FINAL PUBLISHABLE SUMMARY REPORT

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Project acronym:	4G-PHOTOCAT
Project title:	Fourth generation photocatalysts: nano-engineered composites for water decontamination in low-cost paintable photoreactors
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1. Executive summary

Heterogeneous photocatalysis is potentially one of the cheapest and most efficient methods for decontamination of water and air from toxic organic pollutants since highly oxidizing conditions can be established without any further reagents needed – the only prerequisite is the supply of aerobic oxygen and sunlight irradiation. Nevertheless, real-life applications of photocatalysis are still rather scarce, particularly because the photocatalytic degradation rates are not high enough, and the costs associated with the photoreactor construction make the implementation economically unviable. The project 4G-PHOTOCAT (www.4g-photocat.eu) therefore allied the expertise of 7 academic and 3 industrial partners from 5 EU countries (Germany, United Kingdom, Czech Republic, Poland, and Finland) and 2 ASEAN countries (Malaysia and Vietnam) for the development of a novel generation of low-cost nano-engineered photocatalysts for sunlight-driven water depollution.

Through rational design of composites in which the solar light-absorbing semiconductors are coupled to nanostructured redox co-catalysts based on abundant elements, the recombination of photogenerated charges is suppressed and the rate of photocatalytic reactions is enhanced. Within this project, large sets of highly active, novel composite photocatalysts based on commercially available TiO_2 powders (used as benchmark starting materials) coupled to low-cost redox cocatalysts have been developed and tested, exhibiting enhanced activities (by factors of 2 to 7) as compared to conventional benchmark TiO_2 photocatalysts.

Furthermore, protocols have been developed by an industrial partner (Advanced Materials JTJ) for implementation of the photocatalysts into a liquid paint, allowing for deposition of robust photoactive layers onto flat surfaces. In addition, several types of novel photocatalytic reactors have been designed and developed. Such photoreactors based on paintable coatings have been successfully tested under real-sunlight conditions, and they are envisaged as low-cost devices for detoxification of water from highly toxic persistent organic pollutants in remote rural areas of Vietnam and other countries.

In order to achieve fabrication of optimal nanostructures, advanced chemical deposition tools have been developed. Design and optimization of new ALD (Atomic Layer Deposition) reactor constructions was performed by Picosun. These ALD reactor constructions for modification of larger amounts of powder materials were developed in the project and they are already in industrial use at several customer sites.

Apart from the synergy on the industrial level, the specific EU-ASEAN cooperation within 4G-PHOTOCAT offered unique opportunity of intensified collaboration and mutual scientific exchange between scientists from EU and ASEAN countries. Biannual meetings and short-term research exchange visits were practised in order to assure fast progress within the project. Two conferences in Asia (Bangkok, Thailand; Johor, Malaysia) on photocatalysis have been organized. The cooperation networks established within 4G-PHOTOCAT represent a platform for a long-standing scientific exchange and cooperation. The project provided funding for 48 young investigators in the early stage of their career (PhD students and postdocs) who have had the opportunity to visit other partners' labs and obtain valuable scientific and intercultural experiences. This intense exchange is expected to lead to further cooperation in further collaborative projects in the future.

2. Summary description of project context and objectives

People from many countries of the world extensively use pesticides which contaminate drinking and irrigation water with toxic organic compounds. For example, in rural areas of Vietnam, herbicides and dioxins, which are resistant to degradation, made their way into the water cycle during the Vietnam war. Cancer and abnormalities in newborns can be the consequence.

Heterogeneous photocatalysis is potentially one of the cheapest and most efficient methods for decontamination of water from toxic organic pollutants since highly oxidizing conditions can be established without any further reagents needed – the only prerequisite is the supply of aerobic oxygen and sunlight irradiation. Nevertheless, real-life applications of photocatalytic water treatment are still rather scarce, particularly because the photocatalytic degradation rates are not high enough, and the costs associated with the photoreactor construction make the implementation economically unviable. It is well-established that low reaction rates are mainly caused by low quantum yields of photocatalytic reactions (few per cent), meaning that most of the photogenerated charges in the photocatalyst recombine before inducing the desired redox reactions. In particular, the reduction of oxygen by photogenerated electrons is highly important and represents often the limiting step in photocatalytic degradation reactions.

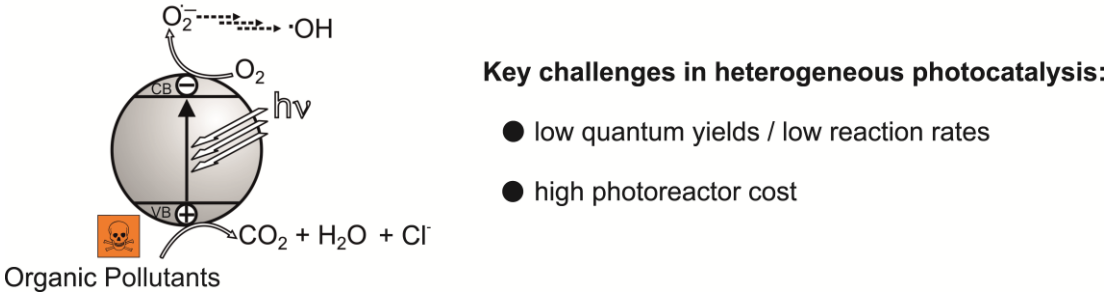

Figure 1: Principle of heterogeneous photocatalalysis: upon light absorption in semiconducting particles electron-hole pairs are generated; toxic organic pollutants are degraded (oxidized) either directly by photogenerated holes or by the action of hydroxyl radicals formed. Efficient reduction of oxygen by photogenerated electrons is highly important for effective photocatalysis.

The **main scientific objective** of the 4G-PHOTOCAT project was to develop a novel generation of low-cost nanoengineered photocatalysts for sunlight-driven water depollution. The newly developed photocatalysts are titanium dioxide particles coupled to nanostructured redox co-catalysts based on cheap and abundant elements. In the presence of the co-catalysts the rate of oxygen reduction reaction is enhanced, which suppresses the recombination of photogenerated charges, and leads to enhanced rates of photocatalytic reactions. In order to achieve fabrication of optimal architectures, advanced chemical deposition techniques with a high degree of control over composition and morphology are being employed and further developed.

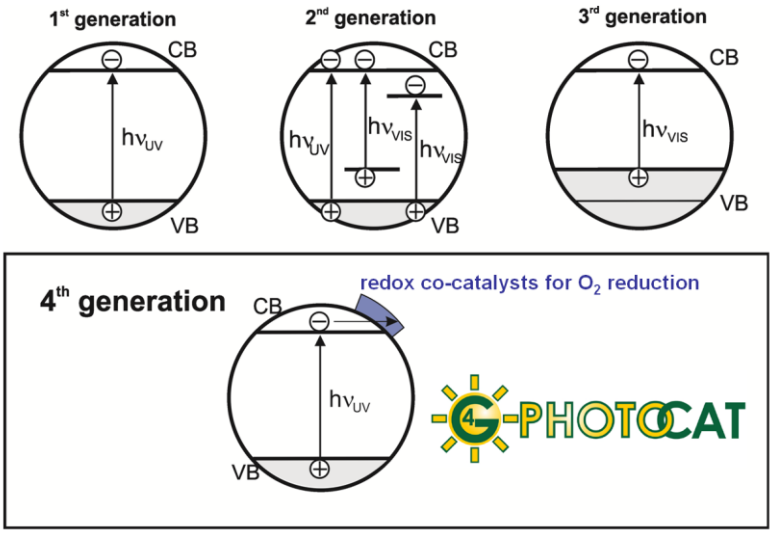

Figure 2: The photocatalyst design concept of **4G-PHOTOCAT** (a low-cost redox co-catalyst is deposited onto TiO_2 photocatalyst to catalyze the reduction of oxygen by photogenerated electrons, and maximizing thus the charge separation and reaction rates) as compared to other strategies for enhancing the photocatalysis at pristine TiO_2 (*1st generation*) by bulk-doping with transition metal ions (*2nd generation*) or main group elements (C, N, S) (*3rd generation*) for visible light activity.

The main **technological objective** of 4G-PHOTOCAT was to develop a highly active composite photocatalyst based on cheap and abundant elements, and to implement it into a liquid paint, allowing for the deposition of robust photoactive layers onto various surfaces on a large scale. Such paintable photoreactors are envisaged as low-cost devices for sunlight-driven detoxification of irrigation as well as drinking water from highly toxic persistent organic pollutants (POPs) in remote rural areas of Vietnam and other countries.

