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A Perspective on Metal Single Atom- Based Electrocatalytsts towards Hydrogen Peroxide Production

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ABSTRACT

The green production of hydrogen peroxide has attracted considerable attention owing to the urge for an alternative production method to the current production. Electrocatalytic reduction via the $2e^-$ pathway has emerged as the brightest approach. However, the finding of catalysts with high efficiency and selectivity to provide a proper interaction between active sites and *OOH is remaining as the primary obstacle. Employing metal single-atom catalysts (SACs) offers a potential manner to address those challenges. The presented review aims to provide cutting-edge development of a single metal catalyst for electrocatalytic H_2O_2 production. Also, perspective is laid out to propose novel approaches for material development in the future.

Introduction

Hydrogen peroxide (H_2O_2) has been considered the essential chemical involved in various industrial processes (e.g., wastewater remediation, chemical synthesis).[1-3] Currently, the annual global market of H_2O_2 has reached \$5 billion and is expected to be considerably higher in the future.[4, 5] The conventional H_2O_2 production, anthraquinone oxidation (AO) process, has raised serious environmental concerns due to its harmful organic wastes and huge energy consumption.[6] In addition, photo- and photo-electrocatalysis have also emerged as potential approaches to produce H_2O_2 [7]. However, the performance of those pathways, which are much lower than that of the expected value, is inappropriate for large-scale production under the current situation [8]. Hence, a robust and greener pathway to produce H_2O_2 is highly urgent and therefore is attracting increasing attention.

Electrocatalytic O_2 reduction has appeared as the potential approach to producing hydrogen peroxide. This method offers four primary advantages: (i) inexpensive reactant (i.e., O_2 and H_2O); (ii) low production cost; (iii) mild production condition and (iv) environment friendly.[9] For those reasons, numerous efforts have been dedicated to setting the stage for industrial H_2O_2 production via electrocatalysis.

As a proof of concept, the electrocatalysis H_2O_2 production involves the participation of O_2 and $2e^-$.

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However, the formation of H_2O, which is associated with $4e^-$, has been considered a competitive chemical reaction. Therefore, the nature of the catalyst surface accounts for an essential function, which not only enhances the efficiency but also improves the selectivity by suppressing the 4e- reduction reaction. However, such materials have been limited.

The bulk and nanoparticles-based electrocatalytic systems have been employed to produce H_2O_2. However, the H_2O_2 selectivity has been poor, which is rooted in the O-O bond cleavage of neighbouring atom centers, leading to the generation of H_2O rather than the H_2O_2 product [10-12]. Recently, the utilization of metal single-atom catalysts has emerged as a novel trend to address the aforementioned challenges owing to their unique surface properties to enhance the performance and selectivity via providing an efficient electron transfer pathway and proper absorption energy toward critical intermediate.[13-16] However, the systematical discussion on the potential of this class of material has been still sporadic. Motivated by those issues, this review aims to provide recent movement in the development of metal single-atom catalysts and an insight into the preparation and pivotal functions of single metal catalysts for electrocatalytic H_2O_2 production.

Experimental

The electrocatalytic production of H_2O_2 could be illustrated through two essential chemical reactions as shown in Figure 1 [17-22]. The nature of the catalytic surface plays a crucial function in the behavior of O_2 molecules. A strong catalyst-O_2 interaction could result in the dissociation of the O-O bond, causing the formation of H_2O instead of H_2O_2. [22, 23] It should be noted that *OOH intermediate is the single and the most imperative product. The binding strength of *OOH to the catalyst surface significantly contributes to driving the final product, which is either H_2O_2 or H_2O. The cathode and anode reactions can be described as follow:

i) Cathode reactions

❖ 4-e^- selective pathway-H_2O production

$O_2(g) + * + (H^+ + e^-) \rightarrow *OOH$

$*OOH + (H^+ + e^-) \rightarrow *O + H_2O$

$*O + (H^+ + e^-) \rightarrow *OH$

$*OH + (H^+ + e^-) \rightarrow H_2O$

❖ 2-e^- selective pathway- H_2O_2 production

$O_2(g) + * + (H^+ + e^-) \rightarrow *OOH$

$*OOH + (H^+ + e^-) \rightarrow H_2O_2$

ii) Anode reaction

$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$

It should be noted that the utilized media significantly contribute to the interfacial charge distribution, local pH, and electric field [24]. In this context, the salt (e.g., Na_2SO_4), acid (e.g., $HClO_4$), and alkaline (e.g., KOH) solutions could be utilized as the primary electrolye for the H_2O_2 production [25]. An appropriate electrolye will go hand-in-hand with utilized catalysts to optimize and preserve the *OOH intermediate.

