Materials Horizons

Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: Z. Zhao, T. Wu, X. Li, Y. Chen and X. Meng, *Mater. Horiz.*, 2024, DOI: 10.1039/D4MH01180E.




ROYAL SOCIETY OF CHEMISTRY

rsc.li/materials-horizons

View Article Online
DOI: 10.1039/D4MH01180E

## Wider Impact Statement

Conventional catalysts preparation methods suffer from mild condition, prolong treatment and low energy transfer efficiency, thus leading to limited inherent nature of catalysts (such as: surface oxidation, agglomeration etc.). Recently, rapid Joule heating method, as novel synthesis method, has attracted widely attention due to the controllable kinetic conditions and eco-friendly operation, while the mechanisms, advantages and recent progress of such method has been concluded by few reviews. Herein, we systematically summarize basic fundamentals, fundamental parameters of Joule heating technique, as well as recent process in terms of effective modification strategies based on Joule heating. Meanwhile, the perspective suggestions and challenges for Joule heating methods on catalytic materials are put forward.

View Article Online
DOI: 10.1039/D4MH01180E

# Progress and perspectives of rapid Joule heating for the preparation of highly efficient catalysts

*Zhan Zhao, Ting Wu, Xiang Li, Yiming Chen and Xiangchao Meng**

Key Laboratory of Marine Chemistry Theory and Technology (Ministry of Education), College of Chemistry & Chemical Engineering, Ocean University of China, Qingdao, Shandong, 266100, China.

*Corresponding author, E-mail: mengxiangchao@ouc.edu.cn*

View Article Online
DOI: 10.1039/D4MH01180E






## Abstract

Functional catalytic materials play an important role in the field of environmental, biological, energy fields, etc., wherein the unique properties can be endowed by various synthesis strategies. However, the conventional catalysts preparation methods suffer from mild condition, prolong treatment and low energy transfer efficiency, thus leading to the situation of limited inherent characterisation of catalysts (such as: surface oxidation, agglomeration etc.). Recently, rapid Joule heating method, as a novel synthesis method, has attracted wide attention due to the controllable kinetic conditions and eco-friendly operation, while the mechanisms, advantages and recent progress of such method has been concluded by few reviews. Herein, we systematically summarize basic fundamentals, fundamental parameters of Joule heating technique, as well as recent processes in terms of effective modification strategies based on Joule heating. Meanwhile, the perspective suggestions and challenges for Joule heating methods on catalytic materials are put forward. This review provides understanding for designing advanced catalytic materials.


***Keywords: catalysis; Joule heating; synthesis; functional nanomaterial; review***

View Article Online
DOI: 10.1039/D4MH01180E

## 1. Introduction

Functional catalytic materials have showed great potentials in environmental, biological, energy fields, *etc.*[1-5]. Typically, by tailoring the compositions, morphologies, sizes of materials, the active sites for surface chemical reactions can be accordingly designed via suitable synthesis methods[6]. Recently, various nanomaterial preparation methods have been widely reported[7-9], including solvothermal reaction[9], electrodeposition[10], ball milling, ultrasonic exfoliation and chemical disposition[11-13]. However, limited by the mild condition of the above methods, the precursor tends to be transferred to thermodynamically advantageous structure (such as: heterostructures and polycrystalline)[14], wherein the inherent nature of materials is hindered. For instance, it is difficult to break through the immiscibility of elemental combinations to synthesize brand new single-phase multi-metallic materials. Meanwhile, the surface oxidation, agglomeration as well as weak interactions between different compositions can occur among most of the common synthesis processes, which leads to unsatisfactory catalytic performance[15-17]. Furthermore, it should be noted that most of the aforementioned methods are time-consuming[18] and limited by the large-scale manufacturing, thus leading to impoverished productivity of catalytic materials. Therefore, it is necessary and meaningful to find a series of facile and effective synthesis strategies, which can also provide harsh kinetic conditions to meet unique chemical and physical properties of catalytic materials.

View Article Online
DOI: 10.1039/D4MH01180E

Recently, Joule heating method has been considered to be an innovative and rapid synthesis of functional catalytic materials with the following advantages[19-21]: 1) Benefiting from the extremely fast heating rate (e.g., $10^5$ K/s)[22], ultra-high temperatures among short period can be obtained, which is conducive to prevent active sites from further oxidation and agglomeration in long-term operation[23]. And the high-temperature treatment facilitates the transfer from metal salts/bulk metals to liquid alloy, which effectively realizes mutual solubility of multiple metals. 2) The following fast quenching provides sufficient dynamic conditions form metastable nanomaterials, which are characterized with structural distortion and defects, thus providing abundant uncoordinated catalytic sites[24]. 3) It should be noted that the short dwelling time (10-1000 ms) can effective synthesis and screen advanced catalysts, wherein the self-heating model with the precursors enables reduced energy consumption and facilitated production efficiency. 4) Materials can be effectively modified and the relevant reliable structure-effect relationships can be established via tuning the technical parameters of Joule-heating in catalyst synthesis[25]. Thus, the novel Joule heating method presents numerous advantageous features and provides a promising pathway to realize effective designing and synthesis of functional catalysts.

Herein, we systematically summarize recent processes for the catalytic materials synthesized via Joule heating as shown in Fig. 1. First, we introduce the basic fundamentals and fundamental parameters of Joule heating technique, including setup, mechanism for the ultra-fast heating/cooling as well as the characteristic advantage of

View Article Online
DOI: 10.1039/D4MH01180E

Joule heating. Then, based on the various functional catalytic materials, we review effective modification strategies via Joule heating, which provide new understanding for designing advanced catalytic materials. Finally, the perspective suggestions and challenges for Joule heating methods on catalytic materials are put forward.

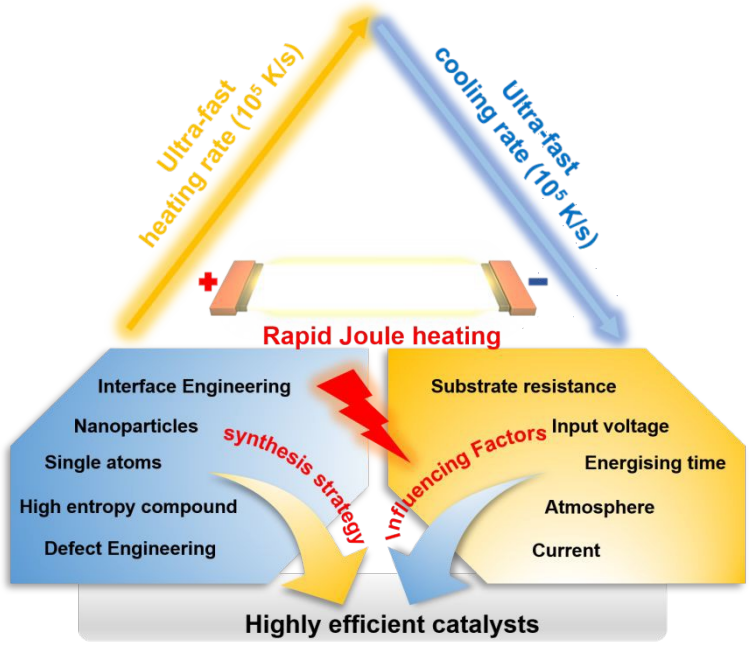



*Figure 1 Schematic illustration of rapid Joule heating method for synthesis highly efficient catalysts.*

## 2. The rapid Joule heating technique

### *2.1 Mechanism of Joule heating*

Joule heating is a novel rapid heating technique based on Joule's law that has recently been employed in the synthesis of catalysts[26], which is also known as ohmic heating. Specifically, the generated voltage different on conductor can endow charge carriers with kinetic energy, which collides with ions in the conductor, thus leading to an amplification of atomic vibrations. This converts energy from the electric field into

View Article Online
DOI: 10.1039/D4MH01180E

thermal energy. In accordance with Joule's law, the heat generated by an electric current through a conductor is inversely proportional to the square of the current (Eq. 1).

$$Q = I^2Rt \qquad (1)$$

In the aforementioned equation, $R$ represents the resistance of the substrate, $I$ denotes the current flowing through the substrate, $t$ signifies the energising time, and $Q$ stands for the heat generated by the current flowing through the substrate.

In Joule heating technology, energy is fed into the system in the form of electrical energy. According to the law of conservation of energy, the input electrical energy can be divided into two parts (Eq. 2). One of these is ultimately converted into the form of heat and absorbed by the material, which is manifested as an increase in the temperature of the catalyst material. The other part is dissipated. The specific heat capacity and mass of the various materials can be related to the elevated temperature. This value is numerically equal to the part of the input electrical energy that is absorbed (Eq. 3).

$$E_i = Pt = E_a + E_d \qquad (2)$$

$$E_a = \xi \cdot E_i = cm(\Delta T) \qquad (3)$$

In Eq. 2, $E_i$, $E_a$ and $E_d$ represent the input, absorbed and dissipated electrical energy, respectively. $P$ denotes the power, and $t$ is the time of the continuous input of electrical energy.

In Eq. 3, $\xi$ represents the absorption coefficient, which is primarily influenced by the material characteristics, reaction environment and heating method. $c$ denotes the

View Article Online
DOI: 10.1039/D4MH01180E

specific heat capacity of the material, $m$ is the mass of the material, and $\Delta T$ is the temperature difference between the starting state and final state of the material.

$$\xi \cdot P/cm = \Delta T/t \qquad (4)$$

Eq. 4 is derived from the aforementioned Eq. 2 and 3. From Eq. 4, suitable heated substrates should be selected to achieve the rapid temperature variation, wherein the factors of substrates, such as absorption coefficient, specific heat capacity and mass, should be considered. At present, the carbon-based materials with satisfactory thermal radiation coefficients as well as thermal conductivities are commonly used as substrates during the rapid Joule heating, which is characterized with the heating rate of $10^3$-$10^5$ $K \cdot s^{-1}$. Meanwhile, in addition to the characteristics of the material, it can be observed that the heating rate $\Delta T/t$ is also influenced by energy, time and space, and Table 1 summarizes the Joule heating setup parameters for the synthesis of catalysts.

Subsequent to the completion of the heating process, the supply of power is terminated, while the cooling process is initiated. The rate of cooling is primarily determined by the physical properties of the material and the manner in which the heat dissipation is achieved. The rate of heat dissipation can be expressed by Eq. 5, where $\kappa$ and $S$ represent the thermal conductivity and area of the material, respectively.

$$Q = \kappa \cdot S(\Delta T) \qquad (5)$$

From Eq. 5, it can be seen that the increase of thermal conductivity can result in high thermal conductivity and fast cooling rate. In addition, the applied gas atmosphere, gas

View Article Online
DOI: 10.1039/D4MH01180E

flow rate and the condition with low temperature in the Joule heating process can significantly affect the cooling rate to obtain the materials with peculiar structure, which should also be rigorously controlled. For example, Hu *et al.* synthesized SF-Ru electrocatalyst with abundant stacking faults (35 and 196 mV @ 10 mA $cm^{-2}$ for hydrogen evolution reaction and oxygen evolution reaction, respectively), which was realized via rapid Joule heating and quenching under liquid nitrogen condition[27]. Compared with the *hcp*-Ru synthesized under Ar atmosphere, the SF-Ru was characterized with the tensile and compressive strain, which could affect the d-band center of Ru, thus adjusting the adsorbate binding.

***Table 1*** *Joule heating setup parameters for several materials*

| Material | Voltage (V) | Current (A) | Temperature (℃) | Response time (s) | Recovery time (s) | Refs. |
|---|---|---|---|---|---|---|
| Ag/C | - | 20 | 500 | 0.5 | - | [28] |
| rGO aerogel | 10 | - | 2727 | 30 | - | [29] |
| $Mo_2C$ | - | - | 1200 | 6 | 1.5 | [30] |
| TMNs | 10 | 4 | 500 | 0.5 | - | [31] |
| CC-S | 80 | - | 1227 | 0.3 | - | [32] |
| CMO/NF-x | - | - | 800 | 60 | - | [33] |
| DA-$Ru_{NP+SA}$/C | - | 20 | 950 | 1.5 | - | [34] |
| NiRu-CNTs | - | - | 1200 | 0.5 | - | [35] |
| Fe/$TiO_2$ | 30 | 300 | 600 | 20 | - | [36] |
| $PdSe_2$NPs/C | - | 12 | 480 | 60 | - | [37] |

View Article Online
DOI: 10.1039/D4MH01180E

### *2.2 Set up of Joule heating*

Recently, two ultra-fast synthesis techniques have been investigated, which are based on the Joule heating effect: Flash Joule Heating (FJH) and Carbothermal Shock (CTS). Typically, the FJH technique relies on the capacitor bank that operates via high-voltage discharge. Meanwhile, the establishment of conductive pathways depends on the additives (such as graphene and carbon nanotube). While the heat generated from CTS technique is directly based on the carbon material, the carbon material and direct/alternating current are assembled to form a conductive pathway.

#### *2.2.1 Set up of Flash Joule heating*

Generally, the FJH setup consists of power supply, capacitor, flashing chamber, vacuum devices, diode electrical inductor and control systems for switching, as shown in Fig. 2a and b. Before the device is activated, the precursor is placed in a quartz or ceramic tube, wherein a certain proportion of conductive carbon material is added to obtain high conductive pathway. Meanwhile, the flashing chamber should be adjusted accordingly (such as gradual compressing) to increase the conductivity of system (1~1000 Ω) as shown in Fig. 2c. Subsequently, the flashing chamber is located between the electrodes (brass screws), which is heated and driven by the discharge of the capacitor under specific gas atmosphere. The power source consists of a series of capacitors, which is characterized with ~0.2 F. Besides, the discharge time can be precisely controlled via a mechanical relay with millisecond delay. Finally, the precursor with carbon source can reach the target temperature (> 3000 K) in a very

View Article Online
DOI: 10.1039/D4MH01180E

short period of time (millisecond level). It should be noted that the temperature and duration of flash chamber can be controlled by setting the conductivity of additives and applied voltage of capacitor. The feedback of the temperature is realised via a temperature measuring system, wherein the real-time temperature is measured by fitting a blackbody radiation spectrum from 600 to 1100 nm as shown in Eq. 6. The $\varepsilon_{gray}$ is the constant emissivity, $T$ represents the measured temperature, $h$, $k_B$ and $\gamma$ denotes the Planck constant, Boltzmann constant and fitting constant, respectively. $\lambda$ and $c$ are the physical quantities associated with light, which are the speed and wavelength of light, respectively.

$$B_\lambda(\lambda, T) = \gamma \varepsilon_{gray} \frac{2hc^2}{\lambda^5} \frac{1}{e^{hc/\lambda k_B T} - 1} \qquad (5)$$

View Article Online
DOI: 10.1039/D4MH01180E



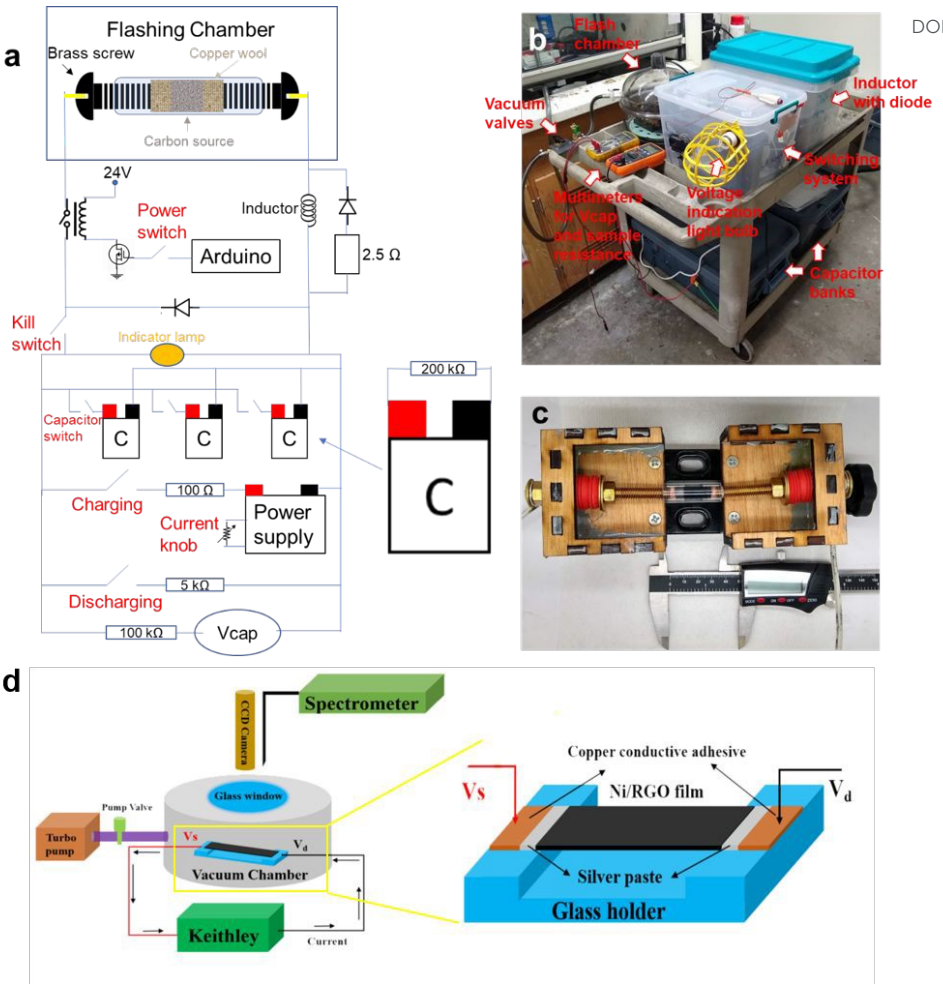



*Figure 2* (a) The detailed schematic diagram of FJH setup. (b) Photo of the FJH setup. (c) Photo of the FJH reaction device. Reproduced with permission.[38] Copyright 2020, Nature. (d) The detailed schematic diagram of CTS setup. Reproduced with permission.[39] Copyright 2017, Wiley-VCH.

### *2.2.2 Set up of Carbothermal shock*

The CTS setup includes electric power sources, conductive electrodes, a vacuum chamber, gas supply system, carbon-based substrate and a temperature sensor, wherein the CTS process utilises the heat generated by delivering a high electrical current to carbon-based substrate. For the operation of CTS device, two conductive electrodes are connected to two opposing ends of the substrate, and the DC power supply is connected

View Article Online
DOI: 10.1039/D4MH01180E

to the electrodes to form an electrical circuit. When the equipment is operated, the current flows through the electrodes to the substrate, which generates heat due to the resistance, thus leading to the instantaneous heating of the substrate. Consequently, the precursor material attached to the substrate can be in-situ transformed to the target material due to the instantaneous heating in the desired gas atmosphere. Meanwhile, in addition to the aforementioned instrumentation, the CTS setup includes a digital camera and a fibre-optic spectrometer, wherein the former is employed to capture images of the sample during the reaction process and the fibre-optic spectrometer is utilised to measure the temperature. Hu *et al.* reported the ultrafast CTS technique to convert micro-level Ni species to ~ 75 nm Ni nanoparticles, which was realized on the rapid heating (~ 2370 K @ 0.06 s) on Ni@C/RGO[39]. It should be noted that the Nano Ni@C/RGO film was connected with copper wire by epoxy and silver colloid as shown in Fig. 2d. The obtained small Ni nanoparticles anchored on the RGO exhibited lager electroactive surface area, thus leading to excellent electro-oxidation activity for $H_2O_2$ fuel (602 mA $cm^{-2}$ @ 0.2 V *vs.* Ag/AgCl). Compared with the complicated operation and the selection of various conductive additives of FJH, the CTS can utilise the carbon-based substrate synthesized by simple process, and is widely applied to synthesize functional alloy nanoparticles, entropic nanomaterials, nanocomposite materials.

