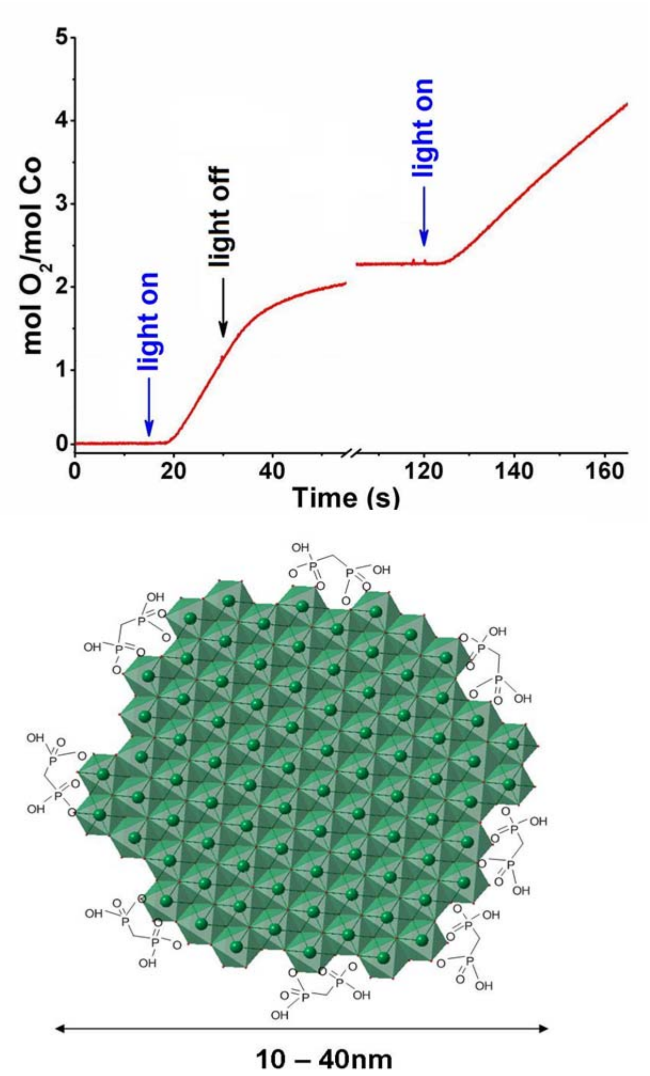
1. FINAL PUBLISHABLE SUMMARY REPORT

The main goal of the WATEROX project was to develop a catalyst for chemical and photochemical water oxidation, which is based on cheap and abundant transition metals. Initially, the project proposal was focused on manganese and manganese-calcium complexes as potential water oxidation catalysts. During implementation of the project, we also included cobalt complexes in the research program in order to increase our chances to achieve the project goal. We have synthesized a series of manganese, manganese-calcium, and cobalt complexes. We were able to grow single crystals for three complexes. Crystal structures of those three complexes have been determined by X-ray diffraction. Their physicochemical properties were studied by IR, UV-Vis, and EPR spectroscopies, ESI mass spectrometry, cyclic voltametry, differential pulse voltametry, controlled-potential electrolysis, and magnetochemistry. We have evaluated catalytic activities of all obtained in the project complexes in the reaction of chemical water oxidation.

The main results of WATEROX project can be divided in two parts, manganese based catalyst and cobalt based catalyst:

Mn based catalyst. We have found that manganese(III) complexes with carboxylic acid ligands hydrolyze in neutral aqueous solutions forming hydrated manganese(III, IV) oxide. The prepared in such a way oxide exhibits catalytic activities in the reaction of chemical water oxidation with Ce(IV) at pH 1 and with $[Ru(bpy)_3](ClO_4)_3$ at pH 7. Also, this oxide shows catalytic activities in the reaction of photochemical water oxidation, where $[Ru(bpy)_3](ClO_4)_2$ and $K_2S_2O_8$ are used as a photosensitizer and a sacrificial electron acceptor, respectively.

Co based catalysts. We have found that during chemical or photochemical oxidation in a neutral aqueous solution cobalt(II) methylenediphosphonate complex forms water soluble catalytically active nanoparticles (Figure 1a). Elemental analysis revealed that those nanoparticles contain cobalt and methylenediphosphonate ligand in the ratio 4:1. Dynamic light scattering indicates the formation of small particles with 10–40 nm radius (Figure 1b).



a **b**

Figure 1. An oxygen evolution curve recorded in the reaction of photochemical water oxidation in a $\{Co^{2+} + 1.4\ M2P + 10\ [Ru(bpy)_3]^{2+} + 100\ S_2O_8^{2-}\}$ system at pH 7 (a). Schematic illustration of a catalytically active Co/methylenediphosphonate nanoparticle. Molecules of methylenediphosphonate ligand adsorb chemically on a surface of the cobalt(III) (hydro)oxide particles and obviate their aggregation (b).

