

A Study of Photoelectrochemical Deposition of Organic Layers on Sol-Gel TiO₂ Surfaces

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Received 7 January 1997

Dedicated to Professor Ľubomír Lapčík, in honour of his 60th birthday

Photoactive TiO₂ surface layers were prepared by the sol-gel process. Their photoelectric activities were judged from measured effective quantum yields of photocurrent. It was found that the photoelectrochemical deposition of *o*-toluidine, pyrrole, and aniline takes place on these surface layers. Changes of hydrophilic-hydrophobic surface nature accompanied with the photoelectrochemical deposition of organic layers were evaluated by measuring contact angle of water drop.

Photoelectrochemical processes on active semiconductor surfaces have gained wide popularity in recent years. Of particular interest are photoelectrochemical reactions of oxidative decomposition of organic compounds and their applications in waste water and air purification systems [1, 2]. However, capabilities of these processes in various chemical reactions were investigated, too [3].

Photoelectrochemical reactions on active planar surfaces may be of interest also for their potential in imaging systems [4–6]. Functionality of such systems is given by a change in certain physical properties of planar semiconductor surface. *Inoue et al.* [4] used photoelectrochemical deposition of metals (Ti, Pb, Co, Ag) on semiconductor electrode in imaging system. Molybdenum oxide was applied in another photoelectrochemical imaging system [7]. Other reported imaging systems utilize photoelectrochromism of conducting polyaniline and polypyrrole films with admixtures of organic dyes and transition metals complexes. The resolution of these systems was enhanced by the aid of nanometre-scaled TiO₂ particles [8] which significantly influenced photoelectrochemical performance.

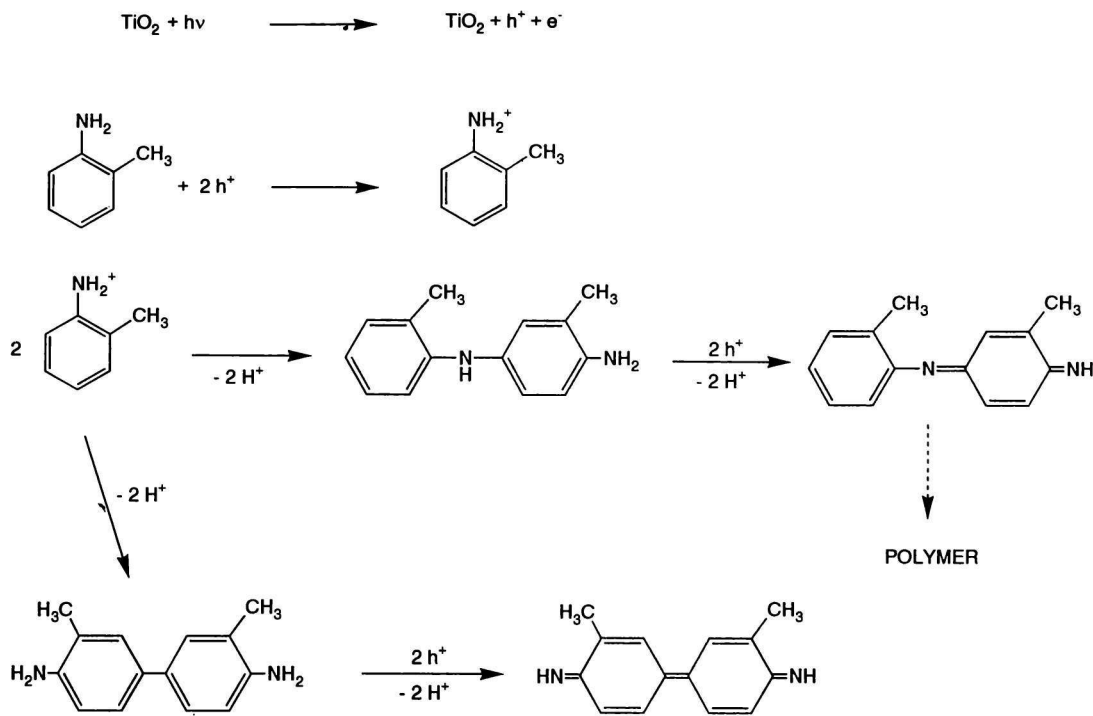
Masuda et al. [9] studied photoelectrochemical deposition of thin organic layers on planar TiO₂ electrodes prepared by thermic and electroanodic oxidation of titanium plate. This system can be described as a semiconductor electrode of *n*-type where electron-

