Photoelectrochemical properties of sol–gel obtained titanium oxide

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Abstract: The photoelectrochemical properties of a sol–gel prepared titanium oxide coating applied onto a Ti substrate were investigated. The oxide coating was formed from an inorganic sol thermally treated in air at 350 °C. The coating consisted of agglomerates of narrow size distribution around 100 nm. The photoelectrochemical characteristics were evaluated by investigating the changes in the open circuit potential, current transients and impedance characteristics of a Ti/TiO$_2$ electrode upon illumination by UV light in H$_2$SO$_4$ solution and in the oxidation of benzyl alcohol. The electrode was found to be active for photoelectrochemical reactions in the investigated solutions.

Keywords: photoelectrochemical activity; titanium oxide; oxide sol; sol–gel procedure; electrochemical impedance spectroscopy.

INTRODUCTION

Owing to its good chemical stability, physico–chemical characteristics, electrical and optical properties, titanium oxide is a widespread material investigated in many fields of fundamental and applied science. The anatase crystalline form is known for its photocatalytic properties upon UV illumination, while the rutile form is most famous as a white pigment in dye technology.[1] In organic reactions, TiO$_2$ is widely used as a photocatalyst in an aqueous (waste water treatment)[2] as well as in a non-aqueous environment (organic synthesis).[3–5] Additionally, it can be used as a carrier for highly dispersed heteropolyacids,[6] electrochemical composite catalysts[7] and as a stabilizing component of electrochemically active oxide coatings on titanium.[8–10] The application of titanium oxide thus envelopes different branches, from the white pigment industry, through sunscreen lotions, so-
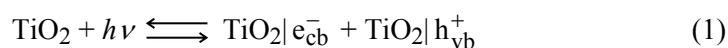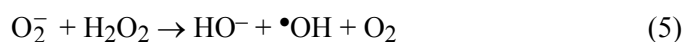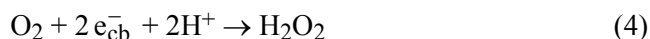
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lar cells and toothpastes, to electrochemistry, random access memory, outdoor air purification and waste water treatments.[11]

The photoreactivity of titanium oxide for oxidation reactions is usually explained by the excitation of valence band (vb) electrons.[1] When TiO_2 is illuminated by light of energy greater than that required by the band gap, electrons are transferred to the conduction band (cb), and positive holes (h^+) remain in the vb. The charge carriers very quickly migrate to surface traps lying within the forbidden gap. From there, the holes are populated by electrons from, *e.g.*, organics (R) adsorbed at the surface of the illuminated TiO_2:[12,13]

$$TiO_2 + h\nu \rightleftharpoons TiO_2|\,e^-_{cb} + TiO_2|\,h^+_{vb} \tag{1}$$

$$TiO_2|\,h^+_{vb} + R \rightarrow TiO_2 + R^\bullet \tag{2}$$

In aqueous solutions, the generated holes can also react with adsorbed water molecules or OH^- to produce $^\bullet OH$ radicals, which are able to react with the organics in parallel to reaction (2).[12]

Reversibility by the electron–hole recombination step (Eq. (1)) decreases the reactivity of illuminated TiO_2. This disadvantage can be suppressed if some sink of excited electrons would be available in the system. For example, in oxygen-containing solutions, the excited electrons can reduce O_2 and generate an avalanche of free radicals:[13]

$$e^-_{cb} + O_2 \rightarrow O^-_2 \tag{3}$$

$$O_2 + 2\,e^-_{cb} + 2H^+ \rightarrow H_2O_2 \tag{4}$$

$$O^-_2 + H_2O_2 \rightarrow HO^- + {}^\bullet OH + O_2 \tag{5}$$

$$O^-_2 + 2H^+ \rightarrow 2^\bullet OH \tag{6}$$

$$H_2O_2 + e^-_{cb} \rightarrow {}^\bullet OH + OH^- \tag{7}$$

$$H_2O_2 + h\nu \rightarrow 2^\bullet OH \tag{8}$$

However, if titanium oxide would be assembled to conducting materials within a closed electrical circuit, the reactivity can be improved by a bias potential, which will drive away exited electrons to the external circuit of the photoelectrochemical (PEC) cell.[14–16]

