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PHOTOELECTROCHEMICAL CHARACTERIZATION OF NITROGEN-MODIFIED TiO_2

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Modification of the chemical structure of titanium dioxide by non-metal elements (nitrogen) allows to move photocatalytic activity of titanium dioxide towards visible light. Three samples of photocatalysts with different nitrogen content and different photocatalytic properties were prepared for photoelectrochemical characterization. The positions of valence and conduction band edges of obtained semiconductors were calculated which enabled better understanding of the mechanism of visible light activity of the photocatalysts.

Key words: titanium dioxide, visible light, modification, photoelectrochemistry

INTRODUCTION

Heterogeneous photocatalysis using titanium dioxide represents efficient method for complete destruction of organic and inorganic compounds in liquid and gas phases which can successfully be degraded in this way. Pollutants containing carbon, hydrogen, nitrogen, sulphur and halogen atoms are mineralized to CO_2, H_2O, NO_3^-, SO_4^{2-}, and halide anions (Hoffmann, 1995). The number of papers and patents related to photocatalytic removal of toxic compounds is constantly on the rise. However, most of them pertain to artificial UV-light application. Photocatalytical methods based on TiO_2 were successfully used in some commercial applications, including water purification, air-cleaning units, antimicrobial coatings and self-cleaning glass (Anpo, 2000).

Although photocatalysis has been investigated for over 30 years, the number of successful commercial applications could be greater. First of all, practical application

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of photocatalysis is limited by the fact that TiO_2 absorbs only UV light due to its high band gap energy (3.2 eV). Only 2 to 5 % of solar spectrum (UV fraction of solar light) can, therefore, be utilized by conventional TiO_2 photocatalysis (Anpo, 2000). UV lamps are needed to use the photocatalytical properties of TiO_2. Application of UV lamps poses a serious disadvantage because of high energy consumption, which increases the operating costs of the UV/TiO_2 system. Sensitization or modification of TiO_2 towards visible light photoactivity can allow to eliminate this limitation.

The most promising approach of activation of TiO_2 in the visible light region is modification of its chemical structure to shift absorption spectrum to the visible light region. This type of modification involves introduction (doping) of metal and non-metal species. To prepare an effective visible light-active photocatalyst doping should produce states in the band gap of TiO_2 that absorbs visible light. The conduction band minimum should be as high as that of TiO_2 or higher than the H_2/H_2O level to ensure its photoreduction activity. The states in the band gap should overlap sufficiently with the band states of TiO_2 to transfer photoexcited carriers to the reactive site at the photocatalyst surface within their lifetime (Asahi, 2001). It is necessary to use anionic species for the doping rather than metal cations, which can give localized *d* states deep in the band gap of TiO_2 and result in recombination centers of carriers (Asahi, 2001).

Recent investigation on titania modification has been mainly focused on applying non-metalic elements: nitrogen (Asahi, 2001; Gole, 2004; Janczarek, 2005; Mrowetz, 2004; Sakthivel, 2004), carbon (Sakthivel, 2003) and sulphur (Umebayashi, 2004). To propose mechanism of visible light activation, one needs to calculate the position of band edges (conduction and valence band) in titania semiconductor electronic structure. This paper presents results of photoelectrochemical investigations on nitrogen-modified titanium dioxide catalysts which were earlier prepared using thiourea and urea as precursors of nitrogen. These N-TiO_2 catalysts were active in visible light – a significant mineralization of 4-chlorophenol (4-CP) was observed (Sakthivel 2004; Janczarek, 2005).

EXPERIMENTAL

The band gap energy of photocatalysts was calculated from their diffuse reflectance spectra (DRS). DRS of the solids were recorded on a Shimadzu UV-2401PC UV-VIS spectrophotometer. Photocatalysts were diluted with $BaSO_4$ (50 mg TiO_2 and 2 g $BaSO_4$) and ground in an agate mortar. Subsequently, 10 mm pellets were prepared for the analysis. The background reflectance of $BaSO_4$ was measured first. Reflectance was converted by the instrument software to $F(R_\infty)$ values according to the Kubelka-Munk theory. The band gap was obtained from a plot of $[F(R_\infty)\cdot E]^{1/2}$ versus energy of the exciting light (E) assuming that undoped titania and modified titanium dioxide are indirect crystalline semiconductors.

