Bimetallic Electrocatalysts for Carbon Dioxide Reduction

Dan Ren, Jing Gao, Shaik M. Zakeeruddin, and Michael Grätzel*

Abstract: Electrochemical reduction of carbon dioxide, using the electricity generated from renewable energy sources, has the potential of rendering a carbon-neutral energy economy. Developing selective, efficient and robust electrocatalysts is the key step towards establishing this promising technology. While different nanostructures of Cu have been extensively studied for the formation of C_1–C_3 alcohols and hydrocarbons, Cu-based bimetallic catalysts showed better activity compared to monometallic Cu. In this review, we will first summarize recent advances in designing Cu-X bimetallic catalysts. We categorized the bimetallic catalysts into different groups based on the CO_2 reduction activities of the 'X' metal, including hydrogen-producing metals, formate-producing metals and CO-producing metals. The key factors in determining the selectivity are discussed. Additionally, representative examples of Cu-free bimetallic catalysts, with appreciable selectivity towards hydrocarbons/alcohols, will also be presented. We will conclude this review with challenges and promising research directions.

Keywords: Bimetallic catalyst · Carbon dioxide · Copper · Ethylene

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Dr. Shaik M. Zakeeruddin joined as a postdoc in 1990 in Prof. Grätzel's group at Lausanne, Switzerland. From then he continues as a senior research scientist and lecturer at the Laboratory of Photonics and Interfaces, Institute of Chemical Science and Engineering, EPFL. The main area of his research focuses on nanomaterials, solar cells (dye-sensitized solar cells and perovskite solar cells), solar fuels such as H_2 from photoelectrochemical water splitting and reduction of CO_2, lithium ion batteries, and biosensors. On a global point of view Zakeeruddin's research activity has yielded more than 400 papers in the best international journals and 35 patents. These contributions have often had a pioneering character and have achieved a very large impact, with over 56,000 citations so far with h-index of 113. In 2011 in the top-100 chemist list of decades by Thomson Reuters, he was ranked 53rd and 29th for the chemist and material scientists list, respectively. He is included in a recently published the world's most influential scientific minds.

Prof. Michael Grätzel is a Professor in École Polytechnique Fédérale de Lausanne and the Director of Laboratory of Photonics and Interfaces. He created the field of molecular photovoltaics, being the first to conceive and realize mesoscopic photo-systems based on dyes as light harvesters that can rival and even exceed the performance of state-of-the-art solar cells based on planar solid state p-n junctions. He is credited with moving the photovoltaic field beyond the principle of light absorption *via* diodes to the molecular level. The prototype of this new photovoltaic family is the dye-sensitized solar cell (DSC), also named 'Grätzel cell', which employs dye molecules, pigments or quantum dots to sensitize the mesoporous oxide semiconductor scaffold. Grätzel is also a leader in the field of fuel generation by sunlight, which is a key technology to provide future renewable energy sources that can be stored. Grätzel's 1645 publications have received some 284'000 citations and his h-index is 243 (Web of Science, September 2019). A recent ranking issued by Stanford

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University places Grätzel in the first position on a list of 100,000 top scientists across all fields.

1. Introduction

Harvesting solar radiation and converting the energy to storable forms, *i.e.* chemicals and fuels, are of great importance for a carbon-neutral future.[1] While photovoltaics have reached industrial scale for solar energy harvesting, there is still a lack of effective ways for energy storage. Electrocatalytic reduction of carbon dioxide (CO_2) to energy-rich chemicals using renewable electricity is one of the promising ways for energy storage to address the intermittency of solar radiation.[2] This process also serves as a means of carbon dioxide utilization and has attracted intense research attention, as well industrial interests.[3]

While most of the metal electrodes catalyze the two-electron transfer process of CO_2 reduction to CO or $HCOO^-$, Cu is unique in catalyzing the production of hydrocarbons and alcohols, as first discovered by Hori and co-workers.[4] However, the selectivity of polycrystalline Cu is poor with the formation of at least 16 products.[5] Tuning the preference of Cu catalysts towards specific products has become one of the major research topics. Different strategies such as modifying crystal facets,[6] changing morphologies,[7] engineering electrolyte,[8] tuning oxidation states[9] as well as designing electrolyzers[10] have been deployed. Recent advances on these methodologies for improving the selectivity of Cu catalysts have been summarized in several excellent reviews.[11]

Apart from these advances on monometallic Cu catalysts, bimetallic catalysts using a second metal to modify Cu have also been investigated.[12] These Cu-X bimetallic catalysts could either be in alloy form or phase separated. Interestingly, the performance of Cu can be dramatically changed, dependent not only on the second dopant but also on how Cu combines with the second element. In this review article, we will summarize the recent progress in the development of Cu-based bimetallic catalysts. Representative examples on non-Cu-based bimetallic catalysts for the production of hydrocarbons and alcohols will also be given. Inspired from these studies, we will discuss the key factors that affect the catalytic activities of these bimetallic catalysts and provide an outlook on future development of bimetallic catalysts for CO_2 reduction.

