



Single-atom catalysis: A practically viable technology?

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Recent advances in single-atom catalysis resulted in readily accessible materials whose application in most catalytic reactions mediated by conventional nanoparticle-based catalysts often results in higher activity and selectivity. Can we expect catalysis by atomically dispersed atoms to find practical applications? Which are the hurdles to be overcome before widespread uptake of atomically dispersed metals in industrial synthetic processes and in hydrogen fuel cells?

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Introduction

Single-atom catalysis (SAC) became a well-established field of contemporary chemical research in less than a decade since the introduction of the term by Qiao et al. in 2011, when the team based in China reported that single Pt atoms supported on FeOx are both active and markedly stable for CO oxidation [1]. Eight years before, Fu et al. in the United States had discovered that nonmetallic gold or platinum species strongly associated with surface cerium-oxygen groups in ceria, and not Au or Pt nanoparticles (NPs), were actually responsible for the activity observed

in the water–gas shift reaction [2]. Comprehensive review [3] and perspective [4] articles have been devoted to the topic, including entire themed issues [5] and reviews focusing on applications of single atom (SA) catalysts in synthetic organic chemistry [6]. Readers are referred to the aforementioned studies, as well as to the recent accounts of Wang et al. [7] and Mitchell et al. [8], to understand how single atoms get stabilized on various supports and the unique features dictating the performance of SA relative to conventional NP catalysts. From a structural viewpoint, contemporary surface science has been and will continue to be instrumental to unravel the unique structural features of these materials [9].

In general, metal atoms in heterogeneous single-atom catalysts are bound to the support surface through heteroatoms such as oxygen and nitrogen or defective metal active sites. Successful synthetic approaches include single atom metal anchoring [10], alloying [11], or atomic layer deposition [12]. Selected exemplary applications of the catalysts thereby obtained include Pt/Al₂O₃ and Pt/CeO₂ for selective hydrogenation and CO oxidation [13], Pt/graphene in electro-oxidation of methanol [14], and non-precious metals such as Fe, Cu, Cr, Co, and Ni on nitrogen-containing carbon in alcohol oxidative dehydrogenation [15]. Remarkably, Malta et al. in 2017 discovered via an *in situ* X-ray absorption fine structure investigation of Au/C catalyst under acetylene hydrochlorination reaction conditions that the active species are coexisting single-site Au⁺ and Au³⁺ cations [16].

Focusing on potential practical application of single-atom catalysis and referring to three selected research outcomes, we aim we provide an answer to a few critical questions in the context of the emerging solar economy in which useful substances and energy will originate, respectively, from biological resources and from solar energy [17].

Can we expect SAC to become a technically and economically viable technology suitable to find application in the chemical industry and in commercial hydrogen fuel cells? Which are, if any, the hurdles to be overcome for single-atom catalysis before become ubiquitous?

Potentially disruptive technologies

Following Christensen, an innovation is called ‘disruptive’ as it eventually displaces established market-leading products and solutions [18]. The three

examples of SAC discussed below hold a disrupting innovation potential in synthetic organic chemistry, in the production of solar hydrogen from water, and in electricity generation in hydrogen fuel cells.

Synthetic organic chemistry

Recently, Zhang et al. in China and in the US reported how a TiO_2 -based catalyst anchoring singly dispersed Pd atoms (Pd_1/TiO_2) is highly selective and highly active for more than 10 Sonogashira C–C coupling reactions ($\text{R}\equiv\text{CH} + \text{R}'\text{X} \rightarrow \text{R}\equiv\text{R}'$; $\text{X} = \text{Br}, \text{I}$; $\text{R}' = \text{aryl or vinyl}$) carried out on 1–2 mmol scale [19].

The catalyst (Figure 1) exhibits high activity and selectivity for C–C couplings between aryl halide ($\text{X} = \text{I}$ and Br) and different terminal alkynes, with the usual lower activity toward chlorobenzene (the C–Cl bond is much stronger than C–Br and C–I bonds) observed with NP catalysts.

In further detail, coupling between iodobenzene and phenylacetylene on 0.20 wt% Pd_1/TiO_2 exhibits a turnover rate of 51 diphenylacetylene molecules per anchored Pd atom per minute at 60°C , with a low apparent activation barrier for the same C–C coupling of 28.9 kJ/mol, and straightforward catalyst separation. For comparison, the activation barrier of C–C coupling of phenylacetylene and iodobenzene catalyzed by molecular catalyst $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ in solution is 51.7 kJ/mol.

