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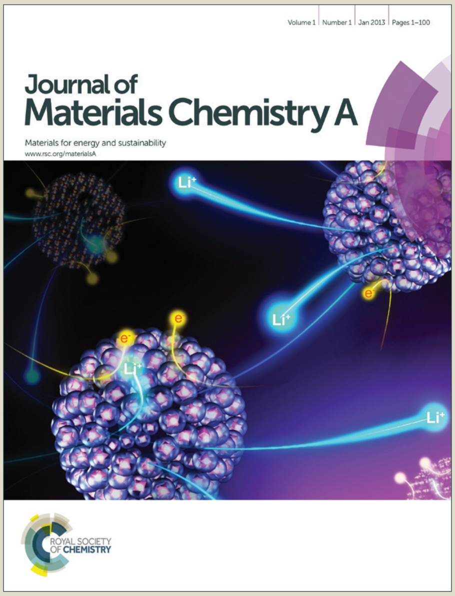

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COMMUNICATION

Novel solid metal-organic self-propagation combustion for controllable synthesis of hierarchically porous metal monoliths

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We demonstrate a solid glycine-nitrate self-propagation combustion route to fabricate hierarchically porous metallic monoliths. Solidifying temperature (*Ts*) and environmental gas pressure (*P*) were effective controlling factor over chemistry, topography and microstructures. This may offer easy up-scaling and controllable synthesis of porous metal monoliths for wide applications like electrode current collectors, catalyst, catalyst substrates and sensors.

Recently, the important roles of porous metal foams have been highlighted by the pursuit of binder-free high-performance supercapacitors[1-3] and lithium-ion batteries electrodes,[4, 5] catalysts,[6] catalyst substrates and sensors,[7] due to their excellent electronic conductivity, low density, high specific surface area and high permeability.[8] However, the porous metallic frames were generally obtained by elaborate process with templates[9] or even highly toxic precursors;[10] still, large pore sizes in commercial Incofoam® Ni foam or the powder forms in most lab experiments limited their applications.[8, 11, 12] Thus, continuous porous metal foams with tuneable microstructures prepared by a facile, cost-effective method would be most enticing.

Combustion,[13] an illustration of sustainable redox reaction, produces not only energy but also valuable materials. Gaseous, liquid or solid combustible precursors like fuel and oxidizer are first mixed (solid precursors are first ground into fine powders and then intimately mixed). After preheating to ignition temperature (T_{ig}), the redox reaction begins to travel through the precursors, giving out heat for reaction sustainability and producing valuable products like carbon nanotubes,[14] advanced ceramics,[13, 15] functional chemicals[15-17] and even pure metals[18, 19] behind the combustion wave. Combustion has been known as an efficient method for in-situ mass production of materials especially for refractory compounds considering its no need for external heating resource.

Conventional solid combustion like thermite reaction, which produces high temperature (>2000K), has been important in the synthesis of refractory metal or ceramic materials for continuous coating or wear-resistant parts by its well-known high–temperature self–propagation synthesis (SHS) mode.**[13, 16]** The newly developed solution combustion, due to its molecular-level blending of precursors in water, much gas release for pore construction and mild synthesis conditions, has been a versatile method for the synthesis of highly porous multi-component powders like advanced ceramics and catalysts.[13, 16] Solution glycine-nitrate (GN) combustion received intensive attention when transition metals/alloys foams rather than chemical compounds powders were obtained in air at room temperature by tuning glycine/nitrate ratio.[18, 20]

However, continuous porous metal monoliths with reliable strength and tuneable microstructures have not yet been realised by neither of the combustion method. Although conventional solid combustion is capable of producing continuous coating or body materials by its controllable SHS mode, it is usually gasless for in-situ pore construction. On the other hand, much gas released within such a short time gives solution combustion spraying nature, which makes the sintering of products insufficient to achieve reliable strength. In addition, the bubbling issue in solution or gel during preheating makes uniform density of monoliths impossible.[13] Note that microstructure control has been especially difficult during instant or even explosive combustion process.

