ($V$) from the experimental quantum yield ($\phi$) of the reaction of acetic acid on both surfaces.

diffusion coefficient, and $\tau$ is the mean carrier lifetime.[9] Taking $\tau = L^2_{\mathrm{Deb}}/\pi^2 D$, where $L_{\mathrm{Deb}}$ is the Debye length, and taking $L^2_{\mathrm{Deb}} = \epsilon\epsilon_o k_B T/2e^2 n_i$, we have estimated $\tau = 0.6$ ps (using $D = 2 \times 10^{-2}$ cm$^2$ s$^{-1}$)[9] and $L$ (mean carrier diffusion length) $= 1.1 \times 10^{-7}$ cm.

The very low reactivity of the {114}-faceted surface is also translated by a negligible barrier height ($eV$) of the depletion layer, computed following eq 4,[8] of 0.023 V (while that of the {011}-faceted surface is 0.18 V).

$$e|V| = \frac{e^2}{2\epsilon\epsilon_o} n_i W^2 \tag{4}$$

$e$ and $\epsilon_o$ have their usual meaning, $\epsilon = 170$,[10] and $n_i$ (the intrinsic carrier density) $= 10^{25}$ m$^{-3}$.

This work shows that in treating photocatalytic reactions on solid surfaces (very relevant for environmental cleanup, energy conversion, and evolution theory), one is poised to consider the last layer atomic arrangement of the semiconductor material as having a major effect on the rate of chemical reactions.

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