



Mini Review

Electrospun nanofibers for electrochemical reduction of CO₂: A mini review

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ABSTRACT

The electrochemical reduction of CO₂ (CO₂RR) into valuable products represents a step towards alleviating global warming and the energy crisis. However, the sluggish kinetics of the CO₂RR and the competitive hydrogen evolution reaction (HER) still limit the application of CO₂RR. In order to solve these problems, catalysts that can reduce CO₂ with high activity, selectivity and stability are required. Recently, electrospun nanofibers have attracted particular interest as CO₂RR catalysts due to their high conductivity, large surface area, superior stability, etc. In this review, we briefly introduce electrospinning technology and the fundamentals of the CO₂RR. Then, the recent progress of CO₂RR catalysts prepared through electrospinning, including heteroatom-doped and metal-decorated carbon materials and metal fiber materials are systematically discussed. Finally, the future perspectives and challenges of electrospun materials for CO₂RR are presented. This mini review is anticipated to inspire better understanding and further development of electrospun materials for promoting CO₂ electrolysis.

1. Introduction

The development of human society relies heavily on the products and energy provided by fossil fuels. However, the reserves of fossil fuels are limited and massive combustion of fossil fuels has led to a sharp increase in CO₂ concentration in the atmosphere [1–3]. Recently, electrochemical reduction of CO₂ (CO₂RR) to chemical feedstocks has been considered as a promising strategy to help reduce these problems [4,5]. Powered by renewable electricity, such as electricity from wind and solar energy, CO₂ can be reduced at room temperature and ambient pressure to a large variety of products, including CO [6,7], HCOOH [8,9], hydrocarbons [10,11] and alcohols [12,13]. However, CO₂ is a thermodynamically stable molecule since the breaking of the C=O bond in CO₂ requires ~800 kJ mol⁻¹. Thus, efficient electrocatalysts are required to decrease the activation energy for the reduction of CO₂, thereby accelerating the reaction rate. In addition, as various different products can be generated as a result of CO₂ reduction, catalysts also need to be selective in order to avoid the need for energy-intensive product separation processes.

In the 1980s, Hori and co-workers carried out a series of pioneering

studies about CO₂RR on different metal electrodes and classified these metals into four groups based on the CO₂RR products: (1) metals that are selective towards CO (Au, Ag, Zn etc.); (2) formate-selective metals (Sn, Pb, In etc.); (3) metals that are not active for CO₂ reduction but mainly reduce H₂O to H₂ (Ni, Pt, Ti etc.); and (4) Cu, which uniquely reduces CO₂ to hydrocarbons and alcohols with considerable selectivity [14]. Since then, much effort has been devoted to developing materials for the CO₂RR and in understanding the catalytic mechanisms. Recently, carbonaceous materials have attracted much attention in electrolysis because of their excellent chemical stability, high conductivity and large surface area [15,16]. However, pristine carbon materials (e.g., carbon nanotubes and graphene) are not active for the CO₂RR due to the lack of active sites for the adsorption and activation of CO₂. Different strategies have been used to introduce active sites into carbon materials, including heteroatom doping (using e.g., N, B, S, F) and metal and/or oxide decoration (using e.g., Cu, Fe, Ni) [17–19]. Electrospinning has been considered to be one of the most efficient methods for synthesizing these types of catalysts, as it can continuously produce polymer nanofibers with controllable size, high purity and high yield. Compared with other

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carbon materials, the carbon fibers obtained via electrospinning have a higher porosity, which is beneficial for gas diffusion. Furthermore, the stacked long nanofibers are favorable for electron transfer. Because the active sites of the catalysts obtained by electrospinning are grown in situ on the carbon nanofibers, they therefore have better stability. In addition, in situ decoration of carbon nanofibers with heteroatoms and metal species can be achieved by electrospinning, which promotes the dispersion of active sites.

To date numerous excellent reviews on CO₂RR have been published, covering catalyst design [5,20-22], reaction systems [23,24], and techno-economic analysis [25,26], as well as discussions on the feasibility of CO₂RR technologies [27]. There have also been some high-quality reviews on electrospun materials for energy storage [28,29]. However, an updated review of electrospun nanomaterials for CO₂RR is lacking. In this mini review, we first briefly introduce electrospinning technology and the basics of the CO₂RR, and then summarize the emerging progress on electrospun nanomaterials as catalysts for the CO₂RR. Finally, future challenges and perspectives are considered.

2. Electrospinning

The birth of electrospinning can be traced back to the 1930s. From 1934 to 1944, A. Formhals [30] published a series of patents describing several innovative electrospinning set-ups and the technical process. In 1969, Taylor performed fundamental studies on the behavior of polymer drops in an electric field and found that the droplets form a conical shape. The angle of the cone (later referred to as the “Taylor cone”) was determined to be 49.3° [31]. In the 1990s, Reneker’s research team conducted extensive and in-depth studies on electrospinning, and the results attracted widespread attention [32]. Since 2000, electrospinning technology has developed rapidly due to the wide variety of spinnable materials and controllable processes, and has been the focus of much scientific research and industrial applications.