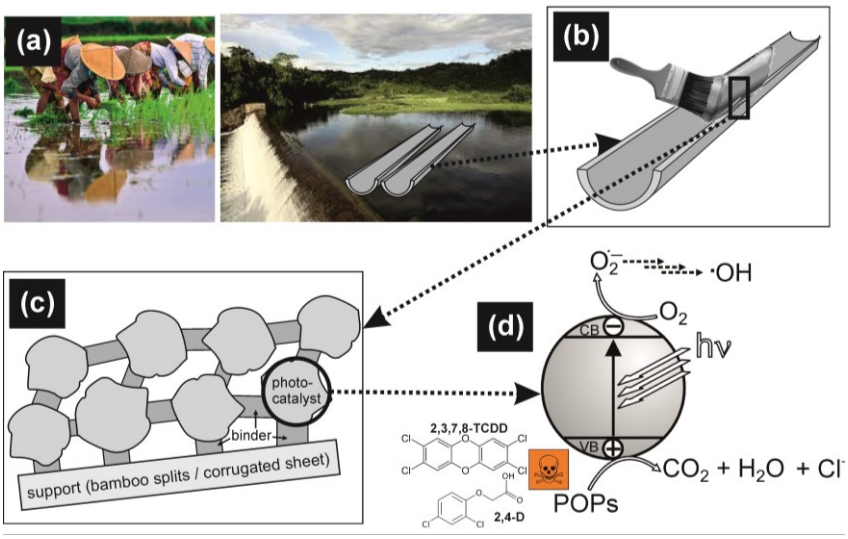

Figure 3: Scheme of the main **technological objective** of 4G-PHOTOCAT: suitable substrates that can be placed into an irrigation water reservoir (a) will be painted by a photocatalyst suspension (b), leading to immobilization of the photocatalyst in the form of a robust layer of photocatalyst particles interconnected by an inorganic binder (c); (d) photocatalytic degradation of highly toxic persistent organic pollutants (POPs).

In order to accomplish these objectives, the 4G-PHOTOCAT project allied the expertise of seven academic and three industrial partners from five EU countries and two Southeast Asian countries:

Table 1: Partners in the 4G-PHOTOCAT consortium.

Participant no.	Participant legal name	Country	Organisation type
1. (Coordinator)	Ruhr-Universität Bochum (**RUB**)	Germany	Academic
2.	University College London (**UCL**)	UK	Academic
3.	Ustav fyzikalni chemie J. Heyrovskeho AV CR, v. v. i. [J. Heyrovský Institute of Physical Chemistry] (**JHI**)	Czech Republic	Academic
4.	Advanced Materials - JTJ sro (**AM**)	Czech Republic	Industrial SME
5.	Uniwersytet Jagiellonski [Jagiellonian University Krakow] (**JUK**)	Poland	Academic
6.	Helsingin Yliopisto [University of Helsinki] (**UH**)	Finland	Academic
7.	Picosun Oy (**PS**)	Finland	Industrial SME
9.	Universiti Teknologi Malaysia (**UTM**)	Malaysia	Academic
10.	Vietnam National University of Agriculture (**HUA**)	Vietnam	Academic
11.	Q&A Ha Noi Ltd (**Q&A**)	Vietnam	Industrial SME

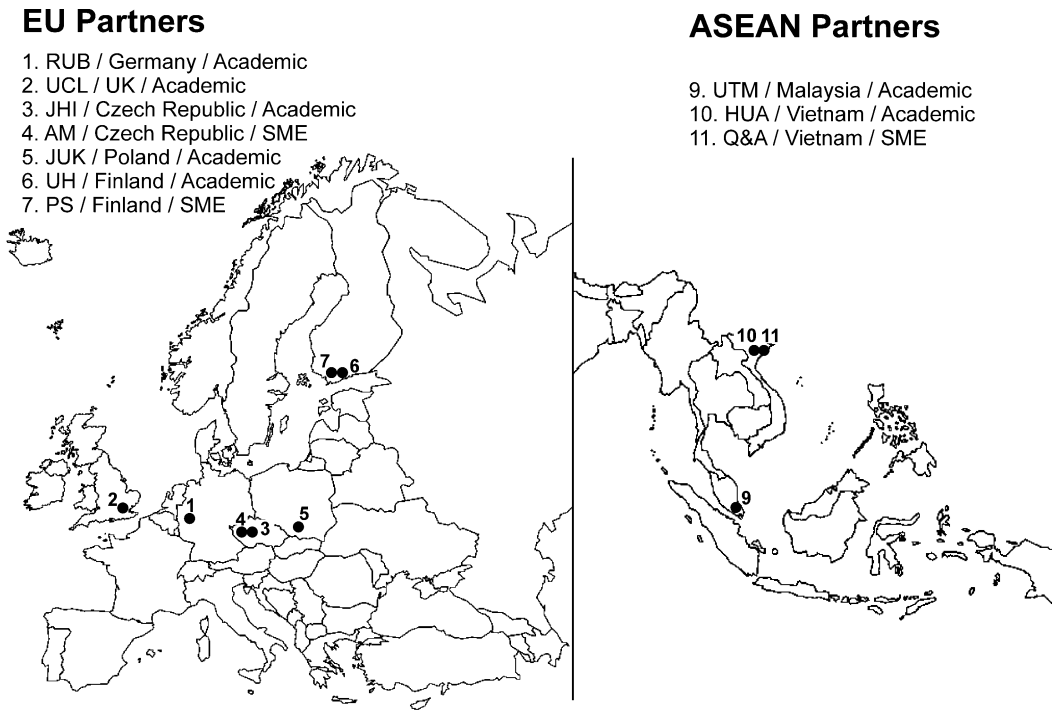

Figure 4: Geographical location of 4G-PHOTOCAT partners.

The 4G-PHOTOCAT project is divided into eight main work-packages plus two WPs for financial and administrative management (WP9), and other activities (WP10). The work-packages were designed in order to ensure smooth workflow from fabrication of novel composite photocatalysts (WP1, WP2, WP3, WP4), their implementation into a paint (WP5), investigating their photocatalytic activity and photochemical/photophysical properties (WP6), supported by theoretical calculations (WP7), to quasi-field tests of detoxification of POP contaminated water in painted photoreactors under real-sunlight irradiation in Vietnam (WP8).

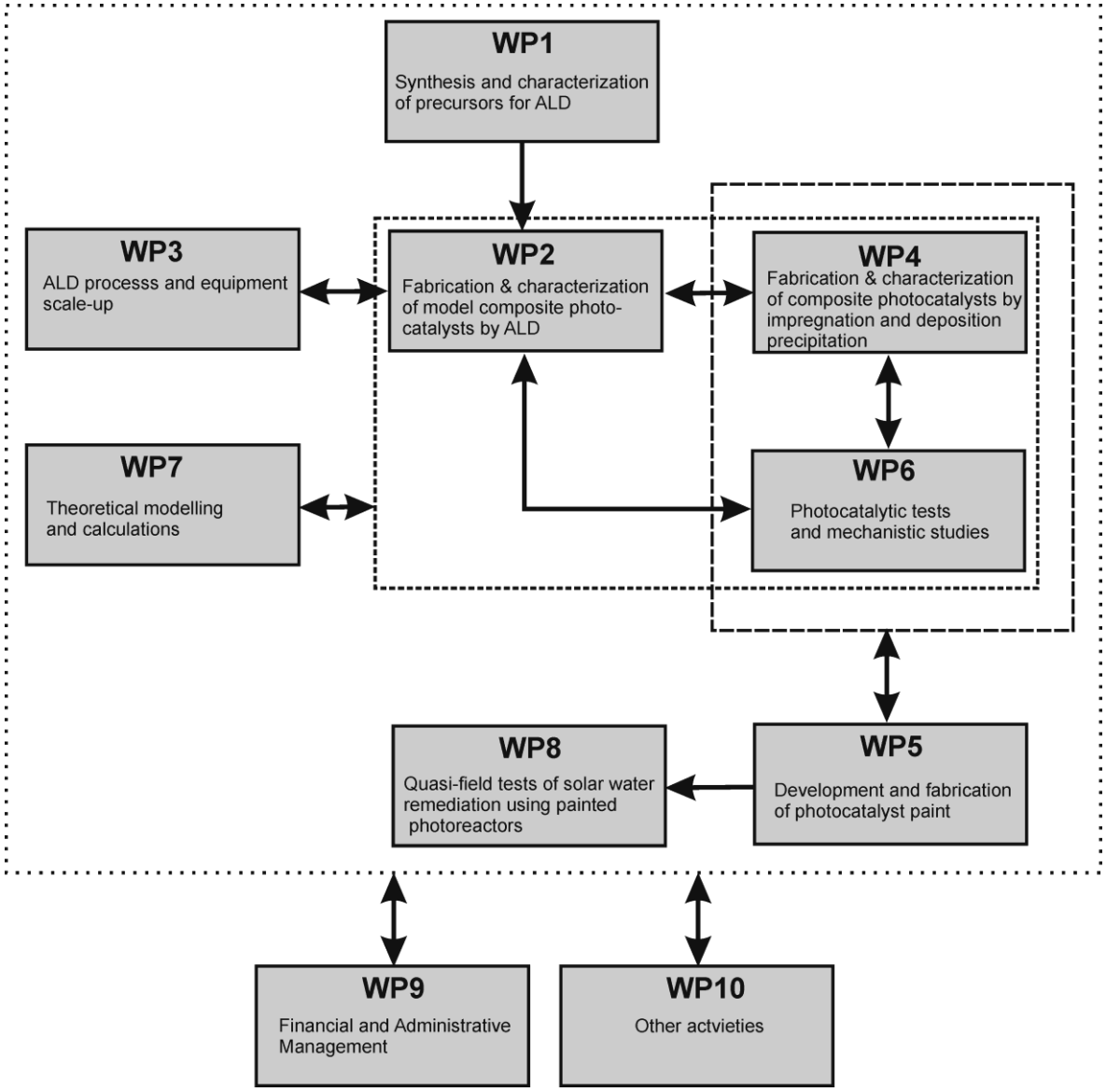

Figure 5: Schematic representation of the 4G-PHOTOCAT workflow (PERT diagram)

3. Description of the main S&T results/foregrounds

The **main achievements** of the 4G-PHOTOCAT project in various work packages are described below.

