

## NANOSTRUCTURAL SEMICONDUCTING PHOTOCATALYSTS FOR MEDICAL APPLICATIONS

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The photocatalysis, according to IUPAC, is a catalytic reaction involving light absorption by a catalyst or by a substrate. This work considers a special type of the photocatalysis – photosensitization. The photosensitization is the process by which an alteration occurs in one molecular entity as a result of initial light absorption by another molecular entity.

Ultrabandgap illumination of the semiconducting photocatalyst can produce the reactive oxygen species (ROS, for example  $\text{OH}^\bullet$ ,  $\text{O}_2^{\bullet-}$ ,  $^1\text{O}_2$ ), which are incredibly powerful oxidants [1]. ROS can cause a lot of damages in an organism, however by a proper targeting of their toxic effect can be applied in many fields, for example in inactivation or killing of cancer cells in the photodynamic therapy (PDT). Unfortunately, the ROS attack is not specific – beside cancer cells also a number of healthy cells is destructed. A possible solution of this problem is based on the connection of the photocatalyst particles with biomolecules (e.g. monoclonal antibodies), which enable a molecular recognition of the cancer cells [2].

The main goal of this project was a modification of heterogeneous photocatalysts (namely  $\text{TiO}_2$ ) in order to enable its connection with antibodies, retaining the photocatalytic activity.  $\text{TiO}_2$  particles could be connected with antibodies through the avidin-biotin bridge, because biotin can be easily linked to antibodies, while avidin – a positively charged protein – can be bound electrostatically to the negatively charged oxide surface. A similar methodology was successfully applied for CdS quantum dots [3]. In order to build the antibody-biotin-avidin- $\text{TiO}_2$  system the surface of  $\text{TiO}_2$  has to be negatively charged. Moreover, the dimensions of the photocatalyst particles have to be comparable with the dimension of the antibodies (a few nanometers) in order to retain molecular recognition properties of the applied antibody.

The  $\text{TiO}_2$  nanoparticles (q- $\text{TiO}_2$ ) synthesized by hydrolysis of titanium isopropoxide [4] were modified with selected organic molecules. The determined band gap energy of the obtained  $\text{TiO}_2$  nanoparticles was close to 3.45 eV, *i.e.* the value by 0.3 eV higher than the band gap energy of microcrystalline  $\text{TiO}_2$ . This increase confirms the nanometric dimension of obtained  $\text{TiO}_2$  particles.

Stable sols were obtained in the case of 4-amino-2-hydroxybenzoic acid, however the surface charge was positive in this case.

