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Article type: Progress Report**Harnessing the Wisdom in Colloidal Chemistry to Make Stable Single-Atom Catalysts***Max J. Hülsey, Jianguang Zhang, and Ning Yan**

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Research on single-atom catalysts (SACs), or atomically dispersed catalysts, has been quickly gaining momentum over the past few years. Although the unique electronic structure of singly dispersed atoms enable uncommon—sometimes exceptional—activities and selectivities for various catalytic applications, developing reliable and general procedures for preparing stable, active SACs in particular for applications under reductive conditions remains a major issue. Herein, we highlight the challenges associated with the synthesis of SACs semi-quantitatively and propose three stabilization techniques inspired by colloidal science including steric, ligand and electrostatic stabilization. Some recent examples are discussed in detail to showcase the power of these strategies in the synthesis of stable SACs without compromising catalytic activity. The substantial further potential of steric, ligand and electrostatic effects for developing SACs is emphasized. A perspective is given to point out opportunities and remaining obstacles, with special attention given to electrostatic stabilization where little has been done so far. We believe that the stabilization strategies presented herein have a wide applicability in the synthesis of a series of new SACs with improved performances.

1. Introduction

A significant portion of noble metals produced on earth are used as supported catalysts, including 40.0% Pt, 79.5% Pd and 80.9% Rh.^[1] Due to the limited availability and imminent depletion of many catalytically relevant transition metals, it is desirable to utilize every atom in heterogeneous catalytic applications where conventionally only surface metal sites directly contribute to a reaction.^[2] Single-atom catalysts (SACs) represent a potential solution to the problem since all atoms are atomically dispersed and are accessible to reactants. The past five years have witnessed an exponential growth in this area, with many single-atom catalytic systems being developed and applied in a broad spectrum of reactions in thermo-,^[3] electro-^[4] and photocatalysis.^[5] As evident from **Figure 1a**, the research interests span a wide variety of 3d-5d elements, while five elements, namely Ru, Rh, Pd, Pt or Au, are particularly important that consistently account for over 50% of all research articles.

Although the immobilization of positively charged species on inorganic supports can be achieved at relatively high weight loadings,^[6] those isolated metal species tend to aggregate under reductive conditions and thus the synthesis of stable and active SACs remains a considerable challenge for reactions under non-oxidative conditions. Many SACs can be prepared by conventional impregnation and precipitation techniques but the metal loadings are normally low and the catalysts often exhibit unfavorable stability upon treatment at elevated temperatures. More sophisticated and specialized procedures have been reported recently using photochemical,^[4d, 7] selective post-synthetic leaching,^[3e] high-temperature atom trapping^[8] or atomic layer deposition strategies.^[3l, 9] Isolated metal atoms have also been stabilized by alloying them into a phase with a second metal, normally in large excess, to reach a sufficient physical separation.^[3b, 3g, 3k, 10] Nevertheless, these newly developed

methodologies may still suffer from issues such as limited scalability and general applicability, and/or unsatisfactory long-term stability under industry relevant reaction conditions.

The reason why it is particularly challenging to synthesize stable single-atom catalysts is shown in **Figure 1b**. For frequently employed transition metals in catalysis, the energy difference (ΔE) between the cohesive energy between metal atoms in the bulk phase and the thermodynamic driving force to form metal-oxygen bonds is generally positive, i.e., thermodynamically it is more favorable to form M–M bonds rather than M–O bonds. Interestingly, the ΔE values for Ru, Rh, Pd, Pt and Au all lay within the range of 100-200 kJ/mol, implying that additional means of stabilization during or after the SAC synthesis need to be considered for those most frequently employed heavier transition metals. Carbon sites seem to provide better protection to Rh and Pt, but the stabilization is still inadequate for Ru and Ir (**Figure S1**). For nitrogen site protection, no substantial conclusion could be drawn due to very limited availability of the thermodynamic data (**Figure S2**).