WP1 (Precursor synthesis) and **WP2 (ALD processing)**

Precursors for atomic layer deposition (ALD) have been synthesized and delivered. Pristine and cocatalyst-modified TiO_2 films have been fabricated by ALD and successfully used in photocatalytic testing as model systems. The photocatalytic properties of these model systems have been studied (Figure 6).

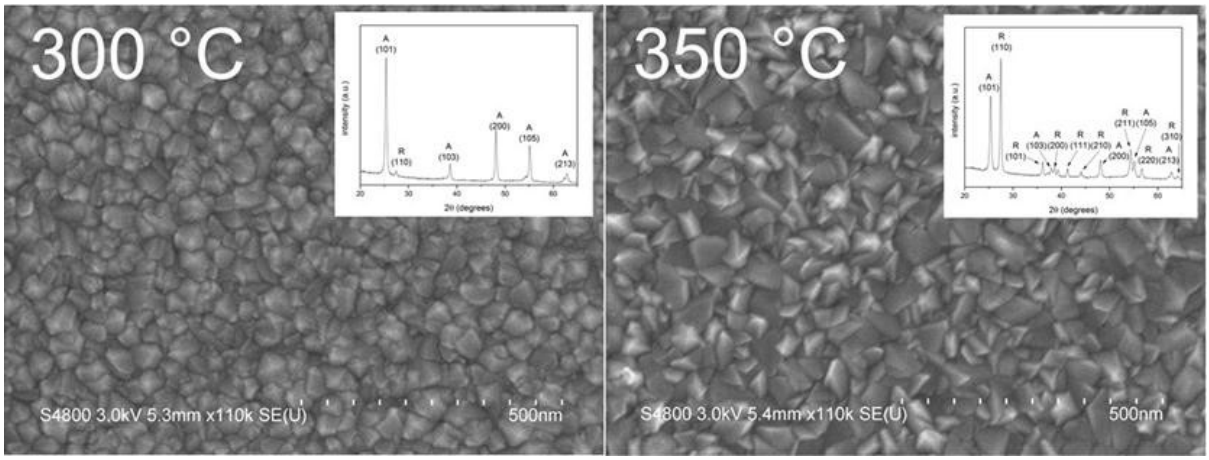

Figure 6. Examples of surface morphologies of about 100–120 nm thick anatase and mixed anatase/rutile TiO_2 films grown on Si wafers using 2500 cycles. Their photocatalytic activities towards Azur B dye, terephtalic acid, and 2,4-D and 2,4,5-T herbicides were evaluated; for more details see: M. Buchalska, M. Surówka, J. Hämäläinen, T. Iivonen, M. Leskelä, W. Macyk "Photocatalytic activity of TiO_2 films on Si support prepared by atomic layer deposition" *Catal. Today* **2015**, *252*, 14-19.

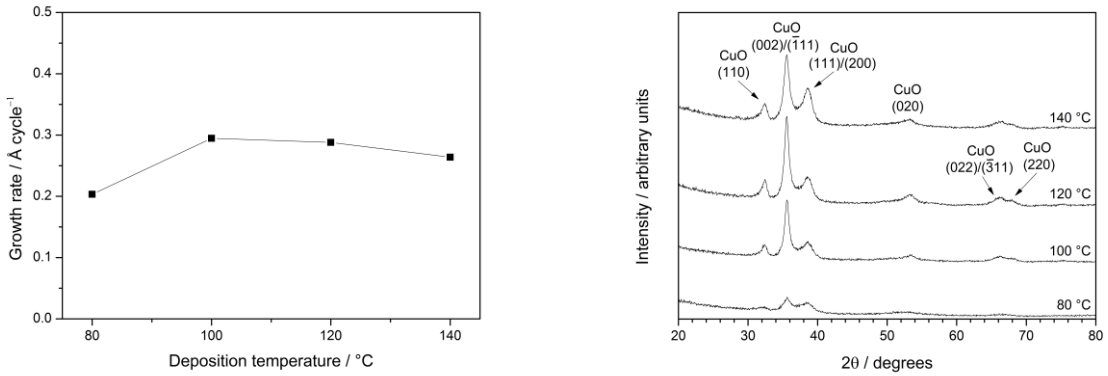

Figure 7. Growth rates and crystallinity of the CuO films deposited on Si (100). For more details see: T. Iivonen, J. Hämäläinen, B. Marchand, K. Mizohata, M. Mattinen, G. Popov, J. Kim, R. A. Fischer, M. Leskelä "Low Temperature Atomic Layer Deposition of Copper(II) Oxide Thin Films" *J. Vac. Sci. Technol. A* **2016**, *34*, 01A109.

A **new ALD process for deposition of copper oxide** using $Cu(dmap)_2$ and ozone was developed and published. Thin films were grown at low deposition temperatures between 80 and 140 °C with a growth rate of 0.2–0.3 Å/cycle (Figure 7). The deposited CuO films were relatively smooth and contained low amount of impurities regardless that the films were grown at low deposition temperatures.

WP3 (ALD reactor development)

Design and optimization of new POCA™ (powder cartridge) ALD reactor constructions for up to hundreds of grams of powders was performed. Simulation of the flow conditions using computational fluid dynamics in complex systems for ALD of powders was also done and it gave valuable knowledge especially for the development of POCA™ systems. The POCA™ construction (Figure 8), especially combined with PicoVibe™, was found to be the best option for upscaling of powders in the present reactor frames of Picosun™ reactors. The new POCA™ constructions with PicoVibe™ designed and tested in the project for the modification of larger amounts of powders **are already in industrial use at Picosun's customers' sites**. The project thus enabled **expansion of ALD technology for new industrial applications**.

Figure 8: ALD reactor constructions (POCA™ 200 & POCA™ 300) for modification of larger amounts of powders (<500 g)

WP4 (Fabrication of photocatalysts) and WP6 (Photocatalytic tests)

Large sets of highly active, novel composite photocatalysts based on commercially available TiO_2 powders (used as benchmark starting materials) coupled to *low-cost* redox cocatalysts have been developed, tested, and investigated in terms of mechanism of photocatalytic performance. These included, for example, TiO_2 modified with Fe_2O_3 cocatalyst by photochemical deposition technique, exhibiting photocatalytic degradation rates enhanced by the factor of 2.2 as compared to pristine P25 TiO_2 materials (Figure 9).

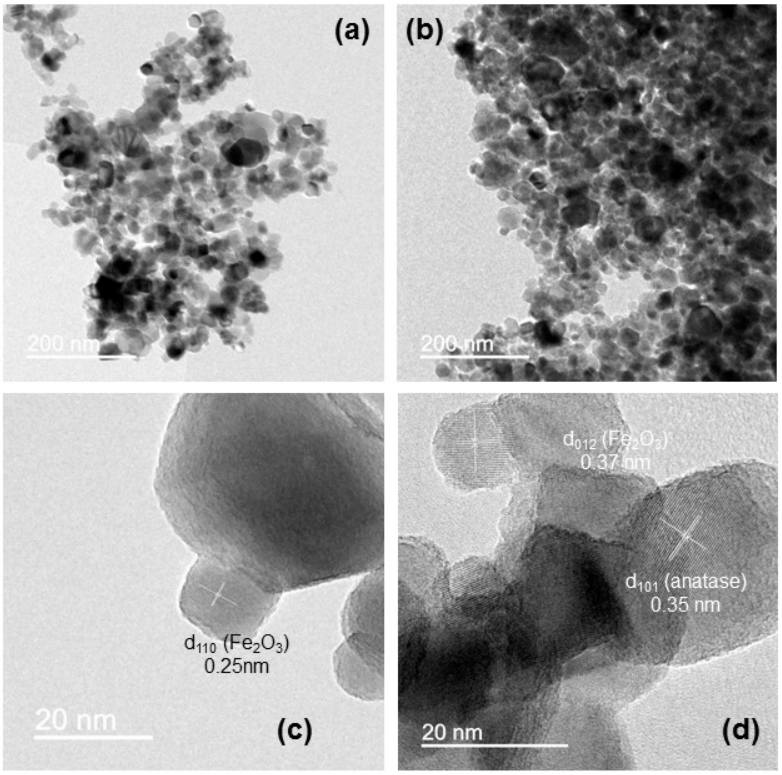

Figure 9: TEM images of (a) P25 TiO_2, (b)10% Fe-TiO_2, (c) and (d) HRTEM images of 10% Fe-TiO_2. Fe2O3-containing photocatalysts have shown highly enhanced (factor of 2.2) photocatalytic activity in degradation of model herbicide pollutants. For more details see: S. J. A. Moniz, S. A .Shevlin, X. An, Z. X .Guo, J. Tang "Fe_2O_3–TiO_2 Nanocomposites for Enhanced Charge Separation and Photocatalytic Activity" *Chem. Eur. J.* **2014**, *20*, 15571-15579.

