GREEN NANOMATERIALS

From Bioinspired Synthesis to Sustainable Manufacturing of Inorganic Nanomaterials

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Preface

This book aims to provide an understanding of emerging bioinspired green methods for preparing inorganic nanomaterials.

Inorganic nanomaterials are used in many applications ranging from sun cream to catalysis and the latest innovations in nanomedicine and high density data storage. In the recent years, we have rightly seen a large quantity of publication activity (including books) on the safety and toxicity of nanomaterials. However, there is a distinct lack of consolidated effort on addressing the sustainability of making nanomaterials. Current methods for nanomaterials synthesis are complex, energy demanding, multistep, and/or environmentally damaging and hence clearly not sustainable. Green chemistry has great promise for future developments, especially in sustainable designs for materials, processes, consumer goods, etc. However, to date, green chemistry has mostly focussed on the synthesis of fine chemicals and very rarely on nanomaterials.

New bioinspired/biomimetic approaches are emerging, which harness biological principles from biomineralisation to design green nanomaterials for the future. With reference to significant body of research performed on understanding biomineralisation, Ozin *et al.* state in their book that "*In molecular terms, it is relatively easy to comprehend the early stages of self-organisation, molecular recognition, and nucleation that precede the morphogenesis of biomineral form. It is not obvious however, how complex shapes emerge and how, in turn, they can be copied synthetically.*"[1] In this book, the aim is to address this highly sought aspect of how to translate the understanding of biominerals into new green manufacturing methods. We cover aspects from the discovery of new green synthesis methods all the way to considering their commercial manufacturing routes.

Who is the book for? The Royal Society of Chemistry and the American Chemical Society's Green Chemistry Institute have both highlighted a "*lack of a deep bench of scientists and engineers with experience in developing green nanotechnology*"[2] as a significant barrier to the development and commercialisation of green nanotechnology. This has motivated us to write this book. When any of us have been educated within a specific traditional discipline of science or engineering for our undergraduate degree, it can be very daunting to take a leap into multidisciplinary science and study within the realms of new disciplines outside our comfort zone, where the experimental approach, culture and even language can be so different, creating barriers and challenges. However, the more we work at this interface the more we realise that these boundaries are artificial for the purpose of our education and do not exist in nature. The purpose of this book is to start with basic explanations to build a foundation, so this area of science can become accessible to students from any related discipline. We hope that this book encourages scientists and engineers to become confident to bridge the gaps between chemistry, nanotechnology, biology, engineering and manufacturing. Specifically, the book combines green chemistry and nanomaterials in a single dedicated monograph.

As such, the book is written with a wider readership in mind including primarily academic researchers focusing on synthetic biology and nanomaterials. This book is targeted towards postgraduate students (taught and research degrees) undertaking studies pertaining to

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[1] Ozin GA, Arsenault AC Cademartiri L, *Nanochemistry: A chemical approach to nanomaterials*, 2nd ed. (Royal Society of Chemistry, Cambridge, 2009), p23.
[2] Matus, et al., Green Nanotechnology: Challenges and Opportunities, ACS Green Chemistry Institute, 2011.

advanced materials and green, sustainable and/or environmental engineering or chemistry. Final year undergraduate students specialising in nanomaterials or green processes will also find this book valuable. Indeed, various universities currently run final year electives on nanomaterials, biomaterials, green chemistry, sustainability, etc., where this book is highly suitable as a textbook. Through the authors' interactions with industry, we know that many industries wish to learn more about these green technologies. Hence, we hope to reach industrialists and raise awareness of the emerging green manufacturing routes.

What is in the book? The book starts by introducing the principles of green chemistry and engineering (Chapter 1). It then highlights the special properties that nanomaterials possess, their applications and ways to characterise them (Chapters 2-3). It describes conventional methods of synthesising and manufacturing inorganic nanomaterials (Chapter 4) and highlights that these techniques cannot always deliver the specifications required for applications or be sustainable (Chapter 5). This will lead to the introduction of biological and biomimetic/bioinspired synthetic methods as a solution to precisely controlled nanomaterials as well as design sustainable manufacturing routes (Chapters 6-7). The book elaborates on various mechanisms and examples of green nanomaterials (e.g. role of organic matrix and natural self-assembly, and advantages and opportunities with green nanomaterials). It will cover two case studies of magnetic and silica materials for advanced readers (Chapters 8-9).

