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Review

Pushing the activity of CO_2 electroreduction by system engineering

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ABSTRACT

As a promising technology that may solve global environmental challenges and enable intermittent renewable energy storage as well as zero-carbon-emission energy cycling, the carbon dioxide reduction reaction has been extensively studied in the past several years. Beyond the fruitful progresses and innovations in catalysts, the system engineering-based research on the full carbon dioxide reduction reaction is urgently needed toward the industrial application. In this review, we summarize and discuss recent works on the innovations in the reactor architectures and optimizations based on system engineering in carbon dioxide reduction reaction. Some challenges and future trends in this field are further discussed, especially on the system engineering factors.

1. Introduction

The excessive dependence of fossil energy in daily life and the resulting environmental pollution of massive emissions of carbon dioxide (CO_2), one of the major greenhouse gases, is a series of global challenges that are facing the human society today [1]. On the one hand, with the rapid economic development and population growth, the global energy demand is continuously increasing. Fossil fuels are limited as non-renewable resources, resulting in an increased energy crisis [2]. On the other hand, due to the large consumption of fossil fuels, the emitted CO_2 is accumulating in the atmosphere year by year, and the continuous increase of artificial CO_2 emissions has caused serious environmental problems [3,4]. On May 11th, 2019, a historic high CO_2 level of 415.26 ppm was recorded by Mauna Loa Observatory in Hawaii, which sounded the alarm for mankind once again (https://www.research.noaa.gov/News/Scientist-Profile/ArtMID/536/ArticleID/2461/Carbon-dioxide-levels-hit-record-peak-in-May). If no active and effective actions were to be taken, the current human development path would become greatly affected in the near future. Thus, technologies that use renewable energies on a large scale to replace the existing fossil energy-based energy structures are urgently needed. Among them, the efficient renewable energy conversion and storage methods should exist in the core position [5].

As a promising technology that may enable the intermittent renewable energy storage and zero-carbon-emission energy cycling, the photochemical or electrochemical catalytic reduction of CO_2 started to be demonstrated in 1970s and has achieved extensive attention in the past decade [6–8]. Researchers have learnt from and then mimicked the natural photosynthesis process of green plants, and proposed a new process that allows clean energy to drive electrocatalytic CO_2 reduction to generate different molecules with energy storage [9]. This process is also known as the artificial photosynthesis (AP) process. Different artificial photosynthesis systems with diverse electrochemical reactions have been developed and studied to convert CO_2 into value-added chemicals or fuels, including photocatalytic [10,11], photoelectrochemical [12–14], electrocatalytic [15–17], and biocatalytic reactions [18].

Among various artificial photosynthesis systems, the development of solar-driven electrocatalytic CO_2 reduction reaction (CO_2RR) is widely considered to have the potential for large-scale practical applications with high efficiency and low cost [19,20], and has thus become a research hotspot of various artificial photosynthesis devices. These successful researches on solar cells have efficiently pushed the solar-to-electric energy conversion to a high level of 39.2% for multi-junction cell and 29.1% for single-junction cell [21]. This artificial photosynthetic system is mainly subject to the low activity and selectivity of electrocatalytic CO_2 reduction reactions [22]. Furthermore, the realization of high activity and high selectivity of CO_2RR requires comprehensive innovation and optimization from electrocatalysts to catalytic systems.

Substantial research developments on electrocatalyst innovation have been made in order to solve the problem of poor activity and selectivity of electrocatalytic CO_2RR [23–25]. Both homogeneous and heterogeneous catalysts have been extensively studied

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for electrochemical reduction of CO_2. In homogeneous catalysis, although many metal complexes [26] and clusters [27] have been reported to reduce CO_2 to small molecules such as CO with high selectivity, the high cost and the difficulty of separation have greatly limited their value for practical use. In contrast, inorganic material-based heterogeneous catalysts have attracted more and more attention from the research community, due to their simplicity of synthesis, environmental friendliness, and high chemical stability in a reductive environment [28]. Both metal-free and metal-based catalysts have shown activity in electrocatalytic CO_2RR. Different product selectivity can be achieved by doping non-metallic heteroatoms with various elemental compositions and site structures on carbon-based metal-free electrocatalysts [29–31]. More heterogeneous catalysts for electrochemical reduction of CO_2 are metal-based materials such as Cu, Ag, Au and Sn [32].

According to the intermediate states of the catalytic process and the main products of the catalytic reaction, the catalysts can be roughly classified into three different categories [33]. The type I electrocatalysts are mainly composed of the main group metal such as Sn, Pb, In, Bi, and Hg, which has a strong binding ability to the intermediate state CO_2^{*-}. The reduction process mainly proceeds to an outer layer mechanism, and the main product is formic acid or in the form of formate at a basic environment [34–36]. The type II electrocatalysts are generally late transition metal materials such as Ag, Au, Zn, and Pd, which have strong binding ability to the *COOH intermediate, but their adsorption to the *CO intermediate is weak, so the main product is carbon monoxide (CO) [37,38]. Copper is the only type III of catalyst. It has a strong binding to the intermediate state *CO and can be further reduced to form a *COH or *CHO intermediate state [39,40]. The products of copper-based material are abundant and can include hydrocarbons and alcohol molecules with 2–3 carbon atoms [41]. Based on the selectivity of different metals for CO_2RR products, researchers have developed electrocatalysts with high selectivity for the synthesis of high value-added compounds such as CO [42], methane (CH_4) [43], formic acid (formate) [44], and ethylene (C_2H_4) [45]. In addition, researchers have also introduced the popular concept of single-atom catalysis to the CO_2RR and created a series of single-atom metal catalysts, such as Fe [46], Co [47], Ni [48], and Cu [49]. By incorporating high-density uniform active sites and facile synthesis, the single-atom electrocatalysts can demonstrate high activity and high selectivity toward CO or formate for CO_2 reduction.

On the other hand, compared to the successful and fruitful catalyst innovation in published research works, the researches on the catalytic reaction system toward commercial and industrial applications are relatively limited. Several types of continuous flow reactors, also known as "flow-cell reactors" that are assisted by gas diffusion electrodes (GDEs), have been demonstrated, which can greatly overcome the limitation of CO_2 mass transport in traditional H-type reactors [50]. This is a big step for CO_2 reduction research towards large-scale industrial applications, and can significantly increase the catalytic current density of the CO_2RR on electrode surface [51]. Depending on the state of the electrolyte in the reactors, these continuous flow reactors can be further subdivided into two types: microfluidic reactors supported by liquid electrolytes, and membrane reactors supported by solid membrane electrolytes [52].

Moreover, CO_2 reduction systems and reactors powered by renewable energy sources, especially solar energy, have also been reported in several works [53–55]. The matching between energy input and catalyst performance provide a significant guidance for efficient renewable energy conversion [56]. The clean and sustainable future energy blueprint can potentially be realized by the feasibility and efficiency of these full artificial photosynthesis systems. In addition, researches have also investigated and optimized different components in electrochemical CO_2 reduction reactors, such as electrodes and electrolytes. Several studies have revealed that the tailoring of catalytic reaction systems may change the activity and selectivity of the catalysts and sometimes even reverse their performance trends [57]. Therefore, system engineering-based research on the full CO_2RR, including the process and device architecture, is equally critical as the catalyst design in order to attain the goal of future industrial application.

In this review, we will summarize recent innovations on the reactor architecture and optimizations based on system engineering in the CO_2RR (Fig. 1). The improvements of the CO_2RR in core metrics of such as the catalytic current density, energy conversion efficiency, and selectivity, will then be discussed based on the reactor design innovation, energy input regulation, as well as electrode structure and electrolyte optimization. These improvements are critical for industrial and commercial applications, and also suggest a guide how to further enhance the performance of CO_2RR from a system engineering perspective. Finally, several critical challenges and future trends focusing on the CO_2RR system engineering will be proposed and discussed.

