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Rational design and controllable synthesis of polymer aerogel based single-atom catalysts with high loading

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Abstract

Recently, single-atom catalysts (SACs) are of great interest in the catalysis field. Current research shows that it is a potential and feasible development direction for precious metal materials to be made into SACs. Reducing the metal content as much as possible gives the single atom catalyst an obvious cost advantage. However, too low metal loading is not always providing the sufficient catalytic activity for SACs. In some catalysis reactions, the deficiency of low catalyst loading can be offset by the increase of catalysts usage. But excessive use of catalyst may lead to the loss of mass transport and then the power density. The single atom and high loading might seem like a paradoxical concept, but
for catalysts, the sufficiently high specific catalytic activity evolves into a most critical parameter for SACs. How to synthesize high loading SACs under control will be an important direction in the next stage of development. In this review, we focus on the progress of precursor selection, material synthesis, content of single-atom, and some possible solutions for high loading SACs. Meanwhile, we also propose a single atom aerogel catalyst with high loading, which provides more possibility for the future development of catalysts.

1. Introduction

Single-atom catalysts (SACs) have attracted great attentions in the field of catalysis. The performance of a catalyst depends on the number of active sites. The single atom catalyst can reduce the amount of metal while ensuring multiple active sites in it, which makes it possess a very competitive advantage. By selecting appropriate supports, SACs have been applied in diverse catalysis for material synthesis, photo-catalytic reactions, electro-catalytic reactions, lithium-sulfur batteries, zinc air batteries, toxic gas adsorption and fuel cells, etc. In order to improve the performance of SACs, researchers have developed various new techniques such as the impregnated method, super mixer, electrofiltration method, high temperature shockwave, in situ photodeposition procedure and high-temperature-synthesized by arc-discharge strategy, etc. Furthermore, additives have been incorporated to the composites to enhance the performance of SACs. The most commonly used synergists or carriers, which serve as hosts and provide stable sites for atoms, include graphene, carbon nanotubes, porous carbon, aerogels, oxides, nitride, sulfides, and alloys. Among these materials, the aerogel show unique properties that suitable for catalyst carrier, such as large specific surface area, tailorable porosity, efficient separation of metal atoms, and chemical/physical stability.
It is worth mentioning that through different processes and composite modification, the properties of the SACs have been significantly improved. However, challenges still remain to from laboratory to real engineering. To realize the engineering of SACs, the following requirements should be fulfilled at least: environmental friend, low cost and good catalytic performance. At present, SACs are still the most state-of-the-art catalysts, which cannot meet all the above requirements. The main challenges are the high cost of raw materials, the too complex preparation process or the low yield, these are the obstacles that cannot get around on the engineering road of the single atom catalysts. For the catalytic performance of the SACs, which affected by multiple factors conclude elements content, specific surface area, micro morphology and particle size, etc. Among these respects, the load of single atoms on the SACs is a crucial parameter but easy to be ignored. The importance of high loading of SACs (it's called sensely packed SACs in some review) was previously reported in various recent review.\textsuperscript{46,47} Usually when researchers consider the sustainable development of catalysts, the metal atoms in the catalyst are kept as low as possible. However, too low metal content is not always providing the sufficient catalytic activity for SACs.

In many catalysis reactions, the deficiency of low metal loading can be offset by the increase of catalysts usage. However, this method of simply increasing the amount of catalyst can only improve the catalytic activity to a certain extent, and with the increase of the amount of catalyst, the specific activity of the catalyst also decreased gradually. Such as in Proton Exchange Membrane Fuel Cell (PEMFC), although excessive usage of catalysts can make up the performance loss of low metal-loading, the thick catalyst layer would lead to the loss of mass transport and then the power density. The unique advantage of the SACs with high loading is that it maintains the high specific activity of the catalyst. The catalyst with high specific activity can significantly reduce the amount of catalyst and
reduce the quality of the whole device, thus improving the energy density and power density of the
device. In addition, high loading of SAC is also important for allowing to establish cooperative effects
between SACs. By developing materials with ligands, metal atoms in different valence states can
coordinate and prevent leaching or nanoparticle formation. So that the gap between homogeneous and
heterogeneous catalysis can be closed.\textsuperscript{48} The controllable synthesis of high loading single atom
catalysts will be an important direction in the next stage of development. At present, there is no clear
definition for the SACs with high loading. This paper tentatively proposes that the low load is less than
1 wt\%, the medium load is 1-3 wt\%, and the high load is more than 3 wt\%.

Some reviews and perspectives about SACs and their applications have been published in recent
years. To the best of our knowledge, there are no reviews emphasizing on the metal content and
summarizing how to synthesize high loading SACs in a controllable way. The SACs with high load
can great improve the catalytic activity of metal atoms, and simultaneously can reduce the amount of
catalyst to reach the same catalytic effect. In this context, this review covers the scope of research
process on the preparation of SACs based on different technologies and carriers. We then primarily
focus on how to adjust and control the effective single atom load of SACs. In addition, based on the
analysis and reasoning of the existing literature and further simulation calculation, a theoretically
feasible preparation scheme for the aerogel supported single atom catalyst is proposed. Through the
implementation of this scheme, SACs can be synthesized in a controllable way in terms of the load
and specific surface area. Finally, challenges and prospects for the future development of single atom
catalysts are also presented.

2. Synthesis of single atom catalysts
The synthetic strategy plays an important role in the synthesis of SACs. The key with SAC materials is that it is difficult to guarantee atomic independence during the synthesis of SACs. Due to the relatively high surface energies of single metal atoms, various general synthetic strategies are not readily adopted for the synthesis of SACs. In recent years, some improved methods based on traditional synthesis methods and some new synthesis methods have been gradually developed and applied in the synthesis of SACs, as shown in Figure 1. The reported synthesis methods can be mainly divided into the following categories, including the homogeneous reaction method, the pyrolysis method, the high energy complex technique, the mass selection with soft-landing method. The reported specific preparation processes are listed in Table 1, advantages and disadvantages of each synthesis method are also included.

1) Homogeneous reaction method is a representative low-cost approach with the benefits of simple prepare process and readily available precursors. Homogeneous reaction is also called "single phase reaction", that is, the chemical reaction only occurred in one phase (gas phase, liquid phase or solid phase). It is characterized by the absence of a phase interface in the reactant system. For monatomic catalysts, the homogeneous reaction mainly occurs in the liquid phase system. Catalyst ions or micro-nanoparticles and carriers are dispersed in the liquid phase system and bonded together by forming new chemical bonds or by van der Waals forces. This type of method mainly include coprecipitation synthesis, wet-impregnation synthesis, and solvothermal synthesis, and these synthesis reactions are usually carried out under mild conditions.\textsuperscript{49-51} During the homogeneous reaction, because most of the reactants are concentrated on the surface of the supports, once the ion concentration increases, the formed single atoms with high specific surface energy are extremely easy to agglomerate.\textsuperscript{52, 53} Therefore, it is difficult to prepare high loading SACs for practical application by
using this method.

(2) High energy complex technique such as ball milling and anti-Ostwald method are likely to be used in large-scale synthetic SAC materials. High energy ball milling is also called mechanical alloying. High energy ball mill should be able to deliver high mechanical energy to the catalysts and supports powder in a short time, so that the milled materials can realize mechanical alloying (mechanical activation) in a short time, and even form nanocrystalline or amorphous materials, and reduce the oxidation and pollution of materials. However, this category has certain requirements for precursors and supports, which set limits to application.54, 55

![Figure 1](image)

**Figure 1.** (a) The schematic diagram of SACs prepared by ALD method.56 Copyright 2018, Oxford University Press. (b) Some conventional and novel synthetic strategies for SACs. (c) The schematic
illustration of single-atom Pt catalysts encapsulated in MOF-808-EDTA via single metal ion trap method. Copyright 2019, Elsevier Inc.

