Single Atoms: A Challenge for Green Chemistry*

Anderson Guarnizo Franco[a] ■ Luis Fernando Rodríguez Herrera[b] ■ Ximena Carolina Pulido Villamil[c]

Abstract: The growing demand for various consumer products due to the increasing world population directly impacts the environment. Recently, the study and development of new materials based on single atoms (SA) is the new paradigm for green chemistry to deal with the negative effect of raw material overexploitation. This paper explains key concepts to understand SA-based materials, their synthesis, applications, the main analytical techniques for their characterization, and their relationship with environmental chemistry as a crucial technological element for sustainable development.

Keywords: Green chemistry; sustainable development; single atom; catalysis; adatom

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a PhD in Inorganic Chemistry and Master's in Applied Materials Chemistry, Universitat de Barcelona. Chemist, Universidad del Quindío. Professor at Universidad del Tolima, Ibagué, Colombia. E-mail: aguarnizof@ut.edu.co. ORCID: https://orcid.org/0000-0002-5841-210X

b Master's in Chemistry, Universidad del Quindío. Chemist, Universidad Nacional de Colombia. Professor at Universidad del Tolima, Ibagué, Colombia. E-mail: lfrodriguezh@ut.edu.co. ORCID: https://orcid.org/0000-0002-6968-6528

c PhD in Biomedicine, Master's in Biomedicine and Biological Sciences, Universitat de Barcelona. Licensed Professor of Biology and Chemistry, Universidad del Tolima. Professor at Universidad del Tolima, Ibagué, Colombia. E-mail: xpulido@ut.edu.co. ORCID: https://orcid.org/0000-0001-6776-0002

Átomos individuales: un reto para la química verde

Resumen: la creciente demanda de diversos productos de consumo debido al aumento de la población mundial impacta directamente el ambiente. En años recientes, el estudio y desarrollo de nuevos materiales basados en átomos individuales (SA) constituyen un nuevo paradigma de la eficiencia en la química verde para enfrentar los impactos negativos de la sobreexplotación de las materias primas. En este documento se explica los conceptos claves para entender los materiales basados en SA, su síntesis, aplicaciones, así como las principales técnicas analíticas para su caracterización y su relación con la química ambiental como elemento tecnológico clave en el desarrollo sostenible.

Palabras clave: química verde; desarrollo sostenible; economía del átomo; átomo individual; catálisis; adátomos

Átomos individuais: um desafio para a química verde

Resumo: A crescente demanda de diversos produtos de consumo devido ao aumento da população mundial impacta diretamente o ambiente. Em anos recentes, o estudo e desenvolvimento de novos materiais baseados em átomos individuais (SA) constituem um novo paradigma da eficiência na química verde para enfrentar os impactos negativos da superexploração das matérias-primas. Neste documento, explica-se os conceitos chave para entender os materiais baseados em SA, sua síntese, aplicações, bem como as principais técnicas analíticas para sua caracterização e sua relação com a química ambiental como elemento tecnológico chave no desenvolvimento sustentável.

Palavras-chave: química verde; desenvolvimento sustentável; economia do átomo; átomo individual; catálises; ad-átomos

Introduction

Since sustainable development is a matter of concern nowadays and for the next generations, access to the use of natural resources, both mineral and organic, envisage new challenges to take advantage of available materials. Rational use is an emerging form of assessment to mitigate the demand for raw materials, especially those that are expensive or toxic but needful for catalysis and the manufacture of electronic devices. Some examples are gold for microprocessors, nickel and chromium for hard disk devices, palladium for catalysts, among many others. From this point of view, as population and needs are growing, it is imperative to minimize the consumption of those important mineral resources (Kim, Guillaume, Chung, & Hwang, 2015).

The reduction of raw materials is a simple assumption to assess material efficiencies or "greenness" that ultimately points towards the impact on metrics of more complex and holistic parameters. Various green metrics have been proposed based on resource consumption, waste coproduction, and environmental performance. The key parameters are divided into mass metrics, environmental metrics, and energy metrics. A complete summary of these parameters was published by Dicks and Hent (2015). Because such parameters include a set of quantitative indexes heavily reliant on data availability and reliability and reciprocal relationship (Andraos, 2012), their application to new materials is limited to accurate green metrics, such as Atom Economy (AE) and Benign Index (BI). This paper aims to focus on the concept of size reduction of some chemicals to exploit the intrinsic size-dependent chemical properties for a greener process, *i.e.*, one that employs fewer quantities of raw materials, especially if they are expensive or toxic.

Parallel to the establishment of parameters to assess the overall green metrics, and as the knowledge of nanomaterials has increased to reduce the demands for raw materials, recent studies have drawn attention to materials based on single atoms (SAs) as a potential tool for the development of greener processes (Zhang, Ren, Liu, Wang, & Zhang, 2018).

Based on the size of the particle domain, materials can be classified into atom, cluster, nanoparticle, and bulk material (Figure 1). As depicted, the physical size limit is the SA. As the size reaches the atom scale, the quantity of active atoms on the surface is expected to be higher. This is an important issue for the chemical industry, which impacts our daily life (Santos *et al.,* 2015). Noble metals (gold, platinum, palladium, among others) have long been widely used as catalysts for petroleum and pharmaceutical chemistry because of their incomparably high activities and stabilities in homogeneous catalysis (Bond, 1974). However, the high costs of noble metals and the increasing demands for them compromise their long-term sustainability. Since only surface atoms are active in a process like catalysis, the efficiency of a bulk catalyst is lower than that of catalysts made of nanoparticles, clusters or SAs (Cheng, Zhang, Doyle-Davis, & Sun, 2019; Liu, Bunes, Zang, & Wang, 2018). From this point of view, SAs or adatoms (Parkinson *et al.*, 2013) become the last conceptual frontier to maximum efficiency because of the major quantity of active atoms. Therefore, this paper comprises the chemical nature, synthesis, applications, and characterization methods for SA-based materials as an emerging class of material for green chemistry.
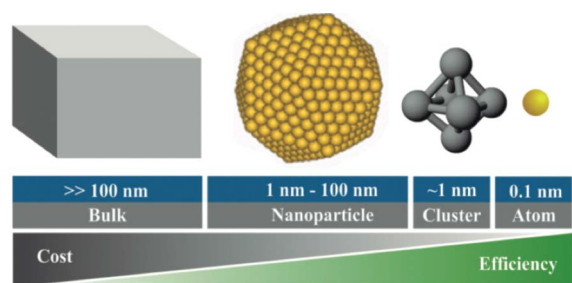

Figure 1. Material size and corresponding idealized efficiency.