Quasi-Fermi level potentials were determined using optical train with XBO 150 W lamp and 100 cm^3 Pyrex flask cell with electrodes (Fig. 1). Twenty mg of catalyst was suspended in 50 cm^3 of 0.1 M KNO_3. The concentration of methyl viologen (MV^{2+}; 1,1'-dimethyl-4,4'-bipyridinium dichloride) was 1.0 mM. The suspension was stirred and sparged with N_2 before and during the measurement. The pH was adjusted with HNO_3 and NaOH solutions, and monitored with a pH-meter. A large surface platinum plate was the working electrode and Ag/AgCl – the reference electrode. The method was based on voltage measurements between these electrodes upon irradiation as a function of pH (Roy, 1995).

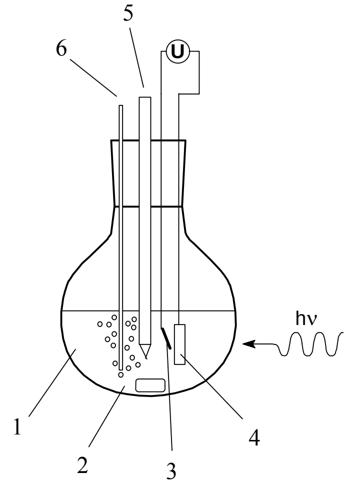

Fig. 1. Laboratory set-up for quasi-Fermi level potential determination: 1- suspension of catalyst, 2-magnetic stirrer, 3-reference electrode (Ag/AgCl), 4-working electrode (Pt), 5- pH electrode, 6-nitrogen inlet

MV^{2+} is used as an electron acceptor. pH-independent reversible reduction of MV^{2+} to $MV^{+\bullet}$ (blue solution) refers to $E°_{MV^{2+/+\bullet}} = -0.445$ V vs. NHE. Energy levels in semiconductors are generally dependent on pH. Assuming that TiO_2 is n-type semiconductor, three cases can be considered, see Fig. 2.

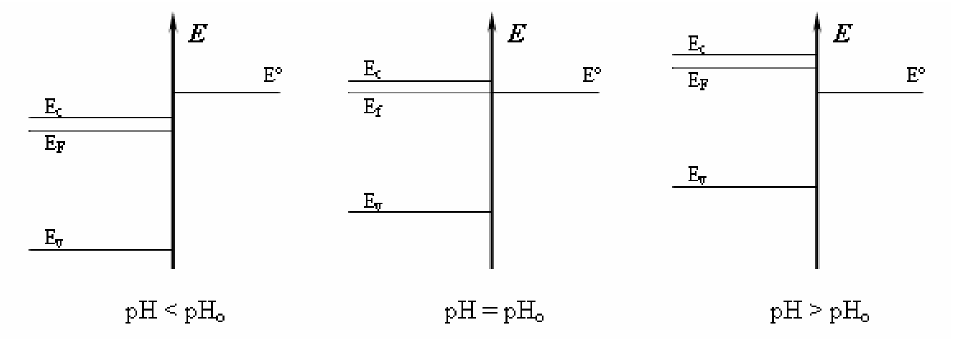

Fig. 2. Positions of energy levels in an *n*-type semiconductor at various pH [Roy, 1995]

At low pH the quasi-Fermi level potential is more positive then the redox potential of an electron acceptor (E^0). Then the excited electron from the conduction band is not able to reduce MV^{2+} what becomes possible at pH ≥ pH_o, when ${}^*E_f \leq E°$. The quasi-Fermi level potential depends on the pH [Roy, 1995]:

$$ {}^*E_f(pH) = {}^*E_f(pH = 0) - k\,\mathrm{pH} \quad (1) $$

At pH_o the redox potential of $MV^{2+/+\bullet}$ couple equilibrates with $E_f(pH_o)$:

$$ E° = {}^*E_f(pH = 0) - k\,\mathrm{pH_o} \quad (2) $$

From equations 1 and 2:

$$ {}^*E_f(pH) = E°_{MV^{2+/+\bullet}} + k\,(\mathrm{pH_o} - \mathrm{pH}). \quad (3) $$

The obtained pH_0 values were converted to the quasi-Fermi level potential at pH=7 using the equation:

$$ {}^*E_f(pH{=}7) = -0.445 + 0.059\,(\mathrm{pH_o} - 7)\,. \quad (4) $$

The reproducibility of pH_o measurements was better than 0.1 pH units.

