https://doi.org/10.1595/205651319x15471379420005 Johnson Matthey Technol. Rev., 2019, **63**, (3), 152–156

JOHNSON MATTHEY
TECHNOLOGY REVIEW

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In the Lab

Bespoke Green Nanomaterials: Discovery, Design, Applications and Manufacture

***Johnson Matthey Technology Review* features new laboratory research**

Siddharth Patwardhan, a chemical engineer and materials chemist, currently leads the Green Nanomaterials Research group with a vision to develop sustainable, scalable and economical routes to functional nanostructured materials. He has experience of sustainable routes to nanomaterials for engineering and biomedical applications. He is a Fellow of the Royal Society of Chemistry, UK, and the Engineering and Physical Sciences Research Council, UK, and is leading a number of projects on the development of green manufacturing routes to functional nanomaterials, for example energy storage materials. He has published over 70 papers.

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About the Research

1. "Green" Nanomaterials

Green chemistry has started to see impact on organic chemistry, where researchers have effectively utilised and embedded some of the 12 principles of green chemistry in designing processes. The total global production of all types of nanomaterials is of the order of several million tonnes per annum, with a global market worth US$3.4 billion, which is enjoying a continuous growth. The applications of nanomaterials span across many areas such as catalysis, coatings, fillers, cosmetics, clothing, healthcare and water treatment. However, nanomaterials have not received much attention in terms of making their production sustainable and green. Traditional methods for nanomaterials production are environmentally damaging because they produce thousands of kilograms of waste per kilogram of product and their manufacturing is generally >1000 times more wasteful than that of bulk chemicals. Given this harsh reality, our aim is to invent green routes to functional nanomaterials that are suitable for a range of applications.

2. Current Methods and their Challenges

Current nanomaterials manufacturing methods suffer from many problems leading to high costs, an extremely adverse environmental impact (for example hazardous waste) and unsustainable production. At present, nanomaterials are manufactured using top-down (lithography, milling and etching) or bottom-up (vapour deposition, sol-gel, precipitation, pyrolysis, solvothermal) approaches. Top-down approaches predominate current manufacturing processes for nanomaterials. Bottom-up approaches, used in electronics, are promising and are known to precisely control properties of nanomaterials, but they also suffer from various issues such as high consumption of water and energy, poor materials utilisation efficiencies, need for ultrapure reagents and use or production of toxic or hazardous chemicals. These issues clearly stress the urgent need for developing fundamentally new production methods for nanomaterials that are green and sustainable.

3. Bioinspired Green Nanomaterials

Biology, *via* biomineralisation, produces large quantities of sophisticated and hierarchically organised nanostructured biominerals under mild conditions. Harnessing this biological approach to develop routes for producing bespoke nanomaterials has exciting prospects and it encompasses most of the 12 principles of green chemistry. We have developed a fully synthetic approach where the use of cheaper synthetic molecules inspired from biology (called 'additives') has been introduced to establish bioinspired green synthesis (**Figure 1**).

Until recently, such syntheses were limited to simple systems where the additives (for example citric acid or tea extracts) acted as reducing agents in the synthesis of metal nanoparticles and the reaction schemes were straightforward (for example gold and silver). However, the vast majority of functional nanomaterials such as metal oxides and ceramics follow more complex reaction pathways which include cluster formation, aggregation, self-assembly, polymerisation and so on. We have extensively investigated bioinspired synthesis of such complex nanomaterials (for example silica) at laboratory scales using synthetic additives (**Figure 2**).

Our proposed process takes only 1–5 min, operates at room temperature in water, produces almost no waste, yet provides superior control of product properties. In contrast, for example, traditional syntheses of mesoporous silica suffer seriously from a range of issues such as the use of toxic precursors, long synthesis (2–6 days), requirement of hydrothermal conditions and extremes of pH. The key benefits of our method are as follows:

- A rapid process (takes only minutes), operates at room temperature and in water
- It is a one-step route, with substantial reductions in time and energy usage
- A mild and facile processing using non-hazardous chemicals
- It offers superior control for producing tailored materials for the desired application.