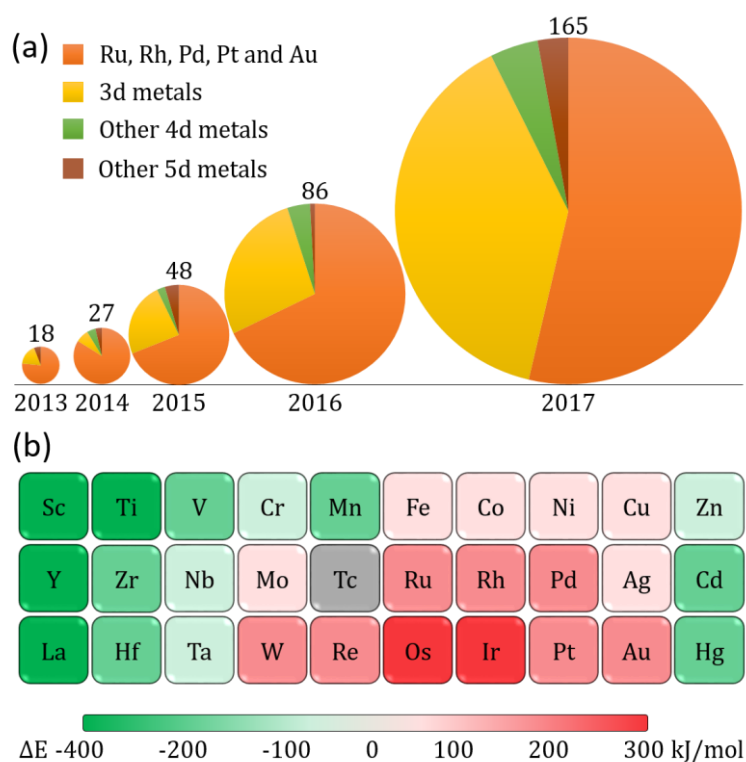


Figure 1. (a) Amount of publications on SACs for different transition metal groups (based on a Web Of ScienceTM search for the keywords ‘Single-atom catalyst’ OR ‘Atomically dispersed catalyst’) over the past five years. (b) Difference (ΔE) between the cohesive energy between metal atoms in the bulk phase and the thermodynamic driving force to form metal-oxygen bonds in kJ/mol. The lowest value indicates the highest stability of M–O bonds and thus the lowest tendency to form metal particles. Due to the limited availability of experimental thermodynamic data, technetium is not considered here.^[11]

We argue that several strategies commonly used in stabilizing colloids may be equally applicable to the stabilization of SACs. In colloidal science, the foremost challenge is the stabilization of small particles in a continuous medium, mainly through three stabilization principles. For steric stabilization, the contact between particles is physically prohibited for example by encapsulating nanoparticles inside cavities of polymers or other porous materials.^[12] Electrostatic stabilization is achieved by adding additional charges around the particles so that the Coulombic repulsion outweighs attractive van der Waals forces.^[13] Stabilizing colloids by attaching organic ligands to particle surface probably is the most obvious stabilization technique mimicking the situation in bio- and homogeneous catalysts, which is particularly powerful for stabilizing metal nanoparticles.^[14] A schematic representation of how those three stabilization principles can be applied to the synthesis of SACs is shown in **Figure 2**. Without any additional stabilization, many metal atoms tend to be mobile on the catalyst surface and thus form particles. If isolated atoms are encapsulated in small cages or placed on spatially separated ‘islands’ that prohibit their direct interaction, SACs are sterically stabilized. Similarly, a charged electrostatic layer can be used to cover the SAC to prevent two atoms approaching each other. In a broad sense, both organic functional groups with a strong affinity to metals and adsorption sites on various inorganic supports can be considered as ligands providing coordination protection.^[15] While these strategies are often employed in the synthetic procedures to prevent atom aggregation during catalyst preparation, they could also be exerted to pre-synthesized SACs to enhance their stability during catalytic reactions.

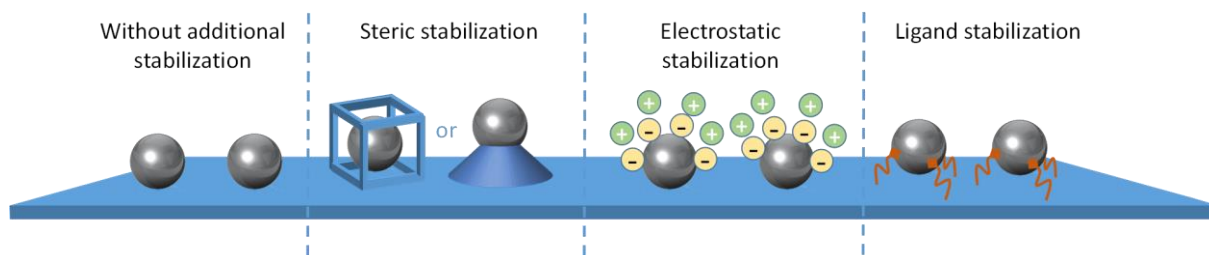


Figure 2. Schematic representation of stabilization principles in colloidal chemistry applicable to the synthesis of stable single-atom catalytic systems. Note that the structure of the final SACs may be different from their precursors.

Although the techniques stabilizing colloids (e.g., nanoparticles) are directly transferrable to the stabilization of SACs, the two have fundamental differences. While steric and electrostatic stabilizations in colloidal stabilization are generally regarded as a kinetic phenomenon, these effects, when exerted on isolated, positively charged metal atoms, bring about an additional thermodynamic stabilization effect. Entropically, SACs are favored as the number of microscopic configurations within the system would increase if metals are isolated in contrast to the case of nanoparticles. As the entropy proportion of the Gibbs free energy vastly depends on temperature, single-atom catalysts have been shown to form spontaneously at elevated temperatures both experimentally^[8] and by simulation^[16]. Colloidal systems, however, are different as upon agglomeration the amount of possible structures increases dramatically and thus in most cases the vibrational and sometimes the rotational entropy increases.^[17] Another key distinction is that stabilized colloidal systems are often designed so that diffusion in solution is unprohibited but that the kinetic barrier for aggregation is sufficiently high. Isolated atoms in SACs, however, are commonly prohibited in surface-diffusion by confinement or strong binding so that aggregation events only seldom occur. In general, no single stabilization principle may be sufficient to make SACs, given the substantial thermodynamic driving force for most metal atoms to aggregate. Multiple

strategies are often employed simultaneously in which no clear distinction can be made, as will be seen in most of the examples discussed below.