hole pairs (h^+ , e^-) are generated as a result of the internal photoeffect upon absorption of light. Electron-hole separation can give rise to various redox processes in which compounds in the vicinity of active surface are involved. If an active surface is in contact with electrolyte containing aromatic compounds, *e.g.* *o*-toluidine, aniline, thin surface layers may be generated by a photoelectrochemical oxidation of these compounds. The deposition takes place exclusively on irradiated surface region. While the uncovered TiO₂ surface is hydrophilic, the nature of surface region covered by thin organic layer is shifted towards hydrophobicity. Thus, the deposited layer creates a hydrophobic image on hydrophilic TiO₂ surface [10]. In [9, 10] a mechanism of the photoelectrochemical oxidation of organic compounds resulting in a generation of oligomeric and polymeric surface layers is assumed. An example for *o*-toluidine is given in Scheme 1.

Techniques entitled sol-gel process are utilized for preparation of glass and ceramic layers of various types in recent years [11]. Basic precursors of these layers are hydrolyzable organometallic compounds or colloidal solutions of metal oxides. Sol-gel process advances through stages of sol and gel formation. Subsequent thermic processing converts gel into glass or ceramic. Sol-gel methods were recently applied also in the preparation of photoelectrochemically active TiO₂ systems [12–14].

The aim of this paper was to study the changes of

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Scheme 1

surface properties generated by photoelectrochemical deposition of thin organic layers on active TiO_2 surface prepared by sol-gel method and to compare this system with that based on thermic TiO_2 surface layers [9, 10].

EXPERIMENTAL

Semiconductor Surfaces

Active semiconductor TiO_2 surfaces were prepared by the solution sol-gel process [15] either on glass plates for deposition of organic layers or on titanium plates for photocurrent measurements.

The plates were dipped into a solution of titanium(IV) tetrabutoxide (6.4 g $\text{Ti}(\text{OBU})_4$, 20.5 g ethanol, 0.7 g H_2O , 0.05 g HNO_3 , and 2.44 g ethyl acetoacetate as a stabilizer) and lifted from there by a constant rate 2 mm s^{-1} . After 24 h of free storage the coated plates were stepwise calcinated in a furnace in an air atmosphere up to the top temperature $150\text{--}500^\circ\text{C}$ and let freely cool to room temperature.

TiO_2 layers prepared by this technique exhibit a good adhesion to the supporting plates and they are both transparent and colourless. However, careful observation can recognize tiny interference. The interference of optical reflectance UV VIS spectra (at the angle of incident beam 12°) was used to determine the thickness of the TiO_2 layers. The refractive index of the TiO_2 layers was determined by the two-angle reflectance method (at 12° and 40°) using a Philips

PU 8800 spectrophotometer equipped with specular reflectance accessory. Details of the method were published elsewhere [16]. Refractive index raises with the temperature of calcination and its value is about 2.2 at 600 nm for the layers calcinated at 500°C . The thickness of TiO_2 surface layers in this study was about 120 nm.

Reproducibility of thickness, optical and photoelectric properties of these layers lay within the interval of experimental errors of the used methods of measurements.

