

Shock synthesis by flash-thermal lamping

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In this issue of *Chem*, Kim et al. report a novel flash-thermal shock (FTS) lamping approach for synthesizing multi-elemental nanoparticles and single atoms supported on the SnO₂ substrate, showing great potential for a range of applications in gas sensing, energy, and catalysis.

Because of their high efficiency, broad material scope, and good tunability, transient high-temperature heating approaches have recently received great attention in materials synthesis and processing. Notably, the fast heating and cooling rates and short heating duration of these approaches are capable of creating a far-from-equilibrium synthesis regime to trap metastable states at the bulk scale,¹ micron scale,² and nano-scale,³ often leading to the discovery of new materials. For example, transient high-temperature heating processes have uncovered a new family of multi-elemental nanomaterials (i.e., medium-entropy and high-entropy nanomaterials), which are often composed of conventionally immiscible elements and not easily obtained by wet chemistry methods.³ The high temperature promotes rapid mixing of multiple elements toward the formation of a solid-solution phase; meanwhile, the transient heating duration and fast temperature quenching “freeze” the homogeneous mixing state while maintaining the desired small particle size. Hu and co-workers first invented a rapid thermal shock method for making unary nanoparticles,⁴ which was extended to the synthesis of high-entropy alloy nanoparticles with up to eight constituent elements via breaking of the thermodynamic immiscibility limit (Figure 1A).³ A number of shock-type processes, such as fast-moving bed pyrolysis,⁵ microwave shock,⁶ and fly-through pyrolysis⁷

(Figure 1B), have been further developed for tailoring various synthetic conditions as well as targeted compositions and crystal structures.

Recently, the laser shock method has been studied for the synthesis of colloidal high-entropy alloy nanoparticles, adding a new member to the shock synthesis family.⁸ Compared with using lasers, using lamps for heating can offer a higher output efficiency with a much larger beam area (cm² versus mm²), making them potentially more scalable than lasers, but they suffer from lower power density ($\sim 10^4$ versus $\sim 10^8$ W cm⁻²), limiting their synthetic capability. What can address this issue is engineering the physicochemical properties of the substrate material so as to create enough photo-thermal effects for efficient surface modification as well as for scalable synthesis of the supported materials. In this regard, metal-oxide-based substrates are particularly suitable and interesting because they exhibit tunable surface defective sites for modulating the photo-thermal response. In addition, metal oxides are feasible substrates in many applications, such as thermochemical catalysis and chemical sensing.

In this issue of *Chem*,⁹ Kim et al. innovatively applied a flash-thermal shock (FTS) lamping process (Figure 1C) on binary white SnO₂ thin-layered porous oxide nanosheets, which were synthesized via calcination of self-assembled

metal-ion precursors on graphene oxide. Through thermal simulations, the authors discovered that the defects, along with the nano-crystallinity and porosity, rendered high light-to-heat conversion efficiencies and low thermal conductivities of the SnO₂ nanosheets, which are critical merits for enabling the highly effective photothermal performance of SnO₂. Based on this effect, the developed FTS lamping approach offers transient high-temperature annealing (temperature > 1,800°C; heating duration < 20 ms) under ambient air, leading to the precise and ultrafast phase-engineered metal oxides (i.e., SnO₂). In addition, this approach provides good tunability of the synthetic conditions: the authors demonstrated a range of temperatures (e.g., 610°C, 892°C, 1,345°C, 1,549°C, and 1,800°C) by varying the energy density of the lamping (i.e., by controlling the photon energy).