Another highly active photocatalysts have been obtained by deposition of CuO cocatalyst using a **novel rapid microwave solvothermal technique**. It was found that a residence time of just five minutes was enough to form crystalline CuO particles in high yield (>80%) using copper(II) acetate hydrate precursor in ethanol solvent at 150 °C (Figure 10). a grey appearance which darkened upon Cu loading. XRD confirm CuO as the crystalline product from the reaction. These materials

exhibited enhanced photocatalytic degradation rates as compared to P25 (enhancement factor of 1.5).

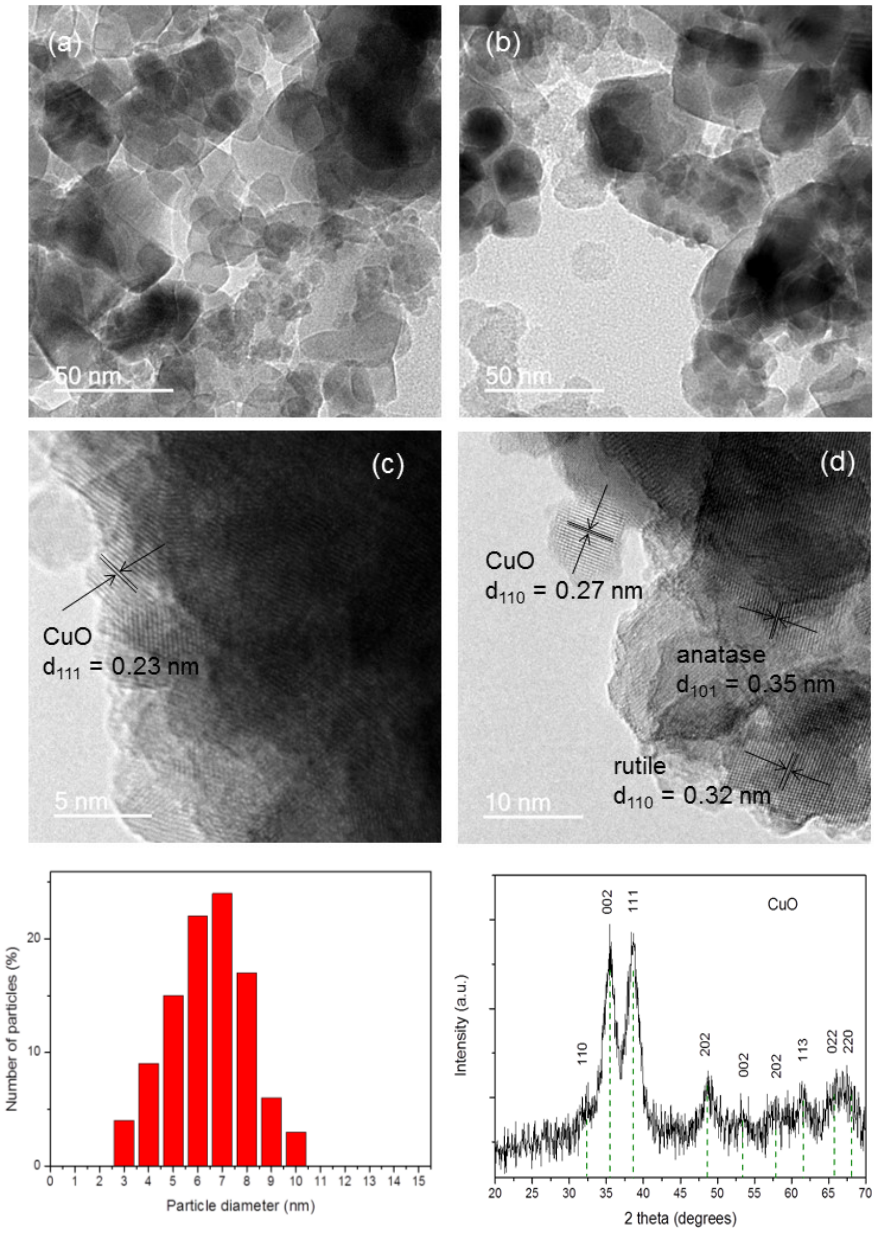

Figure 10: TEM images of (a) P25 TiO_2, (b) 5% CuO/P25; HRTEM of (c) CuO nanoparticles synthesised *via* microwave hydrothermal treatment without TiO_2; (d) 5 wt% CuO-TiO_2 synthesised by microwave hydrothermal synthesis in ethanol. Particle size distribution of CuO nanoparticles formed by microwave treatment without TiO_2 photocatalyst (bottom left); XRD pattern of CuO nanoparticles confirming CuO as the major crystalline phase present (bottom right). For more details see: S. J. A. Moniz, J. Tang "Charge Transfer and Photocatalytic Activity in CuO/TiO_2 Nanoparticle Heterojunctions Synthesised through a Rapid, One-Pot, Microwave Solvothermal Route" *ChemCatChem* **2015**, *7*, 1659-1667.

Another example of newly developed photocatalysts is represented by rutile TiO_2 materials impregnated with ***single*** Cu(II) and Fe(III) cocatalytic sites. Due to the single-ion nature of the redox cocatalytic sites, the parasitic light absorption by the cocatalyst is minimized and the

materials exhibit highly enhanced rates in photocatalytic degradation of organic aqueous pollutants, achieving degradation rates comparable to TiO_2 modified with noble metals like Pt (Figure 11). The exact mechanism of the photoactivity enhancement differs depending on the nature of the cocatalyst. Cu(II)-decorated samples exhibit fast transfer of photogenerated electrons to Cu(II/I) sites, followed by enhanced catalysis of dioxygen reduction, resulting in improved charge separation and higher photocatalytic degradation rates. At Fe(III)-modified rutile the rate of dioxygen reduction is not improved and the photocatalytic enhancement is attributed to higher production of highly oxidizing hydroxyl radicals produced by alternative oxygen reduction pathways opened by the presence of catalytic Fe(III/II) sites. Importantly, the single isolated ion nature of the catalytic sites **makes this type of materials distinct** from more conventional visible light-active modified TiO_2 or TiO_2 composites with heterojunction structure, and also from "single site photocatalysts" based on light-absorbing metal ion species dispersed on the surface of zeolites or silica. As the photocatalytic activity of most photocatalysts is known to be highly substrate-specifc and depending also on a complex interplay of many material properties (crystallinity, porosity, surface area, relative amounts of specic crystal facets, etc.), the demonstrated variety of mechanisms of photoactivity enhancement at single site catalyst-modifed photocatalysts **holds promise for developing many novel, tailored photocatalysts for various applications**.