Measurement of Spectral Photoelectric Activity

The spectral photoelectric activity of the sol-gel TiO_2 layers was measured in the photoelectric cell with aqueous solution of 1 M-NaOH as electrolyte [16]. The cell was a Teflon chamber the bottom of which was the sample with the sol-gel TiO_2 surface layer. The counter electrode was a thick Pt wire. The monochromatic irradiation was provided by the set-up of a 250 W Xe lamp and a grating monochromator (Applied Photophysics, UK). The energy of incident light at the site of the measured TiO_2 layer was determined using standard ferrioxalate actinometry. The photocurrent and dark current spectra were recorded at the short circuit regime over the range $300\text{--}450 \text{ nm}$. After dark current correction the photocurrent values were transformed into an effective quantum yield of photocurrent production η

$$\eta = 1.036 \times 10^{-11} \frac{j/(\mu\text{A cm}^{-2})}{\Phi/(\text{mol cm}^{-2})} \quad (1)$$

where j is the photocurrent density and Φ the photon flux of incident irradiation.

Aromatic Compounds and Electrolyte Solutions

o-Toluidine, aniline, and pyrrole were used as water-soluble redox reagents. All of these compounds were purified by distillation before use. Electrolytic solutions were made from these compounds (0.08 mol dm⁻³), with sodium sulfate (0.2 mol dm⁻³) as the supporting electrolyte. The pH values of electrolytes were maintained by the appropriate additions of NaOH or H₂SO₄ and checked before and after exposure.

Photoelectrochemical Deposition of Organic Layers and Evaluation of Wettability

Photoelectrochemical deposition of organic layers on sol-gel TiO₂ surfaces was carried out in a simple set-up consisting of medium-pressure 250 W Hg lamp (Tesla Holešovice, Czech Republic) irradiating reaction chamber. The plates with sol-gel TiO₂ surface layers were immersed into electrolyte solutions in the reaction chamber. In order to avoid short wavelength irradiation causing direct photolysis of organic compounds the reaction chamber was covered with pyrex glass filter (cutting edge at about 305 nm) during irradiation.

Changes in hydrophilic-hydrophobic nature of the surfaces caused by photoelectrochemical deposition were evaluated by measuring the contact angle of a water drop deposited on the surface, using a contact angle meter (Kernco, USA).

Reproducibility of photoelectrochemical deposition of organic layers on sol-gel TiO₂ surfaces lay within the interval of experimental errors of contact angle measurement (5°).

RESULTS AND DISCUSSION

Spectral Photoelectric Activity of Sol-Gel TiO₂ Surface Layers

Spectral photoelectric activity, *i.e.* the dependence of photocurrent on incident photon energy, is an important characteristic of the active semiconductor layer. The integral parameter corresponding to the spectral activity of semiconductor is the band gap energy, E_g .

The spectral dependence of the effective quantum yield of photocurrent production for surface TiO₂ sol-gel layers with various top temperature of calcination

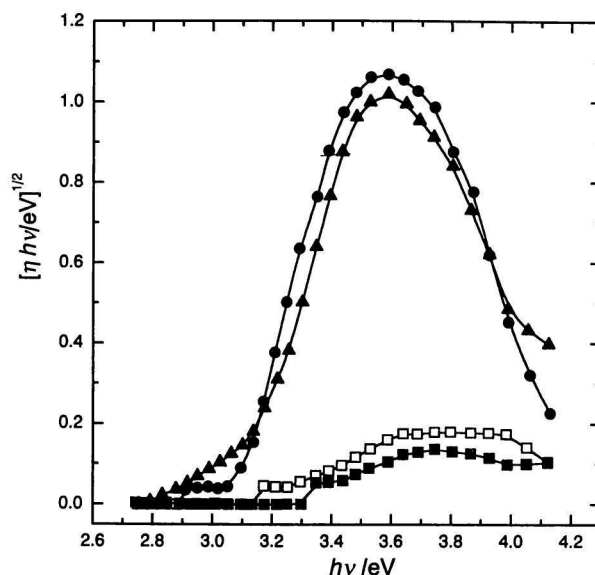


Fig. 1. $\sqrt{\eta h\nu}$ vs. $h\nu$ plot for sol-gel layers calcinated at various top temperatures. ■ 150°C, □ 200°C, ▲ 400°C, ● 500°C.

is presented in the form $\sqrt{\eta h\nu}$ vs. $h\nu$ (Fig. 1). This kind of plot is appropriate for the theoretical equation [17]

$$\eta h\nu = \text{const.} \cdot (h\nu - E_g)^2 \quad (2)$$

where $h\nu$ is the photon energy.