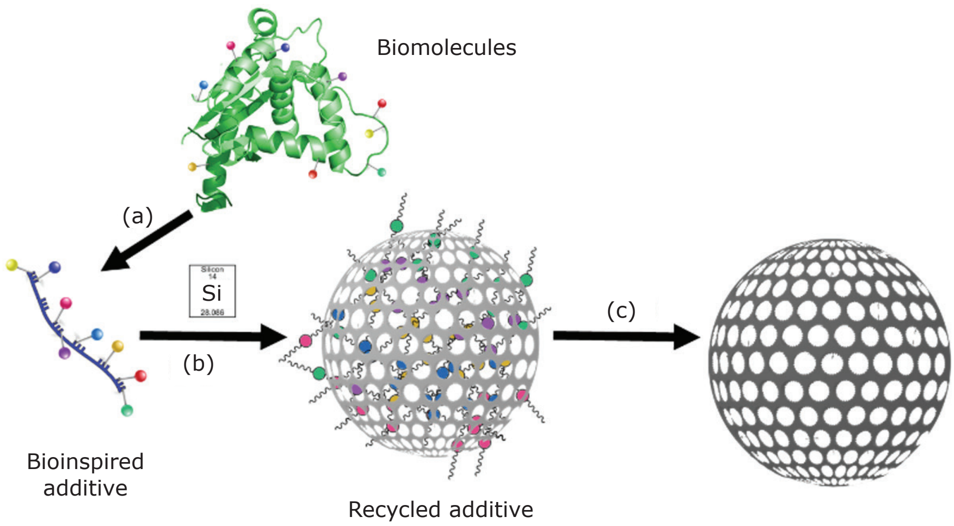

Fig. 1. (a) Learning from biomolecules responsible for biological mineral formation; (b) synthetic bioinspired additives have been developed, which facilitate the rapid formation of silica under mild conditions; (c) these additives can be removed using conventional methods or a recently developed, room temperature purification, which allows the reuse of the additive, yet producing pure porous silica (1) CC-BY

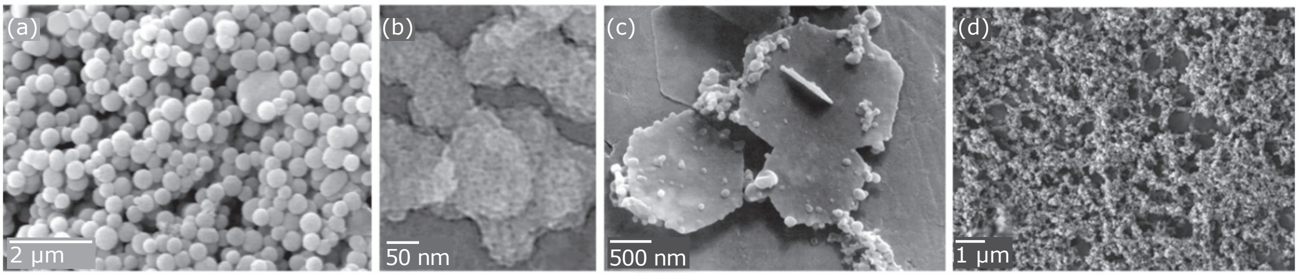

Fig. 2. Representative examples of nanomaterials produced using a bioinspired approach. (a) Spherical nanoparticles synthesised using poly-arginine additive. Reprinted by permission from Springer (2), Copyright 2003; (b) a TEM showing the internal porous structures of nanoparticles; (c) poly-lysine mediated hexagonal plates of silica (3) Copyright (2006) American Chemical Society; (d) bioinspired method used to develop functional coatings on surfaces. Reprinted with permission from (4). Copyright (2007) American Chemical Society

This method is applicable to a wide range of nanomaterials and to date over 50 materials have been produced using a bioinspired green synthesis. Ultimately, our aim is to develop processes that will help reduce environmental burden from nanomaterials, yet without compromising on their utilisation. One of the areas of expertise we have in the group is to undertake the synthesis of bespoke nanomaterials using biologically inspired green routes in order to design novel materials for a range of applications.

