# Electron-Mediated CO Oxidation on the TiO$_2$(110) Surface during Electronic Excitation

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***Abstract:*** The role of electrons and holes in the electronically excited oxidation of adsorbed CO on TiO$_2$(110) has been investigated by tuning the surface electron and hole availability by the adsorption of Cl$_2$ or O$_2$. The presence of an electron acceptor (Cl$_2$ or O$_2$) on the TiO$_2$(110) surface causes upward band bending, increasing the excited hole availability and decreasing the excited electron availability in the near surface region. This enhances O$_2$ desorption and depresses CO$_2$ production during electronic excitation. This result gives clear evidence for the first time that the electronically excited CO oxidation reaction is caused by an electron-mediated process in contrast to O$_2$ desorption which is mediated by holes.

The electronic excitation of a semiconductor using either photons or electron impact results first in exciton formation followed quickly by separation of an electron–hole pair.[1–3] The utility of the hot electron produced is related to its ability to tunnel from the conduction band (CB) to an adsorbed molecule which presents an empty orbital at the appropriate energy. Electron attachment to the adsorbed molecule can produce a temporary negative ion which can then undergo dissociative electron attachment (DEA) producing new products.[4] The utility of the hole produced in the valence band (VB) is to accept an electron from a filled orbital of an adsorbed molecule causing subsequent chemical processes to also occur on the surface. Titanium dioxide is widely used as a photoactive material in which the two processes involving electron and hole charge carriers are balanced, maintaining charge neutrality during photoexcitation.[2,5,6]

The manipulation of the rate of transport of photogenerated charge carriers from the bulk solid to adsorbed species on the surface is a powerful method for the control of surface processes induced by the electronic excitation of a semiconductor. Such control of charge carriers could be useful in enhancing photochemistry on TiO$_2$ particles as well as charge transport efficiency in photovoltaic cells. In previous work,[7] we have shown that electron-withdrawing and electron-donating adsorbates on TiO$_2$(110) are able to strongly influence charge transport to the adsorbed O$_2$ molecule. This is postulated to occur by upward band bending for electron-acceptor surface modifiers and downward band bending for electron-donor surface modifiers, as shown in Figure 1. The upward and downward band bending processes are accompanied by mobile charge carrier displacements in the near surface region of the semiconductor.[8–10]

The present study is carried out on an atomically clean TiO$_2$(110)-1×1 single crystal in ultrahigh vacuum (UHV) using traditional surface preparation and measurement methods used in surface science experiments. Accurate control of surface cleanliness and adsorbate coverage is achieved using these methods. The structure and surface defect density are well-known for this crystal which

was processed to contain 8–10% bridge-bond oxygen (BBO) vacancy defects to act as sites to bind molecular O$_2$. Thus the experiments differ from the usual TiO$_2$ particle-surface modification experiments, where small TiO$_2$ particles with unknown surface inhomogeneities are often employed, and where in such experiments surface impurities, particle size effects, and aqueous solvent effects are often present.
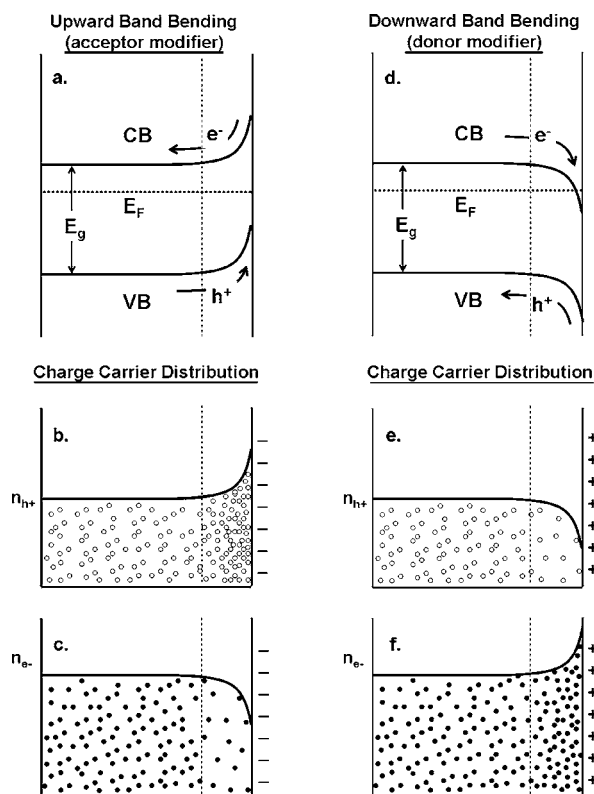