RESULTS AND DISCUSSION

BAND GAP ENERGIES

The determination of band gap energies is essential for identification of changes in the electronic structure of titania after doping with nitrogen. The reference sample of unmodified titania and three samples of surface-modified TiO_2 with nitrogen were considered. In comparison to the reference sample (Figure 3), the diffuse reflectance spectra show entire shift of the absorption spectra for TiO_2-N/1 (1.4 wt.% N) (Figure 4) and TiO_2-N/2 (12.7 wt.% N) (Figure 5). The corresponding calculated band gap energies are 2.48 eV and 2.20 eV, respectively. The presence of this shift and the value of the band gap energy are closely related to nitrogen content. In the case of TiO_2-N/3 sample (0.6 % wt.% N) instead of the shift of the whole spectrum only an absorption shoulder in the 400-520 nm range was observed. The band gap energy for this sample was 2.97 eV (Figure 6). Thus, for high nitrogen-concentrated samples a significant band gap narrowing was observed.

Characterizing surface-modified samples, diffuse reflectance spectra exhibit an absorption shoulder at the range of 400 to 526 nm for TiO_2-N/3 catalyst and complete shift of absorption spectrum for samples TiO_2-N/1 and TiO_2-N/2. Only one absorption edge was observed for each sample. This shift and the band gap energies are strictly dependent on the nitrogen content. It is possible to control the band gap energy by varying nitrogen concentration through adjustment of calcination conditions. Such approach is more repeatable than varying the concentration of nitrogen precursor. Similar strong shift of absorption spectrum was observed by Yin et al. (Yin, 2003a; Yin, 2003b). They prepared nitrogen-doped yellowish rutile titania by high energy ball milling of P-25 titania with hexamethylenetetramine and reported two absorption edges at 400 nm and 520 nm resulting in 3.1 eV and 2.4 eV band gap energies, respectively. It is important to mention that the reflectance spectra were not transformed to Kubelka-Munk function, therefore it is impossible to indicate proper values of the band gap energies. The two band gap energies may not exist since authors did not show the calculation procedure and the reflectance vs. wavelength plot does not allow to determine these values. In the case of TiO_2-N/1 and TiO_2-N/2 samples a clear simultaneous shift for the valence and conduction bands was observed, which has not been shown for any N-TiO_2 yet. In case of TiO_2-N/2 the role of surface states is not so significant because of band gap narrowing.

