"Complex-shaped Metal Nanoparticles: Bottom-Up Syntheses and Applications"

Edited by Tapan K. Sau (International Institute of Information Technology, Hyderabad, India) and Andrey L. Rogach (City University of Hong Kong, Hong Kong), Wiley-VCH Verlag & Co KGaA, Weinheim, Germany, 2012, 582 pages, ISBN: 978-3-527-33077-5, £125.00, €178.80, US$200.00

http://dx.doi.org/10.1595/147106713X664617 http://www.platinummetalsreview.com/

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Introduction

"Complex-shaped Metal Nanoparticles: Bottom-Up Syntheses and Applications" offers a comprehensive review of shaped metal nanoparticles through synthetic strategies, theoretical modelling of growth, discussion of properties and present and future applications. The book is brought together by editors Tapan K. Sau (International Institute of Information Technology, Hyderabad, India) and Andrey L. Rogach (Department of Physics and Materials Science at the City University of Hong Kong). Between them, they draw on their considerable expertise in the synthesis of metal and semiconductor nanoparticles, spectroscopy, photonics and applications of nanomaterials, to combine 16 chapters from a large number of specialist authors. This review will cover the majority of the book, which refers in the main to noble metal particles, with the exception of a few chapters which are specifically related to non-platinum group metal (pgm) materials and are therefore beyond the scope of this review.

The field of nanoparticle preparation has enjoyed an explosion in interest in the last decade as new applications exploiting the novel physical, electronic and optical properties of the particles have been discovered. The properties of nanoparticles are highly dependent on their morphology and thus, a vast number of academic articles have been published tackling the subject of the synthesis of specific shapes of nanomaterials. "Complex-shaped Metal Nanoparticles: Bottom-Up Syntheses and Applications" aims to bring together this research in one volume giving a sound understanding of the general principles, with copious references to more detailed research papers if required and looking towards potential future applications.

Practical Aspects

The book opens with the most substantial chapter, written by the editors, which gives a more general introduction to complex-shaped noble metal nanoparticles and is an essential read for those less familiar with the subject. The brief discussion on the classification of different shaped nanoparticles and accompanying figure of transmission electron microscopy (TEM) images (**Figure 1**) serves to emphasise the breadth of this topic. The synthesis methodologies are introduced by the means of reduction, with a heavy emphasis on chemical reduction but also including electrochemical, photochemical and biochemical routes. It does omit other methods such as sonochemical and hydrothermal reduction, but gives references to alternative sources that cover these.

The chapter provides a useful introduction to topics such as the use of hard templates, for example aluminium oxide porous membranes, and soft templates, for example micelles, to control the growth of the particles. It also covers galvanic replacement and seed-mediated synthesis. Many of these topics are discussed in greater detail in subsequent chapters. In addition to synthesis, the chapter also briefly reviews the many analytical methods that are commonly used to characterise nanoparticles and discusses the pros and cons of each method. It goes on to address the mechanisms of morphology evolution with comprehensive references to the academic literature, for example, the growth of branched platinum nanoparticles from twinned seed crystals or the role of the common growth directing surfactant, cetyltrimethylammonium bromide (CTAB), in the formation of gold nanorods. The editors are pleasingly frank about the limitations of the synthetic methods and emphasise the need for post-synthesis separation due to the prevalence of polydisperse particles in many of the preparations. The chapter concludes with an outlook on where research is lacking and knowledge needs to be improved in order to progress the applications for shaped nanoparticles.

A more in depth look at templating techniques is described in the following chapter by Chun-Hua Cui and Shu-Hong Yu (University of Science and Technology of China). Templating covers a variety of techniques including galvanic displacement, such as the formation of platinum nanotubes from the treatment of silver nanowires with platinum acetate, the use of the porous membrane template anodic aluminium oxide for the electrodeposition of palladium nanowires, hard templates, such as lithographically produced patterns or soft templates, such as CTAB micelles.

Na Tian *et al.* (Xiamen University, China) provide a well set out chapter on high surface energy nanoparticles and their use in electrocatalysis. Nanoparticles with a