(3) Pyrolysis method is usually a post-treatment for the precursors. In the process of high temperature pyrolysis (≥600°C), isolated metal catalyst atoms can be directly doped into the carbon matrix or form strong coordination with carbon atoms, which makes the isolated metal atoms have high stability. Based on mechanisms of pyrolysis, new technologies have also been developed, such as high-temperature-synthesis by arc-discharge strategy, high pressure heating reaction and high temperature shockwave, etc. These methods require a large number of mobile catalyst atoms and a support that can combine with the mobile catalyst atoms. At high temperature, the volatile metal molecules are released and captured by the surface of the support, then the single metal atom can be evenly dispersed on the surface of the support, thus forming the SACs. Pyrolysis methods can afford SACs with high stability, high specific surface area, high metal loading and unique micro hole-structure. However, this method is also not perfect. The formation of specific microstructures requires the use of template agents, high temperature treatment, and hazardous etching reagents (such as HF) to clean the material surface. Moreover, both the supports and the metal atoms are produced simultaneously during the synthesis process, which makes it is difficult to control the number of effective single atoms on the surface of the support and the number of single atoms with catalytic activity.

(4) Atomic layer deposition (ALD) is like an upgraded version of chemical vapor deposition (CVD), the difference is the deposition process between pneumatolytic precursor and support evolving into multistep self-limiting surface reactions, which allows the metal atoms to deposit more evenly on
the surface of the support.\textsuperscript{63-66} ALD usually requires a two-step process, as shown in Figure 1a, the first step is the reaction between the catalyst precursor and the support surface, and the second step is the conversion of the precursor by pulse energy. In the whole synthesis process, the design and control of atomic level can be achieved by adjusting the cycle. ALD is a very promising technology, but so far it is difficult to realize mass production of SACs. On one hand, the high requirement of this method for equipment conditions such as vacuum and elevated temperature leads to high cost, on the other hand, it is selective for material target and support, which makes this method can only be used in part of material systems.

(5) Mass selection with soft-landing is a simple and straightforward technology and it has been successfully applied to the synthesis of SACs. In this method, the pure metal solid is directly gasified in inert gas, and then deposited on the support with inert gas flow. The number of atoms can be controlled by the quality of the added metal solid.\textsuperscript{67, 68} The number of atoms, regardless of single atom or multi-atom clusters, can be directly controlled by controlling the mass of the clusters in the flow. The high dependence on complex equipment and low yield are the major deficiency of this method, which makes it difficult to achieve mass production of SACs. In addition, because the catalyst atoms are adsorbed on the surface of the supports, no chemical bonds are formed, which will cause the catalyst atoms to fall off or agglomerate in the long-term catalytic process, resulting in a sudden decrease in catalytic activity.

3. Metal content in single atom catalysts

With the going deep of the research work, SAC materials have been synthesized in a variety of ways as described above. When the content of metal atoms is very low, the SACs can be easily synthesized
by some specific methods. The commonly used characterization methods mainly include full name and abbreviation: Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), extended X-ray absorption fine structure spectra (EXAFS), X-ray absorption near edge structure (XANES), a high-resolution transmission electron microscopy (HRTEM), high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM), Fourier-transform infrared (FT-IR) spectroscopy, annular bright-field scanning transmission electron microscopy (ABF-STEM). As shown in Table 1, sufficient evidence was provided to prove the existence of single atoms by verifying each other with a variety of characterization methods. The recent reports about SACs (Table 1) show that most of SACs have an atomic payload of less than 3 wt%. The present challenge is that it is difficult to maintain the independence of the metal single atoms with increasing of metal atom content, because high energy metal single atoms are easily migrated and agglomerated in synthesis or subsequent applications. Therefore, choosing suitable precursors is an important prerequisite for the successful synthesis of SAC materials. To this end, some strategies such as spatial constraint, coordination, and chemical bonding have been used to fix metal atoms at the support sites.69, 70

Table 1. Metal loading and construction strategy in single atom catalysts.

| Catalyst | Support | Construction strategy | Structural characterization | Metal content | Ref. |
|----------|---------|-----------------------|----------------------------|--------------|-----|
| Pd       | TiO₂    | Calcined and wet-impregnation method | DRIFTS, EXAFS, XANES | 0.2-1.5 wt% | 71  |
| Pt       | MoC     | High-Temperature-Synthesized by arc-discharge strategy | HRTEM, HAADF-STEM, XANES, DRIFTS | 0.2-2 wt% | 21  |
| Sn-Zn    | CuO     | Impregnated method and | HRTEM, HAADF-STEM, | 0.05-0.2 wt% | 72  |
| Material | Preparation Method | Characterization Techniques | Weight % |
|----------|---------------------|----------------------------|----------|
| Pt       | Ga-Pb/SiO<sub>2</sub> pore-filling co-impregnation method | HAADF-STEM, FT-IR | 3 wt% |
| Ni       | Carbon freeze-dried and Calcined | HAADF-STEM, FT-IR, EXAFS, XANES | 0.44 at% |
| Pt       | g-C<sub>3</sub>N<sub>4</sub> liquid-phase reaction | HAADF-STEM | 0.77 wt% |
| Rh       | CeO<sub>2</sub> adsorption precipitation method | HAADF-STEM, DRIFTS | 0.04 wt% |
| Ni       | MOF Templat and Calcined | HAADF-STEM, EXAFS, XANES, HRTEM | 0.9 wt% |
| Pt       | Mn<sub>3</sub>O<sub>4</sub> high-temperature treatment | DRIFTS | 0.82 wt% |
| Fe       | MOF Silica-mediated MOF-templated | ABF-STEM, HAADF-STEM, EXAFS, XANES | 0.09-0.11 wt% |
| Ni       | N-doped Carbon Annealed and Super mixer | HRTEM, HAADF-STEM, EXAFS, XANES | 1-1.92 wt% |
| Fe       | ZIF-8 Templated and electrofiltration method | HAADF-STEM, EXAFS, XANES | 0.52-0.54 wt% |
| Y/Sc     | Carbon Ball-milling and High-pressure heating reaction | HAADF-STEM, EXAFS, XANES | 0.38-1.24 wt% |
| Au       | LaFeO<sub>3</sub> Homogeneous reaction and Annealed | HAADF-STEM, EXAFS, XANES | 0.3 wt% |
| Element | Support | Method | Catalyst Preparation | Synthesis Method | Analytical Techniques | Metal Loading |
|---------|---------|--------|----------------------|------------------|----------------------|--------------|
| Pd      | ZnO-ZrO2| Homogeneous reaction and Annealed | HAADF-STEM, EXAFS | 0.02 wt% | 80 |
| Cu      | Carbon  | Gas-transport approach | HAADF-STEM, EXAFS, XANES | 0.45 wt% | 81 |
| Pt      | Carbon  | High temperature shockwave | HAADF-STEM, EXAFS | 0.24 wt% | 82 |
| Pt      | CeO2    | Atomic layer deposition | HAADF-STEM, XANES, DRIFTS | 1.1 wt% | 83 |
| Ni      | CN      | Different calcination procedures | HAADF-STEM, EXAFS, XANES | 0.1-1.5 at% | 84 |
| Fe      | Carbon  | Confined carbonization in an inert or reductive atmosphere | HAADF-STEM, EXAFS | 1.15 wt% | 85 |

The catalytic activity and cycling efficiency of the SAC materials and their power/energy density of the SAC-based equipment heavily depend not only on its intrinsic activity but also on the quantity of catalytic sites. One key technical issue is how to balance the relationship between the number of atoms and the agglomeration of atoms. In particular, metal atoms tend to migrate and agglomerate more easily during high-temperature processing, which further increases the difficulty of synthesizing high-loaded SAC materials. The practical use of SACs is confined by limited active sites, which makes high-loading SACs get more attention from researchers. Aim at this problem, some potential solutions have been proposed. Wang et al.\textsuperscript{84} recently reported a two-step wet chemistry method to the synthesis of Ir-NiO/carbon cloth, the metal loading has been raised to 18 wt\% (Ir on the NiO). As shown in Figure 2, the oxygen evolution reaction performance of obtained SACs exhibit significant
improvement with the increase of metal content. Zhao et al\textsuperscript{85} reported a cascade anchoring strategy to synthesize SACs and realize a high metal loadings up to 12.1 wt\%, which indicated high-loading SAC possess better electrocatalytic performance for O\textsubscript{2} reduction and CO\textsubscript{2} reduction. These new attempts opened scientists' eyes to new hope and great potential. Single-atom catalysts with high loading will become the focus of research in the future. Another challenge is the large-scale production, only when the SACs realize industrial production can it be applied in practice. Most synthesis processes of SACs require detailed multi-step regulation to obtain stable single atom sites, while mass production requires commercially available low-cost carriers and preparation processes that can be scaled up. Therefore, it is highly desirable to develop a synthesis method suitable for mass production of SACs with high metal loadings in a controllable manner.
Figure 2. High-loading SACs and their performance comparison with different metal content. (a) HAADF-STEM micrographs of catalyst. (b, c) Corresponding atomic models. (d) Polarization curves and (e) Tafel plots for OER. (f) The estimation of $C_{dl}$. Copyright 2020, American Chemical Society. (g) SEM image of support. (h) Steady-state ORR polarization curves of different SACs. (i) Steady-state ORR polarization curves of SACs with different Fe loading. Copyright 2019, Nature.

