Electrocatalysis in confined spaces: interplay between well-defined materials and the microenvironment

Xue Han, a Qiang Gao, a Zihao Yan, a Mengxia Ji, a,b Christopher Long a and Huiyuan Zhu a

Catalysis in a confined space has attracted much attention due to the simultaneously designable nature of active sites and their microenvironment, leading to a broad spectrum of highly efficient chemical conversion schemes. Recent work has extended the scope of confined catalysis to electrochemical reactions. Mechanistic studies suggest that the confined environment in electrocatalysis can modulate mechanical, electronic, and geometric effects, stabilizing important charge-transfer intermediates and promoting reaction kinetics. In this minireview, we first discuss the fundamental concepts of confined catalysis by summarizing density functional theory (DFT) calculations and experimental investigations. We then present the rational design and applications of space-confined electrocatalysts with emphasis on the confined environment provided by carbon-based materials. We specifically focus on metal-based materials confined in carbon nanotubes (CNTs) and their applications in emerging electrochemical reactions including the oxygen reduction reaction (ORR), water-splitting reactions, carbon dioxide reduction reaction (CO2RR), and nitrogen reduction reaction (NRR). Finally, the existing challenges, opportunities, and future directions of electrocatalysis in confined spaces are highlighted.

1. Introduction

Tailoring active sites to stabilize or destabilize reaction intermediates plays a pivotal role in catalysis and thus has been commonly exploited as a powerful strategy to steer catalytic pathways for desired outcomes. 1,2 Nevertheless, energy scaling...
relations place constraints on optimizing catalytic performances. Consequently, there usually exists a volcano-shaped activity or selectivity trend on various catalyst surfaces.\textsuperscript{3-5} For example, in the electrochemical oxygen reduction reaction (ORR), Pt alloys with different compositions demonstrate a ‘volcano’ relationship between the measured activities and the adsorption energies of key intermediates, \textit{e.g.}, the oxygen-binding energy, along the reaction path.\textsuperscript{3,6,7} Similarly, in the electrochemical CO\textsubscript{2} reduction reaction (CO\textsubscript{2}RR), the activity of transition metal surface is limited by scaling relations between the binding energy of *CO and its hydrogenated species such as *CHO and *COH.\textsuperscript{8,9} The holistic kinetic and transport control to boost catalytic performance has been widely used in the industry. However, this exhaustive sorting of optimum operating conditions remains challenging. Inspired by nature, where enzymes can create a protein environment and incorporate multifunctionality to modulate catalytic reactions, the microenvironment, \textit{i.e.}, the confined space in close proximity to the catalytic active site, is now being recognized as equally important as the active site in regulating catalytic results and thus has been attracting extensive attention in recent years.\textsuperscript{10}

The confinement effect, especially at nanoscale, denoted as nanoconfinement, has been investigated thoroughly in conventional heterogeneous catalysis. For example, carbon nanotubes (CNTs) are a common class of materials that can establish nanoconfinement effects on active sites.\textsuperscript{11-13} Nanoconfinement has also been observed in nanocatalysts under two-dimensional (2D) materials, \textit{e.g.}, graphene and hexagonal boron nitride (h-BN), denoted as “catalysis under cover”.\textsuperscript{14,15} Recently, confined catalysis in emerging porous materials, such as metal–organic frameworks (MOFs), covalent organic frameworks (COFs), and polymer layers, has been considered as an effective strategy in modulating the diffusion and transport of reactants to promote catalysis.\textsuperscript{10,16,17} The comprehensive discussion of confinement effects in conventional thermal catalysis can be found elsewhere,\textsuperscript{15,16,18} and is beyond the scope of this article.

Electrocatalysis enables the conversion of small molecules, \textit{e.g.}, CO\textsubscript{2}, N\textsubscript{2}, and H\textsubscript{2}O, into high-value chemicals or fuels, paving the road to a sustainable energy future with minimal carbon footprints.\textsuperscript{1,19-21} The rational design of electrocatalysts is therefore of crucial importance in achieving this sustainable future. Compared with the abundant literature of confinement effects in thermal catalysis, electrocatalysis in confined spaces is relatively less discussed. Similar to the case of heterogeneous catalysis, a confinement environment in electrocatalysis embraces mechanical, electronic, and geometric effects\textsuperscript{22,23} (Fig. 1), stabilizing important charge-transfer intermediates and promoting reaction kinetics. It may also enable a desired diffusion and transport rate of reactants through the formation of porous nanoreactors.\textsuperscript{12,15} Specifically, mechanical effects induced by the geometric constraint can come into play. For example, a fine-tailored nanospace between CNTs and embedded metals could weaken the interaction between the confined reactants and metal sites due to the mechanical forces.\textsuperscript{22} Electronic effects can also affect the reactivity of
metal sites during electrocatalysis in the confined environment, similar to the case of confined catalysis where electron interactions, charge-transfer, and shifting of \( d \)-band of metal centers can occur.\(^{22}\) Furthermore, geometric effects resulting from the coverage of active sites by CNTs play a crucial role in affecting the catalytic behavior in confined catalysis. For example, the experimental investigations and atomistic simulations of single- and multi-walled CNTs demonstrated that the number of walls and radius of CNTs could determine their structural stability, thus potentially affecting their durability and activity during electrochemical reactions.\(^{24}\)