Thus the plot of Fig. 1 type not only describes the spectral dependence of photoelectric activity but the extrapolation of the left side linear region onto the $h\nu$ axis allows to determine the band gap energy.

The layers calcinated at a low temperature (150°C and 200°C in Fig. 1) do not exhibit significant photoelectric activity. Low-temperature calcination does not remove all organic residuals from semiconductor structure, the quantum yield η is low and the shape of the plot does not allow E_g determination.

On the other hand, as expected, both layers calcinated at higher temperature (400°C and 500°C in Fig. 1) reveal significant photoelectric activity in the region of band gap energy. The value of $E_g = 3.12$ eV (corresponding to 397 nm) was estimated for 400°C TiO₂ layer while $E_g = 3.08$ eV (corresponding to 402 nm) for 500°C layer. Both these values fall into the interval delimited by the band gap energy of anatase phase of TiO₂ (3.2 eV, corresponding to 383 nm) and the band gap energy of rutile phase of TiO₂ (3.02 eV corresponding to 410 nm).

The layers calcinated at 500°C were used in photoelectrochemical deposition experiments.

Photoelectrochemical Deposition of Organic Layers on Sol-Gel TiO₂ Surfaces

Fig. 2 shows the dependence of contact angle val-

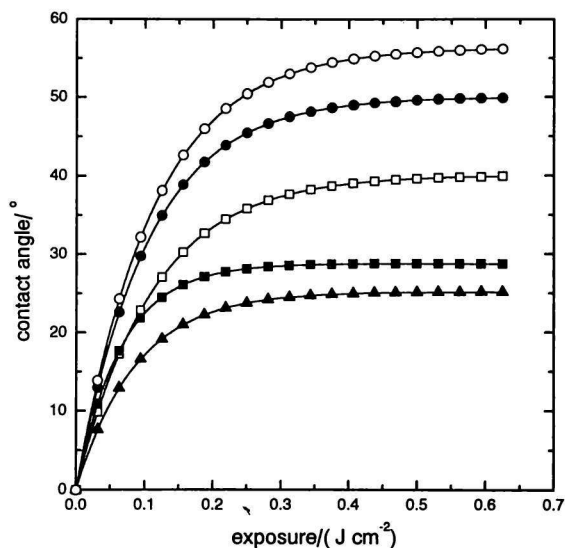


Fig. 2. Dependence of contact angle exposure characteristic of *o*-toluidine electrolyte on pH. ● pH = 4, ○ pH = 5, □ pH = 7, ■ pH = 9, ▲ pH = 10.

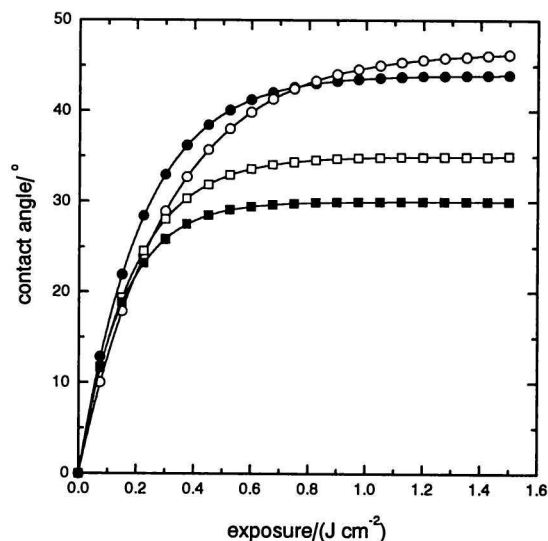


Fig. 3. Dependence of contact angle exposure characteristic of pyrrole electrolyte on pH. ● pH = 4, ○ pH = 5, □ pH = 7, ■ pH = 9.