4. Aerogel catalyst

The number of effective catalytic area in a catalyst is as important as the high loading. For practical applications, the high metal content in SAC materials is not sufficient to catalyze with high efficiency.
It is also of great importance to allow as many active sites as possible to be in full contact with the reaction product, thus those single atoms of metal can perform enough catalytic activity. Among the many candidate support materials, aerogel is a type of nanoscale porous solid material formed by sol-gel process, in which the liquid phase in gel is replaced by gaseous phase (usually by air) through a certain drying method.\textsuperscript{87-89} Aerogels as catalyst support material demonstrates the irreplaceable advantages in comparison with other support materials.\textsuperscript{90-93} Before crystallization at high temperature, due to the three-dimensional porous structure of aerogel materials, the metal atoms composite in aerogel are spatially isolated so that the metal atoms agglomeration can be restrained during the high-temperature process. Secondly, the obtained aerogel SACs possess higher surface area than normal particles, the more contact of active sites lead to sufficient use of SAC's catalytic properties. In addition, aerogels can also be produced as monolithic, flexible structures that can be used without the extra current collector, which will greatly reduce the overall mass of the catalyst devices and improve the bending resistance.

The aerogel catalyst support materials mainly include inorganic oxide-based aerogel and carbon-based aerogel. The typical properties of inorganic aerogels are high specific surface area and high porosity. In addition, some types of inorganic oxide-based aerogels can exhibit specific optical and thermodynamic properties. Compared with the traditional inorganic aerogels (such as silica aerogels), carbon aerogels have many excellent properties and wider application prospects. Carbon aerogels have the advantages of good conductivity, large specific surface area and wide range of density. They are ideal electrode materials for the preparation of electrocatalyst support and electronic double layer capacitor. For different catalytic systems, the requirements of catalyst support are also different. electrocatalysis favors highly conductive substrate while photocatalysis requires substrate with optical
gap. In addition, there are also some characteristics such as mechanical properties, pore structure, hydrophobicity, biocompatibility, transparency, thermal conductivity and so on, which are corresponding to the needs of different fields. In the application, it is necessary to select the catalyst support according to the specific use scenarios, so as to achieve the best catalytic effect.

In a range of catalyst support materials, graphene has received considerable attention in the field of catalysis and has been widely studied. Recently, several articles have reported that graphene can improve the electrocatalytic properties of bird dropping (a bit satiric tone), but the author think researchers should focus their energy on other research directions compared to these efforts. That may be a good suggestion, and it's going to make researchers rethink our attitudes to scientific research. We also believe that the essence of scientific research is to simplify problems, not to complicate them, even bring the learned involution. The combination of single-atom catalysts and graphene aerogels is a very good innovation. In the short term, it is difficult to reduce the production cost of single-atom materials and graphene. With the development of technology and scale, these new materials and technologies will eventually highlight their value. As mentioned above, sufficient catalytic performance, low-cost and environmental friendliness are the three most necessary elements for the application of SACs. Although research has been widely carried out on single atom catalysts and graphene aerogel catalysts, there are much less reports on single atom catalysts supported by aerogels. This review will focus on the synergistic catalytic effects when combining aerogels with single atoms.

The preparation of aerogel can be divided into three typical steps: sol-gel, aging and drying processes. For carbon-based aerogels, an additional carbonization step is required. Sol-gel process is the basic reaction to form three-dimensional skeleton precursor of the aerogel. In general, by controlling temperature, pH value or photo initiation condition, the Individual molecules or ions can
be complexed or cross-linked together to form a solid gel from a colloidal solution. As shown in Figure 3, self-supporting 3D nanostructures can be formed from inorganic precursors, organic precursors and inorganic/organic composite precursors, and the reaction can take place in aqueous solutions system and organic solutions. The transformation of sol into gel can be simply understood as the hydrolysis followed by a condensation reaction between organic and inorganic monomers. For example, the most typical silica aerogel sol gel formation process with tetramethyl orthosilicate (TMOS) as the precursor is shown in Figure 3.

![Figure 3. The sol-gel process of aerogel.](image)

There are also some condensation reactions involving the process that nucleophilic attacks of carbon centers can form three-dimensional networks in non-hydrolytic systems, such as the formation of
oxygen bridge bonds by alcohols, ethers or carboxylic acids to synthesize anhydrous oxides. Detailed mechanism analysis as well as the respective advantages and disadvantages can be referred to the paper of Mutin and Vioux. For organic molecular and biopolymer precursors (e.g. melamine formaldehyde (MF), resorcinol formaldehyde (RF), polysaccharides and polypeptides), the condensation process that forms gel networks include physical polymerization represented by hydrogen bonds and chemical polymerization that initiate crosslinking by light, heat or pH. The reaction process of two representative sol-gel process of MF aerogel and biopolymer aerogel are shown in Figure 3. The sol-gel process of MF aerogel is through the formation of diaminomethylmethyl bridge and diaminomethylmethyl ether bridge under the catalysis of acid. Finally, the gel process is completed to form a 3D network structure. In addition to the crosslinking reactions and dehydration condensations, alginate polymers can also combine with multivalent cations to realize sol-gel process.
Figure 4. The synthetic strategies of aerogel-based catalysts.

After the sol-gel process, aerogel catalysts skeleton structure can be completely formed. Compared with the traditional synthesis methods for catalyst materials (such as hydrothermal method, co-precipitation method, liquid phase reaction method), the synthesis method of aerogel-based catalyst possesses some specific characteristics that the traditional synthesis method does not achievable. In previous years, Schwarz et al.\textsuperscript{102} have comprehensively reported the traditional catalyst synthesis methods mentioned above. In contrast, the synthesis method of aerogel is more straightforward, which allows the direct in-situ compounding of multiple molecular, ions and particles precursors during the
synthesis process. As a product of the sol-gel process, the whole piece of organic-inorganic composite aerogel catalysts can be obtained through the following aging and drying process. Next, we will outline the different synthesis methods of aerogel-based catalysts with aerogel as the support, and provide a comparative analysis of the synthesis steps.

To date, the types of aerogels have been divided into inorganic oxide systems, organic systems and inorganic-organic composite systems. Carbon aerogels are obtained by carbonizing organic aerogels or using carbon materials such as graphene carbon tubes as precursors. Functionalized aerogel is a composite material obtained by compounding specific functional metals, molecules, ions, and compounds with aerogel porous skeleton as a support during the synthesis of aerogels. For aerogel materials with catalytic function, the type of supported catalyst can be single-component, dual-component or multi-component according to requirements. Combined with some reported literatures, Figure 4 summarizes the current routes for preparing various composite aerogel catalysts. In order to ensure that the precursors are fully reacted, the wet gel obtained by the sol-gel process needs to be further aging to enhance the three-dimensional skeleton structure of the gel.

