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Review Article

Single-atom electrocatalysis from first principles: Current status and open challenges

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Abstract

Single-atom catalysts (SACs) are heterogenous catalysts with elements in common with coordination compounds. We discuss some fundamental elements required for the successful computational modeling of SACs for electrocatalytic applications. The first two aspects are the role played by the exchange-correlation functional adopted within a given DFT approach and the role of the local coordination of the active transition metal atom. Next, we discuss new intermediates that can form on SACs and that are not present on extended metal electrodes and how to model solvation, with particular emphasis on the fact that on SACs water can not only act as a solvent but also as a ligand. Finally, we discuss challenges related to the inclusion of pH and voltage in the models and some open issue concerning the rational design of new SACs.

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Single-atom catalysis, Density functional theory, Hydrogen evolution reaction, Oxygen evolution reaction, Intermediates.

Introduction

Single-atom catalysts (SACs) bridge the fields of homogeneous and heterogeneous catalysis [1,2]. A SAC consists of atomically dispersed transition metal (TM) atoms embedded in a solid matrix [3]. Therefore, SACs belong to the class of heterogeneous catalysts where the amount of precious metal used is minimized, and the local coordination can be controlled at atomistic level, as in homogenous catalysts. The attention toward SACs is triggered by various reasons, including the possibility to increase selectivity by playing with the local environment of the active sites [4,5].

SACs have been successfully used in electrochemical processes of interest for the energy transition, such as the hydrogen evolution reaction (HER), the oxygen evolution reaction (OER), the CO_2 reduction reaction (CO_2RR), and nitrogen fixation. [6–10]. Ab initio simulations represent a powerful tool to help understand and rationalize the reactivity of these systems, often making use of concepts derived from classical coordination chemistry [11–13].

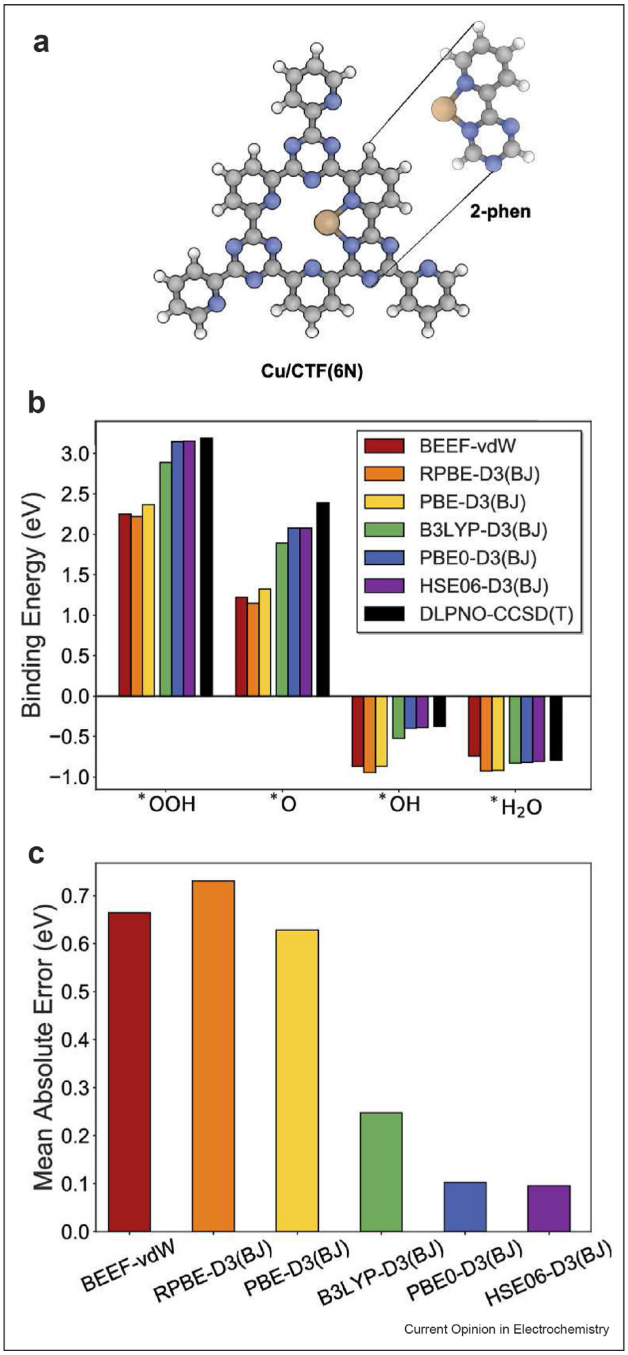
In this work, we will briefly discuss some fundamental aspects that need to be taken into account to perform reliable simulations of SACs for electrochemical applications. Some of these aspects, although essential, are often neglected in many of the simulation studies reported in the literature. The points that we want to address are: (1) the prediction of catalytic activity of a SAC can critically depend on the level of theory used, such as the nature of the exchange-correlation functional. (2) The coordination and structure of the active site need to be known with atomic precision in order to be able to compare theory with experiment. Comparisons are frequently done for experimental systems that are not fully characterized, although the chemistry of SACs is very sensitive not only to the TM but also to its surrounding. (3) All potential intermediates need to be considered to study the reaction mechanisms; neglecting some intermediates because these do not form on metal surfaces can lead to completely different reaction paths. (4) Electrochemical reactions occur in water and solvation can, in principle, affect the thermodynamics and the kinetics of the reaction. The solvent can also act as a ligand, competing with reaction intermediates to bind to the active site. (5) Finally, we will discuss future challenges such as the inclusion of important effects in the simulation of pH and voltage, and the importance to define reliable descriptors of the catalytic activity for the rational design of new SACs.