View Article Online
DOI: 10.1039/D4MH01180E

### *2.3 Advantages for Joule heating technique*

#### *2.3.1 Transient feature*

Currently, most of the conventional synthesis methods of materials are based on the thermochemical reactions, which are characterized with slowly continuous heating under near-equilibrium operating conditions. As a result, such methods suffer from low reaction rate, limited controllability and the waste of energy/reactants, especially for the in-situ synthesis of catalysts on the substrates, such as Ni foam, Cu foam and carbon paper[40]. Generally, the reaction rate based on the collisions of reactants can be adjusted by the high temperature and concentration of reactant, which is reflected by the classic nucleation and growth theories[41], as shown in Eq. 6.

$$\frac{dN}{dt} = Aexp(-\frac{16\Pi\gamma^3 v^2}{3k_B{}^3T^3(InS)^2}) \qquad (6)$$

The $N$ represents the number of nuclei, $k_B$ denotes the Boltzmann constant. $\gamma$ and $v$ are the surface free energy and molar volume, respectively. A is associated with pre-exponential factor. The Joule heating makes it possible for the rapid nucleation of catalysts, which supplies the condition with high concentration and temperature reaction sites. Meanwhile, different from the traditional heating process, the Joule heating has been reported to realize the balance between high rate and controllability, and sensitive thermal modulation and periodic nucleation pulses via pre-set electrified process allows precisely synthesis of catalysts. Recently, Gao *et al.* reported an innovative wet-interfacial Joule heating method to effectively synthesize HKUST-1

View Article Online
DOI: 10.1039/D4MH01180E

with high crystallization rate (~ 2 μm $s^{-1}$), which was characterized with sub-second process and reactant-saving and was 6 orders of magnitude faster than traditional methods as shown in Fig. 3a[40]. The controllable nucleation and particle density could also be realized by the on-off pulses cycled of Joule heating.

Besides, the transient feature of Joule heating exhibits great potential in synthesizing the catalysts with specific morphology and structure, which minimizes the damage to substrate and functional component. For example, to avoid the damage to the transparent conducting oxide (TCO) substrate, Gao *et al.* synthesized metastable protohematite photoanodes for effective water oxidation via rapid Joule heating, which could obtain 3.59 mA $cm^{-2}$ (1.23 V *vs.* RHE)[42]. To solve the aggregation and oxidation of catalyst during the synthesis process, Meng *et al.* utilised rapid Joule heating method to provide ultra-high activation energy (> 1300 K) and synthesized highly active RuMo system, as shown in Fig. 3b. Specifically, the 3D morphology of RuMo catalyst could be remained compared with the catalyst prepared with the traditional temperature-programmed method, which played an important role in active area (Fig. 3c and d). Meanwhile, the rapid heating/cooling rate also endowed RuMo catalyst excellent surface wettability as shown in Fig. 3e.

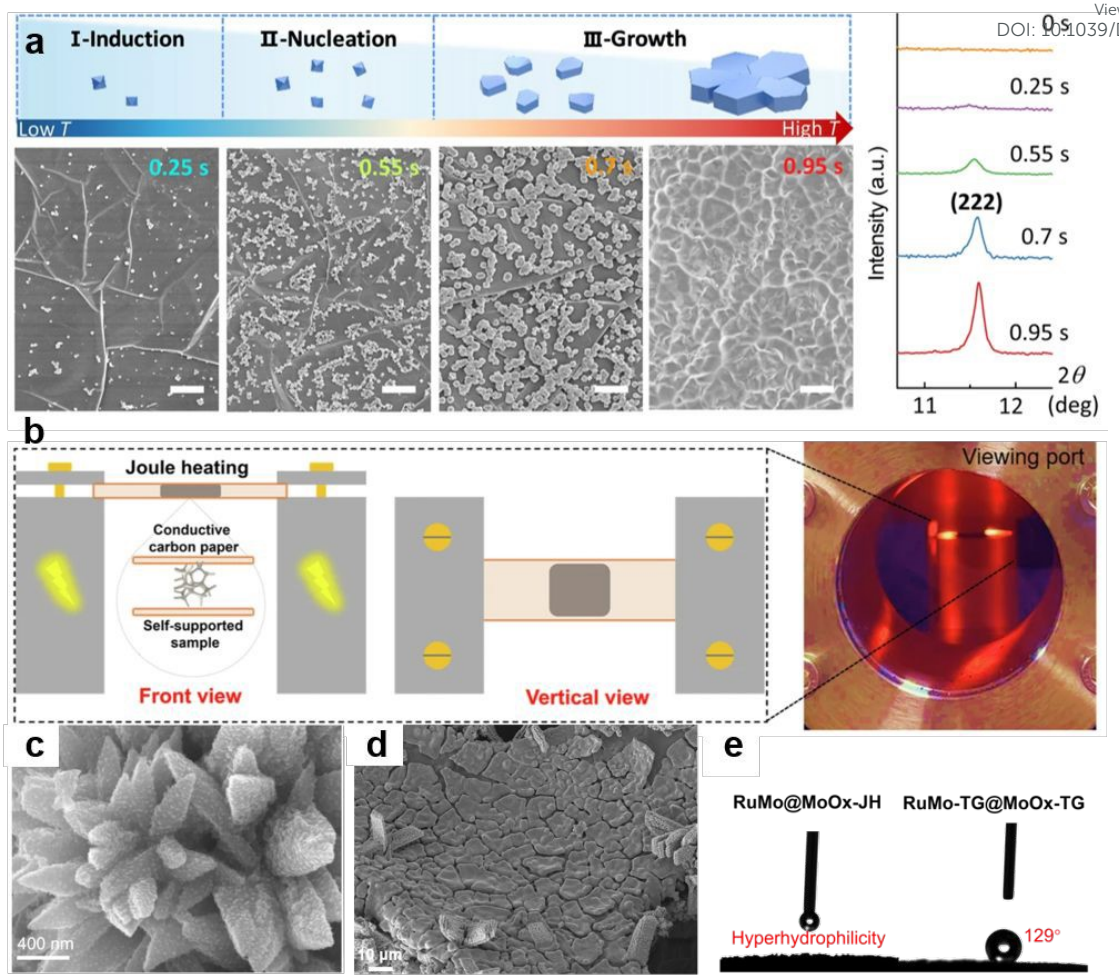



*Figure 3* (a) The schematic diagram, SEM images and XRD patterns of structural evolution for HKUST-1. Reproduced with permission. [40] Copyright 2023, Springer Nature. (b) The schematic diagram and photo of the Joule heating setup. (c) SEM image of catalyst synthesized by Joule heating. (d) SEM image of catalyst synthesized by traditional method. Reproduced with permission.[43] Copyright 2024, Springer Nature.

### *2.3.2 Energy efficiency*

Generally, the conventional heating methods, as indirect heating approach, involve the heating of resistive coil and transferring the heating to precursor, which is based on the radiation mechanism. However, the inferior power and heat dissipation limit the efficient use of energy. Conversely, the Joule heating, by mean of direct heating,

View Article Online
DOI: 10.1039/D4MH01180E

converts the energy of electricity to heating of sample, which is characterized with high heating efficiency and rapid temperature response. Meanwhile, such method can reduce the energy consumption due to the ultrashort reaction, wherein the Table 2 summarizes the reaction time and energy consumption of the Joule heating setup and conventional heating methods for the synthesis of catalysts. Recently, the effective synthesis of carbon nanomaterials from waste plastic via rapid Joule heating has been reported, wherein this synthesis strategy not only converts low-value waste plastics into high-value carbon nanomaterials, but also demonstrates high environmental friendliness and sustainability, with an 86-92% reduction in energy consumption and 92-94% reduction in global warming potential compared to conventional methods[44]. Therefore, the rapid Joule heating possess great potential for the effective synthesis of catalysts with eco-friendliness. Besides, it should be noted that the Joule heating has also been reported to be applied in the industrial thermochemical reactions that might suffer from the heat transfer processes and reaction equilibrium[45]. The temperature difference between the reactants/products and heater tube wall Heat transfer limitations can be avoided by placing the heating element, where the Joule effect occurs, directly in the reaction zone. Thus, the generated low temperature gradient minimizes by-product generation.

***Table 2*** *Synthetic process parameters for several materials*

| Material | Synthesis method | Reaction time | Energy consumption | Conventional synthesis method | Reaction time | Energy consumption | Refs. |
|---|---|---|---|---|---|---|---|
| $MoNi_4/MoO_x$ | Joule Heating | 60 s | 7 W $h^{-1}$ | Tube Furnace Calcination | 2 h | 6 KW $h^{-1}$ | [17] |

View Article Online
DOI: 10.1039/D4MH01180E

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| NiFe alloy/$MoO_2$ | Joule Heating | 180 s | 21 W $h^{-1}$ | Tube Furnace Calcination | 6 h | 2 KW $h^{-1}$ | 16 |
| Mo-Ru/CNTs | carbothermal shocking | 40 s | - | Tube Furnace Calcination | 2 h | - | 46 |
| RuMo@MoOx-JH | Joule Heating | 60 s | 7 W $h^{-1}$ | Tube Furnace Calcination | 11.5 h | 17.2 KW $h^{-1}$ | 43 |
| Ce-Co/CoO@CNTs | Joule Heating | - | - | Tube Furnace Calcination | 2 h | - | 47 |
| $Co_2Mo_3O_8/MoO_2$/NF | Joule Heating | 130 s | - | Tube Furnace Calcination | 2 h | - | 15 |
| HS-NFS | Thermal shock | 100 s | - | Tube Furnace Calcination | 18 h | - | 48 |
| $Pd_3pb$ | Joule Heating | 60 s | - | Traditional annealing | 3 h | - | 49 |
| Inorganic SEI | Fast Heating | 150 ms | - | Hydrometallurgical regeneration | - | About five times higher than Fast Heating | 50 |
| HKUST-1 | Wet-interfacial Joule heating | 0.25 s | $9.55 \times 10^{-6}$ kWh $cm^{-2}$ | Bulk-heating-based methods | - | About $10^6$ times higher than Wet-interfacial Joule heating | 40 |
| Graphite Anodes | Flash recycling process | ~1 s | 10.6 kJ $g^{-1}$ | High-temperature-calcination method | 2 h | - | 51 |
| N-CNTs | Flash Joule heating | 1 s | - | Tube furnace pyrolysis | 2 h | - | 52 |
| Asphaltene-derived flash graphene | Flash Joule heating | 100 ms | 20.55 kJ/g | Conventional chemical vapor deposition | - | - | 53 |

View Article Online
DOI: 10.1039/D4MH01180E

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Ru-Fe@CF | Joule heating | 1 s | - | Traditional calcination method | 3 h | - | 54 |
| Spinel oxides | Joule heating | 15 s | $10^{-1}$ Wh/g | Hydrothermal | hours | $10^{3}$ Wh/g | 55 |
| F-Si@rGO | Flash Joule heating | 120 s | - | Tube furnace pyrolysis | About 12000 times slower than Flash Joule heating | - | 56 |





### *2.4 Materials fabricated by Joule heating*

The Joule heating process consists of several steps. The first step is to attach the precursor to the substrate. Next, a vacuum is applied to create the required gas atmosphere (air, Ar, $N_2$ or $H_2$/Ar). Meanwhile, voltage and energization time are set and current is passed through the substrate, wherein the collision occurs between the precursor electrons and the substrate molecules, thus converting electrical energy into thermal energy. The temperature of the precursor rises rapidly, resulting in the mixing of metal atoms, nucleation and crystal growth. The following sections systematically introduce the progress of Joule heating in synthesizing different materials.

#### *2.4.1 Carbon-based materials*

Currently, the carbon-based materials, as potential catalyst, have attracted wide attention in industrial production, which exhibit exceptional light absorbing properties, excellent conductivity and physical stability[57]. Meanwhile, the abundant resources, eco-

View Article Online
DOI: 10.1039/D4MH01180E

friendliness, no toxicity and low cost-effectiveness endow carbon-based materials with the potential for large-scale generation. Consequently, carbon-based catalysts possess great implementation prospects in plentiful fields, such as energy storage devices, electrocatalysis, photocatalysis, photodetectors[58]. Generally, several common methods have been applied to synthesized carbon-based materials, such as Scotch tape method, chemical vapor deposition, redox reaction and liquid-phase exfoliation[59]. However, the effective synthesis is limited in terms of preparation of large-sized samples, precise design for morphology, product quality and large-scale preparation. The Joule heating, as an innovative method with rapid reaction speed and controllability, can serve as ideal technique for effective synthesize the carbon-based materials. Typically, the extremely fast heating rate (e.g., $10^5$ K/s) generated by Joule heating can rebuild conjugated backbone in defective graphene blocks, which exhibits satisfactory conductivity as well as carrier mobility of carbon films[60]. For example, Gao *et al.* proposed a roll-to-roll process based on Joule heating[61], which was capable of continuously producing large-area, high-quality graphene films (electrical conductivity: $4.2 \times 10^5$ S/m, thermal conductivity: $1285 \pm 20$ W/mK) as shown in Fig. 4a. It should be noted that heating to high temperatures (~2400 °C) at constant voltage can further remove structural defects and impurities. The roll-to-roll Joule heating method offers significant advantages in terms of preparation time and energy consumption over the conventional electric furnace heating methods, wherein the Joule heating consumed less than 3 KW electrical power. James *et al.* synthesized one-dimensional (1D) and 1D/2D hybrid carbon

View Article Online
DOI: 10.1039/D4MH01180E

nanomaterials form plastic waste using Flash Joule Heating (FJH) technology (Fig. 4b), which was characterized with fast reaction, scalable synthesis and avoided the use of solvents or water, thus outperforming conventional chemical vapour deposition as shown in Fig. 4c[44]. Meanwhile, it has been shown that by adjusting the reaction conditions of FJH (e.g. voltage, capacitance, catalyst type and concentration, etc.), the morphology and size of the synthesized carbon nanomaterials can be effectively controlled, including different structures such as nanotubes, nano-fibres and nanoribbons. The rapid heating and cooling process generated by Joule heating provides a simple and rapid method of uniformly loading metal nanoparticles onto carbon carriers, allowing precise tuning of the size, structure and dispersion of the active sites such as alloy nanoparticles, single-atom. For instance, Wang *et al.* realized ultrafine active NiRu alloy nanoparticles (NiRu-CNTs) dispersed on nitrogen-doped carbon nanotubes (N-rich CNTs) by Joule heating as shown in Fig. 4d, which was served as effective electrocatalyst for hydrogen evolution reaction (5.1 mV@10 mA $cm^{-2}$)[62]. The research not only demonstrated that the Joule heating technique is an effective strategy for the preparation of ultrafine-sized and well-dispersed alloys on carbon-based substrate, but also provided an important reference for the design and development of new high-efficiency and low-cost electrocatalysts.

View Article Online
DOI: 10.1039/D4MH01180E



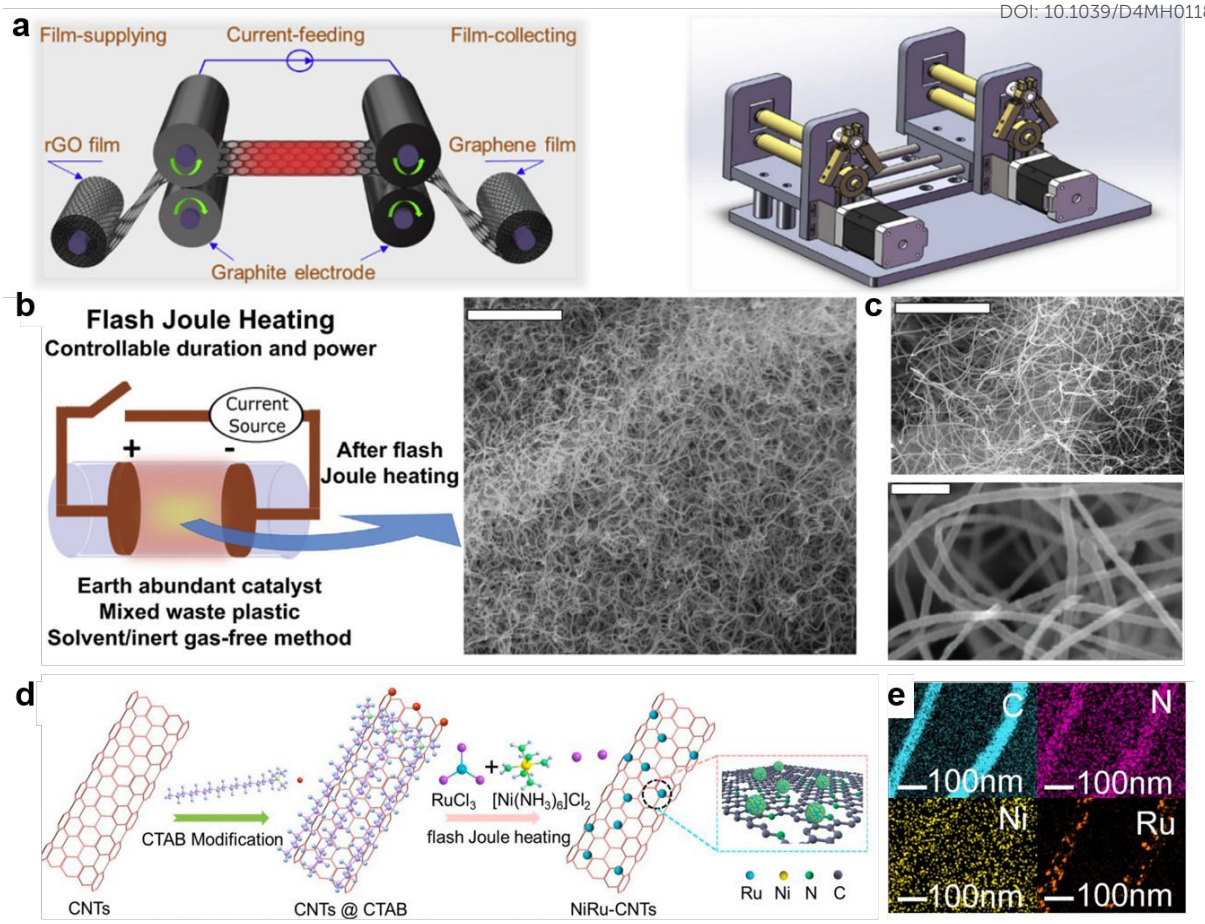



*Figure 4* (a) The schematic diagram of roll-to-roll process based on Joule heating. Reproduced with permission. [61] Copyright 2019, Elsevier. (b) The schematic diagram of the FJH setup with the (c) SEM image of nanomaterials. Reproduced with permission. [44] Copyright 2023, Wiley-VCH. (d) The schematic diagram of sample synthesis process. (e) EDX elemental mapping images of sample. Reproduced with permission. [62] Copyright 2023, Elsevier.

