

Cite this: *Mater. Adv.*, 2021,  
2, 538

DOI: 10.1039/d0ma90053b

rsc.li/materials-advances

## Journal of Materials Chemistry A and Materials Advances Editor's choice web collection: "Recent advances in hydrothermal materials synthesis"

Miriam M. Unterlass  abc

Hydrothermal crystallization occurs in nature as a major mineral formation process. The process has been mimicked in chemical laboratories for over 150 years, with the beginning of hydrothermal synthesis (HTS) tracing back to Schafhäütl's synthesis of quartz microcrystals.<sup>1</sup> To this day, HTS is still extensively used for generating (especially inorganic) materials. More recently, in the last two decades, HTS started to be implemented intensively for the preparation of carbon materials, often starting from biogenic renewable

resources. These syntheses are conventionally termed hydrothermal carbonization (HTC).<sup>2</sup> Research on HTS of carbons has been showing that impressive control – e.g. with respect to morphology and composition such as hetero-atom doping – can be obtained through e.g. the choice of precursors and the fine-tuning of the HTS conditions. Also starting around the end of the 20th century, the feasibility of generating purely organic materials by HTS has been explored.<sup>3</sup> This opened the doors to combining the simultaneous hydrothermal synthesis of organic and inorganic materials as inorganic–organic hybrids.<sup>4</sup> In my opinion, HTS is a tremendously powerful technique for allowing access to a broad range of material types, ranging from inorganic to organic and hybrid materials. For society's increasing environmental and climate concerns, using “nothing but water” as a reaction medium provides sustainability aspects that have given HTS further momentum. A major cornerstone in HTS has been marked by the (commercial) availability of microwave (MW) heating. Heating an aqueous precursor solution is typically more efficient through MW heating than the conventionally employed approach of simply placing batch steel vessels in an electrical oven. MW-assisted HTS has therefore allowed for rapid access to reaction products within reaction times of 1 hour or less. Despite HTS being such a long-standing and established technique, there

are still an impressive amount of open fundamental questions that remain unanswered, in part because of the intrinsic difficulty of *in situ* studies under such conditions.

Part of the Editor's collection is an exquisite study by Reeja-Jayan and coworkers that sheds more light on MW-assisted HTS (DOI: 10.1039/D0TA03721D). They study the effect of the electromagnetic (EM) field generated through MW-heating, on the atomic structure of hydrothermally generated SnO<sub>2</sub> through *in situ* synchrotron X-ray pair distribution function (PDF) analysis. Most interestingly, the authors show that the EM field has a distinct impact on oxygen atomic displacement, suggesting that EM field-assisted growth is mediated by changes to the oxygen sublattice. This finding could have great potential in using EM fields for tailoring atomic arrangements during HTS.

Flow synthesis has – with due right – become a shining beacon of hope for more efficient, rapid synthesis, and has also not stopped at HTS. The beginnings of HTS and synthesis in supercritical water already date back to the 1990s.<sup>5</sup> Also, part of this collection is a contribution by Kellici and coworkers on HTS in flow (DOI: 10.1039/C9TA11781D). They report the synthesis of blue-luminescent nitrogen-doped carbon quantum dots of ~3 nm in size from the precursors citric acid and ammonia, and additionally show that these materials can be used for Cr<sup>VI</sup> ion

<sup>a</sup> Institute of Materials Chemistry, Technische Universität Wien, Getreidemarkt 9/165, 1060 Vienna, Austria. E-mail: miriam.unterlass@tuwien.ac.at

<sup>b</sup> Institute of Applied Synthetic Chemistry, Technische Universität Wien, Getreidemarkt 9/163, 1060 Vienna, Austria

<sup>c</sup> CeMM – Research Center for Molecular Medicine of the Austrian Academy of Sciences, Lazarettgasse 14, AKH BT 25.3, 1090 Vienna, Austria



sensing. Another interesting extension of HTS is reported by Yan and coworkers (DOI: 10.1039/D0TA00870B). The authors combine HTS with electrodeposition for synthesizing a variety of hierarchical nanostructures of CoP, one of the cobalt phosphides. By treating carbon cloths at different HTS conditions with a precursor solution, they show that the cloths can be decorated with a wide range of morphologically different Co(OH)<sub>2</sub> nanostructures. In subsequent phosphidation of the isolated seeded cloths with PH<sub>3</sub>, a variety of CoP hierarchical nanostructures is generated. These CoP nanostructures show catalytic activity in water splitting reactions.

