http://dx.doi.org/10.1595/205651316X689864 *Johnson Matthey Technol. Rev.*, 2016, **60**, (1), 12–15

JOHNSON MATTHEY
TECHNOLOGY REVIEW

www.technology.matthey.com

Faraday Discussion: Nanoparticle Synthesis and Assembly

Recent advancements in nanoparticle research

Reviewed by Anastasia Mantalidi
Department of Chemistry, University College London
20 Gordon Street, London WC1H 0AJ, UK; and
Johnson Matthey Technology Centre, Blounts Court,
Sonning Common, Reading RG4 9NH, UK

Email: anastasia.mantalidi.11@ucl.ac.uk

Introduction

Faraday Discussions are unique international meetings that focus on miscellaneous areas of chemistry and have been held for over 100 years. The format of these meetings is distinctive because delegates submit their papers in advance and these are distributed to all the participants prior to the meeting. During the meeting, the presenting authors are given five minutes to summarise the key points of their work and the remaining time is devoted to discussing the papers. The conference was held at Argonne National Laboratory, USA, from 20th to 22nd April 2015 and was jointly organised by the Royal Society of Chemistry, UK, the Department of Physics, Kansas State University, USA, and Argonne National Laboratory. There were approximately 130 delegates representing 23 countries. The programme consisted of 10 invited talks, 14 paper presentations, 72 poster presentations and 12 lightning poster presentations upon invitation by the scientific committee. The themes that were covered include:

- Nanoparticle synthesis – physical chemistry of nanoparticle shape and ligand control
- Theoretical insights into nanoparticle synthesis and nanoparticle assembly
- Nanoparticle self-assembly
- Nanoparticle directed assembly.

The purpose of this conference was to bring together scientists from a variety of backgrounds to discuss recent advancements in nanoparticle synthesis and assembly, and to enable collaborations. Due to the specified topic of the conference, the majority of the talks focused on these two aspects of nanoscience. Therefore, in this review, examples of these two areas will be presented to give an overview of the discussions that took place.

Further information about the event can be found on the conference website (1).

Nanoparticle Synthesis

Nanoparticles are used in many applications and therefore research in this field is often application driven. However, one of the sessions was focused on research into the fundamental principles behind nanoparticle synthesis. The importance of the synthetic strategies and the phenomena that govern nanoparticle synthesis were explained and the correlation of the synthetic route and of the final properties of the nanoparticles were emphasised.

The challenge to control both the shape and composition of platinum nanoparticles and platinum-based alloys using wet chemistry was highlighted by Christophe Petit (Université Pierre et Marie Curie, France) (2). Petit and colleagues examined the effect of the order of adding the capping agent during the

Invited Talks

Paul Alivisatos (University of California, USA)	Introductory Lecture
David Schiffrin (University of Liverpool, UK)	Concluding Remarks
Lucio Isa (ETH Zürich, Switzerland)	Insights into Mechanisms of Capillary Assembly
Brian Korgel (University of Texas at Austin, USA)	Nanocrystal Superlattices that Exhibit Improved Order on Heating: An Example of Inverse Melting?
Christos Likos (University of Vienna, Austria)	Soft-patchy Nanoparticles: Modelling and Self-organization
Albert Philipse (Utrecht University, The Netherlands)	A Thermodynamic Gauge for Mobile Counter Ions From C Colloids and Nanoparticles
Peter Schurtenberger (Lund University, Sweden)	A New Route Towards Colloidal Molecules with Externally Tunable Interaction Sites
Toshiharu Teranishi (Kyoto University, Japan)	Determination of a Localized Surface Plasmon Resonance Mode of Cu_7S_4 Nanodisks by Plasmon Coupling

synthesis, as well as the effect of the dissolved gases on the structure of the final nanoparticles. They showed that in the synthesis of monometallic Pt nanoparticles, irrespective of the presence of H_2, when the capping agent (an alkylamine) is added to the reaction mixture prior to the chemical reduction of the metal salt, the outcome of the reaction is mostly spherical particles. When the alkylamine is added after the reduction step in the presence of H_2, Pt nanocubes were obtained as the main product whereas in the absence of H_2, spherical and wormlike particles are observed. The schematic illustration presented in **Figure 1** shows the protocols of synthesis that were followed during their experiments.

