# Functionalized nanofiber-enhanced filter media for fine particles and heavy metal removal in flue gases

Project A9.6 NANOFIL (PSI, FHNW, Alstom AG Birr)
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Collaborators: M. Tarik, M. Paraskevopoulos, F. Pilger, A. Testino, M. Waser, U. Pieles, D. Winkler, G. Timothy, I. Thanou, M. Bialkowski

### Introduction

In order to improve the performance of the current fabric filter systems, e.g. more efficient fine particle removal and higher specificity for heavy metals, either in the ionic or in the elemental state, an entirely new approach was planned. The strategy was to develop materials with high specific surface area, thermal and mechanical stability, and functionalized with sulfur (S) groups, which have high specificity for heavy metals.

During the first year, the "NANOFIL" project was devoted to the development of new organic, inorganic, and composite nanofibers. The organic nanofibers are produced by electrospinning, the inorganic material is based on hydrothermally prepared cerium dioxide ($CeO_2$) nanorods, and the composites were produced by electrospinning a polymer solution containing $CeO_2$ spherical nanopowders. Based on the ongoing work, the produced nanofibers are currently under optimization. In the second year of the project, the synthesized fibers will be tested by using an in-house constructed setup, to evaluate their sorption properties, regenerability, and thermal stability.

### Synthesis of nanofibers

For the selection of the base filter material, the flue gas temperature, continuous and peak, is the most important criterion for filter media selection. Fibers can survive short term exposure to temperatures above their continuous operating temperature limit, but the high heat will degrade them. Additionally, chemical attack, such as contacts with acids and alkalis, can have similar effect. For the manufacturing of the project's filter media, two materials have been selected: polyphenylene sulfide (PPS) and P84 (Polyimide). The latter has outstanding properties such as high temperature stability, good chemical resistance, high mechanical strength and minimal abrasion. Since the nanofibers will be applied in the same environment as the base material, P84 was also chosen as the material for the electrospinning. P84 was electrospun as a solution in DMF to produce nanofibers that can be tailored from diameters of approx. 60 nm up to 1 µm.

The innovative idea in this project is to develop nanofiber materials able to capture S, which then can then be used to remove specific heavy metals such as Hg from flue gases. One way to achieve that was to modify the P84 material to bear thiol groups which can sorb mercury. Therefore, P84 was allowed to react with cysteamine. The thiol-modified P84 is also soluble in DMF a can be electrospun as P84, albeit with different conditions, since the polymer properties are changed (Fig. 1).

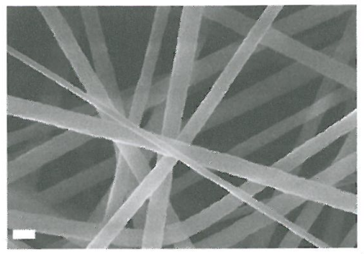

*Fig. 1: Electrospun fibers of thiol-modified P84. Scale bar: 400 nm, magnification: 40000x.*

Alternatively $CeO_2$ nanoparticles were synthesized and their capability to capture sulfur was investigated. The activated nanoparticles can be directly deposited on the base filters or electrospun as composite along with P84 (Fig. 2).

**$CeO_2$ nanoparticles synthesis:** Several batches of $CeO_2$ nanoparticles have been produced with the aim to control the particle morphology. Fig. 3 shows an example of the obtained particles with elongated morphology. These materials can be used in granulated form or integrated in a filtering support. The influence of the particle shape on the S and Hg capturing is currently under investigation. $CeO_2$ nanoparticles with a size of less than 5 nm were produced to be directly immobilized into an inorganic filter material (e.g. glass or quartz). After the synthesis, the particles were washed and dried. The processing promotes particle aggregation (> 1 µm); the aggregates are large enough to be retained by the filtering material. A thermal treatment was applied in order to fix the aggregates on the inorganic support. Some fully inorganic filter with $CeO_2$ nanoparticles have been produced and are currently under testing.