Role of the method: the exchange-correlation functional

Simulation of SACs is based on density functional theory (DFT) and plane waves codes with periodic boundary conditions. The simulation cells must have an acceptable size to avoid spurious effects due to lateral interaction between reactive species [14], and the choice of the exchange-correlation functional is crucial [15]. The large majority of studies are based on the Generalized Gradient Approximation (GGA), with a clear preference for the Perdew-Burke-Ernzerhof (PBE) functional [16]. GGA functionals have intrinsic inaccuracies due to the self-interaction error [17]. The issue can be solved by using self-interaction corrected functionals, such as the hybrid functionals, where a given fraction (α) of the exact Fock exchange is added to the formulation of the functional. α can be determined in a self-consistent way or by fitting some quantities [18]. Three relevant examples are the B3LYP [19] PBE0 [20,21], and HSE06 [22,23]. The latter is a range-separated hybrid, allowing to further improve the description of the electronic structure [24]. Hybrid functionals are computationally more demanding and often this makes the computational effort out of reach. A pragmatic way to overcome this limitation is to adopt the DFT+U scheme, where an *ad hoc* correction is added to the GGA functional on specific orbitals of certain atoms. The critical aspect is the choice of the U parameter. Nevertheless, often DFT+U allows to reconcile GGA calculations with hybrids with nearly zero-additional costs.

An example of the superiority of hybrid functionals was reported by Patel et al. [25] who showed that, for Cu-modified covalent triazine framework catalysts, the DFT thermochemistry estimates with hybrid functionals are close to those obtained with high-level Coupled Cluster Single-Double (Triple) reference calculations, Figure 1. On the contrary, GGA-based functionals provide less accurate results [25]. Also, the PBE+U approach has been tested; although the predicted errors (up to 0.5 eV) are smaller than those for GGAs, it was concluded that some care is necessary with PBE+U since the deviations are not systematic.

Figure 1



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(**a**) Structure of the catalyst; (**b**) and (**c**) the performance of different DFT functionals against the reference CCDS(T) calculations. Reproduced with permission from Ref. [25].

Recently, we showed that PBE+U allows to improve the PBE Gibbs free energies of HER and OER intermediates compared with the PBE0 ones [26]. This is true, in particular, for SACs exhibiting a magnetic ground state with unpaired electrons localized on the TM atom. As an example, we discuss the cases of Mn and Ni atoms embedded in nitrogen-doped graphene (4N-Gr) and their activity in HER. Here, the quantity of interest is the H adsorption free energy, ΔG_H. For Ni@4N-Gr, ΔG_H is virtually the same at PBE (1.72 eV), PBE+U (1.70 eV), PBE0 (1.73 eV), and HSE06 (1.73 eV). This is due to the fact that Ni in this coordination assumes a closed shell configuration. Mn@4N-Gr, on the contrary, with a magnetic ground state, exhibits substantially different ΔG_H values going from PBE (0.45 eV) to PBE+U (0.97 eV), as well as hybrid functionals PBE0 (1.00 eV) and HSE06 (1.01 eV). Needless to say, a ΔG_H of 0.5 eV or of 1 eV corresponds to completely different predictions in terms of catalyst activity.