The FTS lamping approach can enable a far-from-equilibrium synthesis in broad elemental and compositional spaces; the authors demonstrated the synthesis and anchoring of a series of catalytic nanoparticles on the SnO₂ nanosheet support. The phase transformation process of SnO₂ occurs simultaneously with the formation process of the nanoparticles without interfering with it. This *in situ* synthesis was shown to achieve unary, binary, ternary, and even quinary (i.e., PtRuIrFeCo) alloy nanoparticles with a size < 10 nm, which are highly useful for sensing and catalysis applications. Notably, for the multi-elemental nanoparticles, the extreme synthesis conditions (including fast heating and cooling rates) and the high temperature by FTS lamping can together ensure a

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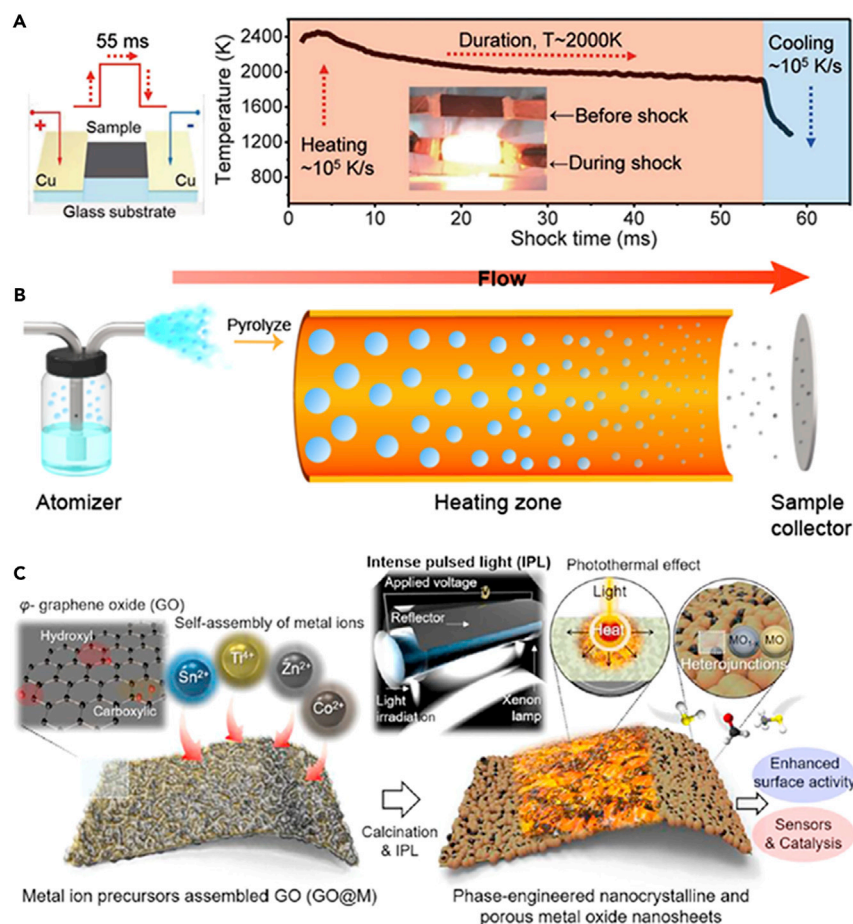


Figure 1. Representative transient high-temperature heating methods for synthesizing multi-elemental nanoparticles

(A) The carbothermal shock method. Reprinted with permission from Yao et al.³ Copyright 2018 AAAS.

(B) The aerosol-based fly-through method. Reprinted with permission from Wang et al.⁷ Copyright 2020 Wiley.

(C) The FTS lamping method reported by Kim et al.⁹

high material quality. The fine shape and size distribution among the nanoparticles and the homogeneous elemental mixing within the nanoparticles are outstanding among the literature. The authors further demonstrated another level of tunability of their approach by transforming nanoparticles to small clusters and finally to single atoms via applying multiple shots to the substrate via FTS lamping. The surface defects play important roles in trapping and stabilizing the single atoms during the transient shots, which has also been shown with other substrates.¹⁰ The concept of using FTS

lamp can be extended to other material platforms, such as Co_3O_4 nanosheets and carbon nanofiber, indicating broad substrate scope and good feasibility of the approach.