2. Activity towards CO_2 Reduction on Monometallic Catalyst

It is of great importance to understand the catalytic properties of each monometallic catalyst before designing bimetallic combinations. The catalytic performances of different metal substrates are summarized in Fig. 1 with their corresponding binding energies with *H and *CO.[13] In general, these metals, excluding Cu, can be categorized into three groups. The first group can be classified as formate-producing metals (shown in the right corner of Fig. 1). These metals, including Cd, Pb, Hg, In and Sn, bind very weakly with *H and *CO. The second group has relative weak binding with *CO, including Zn, Au and Cu. These metals, known as CO-producing catalysts, are selective for CO_2 conversion to

CO. Their weak bindings with CO inhibit the further reduction of CO to hydrocarbons, aldehydes and alcohols. The third group includes Pd, Ni, Pt, Rh, Ir, Fe, Ru and has strong binding with *CO, resulting in CO poisoning of the catalyst, with hydrogen (H_2) being the major product in CO_2 electroreduction. It is well noted that hydrogen is a common by-product in CO_2 reduction due to the competitive reduction of water from the aqueous electrolyte.

Cu is the only metal that has suitable binding with both *CO and *H. The optimum binding between Cu and *CO enables sufficient residence time for intermediated *CO to be coupled with nearby intermediates. This leads to the further dimerization of *CO or protonation of *CO, to produce hydrocarbons and alcohols as the major products. It is also noted that the relatively strong binding with *H is critical in the protonation of these intermediates. As a result, the suppression of H_2 evolution on monometallic Cu is extremely challenging.

The combinations between Cu and these metals for CO_2 reduction have been investigated by many research groups. The presence of a second metal element could significantly change the catalytic behaviour *via* different ways: a) modifying the electronic structure of Cu; b) introducing strain effect on Cu; c) bifunctional catalysis *via* providing active sites for producing critical intermediates and d) acting synergistically for CO_2 reduction.

3. Combination between Cu and H_2-producing Metal

Among all the H_2-producing metals, Pd is the most widely studied as the dopant for Cu catalysts. One of the representative works reported Cu-Pd nanoalloys supported on polymer for CO_2 reduction, which were investigated by Meyer and co-workers.[14] Compared to Cu nanoparticles, Cu-Pd nanoalloys exhibited improved selectivity towards CH_4 with lower onset potential (Fig. 2a). The faradaic efficiency of CH_4 could be further improved
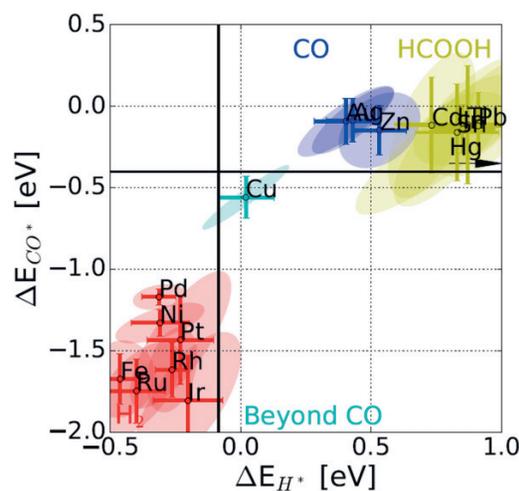

Fig. 1. The binding energies of intermediated *CO and *H on different metal surfaces. Reproduced with permission from ref. [13]. Copyright @ John Wiley and Sons 2017.

Fig. 2. Electrochemical reduction of CO_2 on Cu-Pd nanoalloys (a) as a function of applied potentials and (b) as a function of Cu to Pd ratio in CO_2-saturated 0.1 M TBAPF$_6$/CH_3CN solutions with 1 M added H_2O. Reproduced from ref. [14].
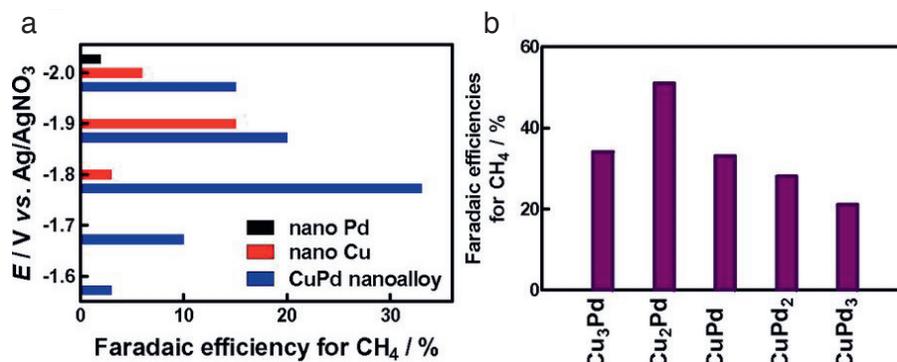
to 51% by tuning the ratio of Cu/Pd to 2:1 (Fig. 2b). The improved CH_4 formation is believed to be caused by the synergetic effect between Pd–H sites and Cu–CO sites. Pd is known for the optimum binding with *H, which enables further protonation of nearby *CO on Cu to CH_4. At the same time, the Cu atoms are mostly isolated from each other due to the alloy nature of CuPd, resulting in the reduced number of active sites (adjacent Cu atoms) for C–C coupling.

Yeo and co-workers have reported the selective production of C_2H_6, using oxide-derived Cu with $PdCl_x$ as the co-catalyst.[15] The $PdCl_2$ was suspended into the electrolyte and is believed to be adsorbed on oxide-derived Cu electrode in the form of $PdCl_x$, which provides binding sites to *H. C_2H_4 produced on oxide-derived Cu sites is believed to diffuse to $PdCl_x$ sites and be further protonated to C_2H_6. Later, Kenis and co-workers systematically studied Cu-Pd bimetallic catalysts with different mixing patterns.[16] The phase-separated Cu-Pd is found to show higher selectivity towards C_2 hydrocarbons and alcohols, whereas ordered Cu-Pd alloy is more favourable towards the formation of CO with the suppression of C_2 products.