How to use the book. We acknowledge this book covered many different traditional disciplines and as such we cannot go into too much depth in every area. Furthermore, this is a very current and fast-moving research area. As new methods, materials and characterisation techniques are discovered, invented and developed, fairly recent advances become old quickly. For both reasons we recommend this text book be supplemented with more detailed, specific and contemporary science and engineering research journal papers. Indeed, in the courses we teach on this subject, the material content of this book is used to explain the background and introduce current research papers as relevant examples.

Acknowledgements

We would like to acknowledge those who helped us complete this book. SP is sincerely grateful to Professor Steve Clarson and Professor Carole Perry who have been the sources of inspiration. SS would like to acknowledge Prof Andrew Harrison and Prof Steve Evans for inspiring and enabling her to begin her research in this area. We thank the scientific communities to which we belong: The networks of academics we work and collaborate with and meet at conferences where we share and develop new ideas, converse and debate. You are a constant source of inspiration for us and for science and engineering in this field to continue to develop. Our collaborators are acknowledged for sharing their wisdom and for the many stimulating discussions over the years. In particular, SS is grateful to Dr. Bruce Ward and Prof. Steph Baldwin for biological training and insight. We thank many of our current and past group members who have been instrumental in providing the ammunition for this book and for their patience during the writing stages. SS thanks Andrea Rawlings and SP thanks Dr. Joe Manning and Dr. Mauro Chiacchia for their help with conceptualising some of the complex aspects/mechanisms included in this book. We are grateful to have the support from Ms. Yung Hei Tung (Jodie) and Drs. Johanna Galloway & Scott Bird for artwork for some of the figures and Ms. Amber Keegan for help with copyright permissions. Finally, we thank the reviewers for their insightful feedback: From the initial book proposal, to friends providing comments on early drafts (thanks to Prof. Maggie Cusack, Prof. Marc Knecht and Dr. Fabio Nudelman) and the reviewers of the completed draft. We offer sincere thanks to the publisher for their support and patience.

Finally, we would both like to thank our families. Academia is a challenging and intense career and this is only amplified when one choses to write a book on top of our other commitments. We are most grateful to our families for their love and support both generally and specifically over the period of writing this book. We both have young children and are especially grateful: SP to his wife Geetanjali and SS to her husband Luke and our parents, for unquestioning childcare that enabled us to achieve this body of work. We are also grateful to our children; Ninaad and Nishaad; Owen, Alex and Joel for their interest in our work, for making us laugh and their inquisitive nature that reminds us every day what this is all for.

…and ongoing: In order to allow a dialogue between the readers, the authors and the publisher, we have created a dedicate web-portal in order to receive feedback from readers and to allow authors and readers to post recent updates relevant to this book. This can be accessed at www.greennanobook.com.

Siddharth V. Patwardhan and Sarah S. Staniland
Sheffield, August 2019.

Author biographies

Siddharth V. Patwardhan

Siddharth is currently a Professor of Sustainable Chemical and Materials Engineering at the University of Sheffield. He obtained a first degree in chemical engineering at the University of Pune (India) followed by masters and doctorate in materials science at the University of Cincinnati (USA). He gained post-doctoral experience in inorganic chemistry at the University of Delaware (USA) and Nottingham Trent University (U.K.). After taking up a short-term lectureship in Chemistry, he became a Lecturer in Chemical Engineering at the University of Strathclyde in 2010. He then moved to Sheffield to take up a position of Senior Lecturer, where he was promoted to a Professor in 2018.

Siddharth leads the Green Nanomaterials Research Group (www.svplab.com) with a vision to develop sustainable routes to functional nanomaterials. His group focusses on the discovery of bioinspired nanomaterials, assessing their scalability and developing manufacturing technologies for energy, environmental, biomedical and engineering applications.