To this point, it can be said that the nature of metal single-atom provides a great platform to regulate the desorption energy toward the *OOH intermediate.[20] The following section will provide cutting-edge development of the production of H_2O_2 through the $2e^-$ reduction pathway.

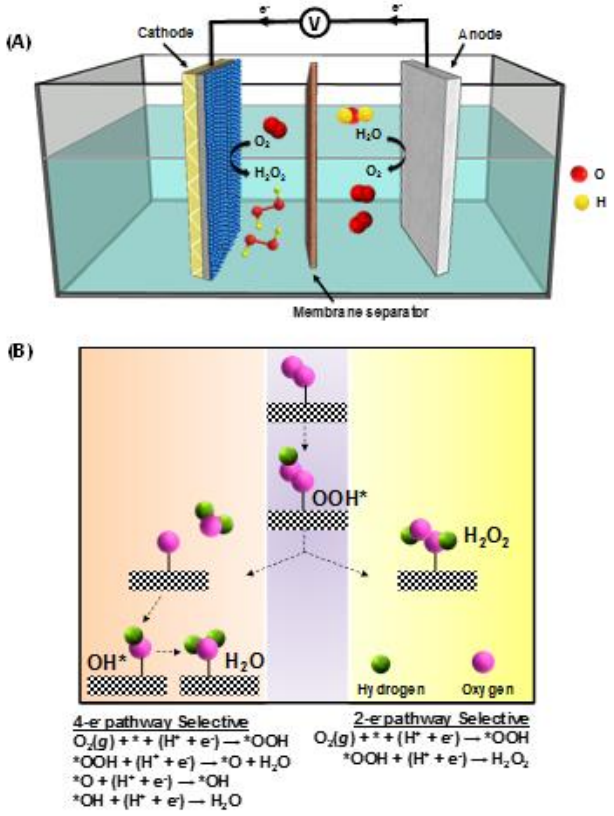

Figure 1: (A) The electrocatalytic production of H_2O_2, (B) Schematic diagram of the comparison between $4e^-$ pathway selective and $2e^-$ pathway selective in the electroreduction reaction. Adapted with permission from ref [26]. Copyright (2020) Electroanalysis

Results and discussion

State-of-the-art development of metal single atom-based electrocatalysts for H_2O_2 production

As aforementioned, electrocatalysts account for an imperative function for the efficiency and selectivity of H_2O_2 evolution performance. Hitherto, metal-based electrocatalysts have emerged as an essential tactic to improve the production and selectivity of H_2O_2. Numerous candidates have been discovered and displayed promising activities for the evolution of H_2O_2. To this end, single metal catalysts appear as a top option as the robust active sites to promote H_2O_2 production. The metal single-atom catalysts can be obtained through various synthetic strategies (e.g., wet chemical, impregnation, electrodeposition, coordination, molten salt, etc.). The selection of a preparation method is strongly associated with opted metals, support environment and condition requirements. In this context, the support functions a critical role in the dispersion and stabilization of atom sites, restricting the formation of metal clusters or nanoparticles [27].

As mentioned, the formation and adsorption of OOH* intermediates manoeuver the generation of H_2O_2. Either strong or weak OOH* adsorption can cause a high overpotential or a low selectivity. To this end, the utilization of metal single-atom catalysts can offer an appropriate medium for the OOH* intermediates without the cleavage of the O-O bond [28]. Various single metal single site-based electrocatalysts have been proposed and synthesized. Heretofore Ni, Co and Pd-based single-atom catalysts have attracted increasing attention and proven their capabilities for electrocatalytic H_2O_2 production. The following section will devote a significant effort to exploring each class of catalysts in detail.