### *2.4.2 Metal-based materials*

The metallic materials have been considered as essential components in industrial catalytic production due to the excellent electrical and thermal conductivity, associated with high hardness and strength, which can also be applied as effective catalysts with abundant active sites and high intrinsic activity [63]. However, the conventional methods

View Article Online
DOI: 10.1039/D4MH01180E



for synthesising metallic materials such as intermetallic compounds typically rely on prolonged annealing treatments, which tend to sinter and aggregate the metallic particles, thus degrading the catalytic properties. Consequently, synthesising the metallic catalysts with highly ordered and uniform distribution on the substrate in a short time has been considered as a challenge in the field of materials science. Recently, the rapid Joule heating method with ultra-fast high-temperature sintering is recognized as an effective technique, which is particularly beneficial to the application with large-scale production of material and effectively avoids the thermodynamically driven aggregation and oxidation of metal active sites[43]. Meanwhile, the rapid Joule heating method also allows materials to be produced with high densities, which is important for specific applications such as solid-state batteries. Hu *et al.* obtained ultrafine silver (Ag) nanoparticles on carbon nanofibers via a fast Joule heating method (~1600 K@20 ms), wherein the uniform Ag nanoparticles served as nano-seeds to guide the deposition of lithium to effectively address the problems of dendrite growth and interfacial instability on lithium metal battery anodes[64]. And the as-prepared Ag-based anode exhibited low overpotential (0.025 V) with long cycle life. Meanwhile, Zachariah *et al.* utilized Joule heating to synthesize uniformly distributed nanoparticles (Al, Pd, Si, Sn) in reduced graphene oxide (RGO) matrices, which could realize the melting and self-assembling micron-sized metal or semiconductor particles into nanoparticles in a short time (1700 K@ 0.01 s)[65]. Benefiting from the barrier effect of the defects on RGO and rapid melting under Joule heating, the Al nanoparticles could avoid the merge and

View Article Online
DOI: 10.1039/D4MH01180E

agglomerate, which were driven by the surface energy. And the molecular dynamics (MD) simulations proved the generated defects and graphene boundaries provided barrier to limit the thermo-activated random walk of Al species, thus leading to the uniform distribution.

It should be noted that the Joule heating process can reach high temperature (up to 3000 ℃), which is appropriate for sintering various high melting point metals and obtaining wide range of meatal and alloys. The non-equilibrium Joule heating-based approach can also effectively solve the problem of phase separation of high entropy nanoparticles/alloy due to the rapid heating/cooling rates, even in immiscible elemental combinations. Chen *et al.* ensured the well mixing and reaction of component to successfully synthesize high entropy metal selenides via Joule heating, which avoided the problem of temperature gradients that are common in conventional heating methods[66]. It should be noted that the HEMS exhibited a low overpotential of 222 mV to obtain the current density of 10 mA $cm^{-2}$ for OER and showed little degradation in a 1000 h durability test. Theoretical investigations showed that the asymmetric Cu-Co-Ni active unit played an important role in improving the activity and durability by modulating the interplay of oxygen-containing intermediates. In addition, such synthesis process is capable of modifying the microstructure of the material to form a more homogeneous and stable nanostructure, thereby improving the catalytic properties of the material[67]. Xu *et al.* successfully synthesized PtFeCoNiMn high-entropy nano-alloy on nitrogen-doped carbon (PtFeCoNiMn/NC) as effective electrocatalysts for

View Article Online
DOI: 10.1039/D4MH01180E

oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) via the ultra-fast Joule heating technique, wherein the strong thermal driving force of the Joule heating process promoted the formation of high-entropy alloy nanoparticles from the absorbed metal ions on NC[68]. Meanwhile, the rapid Joule heating plays an important role in enabling the formation of a strong bond between the alloy nanoparticle catalyst and the conductive substrate, which improves the long lifetime of the metal-based catalyst for catalysis and energy conversion. Recently, Yao *et al.* induced the high-entropy alloy to the defect sites of carbonised wood, wherein the carbon atoms could move to the surface of high-entropy alloy nanoparticles to form a carbon protective shell. This treatment significantly strengthened the interface between the high-entropy alloy nanoparticles and the activated carbon protective layer, which remained active (7 mV@10 mA $cm^{-2}$) during 500 hours electrolysis[69].

*2.4.3 Inorganic non-metal-based materials*

The range of inorganic non-metal-based materials is wide, such as glass, ceramics, and cement etc, which consists of oxides, carbides, nitrides and silicon-based material. Among them, porous ceramic materials are widely applied in the fields such as electrodes, photopolarimetry and catalyst supports, which have also attracted much attention in the field of thermal insulation materials with the features of low thermal conductivity as well as excellent chemical inertness[70]. Recently, Chu *et al.* have successfully developed a 9-cation porous high-entropy diboride ceramic ($(Hf_{1/9}Zr_{1/9}Ta_{1/9}Nb_{1/9}Ti_{1/9}Cr_{1/9}Mo_{1/9}V_{1/9}W_{1/9})B_2$) with a unique multi-scale structural

View Article Online
DOI: 10.1039/D4MH01180E

design via Joule heating[71], wherein the such ceramic material not only exhibited excellent mechanical strength (337 MPa) at room temperature, but also good thermal insulation properties (thermal conductivity of 0.76 W/(m K)) as shown in Fig. 5a. In detail, under the borothermal reduction, the uniformly distributed submicron pores could be generated due to the production and release of the significant amount of $B_2O_3$ gas. Meanwhile, the authors sintered the diboride ceramic with 10 seconds by using rapid Joule heating synthesis technology, wherein the generated strong connections between grains as well as interface between building blocks in the nanoscale played important roles in thermal insulation and mechanical properties.

Currently, the energy density of graphite as an anode material for lithium-ion batteries is close to its theoretical limit, and the inorganic non-metal-based materials (such as silicon-based material), with extremely high theoretical specific capacity and low delithium potential, have emerged as a promising candidate for improving the energy density of batteries[72]. However, the volume expansion of inorganic non-metal elements (such as silicon) during charging and discharging can lead to particle fragmentation and continued formation of SEI layers, which in turn degrades battery capacity degradation. Recently, strategy of encapsulating silicon nanoparticles in carbon matrices to improve stability and electrochemical performance via Joule heating has been reported. Tang *et al.* anchored silicon nanoparticles through the formation of silicide 'rivets' between silicon and graphene via FJH technique to avoid the phase separation and structural instability (Fig. 5b)[56]. After the electrochemical cycling, the F-Si@rGO synthesized via

View Article Online
DOI: 10.1039/D4MH01180E

FJH maintained the structural integrity due to the strong anchoring between the silicon and carbon matrix, while the S-Si@rGO synthesized with slow heating rate showed severe fragmentation of silicon particle and overgrowth of the SEI layer. Therefore, the homogeneous lithiation and interfacial stability of F-Si@rGO, endowed by rapid Joule heating, contributed to the reduction of microcrack formation during the long-term cycling process, thus maintaining the electrical conductivity of the electrode. Meanwhile, the feasibility of mass-producing of sample has been verified by integrating freeze-drying and FJH techniques as shown in Fig. 5c.

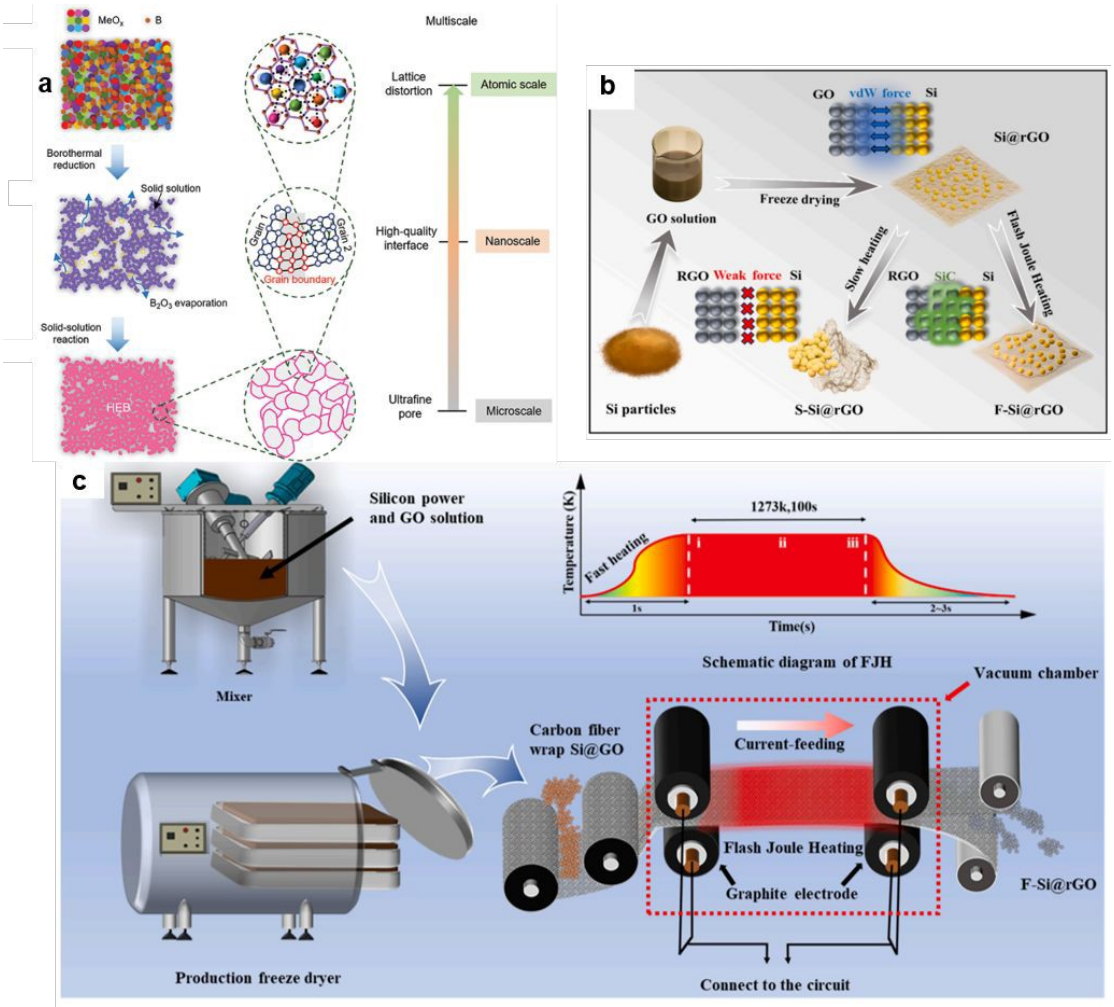


*Figure 5* (a) The schematic diagram of the fabrication of 9-cation porous high-entropy diboride ceramic. Reproduced with permission. [71] Copyright 2024, Wiley-VCH. (b) The schematic diagram of the fabrication of silicon-carbon matrix with (c) the schematic diagram of FJH setup for mass-producing of sample. Reproduced with permission. [56] Copyright 2024, Elsevier.

### *2.5 Characteristics of materials synthesized via Joule heating*

#### *2.5.1 Dispersibility*

Heterogeneous catalysis plays a pivotal role in contemporary industrial processes, with the catalytic reaction predominantly occurring on the surface of solid catalysts[73]. In order to enhance the performance of catalysts, researchers have sought to increase the surface area to volume ratio, such as reducing the size of metallic/non-metallic particles while maintaining a high particle density on the surface[74]. However, the increased surface energy of metal atoms, during the preparation of catalysts at high temperature, gives rise to the tendency to aggregate and form bulky catalysts[43]. The conventional high-temperature pyrolysis methods, despite the widespread application for catalyst synthesis, are hindered for the industrial applicability due to the limitations in thermal diffusion, particle aggregation, and phase separation. Ultrafast Joule heating technology is capable of effectively circumventing metal atom aggregation and maintaining the stability of catalytic particle dispersion through rapid energy input and instantaneous quenching[65]. Tian *et al.* presented the versatile and efficient CTS method for the synthesis of ultra-small and high-density nanoparticles that are homogeneously dispersed and anchored on two-dimensional porous carbon[75]. Typically, in comparison

View Article Online
DOI: 10.1039/D4MH01180E

with conventional tube furnace annealing, the CTS has the advantage of reducing the time by at least five orders of magnitude, and shrinking the size from 27 nm to 1.9 nm with the increase of electrochemical surface area (ECSA) by a factor of 3.8. It should be noted that the rapid Joule heating provides a simple and efficient universal transient nanoparticle synthesis route.

*2.5.2 Phase purity*

The conventional methods of materials synthesis typically necessitate elevated temperatures in excess of 600°C and protracted reaction times spanning hours to days, which are predicated on equilibrium thermodynamics, thereby rendering it challenging to precise control over the phase structure and crystal morphology of the material[76]. In recent years, researches investigating the synthesis of highly ordered and well-dispersed intermetallic nanoparticles using the Joule heating technique have been conducted. For example, Hu *et al.* employed rapid Joule heating method to synthesise *L*12 ordered $Pd_3Pb$ nanoparticles with an average diameter of approximately 6 nm[49], which was achieved by subjecting the reaction mixture to a heating period of 60 seconds at 1600 K. It should be noted that the degree of orderliness of the $Pd_3Pb$ structure could be evaluated by analysing the intensity of the superlattice XRD peaks (100) and (110), wherein the degree of ordering in $Pd_3Pb$ increased gradually with the duration of the heating period and reached complete ordering after 60 seconds. In the contract, the conventional annealing method (~1273 K@3 h) yielded $Pd_3Pb$ intermetallic nanoparticles with large average size of approximately 85 nm and a low ordering degree

View Article Online
DOI: 10.1039/D4MH01180E

of merely 60 %. Tour *et al.* designed novel Flash-within-flash synthesis technique to avoid the possible impurities in the product[76], which might be caused by the conductive additives or substrates. In detail, The Flash-within-flash synthesis technique utilised two quartz vessels, wherein the external flash vessel contained a conductive feedstock such as metallurgical coke, while the internal semi-closed reactor contained the target reactants. Most importantly, the novel technique, based on Joule heating, not only enabled the gram-scale synthesis of target samples, but also realized the phase-selective and single-crystalline bulk powders, which effectively produced target samples with high purity.

Besides, the Joule heating, with high temperature (up to 3000 ℃) and rapid heating rate, can also effectively deconstruct and recycle real-life waste materials such as polyolefin plastic waste and waste lithium-ion battery cathode to synthesize functional materials with high phase purity[77], which shows high environmental and economic benefits. For example, Viachos *et al.* employed one-step Joule heating method to effectively convert polyolefin plastic waste to light olefins ($C_2$-$C_4$) with 90% product fraction[78]. It should be noted that the pulsed treatment coupled with steam co-feeding could facilitate highly efficient selective deconstruction, while simultaneously reducing catalyst deactivation. Tou *et al.* presented an innovative solvent- and water-free FJH technique for the efficient recovery of waste lithium-ion battery cathode materials[77]. Following the application of FJH treatment, the three-dimensional structure of the cathode material was observed to remain intact, and the presence of metallic impurities was effectively

View Article Online
DOI: 10.1039/D4MH01180E

eliminated through the use of magnetic separation techniques. Meanwhile, the concentration of Cu and Al was found to decrease significantly, thereby ensuring the enhanced purity of the re-synthesised cathode material.

*2.5.3 Structure*

The designed structure of functional catalysts, synthesized via Joule heating methods, plays an important role in determining the catalytic performance, which can optimize essential factors such as adsorption/desorption of reaction intermediates, ion migration and electron transport[79]. For example, Chen *et al.* prepared hetero-structured catalysts (W-$W_2C$/G) using the FJH method, which resulted in the spontaneous generation of an internal electric field at the hetero-structured interface, driven by the difference in the work function of W (5.08 eV) and $W_2C$ (6.31 eV)[80]. Such phenomenon effectively accelerated the movement of electrons and ions in catalysts, thus facilitating the sulphur reduction reaction (SRR) process and effectively suppressing the polysulfide shuttling effect. Finally, benefiting from the construction of work function at interface via Joule heating, the W-$W_2C$/G exhibited excellent performance (665 mAh $g^{-1}$ at 5.0 C). Cao *et al.* utilized the Joule heating with transient discharge to enhance the degree of graphitisation for as-prepared hollow carbon spheres, accompanied by improvement in the crystal structure and electrical conductivity of the materials[81]. The graphene-like hollow spheres (L-GHS), as anode materials for lithium-ion batteries, showed a uniform diameter of 200 nm and an optimal specific surface area (670 $m^2/g$), following

View Article Online
DOI: 10.1039/D4MH01180E

498 excellent performance and cycling stability (sustained specific capacity of 942 mA-h/g
499 for 600 cycles at a 1 A/g).

500 *2.6 Catalytic superiority of materials synthesized via Joule heating synthesis*

501 As one kind of high-temperature shock synthesis strategy, Joule heating can avoid
502 phase separation of materials with complex components, and the macrostructure of the
503 materials can be maintained. Meanwhile, the particles engaged in the reaction process
504 tend to be generated in nanometre scale, thus enabling micro-regulation and
505 improvement of the electronic structure of the material. In terms of catalytic reaction,
506 the Joule heating offers a superior approach to improve the catalytic activity and
507 structural stability of the material. In detail, during the catalytic reaction, Joule heating
508 can improve the electronic structure of the adsorption sites, by inducing and
509 maintaining defects, which leads to the effective combination of intermediates and
510 adsorption sites, thus enhancing the catalytic activity of the material[19]. And the Joule
511 heating enables the formation of single-phase alloys from immiscible elements, thereby
512 offering a novel strategy for the synthesis of multicomponent catalysts with elemental
513 synergy effect. Besides, during the reaction process, the high temperature generated
514 transiently induces a considerable number of heterogeneous interfaces, which
515 significantly increases the active sites on the surface of catalyst[82]. Furthermore, the
516 chemical bond between the catalyst and the carrier is also strengthened during the ultra-
517 fast Joule heating for self-supporting material (such as Ni foam, carbon paper), thus
518 enhancing the mechanical stability of the catalyst on matrix[43]. It should also be noted

View Article Online
DOI: 10.1039/D4MH01180E

that the rapid heating and cooling process can result in the tendency which transform the catalyst from a stable phase to metastable state, leading to a more enhanced catalytic performance. Therefore, the unique physico-chemical properties endowed by Joule heating highlight the significant potential in synthesizing high active materials, which will be discussed as below.

## 3. Applications of Joule heating in synthesis of highly active catalysts

### *3.1 Application of Joule heating in interface engineering*

In general, an ideal catalyst should be characterized with large specific surface area, electronic conductivity, long-term stability[83], which contribute to the efficient conversion of energy. Fortunately, the interfacial engineering can optimize the electron transfer process among heterostructures materials and regulate the interface electronic structure via synergistic effect[84-85]. Meanwhile, the interfacial engineering can be applied to improve the stability and long-term performance of catalytic interfaces by designing stable interfacial structures, introducing protective layers or interfacial modifiers[86]. Typically, two mechanisms have been reported, which could effectively facilitate the catalytic activity via interfacial engineering[87]. In case 1, the interface between component A and component B of the catalyst establishes a transport channel for electron transfer, as shown in Fig. 6, wherein the reaction is mainly triggered on component A, thus the catalytic rate can be governed by the binding energy between component A and reactant. It is worth noting that the adsorption and desorption strengths between the catalyst and the reactants can be effective optimized by inducing

View Article Online
DOI: 10.1039/D4MH01180E

electron modulation through interfacial engineering, which in turn improves the catalytic activity. In contrast to case 1, the component A and B in case 2 is responsible for the adsorption process and the desorption process, respectively. The presence of interface plays an important role in transferring intermediates from A to B.

