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Cobalt Single Atom Heterogeneous Catalyst: Method of Preparation, Characterization, Catalysis, and Mechanism

Baljeet Singh, Surender Kumar and Archana Singh

Abstract

Transition metal nanoparticles and metal oxide have been used extensively for a wide range of applications in electrochemical reactions (HER, ORR, OER) and energy storage (supercapacitors batteries). To make less expensive, the use of transition metal at minimum metal contents without compromising the catalytic activity could be one way. Most of the catalytic process takes place on the surface and reaction dynamic can be manipulated by changing the particle size and shape. For a long time, single metal atom organometallic compounds have been used as a catalyst at the industrial level. However, problems with the homogeneous catalyst to recover back at the end of the process lead to development of heterogeneous single-atom catalysts with equal activity like a homogeneous catalyst. Cobalt single atom has received a tremendous interest of the scientific community due to its excellent catalytic activity and recyclability. Cobalt single-atom catalyst has shown better performance compared with sub-nanometer nanoparticles catalyst for ORR, OER, and HER. This chapter is conferring method of preparation of carbon-based single Co atoms heterogeneous catalyst, their application for ORR, OER, HER reactions, and mechanistic investigations through DFT calculations. The role of single Co metal atoms and anchoring using N or heteroatoms is discussed and compared.

Keywords: single metal atom heterogeneous catalyst, transition metal catalyst, homogeneous, heterogeneous, oxygen reduction reaction (ORR), oxygen evolution reaction (OER) and hydrogen evolution reaction (HER)

1. Introduction

The main aim of current research on catalysis is to find out long-lasting catalyst that can consistently work without compromising its catalytic activity [1–3]. The catalytic activity mostly depends on a number of active sites and their accessibilities. Catalytic activity can be tuned by manipulating the nanoparticles sizes or by producing shaped nanoparticles with exposed facets [2–5]. Keys factors for catalytic properties are not very well known and atoms with the different environments are mostly showed different catalytic activity. For example, an atom on the edges and on corners mostly showed different properties, more catalytic activity compared with the atoms present in the middle of exposed facet.

For catalysis purpose, mostly surface atoms are accessible and catalytically active, remaining bulk atoms are providing support. The amount of metal required to produce catalytic activity can be reduced by bringing down the particle size at the atomic level, it may be enhanced by using single-site metal catalyst. Single-metal atom catalysts (SMACs) have shown better activity compared with sub-nanometer nanoparticles materials. As limited by the change in morphologies of nanoparticles, a concept of SMACs has emerged because it only way remaining to maximize efficiency of catalyst [4, 5]. Many single Co atoms homogeneous catalysts have been reported (**Figure 1a, b**) [7], in which single metal atom is supported by the bulky organic functional groups; their activity and accessibility depends on the organic environment around the single metal atom. These organic functional groups do not allow to agglomerate, provide thermodynamic stability and chemical stability (**Figure 1**). However, it is very tedious and laborious to recover back homogeneous catalyst from solution mixture and hard to reuse it again. Thus we need a catalytic system that is easy to recover and reusable. So, heterogeneous catalysts can be a good choice. However, to achieve the catalytic efficiency equal to homogeneous catalyst, a single-atom catalyst preparation is still challenging.

The preparation of stable SMACs is still challenging because high energy of a single atom leads to agglomeration and makes them unstable under reaction conditions at the industrial level. An effective way for a synthesis of SMACs via increasing the interaction between a metal atom and support [4]. In general process, by reducing the size of nanocatalyst and bring them at atomic scale, we are trying to heterogenize homogeneous catalysts on heterogeneous supports. This can be done by overcoming surface energy of a single atom by anchoring on a support substrate, which might sufficiently active like a homogenous catalyst. Graphene is a good support to stabilize coordinately unsaturated single metal sites (CUMS). Graphene is a

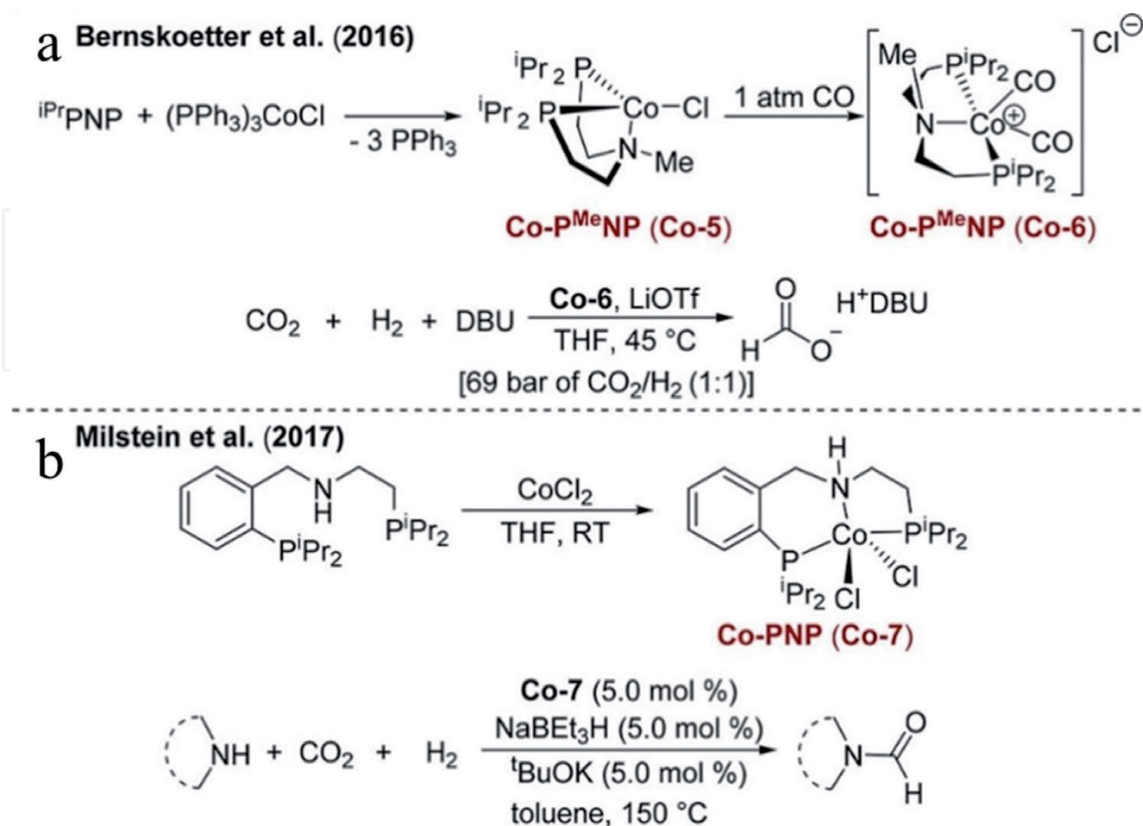


Figure 1.

(a and b) Co-PNP complex catalyzed the hydrogenation of CO₂ to formate and formamides (Reproduced with the permission, Copyright 2018, American Chemical Society [7]).

perfect two-dimensional structure with high specific surface area, high mechanical strength, and thermal stability. Its unique structure and electronic properties are promising for the synthesis of stable CUMS metal atom. Several recent works have been demonstrated the preparation of SMACs using graphene [6–11].

