Keynote Lecture Grasset

Keynote Lecture Kappe

Keynote Lecture Kojima

Keynote Lecture Niederberger

Nanoparticle Synthesis and Assembly for Energy Storage and Conversion

Markus Niederberger[1]

[1]Laboratory for Multifunctional Materials, Department of Materials, ETH Zurich, Vladimir-Prelog-Weg 5, 8093 Zurich, Switzerland.

Introduction

Nanoparticles offer a broad range of size- and shape-dependent properties and are thus the ideal building blocks for the bottom-up fabrication of functional materials. However, to produce macroscopically sized materials with defined architectures, it is critical to have full control over the assembly of the building blocks including their spatial arrangement, orientation and their interaction from the nano- to the macroscale, thus bridging several orders of length scales [1].

Results and Discussion

The success of every assembly experiments depends on the availability of high-quality building blocks, *i.e.*, in a first step nanoparticles with specific sizes, narrow size distributions, defined shapes and tailored surface chemistry have to be prepared. In this talk, we will present the synthesis of nanoparticles, mainly metal oxides, by the so-called nonaqueous sol-gel chemistry. This synthesis methodology involves the reaction of different types of molecular precursors like metal alkoxides, acetates or acetylacetonates with organic solvents in the temperature range of 50-250 °C (Figure 1) [2].

Figure 1. Schematic overview of the nonaqueous sol-gel process.

Nonaqueous sol-gel routes are broadly applicable and give access to a wide range of metal oxide nanoparticles covering different functionalities and various morphologies from spherical particles to nanowires, nanorods or nanosheets (Figure 2).
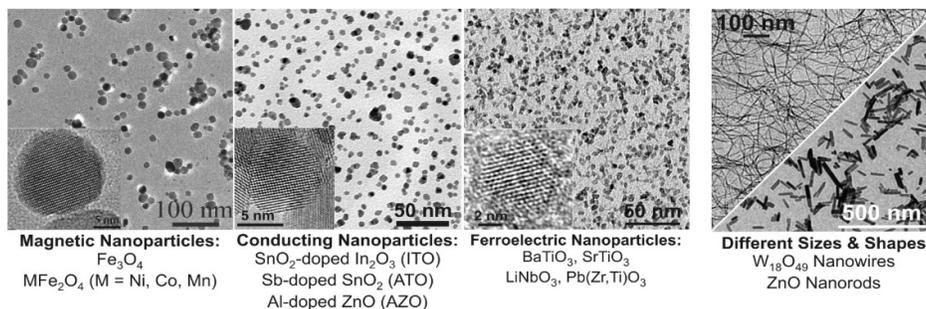
Figure 2. Overview TEM images of metal oxide nanoparticles with different properties and varying shapes.

The nanoparticles can now be assembled and processed into 2- and 3-dimensional geometries like films and aerogels. In monolithic form, aerogels are particularly attractive, because they have macroscopic size, but preserve the nanoscale properties of the initial building blocks, and they offer high porosity, large surface areas and low density [3]. The use of nanoparticles with

anisotropic particle shape and co-assembly of different types of nanoparticles gives access to unique microstructures (Figure 3) and complex nanoheterostructured compositions.
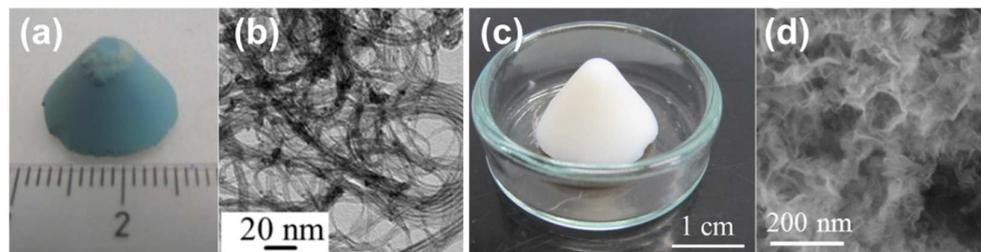
Figure 3. Photograph ((a) and (b)) of selected aerogels composed of (b) tungsten oxide nanowires [4] and (d) yttrium oxide nanosheets [5].