To demonstrate the utility of the SnO_2 -supported nanoparticles, the authors studied the gas-sensing properties of the unary, binary, and ternary nanoparticles (Pt, PtIr, and PtIrRu) loaded on SnO_2 in micro-electromechanical systems (MEMS) to detect trace amounts (250 ppb to 1 ppm) of sulfuric biomarker molecules (e.g., H_2S , CH_3SH , and $\text{C}_2\text{H}_6\text{S}$), which are impor-

tant for the diagnosis of intra-oral and/or extra-oral diseases (halitosis) from the exhaled breath of patients. Interestingly, although the selectivity (i.e., catalytic activity) of the sensor is generally decided by the constituent element, alloying the metal elements as homogeneous multi-elemental nanoparticles is able to fine-tune the sensing behaviors toward different gas molecules. The authors further integrated the material with MEMS sensors for a commercially viable sensing device. Not only did the device exhibit excellent sensing activity, but it also demonstrated good long-term stability without any noticeable degradation after a 9-month aging test period. This proof-of-concept demonstration showcases the great potential of metal-oxide-supported nanomaterials synthesized by FTS lamping for practical utilizations.

Note that the FTS lamping approach is flexible with various substrates, such as SnO_2 , Co_3O_4 , and many more, through surface modification. As such, it can be imagined that the noble-metal nanoparticles supported on the metal-oxide substrates with tunable composition, size, and other physicochemical properties could find applications in many thermochemical catalytic schemes outside of the sensing devices demonstrated in the work by Kim et al. The merit of the FTS lamping approach lies in its capability of continuous fabrication, for which the authors showed a prototype and lab-scale design featuring a roll-to-roll process for high-throughput synthesis on the gram scale. One potential aspect for further exploration using this approach could be integrating several shock-type syntheses (e.g., electrical shock and FTS) together to expand the synthesis capability and create potential synergy.

DECLARATION OF INTERESTS

The authors declare no competing interests.

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From bio-based furanics to biodegradable plastics

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The catalytic conversion of biomass resources into renewable building blocks for the preparation of biodegradable plastics is an open challenge in the modern bio-refinery. In this issue of *Chem*, Li and co-workers propose a tandem homogeneous carbonylation and heterogeneous hydrogenation process for the conversion of (hemi)cellulose-derived furans into hydroxyalkanoates.

The use of renewable feedstocks for the production of biodegradable materials, including polymers and blended or composite products, is one of the cornerstones upon which a sustainable future will be built and a key part of the circular economy.^{1,2} Lignocellulose is a readily available and abundant renewable biomass-carbon reserve on Earth and already represents a key resource for the sustainable production of value-added chemical products and intermediates. Cellulose and hemicellulose fractions, accounting for up to 70% of the dry lignocellulose, can be converted into

a multitude of bio-based molecules, including acids, polyols, alcohols, and furan derivatives. Among the latter, furfural (FUR) and 5-hydroxymethylfurfural (5-HMF) are recognized as versatile C5 and C6 platform intermediates and are included in the list of the 12 most promising bio-based molecules. FUR and 5-HMF are widely used as starting substrates in the preparation of active pharmaceutical ingredients, food additives, biofuels, and a series of functional monomers and polymers.^{3,4} 5-HMF can be employed for the preparation of 2,5-furandicarboxylic acid, which is one of the two mono-

mers for the synthesis of polyethylene furanoate, a bio-based polymer that has the potential to become a valid alternative to polyethylene terephthalate. Unlike 5-HMF, FUR is characterized by a monofunctionalized structure that limits its application in the preparation of polymeric materials.⁵ However, FUR can be easily hydrogenated into furfuryl alcohol (FA), which is the conventional monomer in the synthesis of furfuran resin. It is worth noting that, at the industrial level, more than 60% of FUR production today is devoted to the preparation of FA.

The use of biomass for the production of bioplastics needs to take into consideration two open issues: first, the global production of plastic is expected to exceed 590 million metric tons by 2050;⁶ second, most plastics are mismanaged after use, causing well-known environmental and social problems (a

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