Ni single site-supported graphene brings out novel opportunities to boost activity achievement.[29, 30] Song et al. reported the preparation of Ni_{SAC}-anchored graphene in which Ni atoms were separately decorated onto the graphene under the assistance of DMF as a capping agent protecting the Ni_{SAC} precursor upon the reduction, as shown in Figure 2A. Such the preparation method results in a uniform decoration of unique Ni single sites coordinating oxygen functional groups. Such configuration establishes a proper platform to facilitate the electrocatalytic production of H_2O_2 significantly. Thus, the mass activity and selectivity found to be 2.11 A mg_{Ni}^{-1} at 0.60V vs RHE and >94%, respectively, considerably outperform the conventional Ni-based material (e.g., Ni-NP/G) (Figure 2B). The DFT calculations offer an insight into understanding the role of the as-synthesized material in which the binding of critical intermediates (i.e., *OOH) on the active center could be optimized to promote the two-electron reduction reaction of oxygen without the production of H_2O.[31] It can be said that the development of Ni single atoms-based catalysts has been still limited, which is caused by the following obstacles: (i) preparation methods that offer a proper scaffold to stabilize Ni single atoms. In this context, the functional groups (e.g., $-NH_2$, -OH)- containing material can be an appropriate candidate. However, finding such support possessing highly conductive activity beyond graphene is an obstacle; (ii) a reduction route that could address the agglomeration of Ni atoms into Ni clusters and nanoparticles; and (iii) Further investigation of the nature of active sites should be considered.

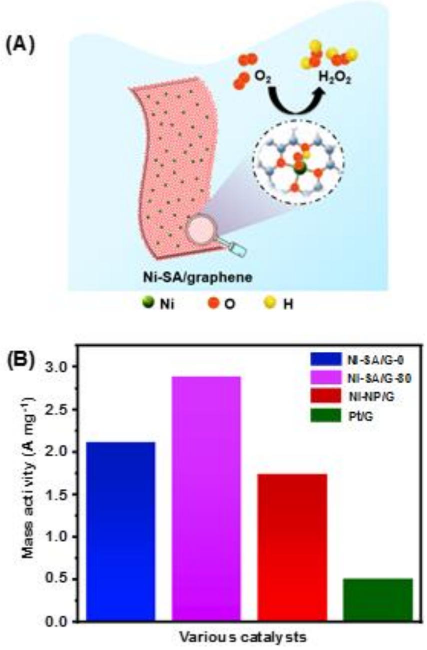

Figure 2: (A) The structure of Ni_{SAC}-anchored graphene, (B) Comparison of the mass activity of various catalysts. Obtained data from ref [31]

In addition to Ni single sites, Co single active sites could have emerged as the brightest consideration for the production of H_2O_2.[32-37] Indeed, the nature of Co single atom could pave the way for the H_2O_2 evolution by providing an appropriate platform to optimize the adsorption energy of *OOH intermediate. In such an investigation, Gao et al. reported the synthesis of Co-anchored N-doped carbon material, exhibiting an extraordinary achievement of H_2O_2 generation. The Co-N coordination leads to the formation of Co single sites without aggregation. As a result, the tailored material exhibited an outstanding electrocatalytic efficiency. The current density and selectivity values achieve 1 mA/cm_{disk}^2 and above 90%, respectively, signifying the robust properties of Co single atom toward the generation of H_2O_2. Theoretical calculations then confirmed that the adsorption energy of *OOH intermediate could be appropriate to facilitate the two-electron reduction rather than four-electrons reduction pathway.[38] In another report, Zhao et al. provided insights into the nature of Co single sites via coordination with nitrogen atoms. It turns out that the $Co-N_5$ configuration is the primary active center boosting the H_2O_2 production under the NaCl solution. [39] Very recently, an alternative coordination environment, the Co-O-C manner, has been explored to be a potentially active center to deliver the two-electron reduction route.[34] For example, Zhang et al. reported a novel form of Co single site-anchored oxygen-modified graphene oxide via the Co-O-C manner, obtained via several acid etching processes as shown in Figure 3A. In this circumstance, the prepared Co-decorated graphene oxide (denoted as Co_1@GO) possessing a $Co-O_3-C$ configuration (Figure 3B) provide a proper platform for manoeuvering the H_2O_2 production and suppressing the production of H_2O, as displayed in Figure 3C. [40] To this end, it can be said that Co single atom-derived materials are thus very potential for electrocatalytic H_2O_2 production. However, modified or functionalized graphene has been considered the primary support for Co atom sites. Therefore, the prepared materials could be restricted due to the graphene limitations. For this reason, probing an alternative support material could disclose a potential avenue to enhance electrocatalytic performance further.