The large surface areas and the high porosity makes nanoparticle-based aerogels attractive for applications as electrodes in lithium ion batteries [6] and as 3-dimensional photocatalysts [7]. Figure 4a shows a Au-TiO_2 aerogel, which has successfully been tested for the photocatalytic CO_2 reduction (Figure 4b) [7].
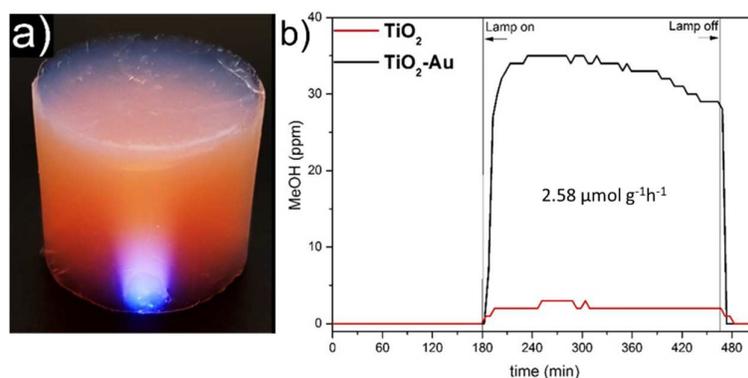
Figure 4. a) Photograph of a Au-TiO_2 aerogel monolith and b) comparison of the photocatalytic activity of a TiO_2 and Au-TiO_2 aerogel monolith for the water-assisted CO_2 reduction (reproduced from Ref. [7]).

Conclusions

The use of nanoparticles as building blocks for the synthesis of advanced materials offers a powerful modular approach to advanced functional materials with complex compositions and architectures optimized for specific applications in energy storage and conversion, sensing, optoelectronics and in (photo)catalysis.

References

[1] M. Niederberger, *Multiscale Nanoparticle Assembly: From Particulate Precise Manufacturing to Colloidal Processing*, Adv. Funct. Mater. **2017**, *27*, 1703647.

[2] N. Pinna, M. Niederberger, *Surfactant-Free Nonaqueous Synthesis of Metal Oxide Nanostructures*, Angew. Chem. Int. Ed. **2008**, *47*, 5292.

[3] F. Rechberger, M. Niederberger, *Synthesis of Aerogels: From Molecular Routes to 3-Dimensional Nanoparticle Assembly*, Nanoscale Horiz. **2017**, *2*, 6.

[4] W. Cheng, F. Rechberger, M. Niederberger, *From 1D to 3D – Macroscopic Nanowire Aerogel Monoliths*, Nanoscale **2016**, *8*, 14074.

[5] W. Cheng, F. Rechberger, M. Niederberger, *Three-Dimensional Assembly of Yttrium Oxide Nanosheets into Luminescent Aerogel Monoliths with Outstanding Adsorption Properties*, ACS Nano **2016**, *10*, 2467

[6] G. Zeng, N. Shi, M. Hess, X. Chen, W. Cheng, T. Fan, M. Niederberger, *A General Method of Fabricating Flexible Spinel-Type Oxide/Reduced Graphene Oxide Nanocomposite Aerogels as Advanced Anodes for Lithium-ion Batteries*, ACS Nano **2015**, *9*, 4227

[7] F. Rechberger, M. Niederberger, *Translucent nanoparticle-based aerogel monoliths as 3-dimensional photocatalysts for the selective photoreduction of CO_2 to methanol in a continuous flow reactor*, Mater. Horiz. **2017**, *4*, 1115.

Character control of calcium compounds by liquid-phase reaction

Yoshiyuki Kojima

Department of College and Science Technology, Nihon University, 1-8, Kanda-Surugadai, Chiyoda Ku, Tokyo 1018308, Japan

Introduction

Calcium compounds include calcium sulfate (gypsum), calcium carbonate, calcium phosphate and calcium silicate, which are abundant all over the world. We have been investigating the synthesis of calcium compounds using liquid-phase reaction techniques and the control of powder properties (character control) such as crystal shape, particle size, morphologies, composition and molecular structure. In this presentation, I will talk about synthesis methods for nano-sized calcium carbonate and calcium phosphate [1] as well as large-sized gypsum (particle size control) [2], the fluorescence properties of amorphous calcium silicate phosphor (composition control) [3],[4] and the structure control of calcium carbonate, and explain using a specific example.