Overall support substrate and metal interaction could help to design long-lasting, stable SMACs which could work without loss of catalytic activity under the operational condition for specific reaction or applications. Using support-metal interaction concept, Sahoo *et al.* investigated a theoretical model of graphene supported transition metal (TM) atom including Iron (Fe) single atom [8]. DFT result showed that graphene supported single-atom catalyst display relative lower activation energy barrier for methane activation. However, of its excellent catalytic performance, it has been proved that a single metal atom can migrate on a surface of graphene defect (**Figure 2**), which allows them to agglomerate into bigger nanoparticles, resultant in loss of catalytic activity. It has been proved that a single metal atom can migrate from one position to another position on graphene layer. Zhao *et al.* observed single Fe atom diffusion on graphene edge [12]. *In situ* electron microscopy was used to investigate diffusion of Fe along edges of graphene via either adding carbon atoms or by removing carbon atom (**Figure 2A–G**). Besley *et al.* also studied the dynamic behavior of single Fe atoms embedded in graphene sheet [13]. Migration of Fe atom was also observed by the aberration-corrected high-resolution transmission electron microscopy (AC-HRTEM) experiments. Anchoring mechanism using heteroatoms has found most effective tool

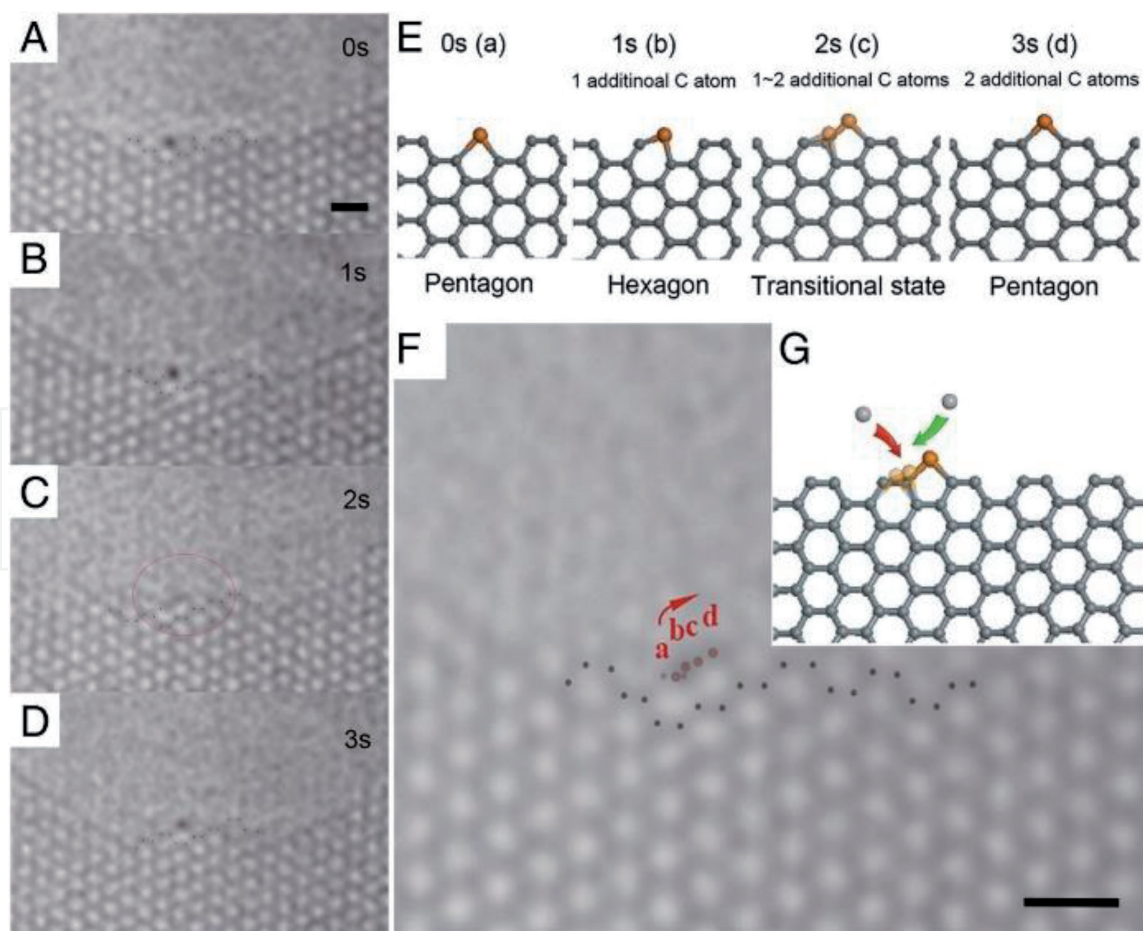


Figure 2.
One cycle growth of graphene edge: (A–D) a series of high-resolution TEM images for 4 s, Fe atom are highlighted with the red dots, nearby carbon atoms are highlighted by black dots. (E) Corresponding atomic structure of A–D. (F) The combination of A–D, which showed the trace of the Fe atom during one unit cell translocations, (G) the atomic structure of the whole growth process (Reproduced with the permission, 2014, Proceedings of the National Academy of Science of the United States of America [12]).

for synthesis of stable SMACs, which could avoid their agglomeration and helps in remain catalytically active. However, anchoring mechanisms is not known completely and this mechanism can vary with substrates. In case of pristine graphene-SMACs void or defect in the single-layer graphene served as a trap site for the single metal atom and help them to stabilize.

2. Synthesis characterization and applications of single metal atom heterogeneous catalyst

The main objective of synthesis of SMACs is 100% dispersion of metal atom on a solid support (**Figure 3**). In SMACs, metal sites may contain different numbers of metal atoms like dimer, monomer, trimer or cluster of a single atom. The main feature of SMACs is highly active low coordination metal site which attracts reactant molecules effectively, and excellent overall rate of reaction. The most important feature of SMACs is metal support interaction which affects the electronic structure and bond formation capability with other molecules in reaction media [15]. However, it is quite challenging to synthesis isolated single metal atoms on desired support. For long-lasting stable SMACs, the interaction between a metal atom and support should be strong. Otherwise, these metal atoms can leached out or migrate on surface of support and slowly convert into metal nanoparticles during reaction process. For synthesis of SMACs, many techniques have been used, including wet chemistry method, atomic layer deposition, modular synthesis based on metal–organic framework, and mass-selected soft-landing method [16]. Out of all techniques, pyrolysis and wet chemistry synthesis are mostly preferred. In pyrolysis, samples are heated at elevated temperature $> 500^{\circ}\text{C}$ under the protected atmosphere of different gases including N_2 , Argon, NH_3 , and H_2 . For the synthesis of carbon or graphene-based SMACs, pyrolysis at high temperatures