As shown in Fig. 1a, a typical electrospinning device consists of three main components: (1) a high-voltage power supply that can provide an electrostatic field for electrospinning; (2) a container containing a polymer solution or polymer melt with a metal spinneret; and (3) a grounded collector that can be designed in various forms (e.g., a flat plate, or a rotating drum etc.).

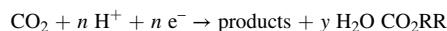
The basic principle of electrospinning is based on electrostatic atomization. Briefly, the spinning solution is pumped out via the spinneret and forms a charged pendant droplet. As the electrostatic repulsion induced by charges counteracts the surface tension, the droplet is stretched and a jet will be formed at a critical point. Subsequently, the jet undergoes a short-distance stable stretching action due to the presence of an external electric field and the surface charge carried by the jet

[33]. The jet then flows at a high speed with an unstable motion, followed by further stretching and an obvious reduction in diameter. At the same time, the solvent in the polymer jet evaporates rapidly, and the jet finally solidifies into fibers with diameters ranging from nanometers to micrometers. The structure and morphology of the resulting fibers are affected by three groups of parameters: (1) solution parameters (e.g., solution viscosity, polymer molecular weight, concentration, conductivity and surface tension); (2) process parameters (e.g., electric field strength, collection distance and feed flow rate); and (3) environmental parameters (e.g., ambient temperature and humidity) (Fig. 1b) [34,35].

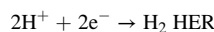
3. CO₂RR fundamentals

Electrochemical reduction of CO₂ can be achieved at room temperature under ambient pressure. In addition to aqueous solutions (e.g., solutions of KHCO₃ and KCl), ionic liquids are also sometimes used as electrolytes. Most reported CO₂RR experiments have been conducted in three-electrode reactors, consisting of a working electrode loaded with catalysts for CO₂RR (cathode), a reference electrode, and a counter electrode (anode). An ion-exchange membrane is normally required to separate the cathode and anode compartments in order to prevent the oxidation of CO₂RR products. Several types of electrolyzer are available for CO₂RR, including: (1) a conventional H-cell, where CO₂ is delivered through the liquid phase; (2) a membrane electrode assembly, where CO₂ is delivered together with water vapor; and (3) a microfluidic reactor, where CO₂ is supplied to the electrode through the gas phase [24]. Like other catalytic reactions, the performance of CO₂RR catalysts are evaluated by activity (current density), selectivity (faradaic efficiency) and stability. Some other parameters are also frequently used as evaluation criteria, including onset potential, overpotential, Tafel slope, and turnover frequency [36].

The CO₂ electroreduction reaction involves multiple electron transfer paths, and the general form of the cathode reaction is:



As mentioned above, a large variety of products, including CO, HCOOH, CH₄, C₂H₄, CH₃OH, C₂H₅OH, acetate and so on, can be produced. Details of the reactions leading toward specific products are described in previous reports [37,38]. H₂ is the major side-product of CO₂RR in aqueous electrolyte since the hydrogen evolution reaction (HER) takes place at equilibrium potentials comparable with that of the CO₂RR.



The main reaction on the anode side is usually the oxygen evolution

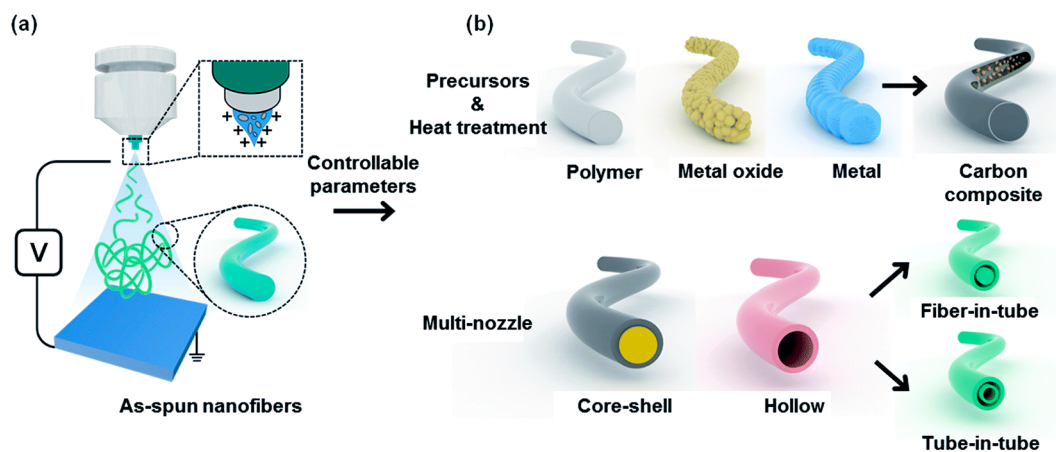
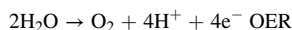


Fig. 1. (a) Schematic illustration of a typical electrospinning apparatus. (b) Diverse electrospun nanofibers obtained by controlling various parameters such as precursors, the calcination atmosphere and the type of nozzle [29].

reaction (OER):



Since CO₂RR is a heterogeneous catalytic reaction, it occurs mainly at the interface of the catalyst, electrolyte and CO₂, and involves the following key steps: (i) the adsorption and activation of CO₂ on the surface of the solid catalyst; (ii) the breaking and formation of chemical bonds (e.g., C-O and C-H bonds), coupled with the transfer of protons and/or electrons; and (iii) the formation, desorption and diffusion of products [38].

