

J. MECH*, K. SZACIŁOWSKI*,**

NEW TYPE OF PHOTOACTIVE MATERIALS BASED ON TiO₂ MODIFIED BY ANTHRAQUINONE DERIVATIVES**NOWE FOTOAKTYWNE MATERIAŁY W OPACIU O TiO₂ MODYFIKOWANY POCHODNYMI ANTRACHINONU**

Anthraquinone derivatives chemisorbed at nanocrystalline TiO₂ present a new type of photoactive hybrid materials. These systems consist of organic chromophores anchored to the semiconductor surface via oxygen atoms of hydroxyl or carbonyl group. The bond between the chromophore and the titanium atom at the semiconductor surface reveals strong covalent character which makes the material stable in wide spectrum of electric potential and in an acidic environment. In alkaline solutions hydrolysis can be observed. The electrodes made of a modified TiO₂ generate photocurrents within 300-700 nm, compared, with 300-400 nm for unmodified TiO₂. Such an efficient photosensitization is a result of mutual arrangement of energy levels of the molecule and energy bands of the semiconductor.

Keywords: titanium dioxide, anthraquinone derivatives, photosensitization

Zaadsorbowane na powierzchni nanokrystalicznego dwutlenku tytanu pochodne antrachinonu tworzą nowy rodzaj fotoaktywnych materiałów hybrydowych. Układy te są zbudowane z organicznych barwników zakotwiczonej na powierzchni półprzewodnika poprzez atomy tlenu grup hydroksylowych lub karbonylowych. Wiązanie pomiędzy barwnikiem a atomem tytanu na powierzchni półprzewodnika wykazuje silny charakter kowalencyjny, co czyni materiał stabilnym w szerokim zakresie potencjałów, a także w środowisku kwaśnym. W środowisku zasadowym materiał ulega hydrolizie. Elektrody na bazie modyfikowanego TiO₂ generują fotoprądy w zakresie 300-700 nm, podczas gdy elektrody z czystego TiO₂ dają fotoprądy w zakresie 300-400 nm. Tak wydajna fotosensybilizacja jest wynikiem wzajemnego położenie poziomów energetycznych cząsteczki oraz pasmami półprzewodnika.

1. Introduction

Over the last several years a huge effort in capturing, converting and storage of the solar energy has been made. Numerous research teams are involved in the development an efficient and economically-viable solar cells. The competition for another fraction of percent in conversion efficiency keeps going but at the same time completely new fields exploring photocurrent have emerged. Among the others there is a completely new branch called photoelectrochemical information processing [1-3]. This new scientific area utilizes the light impulse at the input which, during propagation through the particular light-active system, encodes the information. This device collects information in the form of light pulses and converts it into photocurrent pulses. A discovery of applicability of light in the logical operations arises great enthusiasm as an alternative to the silicon technology, currently exploited, and dominating in electronics. On the other hand an introduction of new materials and phenomena, requires an enormous amount of experimental and theoretical work. The hybrid materials used in the photoelectrochemical information processing should be characterized by certain parameters. One of

them is the ability to generate photocurrents on certain irradiation. Neat TiO₂ has band gap value approx. 3.2 eV – it results in the absorption below 400 nm (near ultraviolet). The idea of exploiting the sun light for information processing brings significant economic benefits. Anthraquinone derivatives embedded at TiO₂ extend the range of interaction with light towards lower energies. The photosensitization can follow different mechanisms due to specific energy levels arrangement and extend of electron coupling. The diversity of energy levels distribution in organic/inorganic hybrid materials is a huge advantage in a context of photoelectrochemical information processing. Usage of diverse hybrid materials characterized by certain energy levels distribution enables the construction of more complex molecular-scale logic devices and additionally provides addressing of individual logic cells. What is more, immobilization of molecular species on semiconducting surfaces increases the stability of the systems. More and more new photoactive materials aimed towards photosensitization have been developed, because of the inexhaustible source of modifiers which are organic molecules absorbing in the UV-Vis range.