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Ning Yan was born in Sichuan, China. He received his B.Sc. and Ph.D. degrees in Chemistry from Peking University in 2004 and 2009, respectively, working with Prof. Yuan Kou. After a stay at École Polytechnique Fédérale de Lausanne in Switzerland as a Marie Curie Fellow with Prof. Paul Dyson, he joined the Department of Chemical and Biomolecular Engineering at the National University of Singapore as an Assistant Professor. The research topics of his group mainly concern advanced catalysis, renewable energy and sustainable chemicals.

2. Active stabilization strategies

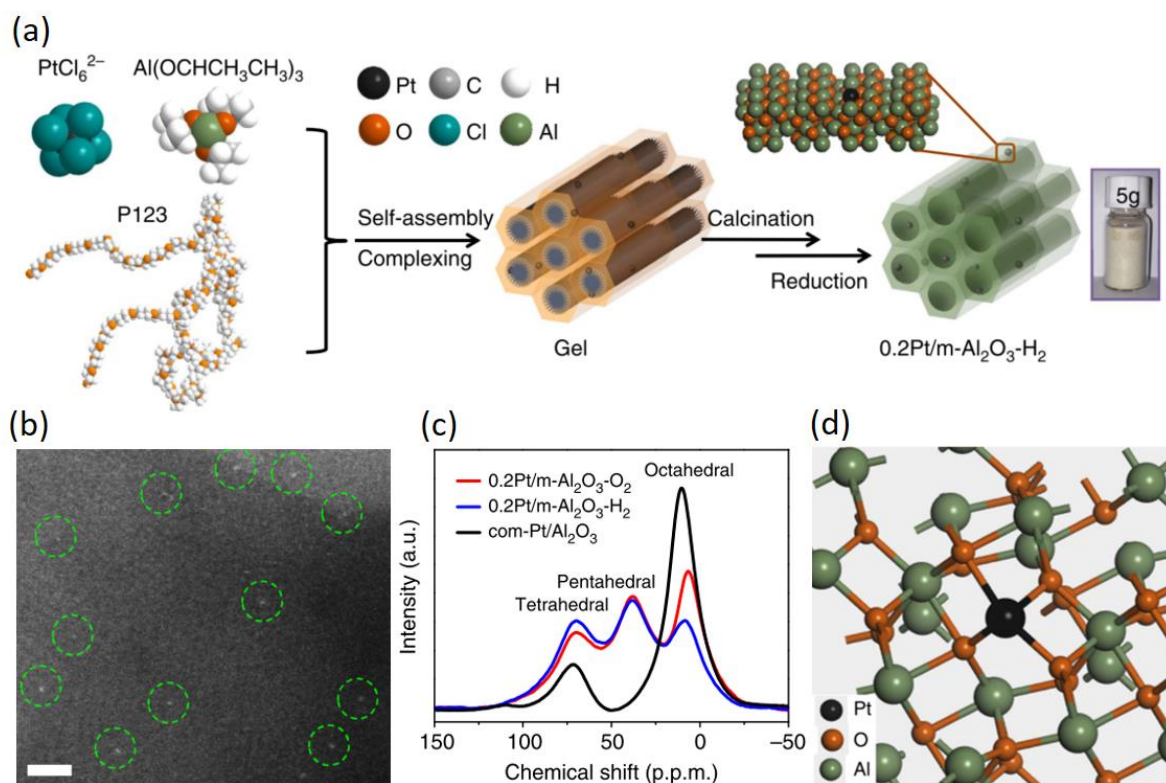


Figure 3. Synthesis of a stable platinum SAC supported on mesoporous alumina by means of steric and ligand stabilization. (a) Schematic synthetic procedure using a sol-gel method on a multiple gram-scale starting from a common platinum salt, an aluminum alkoxide and a commercial polymer. (b) ^{27}Al MAS-NMR spectra for different platinum-containing catalyst samples. (c) High-resolution TEM images of the SAC. (d) Proposed structure of the local environment around the isolated platinum atoms. Adapted under the terms of the CC-BY 4.0 license.^[3m] Copyright 2017, Nature Publishing Group.

Recently, our group has reported a highly stable SAC following a synthetic procedure that adheres to the principles of colloidal chemistry. A mixture of a platinum salt, P123 (an amphiphilic block copolymer) and aluminum alkoxide self-assemble into a gel that yield stable SACs upon calcination and reduction. It is assumed that the aluminum alkoxide precursor forms a stable aggregate with PtCl_3^- species formed by reduction with ethanol, while P123 ensures the formation of a mesoporous alumina matrix during the calcination (**Figure 3 a**, material referred to as $0.2\text{Pt}/\text{m-Al}_2\text{O}_3\text{-H}_2$). Indeed, a reference material prepared without P123 (referred to as $0.2\text{Pt}/\text{p-Al}_2\text{O}_3\text{-H}_2$) exhibited a collapsed pore structure and sintered platinum particles. According to various spectroscopic evidence and high resolution