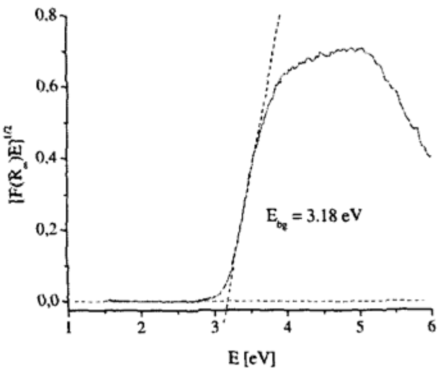

Fig. 3. DRS spectrum for TiO_2

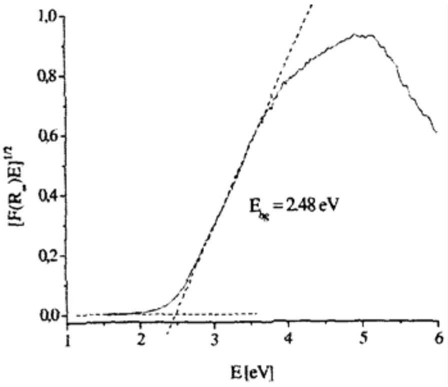

Fig. 4. DRS spectrum for TiO_2-N/1

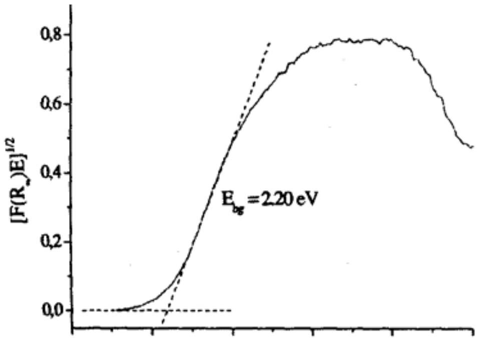

Fig. 5. DRS spectrum for TiO_2-N/2

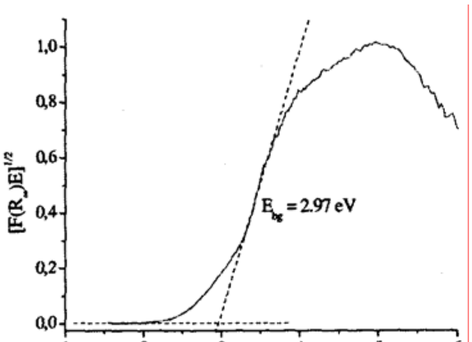

Fig. 6. DRS spectrum for TiO_2-N/3

QUASI-FERMI LEVELS

Figures 7a-d show the dependences of photovoltage (V vs Ag/AgCl) on the pH value of electrolyte for the reference sample (TiO_2) and modified ones. In case of TiO_2-N/2, TiO_2-N/1 -0.47 V and -0.56 V quasi-Fermi levels were determined. The value of the quasi-Fermi levels was the same for unmodified titania (3.18 eV) and TiO_2-N/3 (2.97 eV).

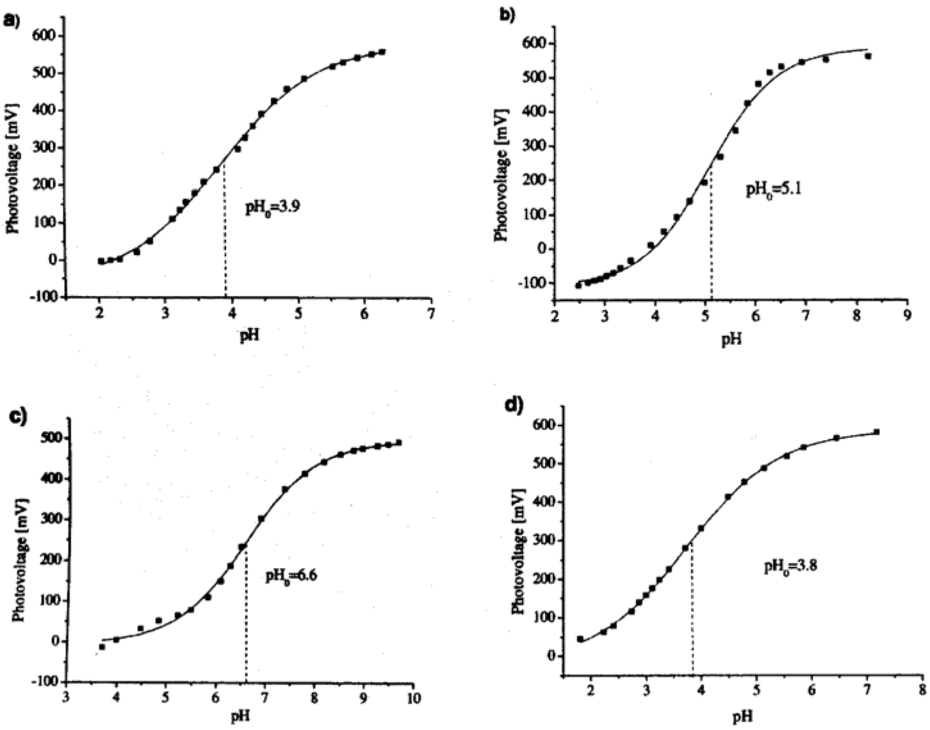

Fig. 7. Dependences of photovoltage (V vs Ag/AgCl) on pH value of electrolyte for: a) TiO_2, b) TiO_2-N/1, c) TiO_2-N/2, d) TiO_2-N/3