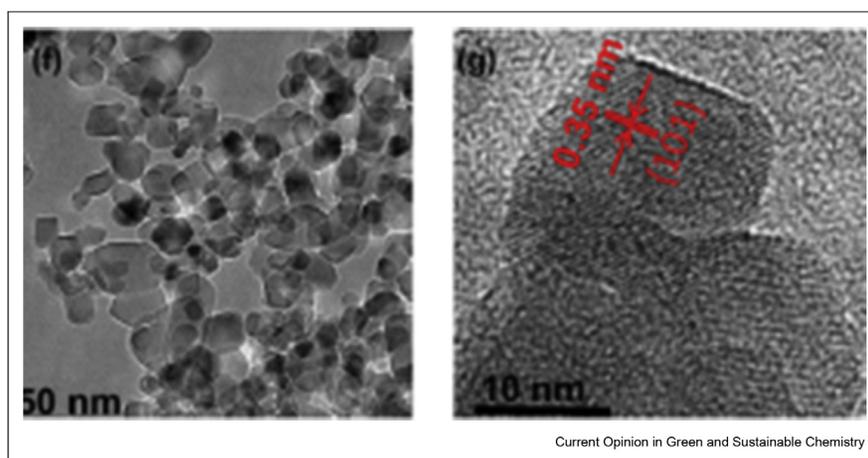
Calculations suggest that the single Pd atom bonded to surface lattice oxygen atoms of TiO_2 acts to dissociatively chemisorb iodobenzene to generate an intermediate phenyl, which then couples with phenylacetylenyl bound to a surface oxygen atom. This coupling of phenyl adsorbed on Pd_1 and phenylacetylenyl bound to O_{ad} of

TiO_2 forms the diphenylacetylene product molecule [19]. Repeated catalytic tests showing stable catalytic activity, though on the usual 1–2 mmol scale of most academic research papers, confirmed the durability of Pd_1/TiO_2 .

Along similar lines, Chen et al. elegantly reported how Pd atoms anchored on exfoliated graphitic carbon nitride (Pd-ECN) capture the advantages of both homogeneous and heterogeneous catalysts in C–C couplings (Suzuki–Miyaura), with an additional robust stability under flow conditions [20]. This material surpasses the performance of state-of-the-art homogeneous catalysts and conventional heterogeneous catalysts based on nanoparticles or grafted molecular complexes, without evidencing metal leaching or aggregation upon reaction completion. The authors nicely explained the enhanced properties with studies at the molecular level, showing how carbon nitride can enable an adaptive coordination to palladium, participating at the same time in the adsorption, stabilization, and activation of substrates and intermediates. The support provides a ligand-like stabilization which minimized catalyst deactivation even under continuous flow conditions [20].

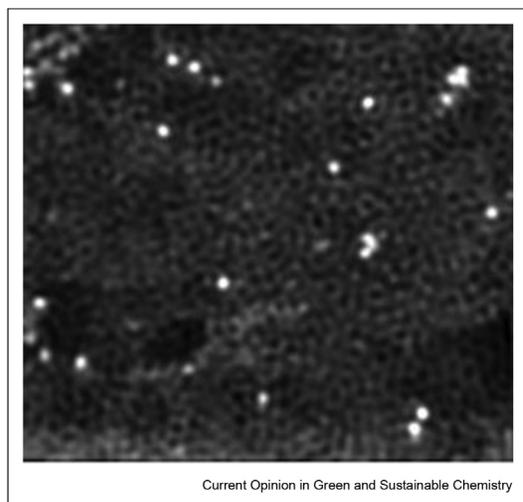
One remarkable recent achievement is the combination of Ru_1/CeO_2 and Rh_1/CeO_2 SACs allowing the synthesis of terminal organosilane compounds with high regioselectivity (>95%) via olefin isomerization and hydrosilylation in one pot, along with easy catalyst recycling and reuse [21]. Showing evidence of the similarity of heterogeneous single-atom catalysis with homogeneous catalysis, catalysis at monoatomic Ru and Rh sites respectively ensures reaction specificity for olefin double-bond migration and *anti*-Markovnikov α -olefin hydrosilylation.

Figure 1



TEM images of 0.20 wt% Pd_1/TiO_2 catalyst particles at different high-resolution (Reproduced with permission from Ref. [19]).