Results and Discussion

Fine particles can be synthesized by increasing the reaction rate, and one method of achieving this is ultrasound irradiation. When ultrasound was used during the synthesis of calcium carbonate and calcium phosphate, nano-particles were easily obtained. Their specific surface areas were 100 and 300 m^2/g, respectively. Figure 1 shows the effect of the ultrasound irradiation on the specific surface area of hydroxyapatite. Note that although short durations of irradiation increased the specific surface area of the hydroxyapatite (HAp), after a certain point (around 6 - 7 minutes), further irradiation had the opposite

Figure 1: Effect of ultrasound irradiation on specific surface area of hydroxyapatite.

effect. Using direct ultrasound irradiation, Horn components are contained in the HAp structure. In contrast, in the case of using indirect irradiation, fine HAp with 99.99% purity could be obtained

On the other hand, large crystals can be obtained by slowing the reaction speed. The thickness of gypsum dihydrate obtained when the hydration temperature of gypsum hemihydrate was raised to 35 μm. The reason for this is that the difference in solubility between gypsum dihydrate and gypsum hemihydrate became smaller and resulted in a hydration time of 8 h.

Phosphor can be synthesized using not only a solid-phase reaction but also a liquid-phase reaction. We succeeded in the synthesis of calcium carbonate phosphor using a liquid-phase reaction, in particular a coprecipitation reaction. Calcium compound phosphors were synthesized by adding rare earth and heavy metal ions (for example, Ce^{3+} and Mn^{2+}) during the synthesis. Ce^{3+}/Mn^{2+}-codoped calcium carbonate emitted red light upon irradiation with black light and Ce^{3+}/Tb^{3+}-codoped calcium carbonate emitted green light.

Generally, if too much activator is added to the phosphor, concentration quenching occurs. However, when an activator is introduced into the calcium silicate hydrate (CSH) layer, concentration quenching hardly takes place. By using CSH, the emission intensity increased up to RE/Ca atomic ratio of 0.5. The CSH phosphor emits red light upon addition of Eu and emits green light at upon addition of Tb. The emission intensity of Tb^{3+}- or Eu^{3+}-doped amorphous

calcium silicate, which was obtained by heating the Tb^{3+} or Eu^{3+} doped calcium silicate hydrate at 850 ºC for 1 h, was maximum. Figure 2 shows the luminescence of Eu^{3+}/Tb^{3+}-codoped amorphous calcium silicate at 850 °C for 1 h. In the emission spectrum of Tb^{3+}-doped amorphous calcium silicate under excitation at 378 nm, the emission spectrum exhibited a major emission band at 544 nm. Eu^{3+}-doped amorphous calcium silicate, which irradiated excitation of 395 nm emitted at 612 nm. When Eu^{3+}/Tb^{3+}-codoped amorphous calcium silicate was irradiated with 377 nm light (excitation wavelength), emission bands at 556 and 612

Figure 2: Emission spectra of Eu^{3+}/Tb^{3+}-codoped amorphous calcium silicate.

nm were observed. By changing the Tb/Eu atomic ratio, the luminescence of the phosphor changed continuously from green to red. Furthermore, by changing the Tb/Ce atomic ratio, the luminescence of the phosphor changed continuously from blue to green. By using three ions (Eu^{3+}, Tb^{3+}, Ce^{3+}), it was possible to synthesize a fluorescent material that emitted across the full range of colors from blue to red.

