# Microwave Shock Synthesis beyond Thermodynamic Equilibrium

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**Abstract:**

Tuning the defect level in reduced graphene oxide (RGO) with proper level of polar groups and π-conjugation can render highly efficient absorption of microwave and extremely short thermal shock up to 1600 K in just 100 ms, opening a pathway for rapid processing of nanoparticles, clusters and individually dispersed atoms beyond thermal equilibrium.

**Main text:** Controllable synthesis of nanoparticles, clusters or even individually dispersed single atoms is central for developing high performance catalysts with maximized atom utilization efficiency. However, the production of catalysts on the atomic or nanometer level is often plagued by undesired thermal diffusion, phase segregation or particle aggregation occurring in relatively long duration (minutes to hours) of high temperature processing. Limited by the thermodynamic equilibrium at high temperature, most catalytic nanostructures, often with high entropy and high surface energy, are difficult to achieve by design. A key strategy to overcome this obstacle and to produce nanostructures beyond thermodynamic equilibrium limitations is to employ ultrashort thermal shock with rapid heating and instant quenching, with which the product is more determined by the kinetics and may deviate considerably from the thermodynamic equilibrium. It could thus promise a new generation of atomic scale materials with unprecedented flexibility in terms of composition, structure and reactivity.[1]

Despite its attractiveness, such rapid thermal shock is usually difficult to achieve in traditional solution-based synthesis due to large heat capacities of the solvents and rapid heat dissipation. Recently, it was found that microwave heating of pretreated reduced graphene oxide (RGO) may induce such thermal shock cartelistic due to the unique microwave absorption properties of RGO. With a common microwave oven, RGO can be rapidly heated to over 1000 K in few seconds, delivering high quality RGO with similar defect level of chemical vapor deposition (CVD) grown

graphene.[2] Two main mechanisms may contribute to the rapid heat generation during the microwave process. First, under the microwave irradiation, polar molecules (e.g., OH groups on RGO) with permanent or induced dipoles can undergo rapid rotation and movement to align the dipoles with the oscillating electric field (2450 million times per second), generating tremendous amount of friction and hence transfer the energy to heat. Second, for materials with charged particles (e.g., π electrons in graphene), the energy of microwave is dissipated in the form of heat via eddy current loss due to the Maxwell-Wagner effect.[3] By precisely tuning the defect level to render appropriate amount of polar groups and the restored π-conjugation in RGO, these heat generation processes can be optimized to reach the highest transient temperature in a very short period of time.

Indeed, by tailoring the defect level in RGO, a group of researchers led by Liangbing Hu, explored this exact strategy for high temperature (1600 K) microwave shock (250 ms) processing of nanoparticles (Figure 1), as reported in this issue of *Matter*.[4] The authors investigated the detailed process of such *microwave assisted thermal shock* on RGO by using a high-speed video camera, computer processing and fitting of the light intensity with Planck's law for gray-body radiation, together with near infrared spectroscopy characterizations. It is found that the abundant surface functional groups and the moderate mobility are both necessary for rapid heat generation. In particular, unlike the graphite with metallic feature that can reflect most of the incident microwave irradiation, the RGO with proper abundance of functional groups and moderate conductivity may function as an optimal microwave absorber. Thus, the heating process on RGO can be ignited in just 100 ms upon exposure to microwave irradiation to reach an ultrahigh temperature up to1600 K in just 250 ms. Under high temperature, the RGO undergoes a rapid loss of surface functional groups and fast lattice reconstruction to nearly fully restore the π-conjugation, which quickly weakens the microwave absorptions efficiency and consequently induces the rapid self-quenching process. Overall, the microwave shock process is divided into three key stages, namely 1) microwave initiation, 2) high temperature shock and 3) rapid self-quenching.

The fundamental heating mechanism of the microwave shock process offers several unique features not possible with conventional thermal process, such as (1) non-contact heating that ensure the uniform heat distribution on the whole body of the materials; (2) fast ignition, rapid heating and quenching to minimize the atom diffusion, agglomeration and achieve nanostructures

beyond thermodynamic equilibrium; (3) high energy efficiency and high potential for controllable scalable processing. Such combined features make microwave shock highly attractive for rapid processing of nanoparticles or clusters with highly tunable composition.