transmission electron microscopy (TEM) (**Figure 3 b**), 0.2Pt/m-Al₂O₃-H₂ predominantly contained isolated platinum atoms. Based on ²⁷Al MAS-NMR, high amounts of pentahedrally coordinated Al³⁺ species were identified (**Figure 3 c**) which are critical to the extraordinary stability of isolated atoms on aluminum oxide.^[18] Combining the experimental evidence, we came to the conclusion that the majority of platinum species have a configuration as depicted in **Figure 3 d**, where isolated metal atoms are bound to under-coordinated aluminum sites *via* oxygen bridges. The obtained SAC exhibited high stability in the oxidation of carbon monoxide at 400 °C for a time span of around 225 h, hydrogenation of butadiene and reforming of *n*-hexane at 550 °C for about 12 hours. The latter one is particularly challenging due to the high reaction temperature and the formation of hydrogen gas – a strong reducing agent – as side-product. Overall, trapping metal precursors inside a gel during the synthesis and then confining the isolated metal atoms inside specialized binding sites (ligand stabilization) in a mesoporous matrix (steric stabilization) seems to be a viable strategy to produce extremely stable SACs. By utilizing other supports, the crucial interaction between the support and the metal species can be further tuned and investigated.^[19]

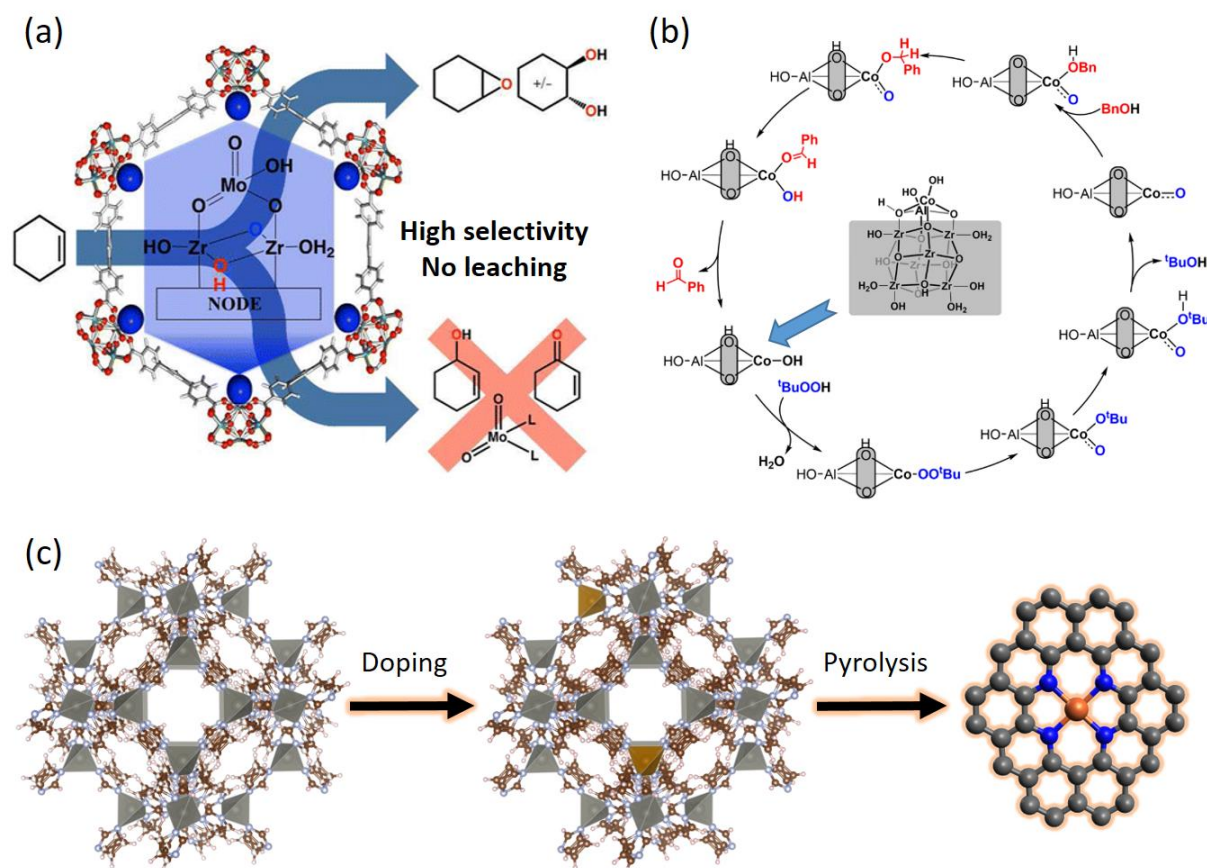


Figure 4. Single-atom catalysts supported on MOFs. (a) Isolated molybdenum atoms on NU-1000 selectively oxidizes cyclohexene. Reproduced with permission.^[20] Copyright 2016, American Chemical Society. (b) Mechanism of the benzyl alcohol oxidation on NU-1000-supported cobalt single atoms determined by DFT calculations. The model in the middle represents the structure indicated by the blue arrow. Adapted with permission.^[21] Copyright 2016, American Chemical Society. (c) Doping ZIF-8 with heteroatoms followed by high-temperature pyrolysis yields stable single-atom catalysts.