2. Catalytic reactor design

2.1. Microfluidic reactor

Due to the mass transport limitation of CO_2 dissolved in the liquid electrolyte, the traditional H-type reactors are subject to a low achievable catalytic current density, which seriously hindered their large-scale application. Gas diffusion electrode (GDE)-assisted microfluidic reactors are pioneered by Kenis and his coworkers in order to solve this problem [58]. In this type of reactors (Fig. 2a), two GDEs are coated with a catalyst for cathodic CO_2RR, and another catalyst for anodic oxygen evolution reaction (OER) catalyst, respectively. Two electrolytes are separated by an ion-exchange membrane and flow between the GDEs. A continuous flow of CO_2 is fed to the back of cathodic catalyst-coated GDE as the reaction substance. The stainless steel plates serve as both reactor shells and current collectors outside the reactor. For continuous flow reactors, the gas phase products can be directly separated from the outlet mixture, and the liquid phase product can be collected from electrolyte as microfluidic reactor. For a typical product analysis, the gas-phase products are determined by gas chromatography (GC) with different detectors like mass spectroscopy (MS), while the liquid-phase products are quantified by nuclear magnetic resonance (NMR). In such work, the production of carbon monoxide (CO), ethylene (C_2H_4), ethanol (C_2H_5OH) in high current density was achieved after applying the copper-based catalyst into this reactor (Fig. 2b). The total current density was up to 400 mA/cm^2 at a low overpotential of 0.7 V with 46% Faradaic efficiency (FE) towards multi-carbon products including

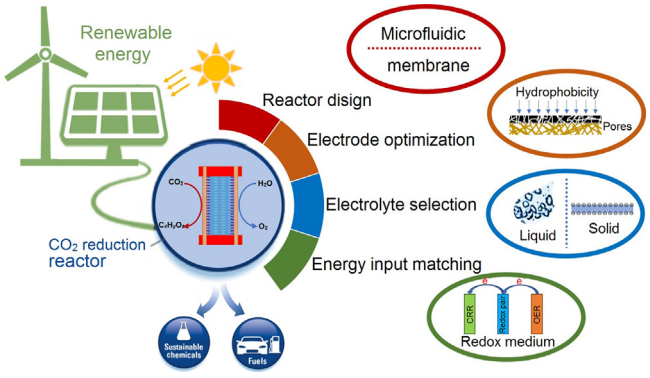

Fig. 1. (Color online) Illustration of pushing the activity of CO_2 electroreduction by system engineering.

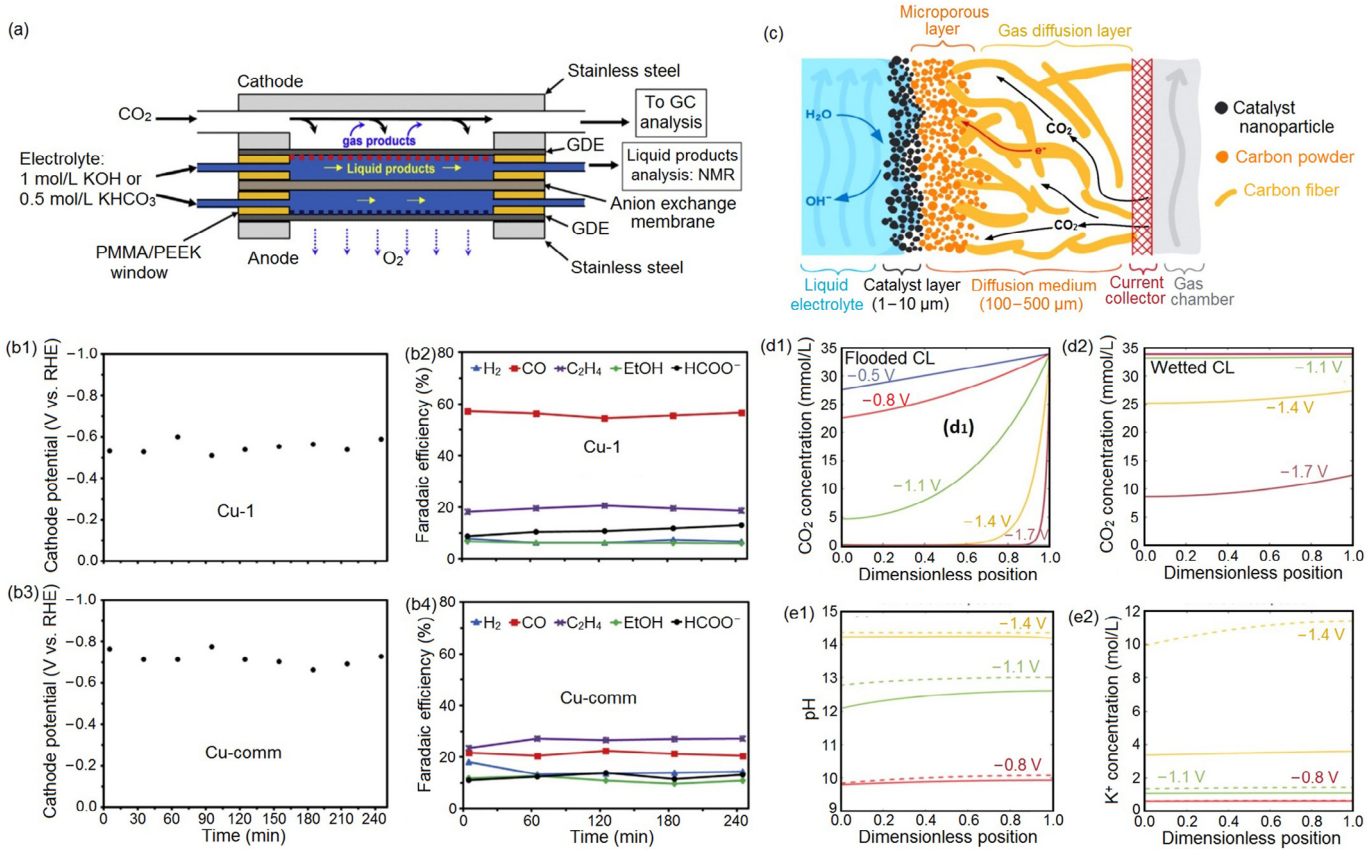

Fig. 2. (Color online) Illustration of microfluidic reactor and gas diffusion electrode. (a) Schematic diagram of gas diffusion electrode-based microfluidic reactor for carbon dioxide reduction reaction. (b) The cathode potential and Faradaic efficiency towards different products of Cu-1 and Cu-Comm electrocatalysts. Reproduced with permission from Ref. [58]. Copyright 2016, Elsevier. (c) Schematic diagram of a typical gas diffusion electrode. (d) The CO_2 concentration of flooded CL and wetted CL under different potential. (e) The pH and K^+ concentration of flooded CL and wetted CL under different potential. Reproduced with permission from Ref. [60]. Copyright 2018, The Royal Society of Chemistry.

ethylene and ethanol. This highly efficient catalytic performance far exceeds those results from H-type reactors and can be attributed to the mass transfer feature enabled by GDE. Furthermore, the onset potential of CO_2RR can be significantly reduced due to the large increase in the CO_2 concentration, which is beneficial to the application of this reaction with high energy efficiency [59].

Beyond improvement in catalytic current density of CO_2RR, a completely different surface environment of catalyst is achieved in the microfluidic reactor. For a better understanding of the actual environment of GDE surface during the CO_2RR, a multi-physics model of GDE was developed by Weber and his colleagues (Fig. 2c) [60]. They investigated the interplay between reaction species transport and electrochemical reaction kinetics by this model, and demonstrated that the wetted porous catalyst layer (wetted CL), which was the normal state of the GDE during the reaction, significantly improved the catalytic performance by offering larger area of active surface and lower mass-transfer resistances. The local CO_2 concentration was maintained at a high level throughout the whole wetted CL, while the flooded CL, which was an abnormal working state and similar to the environment in H-type cell, limited the CO_2 concentration among a large range of CL (Fig. 2d). Furthermore, the local pH and local potassium ion concentration can be improved by GDE, and they are important factors on the activation of CO_2 and the product selectivity control (Fig. 2e).