From the above studies, it appears that the introduction of H_2-producing metals could effectively facilitate the protonation process, such as CO to CH_4 and C_2H_4 to C_2H_6. The constitution of the bimetallic structure established between Cu and H_2-producing metals will also affect the performance greatly. If an alloy is formed, the isolated nature of Cu atoms will assist in the suppression of C–C coupling with decreased activity towards multicarbon products. This is also believed to be applicable to other Cu-X bimetallic systems, discussed below.

4. Combination between Cu and Formate-producing Group

Metals from the formate-producing group have also been mixed with Cu for CO_2 reduction. Takanabe and co-workers have systematically studied these bimetallic systems and found a tunable selectivity between CO and formate.[17,18] Optimized Cu-In alloys were found to be selective for the production of CO (Fig. 3).

Specifically, Cu-In alloy exhibited similar current density compared to oxide-derived Cu catalyst and the presence of In changed the activity of Cu dramatically to CO over a wide potential range from –0.35 V to –0.70 V vs. RHE in 0.1 M $KHCO_3$ (Fig. 3a–c). With the support of density functional theory calculations, the authors proposed that In could induce local geometric and electronic effects on Cu, which will assist in weakening the adsorption of *CO and *H. The further reduction of CO to hydrocarbons and alcohols is thus impaired. Recently, our group has also developed CuSn bimetallic alloy by atomic layer deposition of SnO on CuO nanowires. The reduced form of CuSn exhibited excellent selectivity of CO.[19] Chemisorption of CO on CuSn was found to be different from that on Cu. The reduced binding between CuSn and CO is believed to be the major reason for the suppressed formation of hydrocarbons and alcohols on CuSn alloy.

From these preeminent studies, we can infer that the formate-producing metals could modify the selectivity of CO_2 reduction on Cu towards CO if a phase-blended alloy is formed. If we refer to the volcano plot of CO binding on different metal surfaces (Fig. 1), the binding of CO on Cu is relatively strong while the CO binding on formate-producing metals is rather weak. The alloy form of their combinations exhibits properties of metals in between Cu and formate-producing metals in terms of CO binding energy, showing enhanced selectivity for CO like Au, Ag and Zn. These studies demonstrate that alloying another metallic component is effective in changing the binding energy of *CO on Cu surfaces.

5. Combination between Cu and CO-producing Metal

CuZn, CuAg and CuAu are the most intensively studied bimetallic combinations for CO_2 reduction since these CO-producing metals facilitate the production of CO, which is the key intermediate for hydrocarbon and alcohol production. The sequential CO_2-to-CO and CO-to-hydrocarbons/alcohols process could thus be achieved. This concept was first proposed by us in our study using CuZn bimetallic catalysts,[20] which was inspired by the CO reduction studies on nanocrystalline Cu.[21] The well-mixed bimetallic CuZn showed significantly improved selectivity towards
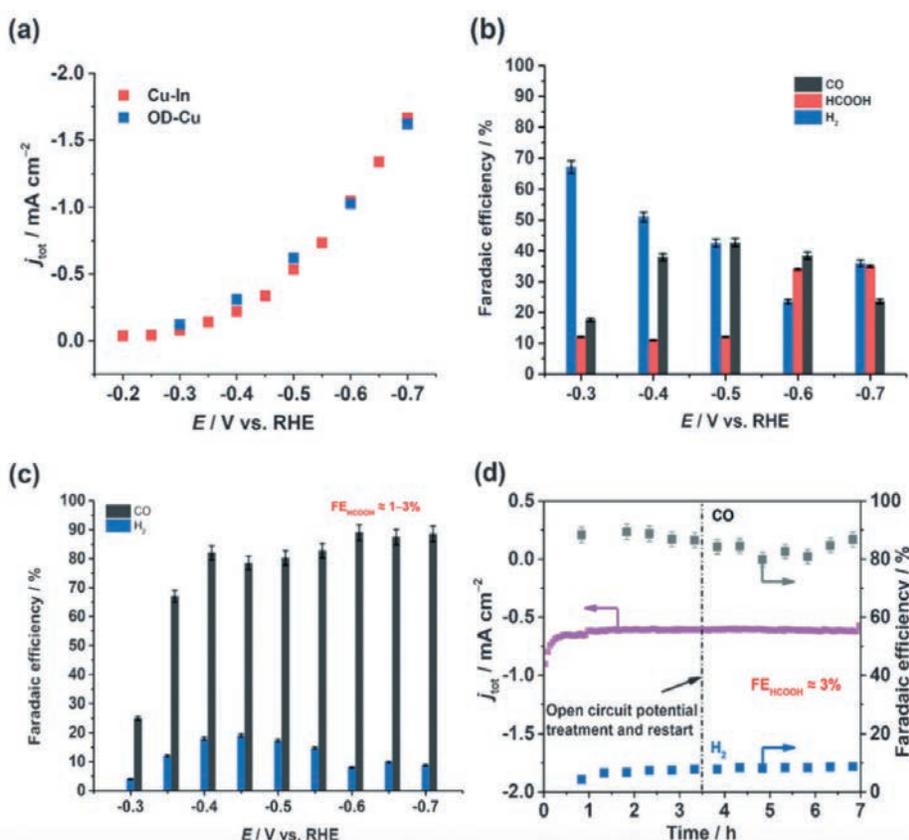

Fig. 3. (a) Current density profiles for oxide-derived Cu and oxide-derived Cu-In, products distribution on b) oxide-derived Cu and c) Cu-In, and d) the long-term stability test for the Cu-In catalyst at –0.6 V vs. RHE in 0.1M $KHCO_3$/CO_2. Reproduced from ref. [17]. Copyright @ John Wiley and Sons 2015.

ethanol. Afterwards, Lee and co-workers reported similar performance on phase-blended CuAg catalyst.[22] On the contrary, CuAg alloy has been reported to be selective for oxygenates or ethylene, by Bell's group and Ager's group respectively.[23] CuAg bimetallic catalysts prepared by different methods were also employed for CO_2 reduction in many later reports.[24] The varying performances observed on CuAg, as well as on CuAu catalysts reflect the difficulties in revealing the key factors determining the catalytic activities.[25] Below, we will summarize these recent findings and provide insights into the key factors in affecting the performance of these bimetallic catalysts for CO_2 reduction.