Their work showed that the different adsorption abilities of the amine-containing capping agent and the dissolved H_2 on the crystal facets of the growing particles may affect the outcome of the reaction.

In the case of Pt-based alloyed systems, the authors explained the difficulties of controlling the composition of Co_xPt_{1-x} or Pd_xPt_{1-x} particles using liquid-liquid synthesis. They attributed the large discrepancies in the composition of the particles to the different reduction kinetics when one of the metal precursors is in the aqueous phase and the second in the organic phase. Additionally, they suggested that better control over the final metal composition can be achieved when the two precursors have similar reduction potentials and are well dissolved in the same media.

Of particular interest was the paper presented by Ger Koper (TU Delft, The Netherlands) (3) that proposed a robust preparation method to obtain ultrafine Au and Pt nanoparticles by bicontinuous microemulsion. The importance of their work lies in the fact that the reactant concentration can be increased, while the size of the particles remains the same. In their experiments, the particle size is controlled by the surfactant size and not by the composition of the microemulsion. A range of surfactants with different charges were used to validate their observations. This could be of particular relevance to industrial processes since a large production of nanoparticles is often required, however increased amounts of the reactants used often lead to undesirable larger particles.

Nanoparticle Assembly

As the main focus of the conference was nanoparticle assembly, a large number of presented papers were devoted to this aspect of nanoscience.

An exceptional paper was presented by Rafal Klajn (Weizmann Institute of Science, Israel) (4), titled: 'Magnetic Field-induced Self-assembly of Iron Oxide Nanocubes'. They examine how the shape of the iron oxide nanocrystals and their surface chemistry affect their self-assembly properties. Several experimental parameters were evaluated and they identified the conditions under which the particles can form superstructures including one-dimensional filaments and helices, as well as carbon-shaped assemblies (**Figure 2**).

These superstructures were reported for the first time and the optical and mechanical properties of each assembly were analysed.