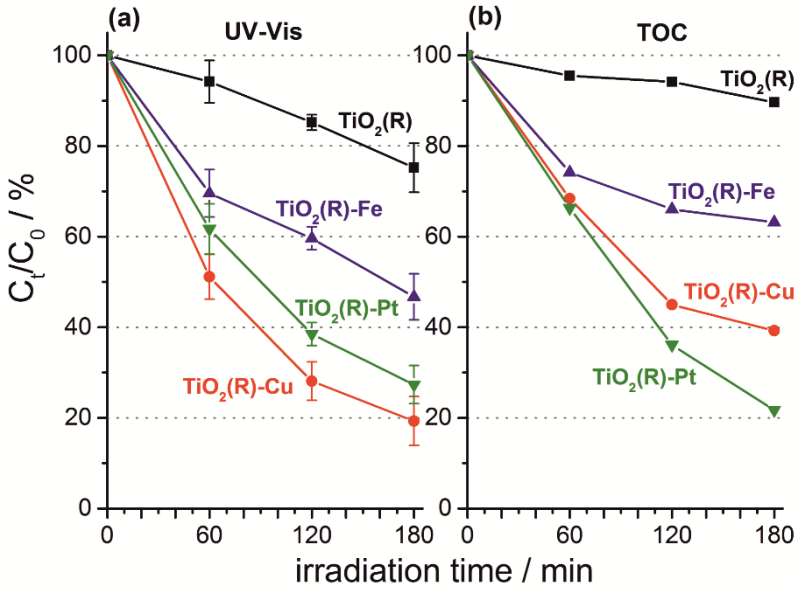

Figure 11. Comparison of test organic pollutant degradation monitored by UV-Vis spectroscopy (a) and Total Organic Carbon analysis (b). The newly developed photocatalyst based on *low-cost* redox cocatalysts (Cu, Fe) exhibit enhanced degradation rates (by the factor of 4 to 7) as compared to pristine TiO_2 photocatalysts, comparable to photocatalysts containing noble metals (Pt). For more details see: S. Neubert, D. Mitoraj, S. A. Shevlin, P. Pulisova, M. Heimann, Y. Du, G. K. L. Goh, M. Pacia, K. Kruczala, S. Turner, W. Macyk, Z. X. Guo, R. K. Hocking, R. Beranek, "Highly Efficient Rutile TiO_2 Photocatalysts with Single Cu(II) and Fe(III) Surface Catalytic Sites" *J. Mater. Chem. A.* **2016**, *4*, 3127-3138.

WP5 (Photocatalyst paint coatings)

The paintable coatings produced by Advanced Materials JTJ have been further developed. The coatings parameters meet requirement of photocatalyst coatings painted onto substrates exhibit long-term (> 2 weeks) stability in aqueous media under irradiation. The coatings are capable of a long-term existence in aqueous environment on most of the common materials while preserving the photocatalytic efficiency.

Bulk quantities of the commercially available TiO_2 coatings were produced and shipped to project partners in Vietnam for the pilot reactor testing. The amount of materials (250 liters) was suitable to run the large reactors for several months and treat 2 000 000-10 000 000 liters of contaminated water. Several personal visits were arranged at HUA and Q&A to help with the experimental design on site.

Synergies of the new compositions with functionalized binding systems were designed and investigated. Hundreds of development compositions of photocatalytic coatings with multifunctional binders were prepared (Figure 12). Samples of the selected compositions were provided to the partners for performance characterization. Durability and photocatalytic performance of the compositions were tested. In the final stage of the project, bulk quantities of photocatalyst paint coatings based on newly developed composite photocatalysts were produced and transferred to partners in Vietnam for the pilot reactor testing.

Figure 12: Advanced Materials JTJ prepared close to 200 composition designed to provide improved mechanical properties, especially adhesion to the substrate and durability in water.

WP7 (Theoretical calculation)

Several different metal-oxide systems were studied. The bulk band structure of these materials was calculated, and experimental data were used to determine what the relative positions of the band edges are. The effects of sensitization of anatase TiO_2 with Fe_2O_3 clusters on the reaction chemistry were studied (based on realistic low energy $(Fe_2O_3)_n$ clusters, particularly their reaction chemistry with the (101) surface and the mechanisms of charge transfer from the anatase TiO_2 to the iron oxide material.

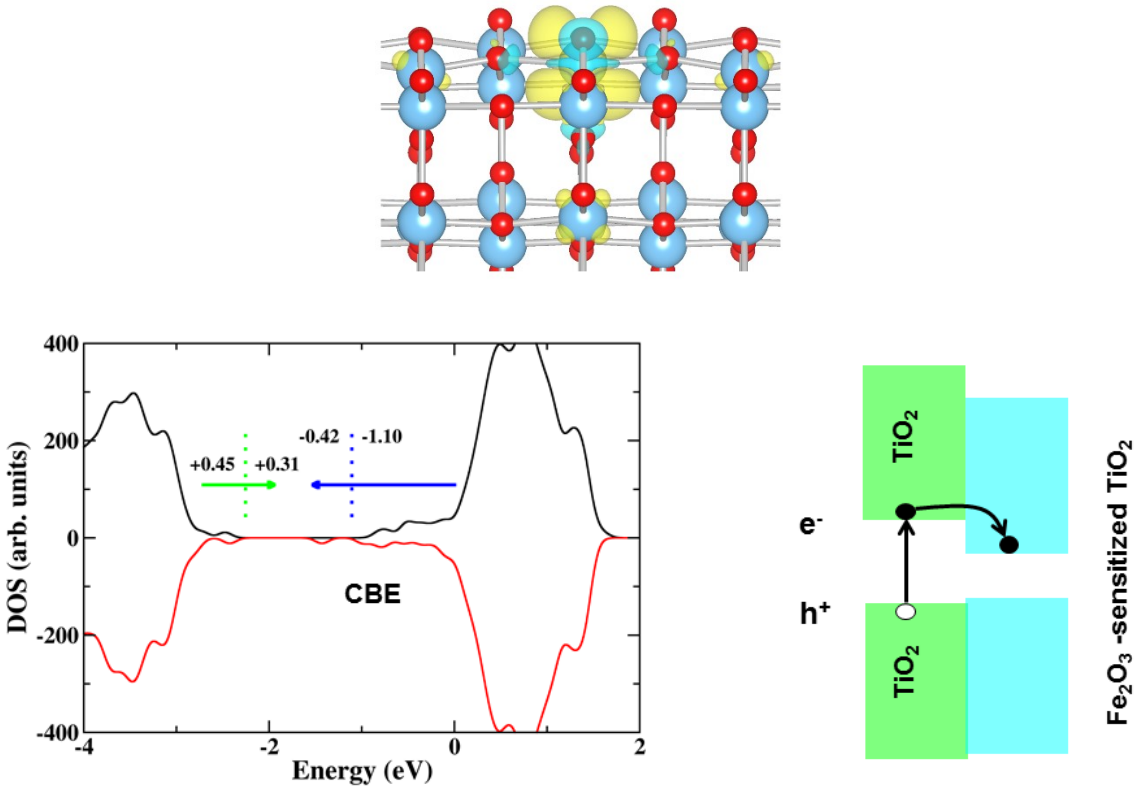

Figure 13: Top is distribution of electron polaron on the (101) surface of anatase, with polaron forming on a single surface Ti atom. Bottom (left) is DOS for anatase-(101) surface co-doped with Fe_2O_3, with alignment of levels and polaron relaxation energies given. Bottom (right) is proposed alignment diagram for this system. The implication is that upon photoexcitation there is a charge transfer of the photoelectron from the anatase to the iron oxide, reducing recombination. For more details see: S. J. A. Moniz, S. A .Shevlin, X. An, Z. X .Guo, J. Tang "Fe_2O_3–TiO_2 Nanocomposites for Enhanced Charge Separation and Photocatalytic Activity" *Chem. Eur. J.* **2014**, *20*, 15571-15579.

Furthermore, the effects of single ion transition metal cocatalysts, specifically Cu(II) and Fe(III), on the charge separation properties of rutile TiO_2-(110) surfaces was investigated, providing valuable confirmation of experimental mechanistic insights (Figure 7).

In addition, the degradation processes of the volatile organic compounds during photocatalysis have been modelled.

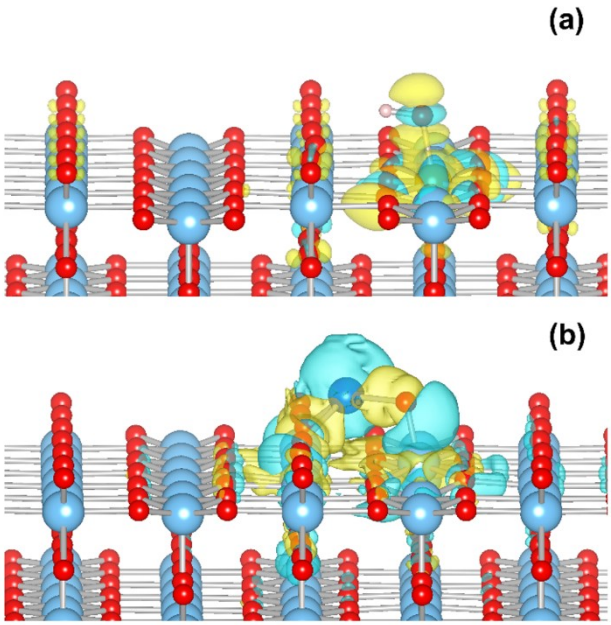

Figure 14. (a) Charge density difference for the TiO_2(R)-Fe(V_{Ti}) system upon electron injection and polaron relaxation. (b) Charge density difference for the TiO_2(R)-Cu system upon electron injection and polaron relaxation. Blue represents charge density accumulation, yellow charge density depletion. These calculations highlight an important difference in the mechanism of photocatalytic degaradtion enhancement at photocatalyst modified with Cu(II) and Fe(III) cocatalytic sites. For more details see: S. Neubert, D. Mitoraj, S. A. Shevlin, P. Pulisova, M. Heimann, Y. Du, G. K. L. Goh, M. Pacia, K. Kruczala, S. Turner, W. Macyk, Z. X. Guo, R. K. Hocking, R. Beranek, "Highly Efficient Rutile TiO_2 Photocatalysts with Single Cu(II) and Fe(III) Surface Catalytic Sites" *J. Mater. Chem. A.* **2016**, *4*, 3127-3138.