By employing X-ray absorption spectroscopy at multiple absorption edges we showed that the catalytically active part of the Co/methylenediphosphonate catalyst is cobalt(III) (hydro)oxide with a layered structure. The methylenediphosphonate molecules bind at the periphery of the oxide particles, preventing their agglomeration (Figure 1b).

The Co/methylenediphosphonate catalytic system developed within the WATEROX project is an important step toward development of an artificial catalyst, which mimics the water oxidation function of Photosystem II in green plants and cyanobacteria. After appropriate chemical modification, M2P ligand can be used to connect directly the photosensitizer to the catalytically active particles thus building a system for direct utilization of the solar energy (Figure 2).

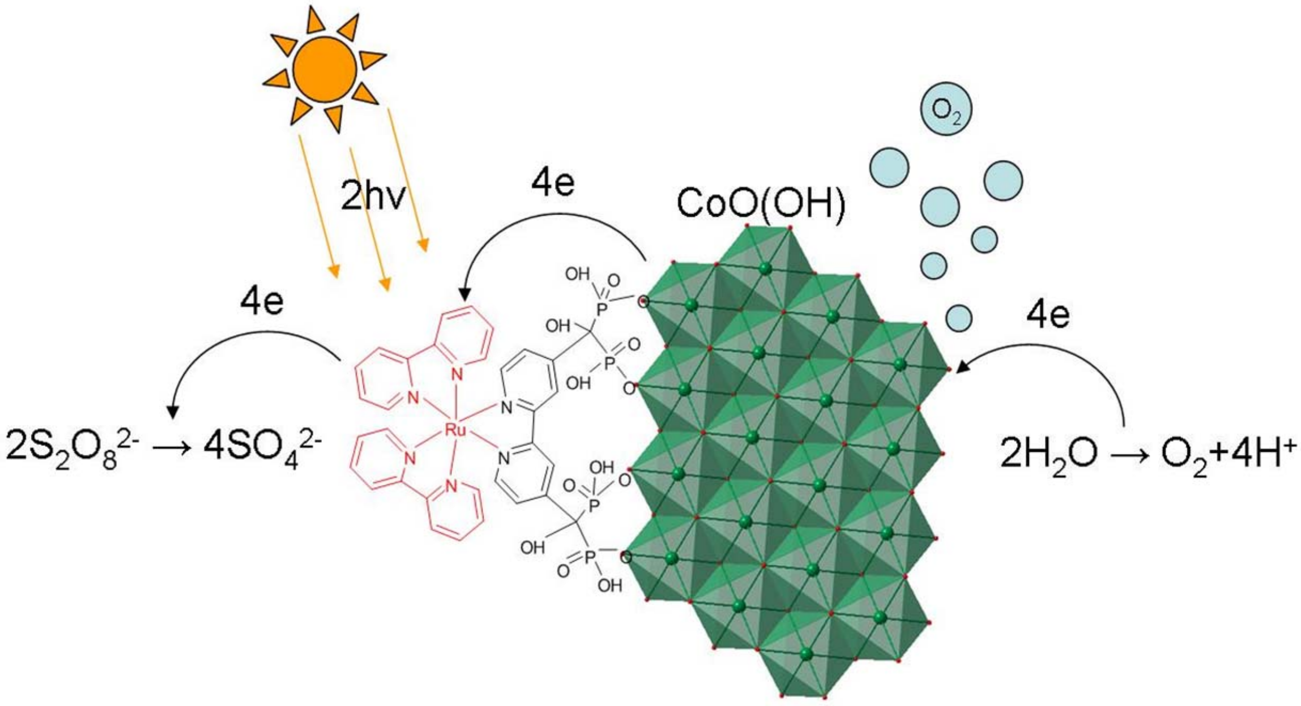


Figure 2. Schematic representation of light-driven water oxidation by a Ru/Co dyad. Upon illumination, the exited state of the ruthenium complex is quenched by electron transfer to a sacrificial electron acceptor peroxodisulfate anion. An electron is then transferred from the cobalt(III) (hydro)oxide nanoparticle to the oxidized ruthenium. In its turn, the nanoparticle withdraws an electron from a water molecule. The catalytic cycle is over when this sequence of electron transfers is repeated four times. As a result, two water molecules are oxidized into one oxygen molecule, and two peroxodisulfate anions are reduced into four sulfate anions. The bipyridyl ligand with two methylenediphosphonate groups, which is shown in black, has been designed and synthesized in this project for the purpose of the connection of a molecular ruthenium photosensitizer with catalytically active cobalt (hydro)oxide nanoparticle.