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Charge Transfer in Photocatalytic Systems: V and Mo Doped TiO_2/Ti Electrodes

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Abstract Charge transfer between the redox couples in solution and the electrodes obtained by surface doping of TiO_2 either by vanadium or by molybdenum have been investigated by electrochemical methods. In both cases the doping metal ions form at the electrode/solution interface surface states which are able to mediate the transfer of electrons between the conduction band of TiO_2 and the redox species in solution.

Keywords Charge transfer in photocatalysis · Titanium dioxide electrode · Vanadium-doped titanium dioxide · Molybdenum-doped titanium · Dioxide · Surface-state mediated charge transfer

1 Introduction

Oxidation of organic molecules at the surface of TiO_2 in photocatalytic processes may proceed either directly, by transfer of electrons from the organic molecules to the valence band holes generated in the process of photon absorption, or indirectly. In the latter case the active oxidants are oxygen-containing intermediates, generated either in the oxidation of water molecules by valence band holes or by reduction of molecular oxygen by conduction band electrons. Transfer of electrons between the electronic bands of a semiconductor and the redox couples in solution may proceed either by direct tunneling, tunneling via surface states (outer sphere mechanism) or via the inner-sphere mechanism (preceded by the adsorption of the molecules being oxidized at the TiO_2 surface). Conditions for direct electron transfer from the molecules in the solution to the valence band holes at the surface of titanium dioxide are rather unfavorable. Valence band edge of TiO_2 is situated at relatively low energy on the electronic energy scale, which places it at the high oxidation potential (approximately +3 V vs standard hydrogen electrode at the pH 0) [1].

Another problem in the application of TiO_2 in photocatalytic oxidation processes is the wide band gap of TiO_2, which causes that only small part of the solar energy may be transferred to the other forms of energy. A simple solution to that problem seems to be doping of TiO_2 by foreign metal atoms that may lead to the apparent narrowing of the band gap [2]. However the doping atoms create also the centers of recombination for the electron-hole pairs which lowers the quantum efficiency of the system. So, the influence of doping on the effectiveness of solar energy transformation by TiO_2 is complex and doping not always leads to the improvement [2, 3]. Foreign metal atoms in the crystal lattice of TiO_2, besides apparent narrowing the band gap, may influence the behavior of TiO_2 by forming surface states at the semiconductor/electrolyte interface. Those surface states can mediate the charge transfer between the redox couples in the solution and the electronic bands in the semiconductor which, in turns, can increase the effectiveness of TiO_2 photocatalyst in the reactions of organic molecule oxidation. That aspect of TiO_2 doping has been much less explored.

In photocatalytic applications TiO_2 is used usually in the form of a powder, either in suspension or deposited on a

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foreign substrate. An appealing alternative is the use of TiO_2 in the form of a thin layer on the surface of Ti metal, despite the fact that mainly rutile, less active crystalline form of TiO_2 is obtained when Ti metal is oxidized in air [4].

In our previous work [4] doping of TiO_2 (created at the surface of titanium sheet) by transition metal ions (V, Mo, Cr, Mn and Nb) was investigated in view of the possible application in photocatalytic oxidation of organic compounds. Samples were investigated by XPS, XRD, SEM and cyclic voltammetry methods. It has been found that TiO_2 samples doped with Cr and Mn were unstable versus anodic decomposition in aqueous solutions, so their applicability in the oxidation processes is questionable. On the other hand in doping vanadium and molybdenum become incorporated in surface of TiO_2 specimens with Mo or V atoms substituting Ti atoms in the surface layer of TiO_2 crystal lattice. The surface states created by doping TiO_2 with those metals were located in the band gap. Three surface states at the interface TiO_2/aqueous solution, located at 0.43, 0.74 and 1.1 eV below the conduction band edge of TiO_2 were found in the case of V-doped TiO_2. In the case of Mo-doped TiO_2 the exact location of the surface states on the electronic energy scale was impossible, because MoO_3 particles were always present at the Mo doped TiO_2 samples, besides the Mo atoms substituting Ti in the crystal lattice of TiO_2. However those surface states were evidently placed also below the conduction band edge of TiO_2.