* AGH UNIVERSITY OF SCIENCE AND TECHNOLOGY, FACULTY OF NON-FERROUS, 30-059 KRAKÓW, AL. A. MICKIEWICZA 30, POLAND

** JAGIELLONIAN UNIVERSITY, FACULTY OF CHEMISTRY, 30-060 KRAKÓW, 3 INGARDENA STR., POLAND

2. Experimental

Four organic dyes, dihydroxy anthraquinone derivatives: alizarin (1,2-dihydroxyanthraquinone), quinizarin (1,4-dihydroxyanthraquinone), anthrarufin (1,5-dihydroxyanthraquinone) and chrysazin (1,8-dihydroxyanthraquinone) of the highest purity available were used in experiment as purchased without further purification. Among the dyes chinizarin, anthrarufin and chrysazin were supplied by Alfa Aesar whereas alizarin was delivered by Acros. TiO₂ P25 delivered by Evonic with anatase content approx. 80%, and 20% of rutile, 50 m² g⁻¹ was used to prepare porous electrodes. Acetonitrile (ACN) HPLC 99.9% grade and dimethylformamide (DMF) was purchased from POCH and Sigma-Aldrich respectively. The absorption spectra of dyes dissolved in either ACN or DMF were recorded using Agilent 8453 spectrophotometer with quartz cuvette (1 cm path length). Perkin Elmer Lambda 950 UV-VIS spectrophotometer with integrating sphere was used for diffuse reflectance spectroscopy of hybrid materials. Barium sulphate (Sigma Aldrich) was used as a matrix for the samples. Recorded reflectance values were converted to the Kubelka Munk function (KM) which quantitatively reflects values of the absorbance Eq. (1).

$$KM = \frac{(1 - R_{\infty})^2}{2R_{\infty}} \quad (1)$$

R_∞ stands for reflectance in the case of infinitely thick sample. Results of spectroscopy measurements were presented as KM*energy vs. energy.

Synthesis. Small amount of TiO₂ powder (ca. 180 mg) was mixed with 5 ml of solution of DHAQ in acetonitrile or dimethylformamide. Acetonitrile is a good solvent for most of the anthraquinone derivatives except anthrarufin (1,5-dihydroxyanthraquinone), which is in turn soluble in DMF. The mixture was stirred for 5 min in an ultrasonic bath. Modified TiO₂ was removed by centrifugation and washed 1 time with ACN or DMF and then 5 times with water. After drying in air, chromophore-modified TiO₂ was obtained as a colour powder.

Photocurrent spectra were recorded in the designed system which is composed of 150 W xenon lamp and a monochromator with a diffraction grating 1200 l/mm. Data were recorded using an Autolab potentiostat (Eco Chemie). The electrode made of modified TiO₂ deposited at the surface of transparent electrode (indium tin oxide, ITO/PET), was placed in the 0.1 M KNO₃ solution.

3. Results and discussion

3.1. Chromophores

All anthraquinone derivatives are based on three ring anthracene moiety in which the central ring bears two carbonyl groups. Two hydroxyl groups are placed respectively: for alizarin in the first and second position, for quinizarin in the first and fourth position, for anthrarufin in the first and fifth position and for chrysazin in the first and eight position, Fig. 1. Each compound is characterized by strong absorption band

428 nm (chrysazin). Very high absorption coefficient is associated with dominant π-π* character of the transitions. The presence of hydroxyl groups enables adsorption of molecules at the TiO₂ surface [2, 4-6].

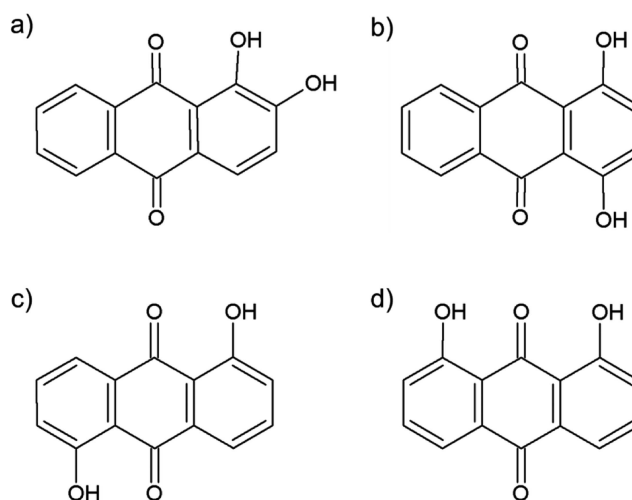


Fig. 1. Schematic representation of anthraquinone derivative molecule. The hydroxyl groups location characterize different species of dihydroxy anthraquinone derivatives (DHAQs), respectively for alizarin in the 1 and 2, for quinizarin in the 1 and 4, for anthrarufin in the 1 and 5, for chrysazin in the 1 and 8 position

3.2. Semiconductor

The surface of TiO₂ may be represented as an 2D array of Ti⁴⁺ and O²⁻ sites [2]. Coordination of surface titanium atoms is octahedral (hexacoordinated). Several types of structural defects may occur on the TiO₂ surface (e.g. oxygen vacancies, titanium interstitials, line defects and impurities) [4]. For example, typically rutile (110) plane contains few percent of oxygen vacancies. UV photoemission spectra of this surface indicates small gap state (about 0.8 eV binding energy) which may be ascribed to hydroxylated oxygen vacancy or titanium interstitial [7].