Overall, an advanced catalyst for the CO₂RR needs to be able to convert CO₂ at a high rate, with high selectivity, over a long reaction time. In the following sections, recent advances in the development of CO₂RR catalysts using the electrospinning method are summarized.

4. Electrospinning nanofibers as electrocatalysts

Nanofiber-structured electrodes prepared by electrospinning have been widely used for the HER and the OER as well as in lithium-ion batteries. The three-dimensional (3D) network nanofibers with their porous structure can efficiently improve the electrochemically active surface area and aid gas transportation [39,40]. Benefitting from these advantages, different types of electrospun nanofibers have been explored for the CO₂RR. In this section, the progress of CO₂RR using electrospun fibers as catalysts is reviewed and the advantages of these materials are discussed. Table 1 summarizes the CO₂RR performance of different electrospun materials reported recently in the literature.

4.1. Carbon-based nanofiber catalysts for the CO₂RR

4.1.1. Metal-free carbon nanofibers as CO₂RR catalysts

As electrocatalysts, metal-free carbon materials benefit from their low cost, high conductivity and high surface area. However, traditional pure carbon materials such as carbon nanotubes and carbon nanofibers cannot provide sufficient active sites for catalytic reactions. Heteroatomic doping is considered to be one of the most effective methods to modify the defect density, electronic structure, and surface chemical properties of metal-free carbon materials. The doped heteroatoms not only play a role as active sites for the adsorption of CO₂ molecules and reaction intermediates, but also activate the adjacent carbon atoms by changing their electronic structure.

In 2013, Kumar et al. reported the application of N-doped carbon nanofibers (CNFs) for the CO₂RR (Fig. 2a, b) [41]. The N-doped CNFs were synthesized by electrospinning of heteroatomic polyacrylonitrile (PAN) solution followed by carbonizing at 1050 °C in Ar. The catalyst

showed 98% Faradaic efficiency (FE) for CO production at −0.573 V vs. SHE in CO₂-saturated 1-ethyl-3-methylimidazolium tetrafluoroborate (EMIM-BF₄) electrolyte. The authors attributed the high catalytic performance of the CNFs to their fibrillar morphology, rough surface and large number of active sites. Interestingly, unlike many other studies that suggest N sites as active centers, this work proposed that the positively charged carbon atoms adjacent to the negatively charged nitrogen atoms are the active centers (Fig. 2c).

Although N is the element most commonly used for carbon doping due to its similar size to the carbon atoms and its larger electronegativity, other elements have been doped together with N to further optimize the electronic properties of the carbon materials. In 2018, Yang et al. synthesized N and S co-doped hierarchically porous carbon nanofibers (NSHCF) via an electrospinning method, using a solution containing ZIF-8 nanoparticles, trithiocyanuric acid (TA) and PAN [42]. After carbonization at 900 °C in an Ar atmosphere, the resulting material (NSHCF900) is flexible and self-supporting and can be used directly as a cathode for the CO₂RR without additional carriers or binders (Fig. 2d–g). In CO₂-saturated 0.1 M KHCO₃ solution, the catalyst showed 94% FE for CO with 103 mA cm^{−2} at −0.7 V vs. RHE. On the basis of density functional theory (DFT) calculations and control experiments, pyridinic N sites were suggested as active centers and S doping was found to further decrease the Gibbs free energy for the adsorption of the key *COOH intermediate.

4.1.2. Carbon nanofibers with metal species as CO₂RR catalysts

As well as heteroatom doping, decoration with metal species is another common way of introducing active centers into carbon fibers. Simply by adding metal salts to the electrospinning solution, carbon nanofiber catalysts embedded with metal nanoparticles or single metal atoms can be fabricated. As the amount deposited and elemental composition are highly flexible, such materials have shown great potential for electrochemical reactions. Typically, supported metal particles exhibit similar product distributions but enhanced activity and selectivity compared to their bulk forms due to their higher surface area and larger number of low-coordinate sites. However, in some cases, the original selectivity of the metal can be changed by the strong interaction between carbon and the metal species. For example, in 2018, Zhao et al. synthesized a Sn-modified N-doped porous carbon nanofiber (Sn-CF) catalyst via the electrospinning method using a solution containing PAN, poly(methylmethacrylate) (PMMA), and SnCl₂, followed by a pyrolysis process at 1000 °C in Ar/H₂ atmosphere [43]. This catalyst showed a morphology of nanofibers decorated with Sn microspheres 0.5–3 μm in size, and exhibited a formate FE of 62% at −0.8 V vs. RHE in 0.5 M KHCO₃. Interestingly, after removing the Sn microspheres by acid

Table 1
CO₂RR performance of various electrospun materials reported in the literature.