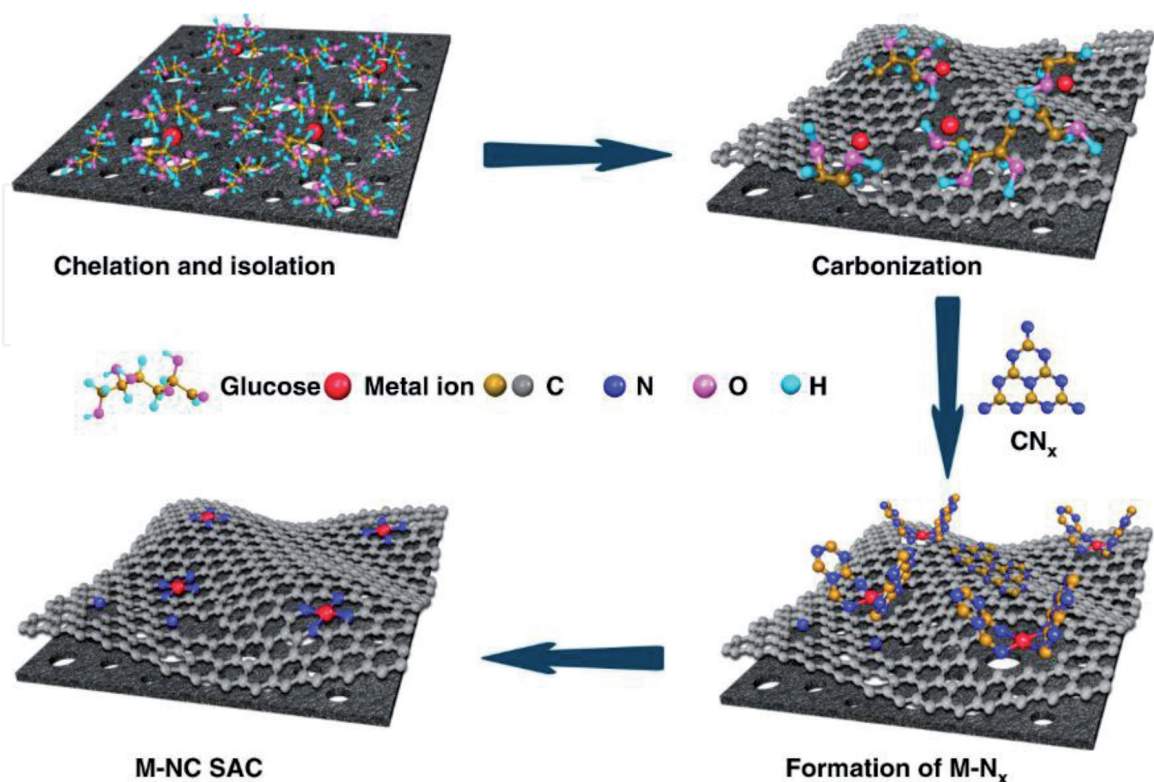


Figure 3. Demonstration of TM single atom anchoring on a carbon support, (Reproduced with the permission, 2019, Nature Publishing Group [14]).

at inert gas conditions has been used extensively. Carbon-based materials including graphite [5], graphene [17, 18], nitrogen-doped graphene [19] were proved to be a suitable support for the synthesis of Co SMACs, because of abundant carbon vacancies at anchoring sites. In general, SMACs synthesis divided into four categories [20].

a. Use of metal–organic framework (MOF) for SMACs synthesis: In recent years use of MOF in heterogeneous catalyst continuously expanding because it well defines porous structure, high-ordered metal and organic arrangements, well-separated metal center, and multi-metallic. MOF is well defined single metal atom catalyst, however, due to its thermal and chemical stability significantly hamper the widespread uses. Also, as prepared MOF cannot be used for electrocatalytic applications, only few examples known in literature [21]. One way is to mitigate these issues to convert them into carbon-supported SMACs. Carbon-based materials do not only provide anchoring with the graphitic skeleton, but also provide thermal and chemical stability to the single metal atoms. Conducting graphitic two-dimensional nature of carbon support help in manipulating charge density and electronic structure of the metal atoms.

b. Use of small metal-containing organic molecules for SMACs synthesis: In this procedure as prepared carbon skeletons are mixed with the metal-containing small organic molecules and subsequent heating at high temperature in the control environment give a single metal atoms doped material [20]. These molecular precursors are mostly low boiling or melting point, low thermal decomposition temperature which creates difficulties during the carbonization of these precursors with the support materials. Hence for the synthesis of SMACs, the selection of molecular precursors is very crucial and important. For example, Chen *et al.* used silver tricyanomethanide and cyanamide as a starting molecular precursor [22]. Both precursors have nitrogen and cyanamide mostly used for the synthesis of g-C₃N₄. Carbonization of a mixture of both leads to the formation of C₃N₄ nanosheet doped with the silver atoms. In this procedure, silver precursors can be replaced with the porphyrin complexes of iron, zinc, or cobalt molecular precursors for the synthesis of different metal atoms on C₃N₄. Besides this, a mixture of two different molecular precursors can help in the preparation of a multi-metallic single-atom catalyst (MM-SACs).

c. Use of sacrificial or hard template for SMACs synthesis: During the heterogeneous catalytic reaction, reactant and product undergoes a series of reactions over the catalyst surface: (1) diffusion of reactant through the solvent used to disperse catalyst, (2) diffusion of reactant in the pore of the catalyst to access catalytic sites, (3) adsorption of reactant on active site, (4) surface reaction or catalysis involved surface diffusion, (5) desorption of product or byproduct from catalytic sites, (6) diffusion of product or bi-product through pores, and (7) diffusion of the product in solvent used for catalysis [20]. Hence, surface area, pore size distribution, and accessibility of active sites are very important parameters for good catalytic activity. Surface area and pore size of catalyst can be manipulated using the templates like silica which can be sacrificed at the end of synthesis to produce a porous network. For example, Liang *et al.* synthesized a series of Co and Fe single atoms heterogeneous catalysts in a mesoporous carbon matrix using silica as a hard template [23]. After pyrolysis in a controlled environment, silica can be leached out with the help of base using HF or NaOH aqueous solutions. Besides that, metal oxide including MgO or Mg(OH)₂ can also be used for the synthesis of SMACs.

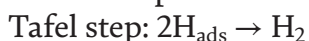
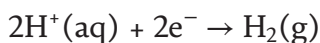
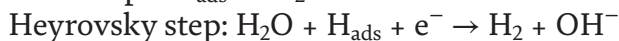
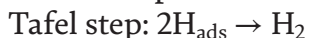
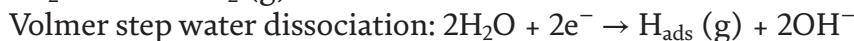
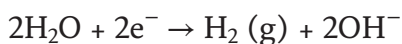
d. Use of metal-containing complexes with carbon matrix for SMACs

synthesis: this procedure widely used for the synthesis of carbon-based SAMCs. Dispersed carbon nanoparticles or graphene oxide was mixed with the metal salt and other necessary chemicals [20]. Heating in a close reactor at high temperature and pressure leads to the formation of metal embedded carbon hydrogel. Dried aerogels are being heated at high temperatures in NH_3 atmosphere which helps in creating an N anchoring site in graphene oxide sheets or carbon networks. In final materials, the M-N_4 site formed, which can be conformed using surface characterization techniques including high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) and Extended X-ray absorption fine structure (EXAFS). NH_3 treatment can also be used for creating an N anchoring site in previously synthesized porous carbon along with the metal salt mixture. This leads to the formation of single metal salt along with bigger metal nanoparticles, which can be eliminated using post-synthesis acid treatment.

2.1 Hydrogen evolution reaction (HER)

H_2 is a next-generation green fuel and H_2 generation using HER can leads to sustainable ways to produce H_2 which can be used for generation of electricity in fuel cells of combustion engine or directly can be used in H_2 engine for transportation. To achieve the high efficiency of water splitting, use of an efficient catalyst to minimize the overpotential is required. Noble metals nanoparticle including Pt, Ag, and Au are known for HER activity and requires very small overpotential with the high reaction rate in acidic solution. However of its excellent catalytic activity, due to high cost, and limited availability, we urgently need to develop an efficient transition metal (TM) catalyst. Co is a known TM, available in large amounts and also not very expensive. The development of Co single-atom catalyst could further reduce the amount of metal required to achieve catalytic efficiency like noble metals.