3.3. Chemisorption of molecule onto TiO₂ surface

Dissociative chemisorption of water results in the formation of three types of sites in the structure of TiO₂ surface. When a molecule, which coordinates titanium dioxide stronger than the water, is present in a solution, ligand exchange reaction occurs. Although all sites of TiO₂ surface undergo hydration reaction, sites occupied by titanium ions are prone to complexation with external ligand. Structure and stability of such a complex depends on a type of ligating sites, TiO₂ crystal plane, accessibility of titanium ions, pH *etc.* [5].

3.4. Molecule-TiO₂ interaction

Adsorption of molecular species onto semiconducting surfaces brings about perturbation of electronic structure of both counterparts [8]. This interaction usually results in a formation of coordination compounds involving surface (coordinatively unsaturated) metal ions. On the other hand these interactions resemble formation of molecular electronic junction,

as molecules reacting with much larger (semi)conducting surfaces with well-defined band structure [9-11]. Modification of energetic structure is much larger on the chromophore side and can be observed as a redshift in absorption spectra or additional absorption peak. The nature of semiconductor-molecule interaction results from the power of coupling. Strongly coupled systems are usually described by the Creutz-Brunschwig-Sutin model [12-14], whereas for weakly coupled systems the Sakata-Hiramoto-Hashimoto model is more appropriate [15, 16]. In the strong electronic coupling regime, the interaction of a ligand with the surface of the semiconductor leads to the formation of surface coordination species. With a proper arrangement of molecular orbitals, new energy levels are formed. In the case of *n*-type semiconductor (TiO_2) a bonding orbital is formed via interaction of the HOMO level of the surface ligand with an empty surface state. Resulting states with both HOMO and LUMO character are mostly located at the surface ligand (electron donor) and belong to the conduction band of the semiconductor respectively. In this case excitation of the surface complex leads to an optical electron transfer from the surface molecule to the conduction band. At the extreme case *d* orbitals of only one Ti^{4+} ion are involved in the electron transfer process [17, 18]. In the case of weak electronic coupling between semiconductor band and surface molecule the photoinduced electron transfer should be considered as the only way of photosensitization. For *n*-type semiconductors electrons are injected from the photosensitizing molecule into the conduction band with possible contribution of the empty surface states. These states are believed to be unsaturated Ti^{4+} surface states with oxygen vacancies. Moreover, the energetics of these states is affected by surface chelation due to Lewis acid-base interactions. This is substantiated by non-exponential kinetics of electron injection from the excited photosensitizer molecules [19]. Strong molecule to semiconductor interaction is commonly encountered in dye sensitized solar cell system where molecular donors are in the resonance with a high density of semiconductor acceptor states [4]. TiO_2 sensitized with alizarin presents system with weak molecule-semiconductor coupling in which the molecular photoexcited state is at the edge of the conduction band. The energetic arrangement of alizarin- TiO_2 system permits efficient electron injection into the edge of the CB by an adiabatic mechanism without the energy loss associated with injection high into the CB in a nonadiabatic process [20].

3.5. Photoactivity of hybrid materials

Photocurrent generation in transparent ITO electrodes covered with modified TiO_2 was investigated as a function of incident-light wavelength and various electrode potentials at pH 7. To have a full overview of photocurrent generation as a function of applied potential and irradiation wavelengths, a set of action spectra was collected at constant potentials (every 50 mV). In this way, three-dimensional photocurrent maps were obtained, Fig. 2. The photoactivity of neat TiO_2 is limited to 300-400 nm range Fig. 2a). The chromophore molecules are good photosensitizers for TiO_2 widening the long wavelength side from 400 nm to 700 nm.