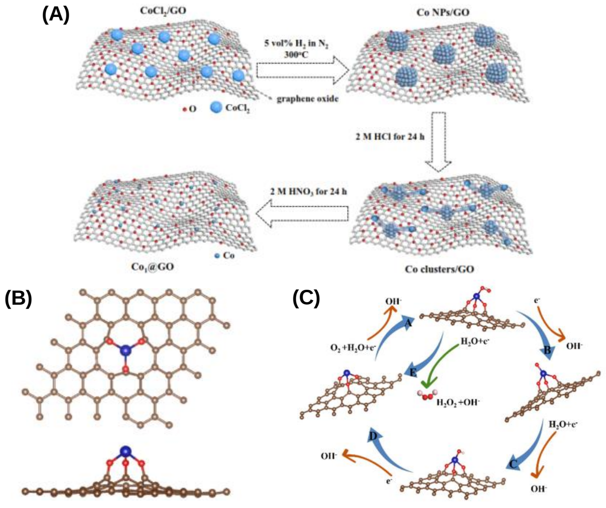

Figure 3: (A) Schematic of Co_1@GO synthesis process, (B) Co-decorated graphene oxide with $Co-O_3-C$ configuration, (C) Scheme depicting the reaction of the intermediates in oxygen reduction reaction process Reproduced from ref [41]. (2022) Communications Chemistry

Recent movements in the development of electrocatalysts have witnessed a novel Mo_{SAC}, W_{SAC}, Nb_{SAC} and Se_{SAC} active sites, which could catalyze the O_2 reduction into H_2O_2. Thus, those single metal atoms possessing a proper interaction with the support could offer outstanding performance for H_2O_2 production. [42-44] However, the preparation of such materials has been limited, requiring double efforts.

Pd-derived materials have been found to be potentially rooted in their nature surface for the two-electron O_2 reduction. Pd-based single-atom catalysts (Pd_{SAC}) have brought out potential strategies among various material designs to boost the H_2O_2 evolution reaction. In a recent investigation, Wei et al. demonstrated the potential employment of the Pd_{SACs} toward the electrocatalytic reduction of O_2 into H_2O_2 via DFT calculations. It turns out that Pb single atoms-decorated defect graphene provides an appropriate platform benefiting the formation of crucial intermediates, lowing the overpotential and therefore benefiting the two-electron oxygen reduction reaction into H_2O_2, as shown in Figure 4 [45] Hitherto, the preparation of such material has been a challenge, caused by the difficulty of synthetic strategy. Therefore, an investigation and production of Pb_{SAC} catalysts could deliver a milestone in H_2O_2 generation in the future.

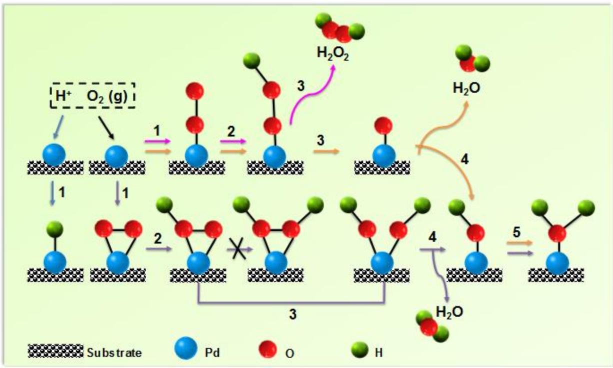

Figure 4: The mechanisms for the oxygen reduction reaction. Adapted with permission from ref [45]. Copyright (2022) Chemical Engineering Journal

Conclusion

In conclusion, the electrocatalytic approach has appeared as a potential tactic to produce H_2O_2, rooted in numerous advantages compared to conventional production methods. To this end, the primary challenge is the interaction between intermediate and catalytic surfaces, which usually drives the formation of H_2O, corresponding to a $4e^-$ reduction reaction. Metal sing atom catalysts, possessing unique surface properties, have emerged as a holy grail to suppress the aforementioned issues. This review has highlighted recent employments of metal single-atom catalysts for electrocatalytic H_2O_2 production. Three primary metals, Ni_{SAC}, Co_{SAC} and other metals, have been mentioned and discussed in details. It can be said that NiSAC and CoSAC-derived catalysts have provided outstanding performance rooted in their capability to provide a proper surface toward the *OOH intermediate. Hitherto, modified and functionalized graphene is considered the major support. Exploring an alternative scaffold could open a milestone in catalytic efficiency and selectivity toward H_2O_2. Other transition metals could also a promising active sites. However, such materials have been still limited, leaving a huge room for researchers to explore in the future. In addition, the working medium should be considered for the large scale adaptability.

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