Catalyst	Electro-lyte	Applied potential (V)	Major products (FE, %)	Current density (mA cm ^{−2})	Electrolyzer	Ref.
Carbon based nanofibers						
N-doped CNFs	EMIM-BF ₄	−0.6 (vs. SHE)	CO (98%)	~3.5	Three-neck cell	[41]
NSHCF	0.1 M KHCO ₃	−0.7 (vs. RHE)	CO (94%)	103	H-cell	[42]
Sn-CF	0.5 M KHCO ₃	−0.8 (vs. RHE)	HCOOH (62%)	~10.0	H-cell	[43]
AD-Sn/N-C	0.5 M KHCO ₃	−0.6 (vs. RHE)	CO (91%)	~2.5	H-cell	[43]
Bi ₂ O ₃ NSs@ MCCM	0.1 M KHCO ₃	−1.3 (vs. RHE)	HCOOH (>90%)	~18.2	H-cell	[44]
Co _x Ni _{1-x} /N-C NFs	0.5 M NaHCO ₃	−0.9 (vs. RHE)	CO (85%)	~13.4	H-cell	[45]
NiN-GS	0.1 M KHCO ₃	−0.8 (vs. RHE)	CO (93.2%)	~4.3	H-cell	[47]
NiSA/PCNFs	0.5 M KHCO ₃	−0.7 (vs. RHE)	CO (95%)	~12	H-cell	[49]
NiSA/PCNFs	0.5 M KHCO ₃	−1.1 (vs. RHE)	CO (88%)	308	Flow-cell	[49]
CoSA/PCNFs	0.1 M KHCO ₃	−0.6 (vs. RHE)	CO (97%)	~23	H-cell	[48]
CoSA/PCNFs	1 M KHCO ₃	−0.7 (vs. RHE)	CO (92%)	211	Flow-cell	[48]
Metal nanofibers						
Sn/SnO ₂ /PHF	0.1 M KHCO ₃	−1.6 (vs. SHE)	HCOOH (82.1%)	~27.9	Gastight cell	[51]
WIT SnO ₂	0.1 M KHCO ₃	−0.89~−1.29 (vs.RHE)	C1 (>90%)	N/A	H-cell	[52]
CuInS	0.1 M TBAPF ₆	−1.5 (vs. NHE)	CO (77%)	0.22	H-cell	[53]

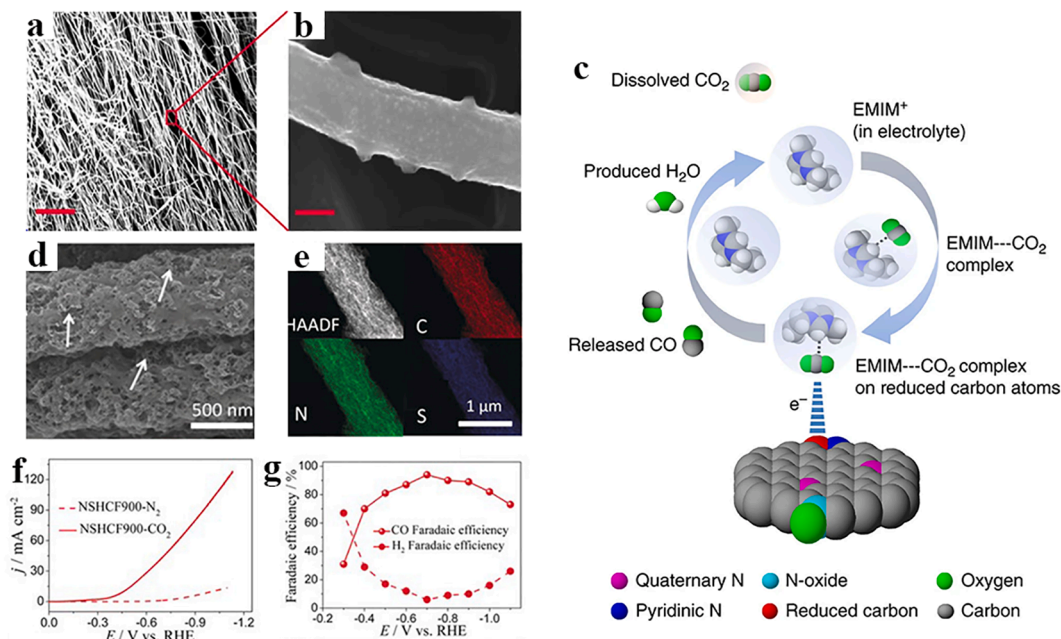


Fig. 2. (a) SEM image of the CNF (scale bar, 5 μm); (b) high-resolution SEM image of an individual fiber (scale bar, 200 nm); (c) schematic diagram of the CO₂ reduction mechanism [41]; (d) high-resolution FESEM images of NSHCF900 (where through-holes are marked with white arrows); (e) EDS mapping of a NSHCF900 nanofiber; (f) LSV curves in CO₂-saturated and N₂-saturated 0.1 M KHCO₃; (g) FE for CO and H₂ of NSHCF900 [42].