$CeO_2$ nanoparticles (< 3 nm) without any drying treatment were synthesized as well. In this case, the material is used for the preparation of the composite fibers by electrospinning. The particles were collected by chemically induced coagulation and re-dispersed in a solvent compatible with the electrospinning process.





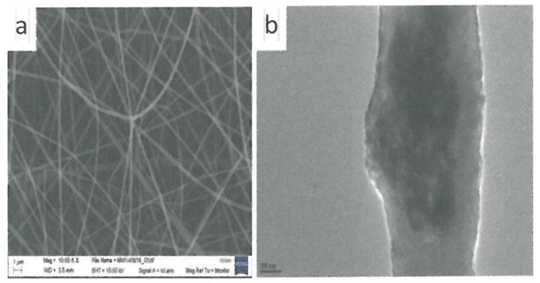


*Fig. 2: Example of electrospun composite fibers: (a) SEM; (b) HR-TEM. A $CeO_2$ nanoparticle aggregate is clearly incorporated in the fiber.*

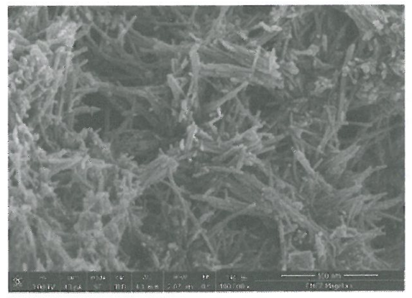

*Fig. 3: Example of synthetized $CeO_2$ acicular particles with tailored size: (a) 500x20 nm.*

**Sulfur adsorption:** Figure 4 reports the preliminary results on S capturing. The sorption was carried out using 1000 ppmV $H_2S$ at 800 °C. The regeneration was done at same temperature with 4 % $O_2$. The material shows excellent sorption capability and it is regenerable. The calculated S/Ce molar ratio is 31 %. The material after S sorption is ready to be tested for Hg capturing.

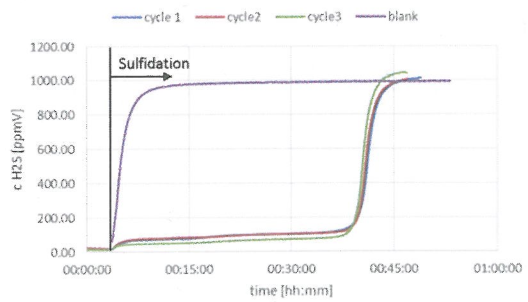


*Fig. 4: Sulfur capturing test carried out on the sample of Fig. 1. The overlapped three curves show the sulfur capturing of the same material after a regeneration cycle.*

### Functionality tests on the developed filters

To test the functionality of nano-coated filters with mercury, a test setup including Hg vaporization, a gas diluter, filter holders, and gas path switch valves have been designed (Fig. 5). A typical Hg concentration in flue gas of coal power plants is 30 µg/m³ [3]. As the vaporization kinetics of mercury may be too slow to achieve saturated Hg atmosphere at 20 °C in a reasonable time, the vaporization should be performed at elevated temperature. The desired saturation concentration at 20 °C will then be achieved by re-condensation of excess vapor. To include any influence of the filter holders and uncoated filter material on Hg content, two identical filter holders for a coated and uncoated filter are provided. This method allows measuring the difference between both filtering materials. The filter holders are maintained at 220 °C and directly connected to the ICP-OES.