Another type of commonly used porous materials are metal-organic frameworks (MOFs) featuring tunable morphology, composition and porosity.^[22] Two major approaches have been developed for the stabilization of isolated metal atoms inside MOFs. One relies on the strong adsorption of metals on the *O*- or *N*-containing nodes and the other on the formation of strong adsorption sites during pyrolysis of the crystalline material. Besides offering suitable binding sites, another crucial factor for enhancing stability is the small pore size of MOFs, which severely restricts the movement of atoms and growth of clusters and particles.

The immobilization of molybdenum species has been achieved on zirconium-nodes of NU-1000 showing a high activity and selectivity in the oxidation of cyclohexene (**Figure 4 a**). In

contrast to molybdenum supported on zirconia which suffers from metal leaching, no decrease in the catalytic activity was observed after three subsequent catalytic reactions.^[20] Similarly, cobalt-aluminum complexes have been deposited on zirconium nodes of NU-1000 and the ligand were removed under mild conditions to yield isolated cobalt atoms in proximity to aluminum active in the oxidation of benzyl alcohol. Due to the structural simplicity, this SAC is a good system to study the reaction mechanism based on DFT calculations (**Figure 4 b**).^[21] Doping transition metals such as nickel, iron or copper into zinc-based ZIF-8 leads to a range of ion-exchanged MOF materials. Subsequent pyrolysis at temperatures up to 900 °C leads to the evaporation of zinc and yields isolated metal atoms embedded in a nitrogen-containing carbon matrix with high metal loading and good reactivity for CO₂ electroreduction and the oxygen reduction reaction.^[23] Different structures for the active sites have been proposed by DFT calculations ranging from near-ideal four-fold nitrogen-bonded sites to less-ideal cases of lower coordination to nitrogen or carbon atoms.^[24] Recently, it was shown that copper species in ion-exchanged zeolites for the catalytic reduction of NO_x form multinuclear sites during the catalytic reaction, indicating a certain mobility throughout different pores and tendency to form dimeric species rather than remain as isolated atoms even when they are confined in small pores.^[25] The tendency of isolated atoms to migrate on porous supports does not only hamper the catalytic activity but may have detrimental effects on the stability of certain supports.^[26] Therefore, the necessity to finetune collaborative contributions of specific binding sites and small cavities that can effectively promote the formation and stability of SACs by steric stabilization strategies cannot be stressed enough.

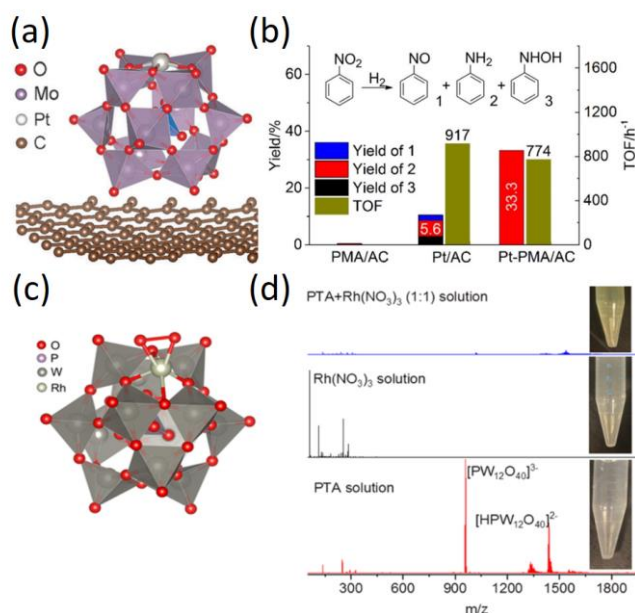


Figure 5. SACs on two different heteropoly acids. (a) Structural model for Pt₁ on phosphomolybdic acid supported on activated carbon. (b) Performance of the platinum SAC compared to a commercial catalyst for the hydrogenation of nitrobenzene. Adapted with permission.^[3ai] Copyright 2016, Wiley. (c) Structural model for Rh₁ on self-assembled phosphotungstic acid. (d) ESI-MS spectra for a mixture of the rhodium salt and the heteropoly acid and each component alone. Adapted with permission.^[27] Copyright 2017, American Chemical Society.

One type of support that offers particularly strong adsorption sites are heteropoly acids, which is a group of solid acids containing oxygen and various metals or non-metals. They offer different possible sites for adsorption but based on our DFT calculations, only the most stable ones on phosphomolybdic acid have been approximated to stabilize isolated platinum atoms by around 550 kJ/mol, very similar to the cohesive energy of metallic platinum (around 550 kJ/mol), and are thus suitable to prevent particle formation. If those platinum-containing heteropoly acids are then immobilized on a support like activated carbon, they act as small ‘islands’ preventing the diffusion of platinum atoms and prohibiting the nucleation and growth of metal particles (**Figure 5 a**). With that strategy, we achieved metal weight loadings close to 1 wt%, much above many other noble metal-based SACs which often have to aim for values below 0.1 wt%. The SAC was superior by at least six times in the hydrogenation of cyclohexanone compared to the commercial platinum catalyst indicating an improved reduction capability towards polar functional groups. Its activity was comparable to

commercial catalyst in nitrobenzene hydrogenation with a superior selectivity to certain products (**Figure 5 b**).