The results obtained by this simulation model are also confirmed by the experimental work. Sargent and co-workers [61] introduced a super alkaline chemical environment (10 mol/L KOH solution) into a microfluidic reactor for CO_2RR. Considering the extreme high reactivity between CO_2 and alkaline solutions, such work was only realized in the GDE-assisted microfluidic reactors. In such strong alkaline environment, the hydrogen evolution reaction (HER), which is the main competitive side reaction of CO_2RR, is greatly inhibited due to the limited proton concentration, while the activation of CO_2 molecules is well improved by the high concentration of hydroxide ion and potassium ion (Fig. 3a). The reaction kinetics toward ethylene is also improved by this chemical environment. The onset potential of ethylene was reduced to −0.165 V (vs. RHE), which was only 0.245 V higher than its thermodynamic potential (Fig. 3b). A GDE architecture with porous PTFE films was also developed with an excellent stability of over 100 h, which was far beyond the performance of commercial GDEs (Fig. 3c). The improvement in stability was mainly attributed to the greatly improved hydrophobicity and resistance of flooding (Fig. 3d).

2.2. Membrane reactor

Membrane reactors have long been used as the reaction device for fuel cells [62], and are increasingly attracting attention from the research community of CO_2RR. The typical architecture of a membrane reactor contains two gas diffusion electrodes separated by an ion-exchange membrane (Fig. 4a). The ion selectivity of membrane varies from proton to anion, which determines the involved ion species for two half-reactions. The polymer membrane between two GDEs is directly contacted with both catalyst layers of two

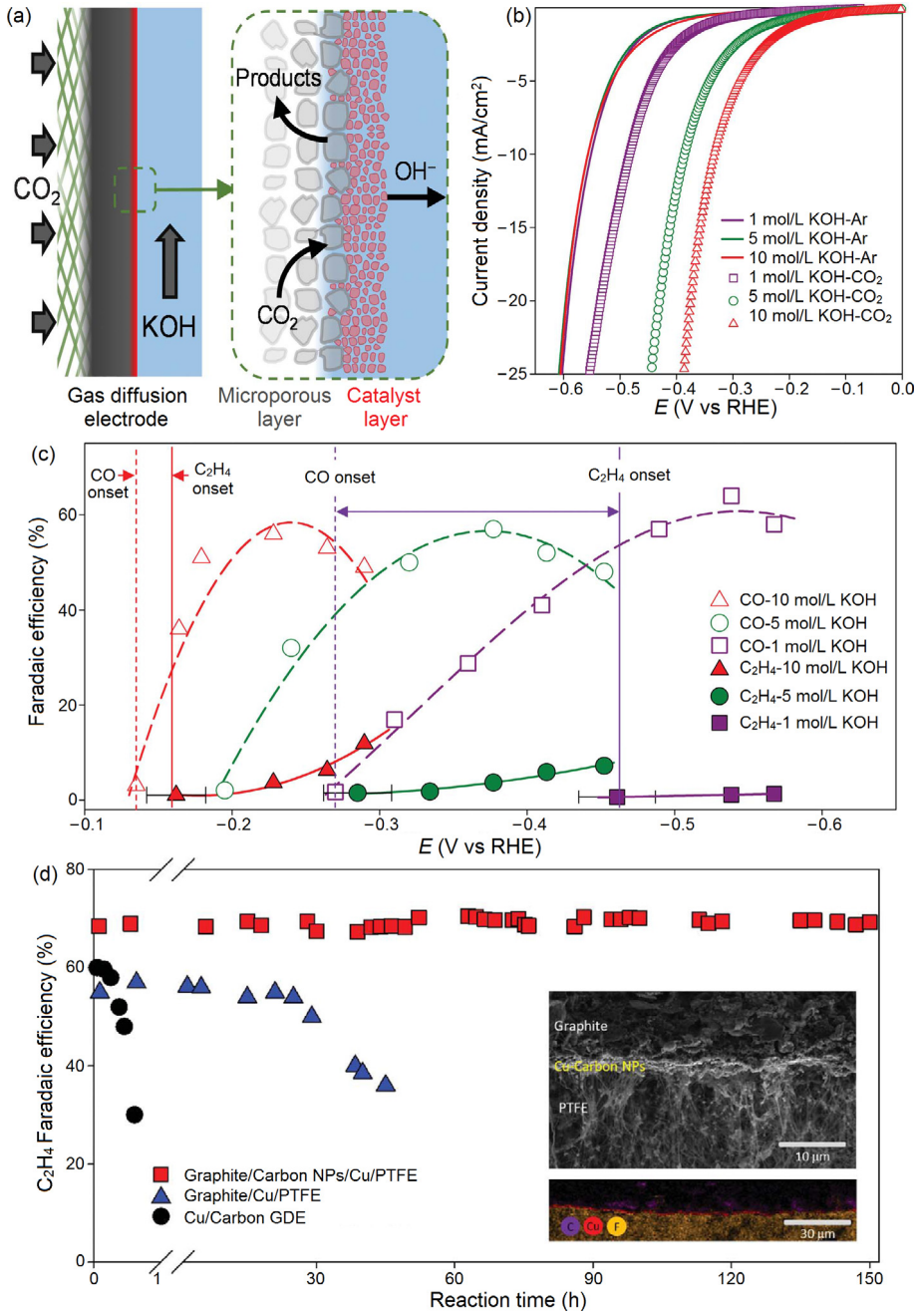

Fig. 3. (Color online) The structure and performance of PTFE-based gas diffusion electrode in CO_2 electroreduction. (a) Schematic diagram of gas diffusion electrode-based CO_2 feeding in electrochemical carbon dioxide reduction. (b) The LSV curve of the copper electrode in basic solution with different concentration of KOH under Ar and CO_2. (c) The Faradaic efficiency of the copper electrode in basic solution with different concentration of KOH. (d) The Faradaic efficiency towards ethylene of different electrode structure. Reproduced with permission [61]. Copyright 2018, AAAS.

GDEs, and acts as charge carrier as well as ion carrier at the catalyst/electrolyte interfaces [63]. In most cases, a certain amount of water remains in the membrane, while the input humidified airflow maintains the water balance of the membrane [64].

The solid-state membrane reactor demonstrates many intrinsic advantages over liquid-phase microfluidic reactor. Compared to various liquid-phase systems, membrane reactors without liquid-solid interface or liquid-phase ion transport process exhibit significantly reduced resistance and allow large catalytic current density. Proton exchange membranes (PEM) and alkaline anion exchange membranes (AAEM) were applied to their membrane reactors [65]. For copper-loaded carbon nanotube cathode catalysts, the AAEM was beneficial to the formation of carbon monoxide in a production rate of 8.88 μmol/(h cm^2), while PEM-based reactor only generated hydrogen on the surface of the electrode under the same conditions (Fig. 4b). Furthermore, many different types of surface ionic environments can be provided by well-designed polymer electrolytes, including super acidity, alkalinity or high ionic strength for specific ion, which is often not possible with liquid phase systems where the surface environment is subject to bulk phase solution components [66].