In this minireview, we summarize the most recent progress in electrocatalysis in confined spaces with a focus on nanomaterials encapsulated by carbon-based materials. More specifically, we provide a comprehensive perspective of metal-encapsulated CNTs (M@CNTs) employed in electrocatalysis. Various types of M@CNTs mainly focusing on non-precious metal-based materials are presented and discussed. Furthermore, applications of M@CNTs in emerging electrocatalysis reactions including the hydrogen evolution reaction (HER), oxygen evolution reaction (OER), ORR, CO\(_2\)RR, and nitrogen reduction reaction (NRR) are summarized and discussed in detail.

2. Fundamentals of CNTs in confined catalysis

2.1 Background of CNTs and their applications in electrocatalysis

Since the discovery of CNTs by Iijima in 1991, this unique one-dimensional (1D) material with a finite carbon structure and a needle-like tube morphology has attracted increasing research attention in the catalysis community.\(^{25}\) CNTs can be categorized into two groups. One is the single-walled nanotube (SWNT), which is a single graphite sheet rolled into a cylindrical morphology. The other is multi-walled nanotubes (MWNTs) consisting of multiple rolled graphene layers with a mutual center. CNTs are wrapped into cylinder tubes by graphene layers through \( sp^2 \) bonds that hold the carbon atoms into an aromatic ring structure.\(^{26,27}\) Such a well-defined structure with the strong \( \pi \)-electron interaction results in outstanding electrical capacitance and intriguing quantum effects of CNTs.\(^{27}\) Recent research has demonstrated that using CNTs as the carbon support in electrocatalysis provides synergistic interactions with metal catalysts and thus improves catalytic activity and selectivity.\(^{28,29}\) To date, many M@CNTs have been engineered into high-efficiency electrocatalysts in a range of electrocatalytic reactions such as ORR, water-splitting reactions, CO\(_2\)RR, and NRR.

2.2 Fundamentals of confined catalysis

Understanding the fundamentals of confinement effect has become an essential topic in the catalysis field. The confined environment is usually established at the space between metal surfaces and 2D materials, 1D nanotubes, and zero-dimensional (0D) porous materials, providing an ideal platform to incorporate site and environment cooperativity for enhancing catalytic performance. For example, compared with the metal nanoparticles (NPs) deposited on the exterior wall of CNTs, metal NPs encapsulated in CNTs exhibit tailored catalytic activities due to the electronic effects.\(^{11}\) Further experimental studies showed that the interplay between spatial confinement and electronic structure leads to significant strains and deformations in CNT channels, resulting in the downshift of \( d \)-band states and thus weakening the adsorption of molecules such as O\(_2\) and CO.\(^{2,11,22}\) Theoretical efforts in identifying the origin of the quantum confinement effect reveal that the spatially confined environment increases the molecular orbital energy, thus changing the adsorption and activation of confined reactants.\(^{14}\) To unify the descriptor of the confinement effect and enable the prediction of its role in catalytic activities, the confinement energy \( (E_{\text{con}}) \) is defined as the adsorption energy difference with

---

**Christopher Long** is an undergraduate student at Virginia Polytechnic Institute and State University. He is currently working in Prof. Huiyuan Zhu’s lab. His research interests are electrocatalysis and heterogeneous catalysis.

**Huiyuan Zhu** received her B.S. degree in Chemistry from the University of Science and Technology in China (2009), and her Ph.D. from Brown University (2014). From 2014 to 2018, she was the inaugural Liane B. Russell Fellow and then research staff in the Nanomaterials Chemistry Group, Chemical Sciences Division at the Oak Ridge National Laboratory. She is currently an assistant professor of Chemical Engineering at Virginia Polytechnic Institute and State University. Her research interests focus on tailoring multifunctional nanostructures for catalysis, energy conversion, and chemical transformation.
and without confinement environment. For example, by analyzing the electronic structure, it was found that the strong interaction between the encapsulated metal sites and the interior surface of CNT leads to the downshift of metal d-band states. A shift weakens the binding energy of oxygen ($E_b(O)$). Consequently, the confined metals are more difficult to be oxidized than those on the exterior walls of CNTs. As $E_b(O)$ differs from the interior walls to exterior walls on CNTs, this difference has been defined as the $E_{con}$, showing as,

$$E_{con} = E_b(in) - E_b(out)$$ (1)

where $E_b(in)$ and $E_b(out)$ are the binding energies of adsorbates over the confined metal and the same metal deposited on the CNT exterior walls, respectively. A positive $E_{con}$ suggests weakened adsorption of reactants/intermediates, which can be confirmed by surface science experiments. Previous investigations demonstrated that $E_{con}$ can effectively explain the confinement effect inside CNTs where the adsorption energy of intermediates/molecules is reduced compared with that of those metals on the exterior walls. This concept has a significant impact on tuning the molecule–metal interaction in a confined system and the corresponding confinement effect can be explicitly explained by $E_{con}$.  