Upon attempts to further extend the synthetic procedure towards several other heteropoly acids and catalytically active metals, we found that a mixture of phosphotungstic acid and rhodium nitrate self-assemble spontaneously in a one to one ratio in an aqueous solution (**Figure 5 c and d**). Surprisingly, the obtained SAC could be used without further supporting the heteropoly acids, showed excellent activity in the CO oxidation and proves that an additional support is not even necessary to prevent the diffusion of rhodium atoms between the heteropoly acid ‘islands’. Due to the high metal loading and very precise structure of anchoring site, we propose that SACs based on heteropoly acids offer an excellent platform to systematically investigate the stability and catalytic mechanism both theoretically and experimentally.^[3r, 28]

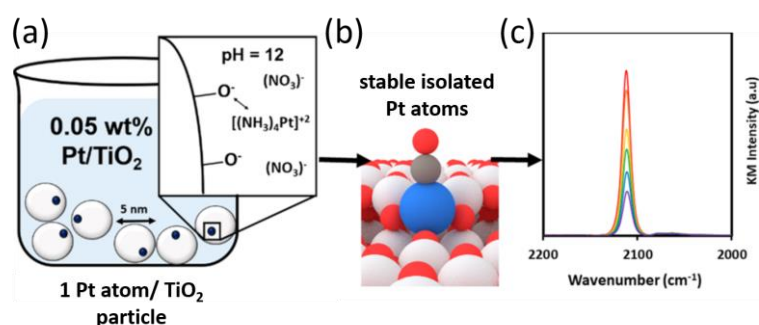


Figure 6. (a) Synthetic approach toward stable SACs using a strong electrostatic adsorption method on small titanium dioxide islands; (b) representation of carbon monoxide adsorbed linearly on isolated platinum atoms and (c) the corresponding infrared absorption spectrum. Adapted with permission.^[3j] Copyright 2017, American Chemical Society.

The aforementioned “islands” do not need to be heteropoly acids but can be more conventional supports such as titanium dioxide. It has been recently reported that finely dispersed titanium dioxide nanoparticles (~ 5 nm) expose excellent adsorption sites for certain metal precursors when the synthesis is performed under very basic conditions. Those conditions not only help for a better dissolution and dispersion of the support nanoparticles in

solution but also deprotonate ubiquitous surface hydroxyl groups. The negatively charged groups then exert a strong Coulombic attraction to positively charged metal precursors (**Figure 6 a**). If the stoichiometry between titanium dioxide nanoparticles and metal salt is tuned appropriately, it is assured that on average less than one metal atom resides on one support nanoparticle increasing the energetic barrier for the sintering of isolated atoms to metal particles (**Figure 6 b and c**). The obtained SACs are stable under high temperature treatment under various atmospheres (**Figure 6**).^[3j, 29]

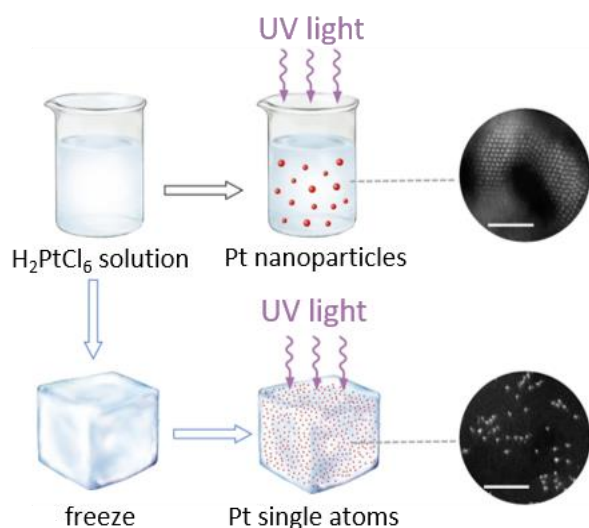


Figure 7. Freezing a solution of metal precursor followed by the UV-light induced reduction can lead to the formation of highly dispersed SACs. Adapted under the terms of the CC-BY 4.0 license.^[4d] Copyright 2017, Nature Publishing Group.

A very straight-forward synthetic approach to prevent the movement of isolated atoms was recently reported by Wei et al.,^[4d] where a homogeneous solution of a metal precursor (H_2PtCl_2 , AgNO_3 or HAuCl_4) in water was frozen and then reduced by UV light (**Figure 7**). This simple protocol yielded almost entirely isolated species whereas the direct reduction of the metal salt solution resulted in the formation of nanoparticles. After forming single atoms in the solution, various supports such as mesoporous carbon, graphene, titanium dioxide nanoparticles as well as zinc oxide nanowires were used to stabilize the metal atoms for

catalytic hydrogen evolution reaction. This study demonstrates that employing a steric barrier during the reduction of the metal precursor led to the formation of isolated atoms even in an aqueous solid matrix that can then be transferred and bind strongly to suitable adsorption sites.

3. Future perspective & concluding remarks

Future research should be devoted to developing more methodologies that are reliable and reproducible for the synthesis of a broad range of single atom catalysts based on various metal atoms and supports. Those advances should be guided by a (semi-)quantitative understanding about thermodynamic and kinetic phenomena affecting the stability of SACs. Knowledge originating from colloidal chemistry provides useful tools to achieve stable SACs: the effectiveness of using steric hindrance and coordination to enhance the stability of SACs have already been adequately demonstrated, and these strategies are to be further explored to release their full potential.