**Figure 1.** Role of (a) electron-acceptor and (d) electron-donor surface modifiers on band bending in an n-type semiconductor such as TiO$_2$. The TiO$_2$ is not electronically excited. The flow of electrons and holes for electronically excited TiO$_2$ is also indicated. For upward band bending: (b) hole density; (c) electron density. For downward band bending: (e) hole density; (f) electron density.

In this study we investigate the oxidation of adsorbed CO by adsorbed O$_2$ molecules on TiO$_2$(110) as induced by electronic excitation of the solid. We employ 100 eV electron bombardment which leads to electron and hole production in the near surface region of the crystal.[11] The CO oxidation reaction is well studied, especially by photon-induced excitation with ultraviolet light with photon energies above 3.1 eV, the bandgap energy of TiO$_2$.[12–15] Our studies have shown that electron impact may also be used to produce electron–hole pairs in TiO$_2$ and that this method of excitation is very nearly equivalent to photon excitation of the TiO$_2$

since electron−hole pair production is involved in both cases.[11,16] The behavior of $O_2$ chemisorbed on $TiO_2(110)$ is also well studied.[5,7,11,16−22] It has been found, both experimentally[5,7,11,16−21] and theoretically,[22] that the electronic desorption of $O_2$, originally adsorbed on BBO oxygen vacancy defect sites, is caused by holes produced either by UV excitation or by holes produced by 100 eV electron impact. The production of holes in $TiO_2$ may be accurately monitored by measuring the yield of desorbing $O_2$ molecules.[11,16] We have found that the rate of the hole-mediated $O_2$ desorption process can be modified by adding either donor or acceptor molecules to the surface containing adsorbed $O_2$. Upward band bending, achieved by the chemisorption of $Cl_2$ (acceptor), has been found to enhance the initial rate of $O_2$ desorption by a factor of up to 25.[7] Conversely, using methanol (donor), it has been found that the initial rate of $O_2$ desorption can be reduced to zero and it is postulated that downward band bending is responsible for this effect by limiting hole transport from the bulk to the surface.[7]
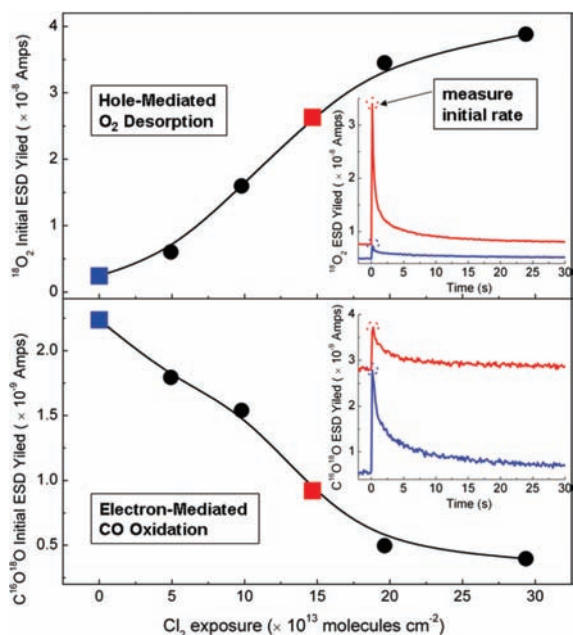