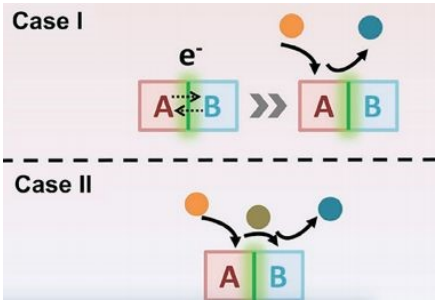



*Figure 6 Mechanisms of* interfacial *engineering effects on catalytic activity. Reproduced with permission.*[88] *Copyright 2019, Wiley-VCH.*

The conventional methods of materials synthesis are characterized with protracted reaction times and slow heating rate, and the equilibrium thermodynamics among the process render it challenging to generate a number of lattice friction as active interface in catalytic reaction[76, 88]. Fortunately, the rapid heating and quenching rates of Joule heating synthesis can be utilized to generated enormous temperature gradient, wherein the subsequently generated thermal stress can drive the formation of multiple dislocations as high active interface[89-90]. For example, Lai *et al.* successfully prepared Ir-based nanoparticles with abundant Frank partial dislocation (FPDs) as shown in Fig. 7a, wherein the 4% compression was generated compared with standard Ir PDF[89]. In contract, less strain and dislocation could be detected in the Ir particles (Fig. 7b), which was prepared via milder high-temperature calcination method. Meanwhile, the Ir-based

View Article Online
DOI: 10.1039/D4MH01180E





558 nanoparticles with FPDs synthesized by Joule heating exhibited excellent HER
559 performance (12 mV@10 mA $cm^{-2}$ in acid solution) and 2.7 times lower than that
560 synthesized via conventional method. Meanwhile, the rapid Joule heating could avoid
561 the accumulation of active sites, which provides feasible pathway to regulate
562 heterostructure, thus providing abundant catalytic sites in designed catalysts. For
563 example, Zhang *et al.* provided a feasible Joule heating treatment strategy to modulate
564 interfacial structures and properties for rational design of advanced electrocatalysts[91].
565 In detail, the Joule heating treatment method was applied to modulate the interfacial
566 oxygen species of graded indium oxide nanosheets (Fig. 7c), which was combined with
567 the subsequent in-situ electrochemical reduction process to prepare metal/metal oxide
568 heterostructures ($In/In_2O_3$-1600). And the interfacial structural oxygen species was
569 rationally regulated. Besides, Sun *et al.* designed a well-lattice-matched
570 $Co_2Mo_3O_8/MoO_2$ heterointerfaces on Ni foam ($Co_2Mo_3O_8/MoO_2$/NF) through a rapid
571 Joule heating method[15]. During the Joule heating process, $Co_2Mo_3O_8/MoO_2$/NF
572 exposed abundant $Co_2Mo_3O_8$ and $MoO_2$ compatible interfaces and lattice dislocations
573 (Fig. 7d-f), which can result in electronic rearrangement on the heterogeneous interface,
574 optimizing the activity of active sites. It should be noted that the sample prepared by
575 conventional CVD heating process showed less interfaces due to the prolong heating
576 treatment. Besides, abundant uncoordinated $Mo^{4+}$ species could be obtained by the
577 rapid Joule heating process, which was of vital importance to optimize the adsorption
578 behaviour of $H_2O$. As a result, $Co_2Mo_3O_8/MoO_2$/NF showed excellent HER activity

View Article Online
DOI: 10.1039/D4MH01180E

(23 mV at 10 mA $cm^{-2}$) and stability (100 mA $cm^{-2}$ @ 200 h) in seawater splitting wherein the activity of $Co_2Mo_3O_8/MoO_2$/NF was much lower than that synthesized by CVD process (56 mV at 10 mA $cm^{-2}$).

The formation of strong interactions between heterogeneous structures represents a crucial factor in significantly enhancing both catalytic activity and stability. Recently, Hu *et al.* designed Ag/Co/C hybrid electrocatalyst with quenched immiscible structure, wherein the formed large immiscibility gab among Ag-Co system, synthesized by ultra-fast heating and cooling, facilitated the strong electronic interaction[92]. Thus, as-prepared Ag/Co/C catalyst exhibited the mass activity of 1.55 A $mgAg^{-1}$ at 0.80 V in alkaline solution. Meanwhile, the interfacial engineering also plays an important role in remaining the mechanical stability when working in harsh operation. It is effective to enhance chemical stability through the strategies of tuning electronic structure via rapid Joule heating. For instance, Liu *et al.* utilized instantaneously formed Mo-C bonds between active MoxC and CNT through Joule heating to greatly hind dissolution and exfoliation of Mo species[82]. The significantly improved charges transfer and binding energy between active MoxC and CNT provided strong coupling. Similarly, to realize the intimate physical contact and low impedance for ion transfer between oxide-based solid electrolytes (SEs) and electrodes, Tour *et al.* applied rapid sintering process based on Joule heating to fabricate ion-conductive SE-cathode interphase within 10 s[93]. Compared with the conventional physical contact of SE-cathode interphase, the rapid sintering reaction could obtain the SE-cathode interphase with well-combination,

View Article Online
DOI: 10.1039/D4MH01180E

wherein the $LiCoO_2$ and $Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$ merged into monolith as shown in Fig. 7g, Meanwhile, the grain boundary growth between $Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$ and electrode was facilitated. Sun *et al.* synthesized a series of $Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$ (LATP)-based solid-state batteries via thermal pulse sintering (TPS) and conventional furnace sintering (FS) to investigated important role in high-energy-density solid-state batteries (SSBs)[94]. As shown in Fig. 7h and i, the TPS technique based on the Joule heating not only improved the ionic conductivity of LATP ($8.20 \times 10^{-4}$ S $cm^{-1}$), but also endowed LATP with enhanced density to facilitate interfacial contact. Meanwhile, the LATP could realize the structural evolution under the TPS methods, thus synthesizing extra $Li^+$ conduction pathways as shown in Fig. 7j, wherein the universality of TPS was also verified Fig. 7k and l.

In conclusion, rational design of interfacial engineering via Joule heating provides a new strategy to effectively optimize the electronic structure as well as heterointerfaces among catalysts.

View Article Online
DOI: 10.1039/D4MH01180E

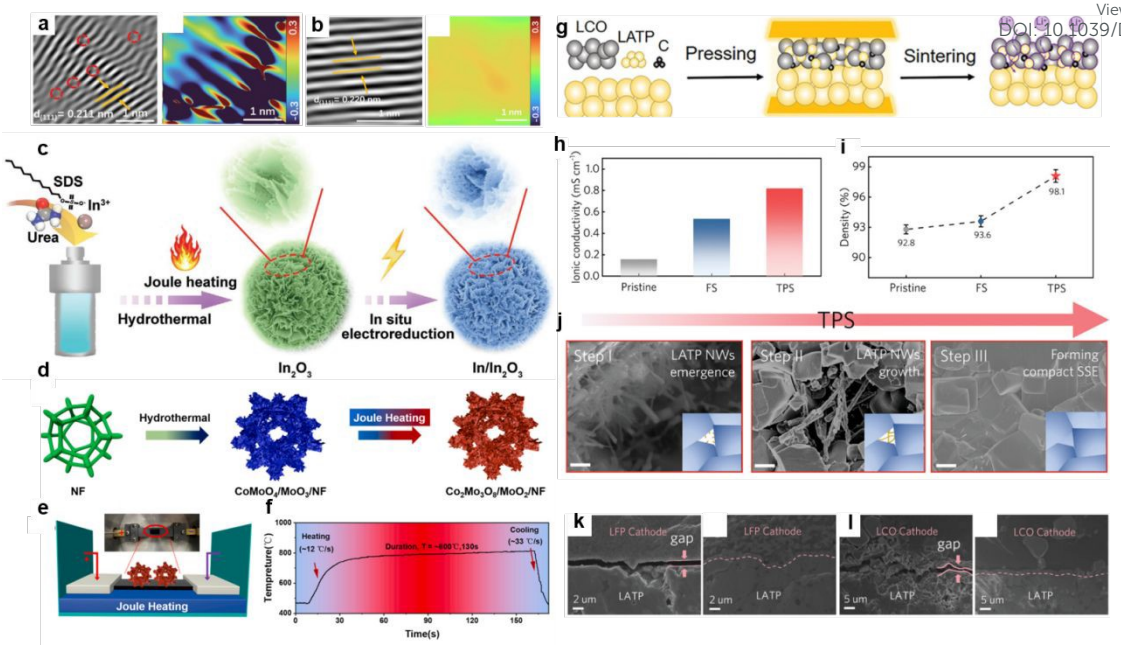



*Figure 7* The IFFT patterns and strain distributions of Ir-based sample synthesized via (a) Joule heating and (b) conventional high temperature calcination. Reproduced with permission.[89] Copyright 2023, Wiley-VCH. (c) The schematic synthesis of $In/In_2O_3$ via Joule heating method. Reproduced with permission.[91] Copyright 2022, Wiley-VCH. (d) The schematic synthesis of Co-O-Mo heterostructure via Joule heating method. (e) Schematic diagram of Joule heating setup. (f) The heating curves of Joule heating. Reproduced with permission.[15] Copyright 2023, Elsevier. (g) The schematic synthesis of electrode based on the Joule heating. Reproduced with permission.[93] Copyright 2024, Wiley-VCH. The measured ionic conductivity (h) and densities (i) for the LATP inorganic solid electrolyte based on different synthesis methods. (j) The SEM images of LATP treated via thermal pulse sintering. (k) The SEM images of $LiFePO_4$ and $LiCoO_2$ cathode/SSE interface with/without thermal pulse sintering. Reproduced with permission.[94] Copyright 2024, Wiley-VCH.

### *3.2 Application of Joule heating in synthesis of nanoparticles*

Nanoparticles are specialized materials with sizes typically in the nanoscale, which exhibit unique properties due to the size-dependence and have attracted much attention in the field of catalysis[49]. The precise control of the size and composition of the metal

View Article Online
DOI: 10.1039/D4MH01180E

nanoparticles on the support can be achieved by finely tuning the synthesis parameters to ensure the suitability and controllability of the nucleation process. However, conventional synthesis methods, such as long-term pyrolysis, hydrothermal method, electrodeposition are characterized with prolonged treatment and slow heating rate, which may lead to the inevitable aggregation of active sites and weak electronic interaction among particles and substrate, thus causing the deteriorated catalytic activity. Fortunately, the use of Joule heating method enables the rapid synthesis of uniformly sized nanoparticles and the regulation of nanoparticle size by adjusting the temperature and duration of the Joule thermal action (10 ms to 10 s)[95].

The rational design of nanoparticles-based materials, via rapid Joule heating method, has been widely reported as the following guidelines: Firstly, the design of ultra-small size of nanoparticles can reduce unnecessary bulk atoms in the catalytic reaction comparing to conventional nanoparticle catalysts, which also exhibits high intrinsic activity. Yao *et al.* realized the uniformly dispersed metallic ultra-small nanoclusters (< 2 nm) on defective substrates via rapid Joule heating[96]. In detail, the particle synthesis duration of rapid Joule heating could be well adjusted in the millisecond scale, thus avoiding the particle coarsening. Similarly, Hu *et al.* showed that high entropy alloy (HEA) catalysts with a homogeneous mixture of multiple elements were successfully prepared by rapid heating and cooling of the metal precursor on the carbon carrier (Fig. 8a), which exhibited well-dispersibility. The method utilized rapid thermal shock (~2000 K, duration: 55 ms, ramp rate: ~$10^5$ K/s) to effectively alloy eight

View Article Online
DOI: 10.1039/D4MH01180E

incompatible elements in nanoparticle (Fig. 8b), breaking through the limitations of conventional synthesis techniques[14]. For comparison, the samples have been treated by the conventional reduction procedures, which tended to exhibited phase-separated heterostructures. And based on the generous adjustable parameters and duration of heating for Joule heating, the concentration of surface-bound residual oxygen on the surface of CNF has been proved to affect the particle fission and corresponding dispersity. This synthesis method has shown great utility in the preparation of multi-membered HEA-nanoparticle catalysts for ammonia oxidation reactions, achieving nearly 100% conversion and more than 99% NOx selectivity.

In addition, ultra-small based nanoparticles catalysts not only provide a large number of active sites for activation of various intermediates, but also maintain an efficient utilization rate, making all highly dispersed nanoparticles available for adsorption and conversion of reactants. *Zhao et al.* utilized rapid Joule heating to decompose the Ni-O-Mo precursor (Fig. 8c) to dense $MoNi_4$ nano-particles on $MoO_2$ nanorods ($MoNi_4$/MoOx) (Fig. 8d)[17]. The rapid heating/cooling rates endowed catalysts with larger specific surface area, smaller nano-particles and larger electrochemical area comparing with the catalysts synthesized by traditional calcination ($MoNi_4$/MoOx-T) (Fig. 4e). Meanwhile, the increased $Mo^{4+}$ species in the $MoNi_4$/MoOx with rapid Joule heating has been proved, which was characterized with low empty d-orbital density and rendered optimized adsorption between *H and Mo species. As a result, the $MoNi_4$/MoOx exhibited ultralow potential for the hydrogen evolution reaction in

View Article Online
DOI: 10.1039/D4MH01180E

seawater (15 mV @ 10 mA $cm^{-2}$), which was much superior than that of $MoNi_4/MoO_x$-T. Meanwhile, it should be noted that the rapid Joule heating method saved ~99% energy among the synthesis process compared with the traditional calcination, indicating the potential in the aspect of low-cost. Besides, Zhao *et al.* alloyed Mo with suitable Ru species via Joule heating to generate RuMo nanoparticle (~3nm) on MoOx, which not only elevated Mo-O* antibonding level by the rational introduction of Ru[43], thus inhibiting oxidative release of Mo among large current density (2000 h @ 1000 mA $cm^{-2}$), but also was beneficial to water splitting through the synergistic effect. Meanwhile, it should be noted that the Joule heating synthesis played an important role in rational control of morphology and active sites, wherein the effective protons transfer kinetics has also been improved in term of hydrogen spillover.

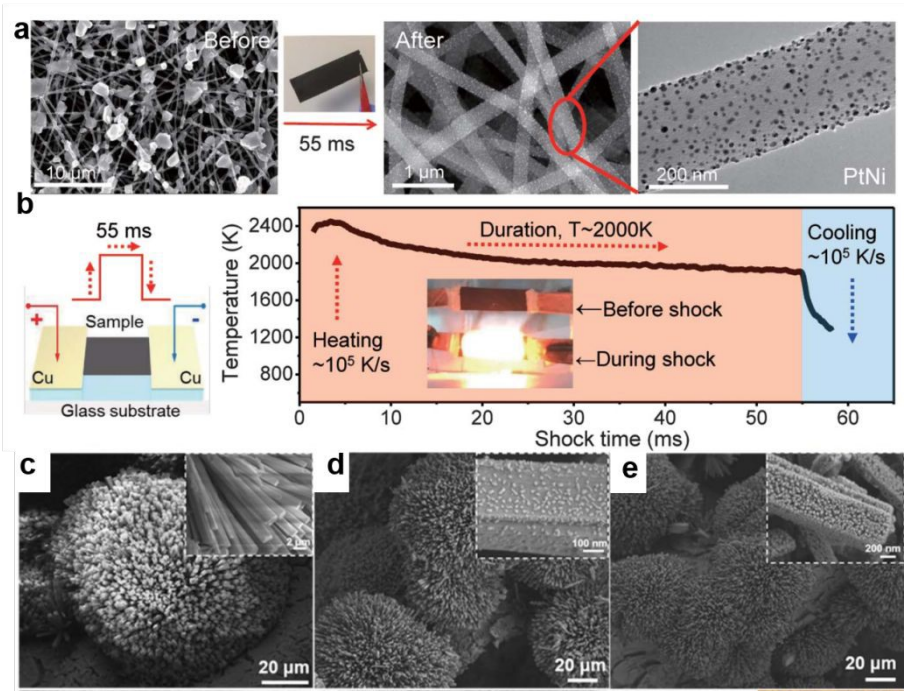



*Figure 8 (a) The image precursor salt on the support (before) and the well-dispersed nanoparticles on the support (after) synthesized by Joule heating method. (b) The schematic*

*synthesis of catalyst via Joule heating method. Reproduced with permission.[14] Copyright 2018, American Association for the Advancement of Science. The scanning electron microscope image of (c) Ni-O-Mo precursor, (d) $MoNi_4/MoO_x$ synthesized by Joule heating and (e) $MoNi_4/MoO_x$-T synthesized by traditional heating. Reproduced with permission.[17] Copyright 2023, The Royal Society of Chemistry.*

### *3.3 Application of Joule heating in synthesis of single atoms based-catalysts*

The concept of single-atom catalysts (SACs) originated in 2011, when *Zhang et al.* successfully prepared iron oxide ($FeO_x$)-loaded single-atom platinum (Pt) catalysts ($Pt_1/FeO_x$) and demonstrated that single Pt atoms coupled with $FeO_x$ carriers had excellent catalytic activity for carbon monoxide (CO) oxidation[97]. Since then, SACs have become a research hotspot in the field of heterogeneous catalysis and have received extensive attention in the past decades[98]. Generally, the SACs consisting of isolated individual metal atoms that are uniformly dispersed on the surface of solid carrier without direct interaction with each other[99]. SACs can be categorized into various types, including metal single atoms anchored to metal oxide surfaces, metals, carbon-based materials, metal-organic frameworks (MOFs), covalent organic frameworks (COFs), and composites[100]. Typically, SACs have been considered as one of the hottest catalytic materials due to the maximum atom utilization efficiency, low coordination metal centers and strong metal-carrier interactions[101]. Unlike conventional nanoparticle-based catalysts, the metal atoms of SACs are highly dispersed on the carrier, which can form bonds with only a few atoms or groups on the carrier, thus leading to the lower coordination number of atoms than bulk phase, wherein the low-

View Article Online
DOI: 10.1039/D4MH01180E

coordination environment in the catalytic center is more conducive to the interaction of active sites with reactant molecules[100]. In addition, the coordinating atoms can effectively optimize the electronic structure of the active center atoms and improve the selectivity of the reaction with the 100% atom utilization (Fig. 9)[102].

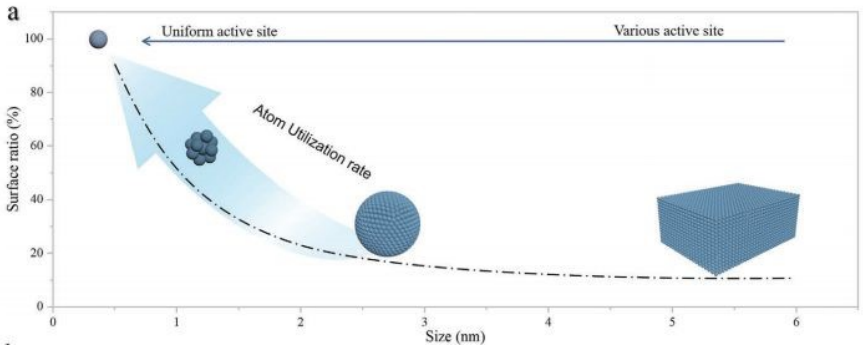



*Figure 9 Schematic illustration of surface ratio of atoms at different particle sizes. Reproduced with permission.[102] Copyright 2024, Wiley-VCH.*

However, the SACs also suffer from the shortcoming that the dramatically increased specific surface area in single-atom level leads to a sharp increase of free energy of the metal surface. The subsequent tendency to agglomerate during synthesis and catalytic processes seriously affects the practical application of SACs. The high temperature pyrolysis (HT) has been demonstrated to facilitate the bond formation between metal atoms and substrates with single-atom stabilization and dispersion[103]. However, the prolong HT can induce the particle migration and coalescence (PMC) and Ostwald ripening mechanisms (OR), which are driven by the Brownian motion and the difference of free energy on the surface, respectively[104]. Thus, the conventional HT methods with prolong treatment and slow heating rate, such as chemical vapor deposition, suffer from the undesired phase segregation and the atomic agglomeration,

View Article Online
DOI: 10.1039/D4MH01180E





727 which limits the synthesis and application of SACs. Fortunately, the Joule heat can
728 realize a rapid temperature increase up to 3000 °C in a short period of time (0-1 s) to
729 achieve an ultrafast thermal shock effect[38], which enhances the stability of single-atom
730 catalysts. Specifically, the rapid ignition with ultra-short heating treatment can
731 effectively prevent atomic diffusion and agglomeration, which also avoids the
732 destruction of substrates such as Ni foam and carbon cloth. Recently, *Yao et al.* reported
733 that single atoms can be effectively synthesized and stabilized at high temperatures
734 (1500-2000 K) via a Joule heat-controllable high-temperature shockwave methods (Fig.
735 10a), which was achieved by a programmable periodic on-off heating mode with a short
736 treatment (e.g., ~1,500 K ≤ 55 ms). The thermodynamically stable metal defect bonds
737 could be formed. Typically, the rapid heating provided activation energy for
738 monoatomic dispersion, and the off-state critically ensured overall stability, especially
739 for the substrate. It should be noted that the reported shockwave approach is
740 characterized with simplication, ultrafast rates, and versatility (e.g., Pt, Ru, and Co
741 elements, as well as carbon, $C_3N_4$, and $TiO_2$ substrates), which provides a platform for
742 the SACs fabrication[105].