Electrostatic stabilization at present is only a viable tool to synthesize colloids, but it may become a simple, feasible strategy to stabilize SACs. We propose to deposit a layer of charged material to cover the isolated metal atoms during a postsynthetic treatment of SACs, and thus stabilize them against surface diffusion and agglomeration. The electrostatic forces provided by the electric double layer normally ranges from several dozen to over a hundred kilojoules per mole, matching well with the gap between M-M bond and M-O bond energy differences (ΔE) (**Figure 8**).^[30] This charged overlayer could be a bifunctional polyelectrolyte, either exhibiting both charges on a single (polyampholytes)^[31] or on two separate polymer backbones.^[32] The latter probably offers more possibilities to combine and tune the properties of the SAC. Ionic liquids are another class of materials highly suitable for the electrostatic stabilization of SACs due to their inherent ionic nature, high stability and known complexation properties towards transition metals.^[33] Recently, atomically dispersed iridium single-site catalyst have been modified by using a coating of different ionic liquids and this approach was shown to significantly alter the selectivity in the partial hydrogenation of butadiene.^[34] It highlights that constructing an ionic layer on SACs is technically viable, and the charged layer influences the electronic state of the metal center, which subsequently should affect the stability of the SACs. Along the same line, the immobilization of frustrated

Lewis pairs on SACs could both enhance their stability and create a more reactive environment for the activation of small molecules such as CO_2 and H_2 as has been shown before in homogeneous and heterogeneous catalytic systems.^[35]

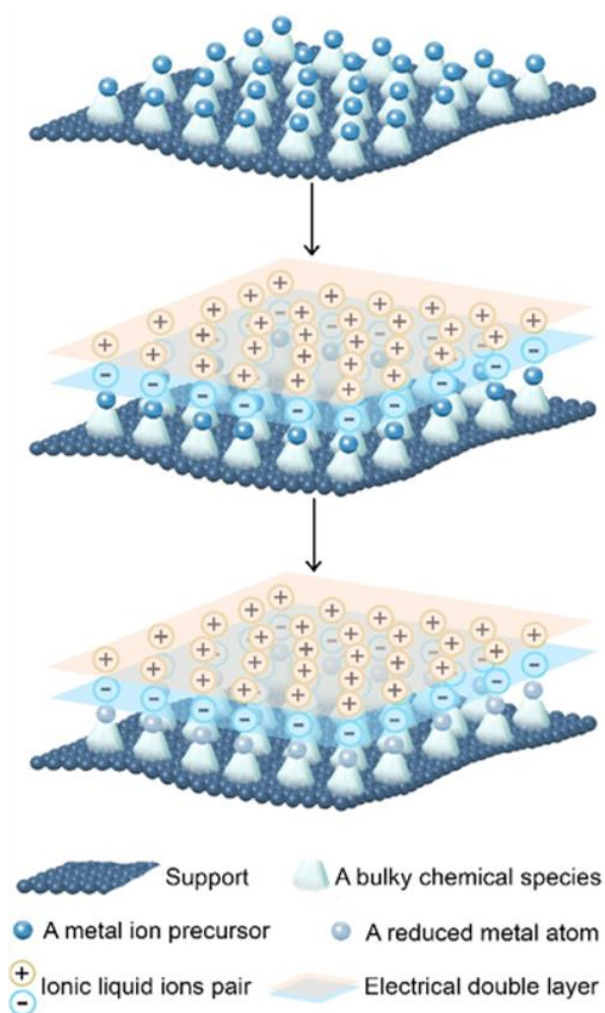


Figure 8. Adding a layer of charged material on top of anchored single atoms before reduction can increase their stability.

A range of questions remain to be addressed regarding the stability of SACs:

1. Does a correlation between the stability and activity of SACs exist? A logical understanding is that more stabilized isolated atoms are associated with a reduced free energy and decreased specific activity. This should be proven or refuted with quantitative analysis, thus providing a guidance of the ultimate stability that a metal atom can reach before it becomes catalytically inactive.

2. How can we create homogeneous adsorption sites that are suitable for the stabilization of SACs? The heterogeneity of SACs has been highlighted recently and severely hampers our understanding of catalytically active sites.^[31, 36] Creating strong and uniform adsorption sites for isolated atoms, such as the case for heteropoly acids, is thus critical.

3. What postsynthetic treatment is suitable to enhance the stability, activity or selectivity of SACs? General methods (e.g., introducing an electrical double layer as proposed in this article) for the alteration of the stability prior to reduction or the modification of the chemical environment around active sites favoring the formation of certain products should be developed.

We believe conventional wisdom to stabilize colloidal solutions accumulated in over a century could help to answer those questions, and potentially give rise to new generations of SACs.

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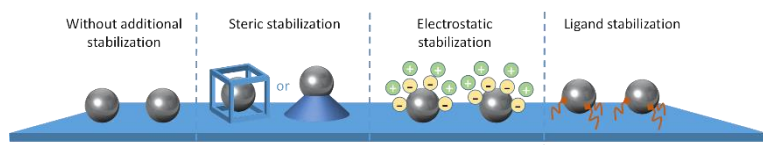
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Teach a young dog old tricks. Conventional knowledge from colloidal science can be employed to stabilize isolated metal atoms for catalytic applications. Critical challenges in the field of single-atom catalysis alongside recent advances in developing strategies to overcome stability issues and future directions will be showcased and discussed.