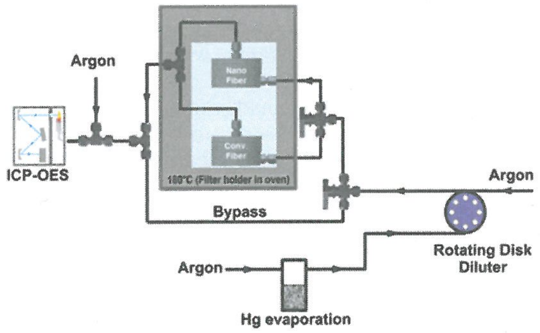


*Fig. 5: Schematic test set up for nanofiber filters for removal of Hg from an argon carrier gas.*

### Conclusions and Outlook

In the first year of the NANOFIL project, novel nanofiber materials able to remove heavy metals (e.g., Hg) were prepared. Chelating groups and $CeO_2$ nanoparticles were used to specifically bind S. For the production of the final functionalized fiber material, direct deposition or electrospinning can be utilized. Preliminary results on the activity of $CeO_2$ as sorbent material for S were obtained. The produced materials are under functional characterization and the synthesis processes under optimization. In the second year of this project, the evaluation of the filters will be performed by using an in-house testing setup coupled to ICP-OES. Furthermore, an in-house developed hyphenated SMPS-ICPMS setup (CCMX "NanoAir" Project) can be used to obtain online and simultaneous elemental and size-resolved information of aerosols loaded with metallic particles. Studies on the strategies to regenerate the active materials are also planned. In the future the developed nano-filtering systems should then be tested for other toxic heavy metals in a real flue gas.

### References for Project A9.6:

[1] Zhou J. et al., Environ Sci Technol. 2013; 47:10056-10062
[2] Adrian H. et al., A hyphenated SMPS-ICPMS coupling setup: Size-resolved element specific analysis of air-borne nanoparticles, submitted to "Journal of Aerosol Science"
[3] R. H. Ahrens, "EU will Quecksilber Emissionen aus Kohlekraftwerken begrenzen", VDI Nachrichten Nr. 15/16, (11. April 2014)

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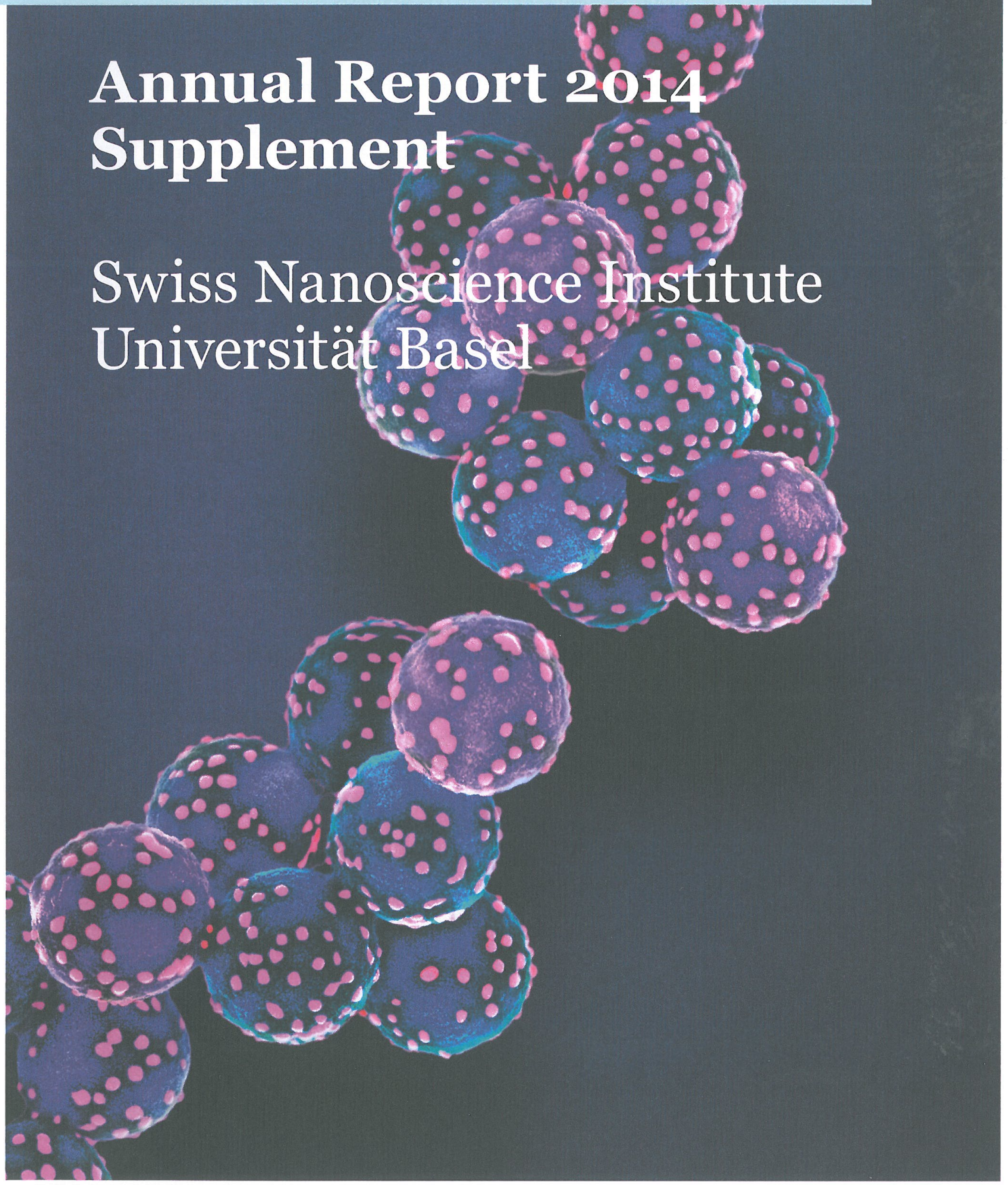

