Faraday Discussions

Volume 181

Nanoparticle Synthesis and Assembly

ROYAL SOCIETY OF CHEMISTRY

Nanoparticle Synthesis and Assembly

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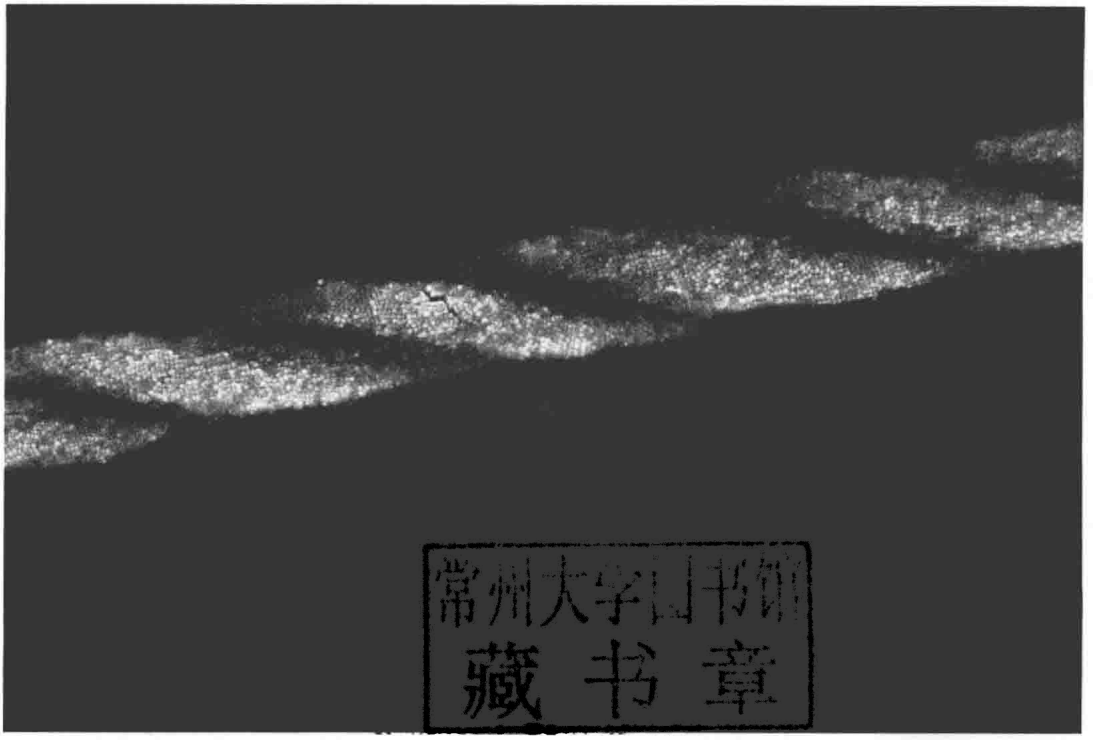

FARADAY DISCUSSIONS

Volume 181, 2015

ROYAL SOCIETY OF CHEMISTRY

The Faraday Division of the Royal Society of Chemistry, previously the Faraday Society, founded in 1903 to promote the study of sciences lying between Chemistry, Physics and Biology.

Faraday Discussions are unique international discussion meetings that focus on rapidly developing areas of chemistry and its interfaces with other scientific disciplines.

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A General Discussion on Nanoparticle Synthesis and Assembly was held in Chicago, USA on the 20th, 21st and 22nd of April 2015.

CONTENTS

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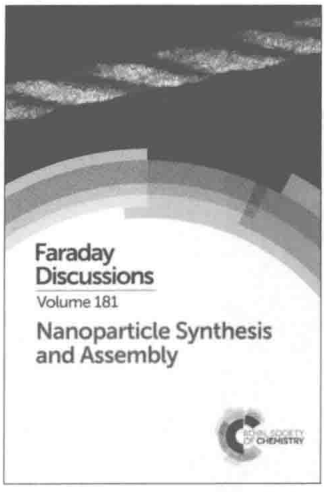

Cover
See Rafal Klajn *et al.*, pp. 403–421.

Under the influence of external magnetic field, cubic nanocrystals of magnetite can self-assemble into helical superstructures.