Source: Own elaboration.

Characteristics of sa materials

The physical properties of materials depend on particle size (Yang *et al.*, 2013). For example, bulk magnetite (Fe_3O_4) is a permanent magnet, but its nanometric version is a non-permanent magnetic

material. So, bulk magnetite is used as the typical black magnet and magnetite nanoparticles are employed, for example, in hyperthermia applications for cancer treatment (Hedayatnasab, Abnisa, & Daud, 2017) because of their inherent superparamagnetic properties. It is expected that SAs have different properties from nanoparticles, clusters, and ions (Liu & Corma, 2018). The size of the particle, therefore, becomes one of the most critical factors in determining the properties of the material (Liu *et al.*, 2018). Essentially, when metal particles are downsized, superficial energy tends to increase to get unstable chemical systems (Liu & Corma, 2018). If the metal particle/atom is adsorbed on a surface by chemical or physical sorption, metal-support interactions will reduce the superficial energy (Yang *et al.*, 2013), resulting in improved chemical stability (Figure 2). In general, the support stabilizes SAs through charge transfer.
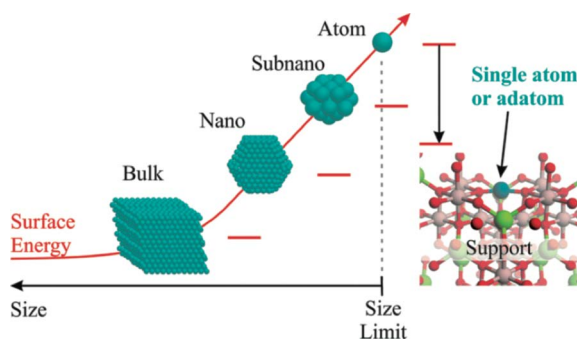

Figure 2. Schematic of changes in surface free energy, specific activity per metal atom with metal particle size, and the effects of the support on stabilizing SAs.

Source: Own elaboration.

Adatoms are metal atoms characterized by a low coordination state and are generally dispersed over a surface of inert or active material. For a simplistic approach, supports act as ligands (Flytzani-Stephanopoulos, 2017; Ogino, 2017). For example, Parkinson *et al.* (2013) obtained Pd adatoms adsorbed on the surface of magnetite (Fe_3O_4) lattice [001] with Pd partial oxidation state of +0.6. In this hybrid material, the palladium +0.6 would be coordinated with oxygen atoms, as depicted in Figure 3. As it is no longer zerovalent palladium or

Pd^{1+}, its physicochemical properties are quite different, as expected for those valences. Nevertheless, some studies point to the existence of SA-support interactions such as weak chemisorption and physisorption (Wu *et al.*, 2017), so a particular physicochemical behavior is expected according to the metal and support characteristics. Over the same support, for example, TiO_2 —the most electronegative metal—, tends to have stronger SA-support interactions in the following order (from the strongest to the weakest): Au < Ag < Rh < Co < Pt < Ni < Cu < Fe (Alghannam, Muhich, & Musgrave, 2017).
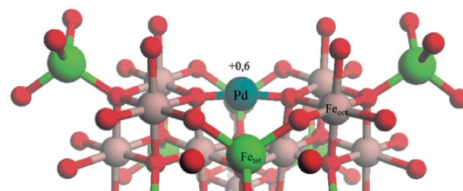

Figure 3. Pd SA adsorbed on magnetite [001]. Oct: Octahedral iron; Tet: Tetrahedral iron.

Source: Own elaboration based on the model proposed by Parkinson *et al.* (2013).

Although adatom is the proper word for that kind of chemical species, when a metallic atom is immobilized on a surface for catalysis applications, the term single-atom catalyst (SAC) have been employed (Yang *et al.*, 2013) to emphasize its use in catalysis. Terms such as "rafts" were mentioned (Qiao *et al.,* 2011) to refer to a disordered grouping of about ten immobilized atoms. The obtaining of adatoms is not trivial because metal SAs are often mobile on the surface and tend to aggregate to form clusters or nanoparticles due to high surface free energy. This is a critical situation under reaction conditions: the activity of this system decreases over time due to particle agglomeration (Hansen, Delariva, & Challa, 2013). It was demonstrated that SAs could hop along the surface and, in some cases, within the support surface (Alghannam, Muhich, & Musgrave, 2017).

The anchoring site of the SA leads to unique electronic properties. The bonding of metal atoms with uncapped sites on the supports causes a charge transfer between metal atoms and the support due to

different chemical potentials, so the effect of the adatom/support pair as a whole should be considered. The electronic structure of a surface, thus the sa-support interaction is quite different from the corresponding structure of semi-infinite surfaces (such as clusters or crystals) or coordination compounds. The electronic structure of these systems is complicated to elucidate. Computationally, the adatom is considered a synergetic sa-support system and it is necessary to simulate the effect of charge transfer, surface potentials, superficial sorption (Doyle, Shaikhutdinov, Jackson, & Freund, 2003), spillover (Pajonk, 2000; Pyle, Gray, & Webb, 2016), surface defects (Castillejos, García-Minguillán, Bachiller-Baeza, Rodríguez-Ramos, & Guerrero-Ruiz, 2018; Liu *et al.*, 2017), and solvent interactions (González-Castaño, 2018).

For a non-reacting system, the approach to solve the electronic problem may be visualized as fixed configurations of nuclei surrounded by an "electron gas." The electronic structure is determined by the solution of the electronic time-independent Schrödinger equation (TISE), and the resulting total energy is interpreted as potential energy for the nuclei. The TISE solution for many different nuclear arrangements permits the construction of potential energy surfaces for the nuclei. Core electrons could certainly be treated with the same quantum techniques as valence electrons, but because core electrons are located in the innermost shells of atoms, they do not generally play an active role in chemical bonding. Hence, it is often not necessary to explicitly include core electrons in quantum calculations. A wider discussion on this topic has been reported by Greeley, Nørskov, and Mavrikakis (2002).

Computational approaches might accurately determine the geometries, energies, electronic structures, and site preferences of adsorbates on well-defined solid surfaces; then, the structure and catalytic mechanism for sa materials are proposed based mainly on theoretical calculations (Parkinson, 2017). The special structure properties of sa-based materials have been researched using tools such as high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) (O'Mullane, 2014), X-ray absorption fine structure (XAFS) spectroscopy (Vilé *et al.*, 2015), scanning tunneling microscopy (STM), and density functional theory (DFT) modeling. The results of these studies have shown that sas have distinctive coordination environments, quantum confinement effects, and very active electronic metal-support interactions (Hu *et al.*, 2014; Qiao *et al.*, 2015).