The Swiss Nanoscience Institute is a research initiative of the Canton of Aargau and the University of Basel.

This report summarizes the work conducted within the Swiss Nanoscience Institute in 2014.

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Cover illustration: Virus-imprinted nanoparticles (Martin Oeggerli, www.micronaut.ch)



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# Jahresbericht 2014

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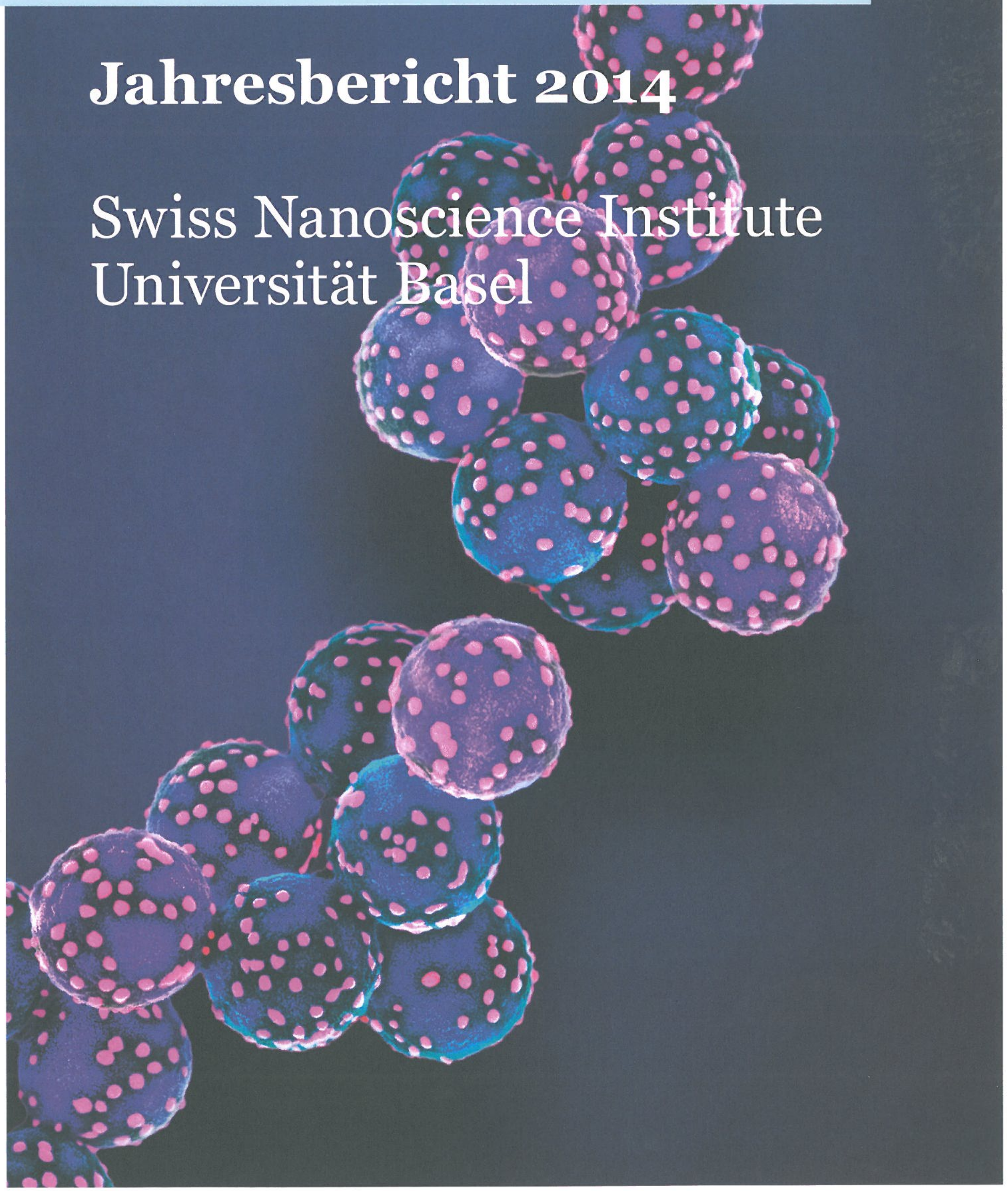

# Argovia-Projekte

## Verlängerte Projekte

(mit und ohne Zusatzfinanzierung)

| Projekt | Projektleiter | Projektpartner |
|---|---|---|
| **A7.4 Nano-LTB:** Low-Temperature Bonding (LTB) of Multichip Modules by Nano-Size Silver Sintering | H. Van Swygenhoven-Moens (PSI) | A. Wahlen (FHNW), N. Hofmann (FHNW Windisch), Ch. Liu (ABB Switzerland Ltd. Baden-Dättwil; AG) |
| **A7.5 NanoFACTs:** nano Functional Active Component Capsules for Textiles | U. Pieles (FHNW) | W. Meier (Univ. of Basel), Ch. Bradbury (HeiQ Materials AG, Bad Zurzach; AG) |
| **A7.6 NanoMorph:** Nanostructured surfaces for the control of polymorphism of active pharmaceutical ingredients | P. Shahgaldian (FHNW) | Th. Jung (PSI), B. Schneider (RPD TOOL AG, Birsfelden; BL) |
| **A7.7 NoViDeMo:** Novel viscosity- and density-meters for process monitoring and biomedical sensing applications | Th. Braun (C-CINA) | J. Köser (FHNW Muttenz), O. Glaied (FHNW), J. Hench (Univ. Hospital Basel), M. Touzin (Endress+Hauser Flowtec AG, Reinach; BL) |