The message is that if predictions have to be made about a new catalyst, these need to be verified against different types of exchange-correlation functionals, in particular, using hybrid or DFT+U approaches when higher-level treatments (coupled cluster, configuration interaction, etc.) are not possible.

Role of the local structure

The local coordination around the metal atom is of primary importance in determining the reactivity of SACs. The paradox is that the surrounding of the TM atom (the active site) can be as important as the nature of the metal. This has been shown recently in a simple, yet convincing computational experiment [27]. A nitrogen-doped graphene scaffold has been chosen to embed 24 TM atoms. These ideal systems have been checked toward the HER, where a common proxy of the reactivity is the free energy of H adsorption, ΔG_{H}:

$$H^{+} + e^{-} + * \rightarrow H^{*} \tag{1}$$

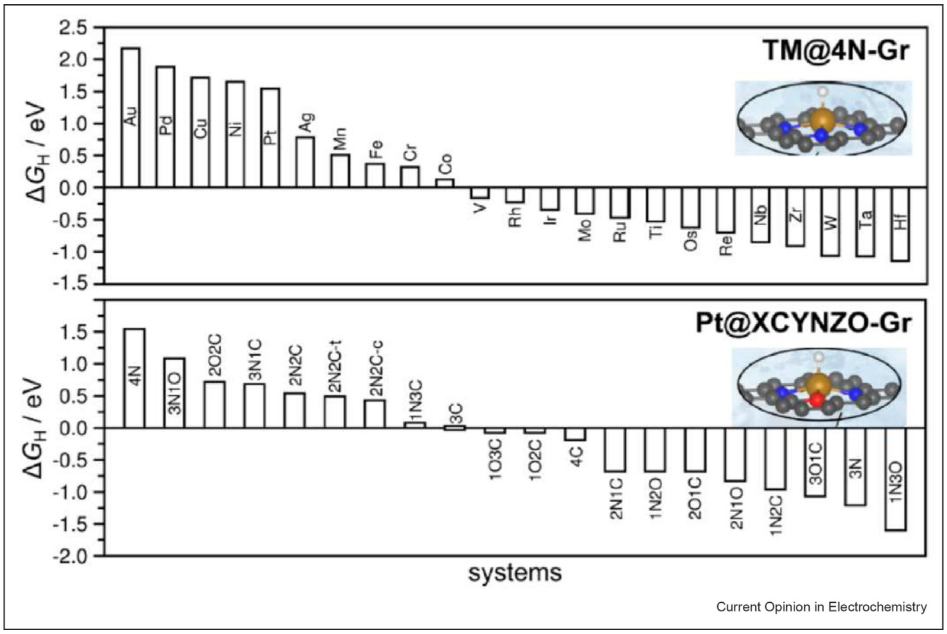
This is a part of the Computational Hydrogen Electrode (CHE) approach [28–30]. If ΔG_{H} is close to zero, the catalyst is expected to have high activity; when ΔG_{H} is too low ($\Delta G_{\mathrm{H}} << 0$) or too high ($\Delta G_{\mathrm{H}} >> 0$), the catalyst is predicted to be inactive. Not surprisingly, by changing the TM atom, one obtains a broad spectrum of H adsorption free energies from −1.14 eV (Hf) to +2.17 eV (Au), with Co exhibiting the highest activity, $\Delta G_{\mathrm{H}} \approx 0.1$ eV, as shown in Figure 2. Interestingly, a qualitatively similar result can be obtained by keeping fix the metal atom, for example, Pt, and changing the neighboring atoms. The first neighbors to the TM have been replaced by C or O atoms, and all possible permutations of the four neighboring N, C, and O species have been generated. With these sets of model catalysts, ΔG_{H} varies from −1.60 eV to +1.54 eV, with a change of about 3 eV, and the same range is obtained by varying the TM atom, as shown in Figure 2 [27].