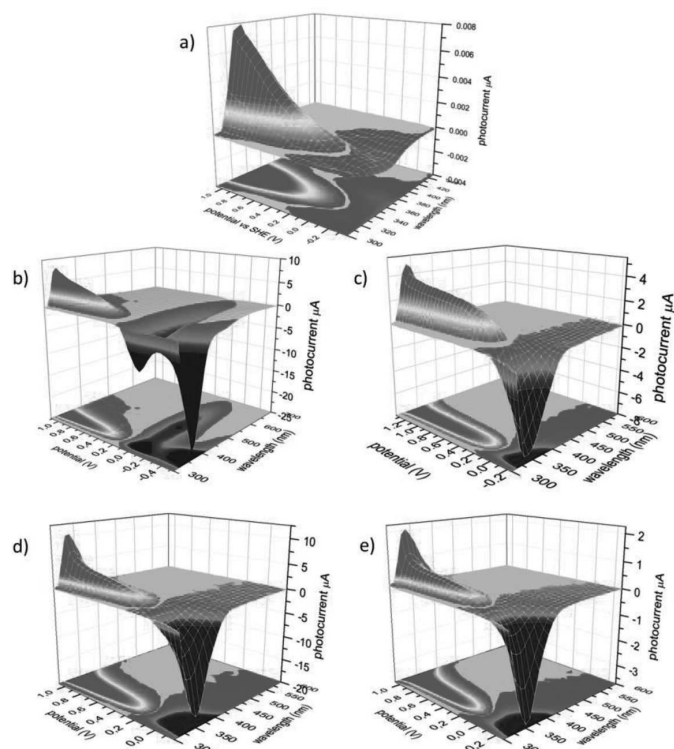


Fig. 2. Photocurrent action spectra recorded at pure TiO_2 photoelectrode and DHAQ@TiO_2 photoelectrodes as a function of the potential applied to electrode and wavelength of incident light. Photocurrent maps have been measured for pure TiO_2 a) and TiO_2 modified by: alizarin b), quinizarin c), anthrurufin d) and chrysazin e)

A photosensitization for alizarin@ TiO_2 is observed within 400-500 nm at positive polarization of the photoelectrode, but it is much more efficient at negative polarization within 400-700 nm Fig. 2b). For other chromophores (1,4-, 1,5-, and 1,8-dihydroxyanthraquinone) photosensitization has narrower range: 400-450 nm at positive polarization, and 400-600 nm at negative polarization. Additionally the intensities of the former are much lower than of alizarin@ TiO_2 . Intensive photocurrents generated by alizarin can be explained by specific molecule geometry and related to the binding mode (alizarin is bound to TiO_2 through oxygens, both from hydroxyl groups). Such geometry is responsible for specific energy distribution in the alizarin- TiO_2 system.

The implementation of additional energy level into the band gap region of semiconductor results in electron injection from donor (molecule ground state) to the acceptor state (semiconductor valence band) using energy lower than band gap value. Photocurrent generation and photosensitization is schematically presented for alizarin at TiO_2 , as an example, Fig. 3. Photocurrent generation occurs upon irradiation of the material with light of sufficient photon energy. We can distinguish two regions of photocurrent generation: high energy excitation from the valence to the conduction band of TiO_2 , and low energy excitation localized at the surface adsorbed chromophore followed by electron injection to the conduction band. Electrons generated in the conduction band can be transferred to the electrode whenever its potential is higher than the potential of trapped electrons Fig. 3. Electrons injected from molecules toward electrode at negative polarization generate anodic photocurrents Fig. 3a). Holes created in the

valence band can recombine with electrons from sacrificial donor in electrolyte. During this process hydroxyl anion (OH^-) is oxidized to the hydroxyl radical (OH^\bullet). Several processes compete with those responsible for anodic photocurrent generation: recombination within the semiconductor (radiative and non-radiative), recombination of holes with electrons from the electrode, as well as reduction of electron acceptors in the electrolyte solution.

Cathodic photocurrents occur at negative polarization, when reduction of the sacrificial electron acceptor, by electrons from the conduction band is more efficient than the mechanisms responsible for anodic photocurrent generation (Fig. 3b). Oxygen dissolved in electrolyte plays a role of the electron acceptor. When the negative polarization of the electrode exceeds a certain level facilitates reduction of alizarin (electron transfer from electrode to the $1,2/1,2^-$ level), the intense dark cathodic currents appear, and photosensitization vanishes, (Fig. 2b).