A derivate of the unique electronic structure of sa materials is their singular magnetic behavior due to quantum confinement restrained by the sa-support interaction. For atoms that bear a single uncoupled electron in an electronic shell, for example, phosphorous [Ne] $3s^2 3p^3$ with an uncoupled electron in the $3p^3$ shell, recent advances demonstrate that a material with a paramagnetic phosphorous sa has a high anisotropy barrier and a high superparamagnetic limit, whereby it is possible to isolate the magnetic momentum of one sa. The manipulation of the magnetic momentum of a sa is important in new electronic devices, as mentioned in the Applications section. Table 1 summarizes the principal effects and properties of sa-based materials.

Table 1. Selected sa physicochemical properties.

Property	Description	Reference
Magnetic	High anisotropy barrier and superparamagnetic limits, short magnetic ground state	Märkl, 2015; Sun *et al.*, 2013
Catalytic	High activity and selectivity	Caparrós *et al.*, 2017; Guarnizo *et al.*, 2016
Conductive	Semiconductor for single-electron transport	Fuechsle *et al.*, 2012; Wu *et al.*, 2017
Diffusive	Aggregates on the surface under reaction conditions or migrates within surfaces	Alghannam, Muhich, & Musgrave, 2017; Matrane, Mazroui, Sbiaai, Eddiai, & Boughaleb, 2017
Chemical	Coordination bonding, weak chemisorption, and physisorption	Gao, Yang, Ding, Lv, & Yan, 2018; Hu *et al.*, 2014; MacLaren, Pendry, & Joyner, 1986; Qiao *et al.*, 2015; Wu *et al.*, 2017

Source: Own elaboration.

Single Atoms: A Challenge for Green Chemistry

Synthesis

The synthesis of SA materials is a challenge for researchers because of the difficulty in obtaining a surface with isolated SAs without the inherent tendency to self-aggregation (Kharissova, Dias, Kharisov, Pérez, & Pérez, 2013; Nath, Jana, Pradhan, & Pal, 2010). This is because noble metal downsized to clusters or single metal atoms are structurally unstable and show high activity and a large specific surface area. The mechanism of self-aggregation can be explained by Ostwald ripening or particle migration (Hansen, Delariva, & Challa, 2013). To prevent these phenomena, it is important to choose a support that prompts SA stability. In the last decade, efforts have been driven towards increasing the efficiency of supported metal due to its fine dispersion on appropriate surfaces. Thus, supports, which can efficiently stabilize SAs, are crucial for the performance of SA-based materials. So far, various metal oxides have attempted to anchor SAs, such as FeO_x (Wei *et al.*, 2014), SiO_2 (Pla *et al.*, 2012), Al_2O_3 (Cui *et al.*, 2017), TiO_2 (Chang *et al.*, 2014; Risse, Shaikhutdinov, Nilius, Sterrer, & Freund, 2008), graphene (Yan *et al.*, 2015), carbon nitride (Vilé *et al.*, 2015), and nanoparticles (Caparrós *et al.*, 2017; Guarnizo *et al.*, 2016). Taking this into account, systems containing adatoms can be successfully synthesized following the chemical or physical approaches shown in Figure 4.
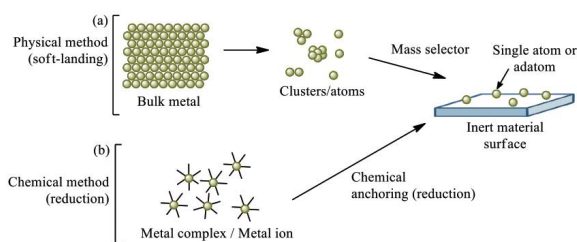

Figure 4. General methods for the synthesis of SA-based materials.

Source: Own elaboration.

The mass-selected soft-landing technique is powerful for preparing supported nanoparticles, clusters or even SAs (Wang *et al.*, 2017) because of its exact control of the size of metal species by using mass-selected molecular or atom beams and precise regulation of the support surface structure by combining these with ultrahigh vacuum (UHV) surface procedures. However, the wide application of such an expensive and low-yield manufacturing method is limited and not suitable for practical industrial applications, except for laboratories.

Atomic layer deposition (ALD) is a thin-film deposition method in which a film is grown on a substrate by exposing its surface to gaseous metal species. It consists in preparing a clean, flat, conductive metal oxide surface by UHV and then sublimating the metal atoms directly onto the support at low temperature (Hansen, Delariva, & Challa, 2013).

The deposit of metal particles involves the formation of sub-nanometric particles, clusters, and SAs by reducing metal salt. The particle size controls the concentration of metal before the reduction. The use of a linker on the surface is an interesting strategy for controlling the size and superficial distribution of NPs and SAs via wet chemistry. Recently, Guarnizo *et al.* (2016) and Rossell *et al.* (2016) carried out the particle size control employing a variable concentration of Pd^{2+} immobilized on magnetite nanoparticles with a phosphine as a linker under sonication. In this case, the surface of the magnetite nanoparticle (Fe_3O_4) was first treated with 4-(diphenylphosphine)benzoic acid (DPA as a linker, Figure 5a). Then, the phosphine group captured Pd^{2+} (Figure 5b) to control the quantity of Pd deposited onto the magnetite surface in the next step of the synthesis (Figure 5c). Bigger metal aggregates were observed at higher Pd^{2+} concentrations as expected. On the other hand, it was established that for magnetite nanoparticles modified on their surface with DPA, an affordable palladium SA could be obtained when its concentration is under 0.1 wt. %.
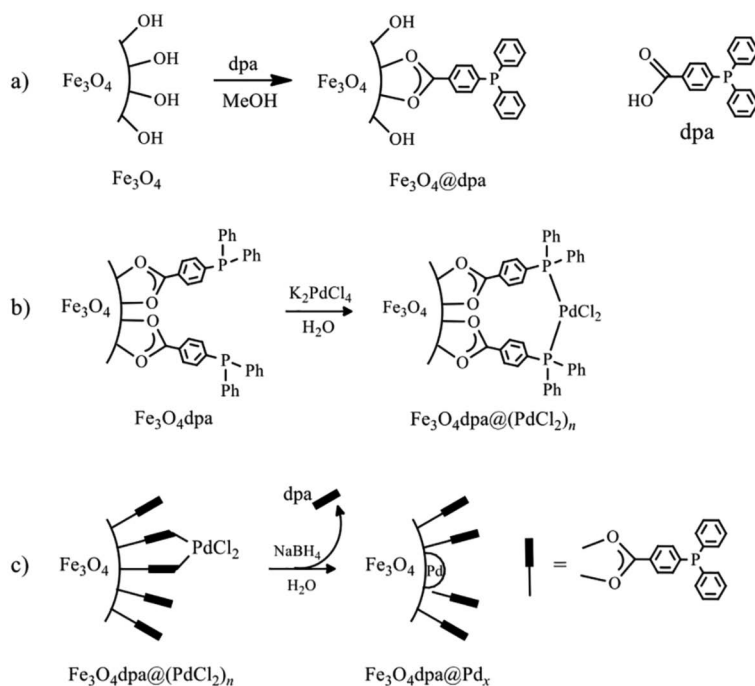
Figure 5. Scheme of the synthesis of nanoparticles and SA materials using wet chemistry. a) Surface modification of magnetite nanoparticles by capping a DPA monolayer; b) Pd^{2+} immobilization; (c) Reduction of Pd^{2+} to deposit Pd SAS, cluster, or nanoparticles.