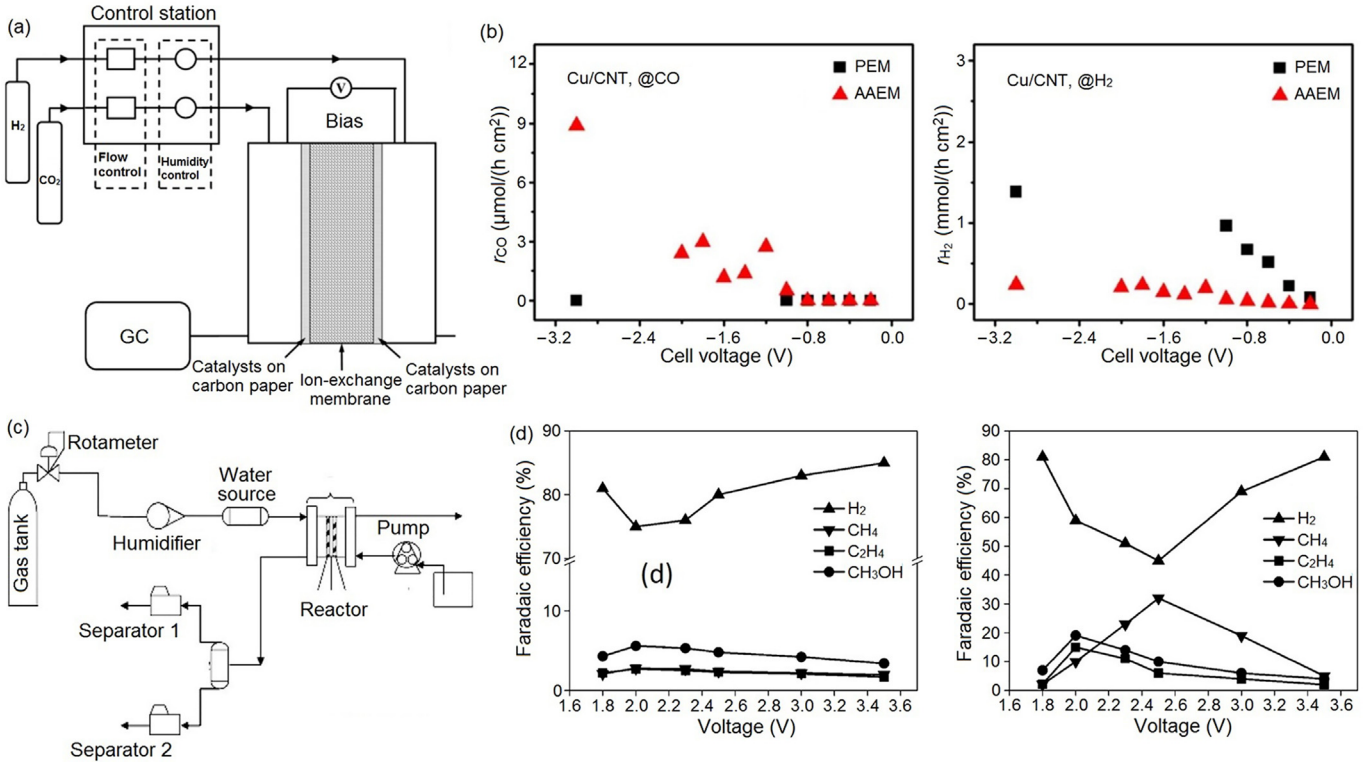

Fig. 4. (Color online) The architecture and performance of membrane reactor and hybrid reactor in CO_2 electroreduction. (a) Schematic diagram of a membrane reactor. (b) The partial current density towards CO and H_2 of PEM-based and AAEM-based membrane reactor. (c) Schematic diagram of a hybrid reactor. (d) The faradaic efficiency towards different product of CMI-based and AMI-based hybrid reactor. Reproduced with permission from Refs. [64,67]. Copyright 2013, 2008, Elsevier.

2.3. Hybrid reactor

Although the membrane reactors show great advantages in many aspects, their energy efficiencies in CO_2RR are limited by the poor activity of anode electrocatalysts. Even by the same electrocatalyst, the exhibited overpotentials of the oxygen evolution reaction (OER) are typically much larger in the membrane-based electrode environment than the super alkaline aqueous environment, due to the insufficient water content and alkalinity on the electrocatalyst surface [67]. More energy input is required to achieve high current density output in membrane reactors even for the low-overpotential noble metal catalysts [68]. This problem can be circumvented in microfluidic reactors with aqueous electrolytes. Thus, a hybrid reactor was developed to take both the advantages of counter electrode in the microfluidic reactor and the advantages of working electrode in the membrane reactor at the same time (Fig. 4c) [69]. Beyond the difference in counter reactions, the difference in performance on the carbon dioxide side may also exist between these two reactors. In such hybrid reactors, the cathodic electrocatalyst is directly contacted with membrane, while the anodic catalyst layer is immersed in an alkaline electrolyte in order to maximize the OER performance [70]. Furthermore, the effect of ion exchange membrane, similar to those reported in membrane reactor, was reported in a hybrid reactor [68]. By comparing the two membranes with same framework structure, i.e., the cation exchange membrane (CMI-7001) and the anion exchange membrane (AMI-7001), it was found that the anion membrane can achieve methane production with a Faradaic efficiency of up to 30% under the same conditions, while no methane was produced in membrane reactor with CMI-7001 (Fig. 4d). In addition to the ion effect, the two reactors have similar trend on the catalytic current toward CO. Under the same membrane and catalyst conditions, the CO partial current can rise rapidly as the voltage increases, and there is no mass transfer limit after the highest Faradaic efficiency due to the high catalytic activity of the catalyst on the membrane surface [71].

3. Renewable energy-driven systems

3.1. Photoelectrochemical system

The direct conversion of renewable energy, especially solar energy, into energy stored in chemical bonds mimics the natural photosynthesis process occurring in green plants and other microbes, and provides a promising future for clean and sustainable energy structure. According to the different forms of energy input, the system for artificial photosynthesis can be divided into various types. Semiconductor-based photoelectrochemical (PEC) CO_2RR system is one of the most promising systems for artificial photosynthesis [72]. In such a system, light is absorbed by the photoactive electrode and the excited charge carriers are subsequently generated, which drives catalytic reactions at both anode and cathode (Fig. 5a). For instance, Yang and co-workers [73] reported a nanowire-based PEC system for CO_2RR. Au_3Cu alloy nanoparticles were directly assembled to the surface of light-harvesting semiconductor nanowires (Fig. 5b). Such Au_3Cu nanoparticle-decorated Si nanowire arrays exhibited high selectivity towards CO with a Faradaic efficiency of 80% at −0.20 V vs. RHE (Fig. 5c). Xiang and co-workers [74] developed an artificial photosynthesis system to convert CO_2 into formate, with a 10% solar-to-formate energy efficiency. A tandem GaAs/InGaP/TiO_2/Ni photoanode was used for light absorption and OER, while the CO_2RR was catalyzed by a Pd/C-coated Ti mesh cathode (Fig. 5d). At a current density of 8.5 mA/cm^2, the cathode exhibited less than 100 mV overpotential and over 94% Faradaic efficiency for converting CO_2 to formate

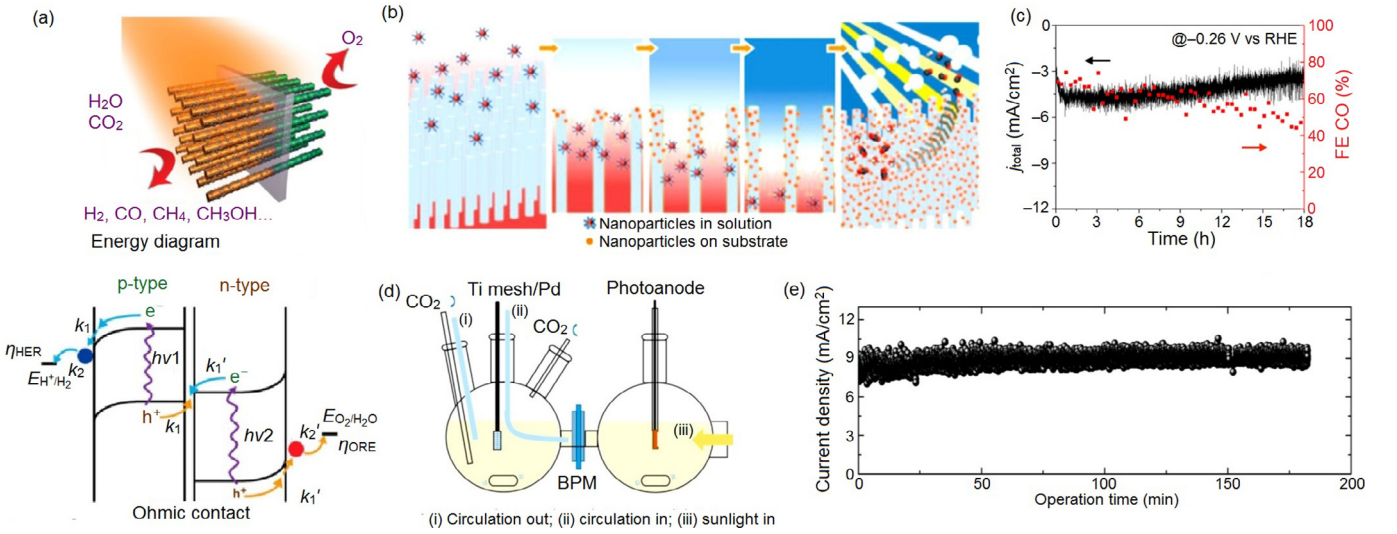

Fig. 5. (Color online) The illustration and performance of CO_2 photo-electroreduction reaction. (a) Schematic diagram of nanowire-based photoelectrochemical artificial photosynthesis. (b) Schematic diagram of nanoparticle-assembled nanowire cathode. (c) The catalytic current and faradaic efficiency towards carbon monoxide of the system. (d) Schematic diagram of bipolar membrane-based photoelectrochemical system. (e) The catalytic current of the system for a test over 180 h. Reproduced with permission Ref. [73,74]. Copyright 2016, American Chemical Society.