In this communication, we report a facile solid glycine-metal-nitrate (GMN) combustion route for the up-scaling synthesis of continuous metal monoliths. This novel solid metal-organic combustion not only inherits merit of molecular-level mixture of precursors from solution combustion synthesis, but also steady and controllable SHS behaviour from conventional gasless solid combustion. Besides, solidifying temperature (*Ts*) and environmental gas pressure (*P*) were found effective controlling factor over chemistry, topography and microstructures. Promisingly, this solid GMN combustion may represent a novel illustration which blurs the boundary between solution combustion and conventional solid combustion and offers easy up-scaling and controllable synthesis of porous metal/alloy/cermet monoliths with tuneable microstructures for wide applications like electrode current collectors, catalyst, catalyst substrates and sensors.

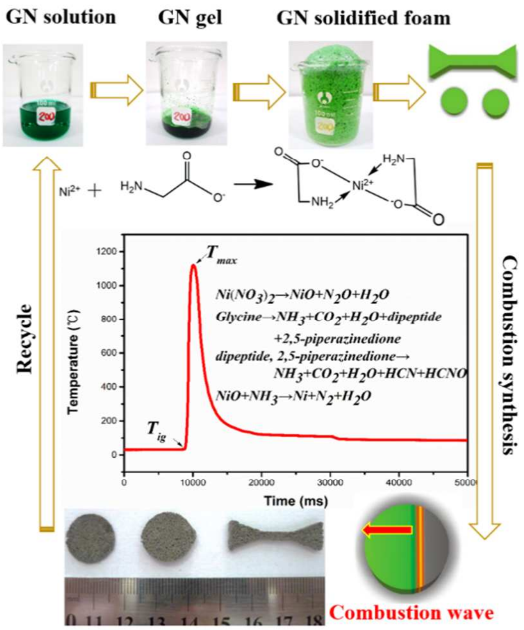

Figure 1 Schematic illustration of solid glycine-metal-nitrate self-propagation combustion route to continuous porous nickel monoliths.

The solid GMN process is facile and efficient for the scalable synthesis of continuous porous Ni monoliths, as illustrated in **Figure 1** and electronic supplementary information (ESI). Nickel nitrate (N) and organic fuels like glycine (G) were first dissolved in water and formed chelated compound, then solvents were removed at different *Ts* according to thermal gravimetric−differential scanning calorimetry (TG–DSC) analysis **(Fig. S 1)** and substance pyrolysis property[19]**,** which gave solidified GN precursors. After grinding and net shaping, the green precursors were locally ignited at room temperature and nickel metallic monoliths were left behind the sustainable combustion wave according to the reaction mechanism equations (see the **inset of Figure 1**) given by Manukyans etal.[20] The as-prepared metal monoliths are continuous with variable shape or size and the process is easy up-scaling. Porous copper monoliths have also been fabricated by substituting metal salts with copper nitrates (see **Fig. S 2**). It is noteworthy that metellic products can be dissolved by nitrate acid, which gives metal nitrate to cycle in solid GN combustion and contributes to rational use of metal resources.

The solid GN precursors inherits merit of molecular-level blending of precursors from solution mixture, as revealed by X-ray diffraction (XRD) and Infrared Spectroscopy (IR). The solidified GN precursors are largely amorphous as revealed by the broad XRD peaks rather than crystalline reflections of glycine or nitrate in **Figure 2(a)**. The characteristic peaks of glycine and nitrate salts remain in IR spectra for solidified precursors, however, the main functional group peaks shift (**Figure 2(b)**). Blue shift of asymmetric stretching peaks of COO$^-$ at 1610 cm^{-1} indicates the coordination between Ni^{2+} and COO$^-$, which is further verified by the vibration band of M-O at about 553 cm^{-1}. [21, 22]The absence of NH^{3+} characteristic peak at 2131cm^{-1} suggests the amino group coordination with metal ions, which is validated by the shifts of stretching vibration and bending vibration of N-H at 3180 cm^{-1} and 1514 cm^{-1} respectively. [21, 22]These XRD and IR results confirm the molecular-level blending of GN precursors in solid state.

The solid GN precursors are combustible and the combustion behaviour is steady by self-propagation mode (see the dynamic movie provided in the supporting information). Propagating parameters such as highest temperature (T_{max}) and velocity of combustion wave *(v)* were carefully monitored, as shown in **Figure 2 (c) and (d)** respectively. Both T_{max} and *v* present a growing tendency with the increase of *Ts* from 70℃ to 200 ℃, which could be ascribed to less heat consumption to remove residual water during combustion, as suggested by Manukyans's experimental study.[20, 23] Note that compared to the extremely high T_{max} (> 2000K) in conventional solid combustion, low T_{max} observed in solid GN combustion is more conducive for the formation of nano-scale microstructures with high surface areas. [13, 16] The propagating velocities were observed to be one order of magnitude lower than that of solution combustion, [18] indicative of controllable combustion behaviour. This allows for enhanced monoliths sintering and further microstructures control.