Structure control of calcium compounds

Calcium carbonate has three polymorphic forms: calcite, aragonite and vaterite. The calcium carbonate formed upon heating calcium bicarbonate ($Ca(HCO_3)_2$) solution. The single-phase vaterite formed upon adjusting the pH with ammonia aqueous solution and the supersaturation degree of the $Ca(HCO_3)_2$ solution. The morphology of the formed vaterite was plate-like. Figure 3 shows a scanning electron micrograph of the hexagonal plate-like vaterite, which shows that the vaterite was neatly arranged. The synthesis and properties of amorphous calcium carbonate (ACC), which formed at the beginning of the liquid-phase reaction, have already been studied. Recently, we have determined synthetic conditions for obtaining single-phase vaterite. To achieve this using a $CaCl_2$ – Na_2CO_3 system, the pH is important, and it is necessary to adjust the pH at the time of crystallization of ACC. Furthermore, when the pH changes, the ratio of hydrogen carbonate ions also changes. Figure 4 shows the effect of HCO_3^- ratio on formation ratio of vaterite in the $CaCl_2$ – Na_2CO_3 system. ACC crystallized to calcite and vaterite after a reaction time of 2 min. The initial pH was controlled with HCl solution. The single-phase vaterite could be obtained when the HCO_3^- ratio was above 80 % at the time of crystallization of ACC.
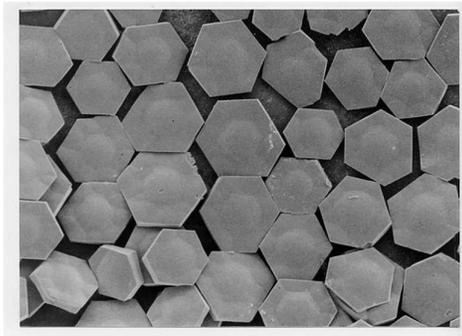
Figure 3: SEM photograph of hexagonal plate-like vaterite.
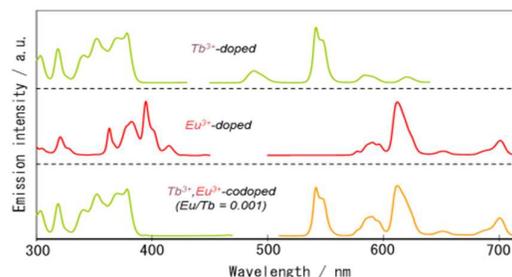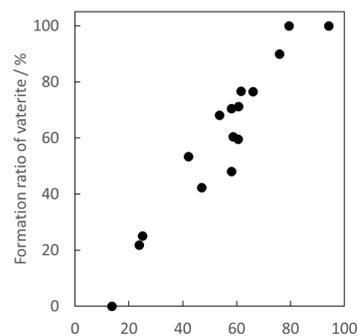
Figure 4: Effect of pH on formation of vaterite in $CaCl_2$-Na_2CO_3 system.

References

[1] Y. Kojima, K. Yamaguchi, N. Nishimiya, *Ultrasonics Sonochem.,* 2010, **17**, 617-620.

[2] Y. Kojima, T. Yasue, *J. Euro. Ceram. Soc.*, 2006,**26**, 771-776.

[3] Y.Kojima,M.Numazawa,T.Umegaki, *J.Luminescence*, 2012, **132**, 2648-2652.

[4] Y.Kojima,M.Numazawa,T.Umegaki, *J.Luminescence*, 2012, **132**, 2992-2996.

Organic Synthesis Goes Flow –

The Use of Continuous Flow Technology for the Synthesis of Active Pharmaceutical Ingredients

C. Oliver Kappe[1,2]

[1] Institute of Chemistry, University of Graz, Heinrichstrasse 28, 8010 Graz, Austria.
[2] Center for Continuous Flow Synthesis and Processing (CC FLOW) at Research Center Pharmaceutical Engineering GmbH (RCPE), Inffeldgasse 13, 8010 Graz, Austria.

Introduction

Continuous flow processes form the basis of the petrochemical and bulk chemicals industry where strong competition, stringent environmental and safety regulations, and low profit margins drive the need for highly performing, cost effective, safe and atom efficient chemical operations. In contrast to the commodity chemical industry, however, the fine chemical industry primarily relies on its existing infrastructure of multipurpose batch or semi-batch reactors. Fine chemicals, such as drug substances and active pharmaceutical ingredients (APIs), are generally considerably more complex than commodity chemicals and usually require numerous, widely diverse reaction steps for their synthesis. These requirements generally make versatile and reconfigurable multipurpose batch reactors the technology of choice for their preparation. However, the advantages of continuous flow processing are increasingly being appreciated also by the pharmaceutical industry and, thus, a growing number of scientists, from research chemists in academia to process chemists and chemical engineers in pharmaceutical companies, are now starting to employ continuous flow technologies on a more routine basis [1]. This will however require a change of mind set on the part of the chemists trained to think entirely in batch mode.

Results and Discussion

Microreactors provide significantly improved control over reaction conditions, and reactions often can be performed under conditions which would be infeasible or impossible to use in batch reactors. Fast mixing can be achieved in microfluidic devices with dedicated mixing structures, and the high surface-to-volume ratio allows rapid dissipation of excess heat. Thus, mass and energy transport limitations can be eliminated even for fast and highly exothermic reactions and the intrinsic reaction kinetics can be fully exploited.