(Fig. 5e). Nevertheless, the relatively low efficiency and current density of photoanodes still limit the further scaling up and application of PEC systems [75].

3.2. Photovoltaic + electrochemical system

As the energy efficiency of solar cells is continuing to be increased by researchers' unremitting efforts, the artificial systems based on photovoltaic (PV) cells and electrocatalysts are presenting unique advantages in energy conversion efficiency [76]. As the selection of catalyst has been greatly expanded by decoupling the light absorption and electrocatalysis [77], a series of photovoltaic cell-based artificial photosynthesis systems have been reported with high energy efficiencies in recent years. For example, Grätzel and co-workers [78,79] reported two perovskite photovoltaics-based artificial photosynthesis systems that converted CO_2 into CO. In the first system, CO_2 was reduced on the oxidized gold cathode while oxygen was generated on the iridium oxide anode in the same cell chamber (Fig. 6a). The system reached a high solar-to-CO efficiency of 6.5% with an overpotential of 700 mV for CO_2RR (Fig. 6b). The FE for CO production was maintained over 80% throughout the 18-h stability test (Fig. 6c). Later, a second system was reported that adopted a two-chamber cell, separated by a bipolar membrane. SnO_2 deposited by atomic layer deposition (ALD) on CuO nanowires was used as cathodic electrocatalyst for CO_2RR. The solar-to-CO efficiency of this system was largely improved, with the lower overpotential for both electrocatalysts and better solar efficiency of a triple junction GaInP/GaInAs/Ge photovoltaic (Fig. 6d). The solar-to-CO efficiency exceeded 13.4% with over 80% FE toward CO production (Fig. 6e).

In addition to the CO_2RR system to produce CO, artificial photosynthesis systems for production of other products have also been demonstrated. For instance, Mougel and co-workers [80] reported a low-cost all-earth-abundant artificial photosynthesis system for the conversion of CO_2 to hydrocarbons. Both the CO_2RR and OER were catalyzed by the dendritic nanostructured copper oxide material with low overpotentials [81]. A 2.3% solar-to-hydrocarbon efficiency was demonstrated in this system. Ager and co-workers [82] developed a system to convert CO_2 to hydrocarbons and oxygenates with a CuAg alloy cathode and an IrO_2 nanotube anode. Under 1 sun illumination, the solar-to-fuel (hydrocarbons and oxygenates) conversion efficiencies of 3.9% and 5.6% were achieved with a Si-based solar cell and 1 four-terminal III–V/Si tandem solar cell, respectively. Nonetheless, the existing system-wide studies are all based on H-type reactors, and further studies and developments with flow reactors are need for industrial applications.

4. System optimization

4.1. Electrode

Electrode acts as the center of the catalytic reaction in any CO_2RR systems, and the activity of electrocatalysts can be directly tailored by optimizing the electrode structure. The electrode structure can be divided into macrostructure and microstructure. The macrostructure mainly includes the uniformity and thickness of the catalyst coating, and the microstructure is mainly the pore structure of the catalyst [83,84]. Thus, the mesoporous and microporous structures on the electrode surface also affect the electrode performance. Jiao and his colleagues developed a nanoporous Ag electrocatalyst for CO_2RR [85]. In their works, it was demonstrated that the pores of the catalyst provided two main aspects for the improvement of CO_2 reduction performance from the perspective of microstructure. On the one hand, the pores provided extra active area for catalytic reaction, which increased the catalytic current density and benefited the product output efficiency (Fig. 7a). The electrochemical surface area of their reported nanoporous Ag electrocatalyst was 150 times larger than the flat polycrystalline Ag. The increase in electrochemically active area was closely related to the increase in current density (Fig. 7b). On the other hand, the activation of CO_2 can be improved by highly curved inner surface of pore structure. Over 90% FE toward CO production was achieved by nanoporous Ag electrocatalyst, while the flat polycrystalline Ag showed no selectivity toward CO_2RR (Fig. 7c). An in-depth study of Tafel slope further indicated this point by showing a dramatic decrease in Tafel slope from 132 mV/dec of flat polycrystalline Ag to 58 mV/dec of nanoporous Ag (Fig. 7d). This decrease indicated that there was a fast initial electron transfer step related to the first reaction intermediate $CO_2^{\cdot-}$ before the

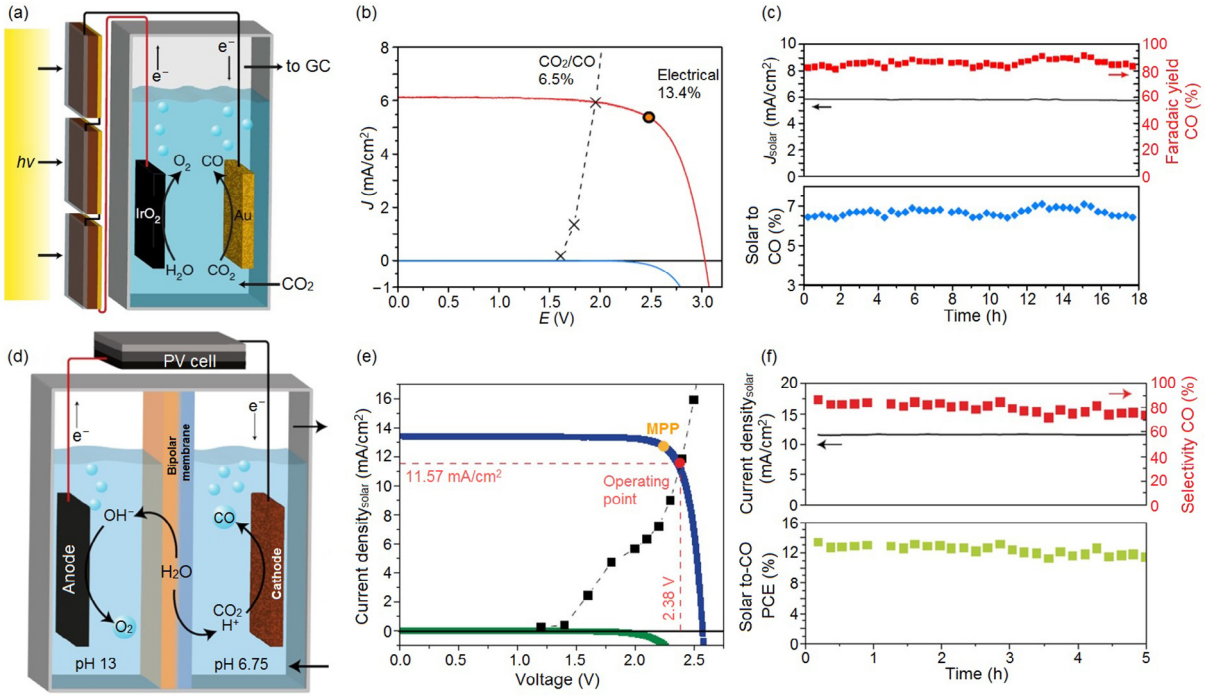

Fig. 6. (Color online) The structure and performance of PV + EC systems in CO_2 electroreduction. (a) Schematic diagram of the artificial photosynthesis system with IrO_2 anode and Au cathode. (b) Photovoltaic cell efficiency curve and catalytic reaction current curve, showing the PCE at their intersection. (c) The Faradaic efficiency towards CO and the solar-to-fuel efficiency of the system. (d) Schematic diagram of the artificial photosynthesis system with CuO cathode. (e) Photovoltaic cell efficiency curve and catalytic reaction current curve, showing the PCE at their intersection. (f) The Faradaic efficiency towards CO and the solar-to-fuel efficiency of the system. Reproduced with permission from Refs. [78,79]. Copyright 2015, 2017, Nature Publishing Group.

subsequent non-electron transfer rate-determining step. The highly curved inner surface of the nanoporous structure was able to stabilize the $CO_2^{\cdot -}$ intermediate [38].