Water electrolysis is performed by passing a current between two electrodes through the acidic or basic solution. Overall HER reaction consists of two half-reactions, at cathode hydrogen evolution reaction (HER) where H_2 is formed and at anode, oxygen evolution reaction (OER) where O_2 is formed. These reaction mechanisms can vary using pH of the reaction media. In acidic medium, the active ions are proton and in alkaline medium, hydroxide ions are active species (below reaction). HER reaction ($2\text{H}^+ + 2\text{e}^- = \text{H}_2$) is a two-electron transfer cathodic reaction in electrochemical water splitting.

Acidic electrolyte:**Alkaline electrolyte:**

Water molecules are the sources of proton in alkaline medium; they react with the OH^- ions, resultant in the formation of hydrogen atom adsorbed on the surface

of electrode. The mechanism of HER reaction can be clearly observed using cyclic voltammetry (CV). A CV is recorded mostly in the range of maximum and minimum potential values. HER mechanism has three reaction steps including Volmer, Heyrovsky, and Tafel. This reaction can have different pathways on the cathode and mostly followed the combination of two reaction pathways. Overpotential is defined as the difference between the equilibrium between thermodynamic potential and the potential at which catalyst operates at a specific current at given operational conditions.

$$\eta = E_{\text{applied}} - E_t$$

where η is the overpotential (V), E_{applied} is applied potential (V), E_t is thermodynamic potential (V). Tafel plots in electrochemistry are used to understand the kinetics of electrochemical cell reactions on the surface of catalyst. This can be used for both anodic and cathodic reactions. Final equation included two Tafel variables including Tafel slope and exchange current density.

$$\eta = \beta * \log\left(\frac{i}{i_0}\right)$$

where β is the Tafel slope (mV/dec), i is the current density (A/m²), i_0 is the exchange current density (A/m²). β is a Tafel slope described the slope of the linear region (**Figure 4c**) within the Tafel plot. A Tafel slope gives information about the rate of reactions; which is inherent properties of the catalyst. For example, a Pt catalyst in acidic medium, Tafel slope is 120 mV for Volmer step, 40 mV for Heyrovsky step and 30 mV for Tafel step. For a good electrocatalyst, a small Tafel slope value

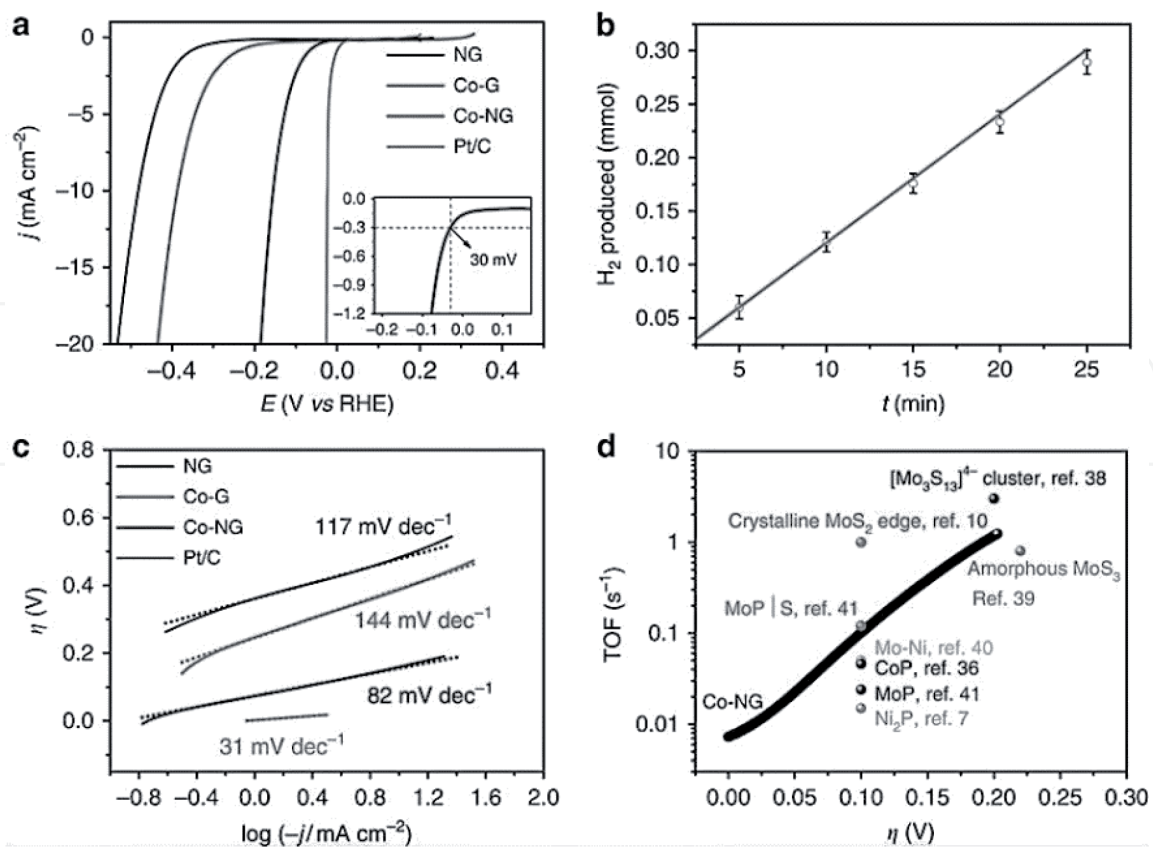


Figure 4. HER reaction performance (a) LSV of Co-NG, NG and Co-G in 0.5 M H₂SO₄ at the scan rate of 2 mV s⁻¹. (b) Rate of H₂ production per unit time. (c) Tafel plots of the polarization curve. (d) TOF value of the Co-NG catalyst along with the TOF values of the recent reports (Reproduced with the permission, 2015, Nature Publishing Group [19]).

is expected. Exchange current density of the electrochemical reactions is another important property of the electrocatalyst. For a good catalyst, current density should be higher. Current density is closely related to reaction rate in the equilibrium state. Higher current density always more stable and does not affect by the external energy sources including temperature. Current density can be calculated using Tafel slope.

Fei *et al.* introduced an inexpensive, easy, and scalable method for synthesis of Co SACs on nitrogen-doped graphene oxide (GO) [19]. A pre-treated mixture of graphene oxide and a small amount of cobalt salt was heated in an NH_3 gas environment. For the synthesis of Co-NG, an aqueous solution of GO was mixed with 1 ml of CoCl_2 (3 mg mL^{-1}) using sonication. It should be noted, for synthesis a very diluted amount of metal salt or organometallic compound always used. Resultant materials could have bigger metal nanoparticles along with a single-atom catalyst, if excess amount is used. Hence, atomic dispersion and number of metal active sites can be controlled using the optimized amount of metal precursor. Then, the whole mixer was freezing dried and heated at 750°C for 1 h underflow of NH_3 gas ($50 \text{ cm}^3/\text{min}$) and argon (150 mL/min). Similarly, a control catalyst was prepared for comparison purposes. HAADF, and EXAFS surface characterization and electrochemical measurements have suggested the formation of Co-N_4 sites (**Figure 5**).