WP8 (Quasi-field photoreactor testing)

Several new devices and techniques for solar photocatalytic detoxification of drinking and irrigation water have been developed and tested. Screening of contaminated sites and relevant pollutants in Vietnam has been carried out. Quasi-field solar experiments of solar photocatalytic purification of real water have been performed and evaluated.

At the J. Heyrovský Institute of Physical Chemistry, Prague, Czech Republic, advanced research has been performed including design, construction and testing of pilot solar photoreactors for decontamination of drinking water and semi-field solar decontamination of surface water by floating photocatalysts.

At the Vietnam National University of Agriculture, investigation of solar photocatalysis has been realized including the design, construction and testing of solar photoreactors for decontamination of drinking water. Several photoreactors have been developed and installed at the Vietnam National University of Agriculture in Hanoi, Vietnam (see Figure 15). Also solar decontamination of surface water by floating photocatalysts has been successfully tested. Parameters like suitability of different support materials, commercial as well as newly-developed for the photocatalytic coating

and investigation of various factors influencing the photoefficiency (such as aeration, surface area of the photocatalytic coating, thickness of the photocatalytic layer, durability of the photocatalytic paint) has been investigated. Experimentation with mirrors led to the enhancement of solar efficiency by factor of 1.3. The enhancement of degradation rates in quasi-field tests using newly developed composite photocatalysts was ca. 1.2 so far (painted coatings based on modified TiO_2 vs. benchmark TiO_2 paint). However, it should be noted that several composite photocatalysts newly developed within 4G-PHOTOCAT have shown much more enhanced degradation rates (by factors 2-7) in laboratory testing. Accordingly, further experimental efforts in quasi-field testing are expected to yield comparable enhancement factors.

Two different photoreactors for solar photocatalytic decontamination of drinking water and one photoreactor for standard tests of photocatalytic activity will be protected as **utility models**.

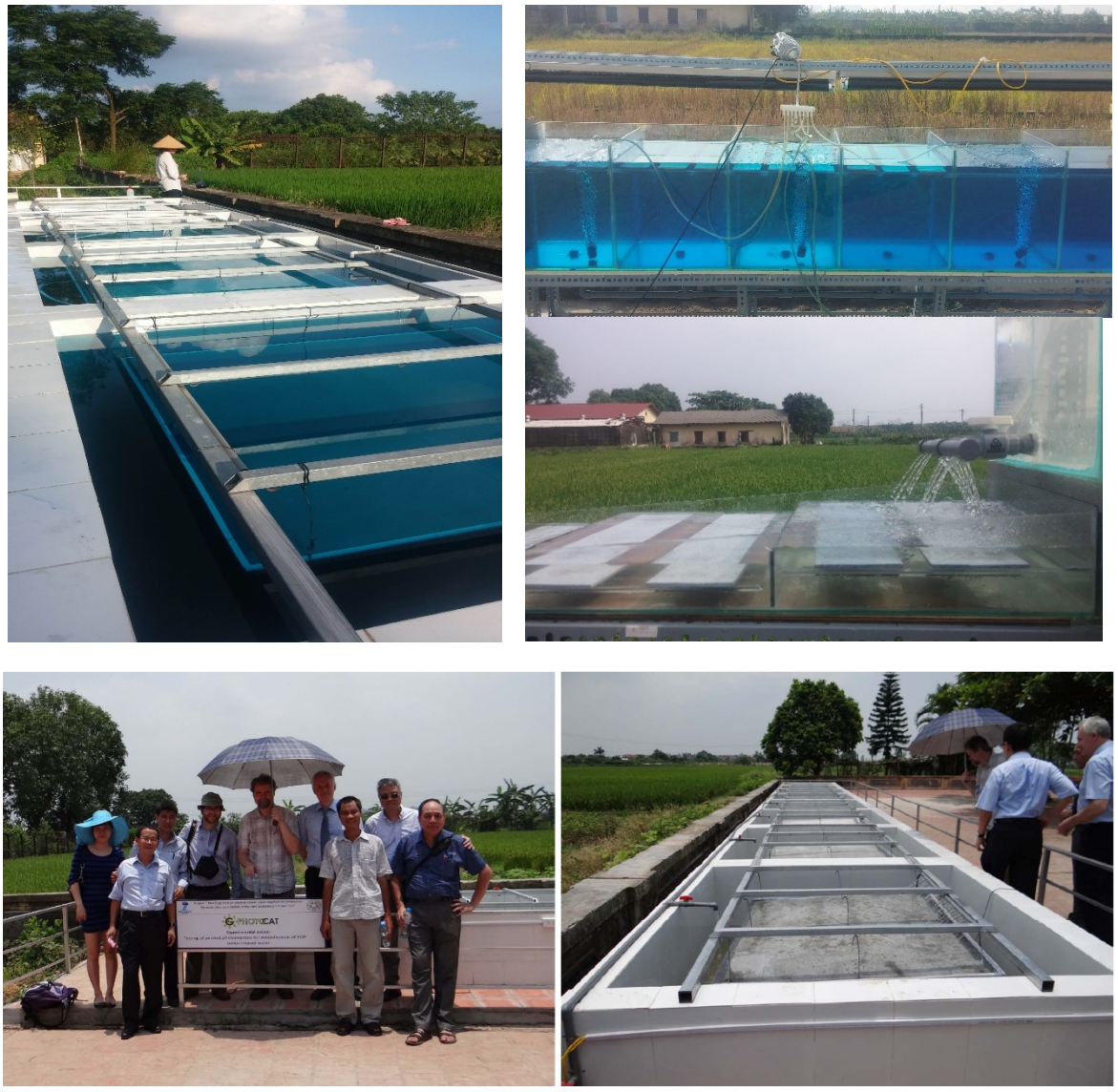

Figure 15. Solar photoreactors installed at the Vietnam National University of Agriculture in Hanoi, Vietnam.

4. The potential impact and the main dissemination activities and exploitation of results

The **main scientific objective** of 4G-PHOTOCAT was to develop novel composite photocatalysts with enhanced efficiency and to understand the correlation between compositional and structural properties of the nanostructured composite, and the photocatalytic reaction rates and degradation mechanisms under solar irradiation. The **main technological objective** of 4G-PHOTOCAT was to develop paintable photoreactors that will be utilized as low-cost devices for sunlight-driven detoxification of water from highly toxic persistent organic pollutants (POPs) in remote rural areas of Vietnam and other countries. The application of the low-cost painted photocatalytic reactors for water decontamination in remote rural areas of Vietnam and elsewhere will in middle and long term lead to **improvement of health standards** of poor and underprivileged people based in areas affected by the overuse of herbicides and other toxic organic substances.

Moreover, the composite photocatalysts developed within 4G-PHOTOCAT find use also in **other photocatalytic applications** including cleaning of air or solar fuel production, as already exemplified by several publications from the 4G-PHOTOCAT the consortium.

It should be noted that novel routes for synthesis of metal oxide nanomaterials, their advanced characterization and better understanding developed within 4G-PHOTOCAT are expected to have a major **impact on nanotechnology in general**, with possible repercussions on sectors of catalysis, health, environment, energy and transport.

Three different types of newly developed photocatalytic reactor constructions will be **protected by utility models**.

The 4G-PHOTOCAT consortium contains **three industrial partners** all of which are eager to pick up the technological progress of the project for future **commercialisation**.

Picosun, a well-established developer of unique ALD reactors, has developed both up-flow (fluidized bed, PicoFloat™) and down-flow (powder cartridge, POCA™) designs for Picosun® ALD reactors for powders. The new POCA™ constructions with PicoVibe™ designed and tested in the project for the modification of larger amounts of powders **are already in industrial use at Picosun's customers' sites**. The project thus **enabled expansion of ALD technology for new industrial applications.**

Advanced Materials, the SME based in the Czech Republic running production of photocatalytic coatings has already established cooperation with **Q&A Ha Noi**, a small Vietnamese SME founded in order to introduce nanotechnologies to the Vietnamese market. Showing the feasibility of water remediation using paintable photoreactors achieved within 4G-PHOTOCAT will for both partners lead to enhancements of product portfolio (photocatalytic coating applicable in aqueous media)

and increase of sales. Moreover, 4G-PHOTOCAT provides for **AM** and **Q&A enhanced visibility on the highly important market segment of Asian region.** This is crucially important since, due to increasing environmental concerns, the market for photocatalytic environmental applications is expected to boom within the next 10 years. **Advanced Materials** has been selected as a National Champion representing Czech Republic in the 2015/2016 European Business Awards.

