Charge transfer from TiO$_2$ into adsorbed benzene diazonium compounds

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Electron transfer from sol–gel–prepared TiO$_2$ into adsorbed benzene diazonium compounds has been investigated using cyclic voltammetry, x-ray photoelectron spectroscopy, contact potential difference, and surface photovoltage spectroscopy. The results show that the potential of maximum electron transfer depends strongly on the dipole moment of the benzene compound. Two reactive surface sites at which electron transfer occurs have been identified. © *2004 American Institute of Physics.* [DOI: 10.1063/1.1777801]

The covalent bonding of organic molecules to semiconductor surfaces is crucial for surface engineering, which has important applications in sensing and medicine.[1] Organic molecules can bond covalently to TiO$_2$ by forming –Ti–O–C≡ surface bonds.[2] Modification of TiO$_2$ surfaces due to covalent bonding of organic molecules has been applied, for example, to dye-sensitized solar cells.[3]

Electrochemical techniques generally allow well-controlled deposition of organic molecules in wet chemical solutions.[4,5] Electrochemical deposition of organic molecules from diazonium salt solutions is initiated by electron transfer from the semiconductor into the diazonium group. During this process, highly reactive organic radicals appear which bond at the semiconductor surface. Extending this approach to metal oxides, such as TiO$_2$, we have found a strong influence of the dipole moment of the benzene compound on the deposition potential. The dipole moments of the diazonium compounds were taken from calculations made by the density functional theory.[6]

Thin TiO$_2$ layers were prepared on Ti-coated glass substrates by a standard sol–gel process such that the formation of preferential surfaces was eliminated as measured by Raman spectroscopy (not shown). 4-bromo-, 4-nitro-, and 4-methoxy-benzenediazonium-tetrafluoroborate compounds (B*, N*, and M*, respectively) were electrochemically grafted at the TiO$_2$ surfaces. The contact potential difference (CPD) and surface photovoltage spectroscopy measurements have been performed using a system described elsewhere.[7]

Figure 1 shows typical cyclic voltammograms of TiO$_2$ in 5 mM diazonium salt solutions for B*, N*, and M*. The current increases significantly when electron transfer into the solution becomes possible. All cyclic voltammograms show a typical current peak between −0.7 V and −1.2 V during which organic layer is deposited. The peak absence during backscan shows that the molecules are stably adsorbed. The

potential of maximum current (U_{peak}) depends strongly on the diazonium salt. U_{peak} is −0.87 V, −0.95 V, and −1.04 V for N*, B*, and M*, respectively. Interestingly, the current shows a double peak where the second peak is smaller and shifted by about 60 mV independently of the organic compound (relating it to the TiO$_2$ substrate). This is discussed later.

X-ray photoelectron spectra were measured for the TiO$_2$ substrate with and without a deposited layer of B*. The results show that the Ti signal does not vanish completely after the deposition, which means that the deposited organic layer is extremely thin. A strong signal of Br appears after deposition, indicating a relative atomic concentration of about 10% versus 76% for carbon. This is in agreement with the ratio of 1:6 between Br and C in B*. We note that the N concentration increases from about 0.5% to only 2.8%, indi-
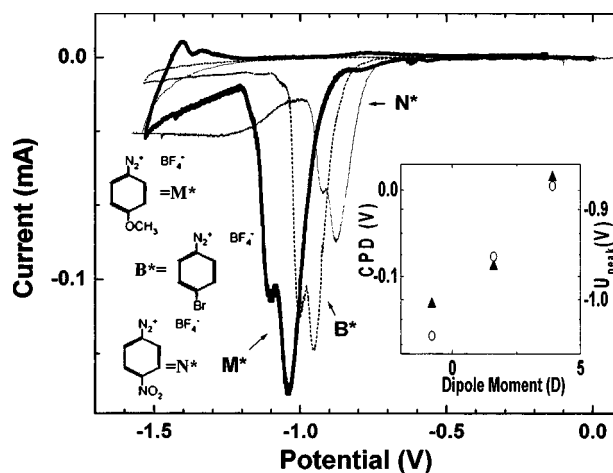