3. Electrocatalysis in confined spaces

The carbon-based materials provide a confined space around the active sites, ultimately affecting the catalytic behavior in various electrocatalytic reactions. In the following session, we highlight the most recent advances in space-confined electrocatalysis with emphasis on the microenvironment created by CNTs. Confinements imposed by other carbon-based materials such as well-defined 2D graphene and oxides are also discussed as an extension of the scope. We present the synthesis, characterization, electrochemical evaluation, and mechanistic investigation of aforementioned systems and emphasize the importance of understanding the interplay between well-defined materials and the microenvironment for the rational design of efficient electrocatalysts. Moreover, electrocatalysis in confined spaces is discussed in detail in the following emerging reactions including ORR, water-splitting reactions, CO$_2$RR, and NRR.

3.1 ORR in confined spaces

As the key process at the cathode of proton exchange membrane fuel cells (PEMFCs) and metal–air batteries, ORR has attracted extensive attention. However, the state-of-art Pt-based catalysts for ORR suffer from high cost and poor long-term stability due to severe agglomeration on supports, limiting their commercial applications. Designing catalysts with confined structures not only offers viable solutions to improve the stability of Pt-based catalysts but also paves the way to the development of Pt-free catalysts with enhancement in both catalytic activity and durability.

Constructing a protective shell to encapsulate Pt-based catalysts can mitigate the agglomeration issue. For example, Cheng et al. designed a zirconia nanocage to encapsulate Pt NPs deposited on nitrogen-doped carbon nanotube (NCNT) as shown in Fig. 2a. The zirconia layer was deposited via the atomic layer deposition (ALD). The zirconia encapsulated Pt NPs, denoted as ALD50ZrO$_2$-Pt/NCNT600 °C, exhibited ten times higher stability than that of commercial Pt/C catalysts in acidic media (Fig. 2b). This is because the presence of the zirconia cage prevented the migration and agglomeration of Pt NPs on NCNT. Interestingly, the ORR specific activity of ALD50ZrO$_2$-Pt/NCNT600 °C was 6.4 times higher than that of Pt/C catalysts. Here the zirconia layer maintained the small size of Pt NPs and resulted in higher activity. Such improvements were also found in other Pt-based nanoalloys with confined structures. For example, Li et al. designed a PtNi nanoalloy catalyst embedded in a few graphitic carbon layers (PtNi@C). The PtNi@C catalyst not only achieved a specific activity of 1.54 mA cm$^{-2}$ at 0.9 V vs. reversible hydrogen electrode (RHE), which showed an 8.4-fold improvement over commercial Pt/C but also very little change in the electrochemically active surface area (ECSA) after 5000 cycles of potential scans in 0.1 M HClO$_4$.

Non-precious metal-based ORR catalysts have gained considerable attention because of their comparable activity to Pt-based catalysts and much lower prices. Unfortunately, unlike chemically inert Pt, non-precious metals, e.g., Fe, Co, and Ni, suffer from severe degradation under harsh environments such as acid and base solutions due to corrosion and subsequent leaching. Therefore, despite their catalytic activity, non-precious metal NPs cannot replace the state-of-the-art Pt catalysts yet. Recent progress has been made on addressing the stability issue by adding a confinement shell that protects metal NPs from harsh environments. For example, Deng et al. encapsulated Fe NPs into pea-pod like CNTs, denoted as Pod-Fe (Fig. 2c), through one-step synthesis using ferrocene and sodium azide as the precursors. Tested in a single H$_2$–O$_2$ fuel cell, the Pod-Fe only demonstrated a voltage loss of 8% after 210 h on stream. To further improve the ORR performance, they performed N-doping and Co-alloying on Pod-Fe, denoted as Pod(N)-Fe and Pod(N)-FeCo respectively. The Pod(N)-Fe and Pod(N)-FeCo showed higher output voltages than Pod-Fe while maintaining similar stability during a 220 h test. Similarly, Kim et al. designed a defect-free encapsulation of Fe NPs using a phenazine-based fused aromatic porous organic network, denoted as Fe@Aza-PON (Fig. 2d). The Fe@Aza-PON exhibited zero current loss even after 100 000 cycles and strong tolerance against methanol and CO poisoning.