5.1 *CuZn Catalysts for Ethanol Formation*

The first reported mixture of Cu and CO-producing catalysts for the production of hydrocarbon and alcohols were Cu-Zn bimetal-oxides, prepared by electrodeposition from an alkaline solution containing Cu^{2+} and Zn^{2+} ions.[20] The selectivity of Cu was found to be tuned towards ethanol by changing the atomic percentage of Zn. The key factor in promoting ethanol formation is believed to be the enrichment of CO near the surface of electrode, as supported by catalytic activities of other metal combinations such as Cu-Ni and Cu-Ag.

To further investigate the enhanced formation of ethanol on CuZn, we have recently prepared bimetallic CuZn catalysts which were derived from atomic-layer-deposited ZnO onto CuO nanowires. Compared to monometallic oxide-derived Cu, our CuZn catalyst exhibited a significantly improved faradaic efficiency for C_{2+} liquid fuels (Fig. 4a). The ratio between ethanol and ethylene has been improved by 5 to 8 times if Zn is doped into Cu (Fig. 4b). More interestingly, we found key factors in determining the selectivity of ethanol by analyzing the trends of the electrochemical activities of representative products including CO, CH_4 and C_2H_5OH (Fig. 4c).

The incorporation of Zn introduces active sites for the formation of CO, which tends to desorb as gas from Zn catalyst due to the weak metal–CO binding. It appears that the formation of ethanol follows a pathway involving reduction of excess free CO near the electrode, since CO formation on CuZn decreased while the ethanol formation improved as compared to Cu catalyst. Moreover, the reaction rate of CH_4 formation on CuZn is only ¼ of that on monometallic Cu catalyst over the potential range from –1.10 V to –1.20 V. This indicates that adsorbed *CH_3 species on Cu, the critical intermediates for the CH_4 pathway,[27] are likely to be consumed for the production of other carbonaceous products. Concurrently, CuZn outperforms Cu catalyst in terms of ethanol formation at –1.15 V. These trends strongly support that ethanol is likely to be produced through the C–C coupling between CO and *CH_3. A similar pathway has also been proposed for the formation of *n*-propanol.[28]

5.2 *Performances of Different CuAu Catalysts*

Cu-Au bimetallic nanoparticles in alloy form for CO_2 reduction were investigated by Yang and co-workers.[25d] Uniform Au_3Cu nanoparticles showed better activity towards CO_2 reduction to CO as compared to pure metallic Au. By analyzing the surface valence band spectra, the authors proposed that the electronic effect plays an important role in determining the catalytic performance. In Au-Cu combinations, the gravity center of d-band gradually shifts downwards from Cu to Au. This electronic modification, together with the geometric effect due to the formation of alloy, is believed to affect the binding of key reaction intermediates.

Our group has recently investigated Cu-Au bimetallic catalysts without the formation of alloy for carbon dioxide reduction (Fig. 5a). Au nanoparticles were galvanically deposited onto Cu_2O nanowires. After the electrochemical pre-reduction, bimetallic CuAu catalysts showed improved selectivity towards C_{2+} products formation. The faradaic efficiency of C_{2+} products reached close to 70% at –1.05 V vs. RHE, which is significantly higher than the 55% of C_{2+} products on oxide Cu catalyst at the same applied potential (Fig. 5b). The major reason for the improved selectivity of C_{2+} products is believed to be the spillover of CO from Au to Cu. This increases the coverage of CO on Cu, which has been proposed to be critical for C–C coupling towards C_2H_4.[29] The further reduction of CO also competes with water reduction, leading to the suppressed hydrogen formation on bimetallic catalyst.

Other than oxide-derived bimetallic CuAu catalysts, metallic CuAu combinations have also been investigated.[25b,30] Jaramillo and co-workers deposited Au nanoparticles on polycrystalline Cu surfaces for CO_2 reduction. The alcohol products were found to be produced at low overpotentials, though the faradaic efficiency is only < 10% at potentials > –0.95 V vs RHE. By analyzing the electrochemical trends, the authors proposed a sequential catalytic pathway for the production of alcohols, similar to what we have proposed before.[20] Shen *et al.* recently also reported the selective ethanol formation on well-dispersed CuAu bimetallic catalyst.[31] The faradaic efficiency of C_2H_5OH could reach 29 ± 4% while the faradaic efficiency of C_2H_4 was suppressed to 16 ± 4% at –1.0 V vs. RHE. The presence of Au is proposed to lower the energy barrier of ethanol formation pathway as compared to the reaction pathway of ethylene, supported by density functional theory calculations.