743 The catalytic activity of SACs is related with the unique local coordination environment
744 between the isolated atom and carrier[106]. And recent researches have proved the role of
745 Joule heating in regulating the coordination and electronic states of SACs, which is
746 superior to conventional methods. For example, *Jiang et al.* reported a thermal shock
747 (TS) methods to tune the local environment of isolated $Pt^{2+}$ for yielding highly active

View Article Online
DOI: 10.1039/D4MH01180E

and thermally stable $Pt_1/CeO_2$ catalysts[106]. Typically, an ultrafast shock wave (> 1200 °C) induced the surface remodeling of $CeO_2$ to generate Pt single atoms with asymmetric $Pt_1O_4$ structure in the inert atmosphere. Due to this unique coordination, $Pt_1^{d+}$ is in a partially reduced state during CO oxidation, resulting in excellent low-temperature performance. Compared with the Atom trapping method (AT), the Joule heating, with ultrafast shockwave, exhibited potential in modulating the electronic structure of the adsorption sites, wherein the near-perfect square-planar $Pt_1O_4$ coordination synthesized with AT limited the potential of Pt active sites as shown in Fig. 10b. Similarly, *Zhang et al.* constructed Pt SAs immobilized on monolayer $Ti_3C_2Tx$ sheets $O_V$ by rapid thermal shock technique. During the heating treatment, the Pt species was reduced to metallic state and coordinated with the positively charged local environment driven by the rapid thermal shock technique. And the resulting $Ti_3C_2Tx$-Pt SA catalysts exhibited excellent hydrogen evaluation reaction (HER) performance compared to 20 wt% Pt/C catalysts with good stability (1000 cycles or 89 h)[107]. The above researches indicate that the rapid Joule heating not only avoid undesired phase segregation and the atomic agglomeration during the synthesis process, but also effectively modulate the local coordination environment of SACs, which exhibits potential in terms of regulation of SACs compared with conventional methods.

View Article Online
DOI: 10.1039/D4MH01180E

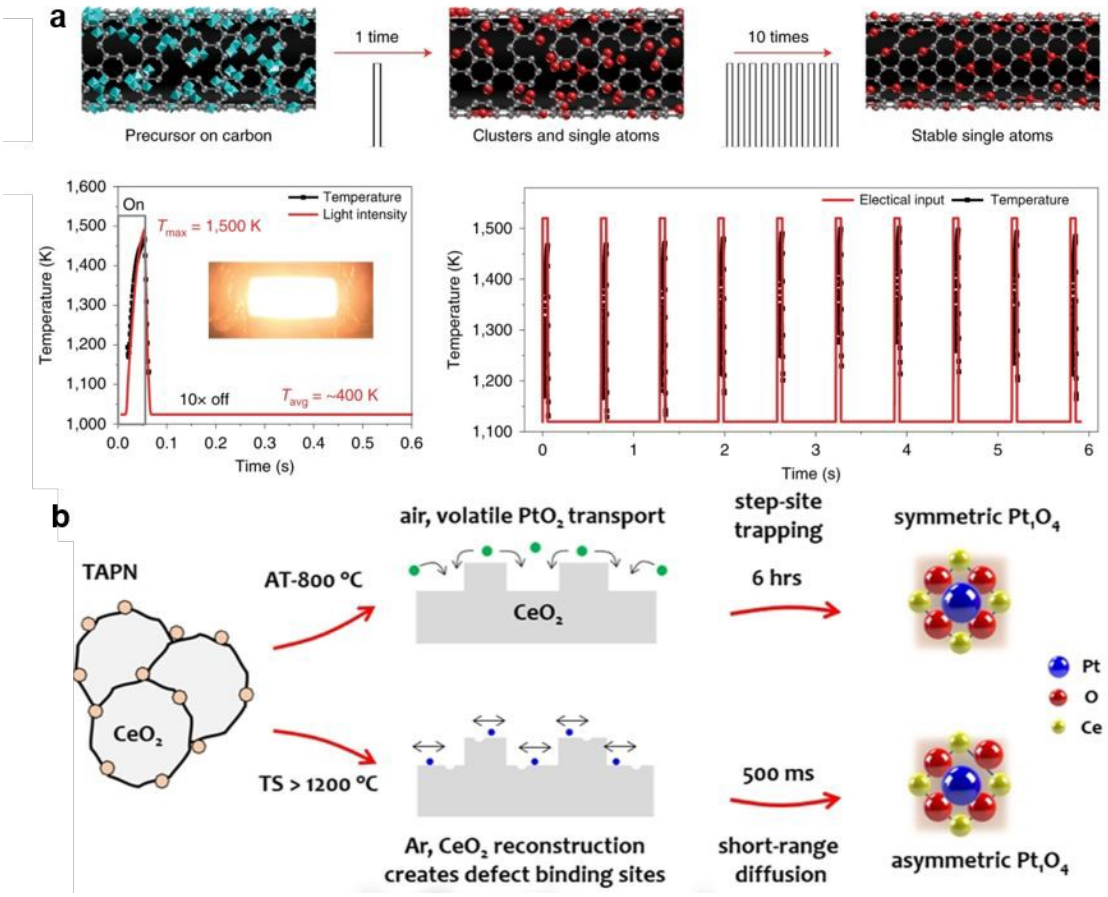



*Figure 10 (a) Schematic illustration of the synthesis of catalyst via Joule heating method with the heating/cooling curves. Reproduced with permission.* [106] *Copyright 2019, Nature. (b) Schematic illustration of the rapid Joule heating process and AT method applied on treatment of precursor. Reproduced with permission.* [107] *Copyright 2021,* Wiley-VCH.

### *3.4 Application of Joule heating in synthesis of high entropy compound*

High-entropy materials (HEMs) are single-phase novel electrocatalysts consisting of five or more uniformly distributed metal elements, which provide an ideal platform for tuning the electronic structure and geometrical configuration of metal centres[108]. Typically, the multiple atomic species are uniformly distributed in the same lattice, wherein the catalytic sites can be effectively expanded. In addition, due to the diverse microenvironments and tunable electronic structures, various HEMs such as high

View Article Online
DOI: 10.1039/D4MH01180E

entropy alloys (HEAs), high entropy oxides (HEOs) are designed and fabricated for improving the catalytic activity[109], which are characterized with better selectivity, stability, and catalytic activity than conventional materials and show good potential for development in the field of functional materials[110]. Based on the thermodynamic theory, the relation between enthalpy and entropy serves to determine whether HEMs is capable of being formed as shown in Eq. 7. And the HEMs is characterized with $\Delta S_M \geq 1.5R$.

$$\Delta G = \Delta H - T\Delta S_M \qquad (7)$$

The $\Delta S_M$ denotes mixing entropy, $T$ denotes temperature, $\Delta H$ denotes enthalpy and $\Delta G$ denotes Gibbs free energy, wherein the $\Delta S_M$ can be calculated as Eq. 8.

$$\Delta S_M = \Delta S_M^C + \Delta S_M^V + \Delta S_M^M + \Delta S_M^E \qquad (8)$$

The $\Delta S_M$ denotes mixing entropy, $\Delta S_M^C$ denotes configurational entropy, $\Delta S_M^V$ denotes vibrational entropy, $\Delta S_M^M$ denotes magnetic dipole entropy and $\Delta S_M^E$ denotes electronic randomness entropy. Meanwhile, the configurational entropy can be calculated as Eq. 9 and is the dominant component in mixing entropy.

$$\Delta S_M^C = klnW = R\left(\frac{1}{N}lnN + \ldots + \frac{1}{N}lnN + \frac{1}{N}lnN\right) = RlnN \qquad (9)$$

The $W$ represents the confusion degree, $k$ denotes the Boltzmann constant.$N$ and $R$ are the number of near-equimolar ratio elements and molar constant, respectively.

According to the Eq. 6, the enthalpy plays an important role in the formation of HEMs, and the enthalpy of element interaction is subjected to the nature of contained elements,

View Article Online
DOI: 10.1039/D4MH01180E

which determines the formed phase under near-equilibrium condition as shown in Fig. 11a. Therefore, the near-zero value of $\Delta H$ can facilitate the formation of HEMs with the domination of entropy, wherein the elements can co-exist without attraction and repelling[111]. However, previously reported synthesis methods are mainly based on thermal treatment via tube furnaces, which requires long heating, holding and cooling processes. Thus, it is challenging to overcome the large physicochemical differences of different elements, leading to the high enthalpy and formation of phase-segregated structures. Meanwhile, the prolonged pyrolysis at high temperatures tends to lead to agglomeration and sintering of the particles. And the relatively complex synthesis conditions can cause low nanoparticle loading. In recent years, the preparation of HEMs by rapid Joule heating has received much attention, which has emerged as a promising method for the synthesis of a wide range of catalysts due to its ultrafast heating and cooling rates as shown in Fig. 11b. It should be noted that the cooling rate plays an important role in the degree of nonequilibrium and structural ordering as shown in Fig. 11c[112]. Meanwhile, the Joule heating also allows for precise heating control in a short period of time, thus leading to instantaneous formation of nano-sized homogeneous phases of disordered metal elements. Recently, the HEMs, synthesized by rapid Joule heating, have been widely investigated in catalytic reaction due to the highly synergistic effect of high entropy, lattice distortion, slow diffusion, and cocktail effect[113].

Firstly, HEOs are emerging as a class of materials consisting of multiple major metal elements[114]. Since the unique properties of HEOs endowed by the enhanced entropic

View Article Online
DOI: 10.1039/D4MH01180E

contributions, it is necessary to explore new element combinations of HEOs through rapid high-throughput synthesis techniques[111]. For example, Wang *et al.* synthesised a carbon substrate by rapid heating using Joule heat for the OER process, which resulted in a high density and homogeneous dispersion of ultra-small HEOs on the carbon substrate (Fig. 11d)[115]. The prepared $(FeCoNiRuMn)_3O_{4-x}$ catalysts owned low overpotentials of only 230 mV and 270 mV to achieve current densities of 10 mA $cm^{-2}$ and 100 mA $cm^{-2}$, which provided a practical and feasible method for the rapid and efficient preparation of large quantities of homogeneous, high-density, and ultra-small nanoparticles (Fig. 11e-g).

Besides, the HEAs, synthesized via Joule heating, have also attracted increasing attention from both theoretical and experimental perspectives. For instance, Lin *et al.* synthesised the multi-electronic metals Cr and Mo by incorporating them into a highly active NiCoFe framework via a rapid Joule heating method (Fig. 11h)[116], which is characterized with uniformly distributed nanoparticles. The catalyst exhibited excellent OER performance that achieved a current density of 10 mA $cm^{-2}$ with only 260 mV (Fig. 11i and j). In conclusion, the rapid Joule heating method provides a practical and feasible method for the rapid and efficient preparation of a large number of well-distributed, high-density HEM.

View Article Online
DOI: 10.1039/D4MH01180E



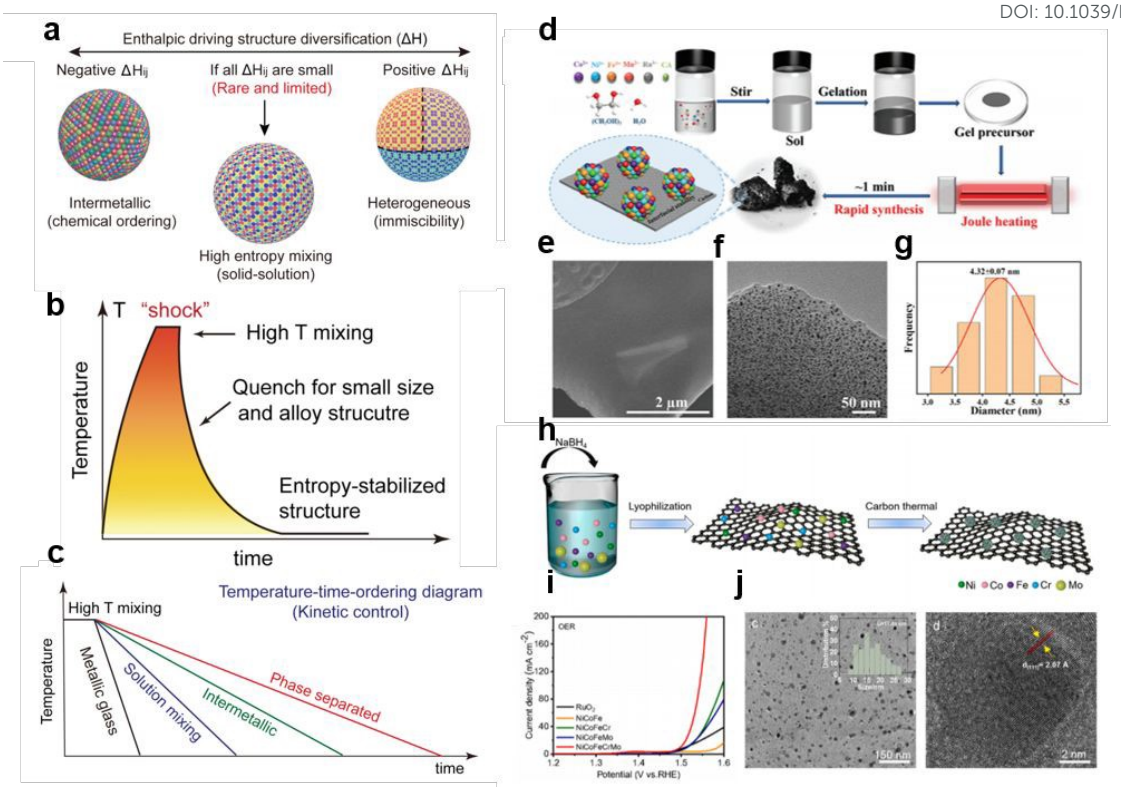



*Figure 11 (a) Thermodynamic analysis of HEMs, (b) Schematic illustration of the heating/cooling rate for Joule heating, (c) Temperature-time-transformation diagram. Reproduced with permission.[111] Copyright 2022, AAAS. (d) Schematic illustration of the rapid Joule heating process applied on gel precursor and corresponding HEOs products, (e) SEM image, (f) TEM image, (g) nanoparticle size distribution of the catalyst, Reproduced with permission.[115] Copyright 2024, The Royal Society of Chemistry. (h) Concise illustration of the synthetic route for NiCoFeCrMo HEA nanoparticles, (i) OER polarization curves, (j) TEM images of NiCoFeCrMo HEA nanoparticles. Reproduced with permission.[116] Copyright 2023, Elsevier.*

### *3.5 Application of Joule heating in synthesis of defect Engineering*

Manufacturing defects is important for improving the electrocatalytic performance of catalysts[117], especially for carbon-based catalysts[118]. Generally, defects in carbon-based catalysts are generated by doping of heteroatoms or in the conjugated network that lead

View Article Online
DOI: 10.1039/D4MH01180E

to anomalous sites (*e.g.* vacancies/holes, edge or topological defects)[119-120]. The resulting defects cause significant changes in the electron density distribution of materials, which potentially enhances electron transfer and electron exchange with exogenous substances, leading to the formation of more active catalytic centres[121-122]. However, the construction of surface defects tends to lead to the collapse of the material structure, which is considered as an unfavourable factor in the electrocatalytic process[123]. The prolonged heating of the traditional heating method tends to cause surface agglomeration and structural collapse of the catalyst, while the rapid heating and cooling process of the rapid Joule heating method leads to structural deformation and lattice strain and the construction of a large number of defects, which provide abundant active sites with well structural stability[46]. For instance, Li *et al.* succeeded in the construction of Ce-doped Co/CoO heterojunctions on CNTs by rapid Joule heating method (Fig. 12a)[47], and the presence of defects was proved by TEM characterisation (Fig. 12b-d). The prepared Ce-Co/CoO@CNTs exhibited low overpotentials (47.6 mV @ 10 mA $cm^{-2}$) in 1 M KOH electrolyte, which was much lower than that of Ce-Co/CoO@CNTs (T) (362.7 mV) prepared by traditional heating method, indicating the significant role of Joule heating in engineering defects. As a result, Ce-Co/CoO@CNTs exhibited a larger electrochemically active surface area and superior intrinsic activity with a Faraday efficiency close to 100%, demonstrating that the construction of defective engineering by rapid Joule heating method is of great promise. Besides, Sun *et al.* prepared superior electrocatalysts (Mo-Ru/CNTs) with cation-rich vacancies Mo-

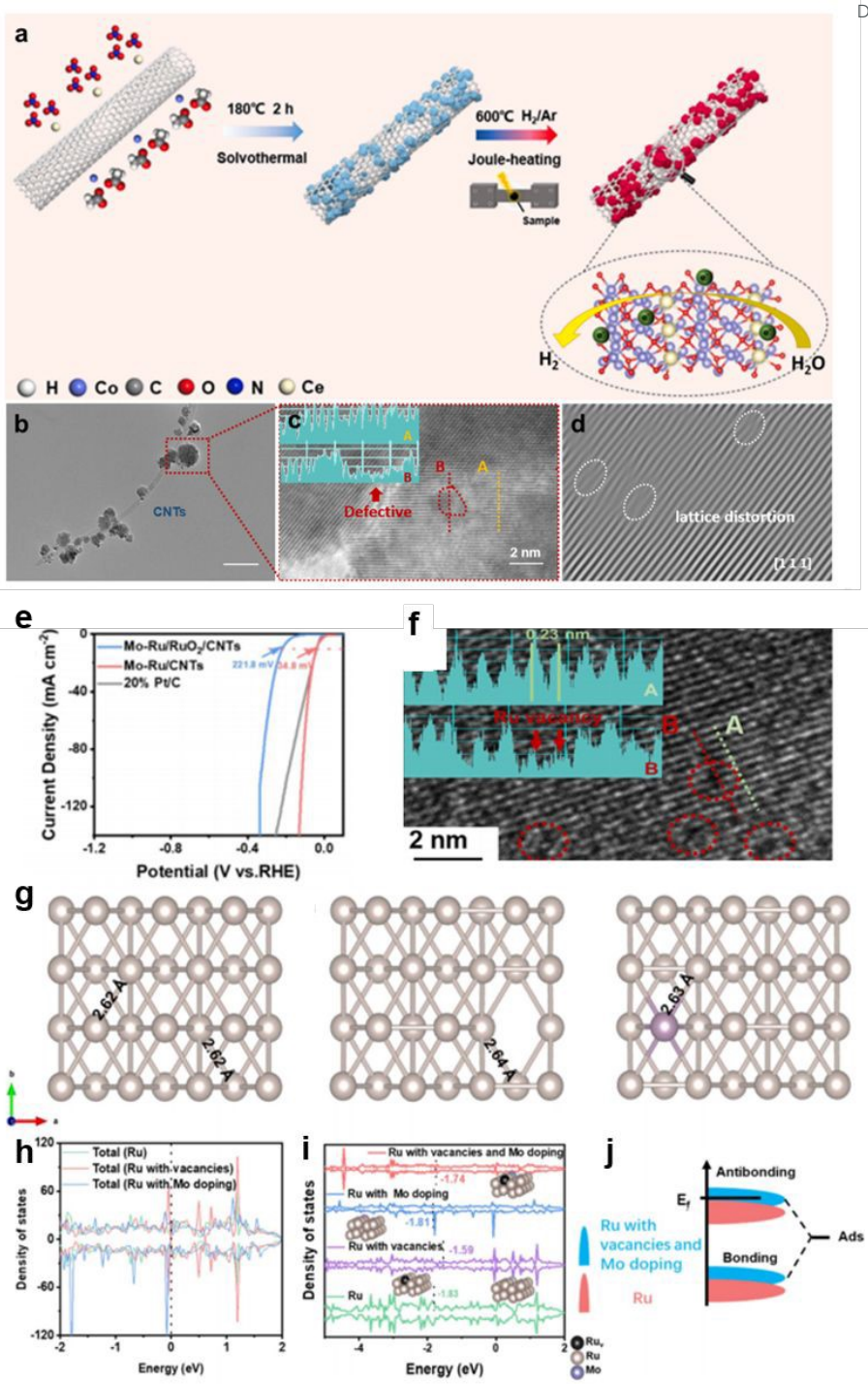
View Article Online
DOI: 10.1039/D4MH01180E

doped Ru nanoparticles on carbon nanotubes by rapid Joule heating[46], wherein the Mo-Ru/CNTs exhibited excellent HER activity in alkaline/seawater with only 34.8 mV/44.9 mV at 10 mA $cm^{-2}$ (Fig. 12e). Compared with the sample synthesized via CVD methods, the available vacancy and abundant lattice dislocations in Mo-Ru/CNTs could be detected as shown in Fig. 12f, while the conventional CVD methods inevitably lead to the oxidation of Ru species due to the prolong heating. Theoretical analyses indicated that Ru vacancies and Mo doping on Ru nanoparticles, facilitated by rapid Joule heating, can modulate the Ru-Ru bond, optimize the d-orbital electronic structure and d-band centre, thus promoting the adsorption of H* on the Ru sites (Fig. 12g-j)[124]. Meanwhile, the TDOS of Ru with vacancies and Mo doping was higher than that of pure Ru, suggesting that the rapid Joule heating could effectively modulate the electronic structure and endow materials better conductivity[125-126].