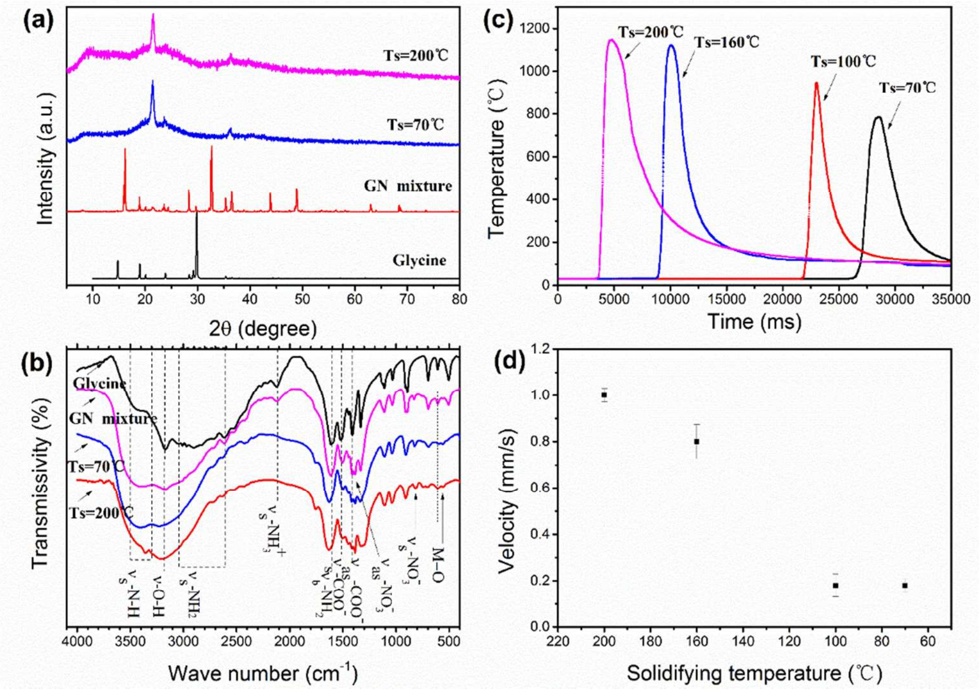

Figure 2 (a) X-ray diffraction patterns and (b) Infrared spectra of GN precursors dried at different *Ts*; (c) Temperature-time profile and (d) propagating velocity of combustion waves with precursors dried at different *Ts* (all ignited at room temperature under air atmosphere).