Recently, Sun and co-workers found that bipyridine-assisted Au assembly on Cu nanowires exhibited excellent selectivity towards aldehyde production, with the faradaic efficiency of 25%. Excellent control experiments using $^{13}CO_2$ for reduction showed that the products are from the reduction of CO_2. It is surprising that the aldehyde is not further reduced to alcohol on the Au-bipyridine-Cu catalyst at –0.9 V vs. RHE, which is negative
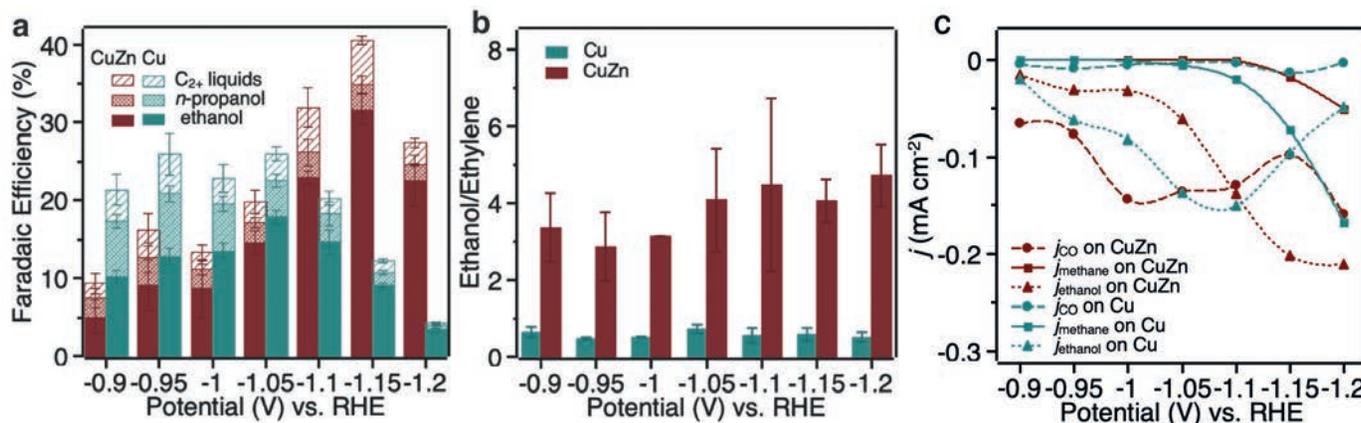

Fig. 4. (a) Faradaic efficiency of C_{2+} liquid fuels; (b) ratio of ethanol/ethylene as a function of applied potential on Cu and CuZn catalysts in an H-cell and (c) partial current density (normalized against the electrochemical active surface area) of ethanol, methane and carbon monoxide as a function of applied potential. Reproduced from ref. [26]. Copyright @ John Wiley and Sons 2019.
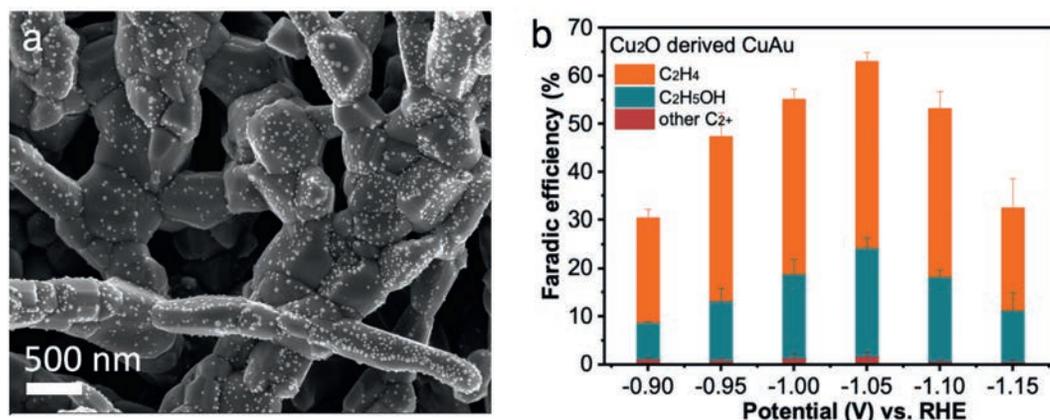
Fig. 5. (a) SEM image of Cu_2O nanowires covered by Au nanoparticles and the faradaic efficiency of C_{2+} products using Au-Cu_2O as the catalyst. Reproduced with permission from ref. [25a]. Copyright @ Royal Society of Chemistry 2019.

enough for the reduction of aldehyde to ethanol.[32] The presence of bipyridine might have played a role in the catalytic behaviour of Cu, which requires further investigation.

Despite these efforts, the understanding of CuAu bimetallic catalysts is still far from satisfactory. While insights on the binding of *CO and *H on CuAu alloy have been gained by recent *operando* Raman spectroscopic studies,[33] how the intermediates bind on the non-alloy bimetallic systems is still unknown. Besides density functional theoretical calculations, *operando* Raman/IR spectroscopic studies on these reported Cu-Au bimetallic catalysts shall be performed to gain more information of the catalytic sites and the key intermediates.

5.3 *Performances of Different Cu-Ag Catalysts*

Various approaches, including electrodeposition,[22,23b,24a] annealing,[23a] galvanic replacement reaction and hydrothermal synthesis[24c] have been explored for designing Cu-Ag combinations as catalysts for electrochemical CO_2 reduction. Different forms of Cu-Ag have been prepared, including alloy, phase-blended bimetallic and phase-separated bimetallic. One representative work reported that phase-blended Ag-Cu_2O showed improved selectivity of ethanol in 0.1 M KCl, compared to phase-separated Ag-Cu_2O and Cu_2O (Fig. 6a). Besides the increased amount of CO molecules provided by the catalytic reduction of CO_2 on Ag sites (Fig. 6b), the number of phasic boundaries is also believed to be critical in determining the ethanol selectivity. This is also consistent with our recent work, showing the improved ethanol selectivity on phase-blended CuZn bimetallic catalysts.[26] The authors also proposed that chloride and residual oxygen are important for C–C coupling process, though detailed evidence is still lacking.