View Article Online
DOI: 10.1039/D4MH01180E








884

885 *Figure 12 (a) Schematic illustration of the synthesis of Ce-Co/CoO@CNTs, (b) TEM image,*

886 *(c-d) HRTEM image, Reproduced with permission.*[47] *Copyright 2024, Elsevier. (e) HER*

887 *polarization curves, (f) HRTEM image, (g) Phase models of Ru, Ru with vacancies and Ru*

888 *with Mo doping, (h) TDOS, and (i) the d-band center of Ru, (j) Scheme of the electron*

*configuration of the Ru d-band center. Reproduced with permission.[46] Copyright 2023, The Royal Society of Chemistry.*

Besides, offering a flexible electron environment via effective modulation strategy has been widely used to improve the performance of various reaction. Generally, it should be noted that the coordination environment of the active sites can be significantly modulated by the induced defects, which plays an important role in optimizing the electronic structure of targeted active sites and facilitating the activation of adsorbed reactants[127]. Meanwhile, defective substrate surface can effectively form the lattice strain, wherein the bonding between loaded active sites (such as single atom, cluster) and designed support may contribute to the strong electron-metal-support interactions, thus leading to well-dispersion and stabilization of the active sites. For instance, Ren *et al.* deposited active Ru clusters on the $BiVO_4$ as shown in Fig. 13a, wherein the rapid Joule heating setup has been used to design oxygen vacancies-rich substrate and promoted the formation of Ru clusters[24]. In detail, the rapid heating and quenching processes could effectively maintain the structure of the Ru/$BiVO_4$-$V_O$, which avoided the aggregation of active metals (about 1.8 nm), thus facilitating the exposed active site. It is vital to note that the induced unsaturated V sites due to the formed oxygen vacancy via Joule heating and modulated Ru clusters played an important role for $N_2$ adsorption and activation. Moreover, the bonding between Ru and designed $BiVO_4$ support contributed to the metal-support interactions, thus resulting intense charge redistribution and reducing energy barrier of $N_2$ fixation reaction. Similarly, Zhao *et al.* innovatively applied specific-size $SiO_2$ as a hard template to form porous honeycomb

View Article Online
DOI: 10.1039/D4MH01180E

$C_3N_4$, and precisely prepared Ni-doped $C_3N_4$ via a controllable Joule heating method as shown in Fig. 13b[19]. Typically, after following Joule heating treatment, the as-prepared catalysts maintained the 3D structure, which also showed compact structure characterized with thinner walls (Fig. 13c), indicating the important role of rapid Joule heating treatment in avoiding the polymerization process. Besides, abundant nitrogen vacancies were endowed by the rapid heating/cooling rates, wherein the strong electronic interaction between Ni and nitrogen vacancies was formed. And reducing the hydrogen adsorption energy of as prepared catalyst was proved by the DFT calculations. Finally, prepared Ni-doped $C_3N_4$ exhibited good photocatalytic hydrogen production performance (420.02 μmol $g^{-1}$ $h^{-1}$ $H_2$ production rate). To improve the synergistic effect of dual active site with vacancies and active metal sites, Zhao *et al.* also synthesized Pt metal clusters and N-vacancies co-modified $C_3N_4$ via Joule heating method[20]. The Fig. 13d showed a decreased $N_{2C}$ peak area ratio, indicating that rapid Joule heating method contributed in constructing nitrogen vacancies, which was favorable to enhance photocatalytic activity. And the above result was consisted to the EPR spectra (g = 2.0034), wherein the materials treated by fast heating methods tended to induce more vacancy. Meanwhile, Fig. 13f indicated the Pt species with transferred to low valent $Pt^0$ benefiting from the Joule heating, thus leading to the facilitated electron transfer between Pt and substrates, which strengthen the performance of photocatalytic hydrogen production. Finally, The DFT calculations achieved good agreements with the above conclusion, wherein the hydrogen adsorption energies of

View Article Online
DOI: 10.1039/D4MH01180E

Pt/NV-CN with Pt active sites as well as N vacancy showed low value of 0.41 eV, thus indicated Pt/NV-CN owned excellent proton adsorption and hydrogen adsorption/desorption behavior.

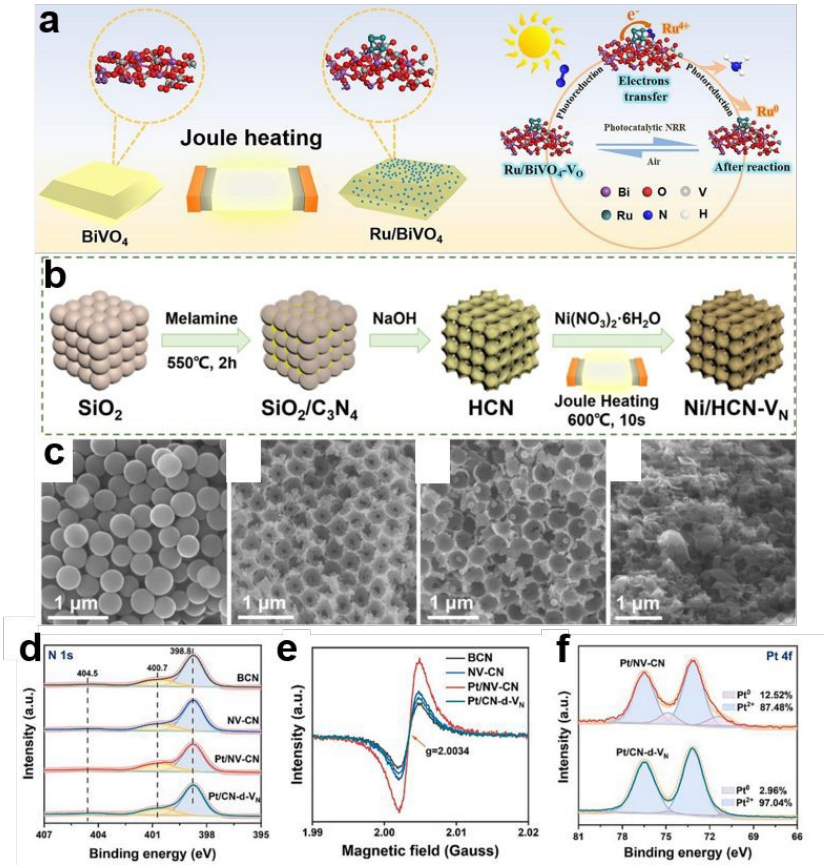



*Figure 13 (a) Schematic illustration of the synthesis of Ru/BiVO$_4$ via Joule heating and the reaction mechanism for photocatalytic N$_2$ fixation, Reproduced with permission.[24] Copyright 2023, Elsevier. (b) Schematic illustration of the synthesis of Ni/HCN-V$_N$ via Joule heating, (c) SEM and HRTEM images of SiO$_2$, honeycomb C$_3$N$_4$, Ni-doped porous honeycomb C$_3$N$_4$ with abundant nitrogen vacancies and relevant catalysts prepared in a tube furnace. Reproduced with permission.[19] Copyright 2024, The Royal Society of Chemistry. (d) N 1 s XPS spectra, (e) EPR spectra, (f) Pt 4f XPS spectra. Reproduced with permission.[20] Copyright 2023, Elsevier.*

View Article Online
DOI: 10.1039/D4MH01180E

## 4. Summary and outlook

In this report, firstly, the equipment setup, basic principles, and advantages of rapid Joule heating on synthesis of effective catalysts are briefly illustrated. Typically, benefiting from the extremely fast heating and quenching rate, the Joule heating method is conducive to prevent active sites from further oxidation and agglomeration in long-term operation, which provides platform for the rational design of high-active catalysts. Consequently, various catalyst-construction strategy (such as heterojunction, well-dispersed nanoparticles, single atom, defect and high entropy alloys) can be effectively realized via Joule heating, and the relevant researches have been reported in this review. Although a number of works based on the rapid Joule heating have been widely reported, there are still several challenges of this method, which should be overcome. 1) Due to the ultrashort processing period of catalysts, it is hard to investigate the forming mechanism of catalysts and the relation between heating parameters and targeted structure, which challenges the in-situ techniques as well as the theoretical computational techniques to understand the catalytic mechanism in depth. Firstly, the critical role of reaction kinetics and mass transport in the Joule heating process remains vague. In detail, the transition of precursor, the removal of noncarbon species and growth rate of target structure should be investigated, wherein the temperature, gas environment, number of pulses and heating time have been proved to affect the materials with different characteristics. For instance, how will the long-range order of multi-element alloys change under different temperature and pulse number? Will the

View Article Online
DOI: 10.1039/D4MH01180E

mass transfer on different substrate limit the nucleation of material? Will the heating rate or gas environment change the coordination environment of SACs? The further researches based on the rapid Joule heating should focus on the relation between obtained structure and electronic environment of sample and modulated heating parameters. Secondly, although it is found that the catalytic properties of samples, synthesized via rapid Joule heating, is superior to that of conventional pyrolysis techniques, which was endowed by the extremely fast heating rate (e.g., $10^5$ K/s) and transient cooling. The mechanistic understanding of performance enhancement is ambiguous. It should be noted that the synthesis parameters need to be set specifically under the two heating methods, aiming to explore the effect of heating rate as well as quenching rate by controlling variables. Generally, loading nanoparticles on the carriers via various methods has been considered as an effective approach to form electronic metal-support interaction (EMSI)[128], thus enhancing the interactions between the carriers and metal atoms, which can modulate the electronic structure and improve the stability of nanoparticles. Accordingly, selecting suitable precursors and Joule heating parameters to fabricate functional materials with EMSI will be important research direction. Finally, the ultra-short treatment and high temperature make the mechanistic researches based on *in-situ* characterisation technology challenging, wherein the specific spectrum with ultra-fast response for high temperature resistance coupled with molecular dynamic simulations close to the real reaction are necessary to understand the formation mechanism and design advanced functional materials.

View Article Online
DOI: 10.1039/D4MH01180E

2) Challenges still exist in precise synthesis of diverse hierarchical and heterostructures. Firstly, the phase transition, size, morphology (hollow, yolk-shell structure etc.) and loading of active sites of materials should be well-defined by tuning the synthesis process. In detail, the functional materials synthesized via rapid Joule heating are universally characterized with nanoparticles, which limit the further application in various fields. For example, it is difficult to realize the selected crystal planes via the tuning of heating parameters, which is vital importance for the reduction and oxidation of reactive intermediates in the photocatalytic reactions. Accordingly, selecting suitable precursors with template strategy to fabricate materials with various structure and morphology will be an important research direction for satisfying the needs of different fields. Besides, the construction of species, during the Joule heating process, for surface functionalization can be removal from precursors due to the ultra-high temperature, which further hamper the effective preparation of functional materials. Finally, current studies based rapid Joule heating methods mainly focus on the high-entropy alloys and carbon-based compound materials. Therefore, the nanomaterials, such as oxides, nitrides, selenides, synthesized via rapid Joule heating with reasonable designing heating process should be focused to garnered recognition in the energy storage and conversion fields.

3) For the field of rapid synthesis of catalysts, the large-scale preparation via Joule heating is still immature, wherein the exposed active sites, catalyst morphology and defect concentration may be changed due to the scaling-up effects. And the design of

View Article Online
DOI: 10.1039/D4MH01180E

large-scale reactor as well as operating parameters should be significantly considered. The rapid Joule heating coupled with roll-to-roll processing technique will be important research direction for satisfying large-scale synthesis of functional materials. Besides, the homogeneous temperature field should be realized for the large-scale synthesis of target sample with specific component and morphology. Therefore, various substrate or conductive additives, such as CNT, GO and carbon paper, with unique structure and characteristics should be investigated to ensure effective heat conduction and dissipation during the rapid heating process. Meanwhile, the reasonable combination of precursors and additives or substrates should be studied as an important research direction. Generally, the high temperature thermal evaporation of additives or substrates at high temperatures inevitably affects the phase composition of the synthesised samples, thus hampering the investigation of the mechanism on catalytic reaction and synthesis of materials with phase purity. Finally, much lager heating area or zone may be required with the increasement of material production via Joule heating, which, coupled with high accurate temperature sensor, heating control unit and vacuum chamber, causes the high capital costs and operating costs. Thus, the feasibility and economic evaluation of large-scale via Joule heating methods are required.

4) Currently, the rapid Joule heating has been applied to facilitate the waste recycling. However, there is still a huge challenge to obtain various high-added value materials via Joule heating method such as polymers, non-conductive precursors, wherein the carbon-based products have been mainly focused. Meanwhile, different kinds of matrix

View Article Online
DOI: 10.1039/D4MH01180E

should be designed according to different precursors and heating parameters. In the future, combining the Joule heating methods with treatment of other waste such as metallurgical slag and seawater may be the potential research direction.

5) Considering the abundant renewable energy and urgency of carbon neutralization, the rapid Joule heating is potential to be extend to the broader thermochemical synthesis, wherein the precise control of temperature in millisecond level and ultra-high heating rate not only facilitate the effective activation of chemical raw reactants, but also modulate the reactive pathways, thus leading to enhanced reactive selectivity. Various reactions, such as methane conversion reactions, carbon dioxide conversion and ammonia synthesis reaction, can utilize Joule heating to realize the precise energy supply, enhance product selectivity and minimise catalyst deactivation. Besides, the Joule heating has great potential for precise heat transfer to reaction zone, which is beneficial to the effective ang highly selective conversion of chemical raw reactants, thus exhibiting distinct advantages in thermochemical synthesis.

6) Based on the generous adjustable parameters and duration of heating for Joule heating, the machine learning coupled with experiment will be a potential way to precisely control the reactive paths and effective synthesis. And such strategy plays an important role in avoiding the limitation of regulatory mechanism due to the complexity of variables. Systematic investigation of heating parameters, such as temperature, gas atmosphere, precursor, substrates and heating/cooling rates, will be needed via machine learning to achieve efficient and selective synthesis of desired materials.

View Article Online
DOI: 10.1039/D4MH01180E

In conclusion, the novel Joule heating method presents numerous advantageous features and provides a promising pathway to realize an effective catalyst-construction strategy, which exhibits tremendous application potentials for effective synthesis and design of functional catalysts in different fields.

## Acknowledgments

This work was financially supported by the Fundamental Research Funds for the Central Universities (No: 202441006, 202364004 and 202461025)

## References

1. Jiang, R.; Da, Y.; Han, X.; Chen, Y.; Deng, Y.; Hu, W., Ultrafast Synthesis for Functional Nanomaterials. *Cell Reports Physical Science* **2021,** *2* (1).

2. Cong, L.; Xie, H.; Li, J. J. A. E. M., Hierarchical structures based on two - dimensional nanomaterials for rechargeable lithium batteries. **2017,** *7* (12), 1601906.

3. Prieto, G.; Zečević, J.; Friedrich, H.; De Jong, K. P.; De Jongh, P. E. J. N. m., Towards stable catalysts by controlling collective properties of supported metal nanoparticles. **2013,** *12* (1), 34-39.

4. Huang, W.; Bo, T.; Zuo, S.; Wang, Y.; Chen, J.; Ould-Chikh, S.; Li, Y.; Zhou, W.; Zhang, J.; Zhang, H., Surface decorated Ni sites for superior photocatalytic hydrogen production. *SusMat* **2022,** *2* (4), 466-475.

5. Sun, J.-P.; Zhao, Z.; Li, J.; Li, Z.-Z.; Meng, X.-C., Recent advances in electrocatalytic seawater splitting. *Rare Metals* **2022,** *42* (3), 751-768.

6. Liu, C.; Chen, Z.; Rao, D.; Zhang, J.; Liu, Y.; Chen, Y.; Deng, Y.; Hu, W. J. S. C. M., Behavior of gold-enhanced electrocatalytic performance of NiPtAu hollow nanocrystals for alkaline methanol oxidation. **2020,** *64* (3), 611-620.

7. Pei, Z.; Zhang, H.; Luan, D.; Lou, X. W., Electrocatalytic acidic oxygen evolution: From catalyst design to industrial applications. *Matter* **2023,** *6* (12), 4128-4144.

8. Zhao, Z.; Sun, J.; Meng, X., Recent advances in transition metal - based electrocatalysts for seawater electrolysis. *International Journal of Energy Research* **2022,** *46* (13), 17952-17975.

9. Zhao, Z.; Li, Z.; Zhang, Z.; Meng, X., Fe/P dual-doping NiMoO4 with hollow structure for efficient hydrazine oxidation-assisted hydrogen generation in alkaline seawater. *Applied Catalysis B: Environment and Energy* **2024,** *347*.

10. Sun, J.; Ren, G.; Qin, S.; Zhao, Z.; Li, Z.; Zhang, Z.; Li, C.; Meng, X., Reconstruction Co-O-Mo in amorphous-crystalline MoOx/Co(OH)2 interface for industry-level active and stable electrocatalytic seawater hydrogen evolution. *Nano Energy* **2024,** *121*.

11. Lan, K.; Liu, Y.; Zhang, W.; Liu, Y.; Elzatahry, A.; Wang, R.; Xia, Y.; Al-Dhayan, D.; Zheng, N.; Zhao, D. J. J. o. t. A. C. S., Uniform ordered two-dimensional mesoporous TiO2 nanosheets from hydrothermal-induced solvent-confined monomicelle assembly. **2018,** *140* (11), 4135-4143.

12. Shi, Y.; Huang, W.-M.; Li, J.; Zhou, Y.; Li, Z.-Q.; Yin, Y.-C.; Xia, X.-H. J. N. C., Site-specific electrodeposition enables self-terminating growth of atomically dispersed metal catalysts. **2020,** *11* (1), 4558.

13. Tang, T.; Jiang, W. J.; Niu, S.; Liu, N.; Luo, H.; Zhang, Q.; Wen, W.; Chen, Y. Y.; Huang, L. B.; Gao, F. J. A. F. M., Kinetically controlled coprecipitation for general fast synthesis of sandwiched metal hydroxide nanosheets/graphene composites toward efficient water splitting. **2018,** *28* (3), 1704594.