ENERGY DIAGRAM

Calculated photoelectrochemical data are shown in Table 1. The positions of the conduction and valence bands for TiO_2-N/1 and N/TiO_2-N/2 samples are strongly shifted (especially catodic shift of the valence band) - a significant band gap narrowing is observed (see Figure 8). Although, in this case the valence band edge is located at +2.34 V. Recalling that light absorbance starts already at 526 nm (2.39 eV), a manifold of surface states localized near the valence band must exist. It is consistent with the first of Asahi's postulates. Sample TiO_2-N/2 is not active but photocatalytic activities of TiO_2-N/3 and TiO_2-N/1 are similar. Therefore, band gap narrowing is not directly responsible for the photocatalytic activity in visible light and the existence of surface states plays a crucial role in this phenomenon.

Table 1. Photoelectrochemical data

Sample name	Bandgap energy [eV]	Quasi-Fermi level [V]	Light absorption onset [nm]
TiO_2	3.18	-0.63	380
TiO_2-N/3	2,97	-0.63	526
TiO_2-N/1	2.46	-0.56	534
TiO_2-N/2	2.20	-0.47	645

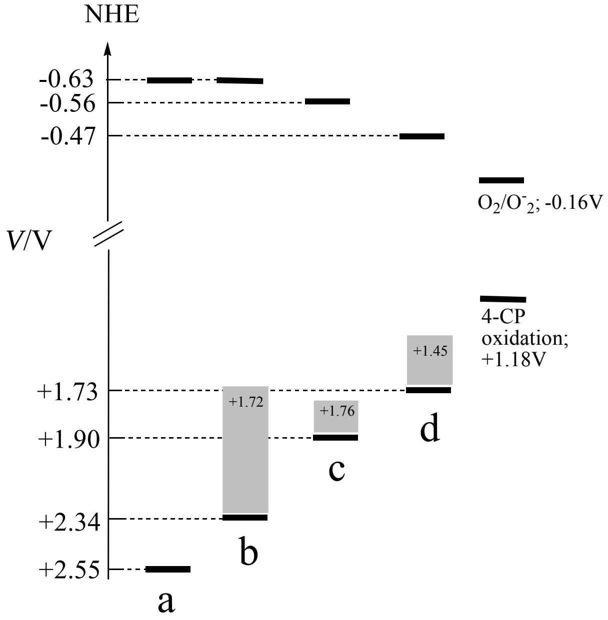

Fig . 8. Electrochemical potentials (vs. NHE) of band edges and surface states (shaded areas) at pH=7; (a) TiO_2, (b) TiO_2-N/3 , (c) TiO_2-N/1, (d) N/TiO_2-N/2

CONCLUDING REMARKS

For the first time nitrogen content in titania catalyst was correlated with the band gap energy. An absorption shoulder (from 400 to 520 nm) corresponding to the band gap energy 2.97 eV was observed in the absorption spectrum of sample containing smallest amount of nitrogen. For other samples, the entire spectrum was shifted towards longer wavelenghts resulting in an even lower band gap energy equal to 2.48 eV. However, nitrogen content of the catalyst exceeding 12 wt.% although resulted in lowering the band gap energy below 2.20 eV, did not further enhanced the photocatalytic potential of titania. The positions of surface states localized near the valence band were calculated.

ACKNOWLEDGEMENTS

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Modyfikacja chemicznej struktury tlenku tytanu(IV) poprzez pierwiastki niemetaliczne (np. azot) jest jednym ze sposobów przesunięcia aktywności fotokatalitycznej tlenku tytanu(IV) w kierunku światła widzialnego. Trzy próbki katalizatorów o różnej zawartości azotu i różnych właściwościach fotokatalitycznych zostały wybrane do charakterystyki fotoelektrochemicznej, której efektem finalnym jest określenie położenia pasma wzbronionego i pasma przewodzenia w otrzymanych półprzewodnikach, co ma istotne znaczenie dla lepszego zrozumienia mechanizmu aktywności przygotowanych fotokatalizatorów w świetle widzialnym.