Publishable Summary Report for the Marie Curie Actions FP7-PEOPLE-IIF-2010-275336-SSNano

On/Off-Switchable Smart Nanobioreactors

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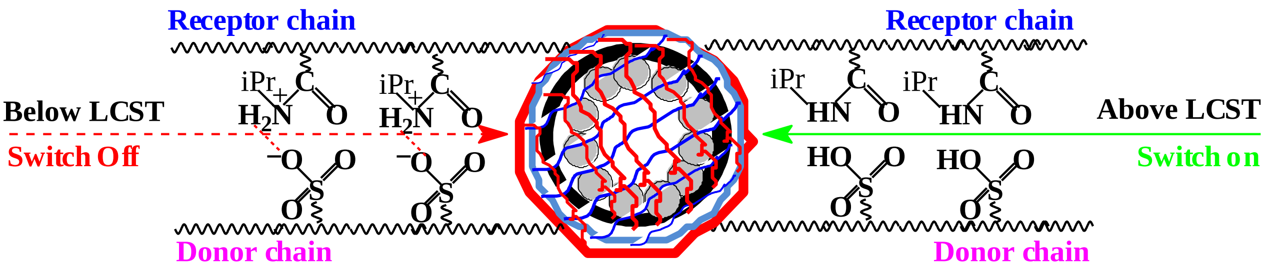
FINAL PUBLISHABLE SUMMARY REPORT

The challenge associated with the growing demands of controlling and/or modulating chemical processes has been driving a number of new methodologies to develop tailor-made stimuli-responsive materials. As a result of extensive effort, a large body of knowledge in this field is now available; however, most of these cannot provide a simple, predictable and straightforward design for tailor-made catalytic materials. A generic protocol suitable for the development of a new generation of tailor-made catalytic materials is urgently needed. Thus, the fundamental goal of this research project is to design, develop and verify a novel bioreactor with self-switchable abilities for advanced applications, offering us new phenomena to tackle key medical, chemical, biological and environmental issues, *etc*. During the fixed two years of this fellowship (15/Oct/2011-16/Oct/2013), we have successfully achieved this objective. We have also realised two-way transfer of knowledge and created links between European host and China.

Building on these previous works, we have exploited the idea of developing a new family of stimuli-responsive nanomaterials based on the combination of hollow silica matrix, metallic nanoparticles or glucose oxidase, and poly (*N*-isopropyl-acrylamide)/poly (2-acrylamide-2 -methylpropane sulfonic acid) (PNIPA/PAMPS) smart interpenetrating network (**Scheme 1**) to construct 'on/off' switchable smart nanobioreactors, which generate the following attractive advantages: 1) capability of freely opening and closing (*i.e.*, auto-switchable by temperature); 2) fast responsive/sensing time (*i.e.* rapidly responsive kinetics); 3) excellent stability and long shelf life; 4) high activity; 5) ease of preparation; 6) cost-effectiveness.

Up-to-date, all experimental results have confirmed that the proposed nanoreactor exhibited positively responsive characteristics and faster response kinetics, because the catalytic behavior of the nanoreactor was induced by an increase rather than a decrease in temperature. This self-switchable nanoreactor not only offered an advantage over the negatively thermo-responsive switches used in pure PNIPA-based nanoreactors, but also achieved tunable catalytic activity and a higher degree of change of the catalytic activity after the external trigger was applied, which allowed better control of reactant accessing to the nanoreactor.



Scheme 1. Schematic presentation of the on/off-switchable nanoreactors.

Four specified work packages, each comprising a number of tasks, were completed during the fixed two years of this fellowship (15/Oct/2011-16/Oct/2013). In details, we have constructed a self-switchable Ag nanoreactor and “on/off”-switchable nanobioreactor in the first package, in order to obtain perfect smart polymer network, the optimised 'stoichiometric ratio of donor/receptor monomers' has been achieved. In the second package, a number of modern methods and instruments including transmission electron microscopy (TEM), scanning transmission electron microscopy (STEM), energy dispersive X-ray analysis (EDX) mapping, scanning electron microscopy (SEM), and BET (Brunauer-Emmett-Teller), dynamic light scattering (DLS), inductively coupled plasma atomic emission spectroscopy (ICP-AES) etc were used to characterise the synthesized nanoreactors. Subsequently, activity evaluation of “on/off”-switchable nanoreactors was carried out in a batch format (Package 3). The self-switching behaviour was investigated by measuring the change of activity at different temperatures ranging from 20-50℃. Package 4 detailed the application of prepared self-switchable nanobioreactor as electrochemical glucose biosensors. As such, by a careful and completive study, major parameters and principles for the design and development of the “on/off”-switchable nanobioreactors have been clarified. Based on the great success, we have further developed methodologies and strategies within this project by exemplifying the efficiency of the process in a range of relevant processes.

In summary, during the fixed two years of this fellowship (15/Oct/2011-16/Oct/2013), we have successfully:1) developed a self-switchable Ag nanoreactor with high catalytic efficiency; 2) constructed an on/off-swtichable glucose nanobioreactor with positively responsive characteristics and faster response kinetics. Besides, this stimuli-responsive nanoreactor not only offers an advantage over the inverse thermo-responsive switches used in pure PNIPA-based nanoreactors, but also achieves a higher degree of permeability change and tunable catalytic activity, which allows better control of reactant access to the nanoreactor. Knowledge/technology generated in this project is now accessible to scientific community via our journal publications, books, conference presentation and seminar presentations. Four high-quality journal publications have been published/accepted: *Advanced Functional Materials* (2013, 23, 2162-2167 (Inside Front Cover) (IF 9.765), *Chemical Communications*, 2014, 50, 118-120 DOI: 10.1039/C3CC47361A (IF 6.378); *Journal of Materials Chemistry,* 2011, 21, 19124-19131(IF 6.101); *Australian Journal of Chemistry,* 2011, 64, 1541-1546 (IF 1.869) along with two book-chapters (*Elsevier B.V.* Molecularly Imprinted Sensors: Overview and Applications. ISBN: 978-0-444-56331-6, 2011, Chapter-3, 57-72 and *Bentham Science Publishers, Frontiers in Biomaterials: The Design, Synthetic Strategies and Biocompatibility of Polymer Scaffolds for Biomedical Application.* 2013, Chapter-9, 195-211). Dr S. Cao, the beneficiary, has also presented results of the project to various international conferences and invited lectures. It is worth pointing out that Dr Cao, as a cofounder, also set up the Chinese Advanced Materials Society (http://www.thecams.org) and international union of advanced materials (www.iuam.org) during the fixed two years of this fellowship (15/Oct/2011-15/Oct/2013)

The implementation of the project could further present important contributions to the development of advanced nanomaterials. European research in this field has been extremely successful and it has helped maintain Europe’s competitiveness in the world. Additionally, due to the unique functionalities of stimuli-responsive smart nanobioreactors, the resulting systems could greatly benefit the current investigation of nanobiotechnology in terms of cost-effectiveness, storage stability, ultra sensitivity and selectivity together with high potentials of industrial production. It coincides directly with the Europe’s social objectives.