EUROPEAN SYNCHROTRON RADIATION FACILITY

INSTALLATION EUROPEENNE DE RAYONNEMENT SYNCHROTRON

Experiment Report Form

	Experiment title: **EXAFS characterisation of magnetic precious metal bio-nanocatalysts**	**Experiment number**: CH-2774
Beamline:	**Date of experiment**: from: 5th November 2008 to: 10th November 2008	**Date of report**: March 2008
Shifts: 15	**Local contact(s)**: Carmelo Prestipino	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

*Dr Victoria COKER SEAES, University of Manchester, UK

*Dr. John M. CHARNOCK SEAES, University of Manchester, UK

*Prof Richard PATTRICK SEAES, University of Manchester, UK

Dr Carolyn Isobel PEARCE SEAES, University of Manchester, UK

Prof. Gerrit VAN DER LAAN Diamond Light Source, Didcot, UK

Dr Neil TELLING SEAES, University of Manchester, UK

Report:

Fe(III)-reducing bacteria, a group of anaerobic microorganisms, are able to precipitate regular shaped nano-sized (20 nm) crystals of the ferromagnetic ferrite spinel, magnetite (Fe_3O_4). This process works by coupling the oxidation of organic matter to the reduction of Fe(III)-oxyhydroxides and is accomplished by direct contact between the terminal Fe(III) reductase in the bacteria and the mineral surface [1]. The use of bacteria in nano-manufacturing is an unexploited area of enormous potential which our research group is actively exploring [2-6]. Understanding the mechanisms of magnetic biomineral synthesis by Fe(III)-reducing bacteria and controlling and manipulating the processes of biomineral production could allow its biotechnological exploitation for a range of applications including bioremediation and the fabrication of magnetic materials and catalytic systems [1]. The successful development of these biomineralising bacteria would revolutionise the manufacture of nano-crystals and provide low energy, environmentally friendly processing methodologies. The element specific nature of XAS and the ability to analyse materials of all crystallinity makes it an excellent tool for investigating these systems and providing local coordination information to compliment ATEM and magnetitc characterisation.

For this experiment we produced biogenic nanomagnetite-supported precious-metal (PM) catalysts using Pd, Pt, Au and, which are all catalytically active and highly conductive elements both individually and as alloys [7-10]. Our aim is to produce a versatile group of novel magnetite-PM nanomaterials with unique

characteristics that can be customised to enhance their properties as catalysts, magnets, and electronic devices. Biogenic nanomagnetite produced by *Geobacter sulfurreducens* was deposited with Pd(II), Pt(IV) or Au(III) and experiments aimed at producing precious metal Pd/Au, Pd/Pt and Pt/Au alloys as nanoparticles on biogenic magnetite were also prepared. ATEM investigation has demonstrated that nanocrystals were superimposed on the pre-deposited Fe minerals suggesting a Fe-oxide support with a precious metal shell. XAS was employed to identify the nature and structure of the PM is the samples and to investigate their association with the Fe-substrate.

Table 1. EXAFS fitting results

Sample	Scatterer	N	r (Å)	$2\sigma^2$ (Å^2)	R factor
		Au L_3-edge			
Au foil	Au	12	2.87	0.019	37.0
	Au	6	3.76	0.023	
	Au	24	4.97	0.026	
	Au	12	5.65	0.017	
	Au	24	6.43	0.024	
PtAu5%	Au/Pt	12	2.87	0.007	25.8
	Au/Pt	6	3.73	0.017	
	Au/Pt	24	4.98	0.011	
	Au/Pt	12	5.65	0.007	
PtAu5%+H_2	Au/Pt	12	2.87	0.008	33.2
	Au/Pt	6	3.73	0.028	
	Au/Pt	24	5.00	0.012	
	Au/Pt	12	5.69	0.005	
		Pt L_3-edge			
Pt foil	Pt	12	2.78	0.012	30.9
	Pt	6	3.92	0.009	
	Pt	24	4.79	0.019	
	Pt	12	5.45	0.009	
	Pt	24	6.20	0.024	
PtAu5%	Pt/Au	12	2.77	0.019	39.5
	Pt/Au	6	3.96	0.005	
PtAu5%+H_2	Pt/Au	12	2.75	0.014	30.8
	Pt/Au	6	3.95	0.015	
PtIr5%	Pt/Ir	12	2.73	0.013	39.9
	Pt/Ir	6	3.90	0.005	
	Pt/Ir	24	4.45	0.022	
	Pt/Ir	12	5.41	0.013	
		Ir L_3-edge			
IrPt5%	Ir	12	2.67	0.017	46.3
IrPt5%+H_2	Ir	12	2.68	0.017	48.9

X-ray absorption data was collected at the Pd K, Pt L_3, Ir L_3 and Au L_3 –edges. Data were collected at low temperature (77 K) and under vacuum to reduce the thermal Debye-Waller factor and prevent oxidation. The concentrations of the PM in the samples was 5wt% and therefore were collected in fluorescence mode. Fitting of the EXAFS data using excurv98 revealed that in all cases that the PM is present as metallic/alloys and no evidence of Fe-PM alloys demonstrating they are particles on the surface of the magnetite (see Table 1 for example data). There is no evidence that all the PM are not reduced to PM^0 as there is no evidence of PM-O interactions. This evidence can be combined with complementary characterisation techniques, especially transmission electron microscopy images of the nanomaterials and will allow us to move confidently into a scale phase and open the way to environmentally friendly manufacture of these novel materials. Early evidence shows excellent catalytic activity.

References

[1] VS Coker, RAD Pattrick, G van der Laan & JR Lloyd. 2007. *Microbiology Monographs*, 3, 276-296

[2] JR Lloyd, RAD Pattrick, VS Coker, G van der Laan. (2004) Patent MG/MSD/JM/P/29368.GB "*Use of bacteria to produce spinel nanoparticles*"

[3] VS Coker, CI Pearce, C Lang, RAD Pattrick, G van der Laan ND Telling, D Schuler, E Arenholz & JR Lloyd. (2007) *Eur J Mineral*, **19**, 707-716.

[4] VS Coker, CI Pearce, RAD Pattrick, G van der Laan, ND Telling, JD Charnock, E Arenholz and JR Lloyd.(2008) *Am Mineral*, in press.

[5] VS Coker, AG Gault, CI Pearce, G van der Laan, ND Telling, JM Charnock, DA Polya, & JR Lloyd. (2006) *Environ Sci & Technol*, 40, 7745-7750

[6] VS Coker, AM Bell, CI Pearce, RAD Pattrick, G van der Laan & JR Lloyd (2008) *Am Mineral*, in press