The PEC activity of TiO_2 towards numerous organics, from methanol[17] to herbicides,[18] has been investigated intensively.[1,13,16,19,20] It was found that PEC reactivity depends strongly on the conditions of formation of TiO_2, such as preparation procedure,[21,22] precursor type,[18] annealing temperature,[19,23] but also on the possible implantation of electrochemically active metals, such as Pt.[24] Titanium oxides prepared by different procedures can show different PEC activity, although their crystalline structures are quite similar.[22] Generally, a mixture of

anatase and rutile crystalline forms is more active than these forms alone,[19,22] although in the case of commercial Degussa P25 TiO$_2$, increasing the rutile content (higher annealing temperature) can lead to a considerable decrease in, *e.g.*, the total organic carbon removal efficiency in phenol oxidation.[19]

The aim of this work was to investigate the PEC activity of TiO$_2$ prepared *via* the sol–gel route employing forced hydrolysis of titanium chloride.[25] Titanium oxide prepared by this procedure already showed some advantages for chlorine and oxygen evolution and phenol oxidation[26] on activated titanium anodes.[10,27] The PEC activity was investigated in H$_2$SO$_4$ solution and for the oxidation of benzyl alcohol, which is known for its simple oxidation kinetics.

EXPERIMENTAL

The synthesis of the oxide sol

Titanium oxide sol was prepared by the forced hydrolysis of titanium chloride (15 % TiCl$_3$ in 10 % HCl, Merck) in acid solution.[25] An appropriate amount of titanium chloride was slowly added into boiling 5.0 mol dm^{-3} HCl and aged for 24 h under reflux in an experimental setup equipped with a magnetic stirrer. Vigorous agitation at the boiling temperature results in slow hydrolysis, which results in a solid oxide phase of narrow particle size distribution.[27,28] The size of oxide particles increases with ageing time, while the TiO$_2$ sols aged more than 20 h were found to be beneficial for good electrochemical properties of binary RuO$_2$–TiO$_2$ coatings of activated titanium anodes.[10,27]

The concentration of the solid phase in the prepared oxide colloidal monodispersion, evaluated by evaporation to dryness at 120 °C for 24 h, was 17 mg cm^{-3}.

Preparation of the photoelectrode

The photoelectrochemical properties of the prepared titanium oxide were examined using an electrode assembly consisting of a titanium substrate coated with the prepared oxide sol. A Ti plate, 1 cm×1 cm×0.7 cm in size, etched in 1:1 v/v hot 35 % HCl:H$_2$O mixture, was used as the substrate. The coating was prepared by painting the oxide sol over the substrate, which was followed by slow evaporation at 70–90 °C. The painting and evaporation steps were repeated until a coating mass of 3 mg per cm^2 of the geometric surface area was attained. The electrode was then subjected to the thermal treatment at 350 °C for 2 h.

The coating was characterized by atomic force microscopy (AFM) technique in air at room temperature. The structural characterization was performed with a NanoScope 3D (Veeco, USA) microscope. The AFM observations were performed in tapping mode using etched silicon probes with a spring constant 20–80 N m^{-1}.

Photoelectrochemical (PEC) characterization

The PEC properties of the prepared Ti/TiO$_2$ electrode and its photovoltaic activity in the oxidation of benzyl alcohol (BA), 0.010 mol dm^{-3}, were investigated in 1.0 mol dm^{-3} H$_2$SO$_4$. Chronopotentiometric, chronoamperometric and electrochemical impedance spectroscopy (EIS) measurements were performed in a standard electrochemical cell equipped with a Pt wire as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode. All experiments were performed at room temperature.

The photoelectrode working area of 0.79 cm^2 faced the electrolyte/air interface at a distance of 5 mm and was illuminated directly in the PEC experiments from above using a UV lamp ($\lambda = 356$ nm, 2×8 W, DESAGA UVIS, Germany) placed about 5 cm away from the electrode surface.