In the present work the electrochemical oxidation of several organic compounds in either aqueous or non-aqueous solutions on V-doped and Mo-doped TiO_2/Ti electrodes was investigated to reveal the nature of the surface states created by doping and to find whether these surface states may effectively mediate the charge transfer processes at the TiO_2/solution interface in the oxidation of organic molecules. Note also, that the systems V_2O_5/TiO_2 and MoO_3/TiO_2 play a very important role in heterogeneous catalysis and any new information on the physical and chemical properties of these systems may be useful in elucidation of the mechanisms of heterogeneous catalytic processes.

2 Experimental

2.1 Materials

In view of the possible practical applications commercial Ti foil, used for fabrication of the electrodes in the industry was used as the substrate. TiO_2 layers were created on the surface of Ti foil either by anodic oxidation or by heating in air. Doping of TiO_2 layer was performed by sintering the TiO_2/Ti foil covered with either V_2O_5 or MoO_3. More information on the preparation procedure and properties of the samples may be found in our previous paper [4]. All chemicals used were of analytical reagent grade purity. Electrochemical measurements were performed either in aqueous or in non-aqueous solution. In the former case H_2SO_4 or Na_2SO_4 of the concentration 0.5 mol dm^{-3} or NaOH of the concentration 1 mol dm^{-3} were used as base electrolytes. In the latter case acetonitrile (Aldrich, 99.93% HPLC grade) was used as received. In some experiments acetonitrile additionally purified from the traces of water was used. The traces of water were removed from acetonitrile by twofold distillation with P_2O_5 and then twofold distillation with calcium hydride. In the case of acetonitrile solutions $(n\text{-}C_4H_9)_4NClO_4$, dried first at the temperature of 95 °C then kept in the desiccator over P_2O_5 was used as a base electrolyte.

2.2 Apparatuses and Procedures

Typical electrochemical cell in three-electrode configuration with investigated titanium foil covered by TiO_2 layer as a working electrode, saturated calomel electrode in alkaline to slightly acidic solutions or a mercury-mercurous sulfate/0.5 mol dm^{-3} sulfuric acid electrode in acidic solution as reference electrodes, and Pt foil as a counter electrode was used in electrochemical experiments. All potentials in this paper are quoted versus standard hydrogen electrode, assuming that saturated calomel electrode has the potential +0.242 V and mercury-mercurous sulfate electrode has the potential +0.682 V. In acetonitrile solutions aqueous saturated calomel electrode was also used as a reference electrode. This electrode was separated from the acetonitrile solution by a salt bridge filled with acetonitrile solution of the base electrolyte. All measurements were performed in the dark, in a constant temperature (25 °C) box, which served at the same time as a Faraday cage. Before experiments the solutions were bubbled with argon to remove dissolved oxygen. The behavior of the electrodes was investigated by cyclic voltammetry with the use of ECI 1286 digital potentiostat (Schlumberger-Solartron).

3 Results and Discussion

3.1 Behavior of Electrodes in Pure Base Electrolyte

Figure 1a and b present the comparison of the cyclic voltammetry curves obtained in aqueous and acetonitrile solutions containing only pure base electrolyte, for vanadium-doped and molybdenum-doped electrodes, respectively. In both cases dramatic differences in the shape and the current values between the voltammetric curves performed in aqueous and in acetonitrile solutions were observed. Similar differences were observed previously in the case of vanadium doped monocrystal rutile electrodes [5]. Evidently, in aqueous solution hydrogen ions participate in the redox transformations of both vanadium and molybdenum at the surface of TiO_2 as it was proposed earlier [4, 5]. The two more cathodic voltammetric waves observed on V-doped TiO_2/Ti electrode occured at the potentials close to the standard potentials of the reactions:

$$V_2O_5 + 2H^+ + 2e^- = V_2O_4 + H_2O \qquad (1)$$

$$V_2O_4 + 2H^+ + 2e^- = V_2O_3 + H_2O \qquad (2)$$

and may be correlated with the redox transformations of vanadium in the crystal lattice of TiO_2, with the simultaneous insertion/ejection of H^+ ions. The formation of transition metal oxide bronzes by electrochemical insertion of hydrogen or alkali metal cations to the crystal structure of transition metal oxides is well documented in the literature – see our previous papers [4, 5]. The only cation present in H_2SO_4 solution was hydrogen cation. No insertion of a cation was possible in the case of acetonitrile solution used in our work because tetrabuthylammonium cation is very spacious in comparison with simple inorganic cations and cannot enter the solid body lattice. The insertion of hydrogen into the lattice of metal oxides is a common phenomenon and plays an important role in catalysis [6]. Transport of hydrogen through thin layers of metal oxides (including TiO_2) accompanies the reaction of hydrogen evolution on some metals and was investigated by electrochemical methods [7]. The formation of hydrogen at the surface of particulate TiO_2 by reduction of adsorbed hydrogen ions by conduction band electrons excited during the adsorption of light has been investigated by Torimoto et al. [8]. It was established that hydrogen formed at the surface diffused spontaneously into the lattice of the oxide creating there Ti^{3+} donor centers. Those centers were located deeply below the surface of the oxide and were stable in time. However in the case of the experiments presented here the insertion of hydrogen into the TiO_2 crystal lattice occurred at the potential more anodic then the reversible potential of hydrogen evolution, which is approximately 0 V in the case of 0.5 mol dm^{-3} H_2SO_4 [1] (see Fig. 1). So, hydrogen entered the crystal lattice of TiO_2 rather as a hydrogen ion, not as a hydrogen atom.

In Fig. 2 cyclic voltammograms in acetonitrile solution for vanadium-doped, molybdenum-doped and undoped electrodes are compared. The current flowing in the case of doped electrodes was at least one order of magnitude higher than in the case of the undoped ones, despite the fact that no reactant was present in the solution. The charge confined within the voltammogram was very high, at least an order of magnitudes higher than may be expected for the process of charging-discharging of the space charge layer even in the case of a semiconductor with very high density of free charge carriers. That charge may be undoubtedly ascribed to the charging/discharging the surface states created by doping metal in the band gap of semiconducting TiO_2. The differential capacitance of the electrode estimated from the formula: $C = \Delta j/2\upsilon$ (υ—potential sweep rate, for the meaning of the Δj see Fig. 2) was of the order of 300 $\mu F\ cm^{-2}$, i.e. in the range expected for very rough metal electrodes, not for semiconductor electrodes.

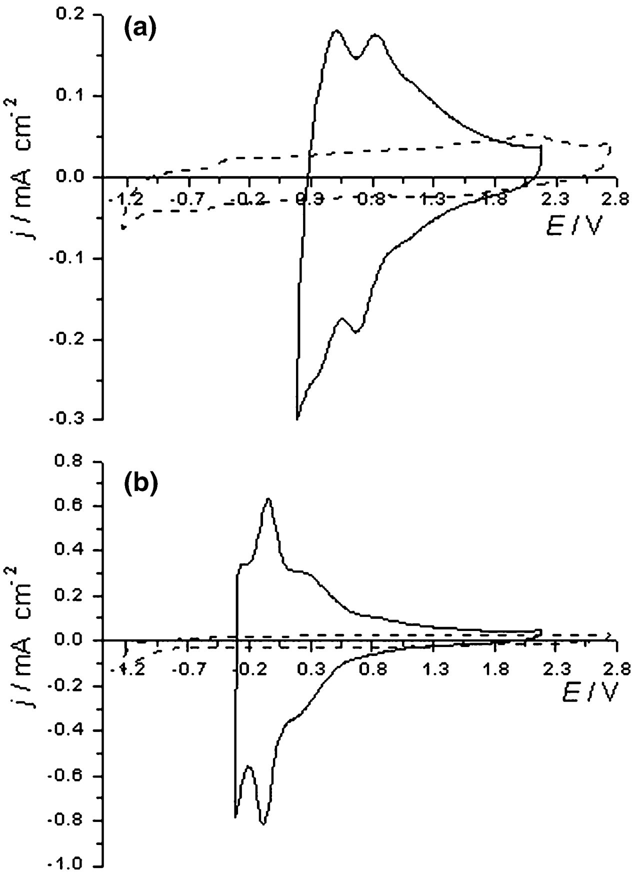


Fig. 1 The cyclic voltammetry of V_2O_5/TiO_2/Ti (**a**) and MoO_3/TiO_2/Ti (**b**) electrodes in 0.5 mol dm^{-3} aqueous H_2SO_4 solution (full line) and 0.1 mol dm^{-3} tetrabuthylammonium perchlorate solution in acetonitrile (dashed line). Potential sweep rate 50 mV/s. Before cycling in acetonitrile solution electrodes were heated during 8 hours at the temperature of 573 K in flowing air to remove adsorbed and chemisorbed water