Figure 2



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TEM of Co on N-doped graphene. White spots correspond to Co atoms [Photo courtesy of Professor James M. Tour, Rice University].

Indeed, as put it by Parkinson [22], knowledge in homogeneous catalysis serves as inspiration for developing new SACs based on better understanding of coordination effects of metal adatoms adsorbed at the surface of different supports, including oxides, carbon, carbon nitride, and graphene [23].

Solar hydrogen from water

In the emerging solar economy in which sun, wind, and water will be the renewable energy sources for all end energy uses [24], renewable hydrogen generated splitting water via both concentrated solar power and electrolysis will emerge as key clean fuel [25].

Hydrogen refueling stations installed across the world will make use of water electrolysis to generate hydrogen gas on site. The gas is then compressed at the required 350 or 700 bar at which H₂ is dispensed at hydrogen fuel cell cars, buses, and trucks. Today, most water electrolyzers use alkaline water electrolysis relying on nickel to mediate both the hydrogen evolution reaction at the cathode and oxygen evolution reaction at the anode (nickel-plated mild steel) [26]. Therefore, the production of solar hydrogen at the large scale needed by massive deployment of hydrogen fuel cell electric vehicle will greatly benefit from advances in the electrode catalytic performance (lower voltage and reduced energy demand) [27].

In 2015, a joint team of scholars in China and in the US led by Tour reported that single cobalt atoms at the surface of graphene doped with nitrogen efficiently mediate the hydrogen separation from water [28]. The resulting electrocatalyst was found to be robust and highly active in both basic and acidic conditions with very low over-potential (30 mV).

TEM analysis shows cobalt atoms widely dispersed throughout the graphene sheets (Figure 2). The N-doped graphene molecular sheets have a dual important role, enabling high electron mobility and strong metal-support interaction. Thanks to strong coordination between the Co and N atoms, the electrocatalyst shows a negligible decrease in activity after 10 h of accelerated degradation studies in both acid and base conditions. In detail, the cathodic polarization curves obtained after 1000 continuous cyclic voltammograms showed a negligible decrease in current density compared with to initial values, whereas extensive characterization of the catalyst suggests that cycling operation did not change the atomic Co dispersion or the chemical states of Co and N [28].

Finally, the catalyst synthetic protocol is simple and highly reproducible involving only sonication of graphene oxide (GO) in the presence of CoCl₂•6H₂O dissolved in water (weight ratio GO/Co = 135:1), followed by freeze-drying to minimize re-stacking of the GO sheets and calcination of the dried sample under an Ar/NH₃ atmosphere at 750°C [28].

Low platinum and platinum-free fuel cells

Today's hydrogen fuel cell cars contain on average about the same amount of Pt contained in the catalytic converters of diesel vehicles (3–7 g, depending on size and power of the automobile) [29].

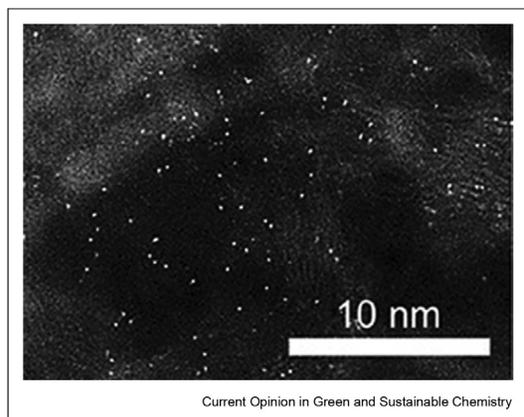
To put progress into perspective, thanks also to a new alloyed platinum catalyst now dispersed onto a solid core-type carbon support, the new 'Mirai' H₂ fuel cell car commercialized in 2015 by a Japan's carmaker contains less than half the amount of Pt contained in the 2008 FCV model of the same manufacturer, with a >2 larger volumetric power density than the previous version (3.1 kW/L vs 1.4 kW/L) [30].

In 2016, Kamai *et al.* achieved a 10-fold reduction in the amount of Pt needed in the electrocatalytic hydrogen oxidation in polymer electrolyte membrane fuel cell by replacing commercial 20 wt% Pt/C with a 2.8 wt% single atom Pt catalyst comprised of covalent triazine framework (Pt₁/CTF) with atomically dispersed Pt atoms [31] (see Figure 3).

The electrocatalytic activity of the resulting electrode in hydrogen oxidation reaction proceeds on single Pt atoms and requires almost no activation energy. Hence, the activity was dramatically higher when compared with that of commercial Pt/C.