Besides the local coordination, the oxidation state of the SAC is a key aspect for the catalytic activity. Lopez and co-workers showed that the reactivity of a Pt@CeO$_2$ SAC is driven by the coexistence and interconnection of different possible charge states of the metal [31].

The main techniques to identify the nature of a SAC are X-ray adsorption spectroscopy for the determination of the charge state of the metal, as well as extended X-ray absorption fine structure (EXAFS) spectroscopy for the identification of the coordination of the metal atom [32]. Combining infrared spectroscopy and thermal desorption spectroscopy of adsorbed probe molecules with DFT calculations provides a powerful tool to identify the actual coordination of a SAC [32,33].

The computational results reported above show that the atomistic identification of the structure of the active

Figure 2



Top: Gibbs free energy (ΔG_{H}) of H adsorbed on transition metal (TM) atoms stabilized in N-doped graphene, TM@4N-Gr. Bottom: Gibbs free energy of H adsorbed on Pt stabilized in N-doped graphene where C and O atoms are replacing some of the N atoms, Pt@XCYNZO-Gr. Adapted from Ref. [27].

phase of SACs is of primary importance to compare theory with experiment. Changing also a single neighboring atom can produce substantial changes in reactivity.

Classical reactions intermediates vs unconventional adducts

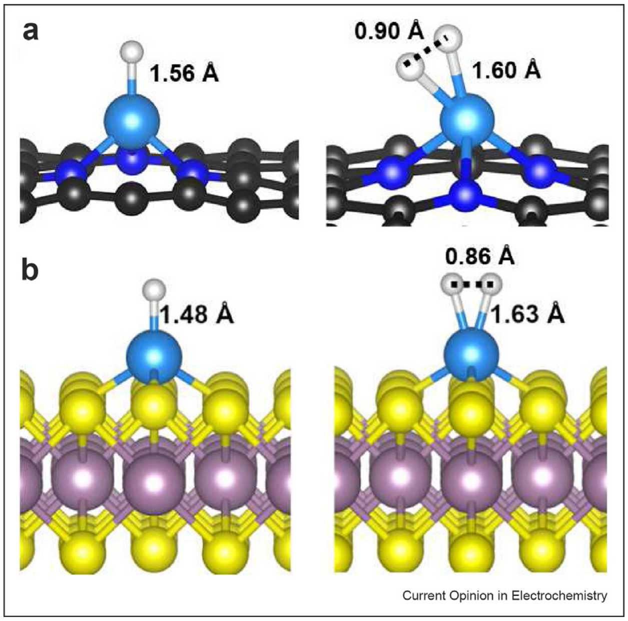
SACs form intermediates that do not commonly exist on extended metal electrodes. The formation of these "non-classical" intermediates, which are not considered in the classical reaction paths of HER, OER, CO_2RR, etc., has been highlighted only recently [34,35] and can be considered a direct consequence of the similarity of SACs with TM complexes. Their formation can radically change the reaction path and profile.

A relevant example is that of HER. As we mentioned above, a simple descriptor to model HER on a catalyst is the Gibbs free energy of an adsorbed hydrogen atom (H*). According to this model, a good catalyst of HER, as Pt, binds H* not too strongly nor too weakly to the catalyst ($\Delta G_H \approx 0.1$ eV) [28]. Based on this assumption, hundreds of theoretical papers have been published in recent years where the screening of optimal catalysts for HER has been performed. However, the assumption is correct if the HER occurs on the surface of a metal electrode, where only H atoms, and not dihydrogen complexes, exist. Things on SACs may differ.

Back in the 1980's, Kubas and Crabtree demonstrated that some metal complexes are able to bind two hydrogen atoms, forming dihydrogen complexes [36,37]. The distance between the two hydrogen atoms is an indicator of the residual strength of the H—H bond, and one can identify two families, dihydrogen complexes (H_2*), where an activated H_2 molecule is coordinated to the metal center, and dihydride ones, H*H*, characterized by a complete H—H bond breaking.

In a similar way, dihydrogen complexes can form on SACs, Figure 3, and they should be accounted for in order to provide reliable estimates of the catalytic activity [34]. In fact, when these species form, the kinetics of the reaction is affected. This has direct implications on screening studies of new SACs, since neglecting the formation of a stable species can alter completely the prediction of the catalyst activity. Similar results have been shown for the OER [12,13].

