Nanocomposites and nanomaterials

Design of photocatalysts for reduction of small molecules

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Photocatalytic reduction of small molecules is usually a key step of every photocatalytic reaction. Reduction of water or carbon dioxide can be used to convert solar energy into fuels, while reduction of oxygen plays the central role in photodegradation of pollutants. In the latter case generation of superoxide ($O_2^{\bullet-}$) influences the overall efficiency of the photocatalytic reaction.

Redox properties of the material, adsorption of reactants, number of electrons participating in the reduction reaction, the oxidation counterpart of the reaction are examples of crucial parameters influencing photocatalytic reduction processes. Redox properties of the photocatalysts can be easily determined using spectroelectrochemical methods developed recently in our laboratory [1,2]. Recognition of the density of electronic states appears fundamental in understanding and predicting applicability of the photocatalyst. Basing on such measurements we were able to understand the differences in photocatalytic properties of rutile-TiO_2 and anatase-TiO_2 [3]. The results revealed significantly better reduction properties of rutile than anatase. Therefore the reduction of oxygen is more efficient at rutile than at anatase. On the other hand, holes generated within anatase particles are stronger oxidants than holes from the valence band of rutile, so oxidation of water to hydroxyl radicals proceeds efficiently at anatase-TiO_2, but not at rutile-TiO_2. These properties explain the differences in photocatalytic activities of both crystalline forms of titanium dioxide.

During the presentation selected examples of photocatalytic materials (not only oxides) designed for the reduction of small molecules will be presented. Factors influencing these reactions will be discussed.

1. *Świętek E., Pilarczyk K., Derdzińska J., Szaciłowski K., Macyk W.* Redox characterization of semiconductors based on electrochemical measurements combined with UV-Vis diffuse reflectance spectroscopy // PCCP 2013, **15**, 14256.
2. *Kobielusz M., Pilarczyk K., Świętek E., Szaciłowski K., Macyk W.* Spectroelectrochemical analysis of TiO2 electronic states – implications on the photocatalytic activity of anatase and rutile // Catal. Today, submitted.
3. *Buchalska M., Kobielusz M., Matuszek A., Pacia M., Wojtyła S., Macyk W.* On oxygen activation at rutile- and anatase-TiO_2 // ACS Catalysis 2015, **5**, 7424.