Siddharth is an EPSRC Fellow in Manufacturing and a Fellow of the Royal Society of Chemistry. He has played a key role in a number of national and international networks as well as conference organisation. One such symposium relevant to this book is on “Green Synthesis and Manufacturing of Nanomaterials” as part of the ACS Green Chemistry and Engineering conference in 2017. Siddharth is passionate about mentoring early career researchers and has received numerous awards including Dedicated Outstanding Mentor awards, Teaching Excellence awards and recognition as a *SuperVisionary* for all-round supervision.

Sarah S. Staniland

Sarah is currently a Reader of Bionano-Materials in the Department of Chemistry at the University of Sheffield. She obtained an integrated undergraduate Masters degree in

Chemistry followed by doctorate in Materials Chemistry (2001, 2005) both at the University of Edinburgh (UK).

After her PhD she won a prestigious independent EPSRC life science interface fellowship (2005-2008) at the University of Edinburgh where she initiated the research, she is currently active in. This helped her transition from the chemical material sciences to interdisciplinary work at the interface with biology. She took this opportunity to live and work in various places globally, from Cape Town to Tokyo, forming lasting collaboration. She then took up a Lectureship in Bionanoscience in the School of Physics and Astronomy, University of Leeds in 2008 where she was promoted to Associate Professor in 2013. She moved to Sheffield in 2013 and was promoted to Reader of bionanoscience in 2016.

Sarah leads the bionanomagnetic research group which studies the biomimetic synthesis of magnetic nanomaterials, particularly inspired from how magnetite nanoparticles are produced within magnetic bacteria. From a basis of material chemistry and PhD in magnetic materials, Sarah has moved into a multidiscipline approach of using biology to control material synthesis. She has been invited to speak at and organised national and international conferences to promote this research area and been a board member of the royal society of chemistry (RSC) materials chemistry division. This multidisciplinary research field requires a highly-skilled, open-minded and diverse research team, which she is passionate about training, developing and mentoring and is very grateful to them all. Sarah is Committed to teaching, especially multidisciplinary science that falls at the interface between several standard degree subjects and is always experimenting with novel methods and techniques to improve her teaching in this area. She has taught a course on bionanoscience (covering much of the material in this book) for 10 years. Sarah has won 3 prestigious awards recently: 2 for her research: the acclaimed RSC Harrison Meldola award in 2016 and the Wain award in 2017. She has also won the Suffrage science award in 2017 for her work on the promotion of gender equality.

CHAPTER 1
GREEN CHEMISTRY AND ENGINEERING

Key Lessons

This short section consists of a chapter on green chemistry and engineering. It introduces the 12 principles of green chemistry and various drivers for making a given process or product greener, and ways to improve sustainability are discussed mainly in terms of the cost of waste produced. A brief introduction is provided on how to evaluate sustainability or green credentials of a given process or product leading to a discussion on ways to improve sustainability. These concepts will be used in other chapters in the book in order to explore potential (un)sustainable aspects of a given method for nanomaterials synthesis. This section is aimed to set the scene for the book and the principles explained will be revisited in latter sections of the book in order to put them in the context of nanomaterials synthesis and manufacturing.

CHAPTER 2
NANOMATERIALS: WHAT ARE THEY AND WHY WE WANT THEM?

Key lessons

Nanomaterials have a very high surface area to volume ratio. This mean surface chemistry and physics dominates their properties. The large surface area is also useful for increasing activity of surface reactions (i.e. heterogeneous catalysis) and ideal for delivery of an active species attached to the surface (i.e. high loading od drugs etc.). Small size also lends itself to nanomedical applications as the small size warrant access to everywhere in the body and it also makes their nanomaterials a comparable size to biological targets such as proteins. A number of phenomena key to nanoscale are discussed and include surface plasmon resonance (SPR), quantum confinement and superparamagnetism. Valuable applications arising from these special properties are discussed such as nanomedicine, nanodevices and a selection of consumer products. Nanotoxicity and biocompatibility are considered when designing all types of nanomaterials, not just those for biomedical use.

Across the applications it is clear that as the design of our nanomaterials becomes more sophisticated, we are challenged to see if the synthesis of more intricate nanomaterials with more demanding specifications can keep up and deliver these materials precisely and consistently. This is ever more important for nanomaterials for *in vivo* medicines. These need to be precise, consistent but also produced in a non-toxic way that ensures the nanomaterials are biocompatible and safe for medical use.