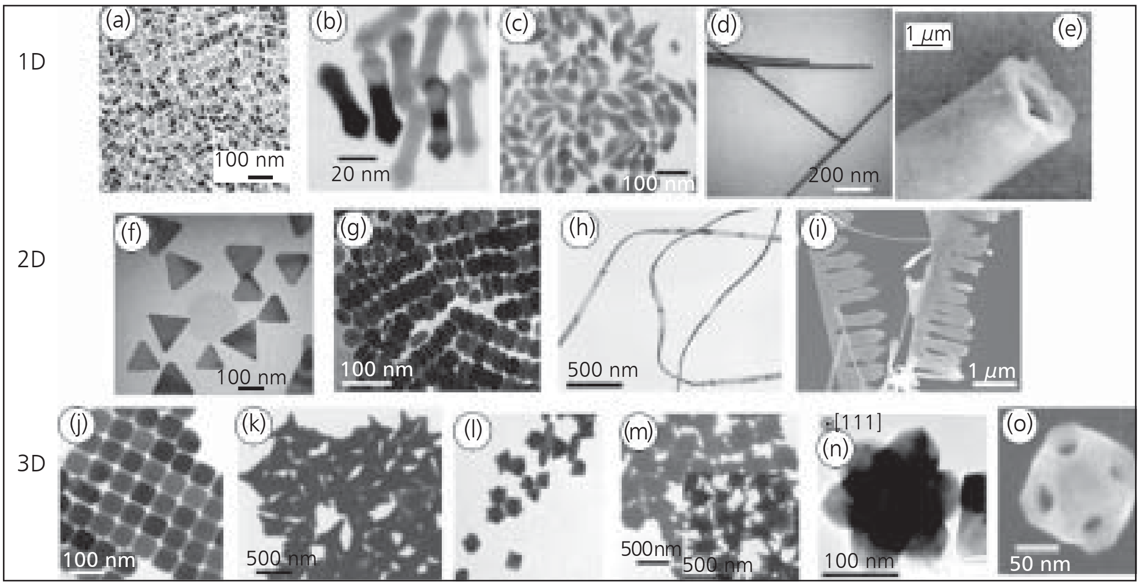


Fig. 1. TEM and SEM images of one-, two- and three-dimensional noble metal nanoparticles: (a) nanorods; (b) nanoshuttles; (c) nanobipyramids; (d) nanowires; (e) a nanotubule; (f) triangular nanoplates; (g) nanodiscs; (h) nanoribbons; (i) nanobelts; (j) nanocubes; (k) nanotetrapods; (l) and (m) star-shaped nanoparticles; (n) a nanohexapod; and (o) a nanocage (Reproduced with permission from Wiley-VCH)

high surface energy have an increased proportion of active surface atoms, with obvious advantages in fuel cells, electrooxidation of ethanol and other catalytic applications. The pgm nanoparticles have a face-centred cubic structure and under thermodynamic equilibrium conditions are enclosed by low energy facets {111} giving an octahedral or tetrahedral shape. The authors describe electrochemical and wet chemistry routes to alternative high energy shapes – concave hexaoctahedrons, 5-fold twinned nanorods, rhombic dodecahedrons and many more. They provide a very useful table including pictures of the shapes, the indices of their facets and references to the literature.

Chapter 9, written by Christophe Petit and Caroline Salzemann (Université Pierre et Marie Curie, Paris, France) and Arnaud Demortiere (Argonne National Laboratory, USA), is specific to platinum and palladium nanoparticles, bringing together some of the more general principles covered earlier in the book. It illustrates the complexity of controlling the numerous variables involved in defining particle morphology. The authors compare the use of alkylamine capping agents in the Brust and reverse micelle synthesis methods, resulting in faceted platinum nanocrystals and polycrystalline worms, respectively. They go on to discuss the effect of reaction conditions, for example the timing of capping agent addition or the presence of dissolved gasses, on the resultant particle shape. Platinum rods, cubes or tripods can be generated by using a nitrogen atmosphere; in the presence of hydrogen, platinum nanocubes are formed. The chapter is completed by a short discussion on self-assembled supercrystals, for example square-based pyramidal or triangular superlattices made up of truncated platinum nanocubes (**Figure 2**).

This leads nicely into a chapter on ordered and non-ordered porous superstructures written by Anne-Kristin Herrmann (Technische Universität Dresden, Germany) *et al.* These have applications in a variety of areas including gold substrates for surface-enhanced Raman spectroscopy and ordered hollow palladium spheres for use as catalysts in the Suzuki reaction. The authors cover techniques including the use of artificial opals or polystyrene spheres as templates, which can be removed by acid etching leaving metal nanoparticle shells. Biotemplates and non-ordered templates, such as aerogels and hydrogels, are also discussed.

Theory

Chapters 6–8 cover the theoretical aspects of complex-shaped nanoparticles. Tulio C. R. Rocha (Fritz-Haber-Institut der Max-Planck-Gesellschaft, Germany) *et al.* discuss Monte Carlo simulations of growth kinetics with an emphasis on defects, such as stacking faults and twin planes, using the synthesis of shaped silver particles as an illustration. Vladimir Privman (Clarkson University, USA) looks at the modelling of nucleation and growth and its application to shape selection and control of the morphology of growth on surfaces. Amanda S. Barnard (Commonwealth Scientific and Industrial Research Organisation (CSIRO), Materials Science and Engineering, Australia) takes a thermodynamic rather than a kinetic approach with the emerging technique of thermodynamic cartography. This involves mapping the thermodynamically preferred structure within specified parameters such as temperature, pressure or chemical environment.