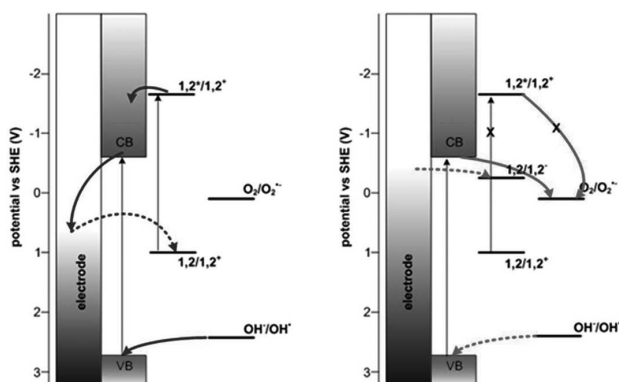


Fig. 3. Mechanism of photocurrent generation: anodic photocurrent is generated at positive potentials upon excitation of the inner part of the TiO_2 particle and alizarin moiety adsorbed on the surface a), while cathodic photocurrents are generated at negative potentials upon excitation of TiO_2 and alizarin b). Shaded vertical bar indicates the photoelectrode potential. $1,2/1,2^+$ indicates oxidation potential of alizarin in the ground state, whereas $1,2^*/1,2^+$ is the oxidation potential of alizarin in the excited state

4. Conclusions

Hybrid materials obtained by immobilization of anthraquinone derivatives onto the surface of nanocrystalline titanium dioxide reveal promising photoelectrochemical properties. They exhibit pronounced photosensitization toward visible light. Photoelectrodes built from DHAQ@TiO_2 generate photocurrent within the 300-700 nm window. The polarity of the photocurrent can be tuned by changing the photoelectrode potential or energy of incident light. The mechanism of this process was described in terms of photoinduced electron transfer involving both anthraquinone molecule and titanium dioxide. DHAQ molecules acts here as an electron buffer, accepting or donating electrons depending on potential applied to the electrode. These materials are especially suited for applications in various optoelectronic switches, since these applications do not require the highest energetic efficiency. Similar to other switchable photoelectrochemical systems [21-32] the DHAQ@TiO_2 hybrid material can be applied for construction

of optoelectronic switches, logic gates, and other functional devices. The mechanism of working of such devices is quite simple. Incident light wavelength and photoelectrode potential can be regarded as input channels, light impulse is an information bit, while photogenerated currents can be regarded as output channels. In this regime, various devices as simple switches, logic gates, and more complex combinatorial circuits can be implemented without any obstacles [23, 33]. Information processing of devices based on hybrid semiconductors should lead to simpler than in the case of silicon electronic devices constructions. Their performance is defined by the nature of the chemical species adsorbed at the surface (or immobilized within the nanocrystals) and is a result of subtle interplay between the components of the system. The phenomenon of photocurrent polarization switching upon changes of photoelectrode potential and incident light wavelength constitute a good platform for construction of various logic devices [23, 27, 33-35].

Furthermore, because of the ability of dihydroxy anthraquinone to form a series of hydrogen bonds with a wide variety of substrates, the DHAQ@TiO_2 system can be a platform for various photoelectrochemical sensors. Because of catalytic activity toward photoreduction of molecular oxygen, DHAQ -titanium dioxide photoelectrodes may also be a good starting point for development of photofuel cells [36] and as a model system to study interfacial electron transfer processes at nanoscale [14, 37].

Acknowledgements

This work was supported by National Science Centre (Grant 2011/03/N/ST5/04470) AGH University of Science and Technology (contract no. 11.11.180.509) and also by Malopolska Scholarship Found for PhD students (ZS.4112-212/2010). Authors also thank Kacper Pilarczyk for valuable discussions and preparation of the manuscript.

