

Studentship Project

Molecular Junctions Made to Measure

Robert French and Frank Marken, University of Bath

Project aims:

To develop simple and novel methodologies to deposit or grow molecular junctions using electrochemical deposition.

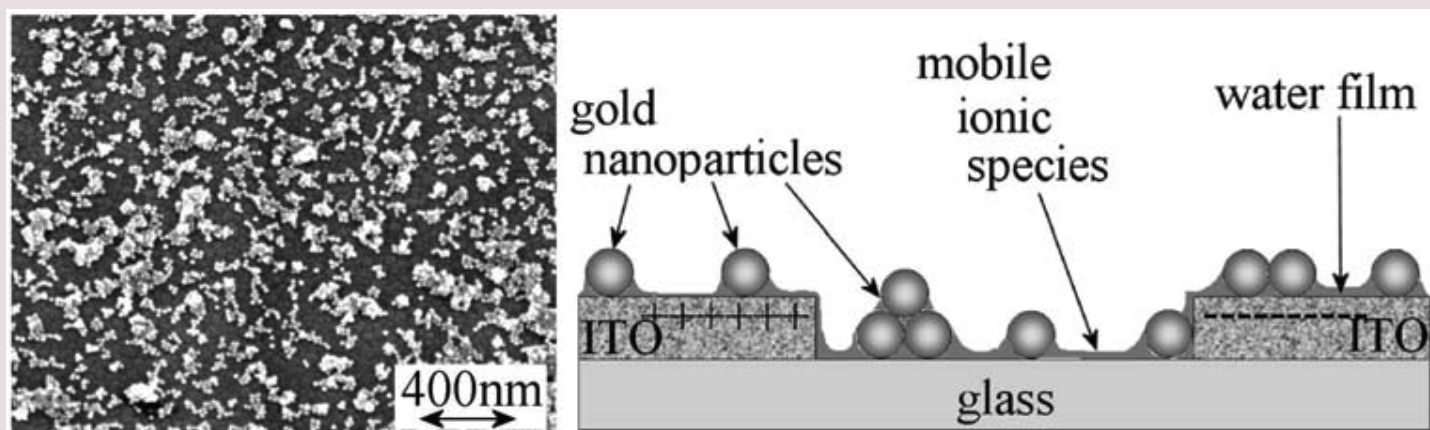
To employ a generator-collector electrode configuration to control the growth of metalmetal junctions.

To develop and exploit the resulting junctions for sensing applications.

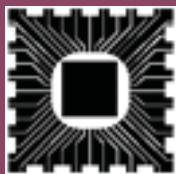
The project has developed considerably from work with gold nanoparticle assemblies in the early stages to the design of "shuttle junctions" (in collaboration with Dr. Sergey Gordeev, Physics, Bath), the formation and optimisation of metal-metal junctions based on gold electro-deposition, to a range of applications of these new type of junctions (in collaboration with Dr. Michael Vagin, Lomonosov Moscow State University). Robert French presented his work at conferences and he visited Lomonosov Moscow State University. In the final part of the project we are now developing liquidliquid ion transfer sensors within nano-scale junctions.

Layer-by-layer assembly of gold nanoparticle junction arrays:

Junctions are highly interesting and the controlled assembly of junction arrays for electrical and electrochemical tunnel processes has been explored in this project as a first approach. Gold nanoparticles with 20 nm diameter (see image) were assembled on a glass substrate with tin-doped indium oxide (ITO) contacts. During assembly, clusters of nanoparticles were formed and the electrical conductivity increased with each layer. The novel device is cleaned with ozone and then treated with thiols to give a novel multi-junction device for the detection of humidity or "sticky" airborne molecules.



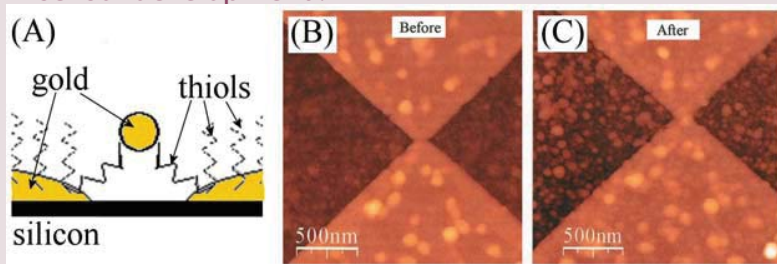
This work was extended to the electro-aggregation of gold nanoparticles at electrodes and the use of the resulting high surface area devices for arsenite detection.



Studentship Project

Assembly of shuttle junctions

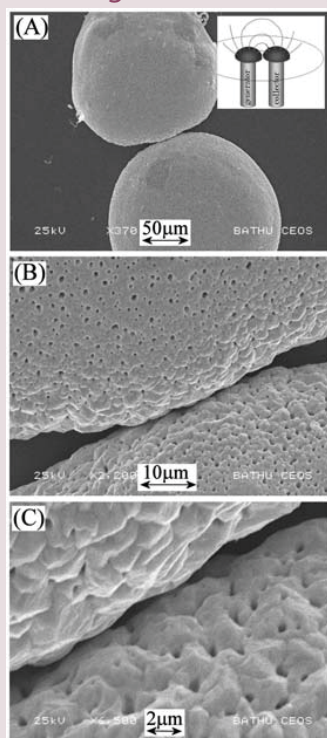
In collaboration with Professor S. Gordeev (Department of Physics, University of Bath), the feasibility of the assembly of individual “shuttle junctions” with a gold nanoparticle bridging to nanoscale gold contacts was explored. Novel junction devices were investigated and in future these devices will be of considerable interest in sensor development.



In situ electrochemical growth of paired electrode junctions

A bipotentiostatic method with a commercial system has been developed to grow paired gold junction electrodes. Gold metal is simultaneously deposited on two adjacent

platinum discs electrodes (approx 100 μ m diameter, separated by 120 μ m) until short circuiting conditions trigger the end point of deposition. By altering the overpotential (-250 mV to -20 mV), junctions of varying sizes can be formed reproducibly, ranging from approximately 5 μ m down to 200nm. The figures shows the scanning electron micrographs of a gold-gold junction with ca. 200 nm junction gap.



The sensing application of these novel junctions have been investigated using generator-collector signals allowing low concentration sensing (e.g. sub-micromolar chloramphenicol or dioxygen). Diffusion processes within the junction have been studied for a range of redox system as a function of the diffusion coefficient. One particular benefit of the small junction gap is the possibility to “catch” unstable reaction intermediates before they can decay in the solution phase. The oxidation of NO (nitric oxide) at the generator electrode resulted in a surprising collector response which was interpreted in terms of a nitrosonium phosphate intermediate.

The junction design was further improved and in particular the formation of small junctions was optimised down to ca. 200 nm gapseize. The true chemical reason for the cut-off mechanism for junction growth needs still to be investigated further, but the ease and reproducibility of junction formation are important benefits of the new methodology.

Paired triple phase boundaries within electrode junctions

By depositing a small volume of a water immiscible redox liquid within the gap anion uptake into the organic phase (oxidation) and anion expulsion into the aqueous phase (reduction) can be combined to result in a generator – collector anion transport system across the liquid | liquid interface. This has been demonstrated with perchlorate anions. Currently, a wider range of anions is investigated and the presence of two mechanistic pathways (surface transport, bulk transport) for ion transport through a liquid studied.