3.2 Electron Exchange with the Redox Couples in Solution. Aqueous Solutions

The undoped TiO_2/Ti electrodes did not show any activity in anodic oxidation reactions at moderate overpotentials, in

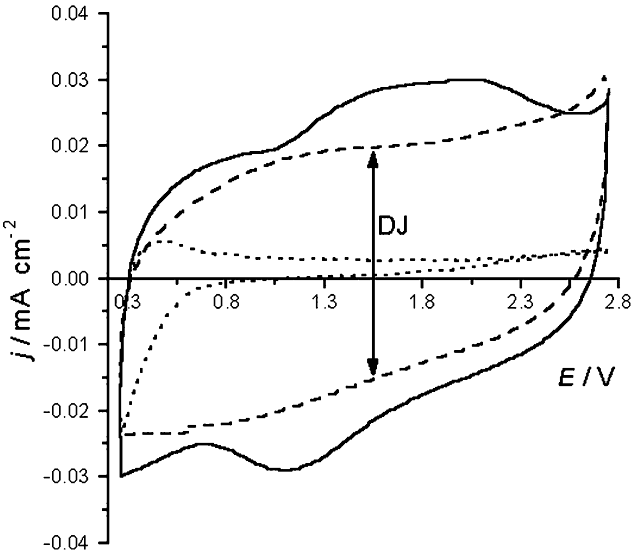


Fig. 2 The comparison of voltammograms performed on $V_2O_5/TiO_2/Ti$ (full line), $MoO_3/TiO_2/Ti$ (dashed line) and undoped TiO_2/Ti (dotted line) electrodes in 0.1 mol dm^{-3} tetrabuthylammonium perchlorate solution in acetonitrile. Potential sweep rate 50 mV/s. Before cycling in acetonitrile solution electrodes were heated during 8 hours at the temperature of 573 K in flowing air to remove adsorbed and chemisorbed water. In the case of TiO_2/Ti electrode the current was multiplied by the factor of 10 for the sake of clarity

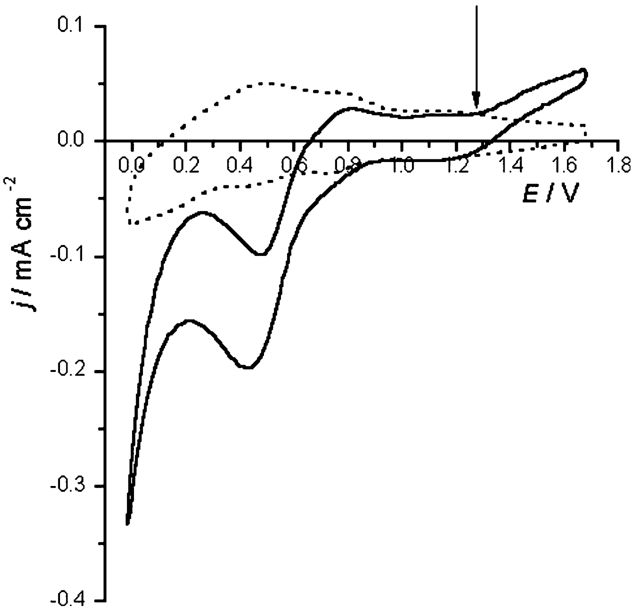


Fig. 3 Cyclic voltammetry of hydrogen peroxide (0.01 mol dm^{-3}) on $V_2O_5/TiO_2/Ti$ electrode in 0.5 mol dm^{-3} aqueous H_2SO_4 solution (full line). Potential sweep rate 20 mV/s. Dashed line 6 voltammogram in pure base electrolyte. Arrow shows the potential where the reaction of H_2O_2 oxidation starts at the Pt electrode

