Abstract

The dynamic development of civilization resulted in the continuous increase of environmental pollution induced by CO_2 emission and with the contamination of water, soil, and air by hazardous chemicals. Considering the tendency of sustainable development of technology, the current economic situation, and the state of the environment and the prospect of exhaustion of mineral oils reserves, there is an urgent need for efficient and cost-effective methods of degradation of environmental contaminants, using renewable energy sources such as solar radiation.

These problems potentially could be solved by heterogeneous photocatalysis in the presence of semiconductor nanoparticles (particles ranging in size from 1 to 100 nm, NPs) and solar light. Enhancing the efficiency of catalytic processes in the presence of visible light is possible by surface modification of the structure of "traditional" semiconductor nanoparticles (so-called homogeneous nanoparticles), with smaller noble metal nanoparticles (so-called heterogeneous nanoparticles). However, up today there is no photocatalytic systems, that allow complete degradation of pollutants using renewable energy sources (sunlight). Moreover, environmentally safety of novel developed heterogeneous photocatalysts is still an open question. Therefore, the main problem in designing new nanomaterials with desirable photocatalytic properties is the lack of systematic knowledge about the photocatalytic activity of the designed heterogeneous nanoparticles. In addition, experimental testing of the significant number of all possible combinations of nanoparticles is the time- and cost-consuming procedure that significantly limits experimental examination of both activity and toxicity.

Based on above, the main purposes of my doctoral research were: (i) the development of computational methods supporting experimental design of surface-modified metal oxide nanoparticles that demonstrate photocatalytic properties; (ii) the application of the developed methodology in order to systematize current knowledge about the influence of structural modifications on photocatalytic activity and toxicity of modified metal oxide nanoparticles.

These goals have been achieved through the series of research tasks completed in five thematic areas:

(i) choosing a core metal oxide nanoparticle (MeOx) for further investigation;

(ii) building the convectional strategy for the development of simplified molecular representation of heterogeneous nanostructures; was realized through the modeling of surface-modified nanoparticles with monometallic NPs (Au);

(iii) implementation of QSPR methods for modeling of photocatalytic activity of heterogeneous nanoparticles; was realized through the modeling of TiO_2 surface-modified bimetallic nanoparticles (Au and Pd);

(iv) development of the methodology for calculating the so-called additive descriptors for heterogeneous nanoparticles; was realized through the modeling of surface-modified TiO_2 trimetallic nanoparticles (Au, Ag and Pt);

(v) implementation of developed additive descriptors in QSAR methods; was realized through modeling of *in vitro* cytotoxicity of surface-modified TiO_2 nanoparticles with Au, Ag and Pt.

The most important quantitative outcome of conducted research and discussion of the obtained results was the confirmation of the validity of four research hypotheses:

First, I found that the combination of modeling techniques allows to fill the lack of knowledge about the quantitative relationships (Nano-QSPR$_{mix}$) between the chemical structure of $Me_{mix}@TiO_2$ nanoparticles and their photocatalytic activity ($\%\tau_{PhOH}$) in visible light and *in vitro* cytotoxicity CHO-K1 cells (Nano-QSAR$_{mix}$).

Secondly, I have demonstrated, that the application of the developed additive descriptors to heterogeneous nanoparticles increase the quality of nano-QSAR models: (i) it allows to represent features of the $Me_{mix}@TiO_2$ nanoparticles, and (ii) it benefit mechanistic interpretation of models, revealing differences in their cytotoxic effects towards Chinese Hamster Ovary CHO-K1), Nano-QSAR$_{mix}$.

Thirdly, I have evaluated the applicability and usefulness of developed *in silico* methods on the modeling of selected physicochemical properties/*in vitro* cytotoxicity of heterogeneous nanoparticles (based on functionalized $Me_{mix}@TiO_2$ nanostructures).

In fourth, I have proven, that the combination of experimental and computational techniques lies within intelligent testing strategy that supports the ideology of design of new nanoparticles with pre-selected properties (in my case it was heterogeneous photocatalysis).

Developed models (Nano-QSAR$_{mix}$/Nano-QSPR$_{mix}$) are the first models presented by scientific community, that allow to quantify the relationships between structure and photocatalytic activity in visible light or *in vitro* cytotoxicity of heterogeneous Me_{mix}@TiO_2 nanoparticles.

The developed research methodology that is based on the combination of computational chemistry with experimental data is a first step towards the development of an intelligent test strategy. This strategy potentially will result in increased efficiency of the design process of novel photocatalytic systems, as will answer important questions about properties of nanomaterials at the design stage (before synthesis) and risk assessment (before transfer nanomaterials in to the market).