From the perspective of macrostructure, the uniformity and thickness of the catalyst coating can significantly affect the CO_2RR catalytic performance. This uniformity requires both the thickness and coverage of electrocatalysts on a large-area electrode surface, and also needs the electrode-to-electrode variability to be as little as possible. Kenis and co-workers [86] compared three different catalyst coating methods including hand-painting, air-brushing and screen-printing. By X-ray micro-computed tomography (Micro-CT) and SEM methods, the uniformity in the macrostructure of the electrode catalyst layer was visualized and improved along with the increase of the automation degree in the coating methods from hand-painting to screen-printing (Fig. 8a). Significant improvements in electrode-to-electrode reproducibility were attributed to the highly automated nature of air-brushing methods. The air-brushed electrocatalyst layers showed a 3-fold increase in the partial CO current density in the CO_2RR with over 94% FE, compared to the hand-printed one at the same loading (Fig. 8b). Thus, the optimization of the CO_2 reduction electrode catalyst layer in macrostructure enabled higher current densities and better uniformity among various parts of the same or different electrodes.

Hydrophobicity of the electrode surface is also a key factor. Only wetted porous catalyst layer in gas diffusion electrode can provide both abundant contact interface of CO_2 and proton for the CO_2RR. The existing commercial GDEs are mainly designed for fuel cell applications with humid gas atmosphere and not suitable to stay in bulk aqueous solution under negative potentials for a long time. Hence, new GDE design and preparation strategy specifically for CO_2RR are urgently needed. Sargent and co-workers [61] reported a "sandwich-like" polytetrafluoroethylene (PTFE)-based GDE with excellent stability in a super alkaline solution due to the high hydrophobicity and chemical stability of PTFE. Furthermore, a variety of structures, especially nanostructures, have been reported to generate hydrophobicity and even superhydrophobicity on their surface [87]. For instance, Cui and co-workers [88] demonstrated that a multilayered, nanoporous polyethylene (PE) membrane pre-sputtered with Au nanoparticles enabled solid-liquid-gas three-phase contact lines for enhanced CO_2 diffusion and better sustainability against flooding. Compared to the single-layered PE membrane or other flat carbon substrates, both the Faradaic efficiency and partial current density for the CO_2 reduction to CO were significantly increased. While it is useful to enhance electrode hydrophobicity by applying selected support materials such as polymers and carbon-based materials, intrinsic hydrophobicity can also be achieved through the controlled synthesis of electrocatalysts with specific micro- or nanoscopic morphology. As the ideal catalyst layer may not contain electrode support materials, the regulation of the intrinsic hydrophobicity can better optimize the wetting level of the catalyst surface, which is important to the catalytic reactions.

4.2. Electrolyte

Electrolyte is another critical part of the catalytic interface in which CO_2RR takes places. The liquid electrolytes are widely used in both conventional H-type reactors and microfluidic reactors. Among different types of liquid electrolytes, the aqueous electrolytes are the most commonly used system for research and practical applications [89]. The ion compositions, concentrations and pH of aqueous electrolytes can influence the catalytic performances of electrocatalysts [90]. Hori and co-workers [91] demonstrated that the hydrogen evolution reaction was favorable in the Li^+ electrolyte, whereas the selectivity toward CO_2RR was preferred against hydrogen evolution reaction in other alkali-metal ion electrolytes, such as Na^+, K^+, and Cs^+. Comparing the high reactivity between CO_2 and alkaline solutions, the common aqueous

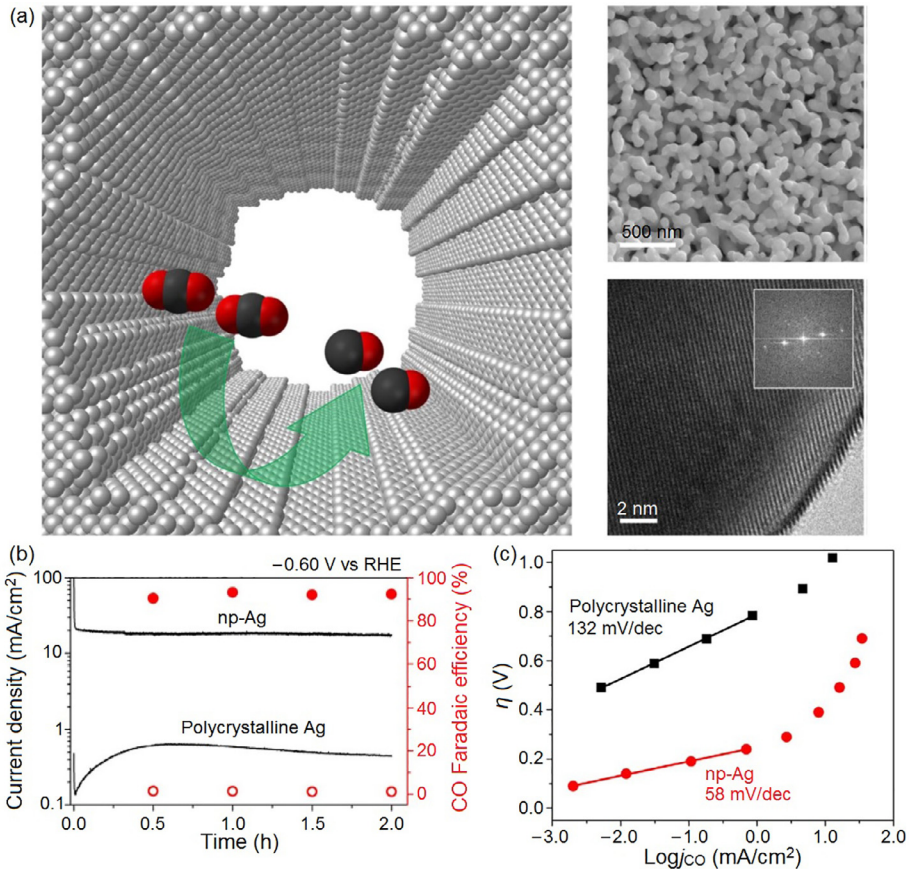

Fig. 7. (Color online) The structure of nanoporous silver and its performance in CO_2 electroreduction. (a) Schematic diagram of curved surface in nano-porous Ag electrode along with its SEM and TEM image. (b) The current density and faradaic efficiency towards carbon monoxide of nanoporous Ag and polycrystalline Ag. (c) The Tafel slope of nanoporous Ag and polycrystalline Ag. Reproduced with permission from Ref. [85]. Copyright 2014, Nature Publishing Group.

solutions for H-type reactors are acidic or neutral, which both have serious tendencies for the hydrogen evolution reaction. In microfluidic reactors, strong basic aqueous electrolytes can be used for the CO_2RR [61].