RESULTS AND DISCUSSION

The typical appearance of the TiO$_2$ coating surface is illustrated in Fig. 1 by AFM images taken at two different magnifications. The spherical grains of a uniform size of around 100 nm are continuously distributed all over the coating surface. Earlier X-ray diffraction investigations of the solid phase of prepared sol[25] indicated the oxide amorphous structure, while anatase crystalline structure was formed by thermal treatments up to 450 °C, with only a negligible presence of the rutile phase at higher temperatures. The crystallite size, according to the Scherrer Equation, was about 8 nm. The examination by transmission electron
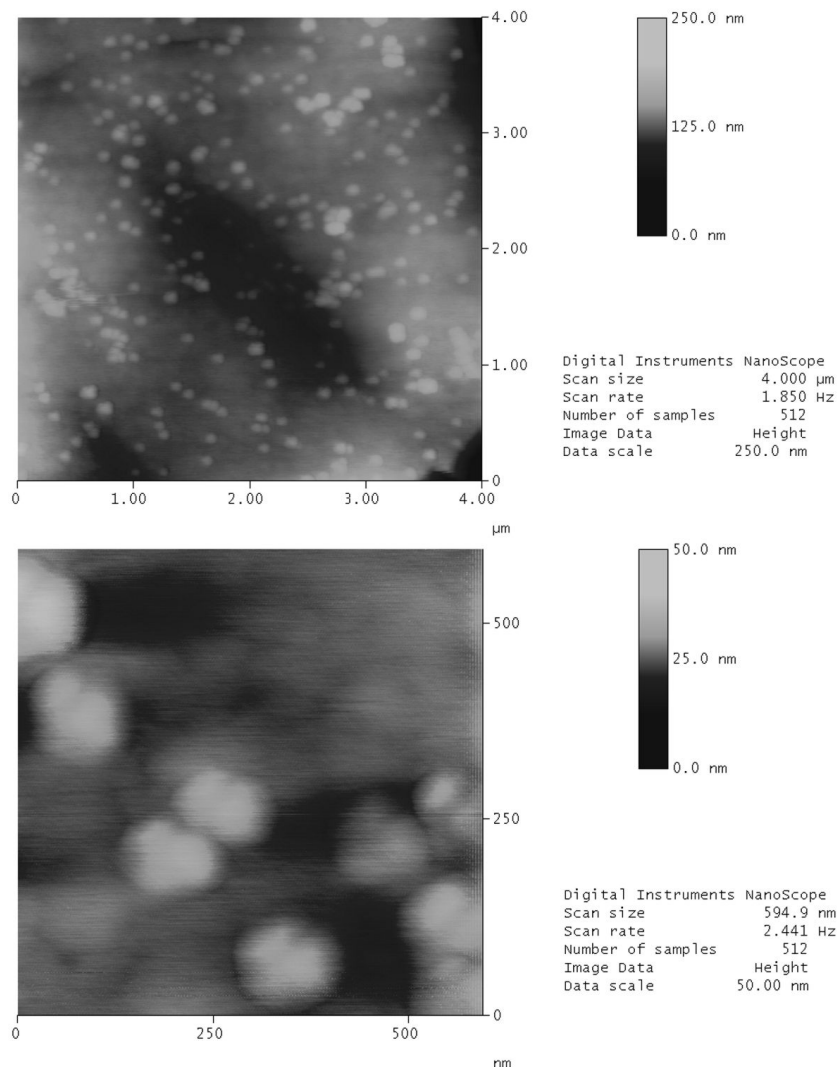

Fig. 1. Typical AFM images of the Ti/TiO$_2$ electrode surface.

microscopy showed the presence of the 5–25 nm particles, depending on the ageing time.[27] According to these earlier results, it can be emphasized that the grains seen by AFM (Fig. 1) must be agglomerates of small crystallites. The structural AFM investigations indicate that the ageing of the oxide sol under the applied conditions of sol synthesis rather results in the sticking of the formed nanoparticles into large agglomerates than in their primary growth, as is to be expected in the forced hydrolysis process.[27,28]