Since the sol-gel process of aerogel is carried out in a liquid phase system, the aging wet gel contains a large amount of solvents. It is necessary to select a suitable drying method to dry the wet gel to obtain porous aerogel products. In order to ensure the high porosity structure of the aerogel, the drying process must be carried out without affecting the microstructure of the wet gel. According to different gel systems, the subcritical drying, supercritical drying, freeze drying and vacuum drying methods have been selected to remove the solvent in the wet gel. In general, for the production process of aerogels, atmospheric drying is the most common and easiest way to achieve, which is a factor of great significance for large-scale production of aerogels. However, the pores of the aerogel are nanometer-
scale, the internal solvent will generate greater stress due to capillary action during the drying process, which will cause the aerogel microstructure to collapse. In this case, some non-polar functional groups can be introduced to modify the pore surface. At the same time, after the aging process of the wet gel is finished, the low surface tension solvent is used to replace the liquid in the pores to reduce the capillary stress, so that the aerogels with complete structure can be prepared. After solvent exchange, the wet gel can be dried by conventional drying methods to obtain solid aerogels. If we want to further increase the specific surface area of the aerogel, supercritical drying is the best choice at present. This method is to replace the solvents in wet gel by using supercritical CO$_2$ or ethanol as medium, which can protect the microstructural stability at the largest degree of aerogels.

For carbonaceous aerogels, the carbonization process is necessary after drying process. The carbonization process is usually carried out at temperatures above 500$^\circ$C with inert gas protection. With the increasing of temperature, the organic matter is pyrolyzed, and the hydrogen and oxygen in the polymer gradually volatilize, leaving a porous carbon skeleton. At the same time, the supported catalyst is reduced and crystallized at high temperature. Figure 4 shows the synthesis process of the organic-inorganic composite aerogel, and as shown in Figure 4, before the carbonization process is carried out, one or more kinds of molecular, ions or particles can be directly compounded in aerogels in the case of without affecting the physical properties of aerogels. In addition, the prepared aerogel can also support the catalyst by immersing solid aerogel in a metal salt solution or vapor deposition and other methods. These methods are generally considered to be the simplest and economical methods to prepare multiple composite catalysts. In recent years, the development of organic-inorganic multiple composite catalysts has brought great opportunities for applications such as photocatalysis, electrocatalysis and heterogeneous catalysis. The introduction of some new
concepts, such as quantum dots and single atoms, also brings new potential for aerogel based catalysts. The development of these cutting-edge aerogel catalysts will certainly push the whole catalytic field to a new stage.

5. Rational design of single atom aerogel catalyst by host-guest interaction

The catalytic performance of catalyst materials is mainly affected by electronic structure effect and surface structure effect. The electronic structure effect mainly includes the influence of the energy band and surface density of states on the catalytic performance. The surface structure effect mainly refers to the influence of the electronic interaction on the surface interface layer between the catalyst material (the surface chemical structure and the atomic arrangement structure) and the reaction system on the catalytic rate.\textsuperscript{111, 112} The influence of the activation energy of the catalyst on the reaction rate is several to dozens of orders of magnitude, while the effect of the surface electric double layer structure on the reaction rate is one to two orders of magnitude. In the practical work of catalysts, the electronic structure effect and the surface structure effect are complementary, and they cannot be completely independent. Even so, the electronic structure effect should be given priority in the selection of catalyst material system, and the catalyst with low power consumption and high activity can be obtained by selecting the appropriate material system. Some high-frequency reported elements that have been used as SACs are shown in Figure 5.\textsuperscript{6} After the catalyst material system is finalized, it is necessary to consider the effect of catalyst surface structure effect on catalytic activity.
According to the electronic structure effect of the material system, the selection of catalysts is mainly concentrated in VIIIIB and IB group. Every single element or their compounds have their inherent physical and chemical properties. In view of these physical and chemical properties, it is necessary to design a reasonable synthesis method to obtain SACs with sufficient performance. The development direction of noble metal SACs is to reduce the metal content as much as possible under the premise of ensuring catalytic activity, while the development direction of base metal SACs is to give priority to ensuring catalytic performance. Among the candidate systems of catalyst materials, the most potential substitutes for noble metals are Fe, Co, Ni and Cu. Some recent studies have also shown that Fe, Co, Ni and their composites possess great potential in the field of SACs.\textsuperscript{86, 113-121} Lausanne Institute of technology and National Taiwan University jointly reported a catalyst composed of dispersed monoatomic Fe active sites (Figure 6).\textsuperscript{113} The catalyst produces carbon monoxide at an overpotential as low as 80 mV. At an overpotential of 340 mV, the partial current density reaches 94 mA/cm\textsuperscript{2}. Du et al.\textsuperscript{114} found that nitrogen doped graphene supported cobalt single atom material can trigger the
surface mediated reaction of lithium polysulfide. A promising lithium sulfur battery with high specific capacity of 1210 mAh/g and good cycle performance was prepared.

Figure 6. (a-d) TEM images and the corresponding EDS mappings. (e) EDS spectrum of the red square region. (f) XANES spectra of samples. (g) Faradaic efficiency of CO and H₂ production. (h) The j_{CO} in an H-cell. Copyright 2019, American Association for the Advancement of Science.

Through a series of systematic investigations on the physical and chemical properties of these base metals of Fe, Co, Ni and their compounds, and we have also found some valuable information. Fe, Co and Ni can form organic transition metal compounds with aromatic properties such as ferrocene,
cobaltocene and nickelocene. These compounds exhibit some unique properties, Masaki et al. invented a supramolecular hydrogel actuator driven by redox, which exploits the mechanism of host-guest interaction. As shown in Figure 7a-c, the gel network of hydrogel drivers consists of N, N-methylenebisacrylamide crosslinked poly(acrylamide) grafted with two functional molecules, beta-cyclodextrin and ferrocene, which make the hydrogel network exhibit redox expansion-contraction function through by host-guest interactions between these two molecules. Duan et al. synthesized ferrocene-cellulose with substitution degree of 0.5 wt% and beta-cyclodextrin-chitosan with substitution degree of 0.35 wt%, and then synthesized cellulose-chitosan gel with these two polysaccharides. Benefiting from the intermolecular inclusion, the cut gel showed self-healing ability after 24 hours (Figure 7d-e). Similarly, Fig. 7f further demonstrates the reaction mechanism during the self-healing process of cyclodextrin and ferrocene. The special properties of the first three materials have one thing in common, that is, the use of the host and guest functions of ferrocene and cyclodextrin. This special property also brings some enlightenment to the synthesis of single atom materials.
Figure 7. (a) Photographs of the gel. b) Illustration of redox-responsive expansion contraction of the gel. c) Illustration of gel actuator in response to redox stimuli. Copyright 2013, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim. (d) Intermolecular inclusion interaction of hydrogel. (e) Self-healing experiments. Copyright 2015, Hindawi Publishing Corporation. (f) Photographs and schematic diagram of Self-healing experiments. Copyright 2011, Nature.
After discovering this particular property, we evaluated this series of organic transition metal compounds. In addition to ferrocene, there are similar organic transition metal compounds such as nickel and cobalt. As shown in Figure 8a, metallocene (general formula (η5-C5H5)2M or (CP)2M) is the generic names of dicyclopentadiene-based metal coordination compounds. Among them, M mainly refers to transition metals, while both cyclopentadienyl groups (CP=C5H5) are pentadentate ligands, like two pieces of bread, sandwich metal M in the middle, commonly known as sandwich compounds.

Cyclodextrin (CD) is a general term for a series of cyclic oligosaccharides produced by amylase under the action of cyclodextrin glucosyltransferase produced by Bacillus sp., usually containing 6-12 D-glucopyranose units. Among them, the most studied and important practical significance is the molecule containing 6, 7, and 8 glucose units, which are called alpha-, beta- and gama-cyclodextrins, respectively (Figure 8b). The upper end of the outer side of the cyclodextrin molecule (larger open end) is composed of C2 and C3 secondary hydroxyl groups, and the lower end (smaller open end) is composed of C6 primary hydroxyl groups, which is hydrophilic. The cavity is affected by the C-H bond and the shielding effect forms a hydrophobic zone. Because the outer edge of cyclodextrin is hydrophilic while the inner cavity is hydrophobic, it can provide a hydrophobic binding site like an enzyme, as the main body (host) envelopes various appropriate objects (guest), such as organic molecules, inorganic ions and gas molecules.

