Final Publishable Summary, Proposal No. 622091: ACRONYM: SONO-ENGINEERING

Execution of the two years of Marie Curie Fellowship SONO-ENGINEERING was focused on:
1) The inorganic micro/nanostructures engineering via high intensity ultrasonication. Three interfacial strategies were developed for sonoengineering of small (<100 nm) nanoparticles), and the main point is how to put nanoparticles on the surface of cavitation bubbles for electronic structure evolution of semiconductor nanoparticles. The first strategy is to sonicate hydrophilic nanoparticles directly in oil phase. Second strategy involves modification of ZnO nanoparticles by span-60 block-copolymer to attract them to the surface of the cavitation bubbles. The third strategy introduces oppositely charged surfactant in the sonication system and nanoparticles would become hydrophobic due to the static electricity attraction. For all approaches, evolution of the evolution of photoluminescence spectra evidenced the annealing effect of the cavitation hot spot to the initially hydrophilic ZnO nanoparticles.
The application of developed interfacial strategies in photoelectrochemical water splitting was demonstrated on another nanomaterial, carbon nitride nanorods with the size of 100-300 nm. In the present of 6 mM surfactant CTAB, nanorods were subjected to the sonication. UV-Vis and PL measurement of resultant nanorods showed sonication has indeed influences to the electronic structures of nanorods. However, when the nanorods were tested for PEC water splitting, it was found the sono-engineered nanorods presented weak photoactivity. One of the reasons could be the low conductivity of carbon nitride film electrode that is prepared via spin coating. To elucidate that the acquired low solar energy conversion could be due to the low conductivity, a graphitic carbon nitride film that has good affinity to FTO substrate was synthesized based on a microcontact-printing-assisted approach. A good motivation of this study is a graphitic carbon nitride film that promises important applications especially in photoelectrochemistry has always been pursued but not yet achieved. What is equally important is that the acquired film can be formed on any desired substrates especially conductive ones, which assures for the further exploitation of its diverse applications. Thanks to the flexibility of the synthetic procedure, the strong affinity of graphitic carbon nitride film to fluorine-doped tin oxide glass substrate leads to a photocurrent density of 30.2 μA/cm2 at 1.23 V RHE , which is so far the highest reported value for pure graphitic carbon nitride based photoelectrochemical devices.
2) Training and development of the Fellow in Interfacial Sonochemistry. The Fellow succeeded in the use of the interface of the cavitation microbubbles for synthesis of different types of nanomaterials starting from nanoparticles to the nanoengineered capsules. Sonication assisted fabrication of porous protein capsules has been performed at the cavitation interface. The superoxide radicals generated during sonication can be effectively utilized to achieve the S-S bonding for proteins containing –SH residuals, such as HSA, BSA, and ferritin. Further studies revealed the pore sizes are adjustable via putting capsules into different pH environments, indicating the potential application of the capsules in loading and releasing drugs. The Fellow also explored cavitation interface for sonoassembly of liquid metal Pickering emulsions using silica nanoparticles.
At the end of the fellowship, the Fellow received skills in the development of the systems for Solar energy harvesting and conversion based on the ultrasonically prepared semiconductor nanoparticles. Increased photoelectrochemical activity was observed for films made from α-Fe_2O_3 nanoparticles after microbending. Additionally, the Fellow developed and studied $CsSnI_3$-based perovskite solar cells.

The results achieved during SONO ENGINEERING project execution are important for the application of the ultrasonic technologies for the development of new nanomaterials for renewable energy harvesting and storage. The results are summarized in the following publications:

1. S. Y. Gao, X. J. Wei, H. Y. Liu, K. R. Geng, H. Q. Wang,* H. Moehwald and D. Shchukin, “Transformation of Worst Weed into N-, S-, and P-tridoped Carbon Nanorings as Metal-Free Electrocatalysts for Oxygen Reduction Reaction”, **J. Mater. Chem. A** 2015, 3, 23376-23384.
2. J. Liu, H. Q. Wang,* M. Antonietti “Graphitic Carbon Nitride “Reloaded”: Emerging Applications Beyond (Photo)catalysis” **Chem. Soc. Rev.** 2016, 45, 2308-2326.
3. X. Qiu, B. Q. Cao, S. Yuan, X. Chen, Z. Qiu, Y. Jiang, Q. Ye, H. Q. Wang,*, H Zeng, J. Liu, M. G. Kanatzidis “From unstable $CsSnI_3$ to air-stable Cs_2SnI_6: A lead-free perovskite solar cell light absorber with band gap of 1.48 eV and high absorption coefficient” **Solar Energy Materials & Solar Cells**, 2017, 159, 227-234.
4. H. Q. Wang, H. Moehwald, D. Shchukin, “Interface Controlled Cavitation: Recent Achievements and Future Perspectives”2017, **Chem. Soc. Rev.** (submitted)
5. H. Q. Wang, J. Jian, G. Jiang, R. van de Krolb and B. Q. Wei, “Engineering of Emerging Multinary Semiconductors for Viable Photoelectrochemical Water Splitting”, 2017, **Adv. Energy Mater.** (submitted).
6. L. Jia, H. Q. Wang, P. Bogdanoff, M. Schmid, U. Bloeck, R. van de Krol and S. Fiechter “Reconfiguration of Solar Fuel Ultrathin Films via Periodically Micro-Bending for Efficient Photo-electrochemical Water Splitting”, **ACS Nano** 2017 (submitted).