accordance with the literature [1]. Doping the surface of the electrode with either vanadium or molybdenum changed the situation dramatically. In the case of cyclic voltammetry of $K_3Fe(CN)_6$ on $V_2O_5/TiO_2/Ti$ and $MoO_3/TiO_2/Ti$ electrodes in the 0.5 mol dm^{-3} aqueous Na_2SO_4 (pH = 4) solution well developed voltammetric maxima in the reaction of the reduction of $Fe(CN)_6{}^{3-}$ ion as well as in the reaction of the re-oxidation of the obtained reaction product ($Fe(CN)_6^{4-}$ ion) gave the evidence that the electron exchange between the electrode and the solution is fast enough to make the reaction diffusion-limited. Similar behavior was observed in the reaction of the reduction of $I_3{}^-$ ion and subsequent oxidation of produced I^- ion. However no activity of either vanadium or molybdenum doped electrodes in the oxidation of simple aliphatic compounds like: methanol, formaldehyde, formic acid or oxalic acid in aqueous solutions has been noted. We paid most attention to the studies of oxalic acid. That substance may be oxidized easily and quantitatively by many oxidants in homogeneous oxidation reactions. It oxidizes also easily on metal electrodes (though poisoning of gold electrode by the products of reaction was observed [9]) but no oxidation currents of oxalic acid in the wide range of pH, concentration and overpotential have been observed in the case of either vanadium or molybdenum doped TiO_2/Ti electrodes. Apparently, oxalic acid molecules are not adsorbed on TiO_2 surface pure or doped with vanadium or molybdenum.

Hydrogen peroxide may be oxidized on $V_2O_5/TiO_2/Ti$ electrode (but not on the TiO_2/Ti electrode nor on the $MoO_3/TiO_2/Ti$ electrode), and the oxidation started at some 0.6 V above the thermodynamic potential of H_2O_2 oxidation, but close to the potential at which the oxidation of H_2O_2 on Pt electrode started (Fig. 3). In the case of molybdenum doped electrode the reduction of H_2O_2 occurred in the same potential range as in the case of undoped one, which means that molybdenum does not exert any catalytic effect in that reaction. In the case of vanadium-doped electrode significant current of H_2O_2 reduction started to flow in the potential range where the redox transformations of vanadium occurred (Fig. 3).

Anodic oxidation of phenol in 1 mol dm^{-3} NaOH solution was observed, but the phenol oxidation current started to flow just before the onset of the reaction of oxygen evolution, so at relatively high overpotential.

High activity was observed both in the case of hydroquinone as well as catechol oxidation on vanadium and molybdenum doped TiO_2 electrodes (Fig. 4).

The positions of the surface states created by vanadium at the interface TiO_2/aqueous solution on the electronic energy scale, observed in this work are completely different from the positions of the impurity states created by vanadium in the bulk of TiO_2 as reported by Mizushima et al. [10]. It may be ascribed to the participation of the hydrogen ion in the reaction of charging/discharging of these surface states (reactions (1) and (2)). According to Mizushima et al. [10] the position of the V^{4+} impurity state

