Karolina Ordon

Functionalized semiconducting oxides based on bismuth vanadate with anchored organic dye molecules for photoactive applications

Abstract

Photoactivated processes are involved in several phenomena and serve as the basis of technological applications in different domains such as eco-construction, energy, environment, medicine, optoelectronics or cosmetology. Among the whole range of photoactivated processes, the key part lies in the photocatalytic reactions. Therefore, photoactive materials are used under radiations within defined spectral ranges contributing inter alia to photodynamic therapy, the production of self-cleaning glasses, hydrogen production for new sources of energy as well as in eco-friendly water purification from harmful organic pollutants.

From the pioneer work of Fujishima et al. (*Nature 1979, 277, 637–638*), the most commonly used semiconductors in photocatalysis is titanium dioxide (TiO_2). An alternatives to the TiO_2 were searched based on ZnO materials (*Chem. Rev. 1995, 95, 69-96*). Unfortunately, due to the high values of their band gap they cannot absorb visible light radiation limiting then their applications. Therefore, the search of new materials as visible light photocatalysts has attracted a wide research community. Among the promising systems, the monoclinic bismuth vanadate ($BiVO_4$) with energy gap equal to 2.4 eV is proposed as an alternative to the mentioned materials because it can harvest large fraction of the solar visible light radiations. Nowadays, exhaustive investigations are carried out to improve the properties of some families of known photocatalytic materials, as well as to develop the synthesis of new functional materials that would replace classic photocatalysts. Among numerous methods, the photocatalytic properties of semiconducting oxides can be improved by increasing their active surfaces, a narrowing of their band gap as well as the use of photoactive organic dyes to sensitize the inorganic semiconducting surfaces.

The aim of the presented work is to realize mesoporous architectures based on bismuth vanadate and to investigate an influence of selected organic sensitizers on the electronic, optical, vibrational and photocatalytic properties of the monoclinic $BiVO_4$. The increase of the active surface area was proposed as the first element improving the photocatalytic properties of the crystalline $BiVO_4$. For this purpose, the $BiVO_4$ was synthesized in a

mesoporous form applying an original approach based on the P123 surfactant. Then, the structural, electronic and optical properties of the obtained materials were exhaustively investigated and optimized. It was found that the mesoporous $BiVO_4$ is a good starting material to obtain an efficient photocatalyst. In addition, it was determined that the synthesis of hybrid materials by anchoring organic dye molecules on a surface of the mesoporous $BiVO_4$ will allow a more efficient transfer of electric charge between the organic molecule and inorganic oxide positively affecting its photocatalytic properties. Therefore, commercial D149 and two new dyes based on imino-pyridine moieties were selected as the organic sensitizers and their performances compared in the process of photoinduced charge transfer .

In order to determine the mechanisms of physical phenomena responsible for photocatalytic effects occurring in hybrid materials, a series of computer simulations and quantum-chemical calculations were performed. Applying the cluster methodology the electronic and optical parameters as well as structural and vibrational features of nanostructured $BiVO_4$ were calculated. The considered simulations were also performed for organic dyes and hybrid materials using a semi-empirical method with the PM6 parameterization. The obtained results from computer simulations were compared to the experimental data in order to validate the relevance of the developed theoretical models. Thus, based on computer simulations through quantum-chemical methods and the carried out experimental works, the involved charge transfer phenomena were characterized in the aim to understand the transfer of electric charges in the hybrid material and the effect of the photocatalytic responses. The role of dyes in enhancing the photocatalytic effects for some organic groups or a quenching of such effects by using other molecules was also explained. It was shown that the combination of experimental and theoretical research methods leads to quantitative understanding of the physical phenomena governing the photocatalytic properties of the photoactive semiconducting structures as $BiVO_4$.

The performed work develops a relevant methodology applied on a promising class of photoactive materials for visible-light driven photocatalysis. The numerical approaches offer the support of experimental investigations for exhaustive understanding of the phenomena involved in the photoinduced charge transfer efficiency in the hybrid systems. The works associate complementary expertise contributions of two research teams responsible for quantum-chemical calculations carried out at the Jan Dlugosz University in Czestochowa (Poland) and the experimental developments of relevant materials features carried out at Le Mans University (France). The results of the present work were disseminated by publishing in high impact journals and by communications during international conferences.