FIG. 1. Cyclic voltammetry of TiO$_2$ in a 5 mM solution of N*, B*, M* compounds in 0.01 M H$_2$SO$_4$. (The molecular structure is shown next to each compound abbreviation). Inset shows the potential of maximum current $-U_{peak}$ (circles) and the CPD (triangles) as a function of the dipole moment of the organic molecules.
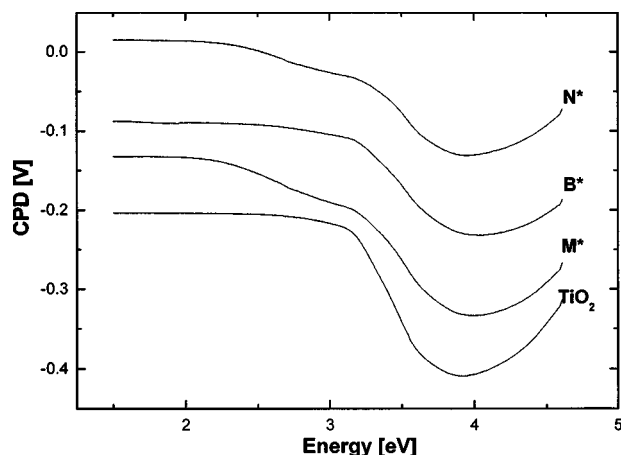
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FIG. 2. CPD spectra of the TiO$_2$ substrate before and after electrochemical grafting of B*, N*, and M*, respectively.

cating that N does not bond significantly at the TiO$_2$ surface after splitting from the diazonium compound due to electron transfer.

The inset in Fig. 1 shows U_{peak} and CPD as functions of the calculated value of the dipole moment of the various organic compounds. The strength of the dipole moment is -0.8, 1.6, and 3.9 Debye for M*, B*, and N*, respectively. The relation to the dipole moment is similar for both signals, indicating the formation of a well-oriented dipole layer at the TiO$_2$ surface. The dipole layer is responsible for limiting the electron transfer from the TiO$_2$ into the diazonium salt solution and it is stable after the electrolyte is removed.

Figure 2 shows CPD spectra of the TiO$_2$ substrate before (bottom curve) and after electrochemical deposition of M*, B*, and N*. The CPD of the clean surface is negative, indicating an *n*-type substrate. A negative CPD for all samples means that the basic electronic properties of the surface region do not change qualitatively by the electrochemical deposition. The significant decrease of the CPD starting at a photon energy of about 3.2 eV indicates the onset of band gap absorption in the TiO$_2$ substrate. This behavior is similar for all samples.

At photon energies below 3.2 eV, the CPD spectra of the various samples are different. A well pronounced shoulder starting at a photon energy of about 2.2 eV appears in the CPD spectra after electrochemical deposition of M* or N*. The shoulder is absent for the clean TiO$_2$ substrate and the B* deposited surface. This shoulder, indicating enhanced formation of the energy states within the band gap of TiO$_2$, correlates with the increase of the negative current at potentials U_{peak} for the electrochemical deposition of M* and N* (see Fig. 2). The latter is absent for B* (compare, for example, the currents for the different samples at -1.4 V).

The formation of gap states seems to be due to reduction of the TiO$_2$ surface.[8] This process may be induced by the

incorporation of hydrogen, which develops at higher negative potentials. However, the B*-coated TiO$_2$ surface is much better protected against hydrogen evolution and defect formation than the N*- or M*-coated TiO$_2$ surfaces. The reason for the improved protection is not understood yet but is apparently unrelated to the surface dipole.

The benzene compound binds to the TiO$_2$ surface by forming a $-$Ti$-$O$-$C bond. This is similar to the bonding of carboxylates to the TiO$_2$ surface.[9] The following idealized reaction scheme may be proposed for the electrochemical grafting of benzene compounds to TiO$_2$ surfaces in acidic solutions: Initially, an electron is transferred to a diazonium group (N$\equiv$N$-$) of the organic compound. As a result, a N$_2$ molecule leaves and a C$_6$H$_4-$X radical is formed (X is $-$Br, $-$OCH$_3$, or $-$NO$_2$ in our case). Next, the C$_6$H$_4-$X radical takes up a hydrogen atom from a $-$Ti$-$OH surface group, forming a $-$Ti$-$O radical. Finally, another C$_6$H$_4-$X radical bonds to the $-$Ti$-$O radical, forming a $-$Ti$-$O$-$C$_6$H$_6-$X surface complex.

The double peak structure of the deposition current corresponds to the presence of two different sites at the TiO$_2$ surface, from which electrons can be transferred into the benzene compound. Protonation of the TiO$_2$ surface in the acidic electrolyte seems to play an important role during electrodeposition. The *p*H of the electrolyte determines the ratio between the $-$Ti$-$OH and $-$Ti$-$O$^-$ surface group concentrations, via which charge transfer can occur. Usually, the $-$Ti$-$OH surface group dominates in acidic solutions. These two different adsorption sites may explain the double peak. However, more detailed investigations are needed to specify the microscopic mechanism of electron transfer during grafting of benzene compounds from diazonium salt solutions.

Electrochemical modification of TiO$_2$ surfaces by organic molecules has been demonstrated. The electrochemical approach demonstrated here may enable obtaining direct $-$Ti$-$O$-$C$\equiv$ bonding in a simple and well-controlled way from aqueous solutions. Electron transfer from TiO$_2$ into diazonium salt solutions is limited by the dipole moment of the benzene compound.

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