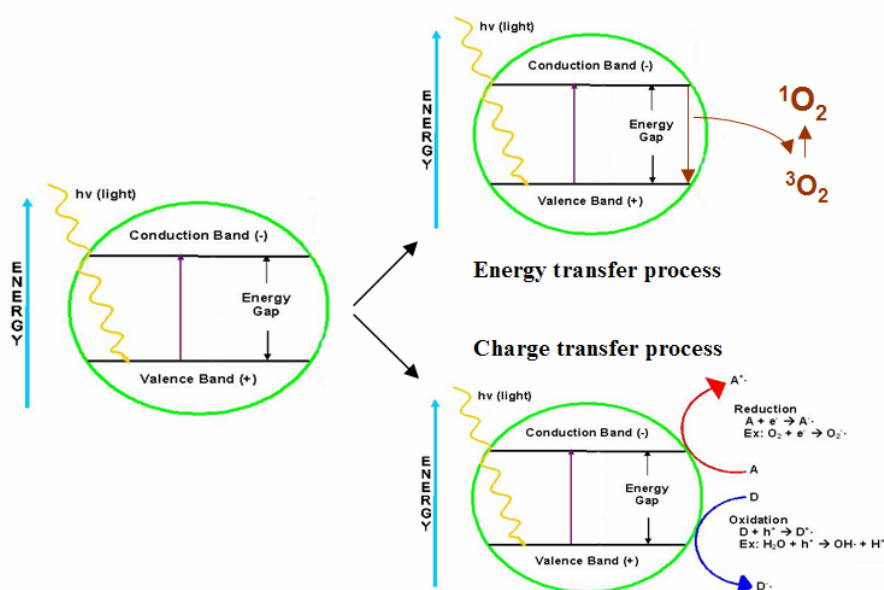
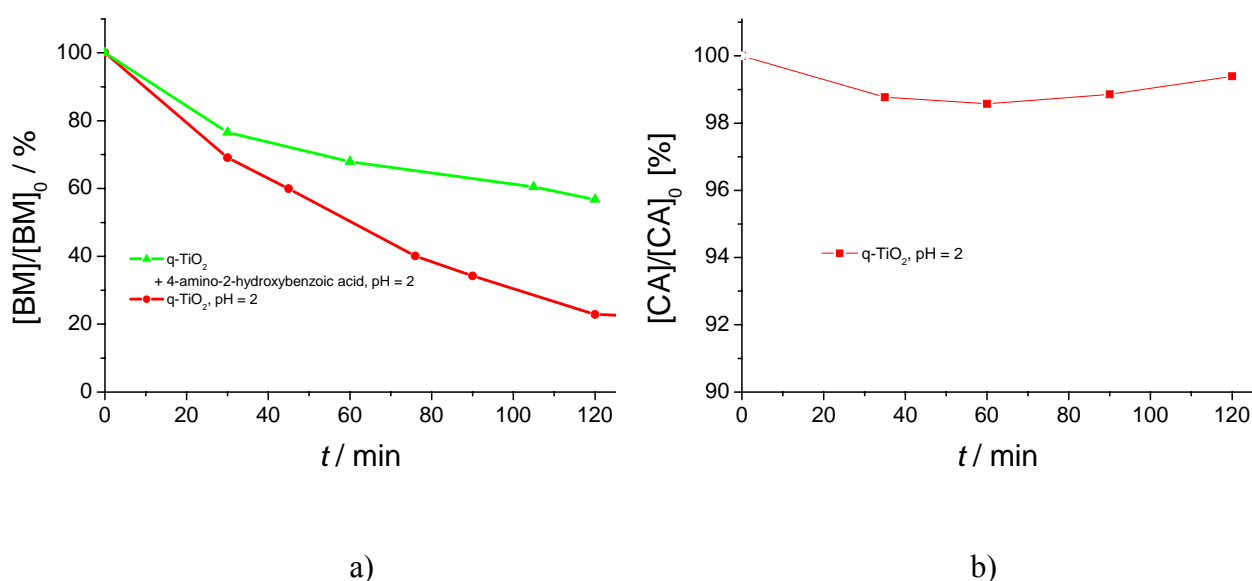
The photocatalytic properties were tested by monitoring the photodegradation of the standard compounds – methylene blue and cyanuric acid. Photodegradation of methylene blue requires hydroxyl radicals which are generated in the processes of charge transfer, while the photodegradation of cyanuric acid undergoes in the presence of singlet oxygen which is formed in the energy transfer processes.

The results show that unmodified q- $\text{TiO}_2$  exhibits a significant photocatalytic activity in the charge transfer processes. Only q- $\text{TiO}_2$  modified with 4-amino-2-hydroxybenzoic acid exhibits a significant photoactivity in analogous processes. Photodegradation of the cyanuric acid was not observed upon ultraviolet light illumination neither in the presence of unmodified nor modified q- $\text{TiO}_2$ . These results reflect a negligible efficiency of the energy transfer processes.

## References:

- [1] Jańczyk, A.; Krakowska, E.; Stochel, G.; Macyk, W., *J. Am. Chem. Soc.*, **2006**, *128*, 15574-15575.
- [2] Barber, P.; Barr, H.; George, J.; Krasner, N.; Morris, A., I.; Sutedja, T., G., *Clinical Oncology*, **2002**, *14*, 110-116.
- [3] Goldman, E. R.; Balighian, E. D.; Mattoussi, H.; Kuno, M.; Mauro, J. M.; Phan, T. T.; Anderson, G. P., *J. Am. Chem. Soc.*, **2002**, *124*, 6378-6382.
- [4] Weng, Y.-X.; Wang, Y.-Q.; Absury, J. B.; Ghosh, H. N.; Lian, T., *J. Phys. Chem. B*, **2000**, *104*, 93-104.

## Figures:

Fig. 1 Mechanism of TiO<sub>2</sub> photocatalysis.

**Fig. 2** Photocatalytic properties of obtained materials in the:  
 a) charge transfer processes; b) energy transfer processes.