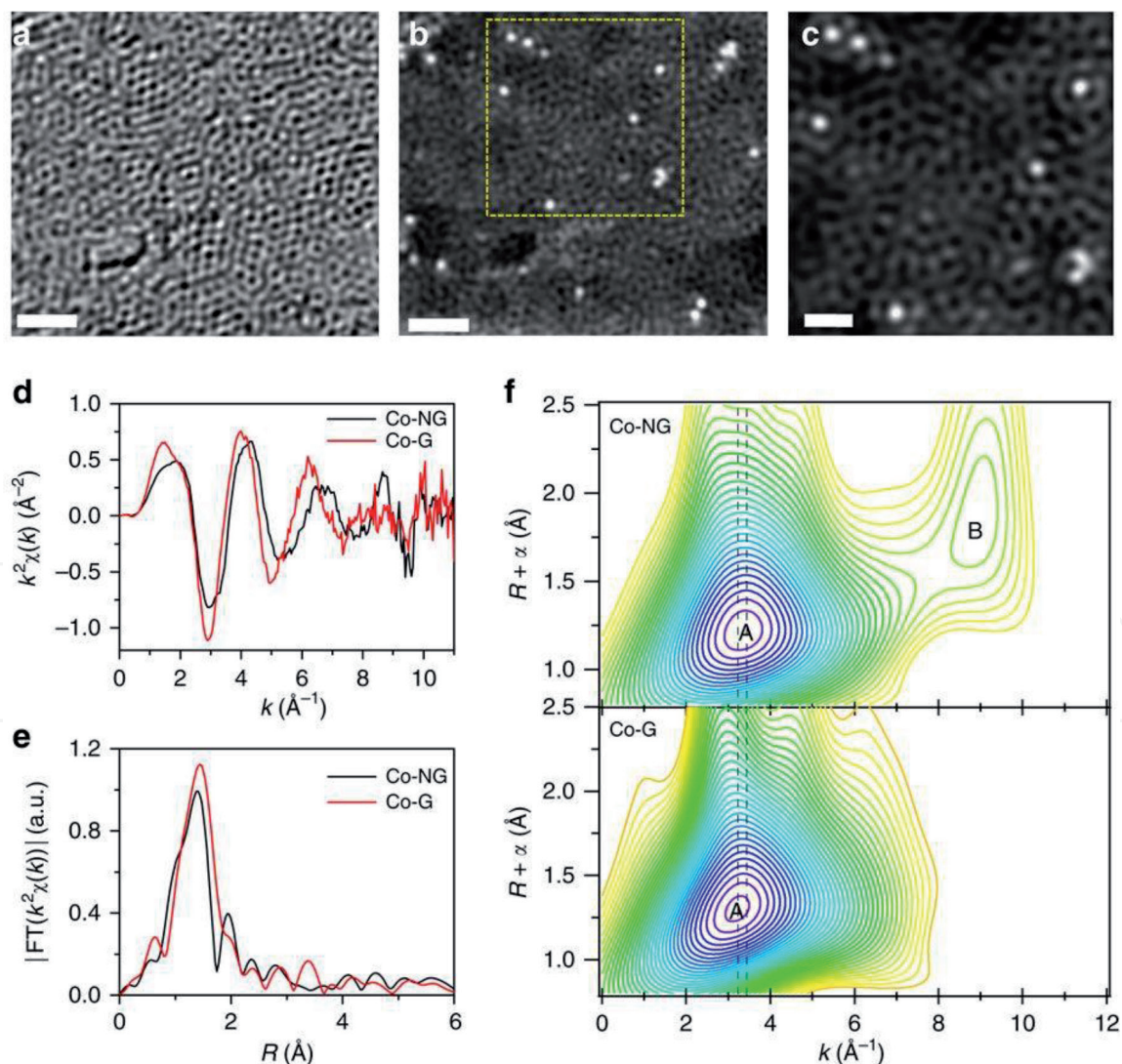


Figure 5.

Structural characterization of Co-NG catalyst. (a) Bright field aberration-corrected STEM images, scale bar 1 nm. (b) HAADF-STEM image. (c) Enlarge view of a selected area in image b, scale bar 0.5 nm. (d, e) K_2 weighted EXAFS in K space and their Fourier transformation in T space for the Co-NG and Co-G, respectively. (f) Wavelength transformation of Co-NG and Co-G (Reproduced with the permission, 2015, Nature Publishing Group [19]).

All these data indicating that Co is atomically dispersed in nitrogen-doped graphene support (**Figure 5**). Bond distance calculation clearly revealed the formation of a Co-N bond (**Figure 5d-f**). This proved that N-atom in graphene support provide anchoring to Co atom and did not allow to agglomerate during catalytic cycles. After that, Co-NG was checked for HER catalytic activity using standard three-electrode electrochemical cell. A glassy electrode was prepared and loaded with $285 \mu\text{g cm}^{-2}$ catalyst. **Figure 4a** showed LSVs curves of the samples which were recorded at 2 mV s^{-1} scan rate in $0.5 \text{ M H}_2\text{SO}_4$ aqueous solution. Co-NG catalyst showed excellent HER catalytic activity with a 30 mV onset potential at a current density of -0.3 mA cm^{-2} , where in comparison commercial available Pt catalyst showed zero onset potential as expected. Onset potential was 70 and 147 mV at 1 and 10 mA cm^{-2} current density, respectively. **Figure 4b** showed 100% Faradaic efficiency, which was due to the generation of H_2 . Faradaic efficiency calculated based on amount of charge transferred through an electrochemical system and amount of reaction happened. In their work, authors were able to achieve better onset potential compared with the Co-based molecular complexes. Further comparison with control catalysts nitrogen-doped graphene and Co-G, single-atom Co-NG catalyst performed much better (**Figure 4c**), which clearly indicated the role of N atom graphene matrix. These catalysts were also tested in alkaline media (1 M NaOH) solution. Single-atom Co-NG catalyst also showed improved catalytic activity compared with the Co-G, NG, and some of other catalysts such as MoS_2 and Ni_2P , were found unstable in a base solution (**Figure 4d**).

TOF is the most important parameter to compare the catalytic activity per unit active sites. In Co-NG, every single atom considered as the active site and if contribution from the NG matrix ignored, the exchange current density by Tafel plots, Co-NG showed $1.25 \times 10^{-4} \text{ A cm}^{-2}$ which is much better than NG ($8.43 \times 10^{-7} \text{ A cm}^{-2}$). To evaluate the stability of the catalyst, accelerated degradation experiments in both acidic and basic media were carried out. One thousand continuous cathodic polarization CV curves showed the excellent stability of the Co-NG compared with the other controlled samples. In addition to the 1000 CV cycles, galvanostatic measurements at a current density of 10 mA cm^{-2} were showed the 35 and 15 mV decrease in offset value after 10 h continuous operation.

2.2 Oxygen reduction reactions (ORR)

ORR is a common relevant process in many electrochemical energy conversion and storage technologies including the air batteries and fuel cells. In most of the cases, ORR reaction is carried out in alkaline conditions, because ORR is much more facile and also provides the high activity in non-noble metal catalyst including TM oxide, SMACs, and heteroatoms doped nanostructured carbon. ORR reaction also proceeds with two electrons reduction mechanism in aqueous medium.

Acidic medium:

Direct pathway: $\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}$ $E_0 = 1.23 \text{ V}$

Series pathways: $\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow \text{H}_2\text{O}_2$ $E_0 = 0.69 \text{ V}$

$\text{H}_2\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow 2\text{H}_2\text{O}$ $E_0 = 1.23 \text{ V}$

Alkaline medium:

Direct pathway: $\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \rightarrow 4\text{OH}^-$ $E_0 = 1.23 \text{ V}$

Series pathways: $\text{O}_2 + \text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2\text{O}^- + \text{OH}^-$ $E_0 = 0.69 \text{ V}$

$\text{HO}_2^- + \text{H}_2\text{O} + 2\text{e}^- \rightarrow 3\text{OH}^-$ $E_0 = 1.23 \text{ V}$

Yang and co-workers produced a single Co atom using N doped carbon nanofiber for ORR application [24]; 1 g of polyacrylonitrile powder was dissolved in 12.5 g of

dimethylformamide under stirring at 60°C for 2 h. Then, 2 g of 4-dimethylamino pyridine powder and 150 mg of cobalt acetate were added and stirred further at room temperature for 2 h. The paste was used to electrospinning at 35°C. The film was dried under vacuum at 60°C for 12 h and then stabilized by annealing at 250°C for 2 h in the air. Finally, Co-containing film was heat-treated at 900°C for 2 h under inert gas condition. As prepared, sample could have bigger Co nanoparticles along with the single atom embedded in the carbon framework. Samples were treated with the aqueous solution of 5 M H₂SO₄, washed and dried under vacuum at 60°C. The authors also prepared nitrogen-doped carbon fiber and only carbon fiber for comparison.