4. From Lab to Manufacturing

In order to make this new method accessible and impactful, we have started designing scale-up strategies. We have taken a systematic approach in terms of both process scale-up and process intensification, as summarised next. We performed a techno-economic analysis of our method in order to assess the economic feasibility. The results show that using our green methods can reduce the energy usage of the reaction step by ~95% when compared with a traditional process and the 'green' nanomaterials (GN) would cost the same as the lowest grade commercial counterparts, yet provide significantly better quality and properties. This is promising and supported further development work.

We performed a number of scalability assessments of our method next (**Figure 3**). Initially, the synthesis was carried out in laboratory-scale continuous flow reactors (at small scale: 10–50 ml). Constantly learning from the results and refining the process, we have increased the scale from a few millilitres to 1 l, 5 l and reaching 40 l. The process seems to work in both batch and continuous mode in tank and tubular reactors. Key learning from these scale-up trials include that the method is readily scalable and the recoverable yield does not change with scale.

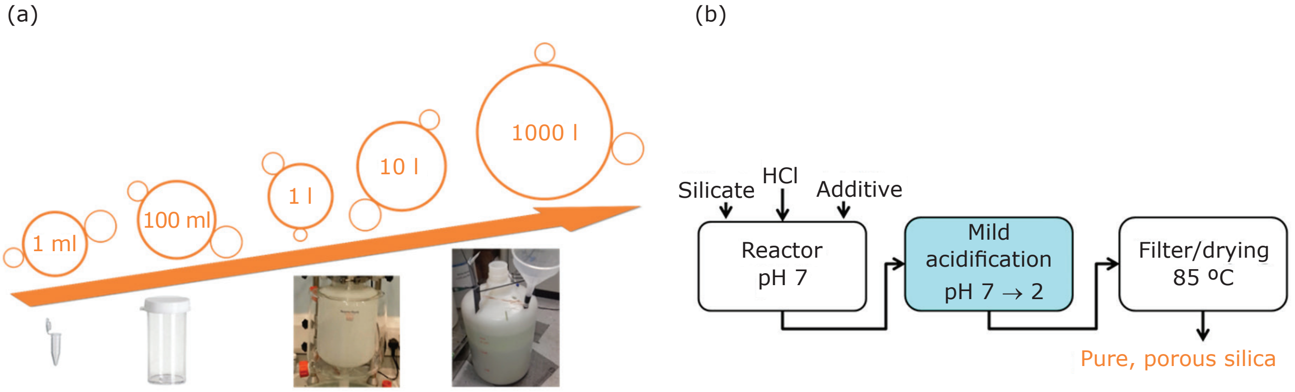

Fig. 3. (a) Pictorial representation of our scale-up journey from 2 ml – 40 l scale; (b) the new purification method developed is show as a block flow diagram, adapted from (5)

However, as expected, we noticed that transport properties, in particular mixing, significantly affected the materials' properties. We are currently developing models and design rules for enabling larger scale production of the bioinspired method, without compromising materials' properties.

We have also focused on some aspects of downstream processing, in particular, purification of the products. In order to render porosity and purity for organic-mediated synthesis, calcination was typically used. However, it is prohibitively energy intensive. Solvent reflux forms an alternative, but it is not always effective, hard to transfer between systems and energy intensive as it requires solvent reflux. This creates economic barriers to commercialisation and hence prohibits industrialisation. In order to address these issues, we have now invented a new method for purification, which involves mild acidification and operates at room temperature and takes a few minutes (**Figure 3(b)**, (5)). This new method allows a complete removal of organics, with an added possibility of composition and porosity control. Given that this is a non-destructive method, >90% water and additive can be recycled, further improving the sustainability and economics.

5. Applications

We have demonstrated the potential of green methods by applying them to the synthesis of a range of nanomaterials as well as testing them in real-life applications. The focus is on increasing technology readiness level (TRL) and delivering technologies that are ready for commercialisation. Currently, we are developing GN for a number of sectors as shown in **Figure 4** and outlined below.

5.1 Environmental Engineering

By tailoring the porosity and chemical functionality, we have designed GN for removal of pollutants from air and water *via* selective adsorption. Examples include the removal of formaldehyde and volatile organic chemicals from polluted air, in particular, indoor environments. In addition to being scalable and cheaper, these sorbents have better capacity and reusability compared to their commercial counterparts. Similarly, by incorporating specific functionality such as organic or inorganic ligands, we are able to remove water pollutants, for example arsenic or organic dyes (**Figure 4(a)**).

