Electronic Supplementary Material (ESI) for Chemical Society Reviews.

# Electrocatalysis for $CO_2$ Conversion: from Fundamentals to Value-added Products

Genxiang Wang,[a,e] Junxiang Chen,[a] Yichun Ding,[a], Pingwei Cai,[a,e] Luocai Yi,[a,e] Yan Li,[a,c] Chaoyang Tu, [d] Yang Hou,[c*] Zhenhai Wen,[a*] and Liming Dai[b*]

[a]*CAS Key Laboratory of Design and Assembly of Functional Nanostructures, and Fujian Provincial Key Laboratory of Nanomaterials, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, China*

[b]*Centre for Advanced Carbon Materials, School of Chemical Engineering, University of New South Wales, Sydney, NSW2052, Australia*

[c]*Key Laboratory of Biomass Chemical Engineering of Ministry of Education, College of Chemical and Biological Engineering, Zhejiang University, Hangzhou, 310027, China.*

[d]*CAS Key Laboratory of Optoelectronic Materials Chemistry and Physics, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, China*

[e] *University of Chinese Academy of Sciences, Beijing 100049, P. R. China*

**Email:** wen@fjirsm.ac.cn, yhou@zju.edu.cn, liming.dai@case.edu

## 1. Parameters in evaluating electrocatalysis of $CO_2$RR

In this section, the key parameters in evaluating the performance of electrocatalysts for $CO_2$RR, including the onset potential, overpotential, current density, faradaic efficiency, electrochemical surface area, turnover frequency, production rate and Tafel slope, will be elucidated.

### 1.1 Onset potential and overpotential

The onset potential for $CO_2$RR is determined by the potential when product is detected by chemical analysis during testing. The overpotential of the $CO_2$RR is the difference between the onset potential and equilibrium potential, which is an important indicator of the activity of catalysts, and the smaller the onset potential, the higher catalytic activity for the corresponding catalyst. During the electrochemical test, various reference electrodes can be used and should be corrected before testing $CO_2$ reduction. The testing potential is generally converted to the potential relative to reverse hydrogen electrode (RHE). Below listed is the conversion equation between several commonly used reference electrodes:

$$E\ (vs.\ RHE)\ = E(vs. Ag/AgCl(saturated)) + 0.197\,V + 0.0591\,V \times pH$$ **(Eq.1)**

$$E\ (vs.\ RHE)\ = E(vs. Ag/AgCl(3M)) + 0.210\,V + 0.0591\,V \times pH$$ **(Eq.2)**

$$E\ (vs.\ RHE)\ = E\ (vs.\ SCE)\ + 0.24V + 0.0591\,V \times pH$$ **(Eq.3)**

$$E\ (vs.\ RHE)\ = E\ (vs.\ SHE)\ + 0.0591\,V \times pH$$ **(Eq.4)**

where SHE, and SCE are the abbreviations of standard hydrogen electrode and saturated calomel electrode, respectively. The Ag/AgCl (3 M) indicates the filled solution is 3 M KCl, while Ag/AgCl (saturated) indicates the filled solution is the saturated KCl solution.

### 1.2 Current density

The current density, usually mass current density or area current density, is another crucial parameter for evaluating the reaction rate. It should be pointed out that an enhanced cathodic current in $CO_2$ atmosphere relative to that in inert gas (*e.g.*, Ar) atmosphere could not be used for judging the occurrence of $CO_2$RR, because the adsorbed intermediates (*e.g.*, CO) would lead to a lower current density during reducing $CO_2$ into hydrocarbons, and the gradual decrease of pH caused by the dissociation of $CO_2$ in aqueous solution would also enhance the HER current density.[1] The partial current density of the product for $CO_2$RR should be obtained by multiplying the corresponding faradaic efficiency by the overall current density.[25]

### 1.3 Faradaic efficiency (FE)

The faradaic efficiency (FE), also called coulombic efficiency, represents the utilization efficiency of charge (or electrons) involved in a system facilitating an electrochemical reaction, which is normally used to estimate the selectivity of a catalyst for $CO_2$RR product, and the calculation formula is expressed as below (Eq.5):

$$FE = \frac{\alpha n F}{Q} \quad \textbf{(Eq.5)}$$

where α denotes the numbers of transferred electrons (*e.g.* $\alpha = 2$ for reduction of $CO_2$ to HCOOH), n denotes the number of moles of the obtained products, F is the faradaic constant (96 485 C $mol^{-1}$), and Q denotes the total charge.

### 1.4 Energy efficiency (EE)

The energy efficiency (EE) is the overall energy utilization toward the desired product, which can be calculated by the following equation:

$$EE = \frac{E_{eq}}{E_{eq} + \eta} \times \mathrm{FE}$$

Where Eeq stands for equilibrium potential and ŋ stands for the overpotential of the desired product. According to the equation, we can know that the smaller the overpotential for the desired product, the larger the energy efficiengy for the $CO_2$ reduction.