In the past decades, technologies for continuous synthesis advanced tremendously and a plethora of discrete flow components and modules, including pumps, mixers, reactors and separation units, along with an increasing number of integrated standalone flow reactors have become commercially available. The emergence of various reactor designs, addressing the diverse physicochemical requirements of chemical reactions, along with the emergence of technologies for feed delivery, flow metering, continuous separation etc. allows the assembly of specialized, high-performance flow systems by combining these operation units. The modular approach provides the flexibility required for fine chemical synthesis while the advantages inherent to continuous production are maintained (Figure). It is partly because of the commercial accessibility of flow equipment for organic synthesis on small to medium scales that flow chemistry evolved from a pure research topic in chemical engineering to an almost ubiquitously applicable technique in organic synthesis laboratories. Furthermore, the pharmaceutical industry is investing heavily in the development and advancement of continuous manufacturing. In fact, virtually all large pharmaceutical companies now have dedicated groups working on the development and implementation of flow synthesis.
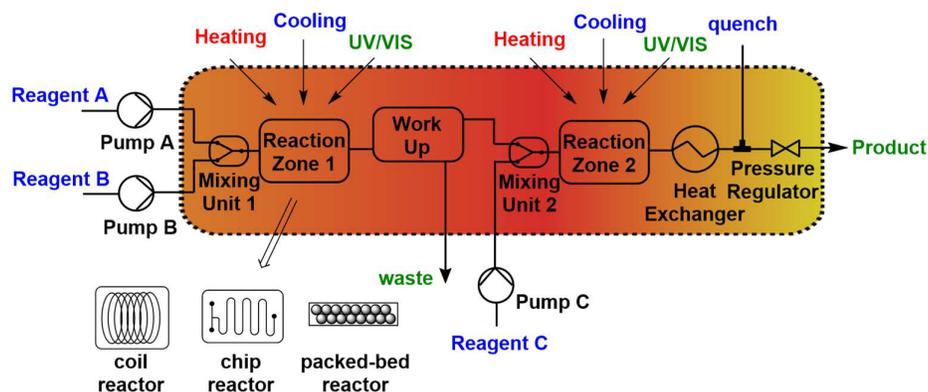
Figure 1. Schematic view of a typical continuous flow set-up.

Conclusions

In this lecture, contributions from our research group in the field of continuous flow processing will be highlighted. Emphasis will be given to highly atom efficient, process intensified and integrated chemical transformations useful for the synthesis of APIs or key intermediates that are often too hazardous to be executed in a batch reactor. These involve azide, diazomethane and nitration chemistry, selective precious metal-free olefin and nitrogroup reductions, and flow photochemistry applications.

References

[1] Review: Gutmann, B.; Cantillo, D.; Kappe, C. O. Angew. Chem. Int. Ed. **2015**, *54*, 6688.

From Colloidal Chemistry to New Nanocomposites Materials for Biomedical, Optical, Energy and Environmental Applications

Fabien Grasset[1,2,3]

[1]CNRS, UMI 3629 LINK, NIMS, Tsukuba, 305-0044, Japan.
[2]Research Center for Functional Materials, NIMS, Tsukuba, 305-0044, Japan
[3]NIMS-Saint-Gobain COE for Advanced Materials, NIMS, Tsukuba, 305-0044, Japan

Introduction

In accordance with the increasingly stringent standards of environmental and cost regulation, chemical solution process to design new materials represents an attractive low-temperature and low-energy approaches to the development of new nanocomposite materials. Several applications could be targeted like biomedical application, opto-electronic application, solar cells applications, or chemical and biological waste degradation. Composite nanoarchitectures represent a class of nanostructured entities that integrate various dissimilar nanoscale building blocks including clusters, particles, wires and films [1]. The heterogeneous composite nanostructured materials are composed by definition of multi-(nano)components, each tailored to address different requirements. As one of the nanocomponents, nanometer sized transition metal clusters (<2 nm), which consist of less than a few dozens of metal atoms, could be defined as a link between atom and nanoparticle [2-5]. Multifunctional properties could be achieved by a combination of several materials in a best-defined architecture.

Results and Discussion

Almost twenty years ago, we started to develop simple, versatile, reproducible and efficient methods based on soft chemistry and sol-gel processes to prepare large amount of multifunctional nanocomposites particles and thin films [6-11]. In this presentation, we will focus on our latest results involving mostly Mo_6 or Ta_6 atom cluster units, SiO_2 and ZnO. The significant role played by the reverse microemulsion process for the synthesis of functional nanoparticles [6, 10-15] and by colloidal solution deposition processes for the synthesis of transparent thin films will be emphasized in this presentation [16-24].