In detail, the maximum power density of the membrane electrode assembly (an assembled stack of proton exchange membranes, catalyst, and flat plate electrode used in polymer electrolyte membrane fuel cells) using

Figure 3



High-angle annular dark-field scanning transmission electron microscopy photograph of covalent triazine framework functionalized with Pt developed by Kamai et al (Reproduced with permission from Ref. [31]).

the single-atom Pt catalyst was 487 mW/cm^2 at 1.2 A/cm^2 , a value nearly identical to that of the same membrane electrode assembly using the conventional Pt/C nanoparticle catalyst (462 mW/cm^2 at 1.0 A/cm^2) containing approximately 5 times more platinum [31].

As extensively shown lately by Artz, covalent triazine frameworks are ideally suited as supports for catalytic species due to their high chemical and thermal stability coupled to easily tunable functionality to support catalytically active sites [32].

An industrially viable technology?

According to Dhiman and Polshettiwar, SACs would be 'still far away from the commercialization, as technologies require stable single and pseudo-single atom catalysts with high metal loadings, which is still a challenge' [33]. In other words, the first main hurdle to be overcome before assist to the uptake of SAC in industry is the increase in the catalyst loading (i.e. high coverage of single atoms) so as to enable the use of acceptable catalyst amounts in existing industrial synthetic plants, in water electrolyser or fuel cell stacks.

In collaboration with Chinese scholars, Beller et al. has lately introduced a single-atom catalyst comprised of single Pt atoms dispersed on Al_2O_3 nanorods of excellent selective activity and stability in olefin hydro-silylation, namely the key process to prepare the silicone precursors [34].

In full analogy to heterogeneously catalyzed reactions mediated by supported nanoparticles [35], the support plays a key role also in single-atom catalysis. For example, the high selective activity of single Rh atoms supported on ZnO nanowires in the hydroformylation of

olefins in batch (2.5 mmol substrate under CO/H_2 pressure of 0.8 MPa at 100°C) [36] fully comparable ($\text{TON} \approx 40,000$) to that of the homogeneous Wilkinson's catalyst $[\text{RhCl}(\text{PPh}_3)_3]$ is because of the ZnO oxide surface in Rh1/ZnO-nw acting 'as robust ligands that tune the electronic structure of isolated Rh centres' [7].

When a new catalyst suitable for an industrial synthetic process is introduced, industry will generally opt for one of two options [37]. If the economic advantages offered by the new catalysts are significant (disruptive technology) [18], a completely new plant will be built whose economics outperform the older process/plant by such an extent to make the investment economically sound. If, instead, the economic advantages offered by the new catalyst do not lead to a return on investment large enough to justify a switch to a new chemical plant or process, industry will use the new catalyst if it can directly replace the catalyst currently employed in the existing process (plant) or fuel cell stack.

Be it synthetic organic chemistry, water electrolysis, or fuel cell energy conversion via reaction at the electrodes of hydrogen and oxygen, these are advanced and highly reliable chemical technologies whose level of reliability will need to be retained when adopting SAC. Otherwise, industry will not switch to new technologies. For instance, water electrolysis is a highly reliable technology. A sugar company in South Africa still uses today a large electrolyser (capacity: $360 \text{ Nm}^3 \text{ H}_2/\text{hour}$) for the production of furfuryl alcohol that was installed at its premises in 1983 during a plant expansion [38]. The electrolyser runs at full capacity 24 h a day, requiring no significant maintenance until the planned routine overhaul.

A catalyst such as the single atom Co–N-doped graphene developed by Fei et al. [28], for example, might replace the existing Ni cathodes in electrolysers, enabling operation at lower voltage and thus saving energy, while not requiring the electrolyser company the complete redesign of the electrolysis equipment.

Introduced in 2015 and obtained starting from GO synthesized from graphite flakes ($\sim 150 \text{ um}$ flakes) using an improved version of the Hummer's method (well known for its high pollution potential and poor atom economy), the electrocatalyst above for hydrogen evolution reaction so far has not been commercialized, despite its impressive chemical and physical stability [28].

Furthermore, owing to the very low content of Co, the Co-containing precursor solution forming a stable suspension similar to the pure GO solution could be easily coated on conductive substrates via drop-casting onto a carbon fiber paper (CFP) in a defined area ($1 \times 1 \text{ cm}^2$)

using directly the Co-NG on CFP as a working electrode for hydrogen evolution reaction, with the electrocatalyst on CFP delivering a remarkable stable current during the testing period [28].

