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PROGRESS REPORT FOR AINGRA09128P

PROJECT TITLE	Synthesis and characterisation novel porous materials for applications in heterogeneous catalysis and nanotechnology	
INVESTIGATOR(S)		**Institution and Department**
Chief Investigator	**Dr Vladimir Golovko**	Chemistry, University of Canterbury
Other Investigators		
Students	Mr. David Anderson	
ANSTO Investigators	Tracey Hanley; Christine Rehm; Robert Knott	
Specialist Committee	N	

SCIENTIFIC OBJECTIVES

The objectives of this research project are to synthesize and characterize novel porous materials for applications in heterogeneous catalysis and carbon nanotube synthesis. These porous materials will be synthesized *via* sol-gel cross-linking of inorganic building blocks templated by self-assembly of metal colloids with a unique (biologically inspired) periphery. The facilities unique to the Lucas Heights Laboratories (and currently missing at the University of Canterbury) will provide us with the exceptional opportunity to characterize these novel materials.

PROGRESS REPORT and RESEARCH OUTCOMES

During our initial (first ever) working visit to the Bragg Institute, we set out to learn how to operate SAXS machine and to examine various triphenyl-phosphine stabilized clusters of gold and intermolecular interaction in solution by small-angle X-ray scattering (SAXS). $Au_{55}(PPh_3)_x$ and $Au_{11}(PPh_3)_8Cl_3$ cluster were synthesized at the University of Canterbury using wet chemical preparative methods. These clusters and their analogs will be tested as templates for the formation of porous TiO_2 materials. $Ti(O^iPr)_4$, a starting material in the synthesis of TiO_2, was purchased from Sigma Aldrich. Various ethanoic solutions of the clusters/TiO_2 colloids were prepared at the Bragg institute.

Our initial visit focused on exploring whether the SAXS technique would be effective for exploring:
a) the detection and adequate modeling of ultra-small Au clusters;
b) assessing inter-particle interaction of gold clusters;
c) whether it could provide information on the self assembly of gold clusters and a TiO_2 building blocks (sols, etc.) to form porous network material.

The early sample runs highlighted, that due to the nature of the gold cluster, very low concentrations of the clusters would be necessary.

Once we had completed leak testing on the sample holders and collected background for each of the sample holders, the samples were run at various low concentrations. Importantly, it appears that even extremely small Au clusters, such as Au_{11}, can be detected by this technique (this is a novel outcome for the SAXS technique as it is "pushing frontiers of the method") and preliminary data processing/modelling using data collected so far give good fit between particle sizes estimated using SAXS technique and estimates of particles sizes based on HRTEM or single X-ray crystal structure analysis. We are currently solving crystal structure for the particular Au11 cluster which was used in our study (our estimate was based on a crystal structure of a similar cluster with slightly different ligand periphery). This piece of work could be published in its own right or become a part of full paper investigating templating. The time we had (2-3 days, with a slight confusion over when we have to finish resulting in somewhat haphazard last set of experiments) only allowed us to gain some practical experience of how to use the apparatus. Promising data obtained for the Au clusters and some preliminary data on TiO_2 sol/gel signal that, should we be granted/approved to use the second portion of this grant, we could achieve our goal – i.e. obtain an insight into templation of the porous TiO_2 with Au clusters. This study would be great to accomplish as it would be a pioneering work in this area and SAXS suits it as a direct, non-invasive, continuous method of data collection.