Organic electrolytes are advantageous substitutes for aqueous electrolytes, as they can have high solubility of CO_2 as well as inhibit the hydrogen evolution reaction by limited proton transfer. For instance, CO_2RR in methanol-based electrolytes is a good choice beyond aqueous reactions, because the solubility of CO_2 in methanol is superior to water under ambient conditions, and the production of hydrogen can also be inhibited by the inactive proton in hydroxyl group of methanol [92]. Nevertheless, the CO_2 conversion in the methanol electrolyte environment is not advantageous in the synthesis of high value-added liquid products, which greatly limits its application. Mizuno and co-workers [93] reported that the methanol electrolyte additive could improve the selectivity toward C_{2+} hydrocarbons. The Faradaic efficiency toward hydrocarbons reached 80% when sodium hydroxide was added into methanol electrolyte. In addition, they also investigated the effect of anionic species as additive of methanol electrolyte on CO_2RR. The selectivity toward ethylene among all possible products can be improved over pure methane in following sequence: bromide > iodide > chloride > thiocyanate > acetate [94].

Ionic liquids are another non-aqueous electrolyte for the CO_2RR. As a group of ionic compounds with special structure that can maintain a liquid state around room temperature, ionic liquids are widely used in support systems for various electrochemical reactions, including organic electro-synthesis [95] and electrocatalytic reactions [96]. The ionic liquids generally feature strong ionic conductivity in liquid phase as well as wide potential windows for operation, which are superior to both conventional aqueous and organic electrolytes systems [97]. Salehi-Khojin and co-workers [98] reported that the nanostructured transition metal dichalcogenide, WSe_2, catalyzed the electrochemical CO_2RR toward CO in an ionic liquid. The ionic liquid played an important role in this electrocatalytic reaction. Their study suggested that the cation of ionic liquid, 1-ethyl-3-methylimidazolium cation ($EMIM^+$), enhanced the mass transportation of CO_2 to the catalyst surface by a coordination between CO_2 and $EMIM^+$ in acidic solution [99].

Beyond the liquid electrolyte, the solid polymer electrolyte is a promising ion carrier for vapor-fed membrane reactor. Commercial ion exchange membranes including proton exchange membrane (PEM), anion exchange membrane (AEM), and cation exchange membrane (CEM) can be used for CO_2RR in membrane reactors. Their chemical components, membrane thicknesses, and the water uptake ability all have substantial influence on the reactor performances. First, the chemical structure and ion selectivity of membrane directly determine the half reaction in membrane reactor. Masel and co-workers [100] reported an anion exchange membrane based on imidazolium-functionalized polymer, polystyrene methyl methylimidazolium chloride (PSMIM), and applied this AEM in CO_2RR. A current density higher than 200 mA/cm^2 with a product selectivity over 98% toward CO was achieved by their membrane reactor with the PSMIM membrane. In comparison to other commercial membranes, PSMIM membrane can be considered as an ideal membrane for CO_2RR. The reactor was operated

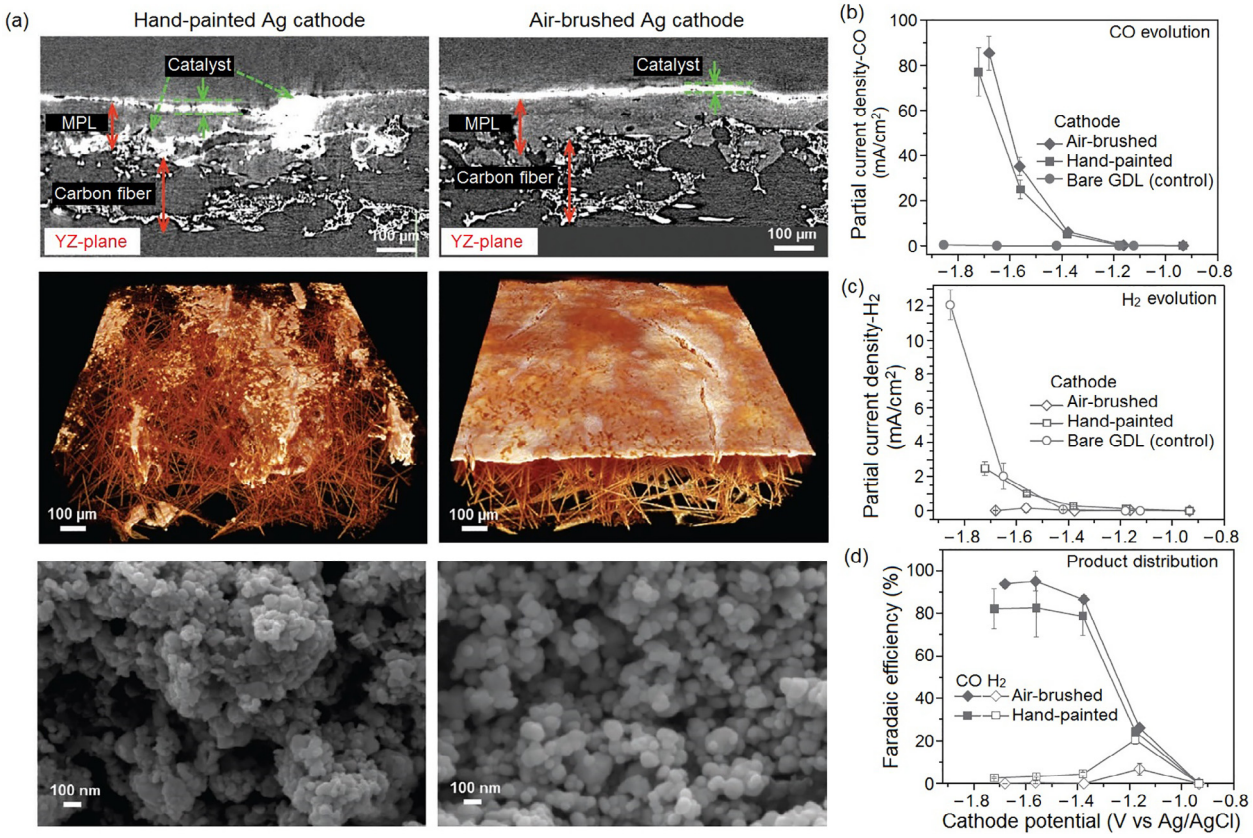

Fig. 8. (Color online) The structures of catalyst layer through different preparation methods and theirs performance in CO_2 electroreduction. (a) SEM and Micro-CT images of silver electrodes after hand-painting and air-brushing. (b) The partial current density for carbon monoxide of hand-painted Ag cathode, air-brushed Ag cathode and bare electrode. (c) The partial current density for hydrogen of hand-painted Ag cathode, air-brushed Ag cathode and bare electrode. (d) The faradaic efficiency towards carbon monoxide and hydrogen of hand-painted Ag cathode, air-brushed Ag cathode and bare electrode. Reproduced with permission from Ref. [86]. Copyright 2013, Wiley-VCH.

continuously for 4,500 h with the help of PSMIM membrane, which demonstrated its exceptional stability. Also, its catalytic current density and CO selectivity remained stable for several months.

In addition to chemical structure, the water uptake ability is also an important factor for membrane-based CO_2RR. Mallouk and co-workers [101] studied the effects of gas input with different humidity on membrane-based CO_2RR. Two CO_2 gas flows with different relative humidity of 15% and 90% were fed into two analogous membrane reactors at same operation current density of 100 mA/cm^2. The membrane reactor fed with 15% humidity CO_2 gas flow only functioned for 1 h, while the other fed with 90% humidity CO_2 gas flow could continuously operate for over 24 h.

4.3. Matching the energy input and catalyst performance

As a promising technology for renewable energy conversion, the current research on artificial photosynthesis system directly driven by renewable energy is focused on systems directly coupled OER and CO_2RR [102]. Although the conversion of CO_2 as well as O_2 generation are conducted in this system, there are many critical challenges that may severely limit the large-scale application of artificial photosynthesis [103]. The main drawbacks include: (1) the poor energy efficiency of the system due to high overpotentials at both cathode and anode caused by poor reaction kinetic; (2) the low catalyst performance of the system whose current input can hardly match the current requirement for the best catalyst performance; and (3) the instability of the system which is inevitably affected by weather changes, especially the fluctuation of solar light intensity.

