Final Report

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Publishable project summary

Using the sun's energy to generate hydrogen from water, green hydrogen, is probably the cleanest and most sustainable source of fuel to drive decarbonisation by 2050. Unfortunately, there are currently no catalysts to produce H_2 in this way in an efficient or economically cost effective manner. The RATOCAT project brought together European expertise in first principles catalyst and ALD process simulation, catalyst synthesis and testing, powder ALD and pilot plant testing with the aim to develop improved photocatalysts, together with the processes for their production by ALD and pilot plant testing.

The core hypothesis was that catalytic performance of cheap TiO_2 powders can be improved by tailoring their surface with nanostructured oxides or metals as co-catalysts with highly-controlable composition, nanoarchitecture, size and chemical state.

Tyndall used first principles simulations, within state of the art density functional theory (DFT) to design the optimum heterostructures of modified TiO_2, with different nanoclusters for each of the water splitting half reactions: metal oxide modifiers for oxygen evolution and chalcogenides or bimetallics for hydrogen evolution. DFT predicted alkaline earth oxide-modified TiO_2 for OER, as well as with MnO_x-modified TiO_2. These showed low overpotentials for OER. For HER, we predicted ZnS and SnS-modified TiO_2, and TiO_2 modified with PdCu bimetallics that show free energies of H adsorption close to the taget of 0 eV.

These catalysts were prepared and characterised at **ICMS**, with a focus on TiO_2 modified with alkaline earth oxide species for OER and modified with PdCu for HER and enhanced stability. The alkaline earth oxide-modified TiO_2 shows that highly dispersed MgO species can be deposited and this catalyst shows a notable enhancement in the oxygen evolution compared to unmodified TiO_2. For HER, the CuPd system, in which Cu is galvanically incorporated into Pd, shows enhanced stability over pure Pd and significant hydrogen production. Finally, arising from these studies, a novel thermal-photocatalytic system was developed which showed a high level of activity, with 8 - 10 % efficiency for HER, and these will be explored further at ICMS.

At **TU Delft** the surface of TiO_2 powders was modified using ALD deposited ultra-fine clusters of different co-catalysts. The experimental results for CeO_2 ALD indicated that the ALD deposition of CeO_2 in our experimental condition is not favourable; this was in line with the results of simulations. Later, TiO_2 nanoparticles were modified using ALD deposited MnO_x and CuO_x clusters. The MnO_x/iO_2 samples showed some improvement toward solar hydrogen production. The CuO_x modified TiO_2 particles showed a significant photocatalytic activity improvement over pure TiO_2. Two catalysts have been tested (Cu/TiO_2 and $CuO+TiO_2$) to produce hydrogen in a solar driven pilot plant scale photocatalytic reactor at **PSA**. Different electron donor aqueous solutions (including municipal wastewater treatment plant influent) have been tested showing and similar or even higher energy efficiency compared to the more expensive noble metal based photocatalytic systems. Glycerol solutions provided the best reactive environments for hydrogen generation. The solar to hydrogen energy conversion factor (STH, amount of chemical energy stored in the produced H_2 vs. amount of solar energy accumulated in the solar reactor) was 2.6%.