This atomic-level confinement effect is one of the most favorable factors for the synthesis of single atom materials. As shown in Figure 8c, using the host-guest interactions of cyclodextrin and ferrocene,
after ferrocene enters the cyclodextrin cavity, the iron atoms in the ferrocene will be restricted by the cyclopentadiene molecule up and down, and the iron atom limited by around cyclodextrin, that is to say, after the inclusion of host and guest, the position of the iron atom cannot move at all, which establishes a prerequisite for the later synthesis of single iron sites. The inclusion products can be directly used for the synthesis of monoatomic materials after separation and drying. Another synthetic route is to add appropriate crosslinking agent and some other functional molecules or nanoparticles into the system to form a hydrogel in situ, and then form an aerogel-based single atom material after aging, drying and carbonization. Through the implementation of this strategy, it has an auxiliary effect on the full synthesis process of the single-atom catalyst in the pre-middle and late stages.
Figure 8. A synthetic strategy of single atom aerogel catalyst by host-guest interaction.
At present, single-atom catalysts still need to face many challenges before it transformed into mature commercial product. As shown in Figure 9, the first one is that single-atom materials are easy to agglomerate during the synthesis process and it is difficult to ensure the independence of atoms. The second is that it is difficult to increase the loading of single atoms. Once the atomic content increases, it will cause the atoms to reunite and lose the advantages of single atom materials. The third is that due to cost and technology constraints, it is difficult to mass produce single atom materials. The fourth is that some of the precursors used in the synthesis process of single atom materials are expensive, which violates the original intention of single atom materials to reduce costs and improve performance, and restrict their practical use. The last key issue is environmental protection. The single atom materials designed by the researchers need to take the issues of adopting environmentally friendly precursors and low-power preparation processes into consideration. For the challenges we are currently facing, we must consider comprehensively and propose reasonable solutions to each problem. The selection of precursor, the selection of synthesis system and the determination of synthesis process need to be considered comprehensively. The choice of precursors is particularly critical. Each precursor has its inherent physical and chemical properties. For different physical and chemical properties, a suitable synthesis scheme needs to be designed. Choosing a suitable precursor can achieve twice the result with half the effort.

Here, we design a possible experimental scheme based on the current literature reports. Ferrocene and cyclodextrin are used as precursors. In the early stage of synthesis, host-guest inclusion complexes between cyclodextrin and ferrocene are used to form inclusion complexes, and sufficient isolation of iron atoms can inhibit iron atom agglomeration to a certain extent in the late synthesis process.
the subsequent mid-term synthesis, inclusion complexes can be directly added to the cross-linker to form gels using functional groups on polysaccharides or implanted into other gel systems. The gels will form a three-dimensional network structure, and undergo supercritical or freeze-drying, which further isolates iron atoms in space and further inhibits atom aggregation during later carbonization.

In this way, iron atoms are well isolated throughout the synthesis phase of the material. Due to the maximum utilization of atoms and molecules, this is also in line with the atom economy proposed today. Through theoretical calculations, the theoretical maximum content of iron atoms can reach 8.2wt% (Table 2). These calculation process takes carbon as the main reference, and the doping of other heteroatoms will change its proportion to a certain extent. After doping with other elements, the iron atom content will be reduced, but it is also much higher than the current mainstream level.

![Diagram](https://via.placeholder.com/150)

**Figure 9. Current challenges and some possible solutions of SACs.**

In addition to inhibiting agglomeration and high loading, this strategy also has obvious advantages in other aspects. Firstly, the inclusion process is a thermodynamic spontaneous process and does not
require additional chemical reactions or energy supply. Secondly, the inclusion process is directly realized in the aqueous system, without additional organic solvents. In the subsequent hydrogel synthesis process, the aqueous solution system is more environmentally friendly and lower cost than the organic solvent system. The obtained hydrogel can be freeze-dried instead of supercritical drying to simplify the process and control the cost. In addition, ferrocene is a mature and cheap industrial raw material, and cyclodextrin is a natural polysaccharide macromolecular material. Both precursors meet the needs of low cost and environmental friendliness. In addition to ferrocene, there are some other molecules with similar properties that can also be used to synthesize SAC materials in this way, and even synthesize diatomic or multiple single atom synergistic composite materials. Only when comprehensively considering all factors and solving all challenges, can we obtain stable, high-load, environmentally friendly, low-cost, and mass-produced SAC materials.

Table 2. The metal load design of single atom catalyst by host-guest interaction.

| Category                  | β-Cyclodextrin (β-CD) | Hydroxypropyl-β-Cyclodextrin (HP-β-CD) | Ferrocene | Nickelocene |
|---------------------------|-----------------------|----------------------------------------|-----------|-------------|
| Molecular formula         | C₄₂H₇₀O₃₅             | (C₄₂H₇₀O₃₅)⁻                        | C₁₀H₁₀Fe  | C₁₀H₁₀Ni    |
| Molecular weight          | 1134                  | 1431-1806                             | 186.03    | 188.88      |
| Carbon content (a)        | 44.44%                | 44.44-45.3%                          | 64.5%     | 63.5        |
| Metal content (b)         | 0                     | 0                                     | 30.1%     | 31.2%       |
| Carbon/Metal (c) | 504/0 | 648/0 | 120/56 | 120/59 |
|-----------------|-------|-------|--------|--------|

| Metal/Carbon (d) | 0     | 0     | CD     | CD     |
|------------------|-------|-------|--------|--------|

6.8 wt% (HP-β-CD), 7.1 wt% (HP-β-CD)  

6.8 wt% (β-CD), 8.2 wt% (β-CD), 8.6 wt% (β-CD)

(a) Carbon content (wt %) in molecule.  
(b) Metal content (wt %) in molecule.  
(c) The ratio of carbon and metal in the molecule.  
(d) The weight ratio of carbon and metal when the metal and CD are combined at a molar ratio of 1:1. The calculation process takes carbon as the main reference, and the doping of other heteroatoms will change its proportion to a certain extent.

6. Conclusion and future perspective

In summary, high-load single-atom catalysts have become an important research direction that cannot be ignored in the development of single-atom catalysts. The main goal of the rapidly developing field of single-atom catalysis is to maximize the loading of metal atoms in the catalyst without agglomeration of atoms. Thus, the single-atom catalysts perform sufficient catalytic activity to ensure the practicability. Meanwhile, the following issues should be considered, such as the ease of technology, the environmentally friendly synthetic process, the controllable cost of raw materials and the feasibility of large-scale production. In addition to traditional experimental research methods, some theoretical calculations and simulations such as DFT and material genes can also be used to the high throughput screening of material systems, and they can be combined with new technologies such as artificial intelligence technology brought about by deep learning and machine learning. With the deepening of research and technological evolution, the difficulties faced by single-atom catalysts will be solved one by one, and the potential of single-atom catalysts will be further highlighted.
Notes