Image courtesy of Rafal Klajn, Weizmann Institute of Science, Israel, from *Faraday Discuss.*, 2015, **181**, 403.

PREFACE

INTRODUCTORY LECTURE

PAPERS AND DISCUSSIONS

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Faraday Discussions

EDITORIAL

Preface

Bruce M. Law

DOI: 10.1039/c5fd90048d

Nanoparticles (NPs) can be viewed as a new type of "atom" with size dependent physical, optical and electronic properties. NPs can be synthesized into monodispersed entities that can be self-assembled into NP superlattice structures *via* the NP–NP interaction. Alternatively, the NP assembly process can occur *via* directed assembly initiated by application of an external electric or magnetic field or induced *via* assembly under non-equilibrium conditions (*e.g.* solvent evaporation can induce NP assembly). When assembled, the NPs form fractal networks or, alternatively, 1D wires, 2D films or 3D superlattice structures. There are numerous open questions in this field. How does the NP–NP potential govern (i) whether or not an NP superlattice forms, (ii) the kinetics of NP assembly and (iii) what type of superlattice crystallographic structure is formed? Can one design a NP from the ground up, according to theoretical predictions, which will self-assemble into a given NP superlattice structure? How does the assembly process vary with NP shape (*e.g.* spherical, rod, triangular, square, *etc.*) and the ligand coating that surrounds each NP? Can one make more robust NP superlattice structures, of macroscopic size (millimeter to centimeter), which can be molded, milled and machined into desired shapes? Can one make NPs that are stable at high temperature so that their assemblies can be melted, alloyed and cast?

These questions cannot be answered in isolation. A successful attack on these difficult questions requires the coordinated and collaborative effects of NP theorists, NP synthesizers and NP assemblers. The purpose of this particular Faraday Discussion meeting is therefore to bring together these diverse groups of scientists, who share related interests, to foment a synergy that will promote significant advances. The open format of the Faraday Discussion will serve as an ideal environment for presentation of the latest developments in NP theory, synthesis and assembly where the discussion between these disparate groups will generate new ideas and engender new collaborations between these groups.

With these thoughts in mind, the idea of hosting a Faraday Discussion meeting on *Nanoparticle Synthesis and Assembly* at Argonne National Laboratory near Chicago in the US was formulated. The Committee, composed of 3 US and 3 UK/European scientists, decided upon the Opening and Closing Speakers, Invited and contributing speakers and general meeting format after much debate, spread over a 4 year period. With bated breathe the meeting date finally arrived, 20–22

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April 2015, and 125 participants from 25 countries gathered to attend only the third Faraday Discussion meeting to be held in the US in its one hundred year history. After brief welcoming remarks from Alfred P. Sattelberger (Argonne Deputy Director) and Bruce M Law (Chair of the Scientific Committee) the Chair had the delightful pleasure of being able to introduce and present the Opening Speaker, Paul Alivisatos (Director of Lawrence Berkeley National Laboratory), with the Spiers Memorial Award for outstanding accomplishments to the field of nanoparticle synthesis and assembly. Each year the Spiers Memorial Award is given to an Opening Speaker who has made outstanding contributions to a particular Faraday Discussion topic. Frederick Solomon Spiers, the founding secretary of the Faraday Society for 20+ years, "was indefatigable in promoting and organising the succession of discussions which have made the Society known throughout the world".[1]

As might be expected, Paul Alivisatos' opening remarks describing *in situ* Electron Microscopy observations of nanoparticle formation in a liquid medium were extremely well received and generated significant discussion. Paul's introductory lecture was followed by 23 contributed papers and 3 invited discussion remarks spread over 8 sessions in this Monday afternoon to Wednesday lunchtime Faraday Discussion meeting.

Two Monday afternoon sessions discussed new synthetic NP methods where the influence of dissolved gases, ionic species, thermally tunable interaction sites, and biologically controlled synthesis were investigated. Thirty second, single slide Lightning Presentations preceded the Monday evening Poster session and wine reception, which was sponsored by Cogent. Seventy posters, including 40 student posters, from around the world stimulated animated discussion. The Committee had the unenviable and challenging task of judging these student posters whose diversity, excellence and novelty led to lively and friendly discourse. A decision had to be made by the Committee before the Conference Dinner on Tuesday

Fig. 1 Paul Alivisatos (right) receiving the Spiers Memorial Award from Bruce M Law.