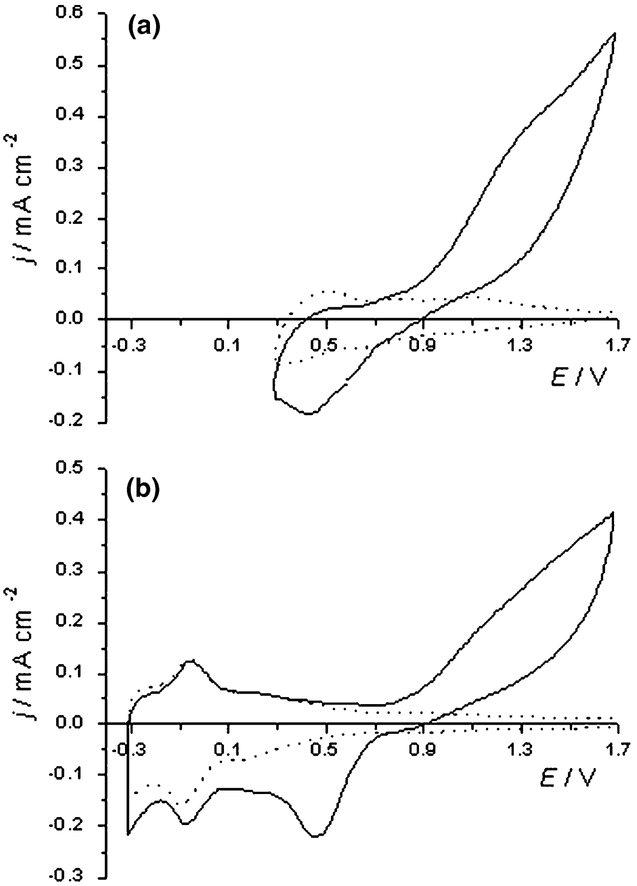


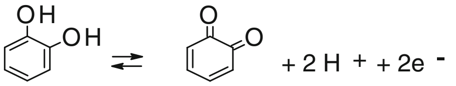
Fig. 4 Cyclic voltammetry of catechol (0.01 mol dm^{-3}) in 0.5 mol dm^{-3} aqueous H_2SO_4 solution on $V_2O_5/TiO_2/Ti$ (**a**) and on $MoO_3/TiO_2/Ti$ (**b**) electrodes. Potential sweep rate 10 mV/s. Dashed lines 6 voltammograms in pure base electrolyte

in the rutile crystal lattice on the energy scale is about 1.8 eV below CBE and that of V^{3+} state about 0.8 eV below CBE. The position of the redox transformation V^{5+}/V^{4+}, which may be identified with the position of V^{4+} state at the TiO_2/aqueous solution interface has been found at the potential of +0.74 V and those of V^{4+}/V^{3+}, which may be identified with the V^{3+} state, at the potential of +0.43 in 0.5 mol dm^{-3} H_2SO_4 solution. In that solution CBE of TiO_2 is located at approximately 0 V [1], so the above mentioned energy levels are situated at 0.74 V (V^{4+}) and 0.43 V (V^{3+}) below CBE. The same situation probably occurs in the case of molybdenum, but no data on the position of molybdenum impurity states in TiO_2 lattice are available in the literature. The difference between the positions of impurity levels created by vanadium (and possibly other transition metals) in the bulk of TiO_2 and at the TiO_2/aqueous electrolyte interface has never been reported in the literature. When discussing the photocatalytic processes at the interface: transition metal ion doped TiO_2/aqueous solution, not the positions of the impurity states, established by Mizushima [10] for bulk doped TiO_2 [2, 11] should be used, but those determined for the interface doped TiO_2/aqueous solution.

3.3 Electron Exchange with the Redox Couples in the Solution. Acetonitrile Solutions

Catechol may be oxidized in acetonitrile solution on both $V_2O_5/TiO_2/Ti$ and $MoO_3/TiO_2/Ti$ electrodes but no reaction of the reduction of the oxidation product formed (o-quinone) could have been seen, because the latter reaction requires participation of hydrogen ions:

However, when 5% of water was added to acetonitrile the reaction proceeded in both directions.



(3)

Similarly like in the case of aqueous solutions neither methanol nor oxalic acid can have been oxidized anodically on either $V_2O_5/TiO_2/Ti$ or $MoO_3/TiO_2/Ti$ electrodes in acetonitrile solution. No oxidation has also been observed in the case of oxalic acid in methanol solution. However many aromatic compounds including hydrocarbons (naphthalene, antracene), phenols (phenol and 2,6-ditertbuthyl-p-cresol), diphenols (catechol and 4-tertbuthylcatechol) could have been easily oxidized on the $V_2O_5/TiO_2/Ti$ electrode in acetonitrile solution. The reaction of the oxidation of naphthalene and catechol proceeded on $MoO_3/TiO_2/Ti$ electrode too. Figure 5 presents the comparison of the voltammograms performed on Pt, $V_2O_5/TiO_2/Ti$ and $MoO_3/TiO_2/Ti$ electrodes in acetonitrile solution containing 0.01 mol dm^{-3} naphtalene. The oxidation reaction on the $V_2O_5/TiO_2/Ti$ electrode starts at approximately the same potential as on the Pt electrode. On $MoO_3/TiO_2/Ti$ electrode the reaction starts at slightly higher overpotential.