In addition to Fe NPs, other Pt-free NPs also exhibited improved stability and activity with the aid of a confinement layer. In 2016, Liu et al. compared the ORR activity of different transition metals encapsulated in NCNTs (denoted as M/N-CNTs, M = Fe, Co, and Ni). The M/N-CNTs were synthesized via a one-step solid-state reaction of cyanamide and transition metal chloride. As illustrated in Fig. 2e, in an O$_2$-saturated 0.1 M KOH solution, the ORR onset potentials of Fe/
N-CNTs, Co/N-CNT, and Ni/N-CNT are 0.96 V, 0.94 V, and 0.91 V, while their half-wave potentials are 0.84 V, 0.81 V, and 0.73 V respectively. The Co/N-CNT catalyst not only outperformed other transition metal catalysts but was also on par with the Pt/C catalyst whose onset potential and half-wave potential are 0.98 V and 0.82 V. The Co-N bonds were identified as the active centers and the electron transfer from Co to carbon lowered the local work function of the carbon surface. In 2018, Cheng et al. reported Co NPs embedded in Co–N doped carbon nanofibers with only ~9 mV decay of half-wave potential after a 10,000-cycle durability test (Fig. 2f). Similarly, Wang et al. reported NCNTs encapsulated Co NPs (Co@NCNTs) with an onset potential of 0.94 V and a half-potential of 0.84 V for ORR. The authors also discussed the effect of N-dopant types (pyridinic-N vs. graphitic-N). According to DFT calculations, graphitic-N-doped carbon exhibited better ORR performance than pyridinic-N because graphitic-N atoms carry more negative charges such that those additional electrons can activate \( \text{O}_2 \) by occupying oxygen’s antibonding orbital. The Co@NCNTs catalyst was robust with cycling durability over 65 h when assembled into Zn-air batteries. Another recent work reported a novel strategy to synthesize Co/N-CNTs with 13 nm diameter from mesoporous silica-coated (mSiO\(_2\)) Co-based MOFs (ZIF-67). The obtained Co/N-CNTs demonstrated outstanding ORR activity and stability which was superior to commercial Pt/C catalysts in alkaline solution. In addition to single-component transitional metals, transition metal alloys with confinement effects have also been developed for ORR. For example, Sultan et al. reported a Co\(_x\)Fe\(_y\) alloy encapsulated in the nitrogen-rich graphitic tube, exhibiting no obvious shift in the linear sweep voltammetry (LSV) curve of ORR before and after 5000 CV cycles in 0.1 M KOH. Table 1 summarizes the performance of representative recently published ORR catalysts with confinement effects.

### 3.2 Water-splitting reactions in confined spaces

#### 3.2.1 Catalysts for HER

Hydrogen, as a clean and renewable fuel, is considered as a potential alternative energy carrier for future global energy demands. Electrocatalytic water splitting is an important hydrogen production process with high energy conversion efficiency. Currently, the state-of-the-art electrocatalysts for HER are noble metal Pt-based catalysts, but their high cost and limited resource impede the commercial application of this water-splitting scheme. Therefore, it is imperative to develop cost-effective and highly-effective Pt-free electrocatalysts to make this technology more economical. Non-precious metal-based materials, such as Ni, Co, and Fe, are promising low-cost alternatives to the state-of-the-art Pt-based electrocatalysts. However, just like the case of ORR, most non-precious metals are not stable in a strong acidic or alkaline medium, thus leading to severe degradation of electroactivity. Embedding these earth-abundant metals in CNTs as electrocatalysts is a potential solution. For example, recent advances showed that encapsulating Ni NPs into CNTs could increase the catalytic activity and mechanical strength as well as improve its corrosion resistance. Olugbode et al. reported a one-step pyrolysis method to obtain Ni encapsulated in CNTs,
denoted as Ni@CNTs. Such well-defined Ni@CNTs exhibited high electrical conductivity and large surface area and thus served as an efficient and stable HER electrocatalyst. Zou et al. reported a nanocomposite consisting of nitrogen-rich CNTs and confined Co NPs (Co-NRCNTs). This nanocomposite was synthesized by a simple and scalable two-step thermal treatment of cobalt chloride and dicyandiamide (Fig. 3). The Co-NRCNTs catalyst exhibited excellent HER activity with low onset potentials, under acidic, neutral, and basic conditions, very close to that of commercial Pt/C. This encouraging result allows it to be coupled with the best available OER catalysts, and play vital roles in the overall water splitting reaction. Meanwhile, the Co-NRCNTs catalyst also demonstrated high performance in HER with an overpotential of 108 and 87 mV in 1 M KOH and 0.5 M H2SO4, respectively. This result is better than the previously reported Co-based materials in a strong acidic or alkaline environment.

Transition metal alloys also demonstrate remarkable activities for HER due to the strong electron coupling of different components; once encapsulated in CNTs, their catalytic performances can be further enhanced. Deng et al. reported a simple chemical vapor deposition (CVD) method to encapsulate Fe, Co, and FeCo alloy into NCNTs and investigated their HER activity in the acidic medium (Fig. 4). The optimized FeCo-NCNTs catalysts exhibited high activity with an onset overpotential of ∼70 mV vs. RHE and long-term durability during the accelerated degradation measurements. In this system, these transition metals are protected by the carbon shell without direct contact with the acidic electrolyte, avoiding corrosion and aggregation of metal NPs during electrochemical cycling. The enhanced activity for HER results from the electron transfer from the metals to CNTs, modifying the electronic structure of the carbon surface. DFT calculations indicated that the adsorption free energy of the H atom on CNTs decreased by the introduction of metal and nitrogen dopants, which synergistically optimized the electronic structure of the CNTs, and thus promoted the HER activity through a Volmer–Heyrovsky mechanism.