TEM imaging (**Figure 6A–F**), EDX mapping revealed the complete dispersion of Cobalt in carbon fiber. HAADF-STEM images confirmed the formation of a single Co atom and there was no signature of bigger Co nanoparticles formation observed (**Figure 6A–F**). XANES and EXAFS were used to investigate the local structure of a single Co atom in the N doped carbon nanofiber. XANES and EXAFS spectroscopy revealed the formation Co-N bond in a carbon matrix, also conforming to the existence of a single Co atom [24].

The catalyst was used to find out its ORR catalytic activity in 0.1 M HClO₄ solution and showed an onset potential of 0.82 and 0.70 V versus the reversal hydrogen electrode (RHE) (**Figure 6a**). Author found as prepared catalyst showed good catalytic activity, however it was still lower than Pt/C with an onset potential of 0.94 and 0.83 V, respectively. In comparison with the other control catalyst, the catalytic order was CNF < NCNF < Co-N-CNF, which confirmed the important role of N in the carbon matrix to anchor Co single atom. The catalyst was found stable in both acidic and basic media, showed high durability (**Figure 6c**), high catalytic activity and stability (**Figure 6f**). The half-wave potential of ORR reaction did not show many changes even after the 10,000 cycles. This is might be due to structural stability of atomically dispersed Co atom in the N doped carbon network [24].

To further clarify unique effect of single Co atom on ORR activity, authors prepared Co nanoparticles and N doped CoP-N/CNFs. It clearly showed 34 mV negative shifts in half-wave potential after 1000 cycles. This is attributed to the stability of single Co atoms anchored on N atom in carbon framework. Now next question is what is chemical nature of Co atom attached to N and expected it can be Co-N₄ as it was proved multiple times in the case of Fe single-atom catalyst. DFT theory was used to prove the nature of active sites on the basis of previously reported (transition metal) TM-N₄-graphene (G) model. **Figure 7a** showed the ion exchange energy landscapes for the Co-N₄-G as well for Fe-N₄-G after the adsorption of molecular and atomic oxygen under acidic conditions. After geometry optimization, O₂ absorption energy in parallel and end on a model for Fe-N₄-G and Co-N₄-G respectively (**Figure 7a**). Structure stability of Co-N₄/CNF can be explained on basis of free energy diagrams of the ORR as showed in **Figure 7b**. The structural stability of Co-N₄/CNF is further increasing after O₂ and O adsorption, which could be the reason for increase in structure stability of the catalyst. Catalyst also showed much better performance for direct methanol fuel cells with a maximum power density of 16 mW cm⁻² for 200 h (**Figure 7c**). The lifetime test of the passive DMFC showed a nearly constant cell voltage of 30 V after the discharge of 200 h (**Figure 7d**), indicating excellent stability of the electrode. This could be used for a robust fuel cell application in the future [24].

Li and co-workers reported the synthesis of a single Co atom catalyst with precise N coordination as superior ORR catalyst [25]. For synthesis, author used Zn/Co bimetallic MOFs, during the pyrolysis process, Zn can selectively be evaporated away and remaining have a carbon framework decorated with a single Co atom. In a typical procedure, Co(NO₃)₂ and Zn(NO₃)₂ was dissolved in 15 mL methanol and which was later mixed with 2-methylimidazole in methanol at room temperature.

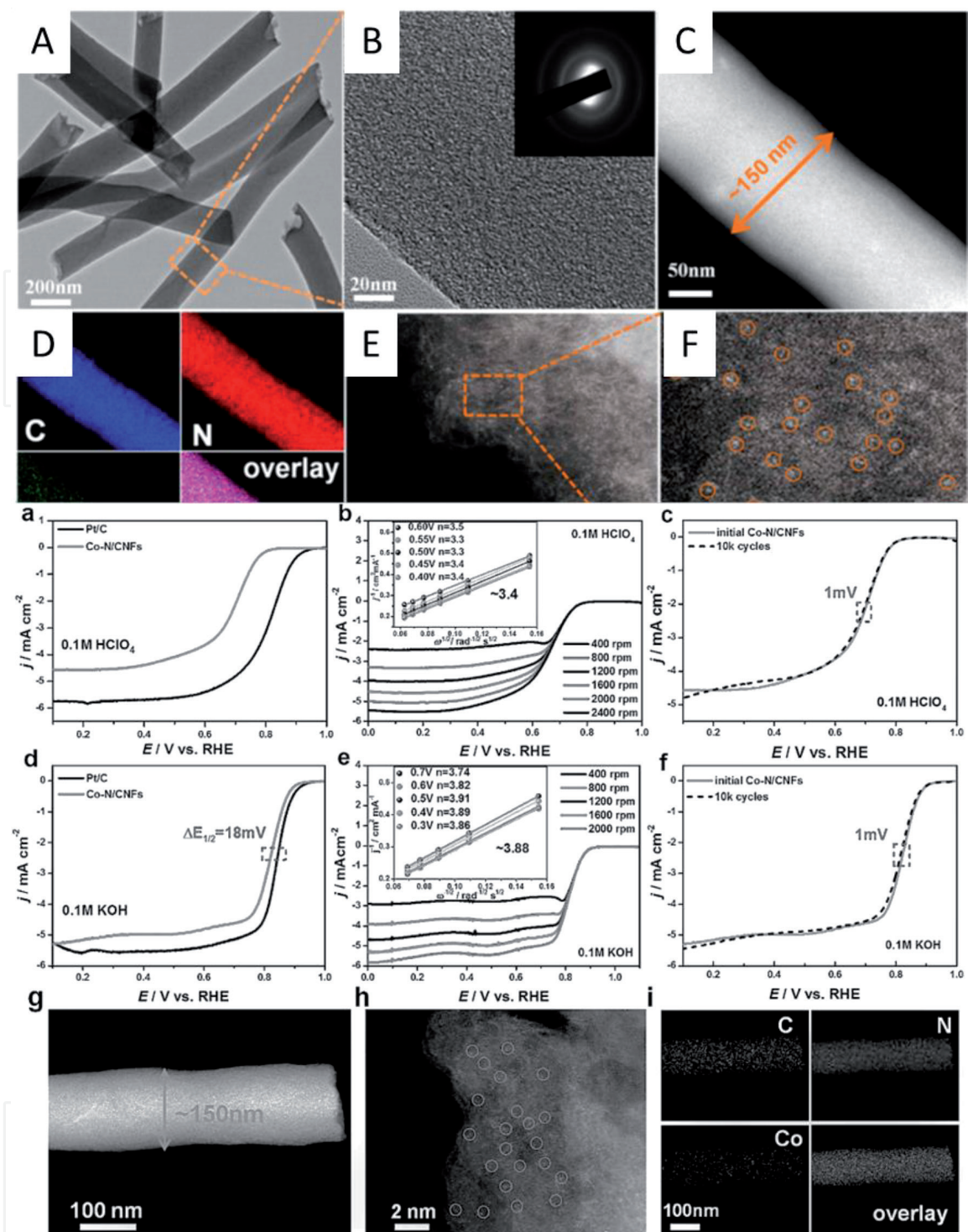


Figure 6. (A) TEM images of fibers, (B) high magnification TEM images of Co-N/CNF, (C) HAADF-STEM images, (D) EDX mapping, (E) aberration-corrected STEM images, (F) enlarge image of Co-N/CNF (single Co atom were highlight by orange circle). (a) LSV of ORR on the Co-N/CNF and Pt/C. (b) K-L plots derived from LSV of ORR. (c) Durability test. (d) LSV of ORR on the Co-N/CNF and Pt/C in basic condition. (e) K-L plots derived from LSV of ORR. (f) Durability test. (g) STEM images of single nanofiber. (h) Aberration-corrected STEM images. (i) EDX mapping for Co-N/CNF after a 1000 cycles ADT test (Reproduced with the permission, 2017, American Chemical Society [24]).

