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Efficient nanoparticle synthesis

Dorota Koziej

Integrating a microwave reactor with a microfluidic platform reduces the synthesis time of nanoparticles to 64ms.

Nanoparticles are essential building blocks for many energy-related applications, ranging from lithium ion batteries, catalysis, and photocatalysis to electrochromic windows. The ability to synthesize nanoparticles with well-defined size, shape, and structure is critically important. In recent years, there have been two main trends to improve the efficiency of nanoparticle synthesis by use of microwave or microfluidic reactors.[1,2] Microwave reactors provide a higher nanoparticle yield in shorter reaction times than conventional batch reactors,[1] and microfluidic reactors have the separate advantage that reaction conditions, such as heat and mass transfer rates, can be independently controlled for small volumes of reaction solution.[2] Integrating such miniaturized reactors with microwave heaters would combine the advantages of both and so improve nanoparticle synthesis.

Several such devices have been developed for aqueous solutions, which are suitable for biochemical applications such as heating a polymerase chain reaction.[3] However, water is not a suitable solvent for low-temperature, low-pressure synthesis of crystalline nanoparticles. Recently, colleagues and I have developed a microfluidic-microwave device, operating at 700–900MHz, which allows precise tuning of the temperature of non-aqueous solvents such as benzyl alcohol, n-butanol, and ethylene glycol.[4]

We used two independent non-contact methods to determine the temperature of benzyl alcohol droplets flowing in fluorocarbon-based oil. Infrared temperature imaging provided quantitative information about the microwave heating of the benzyl alcohol droplets and heat transfer from the droplets: see Figure 1. Additionally, we measured the microwave heating of the benzyl alcohol droplets by fluorescence imaging with high temporal resolution. We can heat the benzyl alcohol droplets to 50°C in 15ms.

We used our microfluidic-microwave device to synthesize tungsten oxide nanoparticles within benzyl alcohol droplets using the synthesis protocol for a conventional reaction in oil bath.

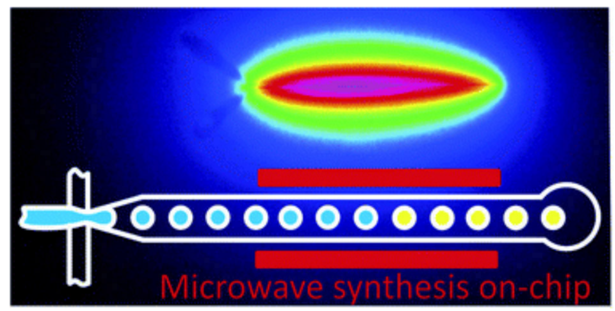

Figure 1. *Top: A 2D temperature map measured at the surface of the microwave-microfluidic device with an IR camera. Bottom: A schematic of the microfluidic-microwave device. (Copyright the Royal Society of Chemistry.[4])*

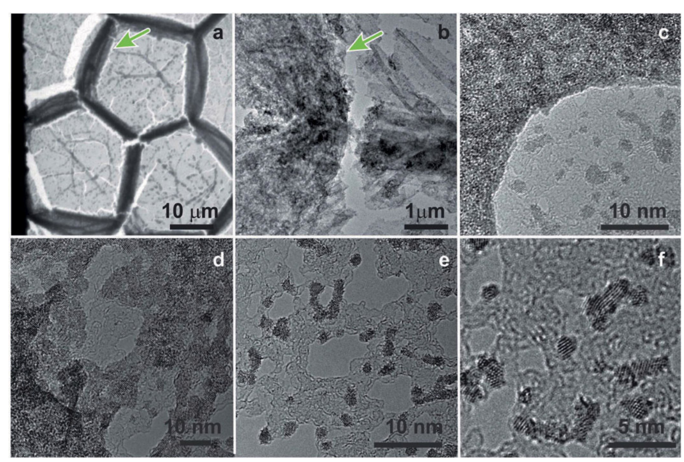

Figure 2. *Transmission electron microscopy (TEM) and high-resolution TEM (HR-TEM) images. The green arrows show the area magnified in the subsequent images. (a) Droplets after heating in microwave oven on the chip, which self-assemble and adopt a honeycomb-like microstructure. (b) A closer look at the dried droplets shows the wrinkled microstructure inside the droplets. (c) Even closer examination shows there is more solid phase collected at the boundaries between the droplets than in the middle of the single droplet. (d) The darker regions inside the droplets consist of assemblies of primary nanoparticles. (e–f) HR-TEM images deliver the final proof of the nanoparticles' crystallinity. (Copyright the Royal Society of Chemistry.[4])*

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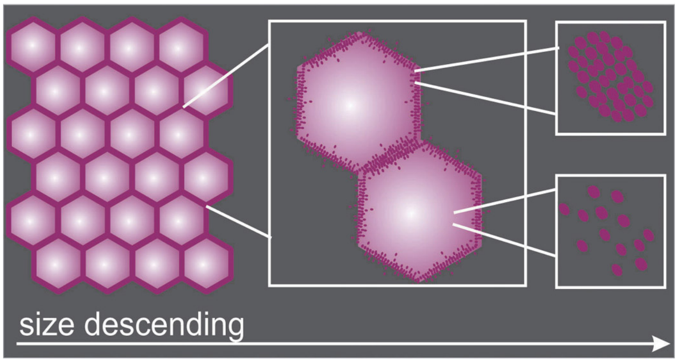

Figure 3. *Schematic showing the complexity of the observed structure at different magnifications. (Copyright the Royal Society of Chemistry.[4])*

The residence time of the droplets in the area exposed to microwave heating of 50°C was 64ms. After drying, the droplets formed a honeycomb-like microstructure: see Figures 2 and 3. There was more solid phase at the boundaries between the droplets than in the middle of the single droplet. Additionally, the dried droplets revealed a subtle nanostructure: inside the droplets we observed individual nanoparticles, whereas at the edge of the droplets they formed assemblies. Thus, our technique offers a route to simultaneously synthesizing and assembling nanoparticles.

In summary, we have shown that microwave heating of picoliter-sized droplets produces appropriate conditions to crystallize inorganic metal oxide nanoparticles and assemble them into complex structures. Although microfluidic reactors are often applied to synthesize crystalline nanoparticles, microwave heating has not previously been used. Our approach meets the requirement to translate the unique properties of nanoparticles to microscale objects.[5] We are now working to develop a next-generation device that will demonstrate microwave-assisted synthesis on a chip as an attractive alternative to batch microwave reactors. By varying the frequency and power of the electromagnetic field, we will tune the nanoparticles' properties. We hope to show that the method is universally applicable and not restricted to synthesis of particular materials.

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Author Information

Dorota Koziej
Swiss Federal Institute of Technology Zurich (ETH Zurich)
Zurich, Switzerland

Dorota Koziej is a team leader in the Laboratory for Multifunctional Materials, Department of Materials, at ETH Zurich. She is developing platforms for on-chip monitoring of nanoparticle crystallization, addressing fundamental questions with in situ spectroscopic synchrotron methods, and developing materials for energy-related applications.

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