Photoelectrochemical properties

The influence of UV light on the value of the open circuit potential (OCP) of Ti/TiO$_2$ electrode in H$_2$SO$_4$ solution is illustrated in Fig. 2. Illumination with UV light caused the OCP to take the negative values with respect to those registered under "UV off" condition. The OCP always shifted cathodically since the number of electrons occupying the conduction band was increased by those excited by photons. The photon–electron interaction process appears to be not completely reversible since the preceding "UV off" OCP value can be hardly recovered after illumination. This also holds for the "UV on" OCP value, which shifts anodically with every subsequent UV on/off period. Consequently, the difference between the "UV off" and "UV on" OCP value decreases with the number of UV on/off periods, which indicates a decreasing ability of the photons to excite the electrons.
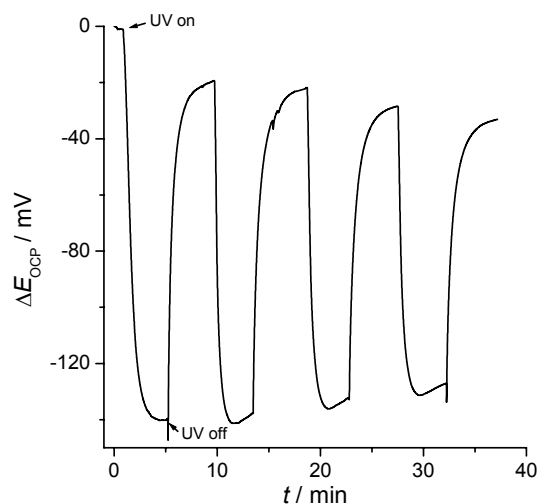

Fig. 2. The time dependence of the open circuit potential of Ti/TiO$_2$ electrode in presence and the absence of UV light. Electrolyte: 1.0 mol dm^{-3} H$_2$SO$_4$.

The Nyquist and Bode plots of EIS data registered at the "UV off" and "UV on" OCP of the Ti/TiO$_2$ electrode in H$_2$SO$_4$ solution are shown in Fig. 3. In the absence and the presence of UV light, loops ascribable to capacitor and resistor in parallel were registered (Fig. 3a). However, the impedance under UV illumination was considerably lower, as the consequence of increased conductivity due to the presence of photon-exited electrons in the conduction band.
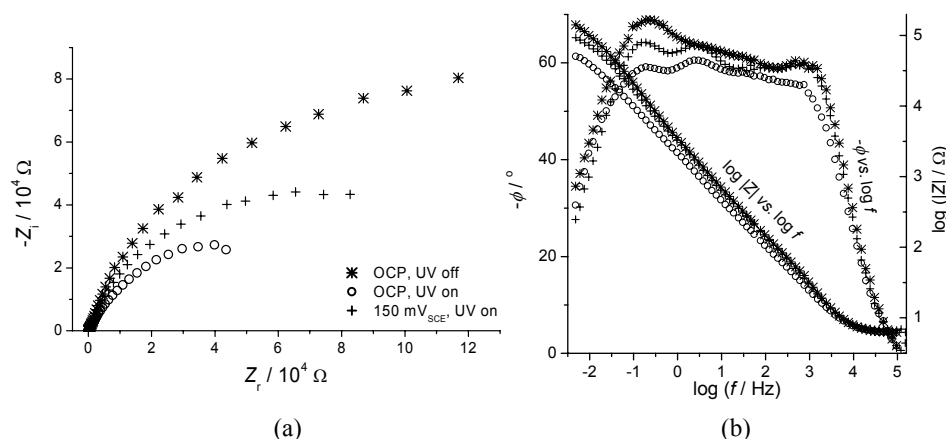
Fig. 3. Nyquist (a) and Bode plots (b) of EIS data of Ti/TiO$_2$ electrode registered at the "UV off" and "UV on" OCP and at 150 mV$_{SCE}$ (UV on) in 1.0 mol dm^{-3} H$_2$SO$_4$.

Although the impedance data generally form a loop in the complex plane plot (Fig. 3a), its fine structure, which depends on whether the UV light was on or off, is clearly resolved in the Bode phase angle plot (Fig. 3b). In the absence of UV light, two well-resolved phase angle maxima are registered at 1 kHz and 200 mHz, both related to the equivalence of a capacitor and resistor in parallel, which indicates that the loop in Fig. 3a is actually comprised of overlapping loops. On the other hand, in the presence of UV light, these maxima were suppressed, while a new, more intense, maximum appeared at around 3 Hz.

In order to resolve which part of the registered impedance characteristics are intrinsic to the presence of UV light, EIS data were registered at a potential of 150 mV$_{SCE}$, which is close to "UV off" OCP value, but in the presence of the UV light. These data are also shown in Fig. 3. As can be seen in Fig. 3b, the EIS characteristics at 150 mV$_{SCE}$ are insensitive to UV down to a frequency of 100 Hz. A new maximum is seen at 3 Hz as in the case of the EIS data at the "UV on" OCP value, while the phase angle peak at 200 mHz is less suppressed. This comparison indicates that the phase angle peak at 3 Hz was completely UV light-induced. On the other hand, the peaks at 1 kHz and 200 mHz, being dependent on electrode potential, are electrochemical in nature.