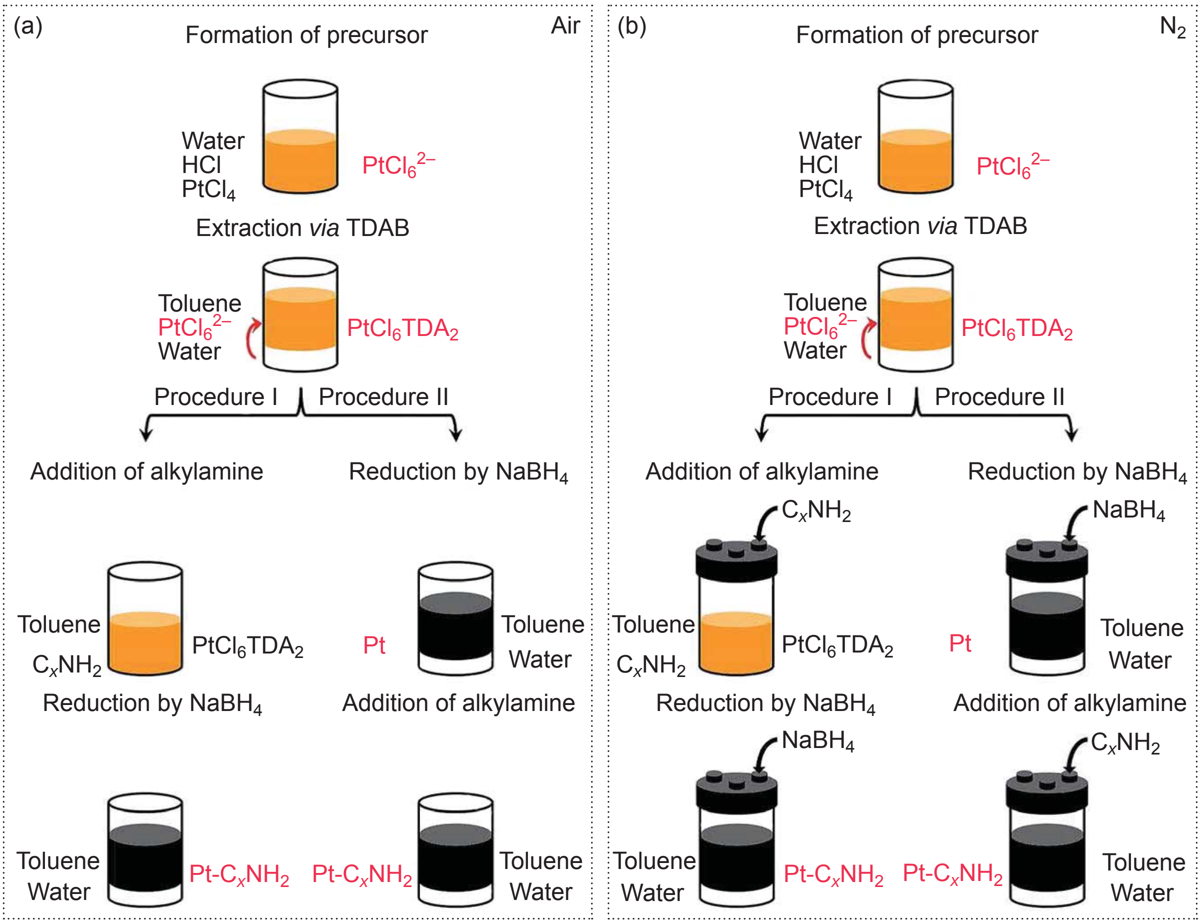

Fig. 1. Description of the two procedures used for the platinum synthesis: (a) in open air; (b) in a glove box, under nitrogen flux. Two procedures are possible and are differentiated by the reduction carried out after (Procedure I) or before (Procedure II) the adding of the alkylamine (2) (Reproduced by permission of The Royal Society of Chemistry)

The experimental conditions were found to be crucial for the final shape of the assembly nanoparticles; by changing the particle density or the direction of the applied magnetic field the organisation of the final assembly can be controlled. However, parameters such as particle size, shape, composition and surface chemistry cannot be overlooked and the interplay between all those factors should be considered. Finally, the authors performed Monte Carlo simulations to further investigate the mechanisms of self-assembly of these superstructures.

On the same topic, outstanding work was presented by Mathias Brust and his group (University of Liverpool) (5), by monitoring for the first time *in situ* pattern formation of drying and wetting dispersions of gold nanoparticles, using an environmental scanning electron microscope (ESEM). This allows direct monitoring of the particle assembly in the nanoscale and offers real time information of how the entire process occurs. This type of investigation offers the possibility to explore further this phenomenon that is as yet poorly understood, and perhaps will provide some information on the mechanistic details that govern this process. The gold nanoparticles that were used were functionalised with hydrophilic thiol ligands since the only dispersant that could be used was water.

During the experiments, significant interactions were revealed between the gold nanoparticles and the substrate, and surprisingly, once the pattern was formed it would either stick on the substrate or could be lifted. Redispersion of the pattern in condensed water droplets was found to be difficult.