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References

1. K. Liu, J. Fu, L. Zhu, X. Zhang, H. Li, H. Liu, J. Hu and M. Liu, *Nanoscale*, 2020, **12**, 4903-4908.
2. R. Lang, T. Li, D. Matsumura, S. Miao, Y. Ren, Y. T. Cui, Y. Tan, B. Qiao, L. Li, A. Wang, X. Wang and T. Zhang, *Angewandte Chemie*, 2016, **55**, 16054-16058.
3. Y. Zhou, G. Gao, W. Chu and L.-W. Wang, *Nanoscale*, 2021, **13**, 1331-1339.
4. K. Chi, Z. Chen, F. Xiao, W. Guo, W. X. J. Liu, H. Yan, Z. Zhang, J. Xiao, J. Liu, J. Luo, S. Wang and K. P. Loh, *Journal of Materials Chemistry A*, 2019, **7**, 15575-15579.
5. S. Wang, J. Li, O. Li, X. Bai and J. Wang, *Nanoscale*, 2020, **12**, 364-371.
6. H. Yan, C. Su, J. He and W. Chen, *Journal of Materials Chemistry A*, 2018, **6**, 8793-8814.
7. Q. Wu, J. Wang, Z. Wang, Y. Xu, Z. Xing, X. Zhang, Y. Guan, G. Liao and X. Li, *Journal of Materials Chemistry A*, 2020, **8**, 13685-13693.
8. Z. Ma, Z. Cui, C. Xiao, W. Dai, Y. Lu, Q. Li and R. Sa, *Nanoscale*, 2020, **12**, 1541-1550.
9. S. Wang, H. Chen, J. Liao, Q. Sun, F. Zhao, J. Luo, X. Lin, X. Niu, M. Wu, R. Li and X. Sun, *ACS Energy Letters*, 2019, **4**, 755-762.
10. W. Zhao, J. Wang, R. Yin, B. Li, X. Huang, L. Zhao and L. Qian, *J Colloid Interface Sci*, 2020, **564**, 28-36.
11. H. Jin, S. Sultan, M. Ha, J. N. Tiwari, M.-G. Kim and K. S. Kim, *Advanced Functional Materials*, 2020, **30**.
12. M. D. Marcinkowski, S. F. Yuk, N. Doudin, R. S. Smith, M.-T. Nguyen, B. L. Kay, V.-A. Glezakou, R. Rousseau and Z. Dohnálek, *ACS Catalysis*, 2019, **9**, 10977-10982.
13. C. Ling, L. Shi, Y. Ouyang, X. C. Zeng and J. Wang, *Nano Lett.*, 2017, **17**, 5133-5139.
14. X. Yang, J. Cheng, B. Fang, X. Xuan, N. Liu, X. Yang and J. Zhou, *Nanoscale*, 2020, **12**, 18437-18445.
15. X. Li, W. Bi, L. Zhang, S. Tao, W. Chu, Q. Zhang, Y. Luo, C. Wu and Y. Xie, *Adv Mater.*, 2016, **28**, 2427-2431.
16. Z. Wang, J. Yang, J. Gan, W. Chen, F. Zhou, X. Zhou, Z. Yu, J. Zhu, X. Duan and Y. Wu, *Journal of Materials Chemistry A*, 2020, **8**, 10755-10760.
17. R. Hu, Y. Li, F. Wang and J. Shang, *Nanoscale*, 2020, **12**, 20413-20424.
18. H. Yin, S.-L. Li, L.-Y. Gan and P. Wang, *Journal of Materials Chemistry A*, 2019, **7**, 11908-11914.
19. Z. Kou, W. Zang, W. Pei, L. Zheng, S. Zhou, S. Zhang, L. Zhang and J. Wang, *Journal of Materials Chemistry A*, 2020, **8**, 3071-3082.
20. L. Zeng, C. Dai, B. Liu and C. Xue, *Journal of Materials Chemistry A*, 2019, **7**, 24217-24221.
21. Q. Bi, X. Yuan, Y. Lu, D. Wang, J. Huang, R. Si, M. Sui and F. Huang, *Research (Wash D C)*, 2020, **2020**, 9140841.
22. X. Jin, R. Wang, L. Zhang, R. Si, M. Shen, M. Wang, J. Tian and J. Shi, *Angew Chem Int Ed Engl*, 2020, **59**, 6827-6831.
23. Z. Chen, Z. Xu, W. Li, C. Chen, J. Yang, J. Liu, F. Gong, J. Liao and M. Wu, *ACS Applied Energy Materials*, 2019, **2**, 5171-5182.
24. Z. Wang, J. Yang, J. Cao, W. Chen, G. Wang, F. Liao, X. Zhou, F. Zhou, R. Li, Z. Q. Yu, G. Zhang, X. Duan and Y. Wu, *ACS Nano*, 2020, **14**, 6164-6172.
25. Y. Yao, Z. Huang, P. Xie, L. Wu, L. Ma, T. Li, Z. Pang, M. Jiao, Z. Liang, J. Gao, Y. He, D. J. Kline, M. R. Zachariah, C. Wang, J. Lu, T. Wu, T. Li, C. Wang, R. Shahbazian-Yassar and L. Hu, *Nature Nanotechnology*, 2019, **14**, 851-857.
26. P. A. Szilagyi, D. M. Rogers, I. Zaiser, E. Callini, S. Turner, A. Borgschulte, A. Zuettel, H. Geerlings, M. Hirscher and B. Dam, *Journal of Materials Chemistry A*, 2017, **5**, 15559-15566.
27. Y. Feng, Y. Guan, H. Zhang, Z. Huang, J. Li, Z. Jiang, X. Gu and Y. Wang, *Journal of Materials Chemistry A*, 2018, **6**, 11783-11789.
28. H. Zhang, G. Liu, L. Shi and J. Ye, *Advanced Energy Materials*, 2018, 8.
29. H. Zhang, W. Tian, X. Duan, H. Sun, S. Liu and S. Wang, *Advanced Materials*, 2019, 32.
30. L. Zhang, K. Doyle-Davis and X. Sun, *Energy & Environmental Science*, 2019, 12, 492-517.
31. L. Zhang, H. Liu, S. Liu, M. Norouzi Banis, Z. Song, J. Li, L. Yang, M. Markiewicz, Y. Zhao, R. Li, M. Zheng, S. Ye, Z.-J. Zhao, G. A. Botton and X. Sun, *ACS Catalysis*, 2019, 9, 9350-9358.
32. L. Zhang, R. Long, Y. Zhang, D. Duan, Y. Xiong, Y. Zhang and Y. Bi, *Angew Chem Int Ed Engl*, 2020, 59, 6224-6229.
33. Z. Zhang, Y. Chen, L. Zhou, C. Chen, Z. Han, B. Zhang, Q. Wu, L. Yang, L. Du, Y. Bu, P. Wang, X. Wang, H. Yang and Z. Hu, *Nat Commun*, 2019, 10, 1657.
34. Z. Zhang, Y. Zhu, H. Asakura, B. Zhang, J. Zhang, M. Zhou, Y. Han, T. Tanaka, A. Wang, T. Zhang and N. Yan, *Nat Commun*, 2017, 8, 16100.
35. Zhou, Zhu and Kang, *Catalysts*, 2019, 9.
36. G. Zhou, S. Zhao, T. Wang, S. Z. Yang, B. Johannessen, H. Chen, C. Liu, Y. Ye, Y. Wu, Y. Peng, C. Liu, S. P. Jiang, Q. Zhang and Y. Cui, *Nano Lett*, 2020, 20, 1252-1261.
37. S. Zhou, L. Shang, Y. Zhao, R. Shi, G. I. N. Waterhouse, Y. C. Huang, L. Zheng and T. Zhang, *Adv Mater*, 2019, 31, e1900509.
38. C. Zhu, S. Fu, Q. Shi, D. Du and Y. Lin, *Angewandte Chemie International Edition*, 2017, 56, 13944-13960.
39. S. Das, R. Ghosh, P. Routh, A. Shit, S. Mondal, A. Panja and A. K. Nandi, *ACS Applied Nano Materials*, 2018, 1, 2306-2316.
40. G. Fu, X. Yan, Y. Chen, L. Xu, D. Sun, J. M. Lee and Y. Tang, *Adv Mater*, 2018, 30.
41. Q. Gao, X. Wang, Z. Shi, Z. Ye, W. Wang, N. Zhang, Z. Hong and M. Zhi, *Chemical Engineering Journal*, 2018, 331, 185-193.
42. Y. Gu, S. Chen, J. Ren, Y. A. Jia, C. Chen, S. Komarneni, D. Yang and X. Yao, *ACS Nano*, 2018, 12, 245-253.
43. Y. Jin, F. Chen, J. Wang, L. Guo, T. Jin and H. Liu, *Journal of Power Sources*, 2019, 435.
44. S. Montes and H. Maleki, in *Colloidal Metal Oxide Nanoparticles*, 2020, DOI: 10.1016/b978-0-12-813357-6.00015-2, pp. 337-399.
45. P. Shanmugam, A. P. Murthy, J. Theerthagiri, W. Wei, J. Madhavan, H.-S. Kim, T. Maiyalagan and J. Xie, *International Journal of Hydrogen Energy*, 2019, 44, 13334-13344.
46. M. B. Gawande, P. Fornasiero and R. Zbořil, *ACS Catalysis*, 2020, 10, 2231-2259.
47. B. Singh, V. Sharma, R. P. Gaikwad, P. Fornasiero, R. Zboril and M. B. Gawande, *Small*, 2021, 17, e2006473.
48. A. Bakandritsos, R. G. Kadam, P. Kumar, G. Zoppellaro, M. Medved, J. Tucek, T. Montini, O. Tomanec, P. Andryskova, B. Drahos, R. S. Varma, M. Otrepka, M. B. Gawande, P. Fornasiero and R. Zboril, *Advances Materials*, 2019, 31.
49. D. Yang, S. O. Odoh, T. C. Wang, O. K. Farha, J. T. Hupp, C. J. Cramer, L. Gagliardi and B. C. Gates, *J Am Chem Soc*, 2013, 135, 7391-7396.
50. D. Yardimci, P. Serna and B. C. Gates, *ACS Catalysis*, 2012, 2, 2100-2113.
51. M. Yang, L. F. Allard and M. Flytzani-Stephanopoulos, *J Am Chem Soc*, 2013, 135, 3768-3771.
52. J. Lin, A. Wang, B. Qiao, X. Liu, X. Yang, X. Wang, J. Liang, J. Li, J. Liu and T. Zhang, *J Am Chem Soc*, 2013, 135, 15314-15317.
53. L. Lin, W. Zhou, R. Gao, S. Yao, X. Zhang, W. Xu, S. Zheng, Z. Jiang, Q. Yu, Y. W. Li, C. Shi, X. D. Wen and D. Ma, *Nature*, 2017, 544, 80-83.
54. X. G. Guo, G. Z. Fang, G. Li, H. Ma, H. J. Fan, L. Yu, C. Ma, X. Wu, D. H. Deng, M. M. Wei, D. L. Tan, R. Si, S. Zhang, J. Q. Li, L. T. Sun, Z. C. Tang, X. L. Pan and X. H. Bao, *Science*, 2014, 344, 616-619.
55. D. Deng, X. Chen, L. Yu, X. Wu, Q. Liu, Y. Liu, H. Yang, H. Tian, Y. Hu, P. Du, R. Si, J. Wang, X. Cui, H. Li, J. Xiao, T. Xu, J. Deng, F. Yang, P. N. Duchesne, P. Zhang, J. Zhou, L. Sun, J. Li, X. Pan and X. Bao, *Science Advances*, 2015, 1.