CHAPTER 3
CHARACTERISATION OF NANOMATERIALS

Key Lessons

This chapter has given a brief overview of several different characterisation techniques used by researchers to understand and assess materials produced. It should be noted these are brief introductions and more in-depth literature can and should be sought from the references in this chapter and from more detailed, focused papers for those intending to specialise in any specific techniques. This chapter gives an assessment of such characterisation with nanoscale materials in mind, and which methods would be most suitable are selected. However, after reading this chapter and before the reader attempt to characterise a nanomaterial they have produced, or assess/review if methods used by others to characterise their new materials are adequate/ suitable and valid, one should first considered the keys lesson of what we find when characterising materials and thus ultimately the purpose of characterisation. On the most basic level it is to "see" the material: The structure, the shape and size, the homogeneity, the chemical elements present. And to "feel" of the material: understand the material in relation to the chemical and physical properties. On the nanoscale this may require more experimental thought and design than on the macroscale, as the materials themselves are not visible to the naked eye.

CHAPTER 5
GREEN CHEMISTRY FOR NANOMATERIALS

Key Lessons

Based on environmental assessment of methods used for nanomaterials synthesis, we have seen that most existing and emerging methods are unsustainable. The reasons behind this include large amounts of waste produced due to low yield, sequential processing, high energy demands and the need for specialised reagents/environments. This highlights the need for change in our perceptions and objectivity when it comes to assessing and progressing a new method for nanomaterials. We identified that biologically inspired methods have the potential to design green methods. In the following chapters, we look for inspiration in biological mineral formation to identify rules and strategies for inventing green methods.

CHAPTER 6
BIOMINERALISATION: HOW NATURE MAKES NANOMATERIALS

Keys Lessons

It is clear that biomineralisation can occur over the whole range of length scales. While it may seem that micro and macro level examples of biomineralisation may not be relevant to the formation of nano-scale materials, this is simple not the case, as common trends and features across the whole range of sizes can be applied to bioinspired nano material synthesis. Furthermore, macro-biominerals are hierarchical across the length scales so have nanoscale intricacies and precision. The common themes that can aid the design of bioinspired approaches to making nanomaterials are the ways in which biology controls:

1. The chemistry of the environment on the nanoscale which affects the nanomaterials formed. This is controlled by ion pumps and redox proteins in biomineralisation, but could utilise other approaches synthetically.
2. The confinement of crystal growth which directs the shape and size of the materials produced, such as formation within liposomes.
3. Organic molecules are adept at forming into a full variety of shapes and architectures at all length scales. However, these are always fundamentally controlled at the molecular level; for example by proteins sequence features that introduce bulky amino acid residues that cause a bend in the protein shape. These form intricate scaffold to template the formation of very specific shaped materials.
4. Patterned arrays of positively charged functional groups can nucleate a specific material by binding metal ions to such an extent they can control the formation of a specific crystal phase and can even direct growth through nucleation of a specific crystal face.
5. Small soluble charged proteins and biomolecules that bind to the forming mineral at specific steps and faces inhibit the growth of these sites and thus control the morphology of the resulting crystal at the nanoscale
6. Mixtures of organic and inorganic (hybrid) hierarchical materials can show superior physical properties which could be utilised when designing new nanomaterials

CHAPTER 7
BIOINSPIRED "GREEN" SYNTHESIS OF NANOMATERIALS

Key lessons

One of the main purposes of developing bioinspired synthesis for nanomaterials is to create sustainable production technologies for desired products. In this chapter, we have learnt the principles of how to translate the knowledge of biomineralisation to designing biologically inspired routes. Important lessons learnt are listed below:

- A molecular level understanding of how biology produces high quality nanomaterials is crucial. One of the key controlling features of biomineralisation is the use of biomolecules. Hence understanding the roles that such biomolecules play in the entire process of biomineralisation is extremely important.
- These biomolecules have unique catalytic or binding sites that offer recognition (selectivity and high affinity), their chemical properties (e.g. amino acid sequence in proteins or peculiar chemical structures, modifications or motifs) and important in this recognition. The structure and conformation of these biomolecules are also important because this leads to particular self-assembly (intra- and inter-molecular) and cooperative assembly with inorganic species.
- These feature together enable controlled synthesis, assembly and/or functionalisation of nanomaterials.
- The direct use of biomolecules causes serious barriers to advancing green synthesis. It is therefore important to design "additives" that can provide the benefits that extracted biomolecules can, yet without the associated issues when it comes to translating the knowledge to the development of new materials, products and processes.
- Confinement for nanomaterials synthesis, especially when combined with the use of additives can be powerful in controlling localisation as well as materials properties.
- It is important to be aware that scale-up is not trivial because the transport properties change non-linearly with the production scale. Which means that the reaction pathways and resultant outcomes change with scale-up and are typically unpredictable for new syntheses.

CHAPTER 8
CASE STUDY 1: MAGNETITE MAGNETIC NANOPARTICLES

8.7 Key lessons

In this case study we have learnt that there are many ways in which to integrate the biomineralisation of magnetosomes. We can look at the genetic and assess sequences as well as perform knockout mutagenesis to investigate which proteins are critical for biomineralisation. We can identify key proteins from their location I the mangetiosome membrane or affinity to the magnetite nanoparticle and assess these for structure, iron binding ability etc. Understanding is most powerful when we can use all these techiques to build up a detailed picture of how biomineralisation proteins function to control magnetite nanoparticle growth.

We have also seen how we can use non-biomineralising protein to screen for function that may not be readily seen in nature. Information extracted from this process can the also be used to look for similar sequences in nature.

From both of these methods the trends noted in Chapter 6 and the implementation shown in chapter 7 are reinforced. We see some very specific rules occurring from which we can design future additives.

We see nucleation of magnetite needs an array of acidic amino acids to bind to iron ion. We see with Mms6 that this should be self-assembled in a specific array to get maximum effect, but the latest work with polymersomes, shows that even just providing this carboxylate charged surface has a nucleation effect.

We see that controlling the crystal growth requires a different set of principle. We see with both MmsF and the MIA that structural conformation of the biomolecule is essential. Both of these need to be constrained in a loop, perhaps to match the crystal surface for high affinity binding. We also see that basic residues dominate the MIAs protein for cubic magnetite interactions. The MmsF sequence is less clear.

Towards the future we can use these principles to design new additive that are more commercially viable. We can adopt these principle into molecules that now consider other factors such as robustness to mixing and other factor of scale up and manufacture that are not considering for biomineralisation in nature.

CHAPTER 9
CASE STUDY 2: SILICA

Key lessons

What we have learnt in this chapter is that intricate biosilica structured are deposited by a range of living system and they do this via an extremely complex process. Molecular biologists and biochemists have studied these systems extensively over decades in order to reveal molecular secrets of biosilicification. They have been able to isolate genes, cellular components and biomolecules that control anything from silicon uptake to biosilica deposition. Further, in vitro studies of these biomolecules have started to provide key information that can be used to develop green synthesis protocols. These outcomes have spurred the interest in developing synthetic additives that can mimic the function of biomolecules in order to synthesise silica in a controlled and a sustainable fashion (see a summary podcast at https://youtu.be/sDUl7urlsxY). In this journey of bioinspired silica, numerous intriguing features of silica formation and silicate-additive interactions have been unveiled. Some of these new concepts include:

- Cationic molecules that are readily water soluble are generally useful in facilitating silica formation under ambient conditions and neutral pH.
- Additives interact with different (and perhaps selective) stages of silica formation, which leads to the differences in their actions and the features of silica produced.
- Dynamic/reversible protonation of the additives is important.
- Additives can self-assemble or co-assemble with silicates, leading to templating final structures.
- The structure, architecture and amine environment, the length of the additive play crucial roles in controlling silica synthesis and materials properties.

The future focus should be on developing robust science underpinning the correlations between the synthesis-structure-property-performance for these materials so that they could be easily applied to existing and emerging markets. Scientists should be working with industry to develop these materials for specific applications and collaborating with engineers to design new sustainable/green manufacturing methods.