### 3.2.2 Catalysts for OER

In addition to the cathode half-reaction HER for the water reduction, the anode half-reaction OER for the water oxidation is kinetically sluggish and severely impedes the overall efficiency of water splitting. At present, the most widely used electrocatalysts for OER are still precious metal-based catalysts, such as RuO2 and IrO2, however, their scarcity and high cost hinder their large-scale commercialization.

Cui et al. reported a facile strategy to synthesize single-layer graphene encapsulating earth-abundant 3d transition metals, including Fe, Co, Ni, and their alloy NPs through a CVD process in a confined channel of ordered mesoporous silica. The OER activity of these single-layer graphene encapsulated metals is following the order of Co < Fe < Ni. The optimized
Fig. 4  (a) STEM image of FeCo@NCNTs. (b) HRTEM image of FeCo@NCNTs with the inset showing the (110) crystal plane of the FeCo NP. (c) Polarization curves of Fe@NCNTs, Co@NCNTs, FeCo@NCNTs, FeCo@NCNTs-NH along with MWCNTs, SWCNTs and 40% Pt/C for comparison (d) stability measurement of FeCo@NCNTs. (e) The free energy profiles of the Heyrovsky route for pristine CNTs, FeCNTs, and Fe@NCNTs. (f) A schematic representation of the HER process on the surface of Fe@NCNTs (this figure has been adapted/reproduced from ref. 59 with permission from RSC Publishing, copyright 2008).
encapsulated FeNi alloy electrocatalyst exhibited the best activity with an overpotential of 280 mV at a current density of 10 mA cm$^{-2}$ and high durability even after 10,000 cycles, superior to that of commercial IrO$_2$ catalyst. DFT calculations demonstrated that the single-layer graphene promoted the electron transfer from the encapsulated metals to the graphene surface, which optimized the electronic structure of the graphene surface and further tuned the binding energies of reaction intermediates (O* and HO*) on the graphene surface.

Another work worth mentioning is the carbon-coated FeCo alloy NPs confined in SWCNTs, denoted as FeCo/SWCNTs. This single carbon layer covered on FeCo NPs could provide electron transport pathways for confined metal NPs, which facilitated the O$_2$ oxidation on the carbon surface, resulting in outstanding OER performance, with an overpotential of 253 mV at 10 mA cm$^{-2}$ and a Tafel slope of 44 mV dec$^{-1}$ in 1.0 M KOH solution. Moreover, the FeCo/SWCNTs maintained most of the original activity after being tested for 50 h, which can be attributed to the protective effect of SWCNTs on the aggregation and corrosion of NPs.\textsuperscript{55}

### 3.2.3 Bifunctional catalysts for overall water splitting.

In order to enhance the overall efficiency of water splitting, the two half-reactions of HER and OER both require efficient electrocatalysts to reduce the overpotential.\textsuperscript{68} Unfortunately, the development of efficient bifunctional electrocatalysts to simultaneously promote HER and OER in the same electrolyte remains challenging.\textsuperscript{69,70} Wang et al. reported a bifunctional catalyst for HER and OER with Co NPs encapsulated in nitrogen-doped carbon (Co@N-C) which was prepared by pyrolysis of cobalt acetate and imidazole followed by acid leaching.\textsuperscript{71} The unique encapsulation structure in Co@N-C leads to high activity and stability for HER in a wide pH range. Furthermore, the Co@N-C catalyst showed promising activity and durability as an OER catalyst in the alkaline medium as well. The HER and OER activities of Co@N-C were superior to that of Fe@N-C with similar content of nitrogen and MWCNTs. Comparative studies suggested that the interaction between Co NPs and surface nitrogen-doped carbon shells is vital for favourable HER and OER activities. Finally, the Co@N-C catalyst was employed as a bifunctional catalyst in a water electrolyzer, paving the road for future practical applications. In addition to monometallic catalysts, Zheng et al. reported a highly efficient bifunctional electrocatalyst for water splitting with CoFe alloy NPs encapsulated in nitrogen-doped CNTs (CoFe@N-C) via simple heat treatment. The as-synthesized CoFe@N-C exhibited low overpotentials of 110 and 292 mV at 10 mA cm$^{-2}$ for HER and OER, respectively. Meanwhile, CoFe@N-C demonstrated excellent stability after 1000 cycles of cyclic voltammetry for HER and OER.\textsuperscript{72}