The mixed solution was then transferred to 50 mL hydrothermal lined autoclave and heated at 120°C for 4 h. As prepared precipitates were then centrifuged and washed with ethanol several times and dried in vacuum at 70°C for overnight. For carbonization, as prepared MOF was then heated at 800, 900, and 1000°C for 3 h under the flow of N₂ gas. Then heated MOFs were then used directly for electro-chemical measurement without further treatment.

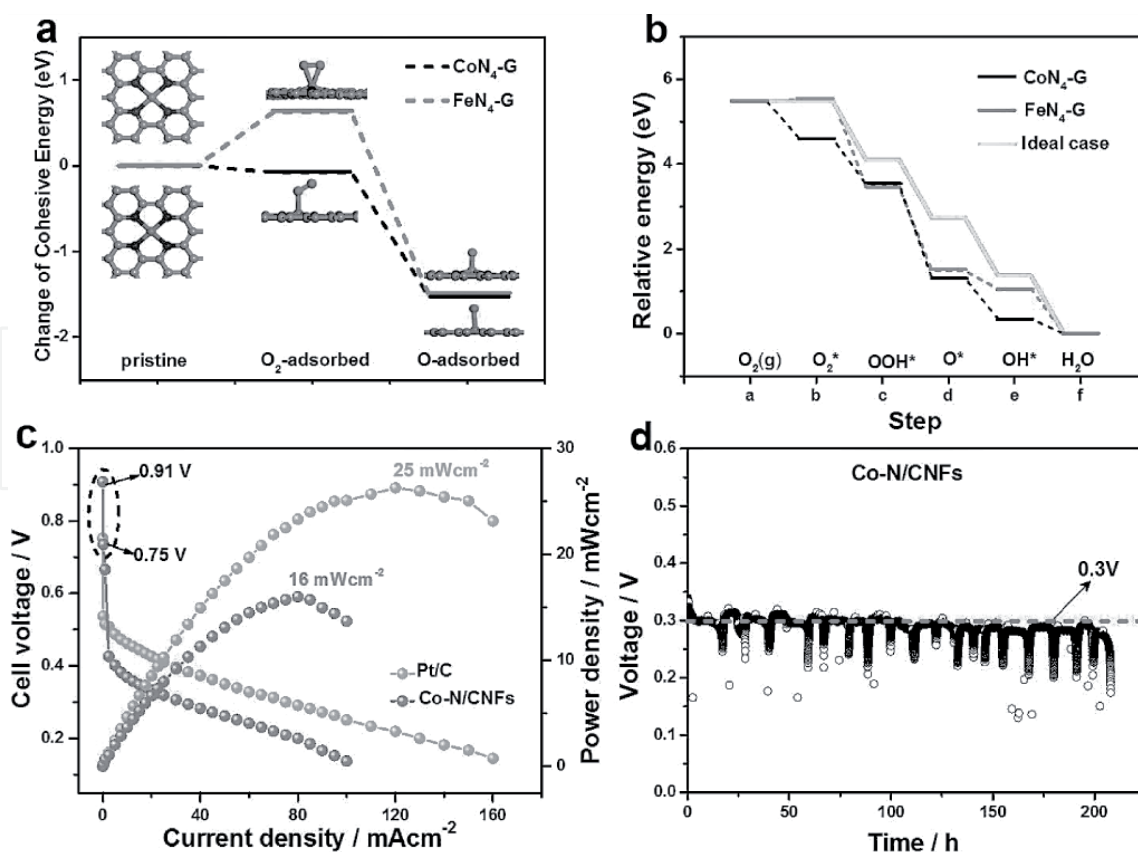


Figure 7.

(a) Relative ion-exchange energy profile. (b) Relative energy profile of the ORR process of the active sites. (c) Steady-state polarization curve of passive DMFCs with 4 M methanol at 40°C. (d) 200 h stability test of a passive DMFC with the cathode catalyst prepared by Co-N/CNFs at a current density of 20 mA cm⁻² (Reproduced with the permission, 2017, American Chemical Society [24]).

MOFs were used as a starting precursor for the synthesis because MOF already has distinguished single metal sites coordinated with the organic ligand. Mixed metallic MOF used because some portion of Co is in pure Co MOF can be replaced with the low boiling point Zn atom, which further helps in maintaining the appropriate distance between the cobalt atoms in the final carbonized materials. Co loading can be tuned by the changing ratio of metal salt added during MOF synthesis. HAADF-STEM images revealed the formation of homogeneous Co atom on carbon support [25].

The special aberration correction spectroscopy and extended X-ray absorption fine structure techniques have been used to confirm the atomic dispersion of Co atom anchored by N atom in the carbon framework [25]. ORR activity of the catalyst was studied using steady-state linear sweep voltammetry (LSV) on the rotating disk electrode in O₂ saturated 0.1 M KOH solution. For comparison, authors also prepared N doped catalyst by pyrolysis of Zn MOFs. This showed low ORR activity, exhibits the role of a single Co atom for its excellent ORR activity. Co-SAs/N-C(900) showed the best ORR activity in comparison with another catalysts, onset potential of 0.881 V was almost equal to the Pt/C catalyst (0.811). This was found in correlation with the DFT calculation. KL plots of Co-SAs/N-C(900) suggesting first-order reaction kinetic. Electron transfer number has been calculated using the rotating ring-disk electrode (RRDE) tests, showing the nearly four-electron ORR pathways over the single Co-N₂ sites. The kinetic current density (J_k) by the Tafel plots at 0.8 V was around 75 mV dec⁻¹. The stability test showed that the catalyst is stable during the operational condition, no change noticed in the CV curve even after 5000 cycles.