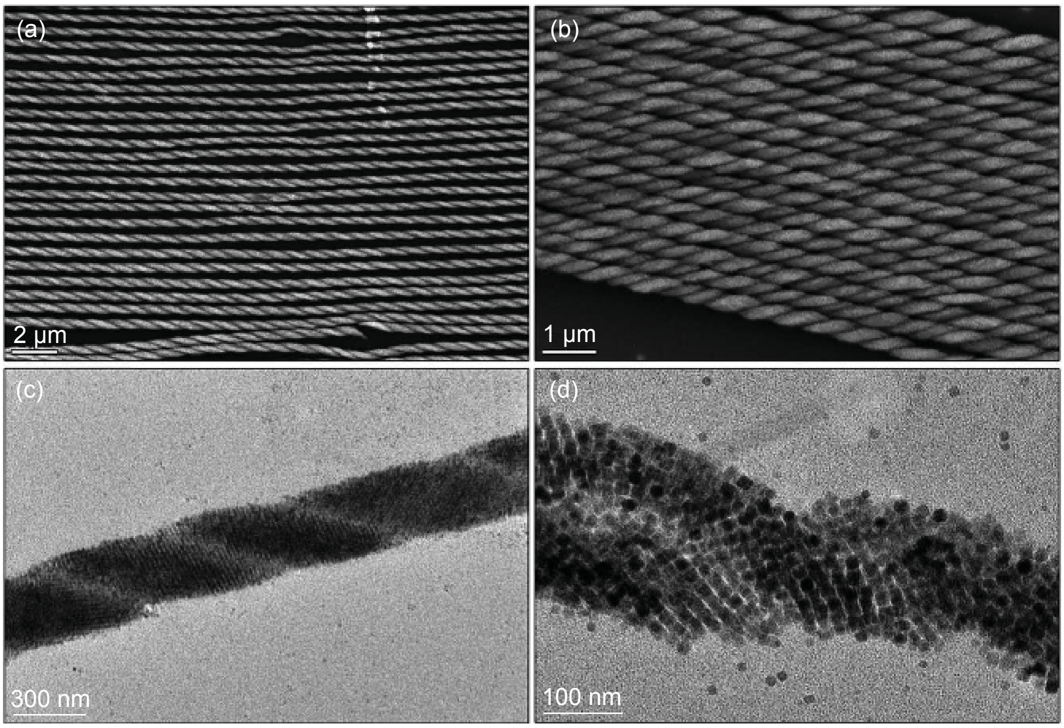

Fig. 2. (a) and (b) Scanning electron micrographs of nanocubes; (c) and (d) transmission electron micrographs showing nanocubes assembled into helical superstructures (4) (Reproduced by permission of The Royal Society of Chemistry)

Conclusions

It is essential to understand nanoparticle synthesis and the effects of experimental conditions on the properties of the final nanoparticles in order to design optimised materials for high-performance applications. Research in this field is ongoing and many aspects in nanoparticle synthesis and assembly are yet to be fully understood. In particular, the much larger number of presentations devoted to nanoparticle assembly – far more than could be described in this brief review – indicates the high level of interest in this area of nanoparticle preparation. This Faraday Discussion meeting provided a good overview of the advances of nanoscience on these topics and the overall content of the presentations and the discussions that took place were very insightful and informative.

References

1. Faraday Discussion: Nanoparticle Synthesis and Assembly: http://www.rsc.org/ConferencesAndEvents/RSCConferences/FD/Nanoparticle-FD2015/index.asp (Accessed on 6th November 2015)
2. C. Salzemann, F. Kameche, A.-T. Ngo, P. Andreazza, M. Calatayud and C. Petit, *Faraday Discuss.*, 2015, **181**, 19
3. R. Latsuzbaia, E. Negro and G. Koper, *Faraday Discuss.*, 2015, **181**, 37
4. G. Singh, H. Chan, T. Udayabhaskararao, E. Gelman, D. Peddis, A. Baskin, G. Leitus, P. Král and R. Klajn, *Faraday Discuss.*, 2015, **181**, 403
5. C. Kunstmann-Olsen, D. Belić and M. Brust, *Faraday Discuss.*, 2015, **181**, 281

The Reviewer

Anastasia Mantalidi graduated with a BSc in Chemistry from the University of Crete, Greece, in 2011, and a MSc degree in Chemical Research from University College London, UK, in 2012. Currently, she is in the last year of her PhD project that is jointly sponsored by the Chemistry Department at UCL and Johnson Matthey. Her project is heavily involved with nanoparticle synthesis employing solution phase protocols and monitoring *in situ* the decomposition of the metal precursors and the subsequent particle formation using synchrotron based techniques.