**Figure 2.** Plots of the initial yield of $^{18}O_2$ (upper panel) and $C^{16}O^{18}O$ (lower panel) as a function of $Cl_2$ exposure during electronic excitation of a $C^{16}O$ + $^{18}O_2$ mixed layer. Inset shows the measurements by QMS for $^{18}O_2$ (upper panel) and $C^{16}O^{18}O$ (lower panel) yields during electronic excitation in the presence of $Cl_2$ (blue curve, $Cl_2$ exposure: 0 molecules cm$^{-2}$; red curve, $Cl_2$ exposure: $1.47 \times 10^{14}$ molecules cm$^{-2}$) on the $C^{16}O/^{18}O_2/TiO_2(110)$ surface. $^{18}O_2$ exposure: $3.84 \times 10^{13}$ molecules cm$^{-2}$; $C^{16}O$: exposure: $1.18 \times 10^{14}$ molecules cm$^{-2}$, at 85 K. The electron bombardment is rapidly initiated at 0 s, and the initial desorption yields of $^{18}O_2$ and $C^{16}O^{18}O$ are measured within the first 0.2 s (as shown in the dashed circles in the insets).

We extend the studies of the modification of hole- and electron-mediated processes on $TiO_2(110)$ to the investigation of the role of charge carrier production on the CO oxidation reaction, finding that the oxidation process is **electron-mediated**. Until now, the role of the electron or hole in the CO oxidation has been unclear and contradictory results have been published. EPR[23,24] and theoretical calculation[23] suggested that the active oxygen in the photocatalytic oxidation process is $O_3^-$, formed by $O_2$ reacted with a hole center ($O^-$), which is a hole-mediated process. In contra-distinction, experiment and kinetics analysis[25−27] showed that, in aqueous media (where water is chemically involved in the production of intermediate species), electron transfer to the $O_2$ may play an essential role in the photooxidation of organic compounds.

In this paper, by fine-tuning band bending at the $TiO_2$ surface using electron-acceptor adsorbates, and hence modifying the surface hole and electron availability and transport kinetics, we show that the oxidation of CO may be strongly modulated.

All the experiments have been carried out in a stainless UHV chamber with a base pressure lower than $3 \times 10^{-11}$ mbar, which has been described elsewhere.[11,28] A clean $TiO_2(110)$-1×1 surface with ~8−10% of a monolayer of bridge-bonded oxygen vacancies can be reproducibly produced by Ar$^+$ sputtering followed by annealing at 900 K in vacuum. The energy of the incident electrons from an electron gun (Kimball Physics ELG-2) is 100 eV with a flux of $6.8 \times 10^{13}$ electrons cm$^{-2}$ s$^{-1}$. An absolutely calibrated capillary array doser[29] has been used to dose $^{18}O_2$ (99% isotopically pure), $C^{16}O$, and $Cl_2$ (Sigma-Aldrich, >99.5%) to the surface. The rate of evolution of $^{18}O_2$ and $C^{16}O^{18}O$ induced by the incident electrons was monitored by a line-of-sight quadrupole mass spectrometer (QMS) (UTI-100C) using 70 eV internal electron impact. All gas dosing and electron stimulated experiments have been done at 85 K. The $TiO_2$ crystal has been cleaned by sputter-annealing after each electron-excited experiment.