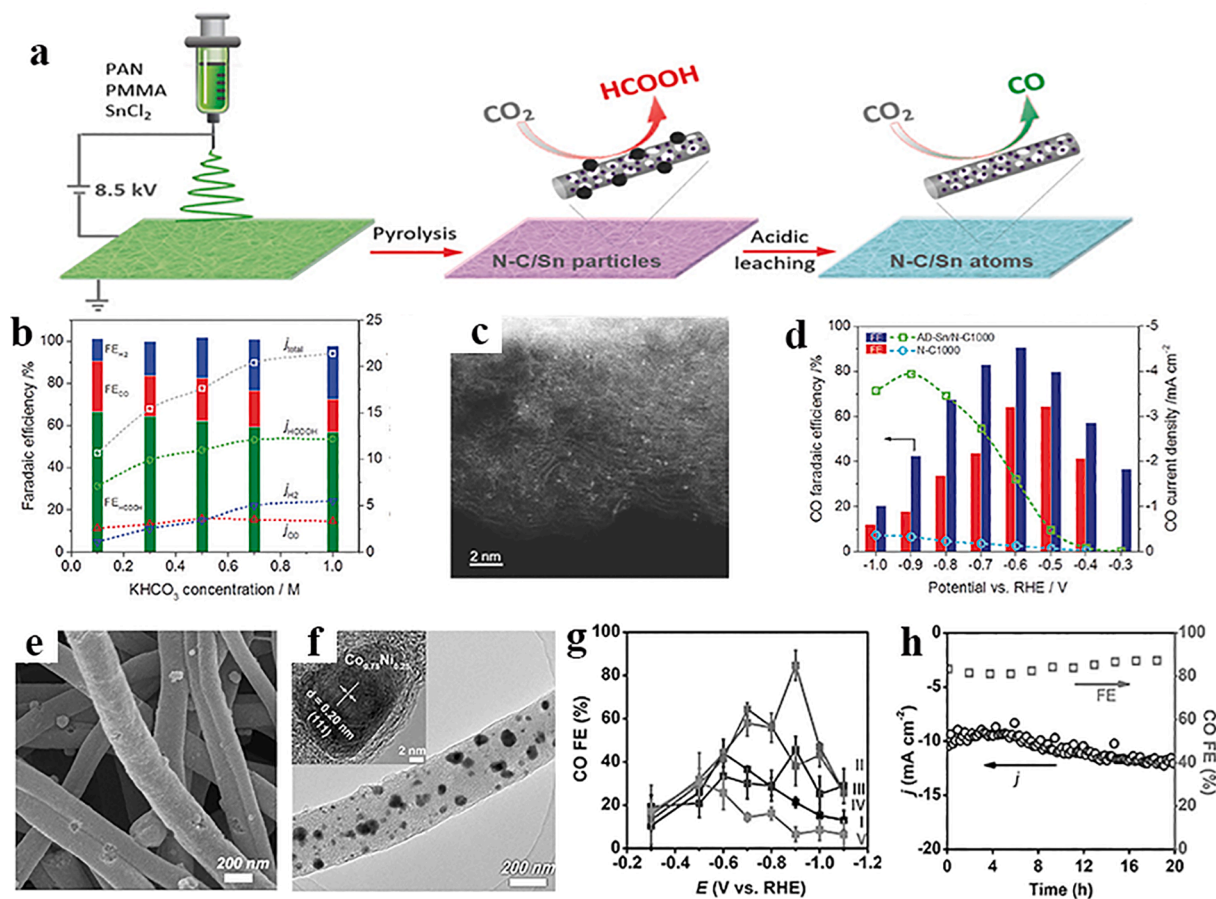


Fig. 3. (a) Schematic illustration of the synthesis of Sn-modified N-doped carbon nanofiber electrocatalysts for HCOOH and CO production; (b) FE of Sn nanoparticle decorated carbon nanofibers; (c) HAADF-STEM image of Sn single atom decorated carbon nanofiber; (d) FE of Sn single atom decorated carbon nanofibers [43]; (e) SEM, (f) TEM, (g) FE of CO; (h) stability test of Co_{0.75}Ni_{0.25}/N-C NFs [45].

etching, the remaining atomically dispersed Sn on the carbon fiber promotes CO production with a maximum FE of 91% at -0.6 V vs. RHE (Fig. 3a, b). Based on electrokinetic studies, the authors suggested that the pyridinic-N-doped-carbon supported Sn nanospheres are active sites for formate production while the Sn-N moieties are active for CO formation.

The above-mentioned catalyst was prepared in a one-step electrospinning process, however, such catalysts can also be prepared through a number of separate steps. In 2019, Liu et al. reported the seed-mediated growth of Bi_2O_3 nanosheets on a conductive multiple channel carbon matrix (MCCM) made by electrospinning [44]. Examined in 0.1 M KHCO_3 solution, the FE of HCOOH approached 90% in a wide potential window and the FE stabilized at $\sim 76\%$ over 12 h. The excellent performance was attributed to the unique properties of the interwoven MCCM and the hierarchical Bi_2O_3 nanosheets. While the MCCM enhances the conductivity of electrons, CO_2 adsorption and a high ratio of pyrrolic-N to pyridinic-N, the Bi_2O_3 nanosheets provide abundant active sites and lower contact resistance.