4 Conclusions

Both in the case of vanadium doped as well as molybdenum doped TiO_2/Ti electrodes the doping metal ions form at the electrode/solution interface the surface states which are able to mediate the transfer of electrons between the conduction band of semiconductor TiO_2 and the redox species in solution. However the nature of those surface states is different at the TiO_2/aqueous solution interface from those created at the TiO_2/non aqueous solution interface. In the case of aqueous solutions the capture of an electron by the surface state is accompanied by the insertion of the hydrogen ion from the solution to the crystal lattice of TiO_2. Due to this fact the surface states created by

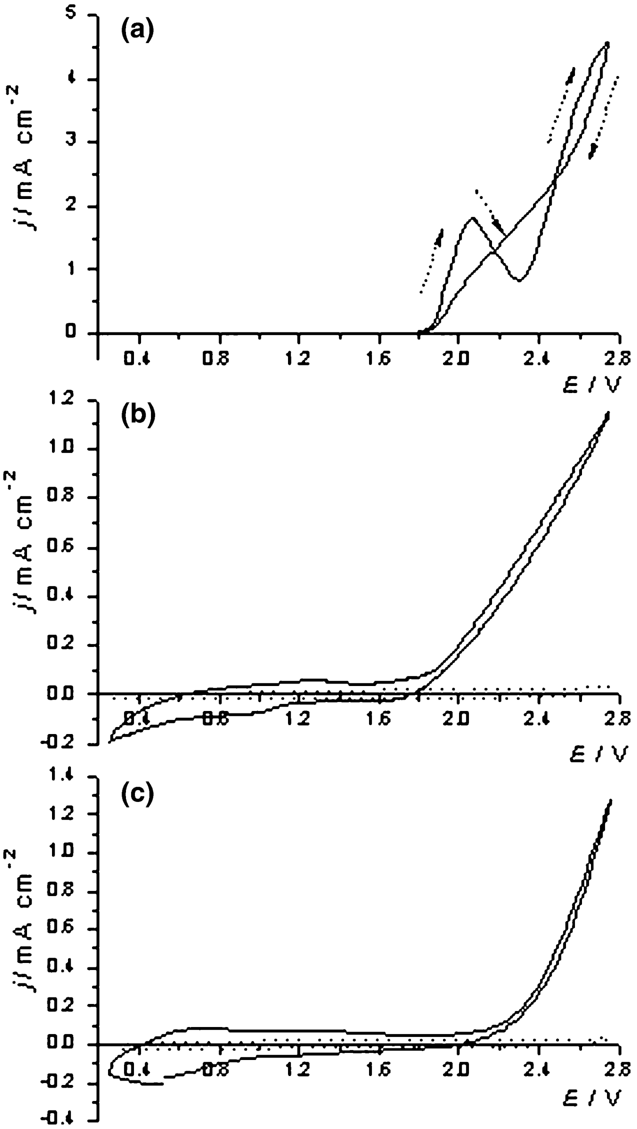


Fig.5 Cyclic voltammetry of naphthalene (0.01 mol dm^{-3}) in 0.1 mol dm^{-3} tetrabuthylammonium perchlorate solution in acetonitrile on Pt (**a**), $V_2O_5/TiO_2/Ti$ (**b**) and $MoO_3/TiO_2/Ti$ (**c**) electrodes. Potential sweep rate 50 mV/s. Dashed lines 6 voltammograms in pure base electrolyte

vanadium at the TiO_2/aqueous solution interface are placed at the energy different from those established for the case of bulk doping of TiO_2 by vanadium and investigated in vacuum. The results of the experiments suggest that hydrogen enters the crystal lattice of TiO_2 as a hydrogen ion, not as a hydrogen atom, and is reduced later on in the vicinity of doping metal ion.

No information on the energy of the impurity states created by molybdenum in the band gap of TiO_2 is available in the literature but the situation in the case of molybdenum is probably the same.

In both cases the density of either vanadium or molybdenum surface states was very high and the Fermi level pinning at the potential of respective surface states evidently occurred.

No activity in the oxidation of simple aliphatic organic compounds was observed in either the $V_2O_5/TiO_2/Ti$ or $MoO_3/TiO_2/Ti$ electrodes, however many aromatic compounds were effectively oxidized on both electrodes in either aqueous or non-aqueous (acetonitrile) solutions. That is probably connected to the fact that aromatic compounds are oxidized by outer-sphere charge transfer mechanism which can operate only when the proper matching of energy levels in the crystal lattice and in the solution occurs. In the case of simple aliphatic compounds the oxidation reaction proceeds according to the inner-sphere charge transfer mechanism that should be independent on the position of energy bands in the solid body but should strongly depend on adsorption of substrates/intermediates of reaction at the surface. Evidently no new adsorption centers facilitating the adsorption of organic compounds are formed as a result of doping.

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