Keywords: atomically dispersed, catalyst syntheses, colloidal sciences, heterogeneous catalysis, atom efficiency

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Harnessing the Wisdom in Colloidal Chemistry to Make Stable Single-Atom Catalysts



Supporting Information

Harnessing the Wisdom in Colloidal Chemistry to Make Stable Single-Atom Catalysts

Max J. Hülsey, Jianguang Zhang, and Ning Yan*

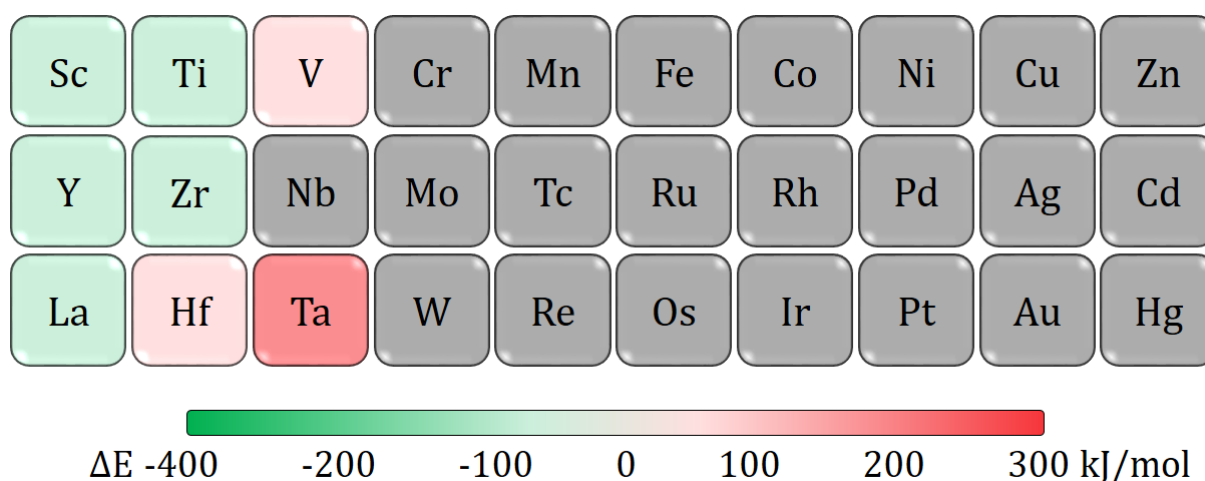


Figure S1. Difference (ΔE) between the cohesive energy between metal atoms in the bulk phase and the thermodynamic driving force to form metal-nitrogen bonds in kJ/mol. The lowest value indicates the highest stability of M–N bonds and thus the lowest tendency to form metal particles. For the elements in grey, no data is available.^[11]

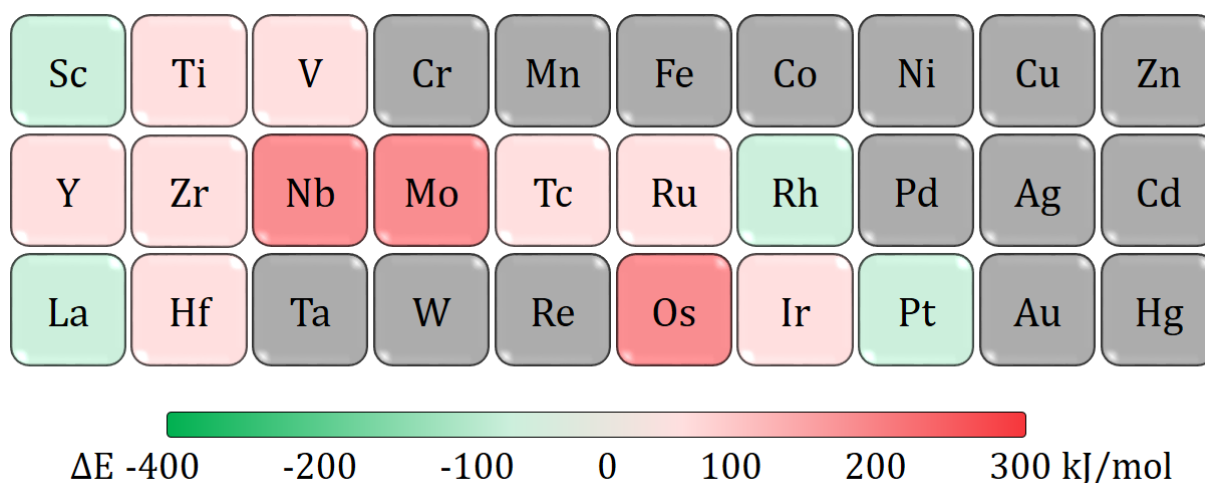


Figure S2. Difference (ΔE) between the cohesive energy between metal atoms in the bulk phase and the thermodynamic driving force to form metal-carbon bonds in kJ/mol. The lowest value indicates the highest stability of M–C bonds and thus the lowest tendency to form metal particles. For the elements in grey, no data is available.^[11]