The photovoltaic contribution to the current transients of the Ti/TiO$_2$ electrode in H$_2$SO$_4$ solution can be seen in Fig. 4. The photoelectrochemical activity was controlled at potentials close to the "UV on" (55 mV$_{SCE}$) and "UV off" OCP (150mV$_{SCE}$). The illumination by UV light caused an increase in the currents due to a positive photocurrent contribution. The photocurrent was stable during several UV on/off periods and depended neither on the bias potential nor on the sign of the UV light-absent current. Since oxidation of water is the only possible anodic process in the given electrolyte, the relatively small photocurrents visible

in Fig. 4 can be ascribed to photocatalytic oxygen evolution. The absolute photo-voltaic effect is rather small, which can be the consequence of the stringent kinetic demands for the oxygen evolution reaction.
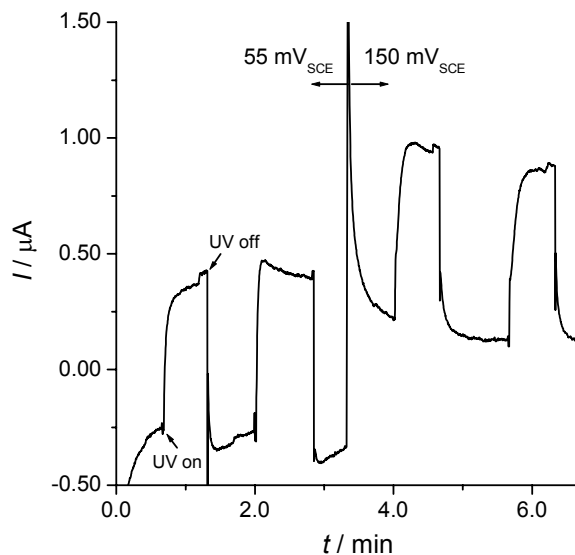

Fig. 4. The current transients of the Ti/TiO$_2$ electrode at the potentials of 55 and 150 mV$_{SCE}$ in the presence and the absence of UV light. Electrolyte: 1.0 mol dm^{-3} H$_2$SO$_4$.

Photoelectrochemical activity for benzyl alcohol oxidation

The change of the OCP of the Ti/TiO$_2$ electrode, induced by UV light in the presence of BA in the electrolyte, is shown in Fig. 5. The OCP values shifted cathodically, as in the case of the BA-free electrolyte (Fig. 2), but in the presence of BA the shift was considerably more pronounced. The OCP can become even
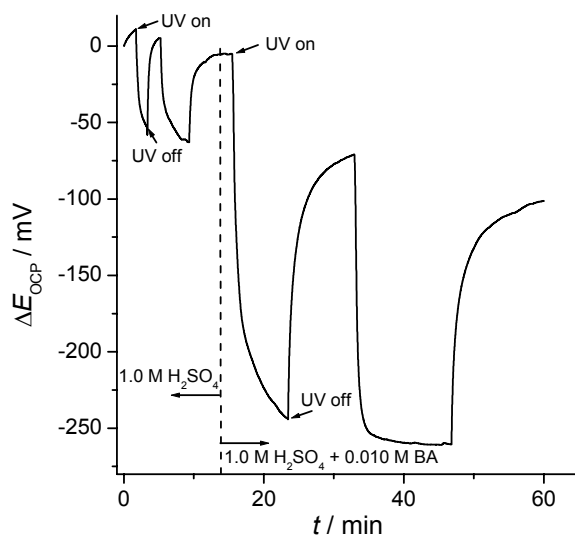

Fig. 5. The time dependence of the open circuit potential of the Ti/TiO$_2$ electrode in presence and the absence of UV light. Electrolyte: 1.0 mol dm^{-3} H$_2$SO$_4$ + 0.010 mol dm^{-3} BA.

250 mV more negative with respect to the "UV off" value. It should be stressed that the "UV off" OCP value did not change upon addition of BA.