Another example worth mentioning is the co-deposition of two metals on carbon fibers. In 2019, Zhang et al. prepared a series of $\text{Co}_x\text{Ni}_{1-x}$ nanoalloys on N-doped carbon nanofiber ($\text{Co}_x\text{Ni}_{1-x}/\text{N-C NF}$) electrocatalysts by electrospinning a N,N-dimethylformamide (DMF) solution containing various amounts of PAN, $\text{Co}(\text{C}_2\text{H}_7\text{O}_2)_2$ and $\text{Ni}(\text{NO}_3)_2$ [45]. With an optimized composition, the $\text{Co}_{0.75}\text{Ni}_{0.25}/\text{N-C NF}$ s catalyst delivered 85% CO FE at -0.9 V vs. RHE in 0.5 M NaHCO_3 (Fig. 3e–h). It is worth noting that earlier studies have shown that metals like Ni and Co are not active for the CO_2RR due to their high activity toward the HER [14]. In this work, although DFT results revealed that $^*\text{H}$ can bind strongly on the $\text{Co}_x\text{Ni}_{1-x}$ surface, the authors suggested that it will not promote H_2 evolution but rather accelerate the CO_2 reduction. Later, the Xiong group also reported the preparation by electrospinning of carbon nanofibers embedded with Cu/CeO_x , which showed greatly enhanced CO_2RR performance due to the synergy between Cu and CeO_x [46].

These works demonstrate that, as a well-established technique, electrospinning can be readily applied to produce a variety of metal-particle-decorated carbon fiber materials for the CO_2RR .

In addition to supported metal-particle catalysts, atomically dispersed metal single-atom catalysts (SACs) have also been developed, and have received much attention in recent years due to their maximum atom efficiency and tunable coordination environments. As single metal atoms are highly unstable, carbon materials (e.g., graphene, CNTs, etc.) are often used as supports to host single atoms due to their high surface area and the possibility of creating a high density of defect sites. Under these circumstances, electrospinning becomes an effective method to prepare SACs since metal precursors can easily be mixed with the polymer solution and the polymer precursors are usually rich in nitrogen functionalities. In 2017, Jiang et al. reported the synthesis of a graphene shell coated Ni nanoparticle sample by electrospinning a polymer solution with Ni and N precursors [47]. They confirmed the presence of a high density of single Ni atoms in the graphene shell using energy-dispersive X-ray spectroscopy (EDS) and atom probe tomography (APT). The catalyst exhibited a remarkable CO FE of 93.2% at an overpotential of 0.7 V. Furthermore, the FE of CO retained around 80% of its original value after >20 h of testing, demonstrating excellent stability (Fig. 4a). They suggest that the Ni atomic sites exhibited a different electronic structure compared with metallic Ni, which can facilitate the conversion of CO_2 to CO and suppress the competing HER.

Carbon fibers made from electrospinning can form a free-standing membrane, which can be used directly as a self-supporting gas diffusion electrode (GDE) in flow cell configurations. Recently, He's group synthesized carbon nanofibers embedded with single atoms and used them in flow reactors to achieve high-current-density electrolysis of CO_2 [48,49]. In their reports, by adding ZIF-8 nanoparticles (as a pore former) and metal salts (as a metal precursor) to the electrospinning solution, single-atom Ni- and Co-decorated self-supporting carbon nanofibers (NiSA/PCNFs and CoSA/PCNFs, respectively) were obtained