Besides being suitable for laboratory scale material syntheses only, the Hummer's method produces reduced graphene oxide (RGO) irregular flakes of small size in which, for instance, the electrical conductivity and charge carrier mobility are reduced because of disruption of the 2D π -conjugation of the RGO sheet electronic structure. In 2014, however, Paton *et al.* at a British chemical company introduced a new surfactant-assisted graphite exfoliation method overcoming the limits of the Hummer's synthesis, affording large amounts of defect-free few-layer graphene [39]. Shortly afterward, high-quality graphene at affordable price became available on the marketplace [40]. This, we argue, is the graphene form that will be used to support the first commercial single-atom electrocatalyst for water electrolysis.

Outlook and perspectives

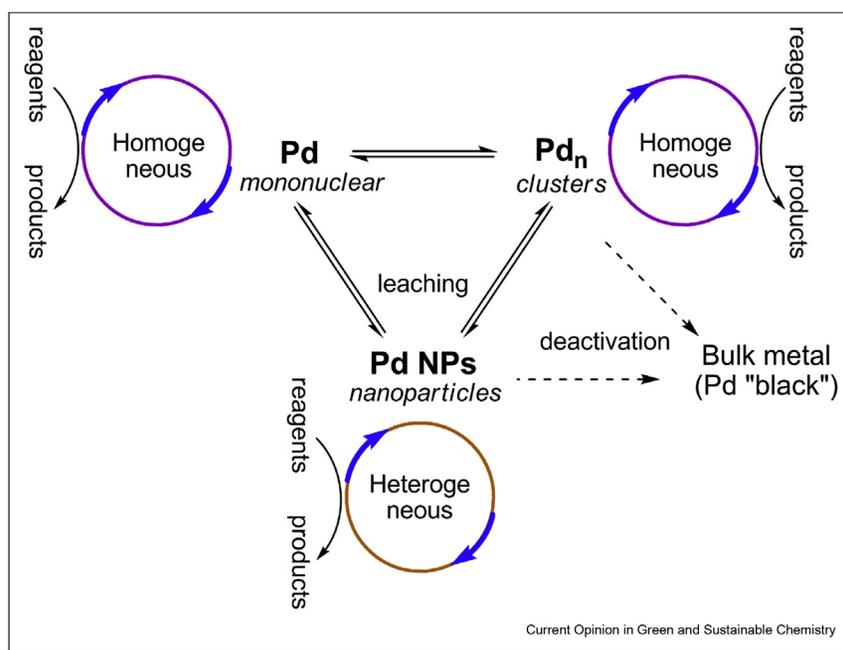
In a series of fundamental works started in 2012, Ananikov and Zalesskiy have shown how homogeneous and heterogeneous catalysts are both involved in transition metal catalysis, disclosing that commercially available samples of $\text{Pd}_2(\text{dba})_3$ readily contain up to 40% of Pd nanoparticles which during catalysis in cross-

coupling reactions progressively decompose to form Pd complexes and clusters in solution, giving place to a 'cocktail' of multiple catalytic species in solution (Figure 4) [41].

Single-atom catalysis can be seen as the ultimate consequence of applying the atom economy concept to heterogeneous catalysis, with full utilization of all metal atoms. In brief, practical application of SAC requires supports tightly binding a large number of single-atom species accessible to reactants at the outer surface, retaining their high selective activity for prolonged reaction times. Chemical and physical robustness, in their turn, depend on the intrinsic stability of the support and on the chemical interaction of the single atoms with the supporting surface.

Two main obstacles now need to be overcome on the route to industrial applicability of SAC. First, developing novel and efficient synthesis methodologies of single-atom catalysts is still desirable. Although, until now, a series of synthetic methods have been reported, including single atom metal wet impregnation [42] (with wet-chemistry synthetic methods for SACs lately reviewed) [43], photodeposition [44], spatial confinement strategy [45], and coordination design strategy [46]. With the exception of photodeposition when Liu *et al.* achieved atomically dispersed Pd/TiO₂ with >1 wt % palladium loading [44], for all these bottom-up

Figure 4



Pd catalysis of cross-coupling reactions using homogeneous Pd complexes involves a cocktail of catalytic species in solution (Image courtesy of Prof. Valentine P. Ananikov, Russian Academy of the Sciences).

synthetic strategies, the metal loading amount of single-atom catalysts is still at a low level. Hence, increasing metal loading amount via stable and repeatable synthetic routes affording SACs of higher metal load at low cost is a prerequisite for forthcoming industrial applications.