Fig. 2 Poster session.

evening, thus, after much Committee debate throughout Monday and Tuesday Igor Fedin's poster on "Probing the surface of nanocrystals with electrochemistry *in situ*" and Daniela John's poster on "Self-assembly of cyclodextrin-functionalized particles" were each awarded a Student Poster prize.

The Tuesday morning session kicked off with a lively discussion on the synthesis and properties of patchy NPs. This was followed by two sessions describing numerous differing routes for self-assembling novel 1D, 2D and 3D superlattice nanostructures mediated by temperature, ions, ionic liquids, ligands, templated capillary assembly, and wrinkles. The mechanical and plasmonic

Fig. 3 Closing Speaker David Schiffrin.

properties of self-assembled nanostructures completed the Tuesday afternoon session just prior to a well attended facility tour of the *Center for Nanoscale Materials* at Argonne. Tuesday evenings' Conference Dinner, which was washed down with extensive quantities of wine, was followed by the announcement and presentation of the Student Poster prizes and a hilarious rendition of the *Loving Cup Ceremony*.

Two sessions on Wednesday morning describing low-current and magnetic field assisted nanoparticle assembly completed the contributed talks for this Faraday Discussion meeting. David Schiffrin provided apt and appropriate Concluding Remarks connecting Michael Faraday's historical investigations of nanoparticle optical properties to the current Faraday Discussion topic on *Nanoparticle Synthesis and Assembly*.

As Chair of this third Faraday Discussion meeting to be held in the US, I would judge this meeting a resounding success. The frequency of US Faraday Discussion meetings is increasing, which undoubtedly is a healthy development considering the level of interest at this current meeting. (The first meeting in the US was held at the University of Notre Dame, Indiana in 1963 on radiation chemistry (FD36). The second meeting (FD146 on superhydrophobicity) took place 47 years later in 2010 at the Jefferson Hotel in Richmond, Virginia.) My hope is that this current Faraday Discussion meeting will generate continuing interactions and developments in nanoparticle synthesis and assembly and that the style of this meeting may encourage further attendance at future FD meetings or, perhaps, as it did for me, stimulate sufficient interest that a fourth FD meeting is planned for the US in the not too distant future.

The success of this FD meeting was dependent upon the dedication and hard work of numerous people at the Royal Society of Chemistry, Argonne National Laboratory and elsewhere. In particular, a debt of gratitude is owed to my Committee, Chris Sorensen (Kansas State University), Fernando Bresme (Imperial College London), Helmuth Moehwald (Max Planck Institute of Colloids and Interfaces), Philip Moriarty (University of Nottingham) and Xiao-Min Lin (Argonne National Laboratory) whose sound advice determined the overall composition of this meeting. Xiao-Min Lin, as the local host at Argonne, carried much of the organizational burden for this meeting. Thank you Xiao-Min. A similar debt of gratitude is owed to the wonderful organization at the Royal Society of Chemistry who provided unending support and advice in the organization of FD meetings and in the publication of FD volumes, in particular, Alisa Becker, Claire Springett, Heather Montgomery, Elisabeth Ratcliffe, and Chris Goodall provided immediate feedback and sage advice. Undoubtedly, there are other members of their team, who work behind the scenes, to whom I also owe a thank you. A large number of individuals at Argonne ensured the smooth and seamless running of this FD meeting. Special thanks to Jacquelin LeBreck (meeting coordination), Eva Stringer (security clearance and gate pass organization), Carmie White (wine, dinner, lunches, poster board and conference room organization), and Tim Donnelly, Jonathon Schmidt, and Stewart Sulphur who ensured glitch free video, audio and PowerPoint presentations. Sean McBride and Jonghun Lee, our friendly "microphone runners", ensured a steady stream of questions for the speakers. Thanks are due to Elena Schevchenko, Yugang Sun, and Subramanian Sankaranarayanan who agreed to be session chairs at the last minute. Thank you also to the Center for Nanoscale Materials Users Office for the

tour, in particular, thanks to Martin Holt, Julie Emery, Ron Tollner, Andrew DiLullo, and Anand Bhattacharya. Financial support for this Faraday Discussion meeting was provided by Argonne National Laboratory, Kansas State University, the Physics Department at Kansas State University, and Cogent. The availability of this funding for student scholarships, travel and conference costs, as well as entertainment costs *etc.* is gratefully acknowledged and certainly made the job of the Committee much, much easier. Finally, thank you to the Opening and Closing Speakers, invited and contributing speakers, poster presenters and conference attendees for the stimulating discussion that pervaded this meeting.