To investigate the influence of $Cl_2$ on the $C^{16}O$ oxidation by electron impact, various exposures of $Cl_2$ were dosed onto the $TiO_2(110)$ surface following the exposure to a constant amount of $^{18}O_2$ (exposure: $3.84 \times 10^{13}$ molecules cm$^{-2}$) and to $C^{16}O$ (exposure: $1.18 \times 10^{14}$ molecules cm$^{-2}$) at 85 K. The insets of Figure 2 show the $^{18}O_2$ (upper panel) and $C^{16}O^{18}O$ (lower panel) yields versus electron bombardment time. In the insets, $Cl_2$ exposures of 0 (blue curve) and $1.47 \times 10^{14}$ molecules cm$^{-2}$ (red curve) were performed on the $C^{16}O/^{18}O_2/TiO_2(110)$ covered surface. Similar to the $^{18}O_2$ yield, the $C^{16}O^{18}O$ yield reaches a maximum value as the electron current is first established and then decreases monotonically over time. The **initial rates** of production of $^{18}O_2$ (upper panel) and $C^{16}O^{18}O$ (lower panel) with various $Cl_2$ exposures are plotted in Figure 2. Measurement of the initial rate (during the first 0.2 s electron exposure) assures that significant electron-beam induced damage effects are not present. Consistent with our previous report,[7] the $^{18}O_2$ desorption yield increases with the $Cl_2$ exposure over a range of exposure maximizing near ~1 ML of $Cl_2$ exposure. In contrast to the $^{18}O_2$ yield, the initial rate of $C^{16}O^{18}O$ production decreases to near zero with the full $Cl_2$ exposure. The opposite trends of the yield of $^{18}O_2$ and $C^{16}O^{18}O$ indicate that the electronic excitation mechanisms for the desorption of $^{18}O_2$ and for the production of $C^{16}O^{18}O$ are different, as will be discussed later.

Previous results[7,8,30,31] have shown that $O_2$ is also an electron acceptor, capable of causing upward band bending when adsorbed on $TiO_2$. Thus, in the case of the electron-induced reaction of adsorbed $O_2$ and CO we have the possibility of the reactant, $O_2$, also being an electronic modifier of the photocatalyst surface by virtue of band bending which it induces. Figure 3 plots the effect of $O_2$ adsorption on the yield of desorbing $O_2$ in the top panel, where a mixture of adsorbed $O_2$ and CO is studied. The $O_2$ yield increases as the $O_2$ coverage increases for two reasons: (1) increasing $O_2$ coverage; (2) increasing upward band bending which promotes hole transport to the adsorbed $O_2$.[7] In the bottom panel of Figure 3, it is seen that two effects are mixed when the production of $CO_2$ is simultaneously monitored. Initially, as the $O_2$ coverage is increased, the yield of $CO_2$ increases due to the coverage increase of the adsorbed $O_2$. However, at intermediate coverages of $O_2$, the rate of $CO_2$ production reaches a maximum and then decreases as the electronic effect of $O_2$ on electron transport **to itself** becomes dominant.

The results shown in Figures 2 and 3 may be rationalized on the following basis. The electron acceptor molecules, $Cl_2$ and $O_2$, when

adsorbed on $TiO_2(110)$, cause upward band bending at the CB and VB band edges. This results in an enhancement of hole transport to $O_2$ molecules upon excitation of the $TiO_2$, resulting in the acceleration of the hole-mediated $O_2$ desorption process (Figures 2 and 3, upper panels). Concomitantly, the upward band bending produced by either $Cl_2$ or $O_2$ causes a diminution of the process mediated by electrons, namely the CO oxidation reaction (Figures 2 and 3, lower panels).
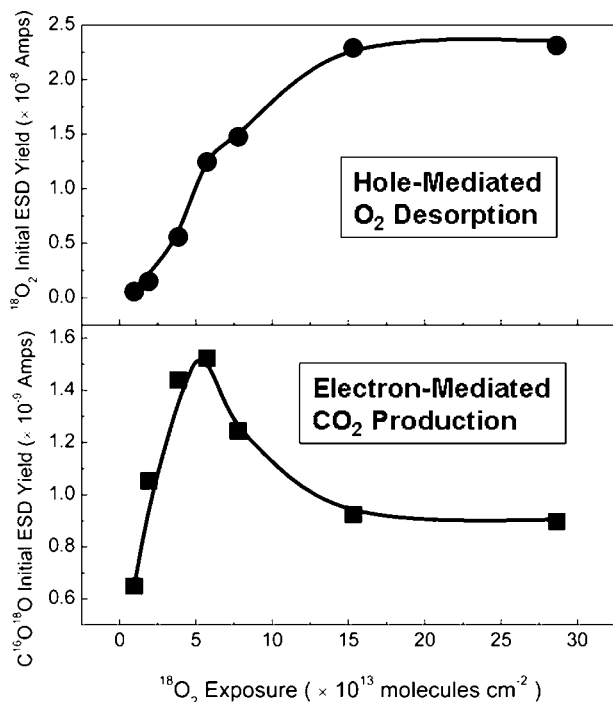