ues during the photoelectrochemical deposition of thin organic layers in *o*-toluidine electrolyte on various pH. Similar dependences for pyrrole and aniline electrolytes are plotted in Figs. 3 and 4, respectively. It can be observed that contact angle increased sharply with exposure and attained a saturated value at an exposure 0.2–0.3 J cm⁻² in all of these systems. This increase of contact angle of water drop with the exposure indicates a significant change of a hydrophilic surface nature towards hydrophobic nature for organic layers deposition in *o*-toluidine, aniline, and pyrrole electrolytes. The effect of the layers deposited in *o*-

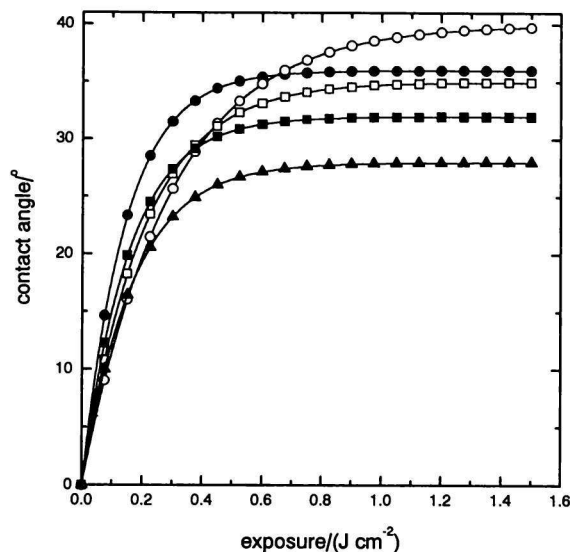


Fig. 4. Dependence of contact angle exposure characteristic of aniline electrolyte on pH. ● pH = 4, ○ pH = 5, □ pH = 7, ■ pH = 9, ▲ pH = 10.

toluidine electrolyte is most significant and higher saturated values were attained.

The changes of contact angle of sol-gel TiO₂ surface during the photoelectrochemical deposition in *o*-toluidine electrolyte are analogous to the changes reported by Masuda *et al.* [10] for the TiO₂ surface layers prepared by a thermic oxidation of titanium plate in a gas burner. However, the studied sol-gel TiO₂ surface layers are about 10 times less sensitive because similar change towards hydrophobicity requires 10 times higher exposure in these systems than the thermic TiO₂ layers do. This indicates that thermic TiO₂ layers are more active in processes of photoelectrochemical oxidation of organic compounds than the studied sol-gel TiO₂ layers. This lower photoelectrochemical activity of sol-gel TiO₂ layers is quite surprising. On the other hand, generally high photoelectric activity of thermic TiO₂ layers (judged from photocurrent measurements) was reported in [18]. The structure and chemical quality of thermic TiO₂ layers is believed to be more suitable for photoelectrochemical deposition of organic layers than that of the sol-gel TiO₂ layers. However, more detailed study is required for an accurate understanding of this finding.

The behaviour of the contact angle changes (Figs. 2–4) was not monotonic with pH. Maximum values, *i.e.* maximum surface hydrophobicity was attained at pH = 5 for all studied electrolytes. This observation is in accordance with earlier findings of Masuda *et al.* [10] for *o*-toluidine electrolyte and TiO₂ surface prepared by thermic oxidation of titanium plate. They assumed that total rate of electrochemical oxidation is independent of pH and pH dependence of contact angle values is caused by the changes of the structure of oxidation products in high pH region.

Acknowledgements. This study was supported by the Slovak Scientific Grant Agency VEGA under the project 95/5195/207.

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Translated by M. Čeppan