Application for a TSM-DTC funded PhD studentship

Please complete this form electronically
and submit to Lilian Wanjohi (l.wanjohi@imperial.ac.uk)
by Friday January 8, 2010

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Please complete the following:

1. Project title
Self-assembly processes in protected metallic nanoparticles for nanomaterial applications:from single particle to nanoparticle networks

2. Project abstract (≤ 200 words please and please add 1 or 2 key references)
Thiol protected metallic nanoparticles have become a very important and fascinating area of nanotechnology with many applications being identified (e.g., catalysis, sensing, molecular switches, … etc). Metal nanoparticles undergo self-assembly processes at different levels; Thiol molecules adsorb at the nanoparticle surface (picosecond-nanosecond scale) and the nanoparticles can self-organise into complex networks (microsecond scale) providing 'hot spots' for catalysis.
The performance of the nanoparticle networks can be enhanced by using mixtures of thiol molecules, which provide both increasing particle free volume, and specific network topology. These properties are desirable in catalytic and sensing processes as well as the isomerisation intrinsic to molecular switches. However, it is very difficult to control the ratio of compositions to achieve the desired performance.
We aim to develop computational approaches to design gold nanoparticles protected with thiol mixtures. We will exploit ab initio electronic structure methods (DFT, ONIOM) (J. Mol. Catalys. A: Chemical, **315**, 28 (2010)) to quantify the strength of thiol-gold interactions and

molecular structure as a function of the thiol composition. We will compute binding energies of different thiol molecules with gold nanocrystals as a function of the thiol molecule composition (alkane-thiol, dithiocarbamates), and thiol molecular orientation. This information will be used in atomistic dynamics simulations to investigate the self-assembly process at a single particle level (J. Am. Chem. Soc., **2006,** 128, 14166). These single particle studies will be combined with parallel replica and mesoscopic simulations, to investigate the self-assembly of nanoparticle networks. Crucially, the success of the method will be validated
through experiments. Our recent experimental contributions to the field (*Inorg. Chem.*, **2009**, *48*, 3866) have involved the use of a new species, dithiocarbamates, which resist displacement from the surface, making them ideal for use in conjunction with thiols. No computational studies exist on dithiocarbamate protected nanoparticles.

3. What is the multi-scale nature of the project? (≤ 100 words please)
Self-assembly at the single particle and network levels involves a range of coexisting time and length-scales. The nanoparticle (~1-20 nm for the individual particle and 1-3 μm for networks) to solvent (~0.1 nm) size ratio requires large system sizes to avoid undesirable finite size effects. Molecular level parameters must also be obtained from static 'electronic' structure calculations. Similarly, long time scales (0.1-1 microseconds) are needed to sample rare events in the network nucleation process. The system we plan to investigate exhibits all the difficulties of a heterogeneous problem: different type of interactions (organic-inorganic), spatial heterogeneity (formation of network structures that evolve in time) and temporal heterogeneity (disparity in time scales from 10^{-1}-10^{3} nanoseconds). The extended time scale
methods currently being implemented in DL_POLY 4 offer an approach to tackle our multiscale problem (EPSRC: EP/F010494/1).

4. How do the expertises of the supervisors complement each other? (≤ 100 words please)
FB has over 10 years experience in the development and application of computer simulation techniques to complex interfaces. He has developed atomistic, mesoscopic models and thermodynamic theories to investigate the behaviour of nanoparticles in solutions and surfaces. JW-E has a decade of experience in experimental organic and inorganic synthesis with seven papers in the last four years focusing on the self-assembly of thiols and dithiocarbamates on gold surfaces, including nanoparticles. MB has over 15 years experience using a wide range of electronic structure methods for molecules containing several to several thousand atoms, including hybrid combinations of electronic structure methods such as ONIOM. He would assist with initial parameter development, and also checking results from snapshots of the simulations.

5. Is there a self-contained 12-week MSc project that would usefully initiate this PhD project? (If the answer is no the project will not be offered as an MSc project)
A suitable computational project would involved the investigation of the self-assembly of a specific thiol or dithiocarbamate molecule at the surface of a single nanoparticle crystal.