Although the "UV off" OCP value can be hardly recovered after the very first UV light switch, as in the case of the BA-free electrolyte, the "UV on" value in the BA-containing electrolyte appeared to be stable and independent of the number of UV on/off periods.

The photoelectrochemical activity of the Ti/TiO$_2$ electrode considerably increased in the presence of BA; the photocurrent was double that of the BA-free electrolyte, as is shown in Fig. 6 by current transient at a potential close to the "UV off" OCP value.
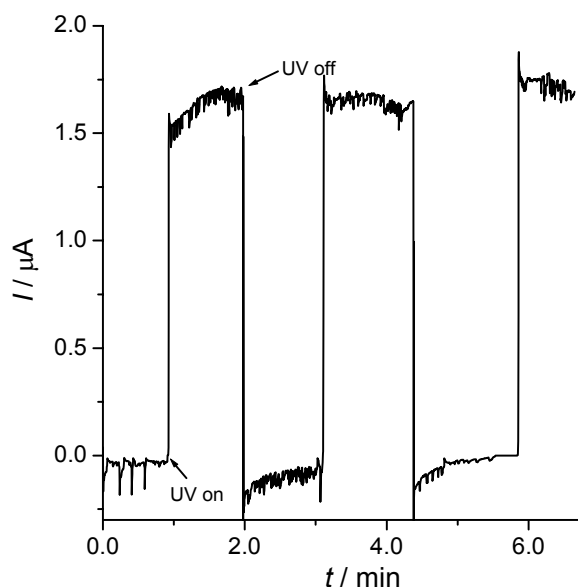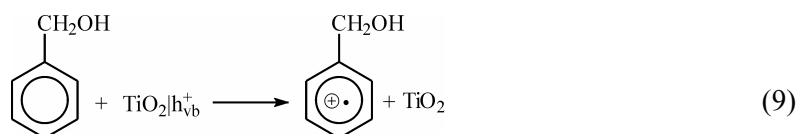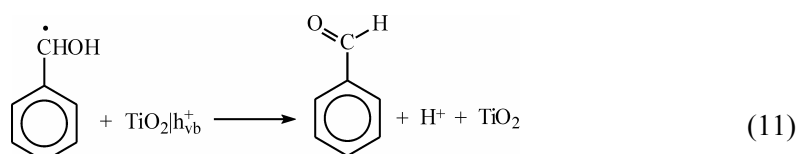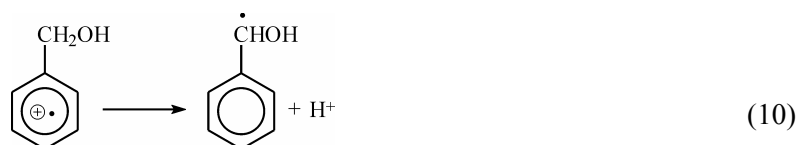

Fig. 6. Current transients of the Ti/TiO$_2$ electrode in the presence and the absence of UV light. Electrolyte: 1.0 mol dm^{-3} H$_2$SO$_4$ + + 0.010 mol dm^{-3} BA.

The considerably larger cathodic shift of the OCP (Fig. 5) and the increased photocurrent (Fig. 6) in the presence of BA indicate that BA is more easily oxidized at TiO$_2$ than water molecules (BA-free electrolyte) because the holes in the TiO$_2$ generated by the excitation of electrons are easily populated by electrons from the BA molecules. BA oxidation to benzenecarbaldehyde proceeds through the benzyl radical as an intermediate and a tentative mechanism of PEC oxidation could be as follows:

$$\qquad\qquad\qquad\qquad (9)$$

$$\overset{\bullet}{CH_2OH} \longrightarrow \overset{\bullet}{CHOH} + H^+ \qquad (10)$$

$$\overset{\bullet}{CHOH} + TiO_2|h_{vb}^+ \longrightarrow \overset{O}{\underset{}{C}}\overset{H}{} + H^+ + TiO_2 \qquad (11)$$

The protons released from the benzyl radical-cation (Eqs. (10) and (11)) are easily adopted by O_2^- (Eq. (6)) generated in the reaction between the exited electrons and oxygen (Eq. (3)).

The Nyquist and Bode plots for the Ti/TiO$_2$ electrode registered at the OCP in the BA-containing electrolyte, in the presence and the absence of UV light, are shown in Fig. 7.