Source: Own elaboration.

Applications

Below are some selected examples of the potential uses of SA materials for microelectronics and catalysis.

Microelectronic devices

Because of its low price, the magnetic recording has been the dominant technology for storing massive information on hard disk devices (HDD). Although the solid-state disk (SSD) has become more popular, magnetic hard disk storage has been continuously improved by ongoing research (Märkl, 2015). To increase the information density on an HDD, SA-based technology is promising to obtain an HDD with a higher storage capacity. The quest for even further miniaturization will find its ultimate goal on an atomic scale such as SA, where quantum magnetism explains the behavior of these objects (Schuh *et al.*, 2011). This technology attempts to use a SA to keep one bit of information in the related

magnetic quantum state of the electronic spin of one SA (qubit). The size of one magnetic bit will approach scales where the superparamagnetic limit is reached. As expected for this kind of nanometric system, thermal fluctuations lead to rapid loss of the magnetization orientation; in practical terms, they cause the loss of stored information.

Single magnetic atoms are known since 1998, when single cobalt atoms over a gold surface (111) were studied (Yazdani, Jones, Lutz, Crommie, & Eigler, 1997). Since then, it has been established that SA materials can eventually pose higher anisotropy barriers than bulk but a shorter lifetime of the magnetic ground state. It means that massive quantities of information could be stored in a very tiny space, but they got lost in a short period. The most promising advance was made by Netterer *et al.* (2017). They showed that it is possible to store one bit of information in just one atom of holmium (Ho) supported on magnesium oxide (MgO) using an external magnetic field for switching the

atomic spin, and the magnetic information could be retained for several hours.

It is possible to produce single-atom transistors, according to Fuechsle *et al.* (2012). A single-atom transistor in which a single phosphorus atom is positioned between a highly doped source and drain leads to a lateral spatial accuracy of +1 atomic lattice spacing. These authors demonstrate that it can trace the source, drain, and gate contacts to the individual donor atom and observe well-controlled transitions for 0, 1, and 2 electron states. That results show that encapsulating phosphorus dopant atoms deep within an epitaxial silicon environment allows them to retain both their discrete quantum states and bulk-like charging energy, despite the presence of highly doped electrodes. Thus, single-atom devices can, in principle, be built and controlled with atomically thin wires, where the active component represents the ultimate physical limit of Moore's law (Fuechsle *et al.*, 2012). Even though the transistor operates under very low temperatures, it is a great effort for next-generation microelectronics.

Catalysis

Catalysis is one of the most important applications. Preparing suitable catalysts that take advantage of sas for the selective and efficient synthesis of desired products from raw materials is a matter of concern for green chemistry. Upon decreasing the size of metal nanostructures from the nanometer to the sub-nanometer scale, and ultimately to sas (Liang, Hao, & Shi, 2015), the catalytic performance could be substantially changed as a result of the low-co-ordination environment, quantum confinement effect, and improved strong metal-support inter-action (Wang *et al.*, 2017). For example, it has been shown in a plethora of cases that gold is a non-reac-tive metal in bulk size, but on a nanometric scale, an important catalytic activity has been registered (Corma & H. Garcia, 2008; Haruta, 2003; Sengani, Grumezescu, & Rajeswari, 2017). As the catalytic activity depends on particle size, with the reactivity increasing as the particle diameter decreases, it was expected that sacs would be the most active cata-lyst. However, sas were inactive in the bio-based aerobic oxidation of thiophenol with O_2 (Corma *et al.*, 2013). Interestingly, these results point to the

possibility of controlling reaction selectivity and ac-tivity by tuning the size of a metal particle on the catalyst from sa to cluster and nanoparticle systems.

Depending on the chemical nature of the cata-lyst entity, either a sa or a cluster, a chemical reac-tion pathway could be shown. For instance, recent studies (Caparrós *et al.*, 2017; Guarnizo *et al.*, 2016; Rossell *et al.*, 2016) observed that immobilized Pd nanoparticles on magnetite nanoparticles had an exceptional catalytic activity in styrene hydroge-nation, but null activity when a sac was used for the same reaction. Conversely, the efficiency in a 4-nitrophenol reduction to 4-aminophenol was the highest when the catalyst was a sac.

Besides an affordable AE, another important aspect of catalytic experiments is the requirement that reactions can be made under mild conditions (affecting BI): using renewable solvents such as water and ethanol, in the air, and at room tem-perature. In the abovementioned experiments (Caparrós *et al.*, 2017; Guarnizo *et al.*, 2016), water pollutant 4-nitrophenol was efficiently reduced to 4-aminophenol under mild conditions.

Recently, attention has been paid to non-noble metal catalysts for long-term sustainable develop-ment, but the performances of such catalysts are currently inferior to those of noble metals. How-ever, the sac concept has encouraged studies for enhancing the catalytic activities of non-noble metal catalysts with properties good enough to be comparable with those of commercial noble metal catalysts. Carbon monoxide chemistry on transition metal surfaces is of great importance in heterogeneous catalysis and a particular matter of concern for the control of emissions from internal combustion motors. Actual catalyst converters of CO into CO_2 for automobiles include Pd and Ru (Kharissova *et al.*, 2013; Dong *et al.*, 2017). Since those metals are expensive, there is a special in-terest in developing new catalysts to address the economy of substituting noble metals for cobalt sa-based materials (Deng, Zheng, & Zhang, 2017). A computational assessment has been used to in-quire into the use of non-noble metal sacs like ti-tanium, versus ruthenium sacs; as expected, the ruthenium sacs were the best in CO oxidation, but titanium sacs showed comparable performances.