In order to solve these severe problems, Zheng and co-workers [104] leveraged the biochemical mechanism of natural photosynthesis and developed a new concept of redox mediation for artificial photosynthesis. In a natural photosynthesis, the light reaction for O_2 production and carbon fixation are carried out in two separated steps, whose energy transfer processes depend on a pair of redox active species, adenosine triphosphate (ATP)/adenosine diphosphate (ADP) [105]. Therefore, the existing artificial photosynthesis systems and natural photosynthesis systems have great difference in reaction details. Inspired by nature, this redox-medium-assisted reaction system proceeded water oxidation reaction under light illumination and then stored the reduction energy using a zinc/zincate redox pair, instead of directly inputting into CO_2RR (Fig. 9a). Benefiting from the excellent reaction kinetics of zinc/zincate electrodeposition and electrochemical dissolution, the full-cell voltage of redox-medium-assisted system was reduced by 20% compared to those of the conventional two-electrode systems (Fig. 9b). The drop in full-cell voltage indicated that the same energy input can achieve more product output, which effectively increases the energy conversion efficiency of the system. Due to the decoupling of the anode and cathode reactions, the loop current involved in the CO_2RR was directly adjusted through current densities, which allowed to optimize performance of the catalyst in such system. Using a Au nanoparticle catalyst, the FE toward CO production was maintained above 90% (Fig. 9c). Moreover, with the buffering of zinc/zincate electrode, the CO_2RR was not directly affected by the photocurrent input or the fluctuation of light intensity, and thus a stable artificial photosynthesis process was achieved. The redox-medium-assisted system was

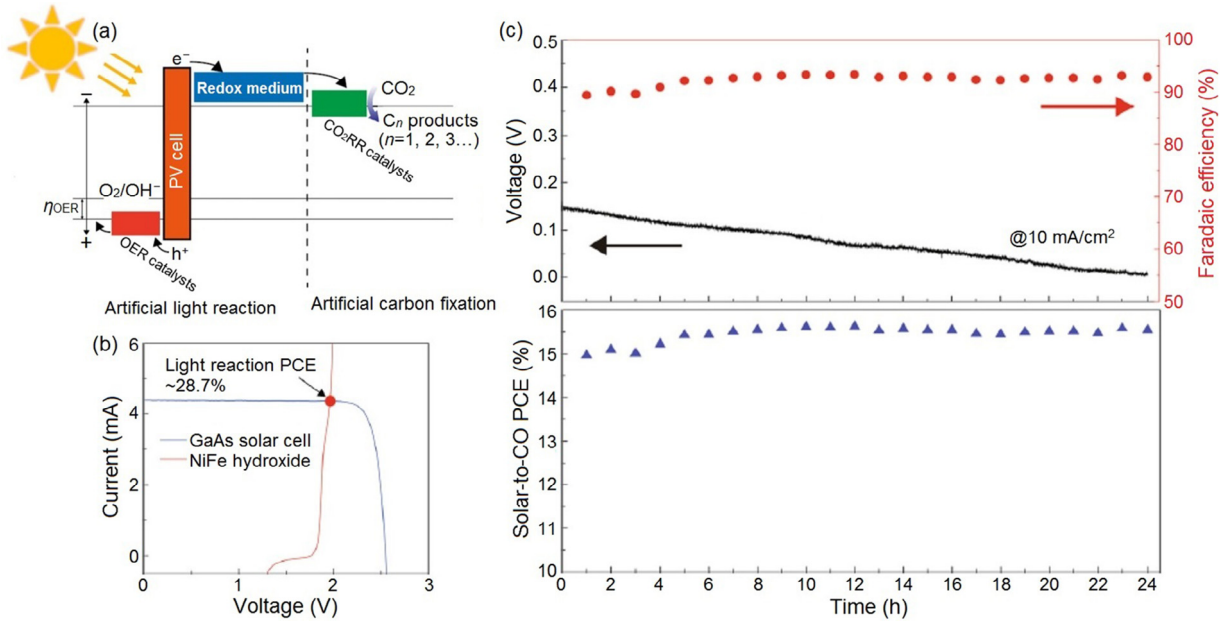

Fig. 9. (Color online) The illustration and reaction performance of redox-mediated artificial photosynthesis system. (a) Schematic diagram of the energy level of the reaction system after adding the redox medium. (b) Photovoltaic cell efficiency curve and catalytic reaction current curve of photoreactive oxygen production, showing the PCE at their intersection. (c) The faradaic efficiency towards CO and the solar-to-fuel efficiency of the system in the continuous test for 24 h. Reproduced with permission from Ref. [104]. Copyright 2018, Nature Publishing Group.

able to maintain an efficient CO_2RR continuously for more than 100 h (Fig. 9d).

The redox-medium-assisted cathode–anode decoupling is proved to be a powerful means to solve the existing problems of artificial photosynthesis process. In addition to zinc/zincate, other combinations of inorganic species and organic species are also potential candidates for redox-medium-assisted artificial photosynthesis systems. The water splitting system studied by Xia and coworkers indicated that nickel (Ni)/nickel hydroxide ($Ni(OH)_2$) was also a suitable redox pair for decoupling electrocatalytic reactions of hydrogen evolution and oxygen reduction reactions [106]. It is noteworthy that the introduction of proton medium is also a promising buffering strategy for electrocatalytic reactions based on proton coupled electron transfer process [107]. Xia and coworkers [108] demonstrated a polymer-based proton-electron medium for two-step water splitting systems. As a solid-state buffer media, pyrene-4,5,9,10-tetraone (PTO) is capable of accepting both electrons and protons from oxygen reduction reaction part and transferring them to hydrogen evolution reaction part. The polymer can obtain and give out protons and electrons at the same time to minimize the influence of pH change. Thus, the OER and HER are separated in space and time without the assistance of membrane. Significant improvements in CO_2RR-based artificial photosynthesis system may also be reached by similar ideas of introducing medium of both protons and electrons.

5. Summary and outlook

The development of electrochemical CO_2RR as a promising technology for our clean and sustainable future is currently making progress in both directions of catalyst innovation and system engineering. In systems engineering, microfluidic reactors and membrane reactors, as well as their variants and hybrids, have been proposed and proven useful in the CO_2RR. Artificial photosynthesis systems based on different energy harvesting methods for the storage and conversion of renewable energy sources are also developed, and the solar-to-fuel conversion efficiency has exceeded 15% nowadays, which shows great promise compared to the natural photosynthesis systems. Optimization of the two key elements of the electrode and electrolyte in the reactor provides guidance for a more efficient catalytic reaction. Methods for matching the energy input and catalyst performance has also been demonstrated in several works. Nevertheless, the state-of-the-art performance of CO_2RR is still far from the requirement of industrial application in many core indicators such as device size, energy efficiency, and stability.

In order to achieve a renewable energy solution that is sufficient to replace existing fossil energy structures and petrochemical processes in the future, more efforts need to be invested in the design and optimization of reaction systems. First, the conversion rate should be considered as a key factor in the evaluation of a reaction system, as well as the product separation in industrial production. Second, membrane reactors for multi-carbon products, especially the liquid products, require further design. The existing systems are hard to separate liquid phase products, while reported polymer membranes have not yet achieved high selectivity for multi-carbon products. Third, high-flux flow reactors driven directly by renewable energy need to be designed and commissioned, which will be a big step for the commercialization of artificial photosynthesis systems.

In summary, we summarize and discuss recent works about the innovations in the reactor architectures and optimizations based on system engineering in CO_2RR in this review. The gap between the existing performance and the actual needs is still huge but not insurmountable. To overcome this gap, both better electrocatalysts and more optimized system engineering are needed. With sustained and extensive efforts, the production of fuel and chemicals from artificial photosynthesis can become a reality in the near future.

Conflict of interest

The authors declare that they have no conflict of interest.

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Author contributions

Hao Shen, Zhengxiang Gu and Gengfeng Zheng organized the literature and wrote the manuscript. Gengfeng Zheng supervised the project. All the authors discussed the manuscript and revision.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scib.2019.08.027.

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