Ouyang et al. reported a highly efficient and stable hybrid electrocatalyst of Co and $\beta$-Mo$_2$C NPs encapsulated in NCNTs (Co/$\beta$-Mo$_2$C@N-CNTs) as a bifunctional electrocatalyst for overall water splitting in an alkaline electrolyte (Fig. 5).\textsuperscript{73} The Co/$\beta$-Mo$_2$C@N-CNTs demonstrated very small overpotentials of 170 and 356 mV at 10 mA cm$^{-2}$, and Tafel slopes of 92 mV dec$^{-1}$ and 67 mV dec$^{-1}$ in 1 M KOH for HER and OER, respectively. The hybrid Co/$\beta$-Mo$_2$C@N-CNTs electrocatalyst in an overall water electrolysis cell showed a stable current density of 10 mA cm$^{-2}$ at 1.64 V with high stability for 24 h. The authors attributed the enhanced electrochemical performance of Co/$\beta$-Mo$_2$C@N-CNTs to the well-defined heterointerface between Co, and $\beta$-Mo$_2$C NPs which could enrich the active sites and promote the electron transfer between the carbon matrix and NPs. Moreover, the confinement effect provided by N-CNTs not only protected the Co and $\beta$-Mo$_2$C NPs from alkaline corrosion but also promoted rapid electron transport between the NPs and the carbon matrix. DFT calculations further proved that the synergistic effect between the N-CNTs, Co, and $\beta$-Mo$_2$C NPs gave rise to a lower reaction free energy of HER and OER. Interestingly, Guo et al. designed an efficient trifunctional electrocatalyst of Co$_9$P$_4$/CoN core–shell NPs encapsulated in NCNTs (Co$_9$P$_4$/CoN-in-NCNTs) for ORR, HER, and OER. The Co$_9$P$_4$/CoN-in-NCNTs with double active centers exhibited excellent activity for water splitting with an overpotential of 1.64 V at the 10 mA cm$^{-2}$. Notably, Co$_9$P$_4$/CoN-in-NCNTs showed high activities toward ORR and OER, making it a promising candidate for Zn-air batteries.\textsuperscript{74} A comprehensive summary of the representative HER, OER, and overall water splitting performance of recently developed electrochemical catalysts is presented in Table 2 for comparison among systems.

### 3.3 CO$_2$RR in confined spaces

Mastery of the conversion of the excess CO$_2$ to high-value-added carbon-based chemicals is paramount to address the energy crisis. CO$_2$RR driven by renewable electricity and using water as the proton source provides a possible route to enable a carbon-neutral cycle.\textsuperscript{75–77} Currently, noble metals including Au, Pd, and Ag predominately convert CO$_2$ into CO under electric bias; while the base metals such as Bi, Sn and In, generate formic acid as the major product.\textsuperscript{78–83} N-CNTs also demonstrate activity for CO$_2$RR with a much lower cost compared with the aforementioned metal systems.\textsuperscript{84} Wu et al. found different types of nitrogen in N-CNTs exhibited different selectivity towards CO. The pyridinic nitrogen possessed the higher adsorption energy in the rate-determining step of the first electron–proton transfer to form the intermediate *COOH, thus weakening the binding of *CO.\textsuperscript{85} In general, the confinement effect in CNTs can help reduce the adsorption energy of the intermediates at the active sites, facilitating the dissociation of target products and promoting the reaction kinetics.\textsuperscript{11} As a result, recent work has been focused on the non-precious metal NPs encapsulated in N-CNTs to exploit the confinement effect on the adsorption energy to steer the pathway of CO$_2$RR.

Ni NPs encapsulated in N-CNTs (Ni@N-CNTs) have been synthesized using a one-step pyrolysis method by annealing the mixed dicyandiamide and NiCl$_2$ under the protection of N$_2$.\textsuperscript{86} TEM shows that Ni NPs with a diameter of 50–100 nm were wrapped by layers of N-CNTs (Fig. 6a). The X-ray absorption fine structure analysis confirmed the metallic state of Ni.
in Ni@N-CNTs. To shed light on the confinement effect in CO$_2$RR by confining Ni NPs inside the N-CNTs, Ni NPs deposited on the exterior surface of N-CNTs (Ni-N-CNTs) were prepared as a comparison. Ni@N-CNTs demonstrated the highest faradaic efficiency (FE) of 99.1% towards CO at $-0.8$ V (vs. RHE), while the maximum FE of Ni-N-CNTs, N-CNTs, and Ni NPs only could reach up to 34.9%, 35.9%, and 0.3%, respectively. The largely enhanced selectivity towards CO in

---

**Fig. 5** (a) Steps for the synthesis of Co/β-Mo$_2$C@N-CNTs. (b) SEM image and (c) TEM image of the Co/β-Mo$_2$C@N-CNTs. (d) Electrocatalytic HER activities in 1 M KOH. (e) Electrocatalytic OER activities in 1 M KOH (this figure has been adapted/reproduced from ref. 73 with permission from John Wiley and Sons, copyright 2019).
**Ni@N-CNTs** was attributed to the benefit of confined metallic Ni, which significantly decreased the charge-transfer resistance and boosted the formation of intermediates *CO*. Moreover, the FE for CO production was maintained at 96% after a 20 h long-term test. In addition, the calculation results on the different sites inside or outside CNTs and N-CNTs of Ni clusters (Fig. 6b and c) further verified the Ni clusters confined in CNTs indeed weakened the adsorption *CO* on Ni surface, facilitating the dissociation of CO molecules. It is noteworthy that Ni was the active site for CO2RR in Ni@N-CNTs and the content of Ni was determined up to 26 wt%. Decreasing the size of metal NPs to the single-atom level emerges as an efficient strategy to maximize the atom efficiency. Hou *et al.* reported a self-sacrifice template method by pyrolysis of core-shell ZnO@ZIF-NiZn nanorods at 800 °C for 5 h to obtain Ni single atoms anchored N-CNTs (Ni SAs@N-CNTs) catalyst, enabling highly exposed active centers to adsorb and activate CO2 molecules.87 Nearly 100% FE of CO was obtained at −0.8 V vs. RHE in Ni SAs@N-CNTs system with Ni content confirmed to be 1.68 wt%.