Hydrogen generation for power supply is a desirable substitute for fossil fuels. Fei *et al.* (2015) synthesized cobalt sa onto nitrogen-doped graphene by a wet chemistry method. This sac was highly active in aqueous media as an electrocatalyst for hydrogen generation.

The replacement of traditional oxidants such as potassium dichromate with oxygen from the air is another focus of attention in green chemistry. Typical oxidation of benzyl alcohols involves the use of potassium dichromate and sulphuric acid, which are environmentally hazardous and very aggressive chemicals for safe handling. In a study by Sun *et al.*, 2017, bimetallic Au-Pd supported on TiO_2 (Au-Pd/TiO_2) catalysts with an Au loading amount of 0.94 wt. % and a Pd loading amount varying from 0.017 to 0.13 wt. % was prepared using a photocatalytic deposition method for solvent-free aerobic oxidation of benzyl alcohol. The characterization of the composites suggested that in bimetallic catalysts, Pd sas were deposited on the exposed Au nanoparticle surface like a shell. Therefore, the highest activity of the bimetallic hybrid was because of the presence of Pd adatoms in the catalyst.

Characterization

The prevailing methods for analyzing sa-based materials are related to their capability to distinguish adatoms from clusters and nanoparticles. Because of this, principal experimental techniques require atom resolution devices. As one of the few laboratory techniques capable of true atomic resolution, stm is potentially ideal for studying adatom materials. Images are obtained by scanning the tip over a surface and recording the tip movements necessary to maintain a constant tunneling current and construct a bidimensional image (Parkinson *et al.*, 2013). Magnetic properties have been studied by spin-polarized stm (sp-stm) as an extension of this technique (Märkl, 2015). stm techniques have permitted the study of chemical reactions in real-time (Hahn & Ho, 2001; Nørskov, 2001). For catalytic activity studies, the idea is to strip away the complexity of a sa material and study well-defined single-crystal samples in a highly-controlled uhv environment to elucidate the active sites of heterogeneous

catalysts and their reaction mechanism step by step (Pfisterer, Liang, Schneider, & Bandarenka, 2017).

A drawback for stm is that only flat surfaces are suitable for analysis, and then sa supported on nanoparticles are difficult to study this way. For this reason, the haadf-stem is a powerful tool for visualizing sas not only on a flat surface but also on an irregular surface such as those of nanoparticles. Heavy atoms are distinguished from lightweight atoms using image contrast. A good example is the lighter image of a palladium sa on a grayish magnetite surface (Figure 6, left). Along with imaging, the energy-dispersive X-ray emission spectrum could be obtained for elemental analysis of the same stem sample. When atoms are impacted by the electron beam in energy-dispersive X-ray spectroscopy (eds), a particular set of emission spectrum peaks (Figure 6, right) is plotted for each element. Some stem devices are coupled to an eds analyzer whereby the imaging of a surface and its chemical composition can be obtained.
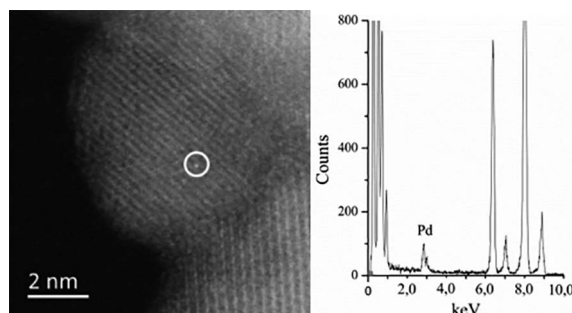

Figure 6. (Left) haadf-stem sa (circled) of palladium on magnetite nanoparticles. (Right) The eds spectrum of the same sample indicates the presence of palladium on the surface.

Source: Guarnizo Franco, 2016.

X-ray photoelectron spectroscopy (xps) has been used to elucidate the oxidation state of the elements of a surface and the strength of the adatom-support interaction (Liu *et al.*, 2017). Although xps is not a technique for imaging, it is appreciated for providing complementary information about the electronic state and element compositional ratio on surfaces. The Auger electron and photoelectron diffraction patterns due to surface adatom emission at low kinetic energies may be used to distinguish isolated

adatoms, neighboring surface site occupation, of adatom chain or cluster formation, and their orientation relative to the substrate (Jonker, 1994; Woodruff, 1994). X-ray absorption spectroscopy (xas) covers X-ray absorption near edge structure (xanes) spectra and extended X-ray absorption fine structure (exafs) spectra, which record the binding energy of the inner n shell (not the valence shell) of an electron and are useful for distinguishing sa-support interactions from metal-metal interactions through binding energy patterns (Chen *et al.*, 2017).

sas anchored to the appropriate supports might have existed for a long time and played significant roles in many catalytic processes, but they have rarely been recognized as active sites. With the emergence of more refined characterization methods and computational modeling techniques such as DTF, sa studies become accessible. A combination of theoretical methods and experimental techniques (Table 2) are needed to enable a better understanding of structure performance relationships.

Table 2. Principal techniques for sa material analysis.

Technique	Information
STM	Atom resolution images and scanning of chemical reactions in real-time. Useful for flat surfaces and diverse analytical methods such as sp-STM to study magnetic properties
HAAD-STEM	Atomic resolution images of surfaces
EDS	Chemical composition of surfaces
XPS	Elemental analysis and electronic state of elements
XAS (XANES, EXAFS)	Photoelectron absorption for local electronic structure determination. Distinguishes sa from metal clusters
Computational modeling	Provides structural information utilizing theoretical calculus such as DTF methods

Source: Own elaboration.

CONCLUSION

Adatom-based materials are hybrids with unique synergetic electronic properties derived from the sa-support interaction. This special feature principally entails the development of new materials for cheaper microelectronic devices and catalysis for pollutant depletion.

sa-based materials are an option for addressing the scarcity and high costs of noble metals. sacs have demonstrated outstanding performances, such as drastic cost-reduction, notable catalytic activity, and selectivity. Although much progress has been made in noble metal sa materials, many issues still need to explore non-noble metals as demanded by green chemistry, especially more efficient chemical synthesis, greener nano-catalysis, a chemical process under solvent-free or non-toxic solvent conditions, and new decontamination technologies.

Recent studies have provided a fundamental understanding of the synthesis, performance, and origin of the superior properties of sa-based materials, although their potential applications under the green chemistry philosophy remain to be unlocked. While many basic topics need to be further discussed, it is expected that, for the next decade, sa-based materials with improved performances will enlarge the number of applications.