56. L. Zhang, M. N. Banis and X. L. Sun, *Nat. Sci. Rev.*, 2018, 5, 628-+
57. D. Yan, J. Chen and H. Jia, *Angew Chem Int Ed Engl*, 2020, 59, 13562-13567.
58. J. Liu, X. Kong, L. Zheng, X. Guo, X. Liu and J. Shui, *ACS Nano*, 2020, 14, 1093-1101.
59. L. Zhang, A. Wang, W. Wang, Y. Huang, X. Liu, S. Miao, J. Liu and T. Zhang, *ACS Catalysis*, 2015, 5, 6563-6572.
60. P. Yin, T. Yao, Y. Wu, L. Zheng, Y. Lin, W. Liu, H. Ju, J. Zhu, X. Hong, Z. Deng, G. Zhou, S. Wei and Y. Li, *Angew Chem Int Ed Engl*, 2016, 55, 10800-10805.
61. X. Wang, W. Chen, L. Zhang, T. Yao, W. Liu, Y. Lin, H. Ju, J. Dong, L. Zheng, W. Yan, X. Zheng, Z. Li, X. Wang, J. Yang, D. He, Y. Wang, Z. Deng, Y. Wu and Y. Li, *J Am Chem Soc*, 2017, 139, 9419-9422.
62. S. Ji, Y. Chen, Q. Fu, Y. Chen, J. Dong, W. Chen, Z. Li, Y. Wang, L. Gu, W. He, C. Chen, Q. Peng, Y. Huang, X. Duan, D. Wang, C. Draxl and Y. Li, *Journal of the American Chemical Society*, 2017, 139, 9795-9798.
63. H. Yan, Y. Lin, H. Wu, W. Zhang, Z. Sun, H. Cheng, W. Liu, C. Wang, J. Li, X. Huang, T. Yao, J. Yang, S. Wei and J. Lu, *Nat Commun*, 2017, 8, 1070.
64. B. J. O’Neill, D. H. K. Jackson, J. Lee, C. Canlas, P. C. Stair, C. L. Marshall, J. W. Elam, T. F. Kuech, J. A. Dumesic and G. W. Huber, *ACS Catalysis*, 2015, 5, 1804-1825.
65. Y. Cao, S. Chen, Q. Luo, H. Yan, Y. Lin, W. Liu, L. Cao, J. Lu, J. Yang, T. Yao and S. Wei, *Angew Chem Int Ed Engl*, 2017, 56, 12191-12196.
66. C. Wang, X.-K. Gu, H. Yan, Y. Lin, J. Li, D. Liu, W.-X. Li and J. Lu, *ACS Catalysis*, 2016, 7, 887-891.
67. M. Nesselberger, M. Roefzaad, R. F. Hamou, P. U. Biedermann, F. F. Schweinberger, S. Kunz, K. Schloegl, G. K. Wiberg, S. Ashton, U. Heiz, K. J. Mayrhofer and M. Arenz, *Nat Mater*, 2013, 12, 919-924.
68. M. D. Kane, F. S. Roberts and S. L. Anderson, *Faraday Discuss*, 2013, 162, 323-340.
69. L. Liu, U. Diaz, R. Arenal, G. Agostini, P. Concepcion and A. Corma, *Nat Mater*, 2017, 16, 132-138.
70. C. H. Choi, M. Kim, H. C. Kwon, S. J. Cho, S. Yun, H. T. Kim, K. J. Mayrhofer, H. Kim and M. Choi, *Nat Commun*, 2016, 7, 10922.
71. F. Yang, S. Ding, H. Song and N. Yan, *Science China Materials*, 2020, 63, 982-992.
72. F. Su, Y. Li, J. Ma, L. Wang, Z. Zhong, L. Wang, S. Tian, Z. Li, H. Liu, J. Li, Y. Zhu, W. Chen, Y. Ji and Q. Shi, *National Science Review*, 2020, 7, 600-608.
73. Y. Nakaya, J. Hirayama, S. Yamazoe, K. I. Shimizu and S. Furukawa, *Nat Commun*, 2020, 11, 2838.
74. S. He, D. Ji, J. Zhang, P. Novello, X. Li, Q. Zhang, X. Zhang and J. Liu, *J Phys Chem B*, 2020, 124, 511-518.
75. B. Han, T. Li, J. Zhang, C. Zeng, H. Matsumoto, Y. Su, B. Qiao and T. Zhang, *Chem Commun (Camb)*, 2020, 56, 4870-4873.
76. Y.-N. Gong, L. Jiao, Y. Qian, C.-Y. Pan, L. Zheng, X. Cai, B. Liu, S.-H. Yu and H.-L. Jiang, *Angewandte Chemie-International Edition*, 2020, 59, 2705-2709.
77. D. Yan, J. Chen and H. Jia, *Angewandte Chemie-International Edition*, 2020, 59, 13562-13567.
78. C.-C. Hou, L. Zou, L. Sun, K. Zhang, Z. Liu, Y. Li, C. Li, R. Zou, J. Yu and Q. Xu, *Angewandte Chemie-International Edition*, 2020, 59, 7384-7389.
79. C. Tian, H. Zhang, X. Zhu, B. Lin, X. Liu, H. Chen, Y. Zhang, D. R. Mullins, C. W. Abney, M. Shakouri, R. Chernikov, Y. Hu, F. Polo-Garzon, Z. Wu, V. Fung, D.-e. Jiang, X. Liu, M. Chi, J. Liu Jimmy and S. Dai, *Applied Catalysis B: Environmental*, 2020, 261.
80. G. Ding, L. Hao, H. Xu, L. Wang, J. Chen, T. Li, X. Tu and Q. Zhang, *Communications Chemistry*, 2020, 3.
81. Z. Yang, B. Chen, W. Chen, Y. Qu, F. Zhou, C. Zhao, Q. Xu, Q. Zhang, X. Duan and Y. Wu, *Nat Commun*, 2019, 10, 3734.
82. J. Li, Q. Guan, H. Wu, W. Liu, Y. Lin, Z. Sun, X. Ye, X. Zheng, H. Pan, J. Zhu, S. Chen, W. Zhang, S. Wei and J. Lu, *Journal of the American Chemical Society*, 2019, 141, 14515-14519.
83. W. Ni, Y. Gao, Y. Zhang, H. A. Younus, X. Guo, C. Ma, Y. Zhang, J. Duan, J. Zhang and S. Zhang, ACS Appl Mater Interfaces, 2019, 11, 45825-45831.
84. Q. Wang, X. Huang, Z. L. Zhao, M. Wang, B. Xiang, J. Li, Z. Feng, H. Xu and M. Gu, Journal of the American Chemical Society, 2020, 142, 7425-7433.
85. L. Zhao, Y. Zhang, L.-B. Huang, X.-Z. Liu, Q.-H. Zhang, C. He, Z.-Y. Wu, L.-J. Zhang, J. Wu, W. Yang, L. Gu, J.-S. Hu and L.-J. Wan, Nature Communications, 2019, 10.
86. L. Zhao, Y. Zhang, L. B. Huang, X. Z. Liu, Q. H. Zhang, C. He, Z. Y. Wu, L. J. Zhang, J. Wu, W. Yang, L. Gu, J. S. Hu and L. J. Wan, Nat Commun, 2019, 10, 1278.
87. X. Xu, H. Chu, Z. Zhang, P. Dong, R. Baines, P. M. Ajayan, J. Shen and M. Ye, ACS Appl Mater Interfaces, 2017, 9, 32756-32766.
88. X. Xu, H. Liang, F. Ming, Z. Qi, Y. Xie and Z. Wang, ACS Catalysis, 2017, 7, 6394-6399.
89. Y. Shang, X. Xu, B. Gao and Z. Ren, ACS Sustainable Chemistry & Engineering, 2017, 5, 8908-8917.
90. H. Maleki and N. Hüsing, Applied Catalysis B: Environmental, 2018, 221, 530-555.
91. B. Zhang, H. Wang, Z. Zuoh, H. Wang and J. Zhang, Journal of Materials Chemistry A, 2018, 6, 15728-15737.
92. Q. Shi, C. Zhu, H. Zhong, D. Su, N. Li, M. H. Engelhard, H. Xia, Q. Zhang, S. Feng, S. P. Beckman, D. Du and Y. Lin, ACS Energy Letters, 2018, 3, 2038-2044.
93. Y. Zhou, G. Zhang, M. Yu, X. Wang, J. Lv and F. Yang, ACS Sustainable Chemistry & Engineering, 2018, 6, 8437-8446.
94. I. Smirnova and P. Gurikov, The Journal of Supercritical Fluids, 2018, 134, 228-233.
95. L. Wang, Z. Sofer and M. Pumera, ACS Nano, 2020, 14, 21-25.
96. H. Maleki, L. Durães and A. Portugal, Journal of Non-Crystalline Solids, 2014, 385, 55-74.
97. P. H. Mutin and A. Vioux, Journal of Materials Chemistry A, 2013, 1.
98. Z. Chen, T. Wang and X. Yan, Journal of Applied Polymer Science, 2017, 134.
99. Z. Chen, T. Wang and Q. Yan, J Biomater Sci Polym Ed, 2018, 29, 309-324.
100. Z. Xu, W. Li, Z. Chen, D. Wang, T. Feng, H. Potapenko and M. Wu, Macromolecular Materials and Engineering, 2019, 304.
101. Z. Chen, T. Wang and X. Yan, Materials Letters, 2017, 197, 156-159.
102. J. A. Schwarz, C. Contescu and A. Contescu, Chemical Reviews, 1995, 95, 477-510.
103. M. Schneider and A. Baiker, Catalysis Reviews, 1995, 37, 515-556.
104. H. Maleki, L. Durães and A. Portugal, The Journal of Physical Chemistry C, 2015, 119, 7689-7703.
105. H. Maleki, L. Durães, B. F. O. Costa, R. F. Santos and A. Portugal, Microporous and Mesoporous Materials, 2016, 232, 227-237.
106. D. Nadargi, J. Gurav, M. A. Marioni, S. Romer, S. Matam and M. M. Koebel, J Colloid Interface Sci, 2015, 459, 123-126.
107. W. H. Lai, Z. Miao, Y. X. Wang, J. Z. Wang and S. L. Chou, Advanced Energy Materials, 2019, 9.
108. N. Leventis, N. Chandrasekaran, A. G. Sadekar, S. Mulik and C. Sotiriou-Leventis, Journal of Materials Chemistry, 2010, 20.
109. S. Mahadik-Khanolkar, S. Donthula, A. Bang, C. Wisner, C. Sotiriou-Leventis and N. Leventis, Chemistry of Materials, 2014, 26, 1318-1331.
110. W. Liu, A.-K. Herrmann, N. C. Bigall, P. Rodriguez, D. Wen, M. Oezaslan, T. J. Schmidt, N. Gaponik and A. Eychmüller, Accounts of Chemical Research, 2015, 48, 154-162.
111. J. Greeley, T. F. Jaramillo, J. Bonde, I. B. Chorkendorff and J. K. Norskov, Nature Materials, 2006, 5, 909-913.
113. J. Gu, C.-S. Hsu, L. Bai, H. M. Chen and X. Hu, *Science*, 2019, **364**, 1091-+