| **A7.9 WGB-NPA:** Wide Band Gap Power Semiconductors Improved by Nanoscale Probe Analytics (bis 31. März ohne Bericht) | E. Meyer (Univ. of Basel) | Th. Jung (PSI), H. Bartolf (ABB, Baden-Dättwil; AG) |
| **A8.1 Bio-DURACLEAN:** Bio-DURABLE self-cleaning painting: development of dirt repellency coatings for large surfaces | O. Glaied (FHNW) | U. Pieles (FHNW Muttenz), W. Meier (Univ. of Basel), G. Siragna (Walter MÄDER AG, Kilwangen; AG) |
| **A8.3 EL-ENA:** Electrophoretic active hybrid core shell silica nanoparticles decorated with dendritic structures for colored electronic ink (e-ink) and e-paper applications | U. Pieles (FHNW) | G. Grundler (FHNW), G. Nisato (CSEM Muttenz), R. Öhrlein (BASF Research Center Basel, BS), A. Hafner (BASF Research Center Basel; BS) |
| **A8.7 NANOX:** Mixed mode nanocomposite catalyst for the effective decomposition of hydrogenperoxide vapour used in sterilization processes of pharmaceutical GMP clean room production facilities and isolator systems | U. Pieles (FHNW) | P. Shahgaldian (FHNW), C. E. Housecroft (Univ. of Basel), O. Scheuber (SKAN AG, Allschwil; BL) |
| **A8.8 NAPOHIC:** Nano carbon based semiconductive polymers for high-voltage cables (bis 31. März ohne Bericht) | J. Gobrecht (PSI) | J. de Pietro (FHNW), M. Kristiansen (FHNW Windisch), L. Xie (ABB Corporate Research, Baden-Dättwil; AG) |
| **A8.9 TIGHTSEAL:** Gastight thin films to minimize emissions of graphite sealings (bis 31. März ohne Bericht) | M. Waser (FHNW) | U. Pieles (FHNW), J. Gobrecht (PSI), U. Wegmann (Klinger AG, Egliswil; AG) |