References

alghannam, A., Muhich, C. L., & Musgrave, C. B. (2017). Adatom surface diffusion of catalytic metals on the anatase TiO 2 (101) surface. *Physical Chemistry Chemical Physics*, *19*(6), 4541–4552. https://doi.org/10.1039/C6CP08789B

Andraos, J. (2012). Inclusion of environmental impact parameters in radial pentagon material efficiency metrics analysis: Using benign indices as a step towards a complete assessment of "greenness" for chemical reactions and synthesis plans. *Organic Process Research & Development,* *16*(9), 1482–1506. https://doi.org/10.1021/op3001405

Bond, G. C. (1974). Homogeneous and Heterogeneous Catalysis by Noble Metals, in B. J. Luberoff (Ed.), *Homogeneous Catalysis* (pp. 25–34). American Chemical Society. https://doi.org/10.1021/ba-1968-0070.ch002

Caparrós, F. J., Guarnizo, A., Rossell, M. D., Angurell, I., Seco, M., Muller, G., ... & Rossell, O. (2017). NH 2-or PPh 2-functionalized linkers for the immobilization of palladium on magnetite nanoparticles? *rsc advances*, *7*(45), 27872–27880. https://doi.org/10.1039/C7RA03639F

Castillejos, E., García-Minguillán, A. M., Bachiller-Baeza, B., Rodríguez-Ramos, I., & Guerrero-Ruiz, A. (2018). When the nature of surface functionalities on

modified carbon dominates the dispersion of palladium hydrogenation catalysts. *Catalysis Today*, *301*, 248–257. https://doi.org/10.1016/j.cattod.2017.05.024

Chang, T. Y., Tanaka, Y., Ishikawa, R., Toyoura, K., Matsunaga, K., Ikuhara, Y., & Shibata, N. (2014). Direct imaging of pt single atoms adsorbed on TiO2 (110) surfaces. *Nano letters*, *14*(1), 134–138. https://doi.org/10.1021/nl403520c

Chen, Y., Huang, Z., Gu, X., Ma, Z., Chen, J., & Tang, X. (2017). Top-down synthesis strategies: Maximum noble-metal atom efficiency in catalytic materials. *Chinese Journal of Catalysis*, *38*(9), 1588–1596. https://doi.org/10.1016/S1872-2067(17)62778-5

Cheng, N., Zhang, L., Doyle-Davis, K., & Sun, X. (2019). Single-atom catalysts: From design to application. *Electrochemical Energy Reviews*, *2*(4), 1–35. https://doi.org/10.1007/s41918-019-00050-6

Corma, A., & Garcia, H. (2008). Supported gold nanoparticles as catalysts for organic reactions. *Chemical Society Reviews*, *37*(9), 2096–2126. https://doi.org/10.1039/b707314n

Corma, A., Concepción, P., Boronat, M., Sabater, M. J., Navas, J., Yacaman, M. J., ... & Mendoza, E. (2013). Exceptional oxidation activity with size-controlled supported gold clusters of low atomicity. *Nature Chemistry*, *5*(9), 775–781. https://doi.org/10.1038/nchem.1721

Cui, X., Junge, K., Dai, X., Kreyenschulte, C., Pohl, M. M., Wohlrab, S., ... & Beller, M. (2017). Synthesis of single atom based heterogeneous platinum catalysts: High selectivity and activity for hydrosilylation reactions. *ACS central science*, *3*(6), 580–585. https://doi.org/10.1021/acscentsci.7b00105

Deng, T., Zheng, W., & Zhang, W. (2017). Increasing the range of non-noble-metal single-atom catalysts. *Chinese Journal of Catalysis*, *38*(9), 1489–1497. https://doi.org/10.1016/S1872-2067(17)62799-2

Dicks, A. P., & Hent, A. (2015). Atom economy and reaction mass efficiency. In *Green Chemistry Metrics* (pp. 17–44). Springer, Cham. https://doi.org/10.1007/978-3-319-10500-0_2

Dong, F., Zhao, Y., Han, W., Zhao, H., Lu, G., & Tang, Z. (2017). Co nanoparticles anchoring three dimensional graphene lattice as bifunctional catalyst for low-temperature CO oxidation. *Molecular Catalysis*, *439*, 118–127. https://doi.org/10.1016/j.mcat.2017.06.022

Doyle, A. M., Shaikhutdinov, S. K., Jackson, S. D., & Freund, H. J. (2003). Hydrogenation on metal surfaces: Why are nanoparticles more active than single crystals? *Angewandte chemie international edition*, *42*(42), 5240–5243. https://doi.org/10.1002/anie.200352124

Fei, H., Dong, J., Arellano-Jiménez, M. J., Ye, G., Kim, N. D., Samuel, E. L., ... & Yacaman, M. J. (2015). Atomic cobalt on nitrogen-doped graphene for hydrogen generation. *Nature communications*, *6*(1), 1–8. https://doi.org/10.1038/ncomms9668

Flytzani-Stephanopoulos, M. (2017). Supported metal catalysts at the single-atom limit–A viewpoint. *Chinese Journal of Catalysis*, *38*(9), 1432–1442. https://doi.org/10.1016/S1872-2067(17)62886-9

Fuechsle, M., Miwa, J. A., Mahapatra, S., Ryu, H., Lee, S., Warschkow, O., ... & Simmons, M. Y. (2012). A single-atom transistor. *Nature nanotechnology*, *7*(4), 242–246. https://doi.org/10.1038/nnano.2012.21

Gao, Z., Yang, W., Ding, X., Lv, G., & Yan, W. (2018). Support effects in single atom iron catalysts on adsorption characteristics of toxic gases (NO2, NH3, SO3 and H2S). *Applied Surface Science*, *436*, 585–595. https://doi.org/10.1016/j.apsusc.2017.12.077

González-Castaño, M., Le Saché, E., Ivanova, S., Romero-Sarria, F., Centeno, M. A., & Odriozola, J. A. (2018). Tailoring structured WGS catalysts: Impact of multilayered concept on the water surface interactions. *Applied Catalysis B: Environmental*, *222*, 124–132. https://doi.org/10.1016/j.apcatb.2017.10.018

Greeley, J., Nørskov, J. K., & Mavrikakis, M. (2002). Electronic structure and catalysis on metal surfaces. *Annual review of physical chemistry*, *53*(1), 319–348. https://doi.org/10.1146/annurev.physchem.53.100301.131630

Guarnizo, A., Angurell, I., Muller, G., Llorca, J., Seco, M., Rossell, O., & Rossell, M. D. (2016). Highly water-dispersible magnetite-supported Pd nanoparticles and single atoms as excellent catalysts for Suzuki and hydrogenation reactions. *RSC advances*, *6*(73), 68675–68684. https://doi.org/10.1039/C6RA14257E

Guarnizo Franco, A. (2016). *Síntesis y propiedades catalíticas de nanopartículas de paladio depositadas sobre nanopartículas de magnetita*. Universitat de Barcelona.