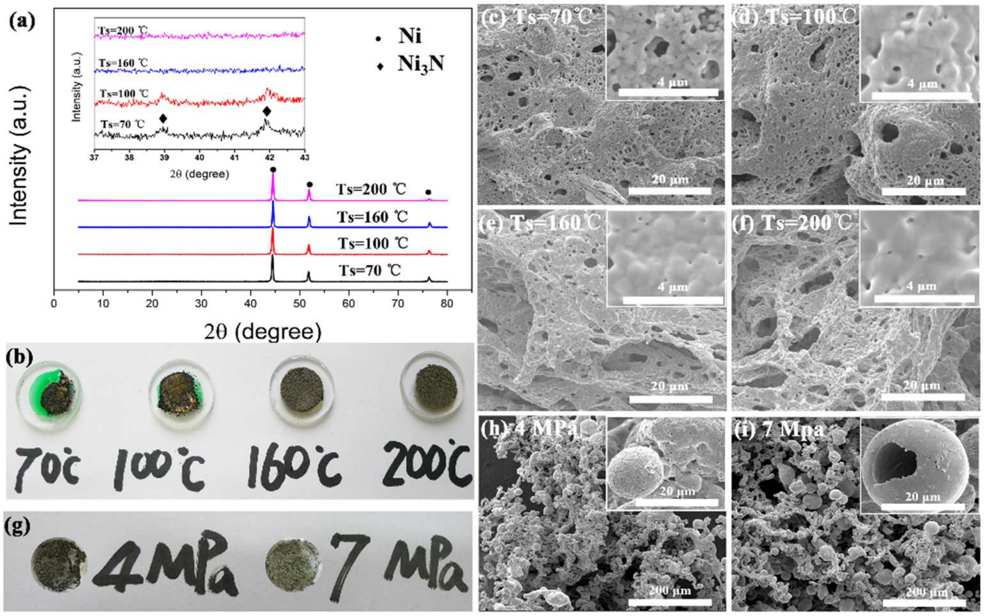

Figure 3 (a) XRD patterns (b) optical photographs and (c) to (f) SEM micrographs of Ni monoliths with precursors dried at different *Ts* (*all synthesized at RT under air atmosphere*); (g) to (i) optical photographs and SEM micrographs of Ni monoliths synthesized at RT but under different environmental N_2 pressures.

The *Ts* affects the purity and bulk phase composition of combustion products, as characterized by XRD and X-ray Energy Dispersive Spectroscopy (EDS). As shown in **Figure 3(a)**, the main phase can be indexed to Ni metal (JCPDS 70-1849) and minute impurities such as C, N and O residue remained in products prepared under lower *Ts* **(Fig. S 3)**. Note that higher *Ts* produces higher T_{max}, which facilitates sufficient pyrolysis of nitrate and glycine, subsequent redox reaction and direct synthesis of metallic foams without post heat treatment. [13, 24]

The *Ts* also exerts a great impact on the as-sintered microstructures of the metal monoliths. The hierarchically porous nickel sheets are composed of sintered grains, which grow from hundreds of nanometers to a couple of microns (**insets of Figure 3(c)-3(f)**) due to less gas release and higher T_{max} for sintering as Ts increases from 70℃ to 200℃. Consequently, the pore structures and void space between sintered structures varied (**Figure 3(c)-3(f)**). The porosity of the continuous nickel monoliths is as high as 95%~98%. The pore structures were further examined by both low temperature N_2 adsorption–desorption method and mercury intrusion porosimeter (MIP). Macropores dominate in the as-synthesized Ni monoliths (Ts=200 ℃) and concentrate at ~10 μm and ~140 μm (**Fig. S 4 (a)**). The specific surface area is about 5.36 m^2/g. The Ni monoliths are also mesoporous with pore size distribution mounting at ~4.9nm, as shown in **Fig. S 4 (b).** Compared with Incofoam® Ni foam (450~3200μm),[25, 26] the optimized hierarchical pore structures and specific surface area may promise improved performances (see **Fig. S 5)**.

Environmental pressure manipulates novel microstructures during this solid gaseous combustion, as shown in **Figure 3(h) and (i)**. Sintered porous metal frames with spherical structures can be observed when environmental N_2 pressure was over 4 MPa **(Fig. S 6)**. Further examination reveals that these microspheres are porous and hollow (**insets of Figure 3(h) and (i)**). The formation of the hollow porous microstructures may result from the interplay of internal released gas and external high gas pressure on the released liquid Ni, which is unique when compared with conventional gasless solid combustion. These hollow porous metal spheres may function as novel structural or functional materials.

Conclusions

In summary, we demonstrate a facile solid glycine-metal-nitrate combustion by self-propagation route for controllable synthesis of hierarchically porous nickel monoliths. Solidifying temperature (Ts) was found an effective controller over propagating velocity (v), maximum temperature (T_{max}) of combustion wave, and consequently compositions and microstructures of products. Environmental gas pressure (P) should manipulate the microstructures into hollow porous metal spheres during this solid gaseous combustion. By substituting the metal or organic fuels in the precursors, we believe that this efficient metal-organic combustion method may inspire more possibilities for continuous porous metal/alloy/cermet monoliths with tuneable microstructures and higher specific area to be employed as electrode current collectors, catalyst, catalyst substrates and sensors.

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Notes and references

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Graphical Abstract

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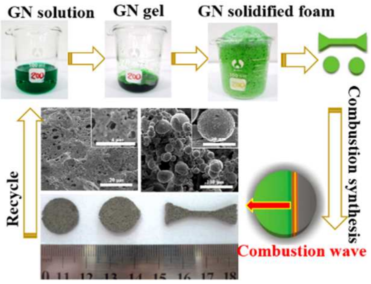

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