<u>Nanocomposite particles:</u> The design, synthesis and characterization of functional SiO_2 nanoparticles is more and more studied during the last decade [12, 25]. However, optimizing the architecture of such materials requires a deep understanding of physico-chemical properties. We demonstrated that colloid-water-in-oil microemulsion is a powerful tool to produce with a high reproducibility large amount of nanoparticles with complex architectures (Figure 1).
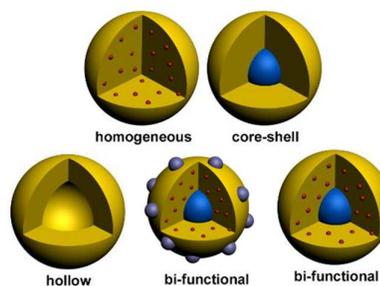
Figure 1: Functional SiO2 nanoprticles with complex architectures

<u>Nanocomposite thin films:</u> Thin films or coatings, with thickness ranging from nanometers to few tens micrometers are playing a very important and indispensable

role in daily life. In recent years, the use of solution processes are highly desirable in order to reduce the cost and waste. These demands are spurring the design of nanomaterials that exhibit engineered physical properties and that can enable fabrication method for low cost, low waste, large area and even flexible devices. In this way, the electrophoretic deposition process (EPD) process has been challenged by the development of transparent functional thin films. Several octahedral atom clusters were characterized and used to prepare thin

Figure 2: Transparent thin films made by EPD

films with high transparency in the visible. Green, yellow, orange, red and brown coloured films were successfully fabricated by coating on an indium-doped tin oxide glass substrate by using electrophoretic deposition process (EPD) (Figure 2). In addition, transparent films with prominent luminescent properties were obtained by using specific Mo_6 clusters whereas UV and NIR filters were realized by using Ta_6 clusters. The EPD process appears a new strategy to fabricate highly transparent and coloured nanocomposite thin films and coatings for optical and energy applications.

Conclusions

These nanocomposites could play a significant role for optical, energy and biotechnology applications in visible and/or near infra-red range.

References

[1] R. Liu et al., *Chem. Comm.*, **2011**, 47, 1384
[2] F. A. Cotton, *Inorg. Chem.*, **1964**, 3, 1217
[3] A. Perrin et al., *C. R. Chimie*, **2012**, 15, 815
[4] Y. Luab et al., *Chem. Soc. Rev.*, **2012**, 41, 3594
[5] V. Fedorov, *J. Clust. Sci.*, **2015**, 26, 3
[6] F. Grasset et al., *Langmuir*, **2002**, 18, 8209
[7] S. Mornet et al., *J. Mater. Chem. C*, **2004**, 14, 2161
[8] F. Grasset et al., *Adv. Mater.*, **2005**, 17, 294
[9] F. Grasset et al., *Adv. Mater.*, **2008**, 20, 1710
[10] F. Grasset et al., *Adv. Mater.*, **2008**, 20, 143
[11] F. Grasset et al., *Chem. Comm.*, **2008**, 4729
[12] T. Aubert et al., *J. Colloid Interface Sci.*, **2010**, 341, 301
[13] T. Aubert et al., *J. Phys. Chem. C*, **2013**, 117, 20154
[14] N. Nerambourg et al., *J. Colloid Interface Sci.*, **2014**, 424, 132
[15] C. Neaime et al., *Phys.Chem.Chem.Phys.*, **2016**, 18, 30166
[16] T. Aubert et al., *Part. Part. Syst. Charact.*, **2013**, 30, 90
[17] S. Cordier et al., *J. Inorg. Organomet. Polym.*, **2015**, 25, 189
[18] A. Renaud et al., *ChemistrySelect*, **2016**, 1, 2284
[19] G. Truong et al., *Sci. Tech. Adv. Mater.*, **2016**, 17, 443
[20] A. Renaud, *J. Mater. Chem. C*, **2017**, 5, 8160
[21] T.K.N Nguyen et al., *ECS J. Solid State Sci. Technol.*, **2016**, 10 R178
[22] T.K.N Nguyen et al., *J. Electrochem. Soc.*, **2017**, 164, 412
[23] T.K.N Nguyen et al., *Coatings*, **2017**, 7, 114
[24] T.K.N Nguyen et al., *J. Mater. Chem. C*, **2017**, 5, 10477
[25] J. Wang et al., *Nanoscale*, **2014**, 6, 4418