Instead of oxide-derived Cu-Ag, pure metallic Cu-Ag alloy was investigated by Bell and co-workers for electrocatalytic CO_2 reduction.[23a] It was found that the activity towards the formation of oxygenates (mainly acetate and aldehyde) is improved while hydrogen evolution is suppressed (Fig. 6c,d). This is believed to be caused by the strain within the CuAg alloy. It is interesting, yet not fully understood, that ethanol selectivity is not greatly affected by this strain. The proposed mechanism of acetaldehyde to acetate formation is also in contrast with most literature reports, which show acetaldehyde is reduced to the exclusive formation of ethanol.[32]

Recently, our group has prepared oxide-derived CuAg with separated phase of Cu and Ag (Fig. 7a).[34] This catalyst is prepared *via* the galvanic exchange between Ag^+ and Cu_2O nanowires, showing isolated nature between Ag nanoparticles and Cu_2O nanowires (Fig. 7b). This metallic catalyst showed 76% faradaic efficiency of C_{2+} products (Fig. 7c). As a contrast, oxide-derived Cu exhibited only 58% faradaic efficiency of C_{2+} products. Specifically, in terms of ethylene production, the faradaic efficiency is improved from 33% to 52% if Ag is decorated in the nanowire structure. Unlike the two cases before (Fig. 6), the selectivity

for liquid products such as ethanol and acetate remained almost the same. We propose that the improved selectivity is mainly due to the CO spillover from Ag to Cu sites.

We also performed state of the art *operando* Raman spectroscopy to gain mechanistic insight into the catalytic difference of Cu and CuAg (Fig. 8). The adsorbed *CO on Cu sites in both Cu and CuAg catalyst is demonstrated by Raman peaks at 282, 355–366 and 2057–2092 cm^{-1}. Moreover, adsorbed *CO on Ag sites is also revealed by additional Raman peaks at 460, 491–494 and 2011 cm^{-1}. This demonstrates that both Cu and Ag could reduce CO_2 to adsorbed CO. Interestingly, the vibration of C–H was also observed at region from 2700 to 3000 cm^{-1}. Two peaks at ~2850 and ~2920 cm^{-1} were detected on both Cu and CuAg catalysts. These peaks could be attributed to reaction intermediates containing C–H bonds (such as *CHO, *C_2H_2O, *etc.*). Remarkably, two new peaks at 2713 and 2816 cm^{-1} appeared on CuAg, which indicates the enhanced coverage of CH-containing intermediates. It is believed that these intermediates, from reduction of CO provided by Ag sites, are critical for the formation of hydrocarbons.

5.4 *Critical Factors that Affect the Catalytic Performance of CuAu, CuAg and CuZn*

CO intermediates: It is generally believed that these catalysts, alloy or not, could significantly enhance the production of CO. This is not surprising since Au, Ag and Zn are all ideal catalysts for selective CO_2 reduction to CO. The produced CO may either release as gas product or be further reduced to other products. Once CO molecules desorb from Au/Ag/Zn surface, they could either couple with adsorbed C_1/C_2 intermediates or re-adsorb on Cu surfaces for further reduction. Both pathways are possible, depending on the amount of CO produced and the binding strength of CO on Cu sites. The excessive amount of CO nearby Cu sites are proposed to be critical for alcohol production on phase-blended CuAg/CuZn. This proposition is further corroborated by the observation of higher alcohol selectivity on Cu surface for CO reduction.[21] If the amount of CO is optimal for further binding on Cu sites, these adsorbed CO species tend to undergo the ethylene formation pathway,[23b] *i.e.* CO dimerization.[35]

Oxide-derived nature of Cu: As supported by extensive studies on oxide-derived Cu catalyst, the C–C coupling process is believed to be facilitated by the grain boundaries, defects, undercoordinated sites, surface/subsurface oxygen, or residual Cu^+ species.[7b,36] Thus, whether the Cu sites in bimetallic systems are derived from oxide or are intrinsically metallic makes a difference to the selectivity of C_2 products. For example, the CuAg nanocoral catalyst, reported by Ager and co-workers, does not effectively suppress the formation of CH_4 since these Cu sites are not oxide-derived. It might even be feasible to design a CuAg catalyst for selective CH_4 formation.

Phase boundaries: The phase boundaries seem to be critical in catalyzing the formation of alcohol products, as shown in the