## 2014 neu gestartete Projekte

| Projekt | Projektleiter | Projektpartner |
|---|---|---|
| **A9.2 em-Select:** Polymer-Emulsion-Segmented Electroconductive Nano Fibres for antistatic textile finishing | U. Pieles (FHNW) | J. Gobrecht (PSI), C. Denier (FHNW Windisch), M. Height (HeiQ Materials AG, Bad Zurzach; AG |
| **A9.6 NANOFIL:** Functionalized nanofiber-enhanced filter media for fine particle and heavy metal removal in flue gas and sewage water | C. Ludwig (PSI) | T. Griffin (FHNW), U. Pieles (FHNW), I.-V. Thanou (Alstom AG, Birr; AG) |
| **A9.7 NanoSiCTrenchFet:** Physical Studies of SiC Nano-Trench-MOSFETs | M. Schnieper (CSEM Muttenz) | N. Marjanovic (CSEM Muttenz), J. Gobrecht (PSI), E. Meyer (Univ. of Basel), R. Minamisawa (ABB Switzerland Ltd. Baden-Dättwil; AG), H. Bartolf (ABB Switzerland) |
| **A9.9 NANOzyme:** Novel Nanobiocatalysts based on confined and concerted artificial and natural enzymes | P. Shahgaldian (FHNW) | P. Corvini (FHNW), T. Ward (Univ. of Basel), A. Cumbo (INOFEA GmBH, Basel; BS) |
| **A9.10 PATCELL:** Surface-patterning of PLGA for Improved Cell Interaction and Tissue Integration of Resorbable Fixation Implants | P. M. Kristiansen (FHNW) | V. Guzenko (PSI), J. Lungershausen (FHNW), J. Köser (FHNW), S. Beck (Synthes, Oberdorf; BL) |
| **A9.12 SCeNA:** Single cell nanoanalytics | Th. Braun (C-CINA) | H.P. Lang (Univ. of Basel), G. Schlotterbeck (FHNW), G. Dernick (Roche, Basel; BS) |
| **A9.15 SINAPIS:** Niederdruckwasserstrahl-injizierte Nanopartikel zur Verbesserung von Implantaten | R. Schumacher (FHNW) | M. de Wild (FHNW), O. Braissant (Univ. of Basel), M. Straubhaar (WATERjet Robotics AG, Oftringen; AG) |