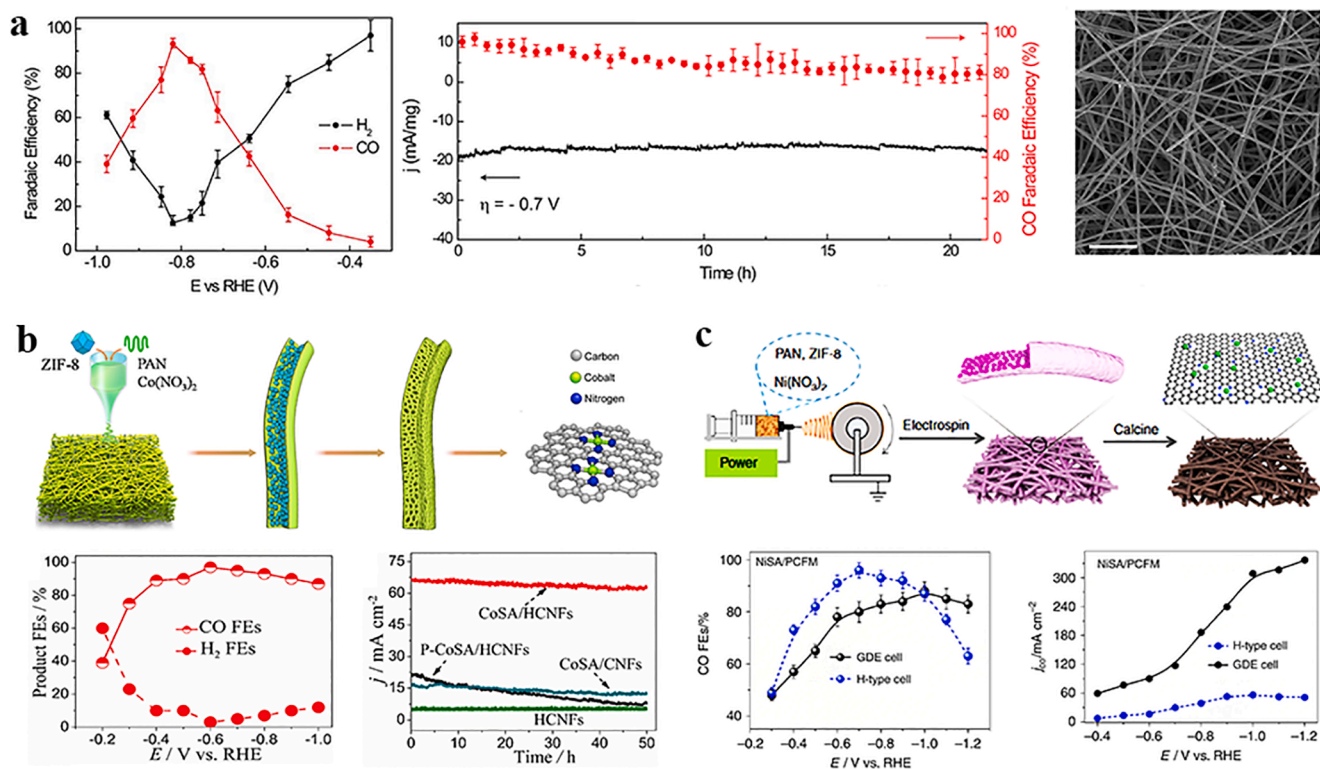


Fig. 4. (a) FE of H_2 and CO, stability test and TEM image (scale bar, 5 nm) for NiN graphene catalyst [47]; (b) schematic illustration of the synthesis, FEs of CO and H_2 and stability test of Co single-atom-decorated carbon nanofibers [48]; (c) schematic illustration of the synthesis, FEs of CO and current density of Ni single-atom-decorated carbon nanofibers [49].

(Fig. 4b, c). In a flow cell device, the partial current density of NiSA/PCNFs can reach a commercially relevant value of 308.4 mA cm^{-2} as well as a CO FE of 88% at -1.1 V vs. RHE for at least 120 h [49]. Similarly, the CoSA/PCNF catalyst exhibited a CO FE of 92% together with 211 mA cm^{-2} at -0.7 V vs. RHE in a flow cell [48]. In these studies, the high current density was attributed to the fast diffusion of CO_2 in the flow cell and the large surface area of the self-supported electrodes providing a large number of active centers. N-coordinated Ni and Co sites were suggested as active centers as they could greatly decrease the energy barrier for the formation of the key $^*\text{COOH}$ intermediate. It is worth noting that there are still debates about the active sites of single-atom catalysts, as the isolated sites can transiently convert into metal nanoparticles during CO_2RR , which then work as catalytically active species [50].

4.2. Metal nanofibers as CO_2 electroreduction catalysts

As shown above, polymer fibers prepared via the electrospinning method are usually carbonized by annealing at high temperature under an inert atmosphere before using them as catalysts, which improves their mechanical and chemical stability, and their electrical conductivity, as well as their interactions with the supported metal species. However, if polymer fibers are electrospun from polymer solution with metal precursors but removed by a later oxidation treatment, they can also serve templates for the preparation of metal/oxide/alloy fibers for catalytic applications. Following this strategy, Hu et al. fabricated Sn/ SnO_2 porous hollow fibers (PHF) by calcination of Sn-containing PVP fibers at $550 \text{ }^\circ\text{C}$ in air for 3 h (Fig. 5a, b) [51]. After the removal of the polymers, the remaining Sn/ SnO_2 fibers are composed of $\sim 12 \text{ nm}$ nanoparticles, showing a high porosity with a high surface area. The catalyst exhibited high selectivity and durability for formate production with a maximum FE of 82.1% at -1.60 V vs. SCE for 10 h (Fig. 5c). The enhanced catalytic performance of the Sn/ SnO_2 PHF catalyst was attributed to an increase in the number of active sites and CO_2 adsorption capacity, as well as a decrease in the activation energy.

Similarly, Fan et al. also prepared SnO_2 fibers for electroreduction of CO_2 to formate [52]. However, ethanol was added in the electrospinning solution to achieve higher SnCl_2 solubility. In this case, the metal precursor can move to the outside of the fibers at the initial stage of the annealing process to form a SnO_2 shell due to the low boiling point of ethanol compared to DMF and PVP. After removing DMF and PVP at $500 \text{ }^\circ\text{C}$ in air for 2 h, one-dimensional SnO_2 nanofibers with a wire-in-

tube (WIT) structure (Fig. 5d, e) were obtained. The catalyst was mainly selective to CO and formate, showing a C_1 FE of $> 90\%$ in the potential range -0.89 to -1.29 V vs. RHE (Fig. 5f). Compared to commercial SnO_2 nanoparticles, SnO_2 nanofibers showed a high specific surface area, a microporous inner tube structure and abundant grain boundaries, resulting in improved CO_2RR performance.