Fig. 6. Faradaic efficiency of (a) CO and (b) C_2H_5OH on phase-separated Ag-Cu_2O, phase-blended Ag-Cu_2O and Cu_2O catalysts; normalized activity for (c) hydrogen formation and (d) oxygenates (aldehyde and acid) formation on CuAg alloy as the function of near-surface composition. Reproduced with permission from ref. [22] and ref. [23a]. Copyrights @ American Chemical Society 2016 and 2017.
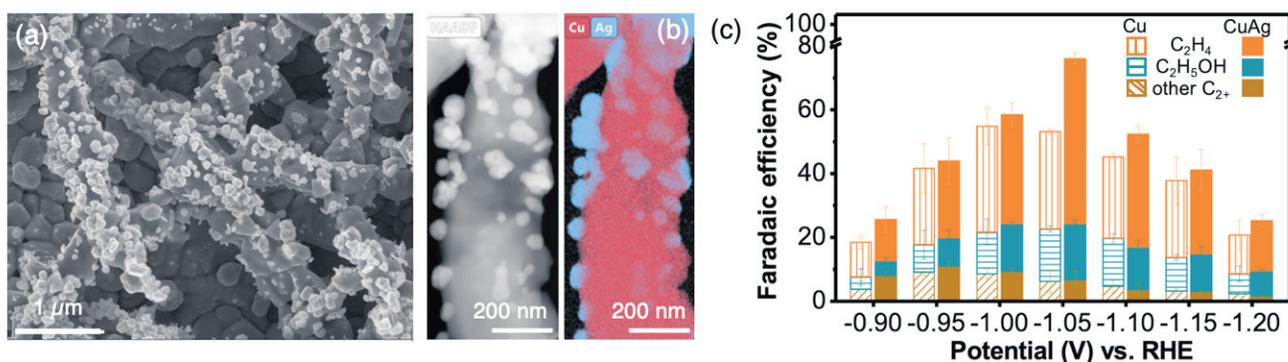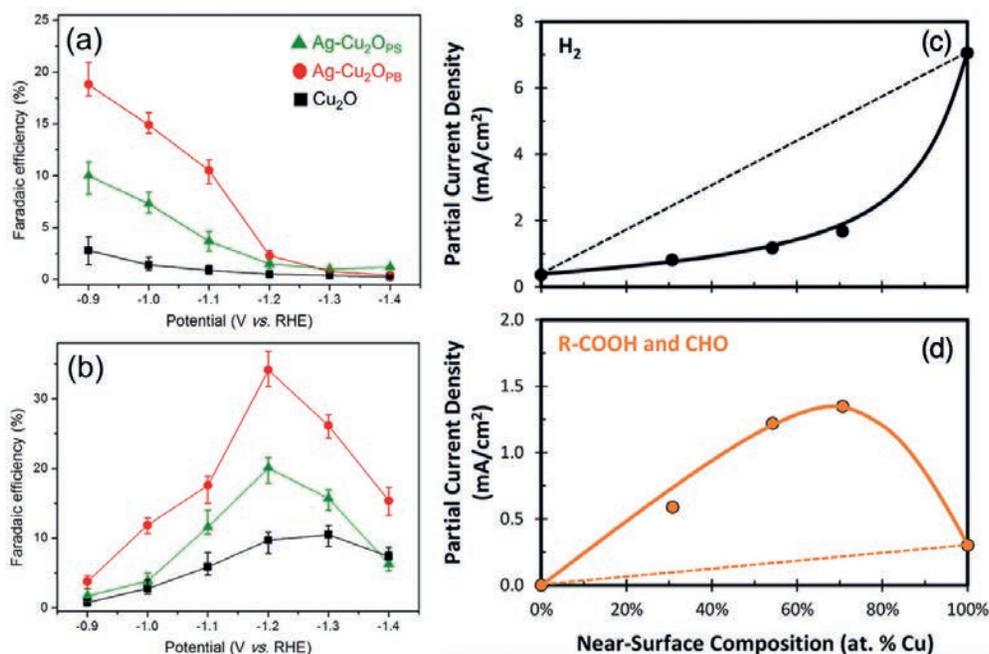

Fig. 7. (a) Scanning electron micrograph and (b) energy dispersive X-ray analysis of Ag-Cu_2O nanowires prepared by galvanic replacement reaction, (c) faradaic efficiencies of C_{2+} products on oxide-derived Cu and CuAg during electrochemical reduction of carbon dioxide.[34] Reproduced with permission from ref. [34]. Copyright @ American Chemical Society 2019.

studies for ethanol production. In contrast, the bimetallic catalysts showing selectivity for ethylene are either phase-separated or isolated nanoparticles. However, the reason why phase boundaries are important remains unclear at this stage. It might be related to the binding with some key intermediates for ethanol formation.

6. Non-Cu-based Bimetallic Catalysts for the Production of Hydrocarbons and Alcohols

Though Cu is the only metal that could catalyze the formation of hydrocarbon and alcohols in appreciable amounts, recent studies showed the formation of products with >2e⁻ transfer using Cu-free bimetallic catalysts. One representative work is reported by Lewis and co-workers using Ni-Ga alloy for CO_2 reduction.[37] Specifically, Ni_5Ga_3 alloy catalyzes the formation of CH_4, C_2H_4 and C_2H_6 with the total Faradaic efficiency close to 4%. Moreover, the onset potential for the formation of these products is more positive as compared to the one on polycrystalline Cu. Recently, Paris *et al.* studied Ni-Al and Ni-Ga bimetallic catalysts for CO_2 reduction and reported the formation of C_2 and C_3 products on both combinations.[38]

Pulse-deposited Zn dendrites on Ag foam were recently reported to be selective for the formation of methanol, an uncommon product in electrocatalytic CO_2 reduction, by Yeo and co-workers.[39] The Faradaic efficiency of methanol reached as high as 10.5% at a constant geometric current density of –26 mA cm⁻². By means of control experiments and DFT calculations, the au-

thors proposed that strained undercoordinated Zn atoms are the active sites for methanol formation and formaldehyde is the key intermediate involved. These representative works showed the possibility of designing Cu-free bimetallic catalysts for hydrocarbon and alcohols formation.