Hahn, J. R., & Ho, W. (2001). Oxidation of a single carbon monoxide molecule manipulated and induced with a scanning tunneling microscope. *Physical review letters*, *87*(16), 166102. https://doi.org/10.1103/PhysRevLett.87.166102

Hansen, T. W., DeLaRiva, A. T., Challa, S. R., & Datye, A. K. (2013). Sintering of catalytic nanoparticles: Particle migration or Ostwald ripening? *Accounts of chemical research*, *46*(8), 1720–1730. https://doi.org/10.1021/ar3002427

Haruta, M. (2003). When gold is not noble: Catalysis by nanoparticles. *The chemical record*, *3*(2), 75–87. https://doi.org/10.1002/tcr.10053

Hedayatnasab, Z., Abnisa, F., & Daud, W. M. A. W. (2017). Review on magnetic nanoparticles for magnetic nanofluid hyperthermia application. *Materials & Design*, *123*, 174–196. https://doi.org/10.1016/j.matdes.2017.03.036

Hu, P., Huang, Z., Amghouz, Z., Makkee, M., Xu, F., Kapteijn, F., ... & Tang, X. (2014). Electronic metal–support interactions in single atom catalysts. *Angewandte Chemie*, *126*(13), 3486–3489. https://doi.org/10.1002/ange.201309248

Jonker, B. T. (1994). Surface adatom-adatom coordination and orientation determined by low energy Auger electron and photoelectron diffraction due to adatom emission. *Surface science*, *306*(1–2), L555–L562. https://doi.org/10.1016/0039-6028(94)91177-0

Kharissova, O. V., Dias, H. R., Kharisov, B. I., Pérez, B. O., & Pérez, V. M. J. (2013). The greener synthesis of nanoparticles. *Trends in biotechnology*, *31*(4), 240–248. https://doi.org/10.1016/j.tibtech.2013.01.003

Kim, J., Guillaume, B., Chung, J., & Hwang, Y. (2015). Critical and precious materials consumption and requirement in wind energy system in the EU 27. *Applied Energy*, *139*, 327–334. https://doi.org/10.1016/j.apenergy.2014.11.003

Liang, S., Hao, C., & Shi, Y. (2015). The power of single-atom catalysis. *ChemCatChem*, *7*(17), 2559–2567. https://doi.org/10.1002/cctc.201500363

Liu, J., Bunes, B. R., Zang, L., & Wang, C. (2018). Supported single-atom catalysts: Synthesis, characterization, properties, and applications. *Environmental Chemistry Letters*, *16*(2), 477–505. https://doi.org/10.1007/s10311-017-0679-2

Liu, J., Jiao, M., Lu, L., Barkholtz, H. M., Li, Y., Wang, Y., ... & Ma, C. (2017). High performance platinum single atom electrocatalyst for oxygen reduction reaction. *Nature communications*, *8*(1), 1–10. https://doi.org/10.1038/ncomms15938

Liu, L., & Corma, A. (2018). Metal catalysts for heterogeneous catalysis: From single atoms to nanoclusters and nanoparticles. *Chemical reviews*, *118*(10), 4981–5079. https://doi.org/10.1021/acs.chemrev.7b00776

Liu, P., Xie, Y., Miller, E., Ebine, Y., Kumaravadivel, P., Sohn, S., & Cha, J. J. (2019). Dislocation-driven SnTe surface defects during chemical vapor deposition growth. *Journal of Physics and Chemistry of Solids*, *128*, 351–359. https://doi.org/10.1016/j.jpcs.2017.12.016

MacLaren, J. M., Pendry, J. P., & Joyner, R. W. (1986). The role of adatom geometry in the strength and range of catalyst poisoning. *Surface science*, *165*(2–3), L80–L84. https://doi.org/10.1016/0039-6028(86)90804-6

Märkl, J. T. (2015). *Investigation of Magnetic Adatoms with Scanning Tunneling Techniques*. Karlsruhe: KIT Scientific Publishing.

Matrane, I., Mazroui, M. H., Sbiaai, K., Eddiai, A., & Boughaleb, Y. (2017). Energy barriers of single-adatoms diffusion on unreconstructed and reconstructed (110) surfaces. *The European Physical Journal B*, *90*(10), 201. https://doi.org/10.1140/epjb/e2017-80235-0

Nath, S., Jana, S., Pradhan, M., & Pal, T. (2010). Ligand-stabilized metal nanoparticles in organic solvent. *Journal of colloid and interface science*, *341*(2), 333–352. https://doi.org/10.1016/j.jcis.2009.09.049

Natterer, F. D., Yang, K., Paul, W., Willke, P., Choi, T., Greber, T., ... & Lutz, C. P. (2017). Reading and writing single-atom magnets. *Nature*, *543*(7644), 226–228. https://doi.org/10.1038/nature21371

Nørskov, J. K. (2001). Surface chemistry: Catalysis frozen in time. *Nature*, *414*(6862), 405–406. https://doi.org/10.1038/35106674

Ogino, I. (2017). X-ray absorption spectroscopy for single-atom catalysts: Critical importance and persistent challenges. *Chinese Journal of Catalysis*, *38*(9), 1481–1488. https://doi.org/10.1016/S1872-2067(17)62880-8

O'Mullane, A. P. (2014). From single crystal surfaces to single atoms: Investigating active sites in electrocatalysis. *Nanoscale*, *6*(8), 4012–4026. https://doi.org/10.1039/C4NR00419A

Pajonk, G. M. (2000). Contribution of spillover effects to heterogeneous catalysis. *Applied Catalysis A: General*, *202*(2), 157–169. https://doi.org/10.1016/S0926-860X(00)00522-6

Parkinson, G. S. (2017). Unravelling single atom catalysis: The surface science approach. *arXiv preprint arXiv:1706.09473*. https://doi.org/10.1016/S1872-2067(17)62878-X

Parkinson, G. S., Novotny, Z., Argentero, G., Schmid, M., Pavelec, J., Kosak, R., ... & Diebold, U. (2013). Carbon monoxide-induced adatom sintering in a Pd–Fe_3O_4 model catalyst. *Nature materials*, *12*(8), 724–728. https://doi.org/10.1038/nmat3667