14. Yao, Y.; Huang, Z.; Xie, P.; Lacey, S. D.; Jacob, R. J.; Xie, H.; Chen, F.; Nie, A.; Pu, T.; Rehwoldt, M. J. S., Carbothermal shock synthesis of high-entropy-alloy nanoparticles. **2018,** *359* (6383), 1489-1494.

15. Sun, J.; Qin, S.; Zhang, Z.; Li, C.; Xu, X.; Li, Z.; Meng, X., Joule heating synthesis of well lattice-matched Co2Mo3O8/MoO2 heterointerfaces with greatly improved hydrogen evolution reaction in alkaline seawater electrolysis with 12.4 % STH efficiency. *Applied Catalysis B: Environmental* **2023,** *338*.

16. Zhao, Z.; Sun, J.; Li, X.; Zhang, Z.; Meng, X., Joule heating synthesis of NiFe alloy/$MoO_2$ and in-situ transformed (Ni,Fe)OOH/$MoO_2$ heterostructure as effective complementary electrocatalysts for overall splitting in alkaline seawater. *Applied Catalysis B: Environment and Energy* **2024,** *340*, 123277-123294.

17. Zhao, Z.; Sun, J.; Li, Z.; Xu, X.; Zhang, Z.; Li, C.; Wang, L.; Meng, X., Rapid synthesis of efficient Mo-based electrocatalyst for the hydrogen evolution reaction in alkaline seawater with 11.28% solar-to-hydrogen efficiency. *Journal of Materials Chemistry A* **2023,** *11* (19), 10346-10359.

18. Xiong, G.; Chen, Y.; Zhou, Z.; Liu, F.; Liu, X.; Yang, L.; Liu, Q.; Sang, Y.; Liu, H.; Zhang, X.; Jia, J.; Zhou, W., Rapid synthesis of various electrocatalysts on Ni foam using a universal and facile induction heating method for efficient water splitting. *Adv. Funct. Mater.* **2021,** *31* (15), 2009580-2009591.

19. Zhao, Z.; Ren, G.; Zhang, Z.; Meng, X.; Li, Z., Rapid Joule heating synthesis of Ni doped into porous honeycomb C3N4 with greatly improved photocatalytic H2 production. *Inorganic Chemistry Frontiers* **2024,** *11* (9), 2634-2647.

20. Zhao, Z.; Ren, G.; Zhang, Z.; Meng, X.; Li, Z., Rapid Joule heating synthesis of Pt clusters on C3N4 with abundant nitrogen vacancies for highly-efficiently photocatalytic H2 production. *Sep. Purif. Technol.* **2024,** *330*.

21. Zhao, Z.; Sun, J.; Li, X.; Zhang, Z.; Meng, X., Joule heating synthesis of NiFe alloy/$MoO_2$ and in-situ transformed (Ni, Fe)OOH/$MoO_2$ heterostructure as effective complementary electrocatalysts for overall splitting in alkaline seawater. *Applied Catalysis B: Environmental* **2024,** *340*, 123277-123294.

22. Chen, W.; Li, J. T.; Wang, Z.; Algozeeb, W. A.; Luong, D. X.; Kittrell, C.; McHugh, E. A.; Advincula, P. A.; Wyss, K. M.; Beckham, J. L.; Stanford, M. G.; Jiang, B.; Tour, J. M., Ultrafast and Controllable Phase Evolution by Flash Joule Heating. *ACS Nano* **2021,** *15* (7), 11158-11167.

23. Yang, H.; Ren, G.; Li, Z.; Zhang, Z.; Meng, X. J. A. C. B. E.; Energy, Fast Joule heating for transformation of Fe-MIL-125 (Ti) to Fe/TiO2 with enhanced photocatalytic activity in N2 fixation. **2024,** *347*, 123795.

24. Ren, G.; Zhao, Z.; Li, Z.; Zhang, Z.; Meng, X. J. J. o. C., Rapid Joule-Heating fabrication of oxygen vacancies and anchor of Ru clusters onto BiVO4 for greatly enhanced photocatalytic N2 fixation. **2023,** *428*, 115147.

25. Dou, S.; Xu, J.; Cui, X.; Liu, W.; Zhang, Z.; Deng, Y.; Hu, W.; Chen, Y., High-temperature shock enabled nanomanufacturing for energy-related applications. *Adv. Energy Mater* **2020,** *10* (33), 2001331-2001346.

26. Liu, Y.; Tian, X.; Han, Y.-C.; Chen, Y.; Hu, W. J. C. J. o. C., High-temperature shock synthesis of high-entropy-alloy nanoparticles for catalysis. **2023,** *48*, 66-89.

27. Jiang, R.; Da, Y.; Zhang, J.; Wu, H.; Fan, B.; Li, J.; Wang, J.; Deng, Y.; Han, X.; Hu, W., Non-equilibrium synthesis of stacking faults-abundant Ru nanoparticles towards electrocatalytic water splitting. *Applied Catalysis B: Environmental* **2022,** *316*.

28. Qiu, Y.; Hu, Z.; Li, H.; Ren, Q.; Chen, Y.; Hu, S., Hybrid electrocatalyst Ag/Co/C via flash Joule heating for oxygen reduction reaction in alkaline media. *Chemical Engineering Journal* **2022,** *430*, 132769.

29. Xia, D.; Mannering, J.; Huang, P.; Xu, Y.; Li, Q.; Li, H.; Qin, Y.; Kulak, A. N.; Menzel, R., Electrothermal Transformations within Graphene-Based Aerogels through High-Temperature Flash Joule Heating. *Journal of the American Chemical Society* **2024,** *146* (1), 159-169.

30. Zhang, H.; Qi, S.; Zhu, K.; Wang, H.; Zhang, G.; Ma, W.; Zong, X. Ultrafast Synthesis of Mo2C-Based Catalyst by Joule Heating towards Electrocatalytic Hydrogen Evolution Reaction *Symmetry* [Online], 2023.

31. Shen, P.; Zhao, J.; Gao, Y.; Lin, Y.; Han, Y.; Xu, K., General synthesis of transition metal nitride arrays by ultrafast flash joule heating within 500 ms. *Science China Chemistry* **2024,** *67* (6), 1976-1982.

32. Liao, Y.; Zhu, R.; Zhang, W.; Zhu, H.; Sun, Y.; Chen, J.; Dong, Z.; Lv, R., Transient synthesis of carbon-supported high-entropy alloy sulfide nanoparticles via

flash Joule heating for efficient electrocatalytic hydrogen evolution. *Nano Research* **2024,** *17* (4), 3379-3389.

33. Wang, Y.; Chen, X.; Meng, X.; Li, Z., Joule Heating Synthesis of Cobalt Molybdate with Unsaturated Mo4+ Coordination for Greatly Enhanced Electrocatalytic Nitrate Reduction to Ammonia. *ACS Sustainable Chemistry & Engineering* **2024,** *12* (17), 6762-6773.

34. Cui, B.; Zhu, H.; Wang, M.; Zeng, J.; Zhang, J.; Tian, Z.; Jiang, C.; Sun, Z.; Yang, H.; Liu, Y.; Ding, J.; Luo, Z.; Chen, Y.; Chen, W.; Hu, W., Intermediate State of Dense Ru Assembly Captured by High-Temperature Shock for Durable Ampere-Level Hydrogen Production. *ACS Materials Letters* **2024,** *6* (4), 1532-1541.

35. Li, J.; Wang, C.; Chen, X.; Zhang, Y.; Zhang, Y.; Fan, K.; Zong, L.; Wang, L., Flash synthesis of ultrafine and active NiRu alloy nanoparticles on N-rich carbon nanotubes via joule heating for efficient hydrogen and oxygen evolution reaction. *Journal of Alloys and Compounds* **2023,** *959*, 170571.

36. Yang, H.; Ren, G.; Li, Z.; Zhang, Z.; Meng, X., Fast Joule heating for transformation of Fe-MIL-125(Ti) to Fe/TiO2 with enhanced photocatalytic activity in N2 fixation. *Applied Catalysis B: Environment and Energy* **2024,** *347*, 123795.

37. Hu, Z.; Huang, L.; Ma, M.; Xu, L.; Liu, H.; Xu, W.; Yang, J., A Quick Joule-Heating Coupled with Solid-Phase Synthesis for Carbon-Supported Pd–Se Nanoparticles Toward High-Efficiency Electrocatalysis. *Advanced Functional Materials* **2024,** *n/a* (n/a), 2405945.

38. Luong, D. X.; Bets, K. V.; Algozeeb, W. A.; Stanford, M. G.; Kittrell, C.; Chen, W.; Salvatierra, R. V.; Ren, M.; McHugh, E. A.; Advincula, P. A.; Wang, Z.; Bhatt, M.; Guo, H.; Mancevski, V.; Shahsavari, R.; Yakobson, B. I.; Tour, J. M., Gram-scale bottom-up flash graphene synthesis. *Nature* **2020,** *577* (7792), 647-651.

39. Li, Y.; Chen, Y.; Nie, A.; Lu, A.; Jacob, R. J.; Gao, T.; Song, J.; Dai, J.; Wan, J.; Pastel, G.; Zachariah, M. R.; Yassar, R. S.; Hu, L., In Situ, Fast, High-Temperature Synthesis of Nickel Nanoparticles in Reduced Graphene Oxide Matrix. *Advanced Energy Materials* **2017,** *7* (11).

40. Zhang, L.; Peng, L.; Lu, Y.; Ming, X.; Sun, Y.; Xu, X.; Xia, Y.; Pang, K.; Fang, W.; Huang, N.; Xu, Z.; Ying, Y.; Liu, Y.; Fu, Y.; Gao, C., Sub-second ultrafast yet programmable wet-chemical synthesis. *Nat. Commun.* **2023,** *14* (1).

41. Thanh, N. T. K.; Maclean, N.; Mahiddine, S., Mechanisms of Nucleation and Growth of Nanoparticles in Solution. *Chem. Rev.* **2014,** *114* (15), 7610-7630.

42. Deng, J.; Li, G.; Yan, D.; Zhang, W.; Feng, K.; Nie, K.; Liu, C.; Lv, X.; Zhong, J., Programmable Wet-Interfacial Joule Heating to Rapidly Synthesize Metastable Protohematite Photoanodes: Metal and Lattice Oxygen Dual Sites for Improving Water Oxidation. *ACS Catalysis* **2024,** *14* (14), 10635-10647.

1194 43. Zhao, Z.; Sun, J.; Li, X.; Qin, S.; Li, C.; Zhang, Z.; Li, Z.; Meng, X., Engineering
1195 active and robust alloy-based electrocatalyst by rapid Joule-heating toward ampere-
1196 level hydrogen evolution. *Nat. Commun.* **2024,** *15* (1), 7475-7590.

1197 44. Wyss, K. M.; Li, J. T.; Advincula, P. A.; Bets, K. V.; Chen, W.; Eddy, L.; Silva,
1198 K. J.; Beckham, J. L.; Chen, J.; Meng, W.; Deng, B.; Nagarajaiah, S.; Yakobson, B. I.;
1199 Tour, J. M., Upcycling of Waste Plastic into Hybrid Carbon Nanomaterials. *Adv. Mater.*
1200 **2023,** *35* (16).

1201 45. Dong, Y.; Rao, Y.; Liu, H.; Zhang, H.; Hu, R.; Chen, Y.; Yao, Y.; Yang, H., Highly
1202 efficient chemical production via electrified, transient high-temperature synthesis.
1203 *eScience* **2024,** *4* (4).

1204 46. Sun, J.; Zhao, Z.; Li, Z.; Zhang, Z.; Zhang, R.; Meng, X., Ultrafast carbothermal
1205 shocking fabrication of cation vacancy-rich Mo doped Ru nanoparticles on carbon
1206 nanotubes for high-performance water/seawater electrolysis. *Journal of Materials*
1207 *Chemistry A* **2023,** *11* (41), 22430-22440.

1208 47. Li, X.; Zhao, Z.; Meng, X.; Li, Z., Rapid Joule-heating fabrication of Ce-doped
1209 Co/CoO on carbon nanotubes for efficiently electrocatalytic hydrogen production. *Appl.*
1210 *Surf. Sci.* **2024,** *669*.

1211 48. Liu, Y.; Han, Y.; Song, Z.; Song, W.; Miao, Z.; Chen, Y.; Ding, J.; Hu, W.,
1212 Accelerating the Phase Formation Kinetics of Alluaudite Sodium Iron Sulfate Cathodes
1213 via Ultrafast Thermal Shock. *ACS Appl. Mater. Interfaces* **2024,** *16* (11), 13828-13838.

1214 49. Cui, M.; Yang, C.; Hwang, S.; Li, B.; Dong, Q.; Wu, M.; Xie, H.; Wang, X.; Wang,
1215 G.; Hu, L., Rapid Atomic Ordering Transformation toward Intermetallic Nanoparticles.
1216 *Nano Lett.* **2021,** *22* (1), 255-262.

1217 50. Ji, Y.; Zhang, H.; Yang, D.; Pan, Y.; Zhu, Z.; Qi, X.; Pi, X.; Du, W.; Cheng, Z.;
1218 Yao, Y.; Qie, L.; Huang, Y., Regenerated Graphite Electrodes with Reconstructed Solid
1219 Electrolyte Interface and Enclosed Active Lithium Toward >100% Initial Coulombic
1220 Efficiency. *Adv. Mater.* **2024,** *36* (19).

1221 51. Chen, W.; Salvatierra, R. V.; Li, J. T.; Kittrell, C.; Beckham, J. L.; Wyss, K. M.;
1222 La, N.; Savas, P. E.; Ge, C.; Advincula, P. A.; Scotland, P.; Eddy, L.; Deng, B.; Yuan,
1223 Z.; Tour, J. M., Flash Recycling of Graphite Anodes. *Adv. Mater.* **2022,** *35* (8).

1224 52. Zhang, X.; Han, G.; Zhu, S., Flash Nitrogen-Doped Carbon Nanotubes for Energy
1225 Storage and Conversion. *Small* **2023,** *20* (3).

1226 53. M.A.S.R. Saadi, P. A. A., Md Shajedul Hoque Thakur, Ali Zein Khater, Shabab
1227 Saad, Ali Shayesteh Zeraati, Shariful Kibria Nabil, Aasha Zinke, Soumyabrata Roy,
1228 Minghe Lou, Sravani N. Bheemasetti, Md Abdullah Al Bari, Yiwen Zheng, Jacob L.
1229 Beckham, Venkataramana Gadhamshetty, Aniruddh Vashisth, Md Golam Kibria,
1230 James M. Tour1, Pulickel M. Ajayan, Muhammad M. Rahman, Sustainable
1231 valorization of asphaltenes via flash joule heating. *Science Advances* **2022,** *8*, eadd3555.

1232 54. Chen, J.; Ma, Y.; Huang, T.; Jiang, T.; Park, S.; Xu, J.; Wang, X.; Peng, Q.; Liu,
1233 S.; Wang, G.; Chen, W., Ruthenium-Based Binary Alloy with Oxide Nanosheath for

Highly Efficient and Stable Oxygen Evolution Reaction in Acidic Media. *Adv. Mater.* **2024,** *36* (26).

55. Yang, W.; Shang, L.; Liu, X.; Zhang, S.; Li, H.; Yan, Z.; Chen, J., Ultrafast synthesis of nanocrystalline spinel oxides by Joule-heating method. *Chin. Chem. Lett.* **2024,** *35* (11).

56. Yang, F.; Deng, P.; He, H.; Hong, R.; Xiang, K.; Cao, Y.; Yu, B.; Xie, Z.; Lu, J.; Liu, Z.; Khan, D.; Harbottle, D.; Xu, Z.; Liu, Q.; Tang, Z., Rapid Joule heating-induced welding of silicon and graphene for enhanced lithium-ion battery anodes. *Chem. Eng. J.* **2024,** *494*.

57. Ding, X.; He, Z.; Li, J.; Xu, X.; Li, Z., Carbon carrier-based rapid Joule heating technology: a review on the preparation and applications of functional nanomaterials. *Nanoscale* **2024,** *16* (26), 12309-12328.

58. Yan, Q.-L.; Gozin, M.; Zhao, F.-Q.; Cohen, A.; Pang, S.-P., Highly energetic compositions based on functionalized carbon nanomaterials. *Nanoscale* **2016,** *8* (9), 4799-4851.

59. Edwards, R. S.; Coleman, K. S., Graphene synthesis: relationship to applications. *Nanoscale* **2013,** *5* (1), 38-51.

60. Li, T.; Pickel, A. D.; Yao, Y.; Chen, Y.; Zeng, Y.; Lacey, S. D.; Li, Y.; Wang, Y.; Dai, J.; Wang, Y.; Yang, B.; Fuhrer, M. S.; Marconnet, A.; Dames, C.; Drew, D. H.; Hu, L., Thermoelectric properties and performance of flexible reduced graphene oxide films up to 3,000 K. *Nature Energy* **2018,** *3* (2), 148-156.

61. Liu, Y.; Li, P.; Wang, F.; Fang, W.; Xu, Z.; Gao, W.; Gao, C., Rapid roll-to-roll production of graphene films using intensive Joule heating. *Carbon* **2019,** *155*, 462-468.

62. Li, J.; Wang, C.; Chen, X.; Zhang, Y.; Zhang, Y.; Fan, K.; Zong, L.; Wang, L., Flash synthesis of ultrafine and active NiRu alloy nanoparticles on N-rich carbon nanotubes via joule heating for efficient hydrogen and oxygen evolution reaction. *J. Alloys Compd.* **2023,** *959*.

63. Sun, J.-P.; Zheng, Y.; Zhang, Z.-S.; Meng, X.-C.; Li, Z.-Z., Modulation of d-orbital to realize enriched electronic cobalt sites in cobalt sulfide for enhanced hydrogen evolution in electrocatalytic water/seawater splitting. *Rare Metals* **2023,** *43* (2), 511-521.

64. Yang, C.; Yao, Y.; He, S.; Xie, H.; Hitz, E.; Hu, L., Ultrafine Silver Nanoparticles for Seeded Lithium Deposition toward Stable Lithium Metal Anode. *Adv. Mater.* **2017,** *29* (38).

65. Chen, Y.; Egan, G. C.; Wan, J.; Zhu, S.; Jacob, R. J.; Zhou, W.; Dai, J.; Wang, Y.; Danner, V. A.; Yao, Y.; Fu, K.; Wang, Y.; Bao, W.; Li, T.; Zachariah, M. R.; Hu, L., Ultra-fast self-assembly and stabilization of reactive nanoparticles in reduced graphene oxide films. *Nat. Commun.* **2016,** *7* (1).

66. Qian, F.; Peng, L.; Cao, D.; Jiang, W.; Hu, C.; Huang, J.; Zhang, X.; Luo, J.; Chen, S.; Wu, X.; Song, L.; Chen, Q., Asymmetric active sites originate from high-entropy

metal selenides by joule heating to boost electrocatalytic water oxidation. *Joule* **2024,** *8* (8), 2342-2356.

67. Dou, S.; Xu, J.; Cui, X.; Liu, W.; Zhang, Z.; Deng, Y.; Hu, W.; Chen, Y., High-temperature shock enabled nanomanufacturing for energy - related applications. *Advanced Energy Materials* **2020,** *10* (33), 2001331-2001346.

68. Xie, M.; Xiao, X.; Wu, D.; Zhen, C.; Wu, C.; Wang, W.; Nian, H.; Li, F.; Gu, M. D.; Xu, Q., MOF-mediated synthesis of novel PtFeCoNiMn high-entropy nano-alloy as bifunctional oxygen electrocatalysts for zinc-air battery. *Nano Research* **2024,** *17* (6), 5288-5297.