### Table 2  Summary of representative electrocatalysts for HER, OER and water-splitting

<table>
<thead>
<tr>
<th>Electrocatals for HER</th>
<th>Catalyst</th>
<th>Electrolyte</th>
<th>Onset potential (mV)</th>
<th>Overpotential at −10 mA cm−1</th>
<th>Tafel slope (mV dec−1)</th>
<th>Stability</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni@CNTs</td>
<td>1 M KOH</td>
<td>110</td>
<td>266</td>
<td>102</td>
<td>10 h</td>
<td>29</td>
<td></td>
</tr>
<tr>
<td>Co-NRCNTs</td>
<td>0.5 M H2SO4</td>
<td>−50</td>
<td>260</td>
<td>69</td>
<td>8.5–10 h</td>
<td>61</td>
<td></td>
</tr>
<tr>
<td>FeCo-NCNTs</td>
<td>0.1 M H2SO4</td>
<td>—</td>
<td>—</td>
<td>72</td>
<td>—</td>
<td>59</td>
<td></td>
</tr>
<tr>
<td>Electrocatals for OER</td>
<td>FeNi encapsulated single layer graphene</td>
<td>1 M NaOH</td>
<td>1440</td>
<td>280</td>
<td>70</td>
<td>—</td>
<td>67</td>
</tr>
<tr>
<td>FeCo/SWCNTs</td>
<td>1 M KOH</td>
<td>—</td>
<td>253</td>
<td>44</td>
<td>50 h</td>
<td>55</td>
<td></td>
</tr>
<tr>
<td>Bifunctional catalysts for HER and OER</td>
<td>Co@N-C</td>
<td>1 M KOH</td>
<td>—</td>
<td>210 (HER)</td>
<td>108 (HER)</td>
<td>10 h</td>
<td>71</td>
</tr>
<tr>
<td>Co/β-Mo2C@N-CNT</td>
<td>1 M KOH</td>
<td>—</td>
<td>170 (HER)</td>
<td>92 (HER)</td>
<td>336 (OER)</td>
<td>67 (OER)</td>
<td>73</td>
</tr>
</tbody>
</table>
In addition to embedding metal particles in N-CNTs, the construction of M–N–C structure via anchoring metal-based hybrid materials inside the CNTs is effective in advancing the electrocatalytic activity. For example, Jia et al. prepared the Fe/Fe₃C NPs wrapped by N-CNTs, denoted as Fe/Fe₃C@N-CNTs via annealing the mixed dicyandiamide and carbon-coated Fe₃O₄ NPs at 650, 750, and 850 °C, respectively. TEM and HRTEM images in Fig. 6d, e show the successful encapsulation of Fe/Fe₃C NPs inside the CNTs. Compared to the samples calcined at 650 and 850 °C, Fe/Fe₃C@N-CNTs calcined at 750 °C showed the lowest onset potential and maximum FE of CO at −0.74 V vs. RHE. Meanwhile, the syngas of H₂/CO ratio could be flexibly regulated in the range from 1:1 to 3:1 (Fig. 6f). The high selectivity for CO production in Fe/Fe₃C@N-CNTs-750 could be attributed to the abundant pyridinic and pyrrolic nitrogen that facilitates the dissociation of *CO. To sum up, intimate contact between CO₂ molecules and metal NPs can be established thanks to the space confinement in N-CNTs. Moreover, the binding and protonation of intermediates can be tuned by controlling the d-band states of metal centers. As previously mentioned, the confinement effect within N-CNTs via enwrapping metallic particles has been investigated in OER, HER, ORR. However, there are only a few examples of CO₂RR in this research area. We envision that the rational design and synthesis of metallic NPs confined in N-CNTs merits further investigations on generating high value-added products, especially C₂⁺ products in CO₂RR.