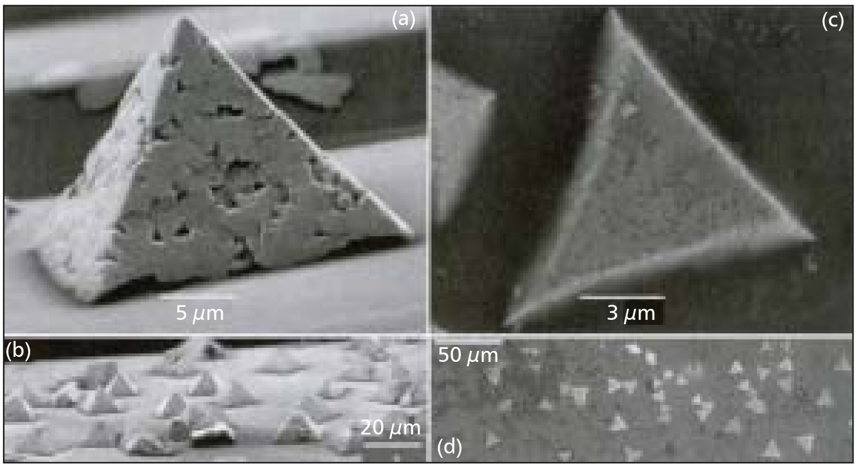


Fig. 2. SEM images of supercrystals of truncated platinum nanocubes: (a) superlattice of pyramidal shape; (b) ensemble of pyramidal supercrystals on a substrate; (c) superlattice of triangular shape; and (d) ensemble of triangular supercrystals on a substrate (Reproduced with permission from Wiley-VCH)

No text on nanoparticles would be complete without a section on surface plasmons and optical responses. This is provided by Cecilia Noguez and Ana L. González (Universidad Nacional Autónoma de México, Mexico) in Chapter 11. It is quite a theoretical chapter, illustrated by numerous equations, which at first appear a little daunting to the synthetic chemist. However, the chapter provides a useful discussion on how surface plasmon resonances are sensitive to particle shape.

Applications

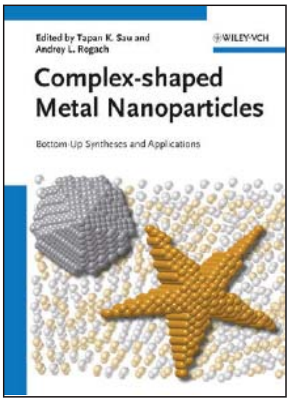
Chapters 12 to 16 take a more detailed look at the applications for complex-shaped nanoparticles. The order of these chapters does appear to be a little haphazard with chapters on biomedical applications interspersed with other topics but as the book is designed as a reference to be dipped into it does not detract too much from the overall experience. In Chapter 12 Thomas A. Klar (Johannes-Kepler-Universität Linz, Austria and Center for NanoScience (CeNS), Germany) and Jochen Feldmann (Ludwig-Maximilians-Universität München, Germany) introduce fluorophore-metal interactions and their application in biosensing. It begins by going through the theories behind the subject, before moving on to the applications, such as ion sensing or immunoassays, but is written in an understandable way for those new to the topic. The chapter would benefit from some concluding remarks on future trends in this area.

Chapter 13 deals with surface-enhanced Raman spectroscopy (SERS) and is written by Frank Jäckel and Jochen Feldmann (Ludwig-Maximilians-Universität München). It gives a good overview of the subject without going into too much detail, and gives references to further reading. The authors clearly emphasise the effect of particle morphology in SERS and compare different particle shapes, in keeping with the aims of this publication. The following chapter, written by Alexander O. Govorov *et al.* (Ohio University, USA) moves back to bioapplications and the photothermal effect of plasmonic nanoparticles. It is mainly concerned with the theory of the plasmonic photothermal effect with a small section on applications and although it is of interest in the more general context of nanoparticle applications, it is not in keeping with the main theme of this book – complex-shaped nanoparticles.

Jun Hui Soh (Institute of Bioengineering and Nanotechnology, Singapore) and Zhiqiang Gao (National University of Singapore) discuss the role of metal nanoparticles in biomedical applications in Chapter 15, covering subjects from diagnostics and imaging to therapy. Some of these topics are discussed in more detail in the preceding chapters, but this chapter gives a well-written overview of all aspects of biomedical applications. The only criticism is the lack of real-world examples, as the references are all based on academic literature. The final chapter deals with thermoelectric materials, which are generally semiconductor materials.

Summary

In conclusion "Complex-shaped Metal Nanoparticles: Bottom-Up Syntheses and Applications" is an extremely useful reference, whether the reader is interested in synthesis, application or theory of complex-shaped nanoparticles. Although there is some repetition between chapters written by different authors this serves to give the reader a choice of the depth to which they wish to explore the subject and I would recommend it as an informative resource to anyone from students to experienced researchers. The book clearly shows the potential for use of noble metals in a broad spectrum of applications, including catalysis, fuel cells, sensors, diagnostics and targeted drug delivery. It becomes obvious that more research into the reliable production of shaped nanoparticles would be highly beneficial.



"Complex-shaped Metal Nanoparticles: Bottom-Up Syntheses and Applications"

The Reviewer

Laura Ashfield received her DPhil in Inorganic Chemistry from the University of Oxford, UK, in 2005 and subsequently joined Johnson Matthey Technology Centre, Sonning Common, UK, where she is a Principal Scientist. Her work centres around the synthesis of nanomaterials with controlled morphology for a range of applications.