Pfisterer, J. H., Liang, Y., Schneider, O., & Bandarenka, A. S. (2017). Direct instrumental identification of catalytically active surface sites. *Nature*, *549*(7670), 74–77. https://doi.org/10.1038/nature23661

Pla, J. J., Tan, K. Y., Dehollain, J. P., Lim, W. H., Morton, J. J., Jamieson, D. N., ... & Morello, A. (2012). A single-atom electron spin qubit in silicon. *Nature*, *489*(7417), 541–545. https://doi.org/10.1038/nature11449

Pyle, D. S., Gray, E. M., & Webb, C. J. (2016). Hydrogen storage in carbon nanostructures via spillover. *International Journal of Hydrogen Energy*, *41*(42), 19098–19113. https://doi.org/10.1016/j.ijhydene.2016.08.061

Qiao, B., Liang, J. X., Wang, A., Xu, C. Q., Li, J., Zhang, T., & Liu, J. J. (2015). Ultrastable single-atom gold catalysts with strong covalent metal-support interaction (CMSI). *Nano Research*, *8*(9), 2913–2924. https://doi.org/10.1007/s12274-015-0796-9

Qiao, B., Wang, A., Yang, X., Allard, L. F., Jiang, Z., Cui, Y., ... & Zhang, T. (2011). Single-atom catalysis of CO oxidation using Pt_1/FeO_x. *Nature chemistry*, *3*(8), 634–641. https://doi.org/10.1038/nchem.1095

Risse, T., Shaikhutdinov, S., Nilius, N., Sterrer, M., & Freund, H. J. (2008). Gold supported on thin oxide films: From single atoms to nanoparticles. *Accounts of chemical research*, *41*(8), 949–956. https://doi.org/10.1021/ar800078m

Rossell, M. D., Caparrós, F. J., Angurell, I., Muller, G., Llorca, J., Seco, M., & Rossell, O. (2016). Magnetite-supported palladium single-atoms do not catalyse the hydrogenation of alkenes but small clusters do. *Catalysis Science & Technology*, *6*(12), 4081–4085. https://doi.org/10.1039/C6CY00596A

Santos, C. S., Gabriel, B., Blanchy, M., Menes, O., García, D., Blanco, M., ... & Neto, V. (2015). Industrial applications of nanoparticles—A prospective overview. *Materials Today: Proceedings*, *2*(1), 456–465. https://doi.org/10.1016/j.matpr.2015.04.056

Schuh, T., Balashov, T., Miyamachi, T., Wu, S. Y., Kuo, C. C., Ernst, A., ... & Wulfhekel, W. (2011). Magnetic anisotropy and magnetic excitations in supported atoms. *Physical Review B*, *84*(10), 104401. https://doi.org/10.1103/PhysRevB.84.104401

Sengani, M., Grumezescu, A. M., & Rajeswari, V. D. (2017). Recent trends and methodologies in gold nanoparticle synthesis—A prospective review on drug delivery aspect. *OpenNano*, *2*, 37–46. https://doi.org/10.1016/j.onano.2017.07.001

Sun, J., Han, Y., Fu, H., Qu, X., Xu, Z., & Zheng, S. (2017). Au@ Pd/TiO_2 with atomically dispersed Pd as highly active catalyst for solvent-free aerobic oxidation of benzyl alcohol. *Chemical Engineering Journal*, *313*, 1–9. https://doi.org/10.1016/j.cej.2016.12.024

Sun, S., Zhang, G., Gauquelin, N., Chen, N., Zhou, J., Yang, S., ... & Li, R. (2013). Single-atom catalysis using Pt/graphene achieved through atomic layer deposition. *Scientific reports*, 3(1), 1–9. https://doi.org/10.1038/srep01775

Vilé, G., Albani, D., Nachtegaal, M., Chen, Z., Dontsova, D., Antonietti, M., ... & Pérez Ramírez, J. (2015). A stable single site palladium catalyst for hydrogenations. *Angewandte Chemie International Edition*, *54*(38), 11265–11269. https://doi.org/10.1002/anie.201505073

Wang, L., Huang, L., Liang, F., Liu, S., Wang, Y., & Zhang, H. (2017). Preparation, characterization and catalytic performance of single-atom catalysts. *Chinese Journal of Catalysis*, *38*(9), 1528–1539. https://doi.org/10.1016/S1872-2067(17)62770-0

Wei, H., Liu, X., Wang, A., Zhang, L., Qiao, B., Yang, X., ... & Zhang, T. (2014). FeO_x-supported platinum single-atom and pseudo-single-atom catalysts for chemoselective hydrogenation of functionalized nitroarenes. *Nature communications*, *5*, 5634. https://doi.org/10.1038/ncomms6634

Woodruff, D. P. (1994). Photoelectron and Auger electron diffraction. *Surface science*, *299*, 183–198. https://doi.org/10.1016/0039-6028(94)90654-8

Wu, C. X., Wen, S. Z., Yan, L. K., Zhang, M., Ma, T. Y., Kan, Y. H., & Su, Z. M. (2017). Conductive metal adatoms adsorbed on graphene nanoribbons: A first-principles study of electronic structures, magnetization and transport properties. *Journal of Materials Chemistry C*, *5*(16), 4053–4062. https://doi.org/10.1039/C6TC05545A

Yan, H., Cheng, H., Yi, H., Lin, Y., Yao, T., Wang, C., ... & Lu, J. (2015). Single-atom Pd1/graphene catalyst achieved by atomic layer deposition: Remarkable performance in selective hydrogenation of 1,3-butadiene. *Journal of the American chemical society*, *137*(33), 10484–10487. https://doi.org/10.1021/jacs.5b06485

Yang, X. F., Wang, A., Qiao, B., Li, J., Liu, J., & Zhang, T. (2013). Single-atom catalysts: A new frontier in heterogeneous catalysis. *Accounts of chemical research*, *46*(8), 1740–1748. https://doi.org/10.1021/ar300361m

Yazdani, A., Jones, B. A., Lutz, C. P., Crommie, M. F., & Eigler, D. M. (1997). Probing the local effects of magnetic impurities on superconductivity. *Science*, *275*(5307), 1767–1770. https://doi.org/10.1126/science.275.5307.1767

Zhang, L., Ren, Y., Liu, W., Wang, A., & Zhang, T. (2018). Single-atom catalyst: A rising star for green synthesis of fine chemicals. *National Science Review*, *5*(5), 653–672. https://doi.org/10.1093/nsr/nwy077