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Thermal Shock Synthesis of Nanocatalyst by 3D-Printed Miniaturized Reactors

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High temperature synthesis and treatments are ubiquitous in chemical reactions and material manufacturing. However, conventional sintering furnaces are bulky and inefficient with a narrow temperature range (<1500 K) and slow heating rates (<100 K min^{-1}), which are undesirable for many applications that require transient heating to produce ideal nanostructures. Herein, a 3D-printed, miniaturized reactor featuring a dense micro-grid design is developed to maximize the material contact and therefore acheive highly efficient and controllable heating. By 3D printing, a versatile, miniaturized reactor with microscale features can be constructed, which can reach a much wider temperature range (up to ≈3000 K) with ultrafast heating/cooling rates of ≈10^4 K s^{-1}. To demonstrate the utility of the design, rapid and batch synthesis of Ru nanoparticles supported in ordered mesoporous carbon is performed by transient heating (1500 K, 500 ms). The resulting ultrafine and uniform Ru nanoparticles (≈2 nm) can serve as a cathode in Li-CO_2 batteries with good cycling stability. The miniaturized reactor, with versatile shape design and highly controllable heating capabilities, provides a platform for nanocatalyst synthesis with localized and ultrafast heating toward high temperatures that is otherwise challenging to achieve.

High temperature is one of the most general and powerful manufacturing methods available for both lab- and industrial-scale syntheses of various materials, including metals, ceramics, and carbon compounds.[1] However, conventional sintering furnaces (e.g., tube and muffle furnaces), which are based on radiative heating within a large chamber,[2] generally display limited temperature ranges (<1500 K), slow heating/cooling rates (<100 K min^{-1}), as well as low energy efficiencies (<10%).[3] The radiative heating strategy employed by such furnaces can also lead to a large temperature gradient and uneven heat distribution for bulk material processing, causing unfavorable structural inhomogeneity in the resultant materials.[4] In particular, the undesired, prolonged heating at high temperature precludes their applications in transient/rapid thermal treatments and reactions far from equilibrium, in particular for nanomaterials synthesis that requires highly controllable and delicate heating conditions to achieve specially-designed surface and nanostructures.[5]

In the past decade, significant efforts have been devoted to the development of rapid, efficient, and controllable heating methods for materials synthesis, including laser heating,[6] microwave-assisted solid state reactions,[7] and solution combustion.[8]. However, these heating strategies are highly dependent on the material properties (e.g., laser and microwave absorption, combustion reactivity, *etc.*) and the resulting synthesis conditions are often less controllable in terms of temperature, duration, and ramping rate.[9] Recently, we reported a rapid and controllable high-temperature thermal shock technique using electrical Joule heating for the in situ synthesis of uniform nanoparticles on a carbon support.[10] Yet the thermal shock method also relies on the materials being conductive films, which limits its wider application to non-conducting materials or powder samples. Therefore, developing a general and highly controllable miniaturized reactor continues to be a significant challenge, though its achievement would be especially beneficial for the rapid synthesis of nanostructures that are sensitive to high-temperature annealing.

In this work, we demonstrate a 3D-printed, miniaturized reactor for efficient and highly controllable heating that can enable batch and scalable synthesis of nanocatalysts. By 3D printing of graphene oxide (GO), we are able to construct versatile reactor shapes with microscale patterns targeted for localized and efficient heating. The reactor itself is triggered by direct Joule heating (>90% conversion efficiency) to reach a temperature as high as ≈3000 K with an ultrafast heating rate of ≈10^4 K s^{-1}. As a proof-of-concept demonstration, we fabricated a miniaturized reactor using 3D extrusion-based printing of a GO slurry by first printing a dense layer of GO as the bottom followed by a microscale grid pattern using six layers of the extrusion filament (**Figure 1**a, Figure S1, Supporting Information). The resulting 3D-printed miniaturized reactor (20 mm × 10 mm × 2.2 mm) has a matrix structure that provides space for the storage of raw materials for subsequent reactions (Figure 1b). We then thermally reduced this reactor at 300 °C under Ar

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