EU-ASEAN cooperation

Apart from the above-mentioned synergy on the industrial level, the specific EU-ASEAN cooperation within 4G-PHOTOCAT offered unique opportunity of intensified collaboration and mutual scientific exchange between scientists from EU and ASEAN countries. Biannual meetings and short-term research exchange visits were practised in order to assure fast progress within the project. Two conferences in Asia (Bangkok, Thailand; Johor, Malaysia) on photocatalysis have been organized. The cooperation networks established within 4G-PHOTOCAT represent a **platform for a long-standing scientific exchange and cooperation**. The project provided funding for 48 young investigators in the early stage of their career (PhD students and postdocs) who have had the opportunity to visit other partners' labs and obtain valuable scientific and intercultural experiences. This intense exchange is expected to lead to further cooperation in further collaborative projects in the future.

Conferences organized

- The 12-months meeting was organized (together with LIMPID and PCATDES consortia) in conjunction with a joint workshop on photocatalysis (over 60 participants) within the EU-ASEAN STI Days in Bangkok (21.-23.01.2014).

Figure 16. Participants of the joint workshop on photocatalysis within the EU-ASEAN STI Days in Bangkok, Thailand.

- The final meeting was organized in conjunction with a joint One Day EU-ASEAN Symposium and Workshop on Photocatalysis in Johor, Malaysia, on 24.11.2015 (over 60 participants).

Figure 17. Photos from One Day EU-ASEAN Symposium and Workshop on Photocatalysis in Johor, Malaysia (24.11.2015).

Engaging with civil society and policy makers

4G-PHOTOCAT members have actively participated in the European Cluster on Catalysis, a coordination and advisory body for the European Commission in the field of catalysis within the Horizon 2020 framework, gathering together EU-funded projects in the field of catalysis, as well as other academic and industrial stakeholders in catalysis at EU level.

Scientific peer-reviewed publications

The project has resulted in 32 peer-reviewed publications so far (as of February 2016; the list of 4G-PHOTOCAT publications will be in future continuously updated at www.4g-photocat.eu).

(32) K. Qi, F. Zasada, W. Piskorz, P. Indyka, J. Gryboś, M. Trochowski, M. Buchalska, M. Kobielusz, W. Macyk, Z. Sojka
"Self-Sensitized Photocatalytic Degradation of Colorless Organic Pollutants Attached to Rutile Nanorods – Experimental and Theoretical DFT+D Studies"
J. Phys. Chem. C **2016**, doi: 10.1021/acs.jpcc.5b10983

(31) S. Neubert, D. Mitoraj, S. A. Shevlin, P. Pulisova, M. Heimann, Y. Du, G. K. L. Goh, M. Pacia, K. Kruczala, S. Turner, W. Macyk, Z. Guo, R. K. Hocking, R. Beranek
"Highly Efficient Rutile TiO_2 Photocatalysts with Single Cu(II) and Fe(III) Surface Catalytic Sites"
J. Mater. Chem. A. **2016**, *4*, 3127-3138.

(30) H. O. Lintang, N. A. Roslan, N. Ramlan, M. Shamsuddin, L. Yuliati
"Photocatalyst Composites of Luminescent Trinuclear Copper(I) Pyrazolate Complexes/Titanium Oxide for Degradation of 2,4-Dichlorophenoxyacetic Acid"
Mat. Sci. Forum **2016**, Vol. „Main Tendencies in Applied Materials Science", 697-701.

(29) L. Yuliati, N. A. Roslan, W. R. Siah, M. Shamsudddin, H. O. Lintang
"Modification of Titanium Dioxide Nanoparticles with Copper Oxide for Photocatalytic Degradation of 2,4-Dichlorophenoxyacetic Acid"
Mal. J. Anal. Sci. **2016**, *20* (1), 171-178

(28) C. Jiang, K Y. Lee, C.M.A Parlett, M. K Bayazit, C.C. Lau, Q. Ruan, S.J.A Moniz, A. F. Lee, J Tang
"Size controlled TiO_2 nanoparticles on porous hosts for enhanced photocatalytic hydrogen production"
App. Catal. A: General doi: 10.1016/j.apcata.2015.12.004

(27) X. An, T. Li, B. Wen, J. Tang, Z. Hu, L. Liu, J. Qu, C.P. Huang, H. Liu
"New Insights into Defect-Mediated Heterostructures for Photoelectrochemical Water Splitting"
Adv. Energy Mater. doi: 10.1002/aenm.201502268

(26) T. Iivonen, J. Hämäläinen, B. Marchand, K. Mizohata, M. Mattinen, G. Popov, J. Kim, R. A. Fischer, M. Leskelä
"Low Temperature Atomic Layer Deposition of Copper(II) Oxide Thin Films"
J. Vac. Sci. Technol. A **2016**, *34*, 01A109.

(25) K. Khaletskaya, A. Pougin, R. Medishetty, C. Rösler, C. Wiktor, J. Strunk, R. A. Fischer
"Fabrication of Gold/Titania Photocatalyst for CO_2 Reduction Based on Pyrolytic Conversion of the Metal–Organic Framework NH2-MIL-125(Ti) Loaded with Gold Nanoparticles"
Chem. Mater. **2015**, *27*, 7248–7257.

(24) M. Buchalska, M. Kobielusz, A. Matuszek, M. Pacia, S.Wojtyla, W. Macyk
"On Oxygen Activation at Rutile- and Anatase-TiO2"
ACS Catal. **2015***, 5,* 7424-7431.

(23) W. R. Siah, H. O. Lintang, M. Shamsuddin, L. Yuliati
"Effect of calcination temperatures on the photocatalytic activities of commercial titania nanoparticles under solar simulator irradiation"
Mal. J. Fundam. Appl. Sci. **2015**, *11*, 106-110.

(22) S. J. A. Moniz, C. S. Blackman, P. Southern, P. M. Weaver, J. Tang, C. J. Carmalt
"Visible-light driven water splitting over $BiFeO_3$ photoanodes grown via the LPCVD reaction of $[Bi(O^tBu)_3]$ and $[Fe(O^tBu)_3]_2$ and enhanced with a surface nickel oxygen evolution catalyst"
Nanoscale **2015**, *39*, 16343-16353.

(21) D. J. Martin, G. Liu, S. J. A. Moniz, Y. Bi, A. M. Beale, J. Ye, J. Tang
"Efficient visible driven photocatalyst, silver phosphate: performance, understanding and perspective"
Chem. Soc. Rev. **2015**, *44*, 7808-7828.

(20) S. J. A. Moniz, J. Tang
"Charge Transfer and Photocatalytic Activity in CuO/TiO_2 Nanoparticle Heterojunctions Synthesised through a Rapid, One-Pot, Microwave Solvothermal Route"
ChemCatChem **2015**, *7*, 1659-1667.
This paper has been featured on the journal front **Cover page**
4G-PHOTOCAT funding has been highlighted in the **Cover profile**

(19) S. Ho-Kimura, S. J. A. Moniz, J. Tang, I. P. Parkin
"A Method for Synthesis of Renewable Cu_2O Junction Composite Electrodes and Their Photoelectrochemical Properties"
ACS Sustainable Chem. Eng. **2015**, *3*, 710–717.

(18) N. A. Roslan, H. O. Lintang, L. Yuliati
"Enhanced Performance of Copper-Modified Titanium Dioxide Prepared by UV Reduction Method"
Adv. Mater. Res. **2015**, *1112*, 180-183.

(17) W. R. Siah, N. A. Roslan, H. O. Lintang, M. Shamsuddin, L. Yuliati
"Photocatalytic Removal of 2,4-D Herbicide on Lanthanum Oxide-Modified Titanium Dioxide"
Adv. Mater. Res. **2015**, *1112*, 168-171.

(16) O. V. Khavryuchenko, L. Wang, D. Mitoraj, G. H. Peslherbe, R. Beranek
"Enabling visible-light water photooxidation by coordinative incorporation of Co(II/III) cocatalytic sites into organic-inorganic hybrids: quantum-chemical modeling and photoelectrochemical performance"
J. Coord. Chem. **2015**, *68*, 3317-3327.

(15) H. M. Stewart, S. A. Shevlin, C. R. A. Catlow, Z. X. Guo
"Compressive Straining of Bilayer Phosphorene Leads to Extraordinary Electron Mobility at a New Conduction Band Edge"
Nano Lett. **2015**, *15*, 2006-2010.

