INDO SWISS JOINT RESEARCH PROGRAMME (ISJRP)

RESEARCH FELLOWSHIPS

EXCHANGE GRANT REPORT

Grant No.: RF 34

Part 1 - General Information

<table>
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<th>Project Title:</th>
<th>Spectroscopic and Scanning Tunneling Microscopic Studies on the Electronic Properties of InP/ZnS Quantum Dots</th>
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<td>Keywords:</td>
<td>Quantum Dots, Gold nanoparticles, STM</td>
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<td>Start date:</td>
<td>March 21, 2012</td>
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<td>Duration:</td>
<td>7 months</td>
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Part 2 - Exchange Participant(s) Details

VISITING SCIENTIST

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HOSTING SCIENTIST

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3.1 Purpose of visit

(Briefly describe the purpose and goals of this exchange.)

The visit was aimed at the synthesis of core-shell metal nanoparticles (gold nanoparticles) and semiconductor Quantum Dots (QDs) and the investigation of their electronic tunneling properties by using Scanning Tunneling Microscopy (STM) and Scanning Tunneling spectroscopy (STS). The patterns formed by different surface bound ligands could control the functional properties of the nanoparticles formed. The formation of these patterns is governed by the entropy factors associated with the crystallization of the ligands on the nanoparticle surface. In this visit we investigated the organization of different thiol functionalized oligoethylene glycol ligands on the surface of gold nanoparticles in the presence of other hydrophobic ligands like alkane thiols, using STM and NMR techniques. These ligand engineered core-shell nanoparticles particles were then used to achieve cell membrane penetration.

3.2 Short description of work carried out during the visit

(Please describe the technologies acquired and the experiments/activities performed during the course of the exchange.)

Thiol functionalised oligo ethylene glycol molecules of varying length were synthesised so as to obtain hydrophobic ligands that can form self-assembled monolayers on the surface of nanoparticles. The synthesis scheme is as follows

\[
\text{H}_3\text{C}\begin{array}{c}\text{O}\
\text{H}
\end{array}\text{nOH} \xrightarrow{\text{TsCl}} \text{H}_3\text{C}\begin{array}{c}\text{O}\
\text{H}
\end{array}\text{nOTs}
\]

\[
\text{H}_3\text{C}\begin{array}{c}\text{O}\
\text{H}
\end{array}\text{nSH} \xrightarrow{\text{thiourea, NaOH}} \text{H}_3\text{C}\begin{array}{c}\text{O}\
\text{H}
\end{array}\text{nSH}
\]

\[n = 3, 5\]

The molecules were purified and characterised using $^1\text{H}$ and $^{13}\text{C}$ nmr spectroscopic measurements. 2-(2-(2-methoxyethoxy)ethoxy)ethanethiol and octane thiol were used as the
ligands for the preparation of mixed ligand gold nanoparticles. Gold nanoparticles were synthesised using Stucky method by reducing the Chloro(triphenylphosphine)gold(I) using borane morpholine complex as the reducing agent in toluene/methanol solvent at 100°C. Nanoparticles were purified by repeated centrifugation until free of unbound ligands. Films of nanoparticles were made using the Langmuir–Blodgett method and these films were then imaged using STM, to understand the organisation of ligands on the nanoparticle surface. NOESY NMR analysis of the mixed ligand nanoparticles can also give information’s on the organisation of the ligands on nanoparticle surface. These studies indicated that the ligands 2-(2-(2-(2-mercaptoethoxy)ethoxy)ethoxy)ethanethiol and octane thiol, form well separated domains on nanoparticle surface.

It has been earlier reported by Stellacci and co-workers (Nature Materials 2008, 7, 588-595) that gold nanoparticles with 11-mercapto-1-undecanesulphonate and octane thiol as ligands in the ratio 2:1 could penetrate the plasma membrane without bilayer disruption. PEG ligands offer hydrophilic character throughout the molecule as against the MUS or octane thiol which has a hydrophobic alkane chain. Gold nanoparticles were synthesized with a mixture of 2-(2-(2-mercaptoethoxy)ethoxy)ethoxy)ethanesulfonic acid and 2-(2-(2-methoxyethoxy)ethoxy)ethanethiol as ligand using the sodium borohydride reduction method. These particles are to be tested for cell penetration.

3.3 Outcomes

(Please describe the main results obtained during the course of the exchange)

Gold nanoparticles with well separated ligand domains were prepared using oligoethylene glycol molecules. 2-(2-(2-mercaptoethoxy)ethoxy)ethoxy)ethanesulfonic acid and 2-(2-(2-methoxyethoxy)ethoxy)ethanethiol capped gold nanoparticle were synthesized to understand the role of hydrophobic and hydrophilic chains in the ligands during cell membrane penetration.

3.4 Future collaboration with host institution

(Please provide information on future collaboration opportunities and follow-up activities.)

This was a great start for both the groups involved in this project. Photophysical properties of various chromophore functionalised nanoparticle systems are currently under investigation at
Prof. George Thomas’ group (Indian side) and the microscopic characterisation and cell studies are to be done in Prof. Stellacci’s group (Swiss side).

3.5 Various comments

(E.g., what worked well, what didn't work well, suggestions and improvement ideas, ...)

We were not able to measure the STM and STS of the InP quantum dots, as the length of the organic ligand used, myristic acid (16 carbon atom) was large enough so that the STM tip could wash away the ligands.

3.6 Projected publications/articles resulting or to result from the exchange

(if applicable)

Manuscript related to the formation of ligand domains on mixed ligand capped (oligoethylene glycol and octane thiol) gold nanoparticles investigated by NMR and STM is under preparation.

Manuscript related to the cell membrane penetration of striped gold nanoparticles formed by ligands 2-(2-(2-mercaptoethoxy)ethoxy)ethoxy)ethanesulfonic acid and 2-(2-(2-methoxyethoxy)ethoxy)ethanethiol is also under preparation.