

# Redox characteristics of photoexcited semiconducting materials

*Wojciech Macyk,<sup>1</sup> Konrad Szaciłowski,<sup>1</sup> Grażyna Stochel,<sup>1</sup> Horst Kisch<sup>2</sup>*

<sup>1</sup> Jagiellonian University, Faculty of Chemistry, Ingardena 3, 30-060 Kraków, Poland

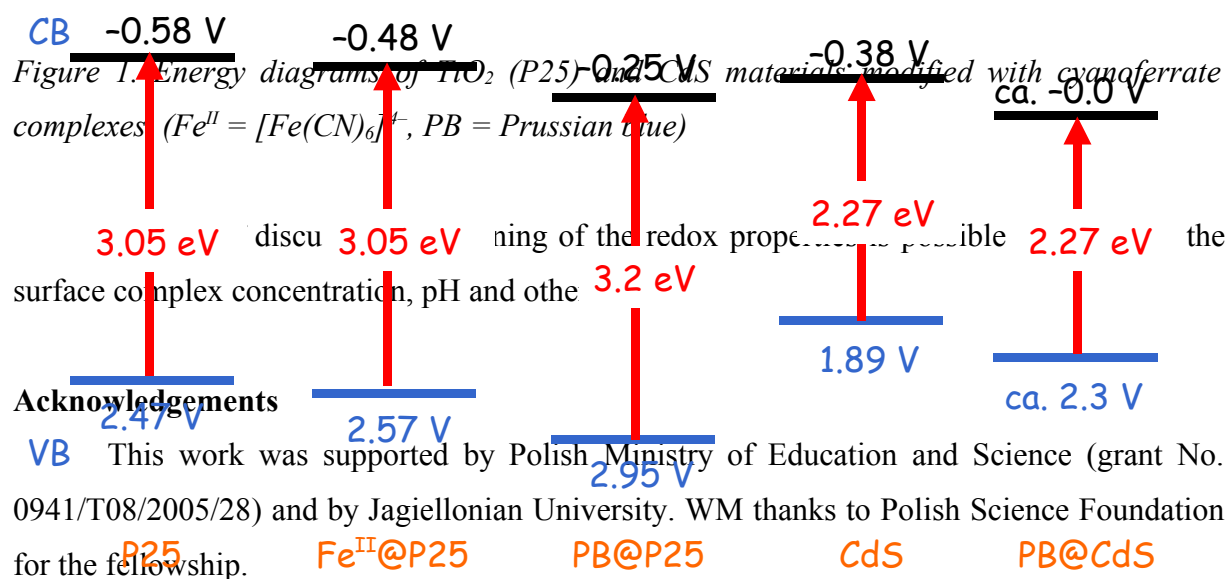
<sup>2</sup> Institut für Anorganische Chemie, Friedrich-Alexander Universität Erlangen-Nürnberg, Egerlandstr. 1, D-91058 Erlangen, Germany

*e-mail: macyk@chemia.uj.edu.pl*

Chemical and electrochemical surface processes attract a growing attention due to their possible practical applications. In particular, semiconducting materials and their modifications are used as catalysts and photocatalysts, (photo)electrodes, (bio)sensors *etc.* One of the crucial features of an appropriate semiconductor suitable for a given purpose is the position of valence and conduction band edges at the energy (or potential) scale. For instance, the redox properties of photogenerated holes and electrons determine the activity of a photocatalyst. Redox properties of photoexcited surface complex may determine the mechanism and direction of interfacial electron transfer processes. Determination of redox potentials of semiconducting materials helps to select a proper material for given application and often allows elucidation of mechanistic details of interfacial charge transfer taking place at the solid-solid and solid-liquid interface.

Although the energy bandgap can be relatively easily estimated from reflectance spectra of semiconductors, the measurement of band edge potentials is more difficult. One of the methods is based on capacity measurements. From the Mott-Schottky plot (the space charge capacity *vs.* electrode potential) it is possible to determine the so called flatband potential. The capacitance method is useful for semiconductor electrodes but not for suspensions. A number of other methods based on spectroscopic determinations,<sup>1</sup> modulation spectroscopy,<sup>2</sup> photocurrent,<sup>3</sup> and photovoltage<sup>4,5</sup> measurements have also been developed. In this presentation selected methods will be presented. Simple photoelectrochemical and spectroelectrochemical methods suitable for flatband potential measurements for semiconducting powders<sup>5</sup> and transparent films<sup>6</sup> will be discussed in detail.

Obtained data allow for a detailed characterization of visible light active photocatalysts (TiO<sub>2</sub> modified with platinum(IV) chloride complexes and chromium(VI) anions), mixed-oxide photocatalysts (containing titanium and iron oxides), TiO<sub>2</sub>-based photocatalysts with exchanged surface –OH groups, and semiconducting materials modified with cyanoferrate complexes working as chemical switches (Fig. 1).



## References

- (1) Boschloo, G.; Fitzmaurice, D. *J. Phys. Chem. B* **1999**, *103*, 2228-2231.
- (2) Chaparro, A. M. *J. Electroanal. Chem.* **1999**, *462*, 251-258.
- (3) Finlayson, M. F.; Wheeler, B. L.; Kakuta, N.; Park, K.-H.; Bard, A. J.; Campion, A.; Fox, M. A.; Webber, S. E.; White, J. M. *J. Phys. Chem.* **1985**, *89*, 5676-5681.
- (4) Roy, A. M.; De, G. C.; Sasmal, N.; Bhattacharyya, S. S. *Int. J. Hydrogen Energy* **1995**, *20*, 627-630.
- (5) Macyk, W.; Burgeth, G.; Kisch, H. *Photochem. Photobiol. Sci.* **2003**, *2*, 322.
- (6) Rusina, O.; Macyk, W.; Kisch, H. *J. Phys. Chem. B* **2005**, *109*, 10858-10862.