**Figure 3.** Plots of the initial yields of $^{18}O_2$ (upper panel) and $C^{16}O^{18}O$ (lower panel) as a function of $^{18}O_2$ exposure during electronic excitation of a $C^{16}O$ layer. The preadsorbed $C^{16}O$ exposure: $1.18 \times 10^{14}$ molecules cm$^{-2}$ at 85 K.

Figure 4 schematically shows the two electronically excited reactions of adsorbed oxygen which have been studied here, under conditions where electrons and holes stimulate different surface reactions. The upward band bending caused by either $Cl_2$ or $O_2$ adsorption results in the enhancement of the hole-mediated process leading to enhanced rates of $O_2$ desorption; at the same time, the electron-mediated CO oxidation process is diminished in rate as the process, driven by electrons from electron–hole pair formation in $TiO_2$, is reduced by upward band bending.

It is well known that adsorbed $O_2$ species on BBO vacancy sites acquire a negative charge upon adsorption.[7,8,22,30–36] We will assign these species as $O_2^-$ superoxide species, based on theory[22,34,35] and on observations by ESR[33,36] and EELS.[32] The chemisorbed $O_2^-$ species, upon electron attachment in an electron-mediated process, produce the $O_2^{2-}$ species, a peroxide ion well-known for its ability to cause oxidation. Peroxide ions participate in oxidation reactions with the production of $O^{2-}$, the oxide ion which has the formal oxidation number $(-2)$, as do the oxygen moieties in $CO_2$. Thus, because of the variable oxidation states available to oxygen, the reaction, driven by electrons interacting with $O_2^-$ adsorbed species, results in the oxidation of CO, forming $CO_2$.

These experiments demonstrate the dual role of adsorbed $O_2$ as a participant in both hole-driven and electron-driven surface processes on the $TiO_2$ surface. Depending on which charge carrier activates $O_2^-$, either $O_2(g)$ (hole-mediated) or $O_2^{2-}$ (electron-mediated) species are produced. The $O_2^{2-}$ species act as oxidizing

agents for adsorbed CO as they are reduced to $O^{2-}$. It is likely that the electron-mediated process, leading to adsorbed $O_2^-$ excitation to a peroxide, is also responsible for various photooxidation reactions involving organic molecules on $TiO_2$ under anhydrous condition; more complex electron-mediated oxidation chemistry occurs when water is present.[25–27]
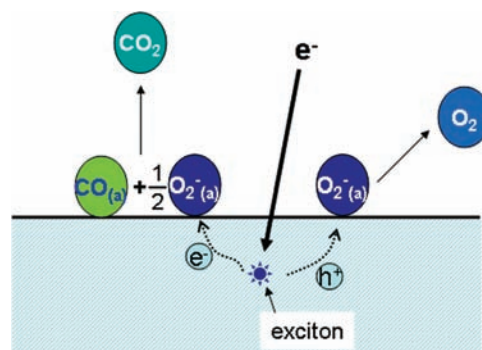


**Figure 4.** Schematic mechanism of $O_2$ desorption and CO oxidation on $TiO_2(110)$ during electronic excitation. Desorption of $O_2^-$ as $O_2(g)$ is induced by holes; Reaction of $O_2^-$ to produce $CO_2$ is induced by excited electrons created in the $TiO_2$.

In summary, the production of electrons and holes can be tuned using $Cl_2$ and $O_2$ as electron acceptors to cause upward band bending of the VB and CB of $TiO_2$. A surface oxidation process (involving adsorbed oxygen), which depends on the excitation of electrons in the bulk $TiO_2$, has been demonstrated, and it is shown that adsorbed acceptor molecules may be used as surface modifiers to modulate the rate of the oxidation process.

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