(14) M. Buchalska, M. Surówka, J. Hämäläinen, T. Iivonen, M. Leskelä, W. Macyk
"Photocatalytic activity of TiO_2 films on Si support prepared by atomic layer deposition"
Catal. Today **2015**, *252*, 14-19.

(13) S. J. A. Moniz, S. A. Shevlin, D. J. Martin, Z.-X. Guo, J. Tang
"Visible-light driven heterojunction photocatalysts for water splitting – a critical review"
Energy Environ. Sci. **2015**, *8*, 731-759.

(12) P. Chen, P. Wang, L. Wang, A. Kostka, M. Wark, M. Muhler, R. Beranek
"CNT-TiO_{2-d} composites for improved co-catalyst dispersion and stabilized photocatalytic hydrogen production"
Catalysts **2015**, *5*, 270-285.

(11) X. An, H. Liu, J. Qu, S. J. A. Moniz, J. Tang
"Photocatalytic mineralisation of herbicide 2,4,5-Trichlorophenoxyaceticacid: Enhanced performance by triple junction Cu-TiO_2-Cu_2O and the underlying reaction mechanism"
New J. Chem. **2015**, *39*, 314-320.

(10) C. Jiang, S. J. A. Moniz, M. Khraisheh, J. Tang
"Earth-Abundant Oxygen Evolution Catalysts Coupled onto ZnO Nanowire Arrays for Efficient Photoelectrochemical Water Cleavage"
Chem. Eur. J. **2014**, *20*, 12954-12961.

(9) M. Buchalska, M. Pacia, M. Kobielusz, M. Surówka, E. Swietek, E. Wlazlak, K. Szacilowski, W. Macyk
"Photocatalytic Activity of TiO_2 Modified with Hexafluorometallates—Fine Tuning of Redox Properties by Redox-Innocent Anions"
J. Phys. Chem. C **2014**, *118*, 24915-24924.

(8) S. J. A. Moniz, S. A .Shevlin, X. An, Z. X .Guo, J. Tang
"Fe_2O_3–TiO_2 Nanocomposites for Enhanced Charge Separation and Photocatalytic Activity"
Chem. Eur. J. **2014**, *20*, 15571-15579.

(7) X. Han, H. M. Stewart, S. A. Shevlin, C. R. A. Catlow, Z. X. Guo
"Strain and Orientation Modulated Bandgaps and Effective Masses of Phosphorene Nanoribbons"
Nano Lett. **2014**, *14*, 4607-4614.

(6) M. Bledowski, L. Wang, S. Neubert, D. Mitoraj, R. Beranek
"Improving the Performance of Hybrid Photoanodes for Water Splitting by Photodeposition of Iridium Oxide Nanoparticles"
J. Phys. Chem. C **2014**, *118*, 18951-18961.

(5) D. J. Martin, P. J. T. Reardon, S. J. A. Moniz, J. Tang
"Visible light-driven pure water splitting by a nature-inspired organic semiconductor based system"
J. Am. Chem. Soc. **2014**, *136*, 12568–12571.

(4) S. M. Ho-Kimura, S. J. A. Moniz, A. D. Handoko, J. Tang
"Enhanced photoelectrochemical water splitting by nanostructured $BiVO_4$-TiO_2 composite electrodes"
J. Mater. Chem. A **2014**, *2*, 3948-3953.

(3) X. An, J.C. Yu, J. Tang
"Biomolecule-assisted fabrication of copper doped SnS_2 nanosheet-reduced graphene oxide junctions with enhanced visible-light photocatalytic activity"
J. Mater. Chem. A **2014**, *2*, 1000-1005.

(2) S. Neubert, P. Pulisova, C. Wiktor, P. Weide, B. Mei, D. A. Guschin, R.A. Fischer, M. Muhler, R. Beranek
"Enhanced photocatalytic degradation rates at rutile TiO_2 photocatalysts modified with redox co-catalysts"
Catal. Today **2014**, *230*, 97-103.

(1) S. Neubert, A. Ramakrishnan, J. Strunk, H. Shi, B. Mei, L. Wang, M. Bledowski, D. A. Guschin, M. Kauer, Y. Wang, M. Muhler, R. Beranek
"Surface-Modified TiO_2 Photocatalysts Prepared by a Photosynthetic Route: Mechanism, Enhancement, and Limits"
ChemPlusChem **2014**, *79*, 163-170.

Publications in professional magazines

(2) S. Ożóg
"Fotokatalityczna degradacja herbicydów – nowe katalizatory na bazie TiO_2"
Wiadomości Chemiczne **2015**, *69* (7-8), 605–616.

(1) R. Beranek, S. Neubert
"Chemie unter der Sonne: Neue photoaktive Materialien für Energiekonversion und Umweltschutz"
GIT Labor-Zeitschrift **2014**, *58/3*, 72-75.

Talks & conference contributions

140 conference contributions (for the full list see www.4g-photocat.eu)

4G-PHOTOCAT posters have been awarded **two Best Poster Prizes** at international conferences:

SP-4, "4th International Conference on Semiconductor Photochemistry", Prague (Czech Republic), 23.-27.06.2013

IPS-20, ”20th International Conference on the Conversion and Storage of Solar Energy”, Berlin (Germany), 27 July – 1 August 2014

Figure 18. 4G-PHOTOCAT researchers Petra Pulišová and Susann Neubert (both RUB) were awarded the best poster prize at the SP-4 conference in Prague (left) and at the IPS-20 conference in Berlin (right).

Theses and Dissertations

4G-PHOTOCAT research has resulted in ten bachelor, master, and PhD theses so far:

- Master thesis: "*Synthesis and characterization of TiO_2 photocatalysts modified with redox co-catalysts"* by Manuel Heimann at Ruhr-Universität Bochum, Germany (13.10.2014).
- Master thesis: "*Powder coating capacity of atomic layer deposition reactor*" by Timo Vähä-Ojala at Aalto University School of Engineering, Picosun Oy, Finland (16.12.2014).
- Master thesis: "*Degradation of methylene blue on commercial photocatalysts under solar light*" by Nguyen Thi Thoa at HOC VIEN NONG NGHIEP VIET NAM (30.11.2015).
- Master thesis: "*Investigating factors effect on photoactivity of commercial TiO_2 (FN2)*" by Nguyen Le Thuy at HOC VIEN NONG NGHIEP VIET NAM (30.06.2015).
- Bachelor thesis: "*Controlled Deposition of Redox Cocatalysts onto Anatase TiO_2 for Water Remediation"* by Alina Gawel at Ruhr-Universität Bochum, Germany (30.07.2015).
- PhD Thesis: "*Interface Engineering of Photocatalysts for Water Decontamination and Artificial Photosynthesis of Fine Chemicals*" by Susann Neubert at Ruhr-Universität Bochum (11.12.2015).
- Master thesis: "*Fotokatalityczna degradacja herbicydów: kontrola fotoaktywności TiO_2 poprzez domieszkowanie tlenkami wolframu i molibdenu*" by Sabina Ożóg at Jagiellonian University in Cracow (18.09.2015).
- Master thesis: "*Preparation and characterization of iron modified TiO_2 photocatalysts utilizing a $[Fe(NH_3)_6]^{2+}$-complex*" by Annika Diekmann at Ruhr-Universität Bochum (December, 2015).
- PhD Thesis: *Title to be announced*; by Jiyeon Kim at Ruhr-Universität Bochum (expected in December, 2016).
- PhD Thesis: Tentative title: “Atomic Layer Deposition of Transition Metal Oxide Thin Films for Photocatalytic Application” by Tomi Iivonen (University of Helsinki); (expected in December, 2016).

Further Dissemination Activities

Further dissemination activities included press releases, numerous TV, radio, and press coverages, distribution of flyers, and presentations of 4G-PHOTOCAT at large interactive events including EuroNanoForum 2013 in Dublin, Ireland (18.-20.06.2013). and EuroNanoForum 2015 in Riga, Latvia (10.-12.06. 2015). A few selected dissemination results are listed below:

- *Fotokataliza – czy farba może oczyścić wodę?* prepared by Polish internet portal (rynekfarb.pl, 25.04.2013).
- A short article Zavádění fotokatalýzy do každodenního života published on the web of Akademický bulletin in Czech republic.
- On April 6th the project has been presented in TVP Kraków (Polish regional television) in "Kronika" magazine. The link to the record is here (it starts at 12:35 of the record).
- A web article prepared by the Centre for Innovation, Technology Transfer and University Development (CITTRU) of JUK (18.03.2013).
- The concrete answer to pollution by Horizon – The EU Research & Innovation Magazine (18.12.2014).
- „4G-PHOTOCAT"- Rettung für das Trinkwasser? by global° - Magazine für nachhaltige Zukunft (ausdruck.AGENTUR), 21.02.2013, updated 03.12.2015.

5. The address of the project public website and project logo

Project webpage: www.4g-photocat.eu

6. The project principal investigators' contact details

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