Notes and references

1 Obituary, Frederick Solomon Spiers, *Trans. Faraday Soc.*, 1926, **22**, 207.

Faraday Discussions

PAPER

Spiers Memorial Lecture

New tools for observing the growth and assembly of colloidal inorganic nanocrystals†

A. Paul Alivisatos,*[abc] Hoduk Cho[abc] and Jungwon Park[de]

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We present two examples of the use of liquid cells to study colloidal inorganic nanocrystals using *in situ* transmission electron microscopy. The first uses a liquid cell to quantify the interaction potential between pairs of colloidal nanocrystals, and the second demonstrates direct imaging of nanocrystal growth and structure in the liquid cell.

Over the last twenty years, colloidal inorganic nanocrystals have evolved into a major building block for solid state chemistry and the design of materials. Today, such nanocrystals are in practical use in biological imaging, in displays, and in many other technologies.[1–4] Further, there is intensive interest in designing new nanocrystals with complex interconnections, spatial arrangements, and topologies, which can be used in more advanced areas of application, in solar to fuel catalysis for example.[5] In order to achieve these goals, it is highly desirable to be able to understand the growth and assembly of these major building blocks as they form in solution. The very recent advent of the *in situ* liquid cell for transmission electron microscopy is just such a tool, and this lecture is dedicated to examining how these liquid cells today are enabling a new period of quantitation of nanocrystal growth and assembly.

In the first segment of this lecture, we review the use of the liquid cell to quantitate the interaction potential between pairs of colloidal nanocrystals.[6] Here we use a conventional liquid cell, one fabricated with two thin SiN windows (each 50 nm thick) separated by a liquid layer of approximately 150 nm at its thinnest point. In such a cell, we can load nanocrystals, such as positively charged Au nanorods in a buffered water solution. Due to the force of attraction between the nanocrystals and the SiN window, we find that typically the nanocrystals are

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† Electronic supplementary information (ESI) available. See DOI: 10.1039/c5fd90056e

confined to a two-dimensional region near one of the windows, and within this thin layer they are free to move about (see Movie 1† and Fig. 1, reproduced from ref. 6). When two nanorods approach each other we can see that they tend to do so end to end, a rather surprising result, since the van der Waals force of attraction will be greatest for side to side attraction. Nonetheless, we can clearly see trajectories where nanocrystals fuse end to end. Further, we find that the nanocrystal aggregation is completely suppressed at lower ionic strengths. In principle, from the trajectories of pairs of nanocrystals in solution, we can reconstruct at each value of the ionic strength the form of the pairwise interaction potential *versus* angle and distance. Using this approach, we were able to show that for separations greater than around 10 nm, where the van der Waals forces become negligible, the effective interaction potential is dominated by screened Coulombic forces, which is consistent with the classical Derjaguin–Landau–Verwey–Overbeek (DLVO) model.[7,8] From this we can understand why it is that the nanocrystals join end to end, because this is the direction for which the repulsive force at long distances is the least. This is just one recent example, showing how it is possible to learn about the forces between nanoparticles in a very direct way using the liquid cell.