3.4 NRR in confined spaces

Ammonia (NH₃), as an essential raw material for the chemical industry and agriculture, is also considered as a potential energy carrier for chemical conversion. In industry, the Haber–Bosch process is an important NH₃ production process. However, this process operates under harsh reaction conditions, requiring immense energy input. The electrochemical nitrogen reduction to NH₃ is considered a promising alternative to the industrial Haber–Bosch process due to its lower energy consumption under ambient conditions. Currently, precious metals, such as Ru, Rh, and Au, demonstrate outstanding NRR activity, but their high price and scarcity impede the practical application; while the non-precious metals such as Fe, Co, Mo, Ti, and Bi prefer HER over NRR, thus demonstrating low selectivity toward NH₃. Recent studies have found that encapsulated nonprecious metal-based materials by CNTs exhibit NRR activities in ambient conditions. Zhang et al. reported a facile strategy to fabricate CNTs with embedded CoP NPs (CoP/CNs) using a pyrolysis-phosphorization approach. The CoP/CN catalyst showed the NH₃ yield rate of 48.9 µg h⁻¹ mgₖₑₕ⁻¹ with FE of 8.7%. Additionally, metal encapsulated in N-CNTs can also enhance the activity of NRR. Yuan et al. developed a new approach by tuning the work function of N-CNTs via Cr, Cu, Mn, Co, Fe, Ni-metal encapsulation. Among these catalysts, Ni encapsulated in N-CNTs (Ni@NCTs) showed the lowest work function of 5.2 eV. As a result, electron transfer on the catalyst surface was facilitated and the rate-limiting step of NRR for converting N₂ to N-NH was accelerated. In detail, Ni@NCTs exhibited a NH₃ yield rate of 53.88 µg h⁻¹ mgₖₑₕ⁻¹ with FE of 7.33% at −0.5 V and −0.3 V vs. RHE, respectively.

In addition to monometallic catalysts, Wang et al. confined Fe and Cu atoms in the narrow surface cavities of graphic carbon nitride, denoted as CNT@C₃N₄-Fe&Cu. The as-prepared CNT@C₃N₄-Fe&Cu showed the NH₃ yield rate of 9.86 µg h⁻¹ mgₖₑₕ⁻¹ and reached the highest FE of 34% at −0.8 V. Furthermore, after a 10 h stability test, CNT@C₃N₄-Fe&Cu still maintained a stable current at −1.6 V. Nevertheless, NRR is a relatively new research area; it still requires an in-depth understanding and further investigation of the reaction mechanism, testing conditions, analysis methods for the future development of efficient catalysts.

4. Conclusions

A critical element in the pursuit of design strategies for advanced electrocatalysts is the simultaneous control of active sites and their surrounding microenvironment. Electrocatalysis in confined spaces is well-suited for this mission and opens enormous opportunities for future catalyst design. One of the crucial concepts here is the confinement effect that describes the difference of binding energy with/without the confined space. With this concept, it enables the prediction of confinement effects on electrocatalytic behavior in different reaction systems. The interplay between active sites and their microenvironment provides synergistic electronic, mechanical, and/or geometric effects in directing electrocatalytic outcomes of confined systems. For example, in the nitrogen-doped CNTs system, the interaction between the N dopants and embedded metal catalysts can generate more efficient active centers to further improve their catalytic activity. As discussed in Section 3, the interplay between active centers and CNTs usually leads to the protective environment against electrochemical cycling, shifting of metal centers, charge-transfer, as well as adjusted work functions of CNTs to regulate the adsorption and activation of reactants and intermediates. Furthermore, non-precious metal NPs confined in carbon-based materials demonstrate comparable performance in ORR, HER, OER, CO₂RR, and NRR with those precious metal-based state-of-the-art catalysts.

5. Challenges and opportunities

Compared with the fundamental investigation of conventional heterogeneous catalysis, the origin of the confinement effect in electrocatalysis has not been fully revealed. Surface science, especially by coupling electrochemical evaluations with on-line spectroscopy, such as surface-enhanced IR, Raman, differential electrochemical mass spectroscopy, and X-ray absorption spectroscopy, will play a pivotal role in pinning down the nature of confinement in electrocatalysis.
Parallel to the suggested surface chemistry efforts, we also emphasize the importance of a highly integrated framework of theory and experimentation. Although this minireview is mainly focused on the experimental progress, close integration of theoretical and experimental investigation is appealing to pinpoint the mechanistic pathways in confined electrocatalysis. For this reason, we anticipate that the well-defined systems including monodisperse NPs and single-atom catalysts will lead to in-depth understanding and further development to establish a feedback loop for adaptive modelling and prediction.

Regarding the materials system, metals confined in other materials systems beyond CNTs will open new opportunities in precisely tailoring the interplay between active sites and their microenvironment. For example, CNTs usually demonstrate weak interactions with metal centers; while metal oxides may establish strong-metal support interactions at the interface between oxides and metals,\textsuperscript{97,98} enabling efficient charge transfer. We also anticipate that by reducing the size of the microenvironment imposed by the cover, the confinement effect may be amplified. Furthermore, the geometric effect, e.g., the porosity, and the size of coating, and the electronic effect, e.g., the charge transfer direction and degree\textsuperscript{98} can be precisely controlled and harnessed for catalysis in these well-defined systems.

In summary, electrocatalysis in confined spaces has far-reaching implications in chemistry, materials science, and sustainable energy applications. We believe that advanced and practical electrocatalysts for next-generation chemical and energy devices can be developed based on the concept of confinement, calling for the understanding of fundamental aspects and precision chemical synthesis.

Conflicts of interest
There are no conflicts to declare.

Acknowledgements
We acknowledge the support from the Jeffress Trust Awards Program in Interdisciplinary Research from Thomas F. and Kate Miller Jeffress Memorial Trust.

Notes and references