7. Challenges and Outlooks

The rapid development of bimetallic catalysts has enriched the materials library for CO_2 reduction to different products, especially hydrocarbons and alcohols. Among these bimetallic catalysts, combinations between CO-producing metals and Cu are the most intensively studied due to the improved performance for the C–C coupling process towards the formation of ethylene or ethanol. Our recently developed CuAg catalyst showed 52% faradaic efficiency of ethylene in an H-cell. Once coupled with perovskite solar cells connected in series, we obtained a record 4.2% solar to ethylene energy conversion efficiency.

Despite these advancements, the understanding of key factors in bimetallic catalysts is still lacking. The strain, oxidation state, and level of phase blending have all been proposed to affect the catalytic performance. How to decouple these factors remains a great challenge. For example, our recently developed CuAg and CuAu catalysts where Ag/Au nanoparticles are isolated from Cu substrate with minimum amount of phase boundaries. However, the effect of phase boundaries could not be fully excluded for the observed catalytic performance.
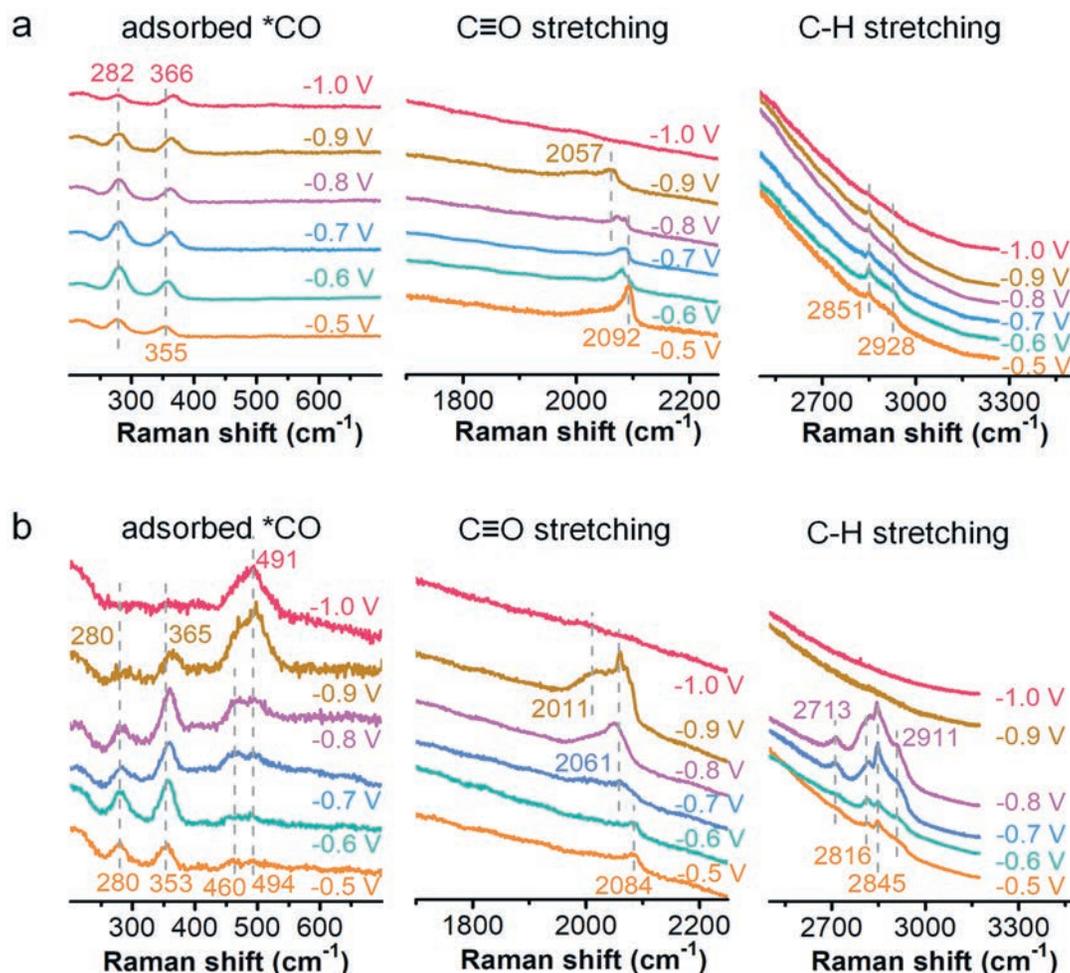
Fig. 8. *Operando* Raman spectra of (a) Cu and (b) CuAg catalysts in 0.1 M KHCO₃ at different potentials. Reproduced with permission from ref. [34]. Copyright @ American Chemical Society 2019.

The reaction intermediates for the product formation also require further investigation. While the presence of CO and protonated dimer has been supported by *operando* Raman and IR spectroscopy,[20,40] most of the reaction intermediates proposed in the reaction pathways are still missing in spectroscopic studies. Our recent Raman spectroscopic studies on CuZn and CuAg suggest the presence of C–H vibrations, which might originate from $C_xH_yO_z$ intermediates for ethylene and ethanol formation. The identification of these vibrations could be supported by future studies using density functional theory calculations and Raman spectroscopy with isotopically labelled H_2O or CO_2.

The studies of CO_2 reduction is also transitioning from using an H-cell to employing an electrochemical flow cell.[41] The significant improvement in reaction rates could enable the detection of more reaction intermediates. However, there is still a lack of studies using *operando* spectroscopy in an electrochemical flow cell system. Investigating the performance of bimetallic catalysts for CO_2 reduction and probing the surface of catalysts using *operando* Raman spectroscopy in an electrochemical flow cell will definitely be an interesting topic that is worthy of study.

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