As well as metal oxide nanofibers, metal sulfide materials have also been prepared for CO_2RR using the electrospinning method. For example, Aljabour et al. synthesized chalcopyrite semiconductor CuInS (CIS) nanofibers for the electroreduction of CO_2 to formate in ionic liquid solution [53]. The only difference between the fabrication of metal oxide and metal sulfide fibers is the addition of dodecanethiol as a sulfur precursor during the annealing process. The CO FE reached 77% in 0.1 M tetrabutylammoniumhexafluorophosphate (TBAPF_6) in anhydrous acetonitrile and the catalyst can be stable for 10 h. The crystallized CuInS_2 nanofiber networks provide the possibility of expanding the active catalytic surface, which is essential for obtaining high selectivity. Notably, the role of sulfur was not discussed in this work, although previous studies have found that sulfur can either act as a promoter [54] or be toxic to the catalyst [55].

5. Conclusions and outlook

Electrospinning is a simple method of producing nanofibers with a high surface area, high porosity, good conductivity and high stability. This mini review summarizes the recent advances in materials synthesized by electrospinning and their applications for the CO_2RR . Heteroatom-doped (e.g., N and S etc.) carbon fibers can be fabricated by simply electrospinning polymers with the target heteroatom, and such materials have shown excellent selectivity towards CO ($>90\%$ FE). By adding metal salts to the polymer solution, carbon fibers decorated with metal single atoms, metal particles or oxide particles have been obtained. The selectivity of these materials can be adjusted by varying the metal used, the particle size and the oxidation state. In addition, porous carbon fibers made by electrospinning can also serve as templates for fabricating metal/oxide/alloy fibers for the CO_2RR . While promising progress has been observed over the last few years, a number of issues still remain to be considered in future studies of electrospun materials for the CO_2RR .

First, the industrial application of electrospinning is still challenging due to the high working voltage and high energy consumption required. To act as electrocatalysts, polymer fibers made by electrospinning often

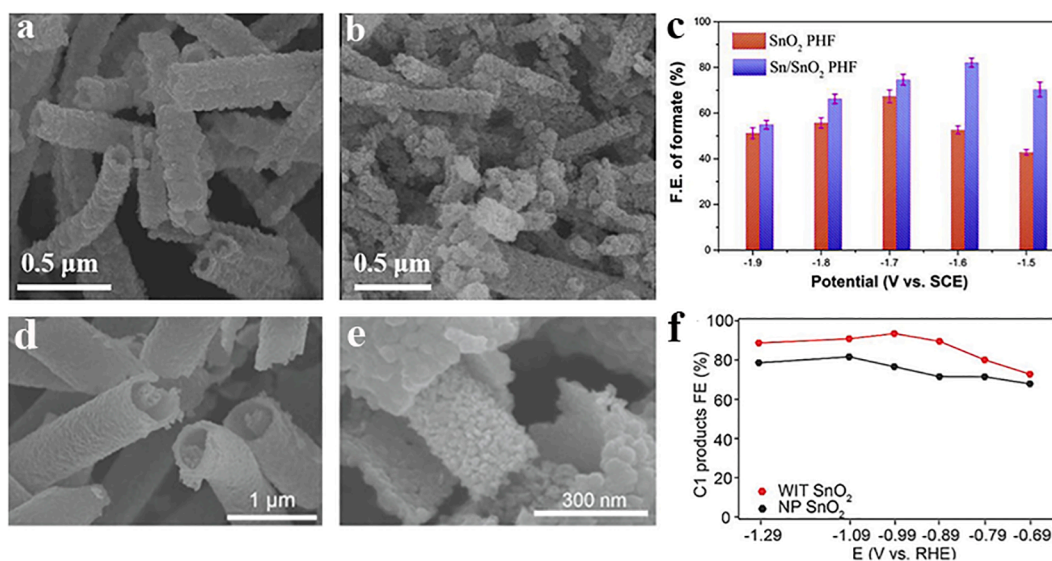


Fig. 5. SEM, bright-field TEM, high-resolution TEM images of (a) SnO_2 PHF and (b) Sn/ SnO_2 PHF catalysts; (c) FE of formate for SnO_2 PHF and Sn/ SnO_2 PHF [51]; (d,e) SEM images of the WIT SnO_2 nanofibers at various magnifications; (f) FE of C1 products for WIT SnO_2 nanofibers [52].

require pyrolysis treatment to increase their conductivity and stabilize the catalytic center, which consumes additional energy. Therefore, it is important to optimize the synthesis process to obtain highly active catalysts with a lower energy consumption. Second, electrospun materials that are self-supporting, with high flexibility and a well-developed pore structure are ideal for use as GDEs, but few studies of this have been reported. Thus, more studies should be carried out on the development of self-supported electrospun materials for use as GDEs in flow reactors, which is another important step toward industrial applications. Third, the major products of electrospun materials for the CO₂RR are still limited to CO and HCOOH; future studies are recommended to focus on the more valuable multi-carbon products. Fourth, previous studies have shown that carbon materials become more hydrophilic during the CO₂RR process, which results in a higher H₂ evolution rate compared to the CO₂RR. Therefore, more attention should be paid to the stability of electrospun carbon-fiber-based electrodes.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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