69. Wang, Y.; Zhang, Y.; Xing, P.; Li, X.; Du, Q.; Fan, X.; Cai, Z.; Yin, R.; Yao, Y.; Gan, W., Self-Encapsulation of High-Entropy Alloy Nanoparticles inside Carbonized Wood for Highly Durable Electrocatalysis. *Adv. Mater.* **2024,** *36* (28).

70. Dittmann, J.; Maurath, J.; Bitsch, B.; Willenbacher, N., Highly Porous Materials with Unique Mechanical Properties from Smart Capillary Suspensions. *Adv. Mater.* **2015,** *28* (8), 1689-1696.

71. Wen, Z.; Tang, Z.; Liu, Y.; Zhuang, L.; Yu, H.; Chu, Y., Ultrastrong and High Thermal Insulating Porous High-Entropy Ceramics up to 2000 °C. *Adv. Mater.* **2024,** *36* (14).

72. Dai, X.; Liu, H.; Liu, X.; Liu, Z.; Liu, Y.; Cao, Y.; Tao, J.; Shan, Z., Silicon nanoparticles encapsulated in multifunctional crosslinked nano-silica/carbon hybrid matrix as a high-performance anode for Li-ion batteries. *Chem. Eng. J.* **2021,** *418*.

73. Friend, C. M.; Xu, B., Heterogeneous Catalysis: A Central Science for a Sustainable Future. *Acc. Chem. Res.* **2017,** *50* (3), 517-521.

74. Yuan, H.; Jiang, D.; Li, Z.; Liu, X.; Tang, Z.; Zhang, X.; Zhao, L.; Huang, M.; Liu, H.; Song, K.; Zhou, W., Laser Synthesis of PtMo Single-Atom Alloy Electrode for Ultralow Voltage Hydrogen Generation. *Adv. Mater.* **2023,** *36*, 2305375-2305385.

75. Shi, W.; Li, Z.; Gong, Z.; Liang, Z.; Liu, H.; Han, Y.-C.; Niu, H.; Song, B.; Chi, X.; Zhou, J.; Wang, H.; Xia, B. Y.; Yao, Y.; Tian, Z.-Q., Transient and general synthesis of high-density and ultrasmall nanoparticles on two-dimensional porous carbon via coordinated carbothermal shock. *Nat. Commun.* **2023,** *14* (1).

76. Choi, C. H. W.; Shin, J.; Eddy, L.; Granja, V.; Wyss, K. M.; Damasceno, B.; Guo, H.; Gao, G.; Zhao, Y.; Higgs, C. F.; Han, Y.; Tour, J. M., Flash-within-flash synthesis of gram-scale solid-state materials. *Nat. Chem.* **2024**, 1-7.

77. Chen, W.; Cheng, Y.; Chen, J.; Bets, K. V.; Salvatierra, R. V.; Ge, C.; Li, J. T.; Luong, D. X.; Kittrell, C.; Wang, Z.; McHugh, E. A.; Gao, G.; Deng, B.; Han, Y.; Yakobson, B. I.; Tour, J. M., Nondestructive flash cathode recycling. *Nat. Commun.* **2024,** *15* (1).

78. Selvam, E.; Yu, K.; Ngu, J.; Najmi, S.; Vlachos, D. G., Recycling polyolefin plastic waste at short contact times via rapid joule heating. *Nat. Commun.* **2024,** *15* (1).

79. Huang, G.; Leng, Y.; Yin, Y.-C.; Das, S.; Wan, J., Perspectives on Ultrafast, Precise Synthesis and Regeneration of Advanced Battery Materials. *Energy Fuels* **2024,** *38* (15), 13722-13736.

80. Dong, H.; Wang, L.; Cheng, Y.; Sun, H.; You, T.; Qie, J.; Li, Y.; Hua, W.; Chen, K., Flash Joule Heating: A Promising Method for Preparing Heterostructure Catalysts to Inhibit Polysulfide Shuttling in Li–S Batteries. *Advanced Science* **2024**.

81. You, L.; Dong, S.; Fang, Y.; Guo, Y.; Zhu, K.; Gao, Y.; Bao, T.; Wu, H.; Cao, D., A graphene-like hollow sphere anode for lithium-ion batteries. *Chem. Commun.* **2024,** *60* (38), 5030-5033.

82. Li, C.; Wang, Z.; Liu, M.; Wang, E.; Wang, B.; Xu, L.; Jiang, K.; Fan, S.; Sun, Y.; Li, J.; Liu, K., Ultrafast self-heating synthesis of robust heterogeneous nanocarbides for high current density hydrogen evolution reaction. *Nat. Commun.* **2022,** *13* (1), 3338-3349.

83. Khan, M. A.; Al-Attas, T.; Roy, S.; Rahman, M. M.; Ghaffour, N.; Thangadurai, V.; Larter, S.; Hu, J.; Ajayan, P. M.; Kibria, M. G., Seawater electrolysis for hydrogen production: a solution looking for a problem? *Energy & Environmental Science* **2021,** *14* (9), 4831-4839.

84. Zhang, Y.; Lin, Y.; Duan, T.; Song, L., Interfacial engineering of heterogeneous catalysts for electrocatalysis. *Mater. Today* **2021,** *48*, 115-134.

85. Zhang, X.; Huang, W.; Yu, L.; García-Melchor, M.; Wang, D.; Zhi, L.; Zhang, H., Enabling heterogeneous catalysis to achieve carbon neutrality: Directional catalytic conversion of CO2 into carboxylic acids. *Carbon Energy* **2023,** *6* (3).

86. Yu, Q.; Luo, Y.; Qiu, S.; Li, Q.; Cai, Z.; Zhang, Z.; Liu, J.; Sun, C.; Liu, B., Tuning the Hydrogen Evolution Performance of Metallic 2D Tantalum Disulfide by Interfacial Engineering. *ACS Nano* **2019,** *13* (10), 11874-11881.

87. Xue, Z.; Li, X.; Liu, Q.; Cai, M.; Liu, K.; Liu, M.; Ke, Z.; Liu, X.; Li, G., Interfacial Electronic Structure Modulation of NiTe Nanoarrays with NiS Nanodots Facilitates Electrocatalytic Oxygen Evolution. *Adv. Mater.* **2019,** *31* (21).

88. Shao, Q.; Wang, P.; Huang, X., Opportunities and Challenges of Interface Engineering in Bimetallic Nanostructure for Enhanced Electrocatalysis. *Adv. Funct. Mater.* **2018,** *29* (3).

89. Liu, P.; Zhang, X.; Fei, J.; Shi, Y.; Zhu, J.; Zhang, D.; Zhao, L.; Wang, L.; Lai, J., Frank Partial Dislocations in Coplanar Ir/C Ultrathin Nanosheets Boost Hydrogen Evolution Reaction. *Adv. Mater.* **2023,** *36* (11).

90. Tao Meng, P. S., Feng Yang, Jie Zhu, Baoguang Mao, Lirong Zheng and Minhua Cao, Double-atom dealloying-derived Frank partial dislocations in cobalt nanocatalysts boost metal–air batteries and fuel cells. *Proceedings of the National Academy of Sciences* **2022,** *119*, e2214089119.

1351 91. Wulan, B.; Cao, X.; Tan, D.; Ma, J.; Zhang, J., To stabilize oxygen on In/$In_2O_3$
1352 heterostructure via joule heating for efficient electrocatalytic $CO_2$ reduction. *Adv. Funct.*
1353 *Mater.* **2022,** *33* (1), 2209114-2209123.

1354 92. Qiu, Y.; Hu, Z.; Li, H.; Ren, Q.; Chen, Y.; Hu, S., Hybrid electrocatalyst Ag/Co/C
1355 via flash Joule heating for oxygen reduction reaction in alkaline media. *Chem. Eng. J.*
1356 **2022,** *430*.

1357 93. Chen, J.; Chen, W.; Deng, B.; Li, B.; Kittrell, C.; Tour, J. M., Cathode Interface
1358 Construction by Rapid Sintering in Solid-State Batteries. *Small* **2023,** *20* (8).

1359 94. Yao, X.; Chen, S.; Wang, C.; Chen, T.; Li, J.; Xue, S.; Deng, Z.; Zhao, W.; Nan,
1360 B.; Zhao, Y.; Yang, K.; Song, Y.; Pan, F.; Yang, L.; Sun, X., Interface Welding via
1361 Thermal Pulse Sintering to Enable 4.6 V Solid - State Batteries. *Advanced Energy*
1362 *Materials* **2023,** *14* (10).

1363 95. Xia, D.; Mannering, J.; Huang, P.; Xu, Y.; Li, Q.; Li, H.; Qin, Y.; Kulak, A. N.;
1364 Menzel, R., Electrothermal Transformations within Graphene-Based Aerogels through
1365 High-Temperature Flash Joule Heating. *J. Am. Chem. Soc.* **2023,** *146* (1), 159-169.

1366 96. Yao, Y.; Huang, Z.; Xie, P.; Li, T.; Lacey, S. D.; Jiao, M.; Xie, H.; Fu, K. K.; Jacob,
1367 R. J.; Kline, D. J.; Yang, Y.; Zachariah, M. R.; Wang, C.; Shahbazian-Yassar, R.; Hu,
1368 L., Ultrafast, Controllable Synthesis of Sub-Nano Metallic Clusters through Defect
1369 Engineering. *ACS Appl. Mater. Interfaces* **2019,** *11* (33), 29773-29779.

1370 97. Qiao, B.; Wang, A.; Yang, X.; Allard, L. F.; Jiang, Z.; Cui, Y.; Liu, J.; Li, J.; Zhang,
1371 T., Single-atom catalysis of CO oxidation using Pt1/FeOx. *Nat. Chem.* **2011,** *3* (8), 634-
1372 641.

1373 98. Zhu, C.; Fu, S.; Shi, Q.; Du, D.; Lin, Y., Single - Atom Electrocatalysts. *Angew.*
1374 *Chem. Int. Ed.* **2017,** *56* (45), 13944-13960.

1375 99. Mao, J.; He, C. T.; Pei, J.; Chen, W.; He, D.; He, Y.; Zhuang, Z.; Chen, C.; Peng,
1376 Q.; Wang, D.; Li, Y., Accelerating water dissociation kinetics by isolating cobalt atoms
1377 into ruthenium lattice. *Nat. Commun.* **2018,** *9* (1), 4958-4866.

1378 100. Xu, G.; Liu, Q.; Yan, H., Recent Advances of Single-atom Catalysts for
1379 Electro-catalysis. *Chem. Res. Chin. Univ.* **2022,** *38* (5), 1146-1150.

1380 101. Guo, J.; Liu, H.; Li, D.; Wang, J.; Djitcheu, X.; He, D.; Zhang, Q., A
1381 minireview on the synthesis of single atom catalysts. *RSC Advances* **2022,** *12* (15),
1382 9373-9394.

1383 102. Yu, Y.; Zhu, Z.; Huang, H., Surface Engineered Single - atom Systems for
1384 Energy Conversion. *Adv. Mater.* **2024,** *36* (16).

1385 103. Giugni, A., Non-locality by nanoconfinement. *Nat. Nanotechnol.* **2019,** *14* (9),
1386 814-815.

1387 104. Xiong, H.; Datye, A. K.; Wang, Y., Thermally Stable Single - Atom
1388 Heterogeneous Catalysts. *Adv. Mater.* **2021,** *33* (50).

105. Yao, Y.; Huang, Z.; Xie, P.; Wu, L.; Ma, L.; Li, T.; Pang, Z.; Jiao, M.; Liang, Z.; Gao, J.; He, Y.; Kline, D. J.; Zachariah, M. R.; Wang, C.; Lu, J.; Wu, T.; Li, T.; Wang, C.; Shahbazian-Yassar, R.; Hu, L., High temperature shockwave stabilized single atoms. *Nat. Nanotechnol.* **2019,** *14* (9), 851-857.

106. Jiang, D.; Yao, Y.; Li, T.; Wan, G.; Pereira-Hernández, X. I.; Lu, Y.; Tian, J.; Khivantsev, K.; Engelhard, M. H.; Sun, C.; García-Vargas, C. E.; Hoffman, A. S.; Bare, S. R.; Datye, A. K.; Hu, L.; Wang, Y., Tailoring the Local Environment of Platinum in Single-Atom Pt1/CeO2 Catalysts for Robust Low-Temperature CO Oxidation. *Angew. Chem. Int. Ed.* **2021,** *60* (50), 26054-26062.

107. Zhang, J.; Wang, E.; Cui, S.; Yang, S.; Zou, X.; Gong, Y., Single-Atom Pt Anchored on Oxygen Vacancy of Monolayer Ti3C2Tx for Superior Hydrogen Evolution. *Nano Lett.* **2022,** *22* (3), 1398-1405.

108. Wu, H.; Lu, Q.; Li, Y.; Wang, J.; Li, Y.; Jiang, R.; Zhang, J.; Zheng, X.; Han, X.; Zhao, N.; Li, J.; Deng, Y.; Hu, W., Rapid Joule-Heating Synthesis for Manufacturing High-Entropy Oxides as Efficient Electrocatalysts. *Nano Letters* **2022,** *22* (16), 6492-6500.

109. Yu, L.; Zeng, K.; Li, C.; Lin, X.; Liu, H.; Shi, W.; Qiu, H. J.; Yuan, Y.; Yao, Y., High-entropy alloy catalysts: From bulk to nano toward highly efficient carbon and nitrogen catalysis. *Carbon Energy* **2022,** *4* (5), 731-761.

110. Chang, R.; Li, H.; Tian, X.; Yang, Y.; Dong, T.; Wang, Z.; Lai, J.; Feng, S.; Wang, L., In Situ, Rapid Synthesis of Carbon - Loaded High Density and Ultrasmall High Entropy Oxide Nanoparticles as Efficient Electrocatalysts. *Small* **2024,** *20* (24).

111. Yao, Y.; Dong, Q.; Brozena, A.; Luo, J.; Miao, J.; Chi, M.; Wang, C.; Kevrekidis, I. G.; Ren, Z. J.; Greeley, J.; Wang, G.; Anapolsky, A.; Hu, L., High-entropy nanoparticles: Synthesis-structure-property relationships and data-driven discovery. *Science* **2022,** *376* (6589).

112. Yonggang Yao, Z. H., Pengfei Xie, Steven D. Lacey, Rohit Jiji Jacob, Hua Xie, Fengjuan Chen, Anmin Nie, Tiancheng Pu, Miles Rehwoldt, Daiwei Yu, Michael R. Zachariah, Chao Wang, Reza Shahbazian-Yassar, Ju Li, Liangbing Hu, Carbothermal shock synthesis of high-entropy-alloy nanoparticles. *Science* **2018,** *359*, 1489-1494.

113. Zhang, Y.; Wang, D.; Wang, S., High - Entropy Alloys for Electrocatalysis: Design, Characterization, and Applications. *Small* **2021,** *18* (7).

114. Rao, P.; Deng, Y.; Fan, W.; Luo, J.; Deng, P.; Li, J.; Shen, Y.; Tian, X., Movable type printing method to synthesize high-entropy single-atom catalysts. *Nature Communications* **2022,** *13* (1).

115. Tian, X.; Li, H.; Chang, R.; Yang, Y.; Wang, Z.; Dong, T.; Lai, J.; Feng, S.; Wang, L., Rapid, self-sacrificing template synthesis of two dimensional high-entropy oxides toward high-performance oxygen evolution. *Journal of Materials Chemistry A* **2024,** *12* (6), 3276-3282.

116. Zhao, J.; Wang, Z.; Fang, X.; Yang, L.; Wu, C.; Gan, W.; Zhou, Y.; Shan, L.; Lin, Y., Fast joule heating synthesis of NiCoFeCrMo high-entropy alloy embedded in graphene for water oxidation. *Journal of Alloys and Compounds* **2023,** *966*.

117. Zhao, Z.; Qin, S.; Li, X.; Sun, J.; Li, Z.; Meng, X., Sulfur-facilitated in situ deep reconstruction of transition metal molybdates toward superior electrocatalytic oxidation of alkaline seawater. *Chem Catalysis* **2024**.

118. Peng, H.; Ren, J.; Wang, Y.; Xiong, Y.; Wang, Q.; Li, Q.; Zhao, X.; Zhan, L.; Zheng, L.; Tang, Y.; Lei, Y., One-stone, two birds: Alloying effect and surface defects induced by Pt on Cu2−xSe nanowires to boost C-C bond cleavage for electrocatalytic ethanol oxidation. *Nano Energy* **2021,** *88*.

119. Huo, S.; Song, X.; Zhao, Y.; Ni, W.; Wang, H.; Li, K., Insight into the significant contribution of intrinsic carbon defects for the high-performance capacitive desalination of brackish water. *Journal of Materials Chemistry A* **2020,** *8* (38), 19927-19937.

120. Yang, S.; Xu, S.; Tong, J.; Ding, D.; Wang, G.; Chen, R.; Jin, P.; Wang, X. C., Overlooked role of nitrogen dopant in carbon catalysts for peroxymonosulfate activation: Intrinsic defects or extrinsic defects? *Applied Catalysis B: Environmental* **2021,** *295*.

121. Li, D.; Ren, B.; Jin, Q.; Cui, H.; Wang, C., Nitrogen-doped, oxygen-functionalized, edge- and defect-rich vertically aligned graphene for highly enhanced oxygen evolution reaction. *Journal of Materials Chemistry A* **2018,** *6* (5), 2176-2183.

122. Shao, P.; Yu, S.; Duan, X.; Yang, L.; Shi, H.; Ding, L.; Tian, J.; Yang, L.; Luo, X.; Wang, S., Potential Difference Driving Electron Transfer via Defective Carbon Nanotubes toward Selective Oxidation of Organic Micropollutants. *Environmental Science & Technology* **2020,** *54* (13), 8464-8472.

123. Gao, Y.; Liang, S.; Liu, B.; Jiang, C.; Xu, C.; Zhang, X.; Liang, P.; Elimelech, M.; Huang, X., Subtle tuning of nanodefects actuates highly efficient electrocatalytic oxidation. *Nature Communications* **2023,** *14* (1).

124. Guo, L.; Chi, J.; Zhu, J.; Cui, T.; Lai, J.; Wang, L., Dual-doping NiMoO4 with multi-channel structure enable urea-assisted energy-saving H2 production at large current density in alkaline seawater. *Applied Catalysis B: Environmental* **2023,** *320*.

125. Zhou, S.; Jang, H.; Qin, Q.; Hou, L.; Kim, M. G.; Liu, S.; Liu, X.; Cho, J., Boosting Hydrogen Evolution Reaction by Phase Engineering and Phosphorus Doping on Ru/P-TiO2. *Angewandte Chemie International Edition* **2022,** *61* (47).

126. Yu, J.; Li, J.; Xu, C.-Y.; Li, Q.; Liu, Q.; Liu, J.; Chen, R.; Zhu, J.; Wang, J., Modulating the d-band centers by coordination environment regulation of single-atom Ni on porous carbon fibers for overall water splitting. *Nano Energy* **2022,** *98*.

127. Ren, G.; Zhao, J.; Zhao, Z.; Li, Z.; Wang, L.; Zhang, Z.; Li, C.; Meng, X., Defects-Induced Single-Atom Anchoring on Metal–Organic Frameworks for High-Efficiency Photocatalytic Nitrogen Reduction. *Angew. Chem. Int. Ed.* **2023,** *63* (2).

1469 128. Ren, G.; Shi, M.; Li, Z.; Zhang, Z.; Meng, X. J. A. C. B. E., Electronic metal-
1470 support interaction via defective-induced platinum modified BiOBr for photocatalytic
1471 N2 fixation. **2023,** *327*, 122462.

View Article Online
DOI: 10.1039/D4MH01180E

View Article Online
DOI: 10.1039/D4MH01180E

## Data availability statements

No primary research results, software or code have been included and no new data were generated or analysed as part of this review.