As in the BA-free electrolyte (Fig. 3a), loops were registered in the presence and the absence of UV light, although the impedance is considerably lower than in the BA-free electrolyte (Fig. 7a). The influence of UV light is not so pronounced; only a decrease in the imaginary value can be seen in the low-frequency domain. Two phase angle maxima are registered (Fig. 7b) with no appearance of a UV light-induced third one, as was registered in the BA-free electrolyte (Fig. 3b). However, the low-frequency phase angle peak is considerably more pronounced in the presence of BA.
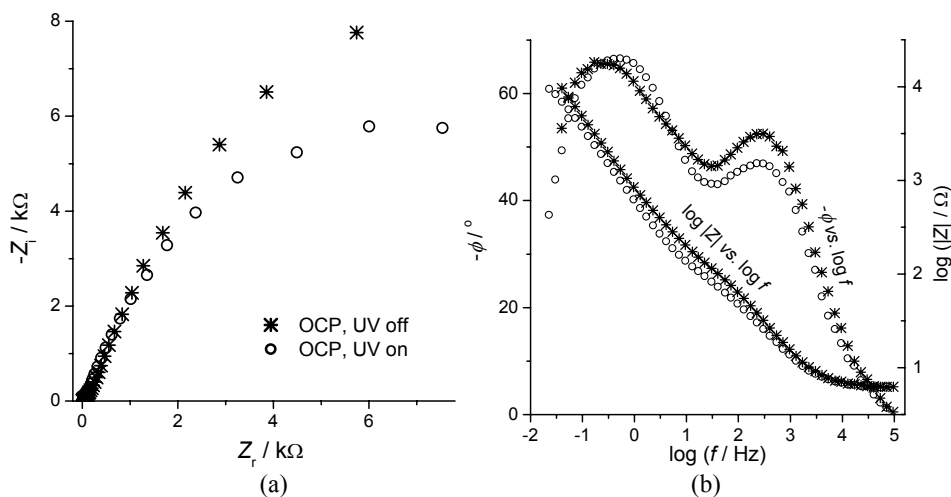

Fig. 7. Nyquist (a) and Bode plots (b) of the EIS data for the Ti/TiO$_2$ electrode registered at the "UV off" and "UV on" OCP in 1.0 mol dm^{-3} H$_2$SO$_4$ + 0.010 mol dm^{-3} BA.

CONCLUSIONS

A titanium oxide coating on a titanium substrate, prepared by the inorganic sol–gel procedure, showed photoelectrochemical activity in H_2SO_4 solution and for the oxidation of benzyl alcohol.

Microscopic investigations of the coating showed the presence of agglomerates of narrow size distribution, around 100 nm. The agglomerates are consisted of 8 nm-sized crystallites.

Illumination with UV light influenced the open circuit potential, current transient and impedance characteristics of the prepared Ti/TiO_2 photoelectrode, in a H_2SO_4 solution and in a H_2SO_4 + benzyl alcohol solution. The cathodic shift of the open circuit potential was more pronounced in the presence of benzyl alcohol than in its absence, while the photocurrent was doubled due to the oxidation of benzyl alcohol. Due to UV illumination, a new phase angle peak appeared in the Bode plot of the EIS data of the photoelectrode in H_2SO_4 solution. However, this peak was not registered in the H_2SO_4 + benzyl alcohol solution.

ИЗВОД

ФОТОЕЛЕКТРОХЕМИЈСКА СВОЈСТВА ТИТАН-ОКСИДА
ДОБИЈЕНОГ СОЛ–ГЕЛ ПОСТУПКОМ

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Фотоелектрохемијска својства титан-оксида добијеног сол–гел портупком испитивана су на оксидној превлаци нанетој на титанску подлогу. Превлака је термички третирана у ваздуху на температури од 350 °C. Превлака се састоји од зрна уједначене расподеле по величини од око 100 nm. Фотоелектрохемијске карактеристике установљене су испитивањем промена потенцијала отвореног кола, временске зависности струје и импедансних карактеристика Ti/TiO_2 електроде при осветљености UV светлошћу у раствору H_2SO_4 и при оксидацији бензил-алкохола. Установљена је фотоактивност електроде у испитиваним системима.

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