Figure 3



Classical H* and unconventional H_2* intermediates of HER on Co-based SACs: (**a**) a nitrogen-doped graphene; (**b**) MoS_2 [34].

Role of solvent

Electrochemical processes occur in water. Solvation is challenging for computational chemistry, because this implies an additional computational effort and an increase in complexity of the model used. The formation of a solid/water interface and the intrinsic fluxional behavior of water are not trivial to model.

Several possible schemes have been proposed to mimic solvation. The simplest approach consists in including the solvent implicitly, as in the polarizable continuum model [38]. This method offers a handy way to account for solvation effects, but at the same time, it misses important aspects, such as the local interactions and the directionality of hydrogen bonding.

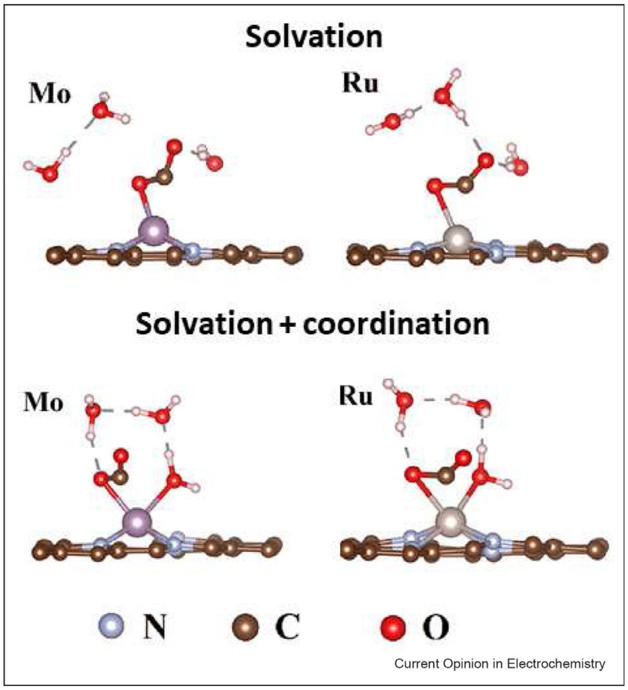
Solvent molecules can be treated explicitly at the DFT level in the simulation box. In this case, one can adopt different frames to mimic the behavior of water. A widespread approximation is to use a static water bilayer as a representative structure of the solvent [39]. This requires only static calculations and implies the inclusion of a number of water molecules without large computational costs [40]. However, the model is quite rigid, and one needs to adapt it to the simulation cell, implying some strain that could lead to spurious effects. Despite some limitations, this method has been rather successful and often very insightful [40,41]. Recently, a related scheme was proposed that approximates solvation by just a few water molecules surrounding the reactive species of interest. This approach, named microsolvation, often provides estimates of solvation energies close to those obtained using the static water bilayer. It is remarkable that this can be obtained by using only three water molecules, thus with a small computational cost [42].

To include statistical effects and to sample the solvent configurational space, ab initio molecular dynamics simulations are needed. This provides a more complete treatment of the complex picture of solvation but is also computationally very intensive [43,44].

When dealing with SACs, one must consider another important role played by the solvent. Water molecules can not only solvate the system but also act as ligands that bind directly to the SAC and compete in bond strength with the reactive species of interest. It is important to underline that these adducts are not characterized by a weak bonding between the solvent and the catalyst, as they have specific chemical interactions. This effect is typical of SACs and directly arises from their capability to form coordination compounds. In homogenous catalysis, it is rather common that, in a catalytic cycle, labile ligands leave the active site and are replaced by a solvent molecule and that water can play the role of a ligand. Needless to say, the neglection of this effect can significantly affect theoretical predictions.

Recently, we found that water competes with CO_2 molecules in binding single metal atoms embedded in nitrogen-doped graphene, as shown in Figure 4. In some cases, the adsorption of solvent molecules to the catalyst prevents the adsorption of CO_2 [45]. Also, such a coordination/solvation effect has consequences on the stability of reaction intermediates in CO_2 electroreduction, and it may change the preferred reaction channels.