REFERENCES

- [1] A. Hagfeldt, G. Boschloo, L. Sun, L. Kloo, H. Pettersson, *Chem. Rev.* **110**, (2010).
- [2] M. Oszajca, P. Kwolek, J. Mech, K. Szaciłowski, *Current Physical Chemistry* **1**, (2011).
- [3] P.V. Kamat, K. Tvrđy, D.R. Baker, J.G. Radich, *Chem. Rev.* **110**, (2010).
- [4] W.R. Duncan, O.V. Prezhdo, *Annu. Rev. Phys. Chem.* **58**, (2007).
- [5] P. Kwolek, M. Oszajca, K. Szaciłowski, *Coord. Chem Rev.* **256**, (2012).
- [6] W. Macyk, K. Szaciłowski, G. Stochel, M. Buchalska, J. Kunczewicz, P. Łabuz, *Coord. Chem. Rev.* **254**, (2010).
- [7] S.-C. Li, J.-G. Wang, P. Jacobson, X.-Q. Gong, A. Selloni, U. Diebold, *J. Am. Chem. Soc.* **131**, (2009).
- [8] Q. Chen, L. Zhao, C. Li, G. Shi, *J. Phys. Chem. C* **111**, (2007).
- [9] R.L. McCreery, *Chem. Mater.* **16**, (2004).
- [10] D.S. Seferos, S.A. Trammell, G.C. Bazan, J.G. Kushmerick, *Proc. Natl. Acad. Sci.* **102**, (2005).
- [11] F. Anariba, R.L. McCreery, *J. Phys. Chem. B* **106**, (2002).

- [12] C. Creutz, B.S. Brunschwig, N. Sutin, *J. Phys. Chem. B* **110**, (2006).
- [13] C. Creutz, B.S. Brunschwig, N. Sutin, *J. Phys. Chem. B* **109**, (2005).
- [14] D.M. Adams, L. Brus, C.E.D. Chidsey, S. Creager, C. Creutz, C.R. Kagan, P.V. Kamat, M. Lieberman, S. Lindsay, R.A. Marcus, R.M. Metzger, M.E. Michel-Beyerle, J.R. Miller, M.D. Newton, D.R. Rolison, O. Sankey, K.S. Schanze, J. Yardley, X. Zhu, *J. Phys. Chem. B* **107**, (2003).
- [15] T. Sakata, K. Hashimoto, M. Hiramoto, *J. Phys. Chem.* **94**, (1990).
- [16] O. Kitao, *J. Phys. Chem. C* **111**, (2007).
- [17] L.G.C. Rego, V.S. Batista, *J. Am. Chem. Soc.* **125**, (2003).
- [18] S.G. Abuabara, L.G.C. Rego, V.S. Batista, *J. Am. Chem. Soc.* **127**, (2005).
- [19] S. Ardo, G.J. Meyer, *Chem. Soc. Rev.* **38**, (2009).
- [20] W.R. Duncan, W.M. Stier, O.V. Prezhdo, *J. Am. Chem. Soc.* **127**, (2004).
- [21] W. Macyk, G. Stochel, K. Szaciłowski, *Chem. Eur. J.* **13**, (2007).
- [22] S. Gawęda, G. Stochel, K. Szaciłowski, *Chem. Asian J.* **2**, (2007).
- [23] K. Szaciłowski, W. Macyk, *Chimia* **61**, (2007).
- [24] M. Hebda, G. Stochel, K. Szaciłowski, W. Macyk, *J. Phys. Chem. B* **110**, (2006).
- [25] K. Szaciłowski, W. Macyk, M. Hebda, G. Stochel, *ChemPhysChem* **7**, (2006).
- [26] K. Szaciłowski, W. Macyk, G. Stochel, *J. Mater. Chem.* **16**, (2006).
- [27] K. Szaciłowski, W. Macyk, *Comp. Rend. Chimie* **9**, (2006).
- [28] R. Beránek, H. Kisch, *Angew. Chem. Int. Ed.* **47**, (2008).
- [29] M. Biancardo, C. Bignozzi, H. Doyle, G. Redmond, *Chem. Commun.* (2005).
- [30] L.F.O. Furtado, A.D.P. Alexiou, L. Gonçalves, H.E. Toma, K. Araki, *Angew. Chem. Int. Ed.* **45**, (2006).
- [31] M. Long, W. Cai, H. Kisch, *J. Phys. Chem. C* **112**, (2008).
- [32] M.-C. Long, R. Beranek, W.-M. Cai, H. Kisch, *Electrochim. Acta* **53**, (2008).
- [33] J. Mech, R. Kowalik, A. Podborska, P. Kwolek, K. Szaciłowski, *Aust. J. Chem.* **63**, (2010).
- [34] K. Szaciłowski, W. Macyk, *Solid State Electron.* **50**, (2006).
- [35] K. Szaciłowski, W. Macyk, G. Stochel, *J. Am. Chem. Soc.* **128**, (2006).
- [36] J.A. Cracknell, K.A. Vincent, F.A. Armstrong, *Chem. Rev.* **108**, (2008).
- [37] B. Ulgut, H.D. Abruña, *Chem. Rev.* **108**, (2008).