5.2 Biomedical Applications

We have exploited the benign nature of the synthesis for development of new drug delivery systems (DDS) *via in situ* encapsulation. We have further assessed their biocompatibility and toxicity. There are a number of nanomaterials-based DDS studied in labs, including one of the most promising candidates – mesoporous silica. However, there are no silica based DDS on the market, despite their promise 18 years ago, due to their unsustainable, uneconomical and energy intensive synthesis. In GN-based DDS, the drug loading and release can be controlled by formulation chemistry, in particular by modulating drug-additive interactions. As shown

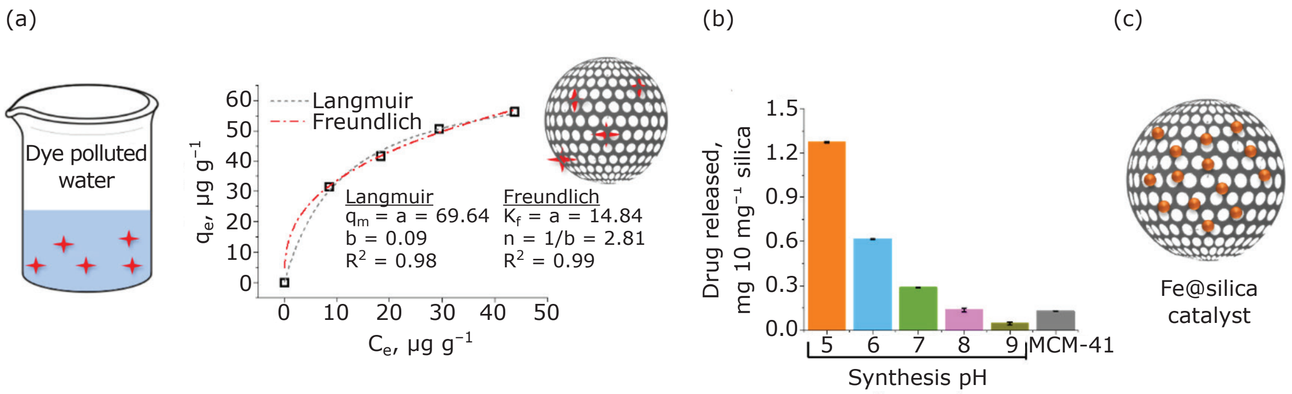

Fig. 4. Applications of GN in: (a) selectively removing pollutants from contaminated water (or air) *via* adsorption (6) Published by The Royal Society of Chemistry; (b) drug delivery systems (7). Copyright (2016) American Chemical Society, reproduced by permission; (c) developing catalysts such as iron supported on porous silica for Fischer Tropsch synthesis

in **Figure 4(b)**, GN show dramatic improvement in drug release performance when compared to a mesoporous silica benchmark. Further, through a number of assessments, we have shown that GN are far more biocompatible than other nanomaterials, thus becoming promising candidates for DDS.

5.3 Catalysts and Biocatalysts

Further utilising the benefits of the mild synthesis, we have been able to immobilise a range of metals (gold, iron, palladium) or enzymes (lipase, anhydrase, peroxidase, invertase) on GN (**Figure 4(c)**), which have great potential for Fischer-Tropsch synthesis, catalytic reduction, C-C coupling reactions of pharmaceutical relevance and hydrolysis reactions for biofuels or chemical feedstock production and beyond. Again, the ability to tune the synthesis in order to tailor materials properties as well as a one-step method provides significant benefits.

5.4 Energy Materials

The bioinspired methods have been applied to design novel materials for energy storage and carbon capture applications. For example, combining the sustainable and economical attributes of the bioinspired method provides great potential to develop materials technologies for next generation electrodes for lithium-ion batteries.

Summary

Learning from biology, we have invented a green platform technology, with the following features:

- Cheaper than existing processes (less waste, low energy needs)
- Scalable technology
- Great control over product attributes.

This technology enables the green preparation of functional materials with wide-ranging engineering and biomedical applications.

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