HTS is exquisitely well suited for generating various metal oxides. Interesting recent contributions showcase the HTS of manganese oxide-based materials, including a report by Wu and coworkers on the mild (100 °C, 12 h) HTS of Fe-doped MnO<sub>2</sub> as a nitrogen reduction electrocatalyst (DOI: 10.1039/C9TA13026H). A report by Xia and coworkers contributes the also relatively mild (150 °C, 24 h) HTS of Cr-doped δ-MnO<sub>2</sub> (Birnessite) as an electrode material for supercapacitors (DOI: 10.1039/D0TA01480J). Furthermore, several recent works provide new examples of the HTS of core-shell hybrid structures. These include works by

Swain and coworkers on Fe(0) nanoparticles (NPs) coated with iron oxides, and Mn(0) NPs coated with manganese oxides (DOI: 10.1039/D0TA00611D); Yu and coworkers on Au(0) NPs coated with CeO<sub>2</sub>, which are additionally functionalized with Pt(0) NPs ≤5 nm in diameter (DOI: 10.1039/D0TA00811G); and by Tonda and coworkers, who report the synthesis of TiO<sub>2</sub> NPs coated with a shell of NiAl-layered double hydroxide (DOI: 10.1039/D0TA00104J). All three examples use NPs synthesized prior to HTS as cores, and hydrothermally deposit the shell of the core-shell NPs, thereby providing nice examples of the use of HTS to deposit materials on premade seeds for the preparation of controlled hybrid NP nanostructures. Aside from the HTS of metal oxide-based materials, several recent reports provide new examples of the amenability of sulfidic materials to HTS. Morán and coworkers report the synthesis of phase-pure polycrystalline Sn<sub>1-δ</sub>S *via* MW-assisted HTS (DOI: 10.1039/D0MA00301H), and Sangabathula and Sharma report the HTS of Mo-doped Nickel sulfide through the HT treatment of a Nickel foam with ammonium heptamolybdate tetrahydrate and thiourea (DOI: 10.1039/D0MA00593B). Finally, recent contributions also highlight the synthesis of zerovalent materials, including

the Jiang *et al.* report on the HTS of tellurium nanowires through hydrothermal reduction of sodium tellurite with glucose (DOI: 10.1039/D0MA00220H).

These are just some of the many recent papers published in *Journal of Materials Chemistry A* and *Materials Advances* on the topic of hydrothermal synthesis of materials. I hope that you will find them an interesting read!

Sincerely yours,  
Miriam Unterlass

## References

- 1 A. Schafhäütl, *Gelehrte Anzeigen München*, 1845, **20**, 577.
- 2 M.-M. Titirici, R. J. White, C. Falco and M. Sevilla, *Energy Environ. Sci.*, 2012, **5**, 6796–6822, DOI: 10.1039/C2EE21166A.
- 3 M. M. Unterlass, *Angew. Chem.*, 2018, **57**(9), 2292–2294, DOI: 10.1002/anie.201713359.
- 4 L. Leimhofer, B. Baumgartner, M. Puchberger, T. Prochaska, T. Konegger and M. M. Unterlass, *J. Mater. Chem. A*, 2017, **5**, 16326–16335, DOI: 10.1039/C7TA02498C.
- 5 P. W. Dunne, A. S. Munn, C. L. Starkey, T. A. Huddle and E. H. Lester, *Philos. Trans. R. Soc., A*, 2015, **373**, 20150015, DOI: 10.1098/rsta.2015.0015.