A second example to be considered here concerns the direct imaging of nanocrystal growth and structure in the liquid cell. For this purpose, higher resolution is required, and this is greatly facilitated by using the graphene liquid cell.[9] Here a thin layer of liquid is trapped between two layers of graphene, either single layer thickness of graphene, or multilayer, depending on what is needed. Inside such a cell, it is possible to use the electron beam itself to induce the nucleation and growth of nanocrystals, and to observe the trajectories of their growth in the fluid. In this cell, the attraction to the "windows" is much less, so the motion is more three dimensional. We have used the liquid cell to observe the growth of Pt nanocrystals as an example. A significant surprise came when we saw that the Pt nanocrystals form through a somewhat unexpected sequence (Movie 2,† reproduced from ref. 9). At the earliest times, we observe a burst of nucleation of rather small (<1 nm) particles. This period of nucleation is followed by a period of coalescence and growth in which there are many particle fusion events, as well as events where individual particles grow by addition of molecular precursors (Fig. 2). This particle fusion is presumably due to the relatively high surface energy of the Pt nanocrystals as compared to the energy of a grain boundary.[10] In such a liquid cell, it also appears to be possible to observe the electron diffraction patterns from individual particles as they rotate freely in the solution, opening the

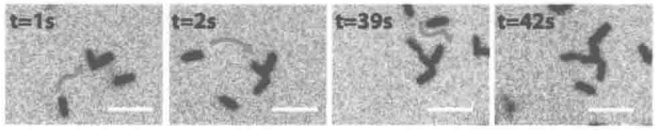

Fig. 1 A time series of TEM images showing how Au nanorods approach and attach to each other to give the final tip-to-tip assembled structure. Red arrows highlight the trajectories of nanorods before they attach to the cluster of growing rod assemblies. Scale bar is 100 nm. Reprinted with permission from ref. 6. Copyright 2015 American Chemical Society.

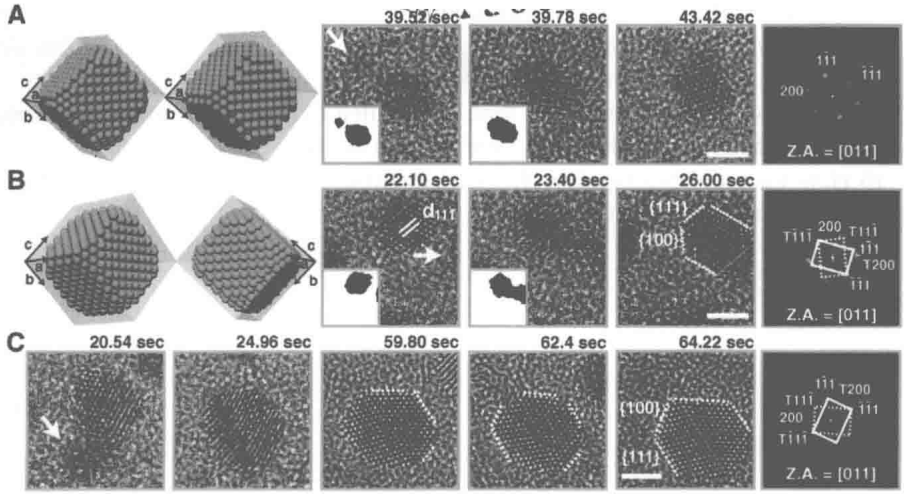

Fig. 2 Still snapshots from Movie 2† of Pt nanocrystal growth *via* coalescence and crystal-structure evolution, observed with atomic resolution in a graphene liquid cell. Schematic illustrations and corresponding TEM images exhibiting nanocrystal coalescence along the ⟨111⟩ direction, evolving into (A) a single crystalline fcc structure or (B) a twinned (red dotted line) fcc structure. (C) Shape evolution of the Pt nanocrystal by straightening of the twin boundary (red dotted line) and evolution toward a hexagonal shape. The right-hand panel in each sequence shows a FFT of the panel adjacent to it. White arrows denote incoming small nanocrystals (as seen in insets). Scale bars, 2 nm. Z.A., zone axis. Reprinted with permission from ref. 9. Copyright 2012 American Association for the Advancement of Science.

door to one day being able to directly obtain the structure of individual nanocrystals.

In the two examples given above we can see that the *in situ* liquid cell for the transmission electron microscope has the potential to provide unprecedented levels of quantitative information about nanocrystal growth and assembly. There are still many aspects of this to be worked out, such as improved understanding of the influence of the electron beam on the chemical environment (we know that heating is negligible), and the nature of the liquid layers that are trapped in such thin cells. Nonetheless, we can see already that a new era of quantitation for nanocrystal building blocks is upon us.

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