DATA

List of Samples

Date	Time	Sample	Sample Loading	Time /s	Sample Position	Run/Frame
25-11-2009	1600	Au_{55}	1 %	3600	SH 1	R7/F1-3
25-11-2009	1600	Au_{55}	0.5 %	3600	SH 2	R7/F4-6
25-11-2009	1600	Au_{55}	0.1 %	3600	SH 3	R7/F7-9
25-11-2009	1600	Au_{55}	1 %	3600	SH 1	R7/F10
25-11-2009	1600	Au_{55}	0.5 %	3600	SH 2	R7/F11
25-11-2009	1600	Au_{55}	0.1 %	3600	SH 3	R7/F12
25-11-2009	2300	$Au_{11}(PPh_3)_8Cl_3$	0.66 %	3600	SH 1	R8/F1-3
25-11-2009	2300	$Au_{11}(PPh_3)_8Cl_3$	0.33 %	3600	SH 2	R8/F4-6
25-11-2009	2300	$Au_{11}(PPh_3)_8Cl_3$	0.16 %	3600	SH 3	R8/F7-9
25-11-2009	2300	$Au_{11}(PPh_3)_8Cl_3$	0.66 %	3600	SH 1	R8/F10
25-11-2009	2300	$Au_{11}(PPh_3)_8Cl_3$	0.33 %	3600	SH 2	R8/F11
25-11-2009	2300	$Au_{11}(PPh_3)_8Cl_3$	0.16 %	3600	SH 3	R8/F12
25-11-2009	2300	$Au_{11}(PPh_3)_8Cl_3$	0.66 %	3600	SH 1	R8/F13
25-11-2009	2300	$Au_{11}(PPh_3)_8Cl_3$	0.33 %	3600	SH 2	R8/F14
25-11-2009	2300	$Au_{11}(PPh_3)_8Cl_3$	0.16 %	3600	SH 3	R8/F15
26-11-2009	0700	$Ti(OiPr)_4$	0.06 %	3600	SH 1	R9/F1-3
26-11-2009	0700	$Ti(OiPr)_4$	0.006 %	3600	SH 1	R9/F4-6
26-11-2009	0700	$Ti(OiPr)_4$ + Au_{55}	0.06 %	3600	SH 1	R9/F7-9
26-11-2009	0700	$Ti(OiPr)_4$	0.06 %	3600	SH 1	R9/F10
26-11-2009	0700	$Ti(OiPr)_4$	0.006 %	3600	SH 1	R9/F11
26-11-2009	0700	$Ti(OiPr)_4$ + Au_{55}	0.06 %	3600	SH 1	R9/F12
26-11-2009	0700	$Ti(OiPr)_4$	0.06 %	3600	SH 1	R9/F13
26-11-2009	0700	$Ti(OiPr)_4$	0.006 %	3600	SH 1	R9/F14
26-11-2009	0700	$Ti(OiPr)_4$ + Au_{55}	0.06 %	3600	SH 1	R9/F15
26-11-2009	0700	$Ti(OiPr)_4$	0.06 %	3600	SH 1	R9/F16-18

26-11-2009	0700	$Ti(OiPr)_4$	0.006 %	3600	SH 1	R9/F19-21
26-11-2009	0700	$Ti(OiPr)_4$ + Au_{55}	0.06 %	3600	SH 1	R9/F22-24
26-11-2009	0700	$Ti(OiPr)_4$	0.06 %	3600	SH 1	R9/F25
26-11-2009	0700	$Ti(OiPr)_4$	0.006 %	3600	SH 1	R9/F26
26-11-2009	0700	$Ti(OiPr)_4$ + Au_{55}	0.06 %	3600	SH 1	R9/F27
26-11-2009	0700	$Ti(OiPr)_4$	0.06 %	3600	SH 1	R9/F28
26-11-2009	0700	$Ti(OiPr)_4$	0.006 %	3600	SH 1	R9/F29

PUBLICATIONS / REPORTS arising as a result of your work

To be written up. As per progress report above, work on Au clusters could be published as is. Activation/roll-over into 2010 of the second part of this grant is needed for completion of our study of templation of TiO_2 porous materials using Au clusters as templates.

PhD STUDENTS

David Anderson [david.anderson@pg.canterbury.ac.nz]

David will have another year or may be two before completion. Add 3-6 months for anticipated date of conferment of a PhD award. At this stage the title of his PhD thesis is NOT finalized. Hopefully it will be along the lines of metal nanoparticles for catalysis and should we succeed with SAXS experiment in our studies of Au/TiO2 it will constitute a breakthrough in his research and will yield a chapter in the thesis and several high quality papers.