As surprising as it may seem to nanochemistry scholars educated to the primary relevance of the bottom-up approach to nanostructured materials, the top-down strategy to making single atom catalysts has ‘simplified the synthesis routes for SACs with exceptional activity and stability enabling to increase the metal loading from <1% to 5% and still allowing to control the metal coordination environment definitely facilitating the development of general protocols for accessing SACs’ [47].

For example, one general method for atomically dispersing Pt atoms on mesoporous metal oxides is the synchronous pyrolysis-deposition route [48], an elegant nanochemistry synthesis starting from the homogeneous precursor solution containing $[\text{Pt}(\text{NH}_3)_4](\text{NO}_3)_2$, nitrates (e.g. $\text{M}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$) and Pluronic F-127 surfactant. Quick (3.7 s in the heating zone) pyrolysis at 600°C ensures water evaporation and decomposition to MO_x (metal oxides) and single-site Pt species to form Pt/ MO_x composite particles with Pt species atomically anchored on MO_x particles. Removal of F-127 template and 5% H_2/Ar reduction of Pt^{2+} ions to Pt^0 single atoms affords atomically dispersed Pt_1/MO_x mesoporous catalysts whose high activity, for example in the water gas shift reaction, linearly correlates with Pt loading from 0.1 to 0.5 wt %, suggesting that the site with the single Pt atom anchored by supports is responsible for reaction.

Second, the stability of single-atom catalysts is another obstacle for industrial applicability. Single noble metal atoms tend to sinter into aggregated particles at elevated temperatures, driven by the decrease of metal surface free energy. Hence, suppressing or avoiding the occurrence of this phenomenon is the other main prerequisite along with higher catalyst load. In a key study providing valuable insight for understanding the stability of SACs, the team led by Wei in China has recently reported the unexpected phenomenon that noble metal (Pd, Pt, Au) nanoparticles can be transformed to thermally stable single atoms above 900°C [49]. The thermally stable single atoms (Pd SAs) exhibit higher activity and selectivity than nanoparticles (Pd NPs) for example in the semihydrogenation of acetylene. *In situ* environmental transmission electron microscopy clearly showed competing sintering and atomization processes during the NP-to-SA conversion, whereas quantum mechanics calculations suggest that the former high-temperature conversion is actually driven by the formation of more thermodynamically stable Pd- N_4 structure when mobile Pd atoms are captured on the defects of nitrogen-doped carbon.

Once single-atom catalysts of sufficient metal load and prolonged stability will be developed, industrial uptake will be rapid both for chemical productions and for hydrogen fuel cells and water electrolyzers currently experiencing dramatic growth [50].

From the practical viewpoint of this study, it is of high and direct relevance the discovery of He et al. of a new mechanochemical method to produce SACs on kilogram-scale via a simple ‘precursor-dilution’ strategy by which salts of palladium, rhodium, ruthenium, and palladium, such as, for example, palladium acetylacetonate are mixed with a large excess of zinc acetylacetonate ($\text{Pd}:\text{Zn} = 1:400$) thereby promoting diffusion of $\text{Pd}(\text{acac})_2$ into the bulk $\text{Zn}(\text{acac})_2$ during the subsequent milling process [51]. The mixture is then thoroughly ground and eventually calcined at 400°C for 2 h in air affording low-cost SACs deposited on zinc oxide.

The method, which can be applied also to deposit single-atoms on copper oxide, avoids the problems encountered with metal agglomeration when the synthesis of SACs is scaled-up, showing the immediate potential for commercial applications. The team estimates that the preparation cost of noble metal SACs is less than \$0.10 per gram [52].

Besides industrial processes currently heterogeneously catalyzed by supported metal nanoparticles in which carbon deposition will be avoided owing to the isolated active sites, there are a number of industrial processes currently mediated by homogeneous catalysts that can be expected to be replaced by single-atom catalysis. In conclusion, the striking structural similarity between single-atom catalysts and metal complexes, with the support of SACs acting as ligands, enables true conceptual merging of heterogeneous and homogeneous catalysis [53], an outcome that also has important educational consequences as chemistry undergraduate education is being reshaped to foster creativity also with the aid of relevant recent research findings [54].

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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