Abruna *et al.* produced structurally disordered intermetallic platinum cobalt core-shell nanoparticles for ORR activity [26]. They demonstrated Pt-metal disordered alloy core-shell nanoparticles with ordered Pt₃Co intermetallic core and 2–3 layer of Pt shell. These Pt-Co core-shell nanoparticles showed a 200% increase in mass activity and 300% increase in specific activity when compared with disordered Pt₃Co alloy nanoparticles as well as with Pt/C. The stability test showed minimal loss of ORR activity after 5000 cycles and core-shell structure was still found stable under operational conditions. Lin *et al.* reported the preparation of a hierarchically porous Co and Fe single-atom catalyst for ORR [27]. In present work, authors used bimodal template bases synthesis strategy for the large scale synthesis of porous single-atom catalysts. For synthesis of hierarchically porous Co-N-C-900 single-atom catalyst, first 2 g D-glucosamine hydrochlorides, ZnCl₂, and CoCl₂ were dissolved in 20 mL colloidal silica suspension. After stirring for 10 min, whole mixture was then freeze-dried and obtained powder was carbonized under the flow of N₂ gas at 900°C for 2 h. Silica was removed using 10 wt.% HF solution for 12 h at room temperature. For comparison, Co-N-C-900 was synthesized without using ZnCl₂ and also porous N-C was also synthesized. Silica was used as a hard template because this creates the porosity in a carbon network and further use of ZnCl₂ produced more nanopores in carbon networks. TEM analysis clearly showed the presence of nanopores of 20 nm size, due to the use of silica nanoparticles as a template. HAADF-STEM images of catalyst represent the formation of a single atom in a carbon framework. No bigger nanoparticles were detected, this is because during HF treatment, it could be possible for bigger particles to dissolve and only those single atoms remain which are strongly bound with the carbon framework. Fe single-atom catalyst was found stable against O₂ and also found most active compared with Co single-atom catalyst. Optimized Fe-N-C catalyst showed half-wave potential of 0.927 V in alkaline medium, which was found even more positive 49 and 55 V than the Co-N-C and Pt/C, respectively. DFT calculation revealed that Fe-N₂ sites are more active compared with the CoN₄ for ORR because of Fe-N₂ functional at lower energy barrier for the intermediate and produced involved.

Sun *et al.* reported synthesis of a single Co atom embedded in hierarchically ordered porous nitrogen-doped carbon (Co-SAS/HOPNC) for HER and ORR applications [28]. Firstly, phenol-formaldehyde resol (Mw < 500) was prepared using 10 g phenol and formaldehyde. For the synthesis of Co-SAS/HOPNC, pluronic F127 and dicyandiamine were dispersed in ethanol and deionized water using magnetic stirrer, followed by adding a resol ethanol solution. Then vitamin B12 protein was added to above mixture at room temperature to produce a homogeneous pink solution. Subsequently, silica template was soaked into the prepared precursor for 2 h and whole mixture heated at 50°C in an electric oven for solvent evaporation for 8 h. After heating at 100°C for overnight for thermosetting, as prepared composite was heated at 900°C for 2 h in an Ar atmosphere. To remove the bigger cluster of Co nanoparticles and silica after carbonization; composite was treated with the HF aqueous solution for 24 h. As prepared catalyst possessed high surface area, good conductivity, high isolated Co atom, and exceptional catalytic performance. Co-SAS/HOPNC exhibited the half-wave potential of 0.892 V for ORR in alkaline medium. This was found 53 mV more positive than Pt/C, high tolerance to methanol and great stability. Co-SAS/HOPNC showed remarkable HER activity with a turnover frequency of 0.41 and 3.8 s⁻¹ at overpotential of 100 and 200 mV, respectively. DFT theory was proposed to explain the nature of single Co site. Co-N₄ was found an active site for this dual character, three-dimensional porous carbon networks; accessible highly active Co-N₄ sites synergistically contribute the excellent catalytic performance.

3. Conclusions and future directions

Single-atom catalyst has established a connection between homogeneous and heterogeneous processes. A single atom catalyst can be better than a homogeneous catalyst because it is easy to recover at the end of the process and equal catalytic activity. Single-atom catalyst can have many fascinating characteristics such as maximize the atomic efficiency, a high activity like a homogeneous system, and selectivity. A single-atom catalyst has been proved to be a very efficient and powerful catalyst for various applications including the ORR, OER, HER, CO₂ conversion, and organic transformation. Significant progress is made to understand the catalyst preparation, characterization using advanced techniques and mechanism interpretation using experimental data and theoretical models.

The microenvironment of a single atomic site needs to investigate more in detail, *in situ* spectroscopy technique can be utilized to study the active site in operation condition, and a specific reaction mechanism can be proposed [29]. It can be understood from literature, the interaction between the metal single atom and support is necessary to stabilize a single metal atom. If we can manipulate these interactions, it can tune the catalytic activity, stability, and selectivity for multiple catalytic applications.

MOFs are the fascinating precursor for single metal atom catalyst design. Multi-metal MOFs can also use for the synthesis of multi-metallic single atom heterogeneous catalyst to utilized the one catalyst for numerous applications [30]. To further change the catalytic phenomena of a single metal catalyst, two-dimensional materials such as MXenes, MoS₂, HBN, black phosphorus, and many more support materials can be successfully explored for the synthesis, industrial, and environmental applications [31].

Porous metal oxide support for the preparation of a single-metal atom catalyst can be also utilized and use for organic transformation, gas phase, and electrochemical applications. Although porosity of metal oxide support is an issue, however two-dimensional metal oxides can be utilized for single-atom catalyst preparation [32]. Silica (mesoporous spherical or nanosheets) can be a good support for the single-atom catalytic application, however, it needs to be explored further [33, 34]. Non-conducting and passive nature of silica might a problem for single-atom catalysts. Porous carbon nanocage using KCC-1 as a hard template was used to prepare a three-dimensional accessible surface carbon sphere [35]. Same carbon morphology can be utilized for the preparation of mesoporous carbon-based SAMCs for various applications. **Figure 8** is demonstrating the overall picture of different ways of single-atom catalyst preparation and their utilization in various applications.

Recently, metal-air batteries have been received to consider a potential candidate for future energy storage materials due to their theoretical high energy density, excellent safety, and abundant TM resources. Typically, metal-air batteries' performance

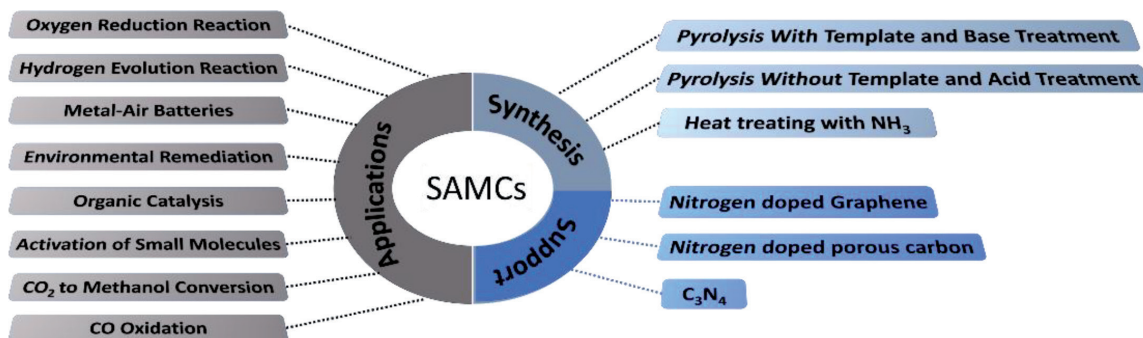


Figure 8. General description of SAMCs, method of preparation, support used and applications.

depends on two catalytic reactions ORR and OER, both occurring on porous cathode surface [36–38]. Due to the unsaturated characteristic of SMACs and its catalytic activity can be utilized to make more highly efficient and cheap metal-air batteries.

Acknowledgements

We thank SERB - DST, New Delhi for their support under EMEQ Scheme.

Conflict of interest

Authors declare that there is no conflict of interest in this chapter.

Acronyms and abbreviations

ORR	oxygen reduction reaction
OER	oxygen evolution reaction
HER	hydrogen evolution reaction
CUMS	coordinately unsaturated metal sites
SMACs	single metal atom catalysts
MM-SACs	multi-metallic single-atom catalyst

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