114. Z. Du, X. Chen, W. Hu, C. Chuang, S. Xie, A. Hu, W. Yan, X. Kong, X. Wu, H. Ji and L. J. Wan, *J Am Chem Soc*, 2019, **141**, 3977-3985.

115. Y. Hou, M. Qiu, M. G. Kim, P. Liu, G. Nam, T. Zhang, X. Zhuang, B. Yang, J. Cho, M. Chen, C. Yuan, L. Lei and X. Feng, *Nat Commun*, 2019, **10**, 1392.

116. Y. Gao, Z. Cai, X. Wu, Z. Lv, P. Wu and C. Cai, *ACS Catalysis*, 2018, **8**, 10364-10374.

117. J. Yang, Z. Qiu, C. Zhao, W. Wei, W. Chen, Z. Li, Y. Qu, J. Dong, J. Luo, Z. Li and Y. Wu, *Angew Chem Int Ed Engl*, 2018, **57**, 14095-14100.

118. Z. Gao, W. Yang, X. Ding, G. Lv and W. Yan, *Applied Surface Science*, 2018, **436**, 585-595.

119. Z. K. Yang, C.-Z. Yuan and A.-W. Xu, *Nanoscale*, 2018, **10**, 16145-16152.

120. Y. Xue, B. Huang, Y. Yi, Y. Guo, Z. Zuo, Y. Li, Z. Jia, H. Liu and Y. Li, *Nature Communications*, 2018, **9**.

121. G. Wan, P. Yu, H. Chen, J. Wen, C. J. Sun, H. Zhou, N. Zhang, Q. Li, W. Zhao, B. Xie, T. Li and J. Shi, *Small*, 2018, **14**, e1704319.

122. M. Nakahata, Y. Takashima, A. Hashidzume and A. Harada, *Angew Chem Int Ed Engl*, 2013, **52**, 5731-5735.

123. J. Duan, C. Han, L. Liu, J. Jiang, J. Li, Y. Li and C. Guan, *Journal of Spectroscopy*, 2015, **2015**, 1-6.

124. M. Nakahata, Y. Takashima, H. Yamaguchi and A. Harada, *Nat Commun*, 2011, **2**, 511.

125. Y.-F. Wang, K. Li and G.-C. Wang, *Applied Surface Science*, 2018, **436**, 631-638.

126. K. Alexopoulos, Y. Wang and D. G. Vlachos, *ACS Catalysis*, 2019, **9**, 5002-5010.

127. J. Hwang, S. H. Noh and B. Han, *Applied Surface Science*, 2019, **471**, 545-552.

128. K. Alexopoulos and D. G. Vlachos, *Chemical Science*, 2020, **11**, 1469-1477.