Figure 4



(**a**) Solvation effect on CO_2 adsorption on Mo and Ru SACs supported on nitrogen-doped graphene. (**b**) Examples of water that coordinates and binds to the catalyst center. Adapted with permission from Ref. [45].

Future challenges

Electrochemical processes not only occur in solution but also occur under an applied voltage and at variable pH conditions. Most of the calculations reported in the literature account for these effects indirectly, that is, by including terms in the working equations of the CHE. In some cases, pH and voltage can have a dramatic impact on specific electrochemical reactions [46]. Oper and co-workers showed that the HER activity undergoes a dramatic drop by modulating the pH; furthermore, they showed that by increasing the electrolyte pH (pH 10—13), one can tune the local field strength and indirectly enhance the HER activity by changing the near-surface cation concentration [46]. Atanassov et al. demonstrated the pH effect in oxygen reduction reaction and, in particular, that this is limited by the proton-coupled electron transfer at pH values below 10.5 [47]. From a theoretical perspective, the effect of applied voltage and pH can be included by explicitly adding in the simulation model excess charges in a grand-canonical fashion, as done by Goddard III and co-workers [48].

Furthermore, voltage and pH can have other important effects, related to the acid-base equilibria at the surface of the catalysts, as demonstrated by Pasquarello and co-workers by means of an approach based on the Grand-Canonical formulation of species in solution [49—51].

A further ingredient in electrochemical experiments is the role of the electrolytes. Recent works demonstrated that dissolved ions, usually assumed to be inert, have in reality a dramatic impact on the catalytic activity [43,52]. The description of these aspects will considerably reinforce the predicting power of ab initio simulations of the chemical activity of SACs in electrocatalytic reactions.

Universal descriptors and scaling relations

Computational electrocatalysis is an important complement to experimental activities both for a better understanding of the underlying principles and for the design of novel catalysts. The identification of descriptors, simple quantities directly related to the activity of a catalyst, and of scaling relations is particularly relevant. Descriptors are. For instance, we have seen above that the free energies of reaction intermediates in a catalytic cycle are often used as descriptors. Descriptors are then used to develop scaling relationships, which are correlations (often linear) that allow one to predict the free energies of all the remaining reaction intermediates in the catalytic cycle. Thus, descriptors not only allow a better rationalization of the chemistry of a catalyst but also, the more general (or "universal") they are, the better their predictions of novel promising candidates [53,54].

Thanks to the increased computing power and to the relative simplicity of SACs embedded in carbon-based supports or on other 2D materials, it has become possible to screen hundreds or even thousands of structures using DFT calculations [55,56]. This has stimulated several high-throughput studies aiming at providing new descriptors (sometimes complex ones) or novel SACs. However, SACs are not as simple as they appear, and their chemistry is rather rich and complex. We have seen above that several new intermediates can form besides the usual ones, and also the stability of the adsorbates is affected by the nature of metal, the ligands, and the coordination. Not surprisingly, this complexity may lead to break the scaling relations, which complicates the rationalization of the processes but, at the same time, opens new opportunities for the catalyst optimization [57,58]. This does not mean that scaling relations do not exist for SACs, but most often they are restricted to a specific class of compounds or even to specific kinds of coordination [12,13]. From this perspective, the discovery of universal descriptors of the activity of SACs, often claimed in the literature, remains the holy grail of the theoretical research on SACs [59].

Conclusions

We discussed some fundamental aspects related to the modeling of SACs for electrocatalytic applications. For state-of-the-art DFT calculations, the choice of the functional is essential for the accuracy of the results. For a direct comparison with the experiment, a one-to-one correspondence between the computed structure and that of the real catalyst is required, as even small changes in the environment of the TM atom can result in large changes in reactivity. In determining reaction mechanisms and energy profiles of catalytic reactions on SACs, all intermediates need to be considered, and not only those that are usually assumed to form for the same reaction on a metal electrode. In treating solvent effects, it is important not only to consider the molecular character of water via more or less sophisticated solvation approaches but also the capability of water to bind to the metal center in a stable way, acting as a ligand rather than as a solvent. Finally, we discussed future challenges related to the inclusion of important effects, such as pH and applied voltage, and the problem to identify proper descriptors that can help the rational design of novel SACs.

Author information

The manuscript was written through contributions of all authors.

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.

Data availability

No data was used for the research described in the article.

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