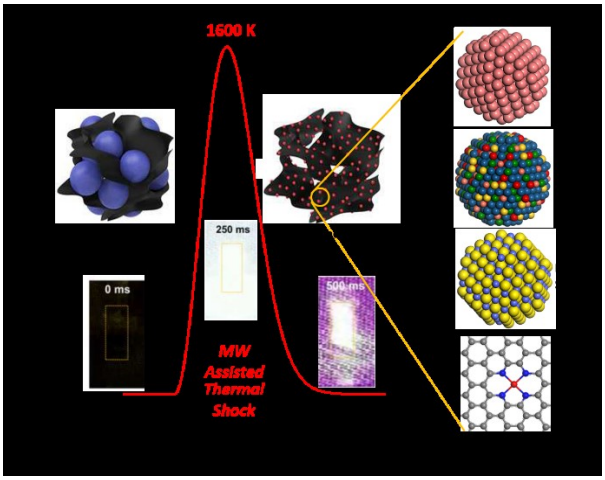
As demonstrated by the authors, this synthetic strategy is effective for rapid and scalable synthesis of CoS as well as other metallic (i.e. Ru, Pd and Ir) nanoparticles with narrow size distributions. Beyond what is demonstrated in this study, the microwave wave assisted thermal shock is attractive for many other processes (Figure 1). In particular, alloy structures with typically immiscible binary or ternary elemental compositions may be produced with such methods since this ultrahigh transient temperature and rapid quenching process may help retain high entropy mixing state of liquid metals to produce single phase solid solution beyond thermal equilibrium, which that are difficult to achive with other more typical methods.[5] Such a capability could lead significant technological opportunities, for example, for the preparation of platinum/transition metal alloy nanocatalysts that exhibit excellent oxygen reduction reaction (ORR) activity and durability for fuel cell applications. Additionally, such high transient temperature may also be used to rapidly remove the poisonous ligands bonded on the surface of solution prepared nanocrystals while minimizing atomic diffusion to maintain their original shape and facets.[6]

Taking a step further, beyond nanocrystal synthesis, this strategy may also be explored for producing individually dispersed single metal atoms in graphene, which represents a new generation of catalysts with the ultimate atom utilization efficiency. For example, it has been shown that single iron atoms dispersed in a nitrogen doped carbon graphene (Fe-N-C) could exhibit comparable ORR activity to commercial Pt/C and and similar Co(Ni)-N-C structures have caught significant interest for efficient water splitting. The practical application of such single atom catalysts (SACs) requires a high metal loading, in which the individual metal sites could seriously agglomerate during the typical high temperature processes needed to incorporate such metal atoms into the graphene matrix. The microwave assisted rapid thermal shock offers a promising approach for providing sufficient kinetic energy to insert the metal atoms or other dopants into the graphene basal plane while minimizing the atom diffusion and agglomeration occurring in the typical long duration thermal process. Indeed, the microwave process has recently been successfully explored for the synthesis of such SACs with improved mass loading and catalytic performance.[7] Additionally, microwave combustion has also been explored for

controllable generation of holes on graphene with tunable sizes from several nanometers to one hundred nanometers.[8] Such tunable porosity may serve as the channels for efficient mass transport of ions and small molecules, making the resulting holey graphene framework an attractive scaffold in various chemical and electrochemical processes.[9]

Together, the microwave assisted thermal shock strategy represents a novel, versatile synthetic approach that can open up a new chapter for rapid processing of a wide range of nanometer and atomic scale materials beyond the thermal equilibrium limitations and can impact diverse technological areas. A fundamental understanding of the microwave absorption, heat generation, dissipation and quenching process will be essential for developing controllable microwave synthesis methods and this article provides an excellent step forward.

Figure 1. The illustrated temperature profile of the microwave assisted thermal shock and its potential applications for the synthesis of pure metal nanoparticles, multi-component alloys, metal sulfides and single atom catalysts (SACs).




**ACKNOWLEDGMENTS**

X.D. gratefully acknowledges support from the National Science Foundation under grant no. NSF 1800580.

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