### 1.5 Electrochemical surface area (ECSA)

The number of electrochemically active sites of an electrode can be evaluated by the electrochemical surface area (ECSA), which is greatly dependent on the nature of electrodes and the preparation method.[2] Notably, not all the electrochemically active sites are catalytically active. The ECSA can be calculated by Eq. 6 as following:[3]

$$ECSA = \frac{C_{dl}}{C_s} \quad \textbf{(Eq.6)}$$

$C_{dl}$ is the electrical double-layer capacitance of which is obtained by scanning cyclic voltammetric stripping of the work electrode in the non-Faradaic regions (non-faradaic current density j) at different scan rates v, *i.e.* the slope of the linearity between j and v, $C_{dl}= j/v$. $C_s$ is the specific capacitance of corresponding smooth metal or oxide electrode.[3]

## 1.6 Turnover frequency (TOF)

The turnover frequency (TOF) is used to quantify the per-site activity of the electrocatalysts, which characterizes the level of catalytic activity. TOF for a specific product i can be acquired by Eq. 7:

$$TOF(i) = \frac{j \cdot FE(i)}{nFN_a} \qquad \textbf{(Eq.7)}$$

where j is the current density (A $m^{-2}$), n is the mole number of electrons transfer per mole of product i (*e.g.*, n = 2 for product CO), and $N_a$ is the active site density of the electrocatalyst (mol $m^{-2}$).

## 1.7 Production rate (PR)

The production rate is used to evaluate the practical applicability of a specific electrocatalyst and defines the reaction rate necessary to obtain a particular product. The PR for a certain product (such as CO, $\alpha = 2$) on an electrocatalyst can be estimated by Eq. 8:

$$PR(i) = \frac{j \cdot FE}{\alpha \cdot F} \qquad \textbf{(Eq.8)}$$

Production rate is a vital parameter for evaluating the practical applicability of a catalyst for a long-lasting experiment under the steady-state, and it is necessary to estimate the production rate of a desired product in studying a catalyst or device for $CO_2RR$.

## 1.8 Tafel slope

The Tafel slope is a plot of overpotential *vs.* logarithm of the partial current density of some product, which is commonly applied to assess electro-kinetic pathway and mechanism of the reaction. The smaller the Tafel slope, the better the catalytic performance of the catalyst. Generally, a Tafel slope of 59 mV $dec^{-1}$ for $CO_2RR$

means it is a one-electron pre-equilibrium step before a later rate-limiting chemical step, while a Tafel slope of 118 mV dec$^{-1}$ suggests that the initial one-electron transfer step forming $CO_2^{-\bullet}$ is the rate-determining step of the reaction.

### 1.9 Adsorption energy of the key $CO_2$-related intermediate

The adsorption energy of $CO_2^{*-}$ ($CO_2^-$ adsorbed on the active site, asterisk (*) stands for the active site) can be used to evaluate the activity of $CO_2$ reduction.[4, 5] Generally, the $OH^-$ acts as the surrogate of $CO_2^{*-}$, and the adsorption energy of $CO_2^{*-}$ on the surface of catalysts is estimated by performing the anodic linear sweep voltammetry (LSV) curves in $N_2$-saturated alkaline electrolyte (such as 0.1 M KOH). The more negative adsorption peak indicates the stronger bond strength of $CO_2^{*-}$ intermediate(s) with active sites, thus facilitates $CO_2$ reduction.

**Table 1.** Performance of Au related materials for $CO_2RR$ with CO as the main product

| Catalysts | Electrolyte | Durability test | Potential | Current density/ mA $cm^{-2}$ | CO FE | References |
|---|---|---|---|---|---|---|
| Au plate | 0.5 M $KHCO_3$ | - | -1.00 V *vs.* NHE | -3.7 (pcd) | 91% | [6] |
| oxide-derived Au | 0.5 M $NaHCO_3$ | 8 h | -0.35 V *vs.* RHE | -2~4 | >96% | [7] |
| 8 nm Au NPs | 0.5 M $KHCO_3$ | - | -0.67 V *vs.* RHE | -8 | 90% | [8] |
| 4 nm Au NPs | 0.5 M $KHCO_3$ | - | -0.59 V *vs.* RHE | -166.1 A $g^{-1}$ | 78% | [9] |
| Au QDDCs | 0.5 M $KHCO_3$ | 80 h | -0.3 V *vs.* RHE | 19 | 95% | [10] |
| ER-Au-UR/C | 0.1 M $KHCO_3$ | 10 h | -0.68 V *vs.* RHE | -4.4 | 94.2% | [11] |
| Au NWs | 0.5 M $KHCO_3$ | 12 h | -0.35 V *vs.* RHE | -1.84 A $g^{-1}$ | 94% | [12] |
| Au-NW stacked electrode | 0.2 M $KHCO_3$ | - | -0.69 V *vs.* RHE | $^{m}$-3 | ~93% | [13] |
| $Au_{25}$ nanoclusters | 0.1 M $KHCO_3$ | - | -0.8 V *vs.* RHE | -1.4 | 90% | [14] |
| Au-IO thin films | 0.5 M $KHCO_3$ | - | -0.51 V *vs.* RHE | - | 99% | [15] |
| Au nanoneedles | 0.5 M $KHCO_3$ | 8 h | -0.35 V *vs.* RHE | -22 | >95% | [16] |
| Au hierarchical nanoneedles | 0.5 M $KHCO_3$ | - | -0.4V *vs.* RHE | -38 | 98% | [17] |
| porous Au film | 0.1 M $KHCO_3$ | 9 h | -0.50 V *vs.* RHE | -8.3 | 91% | [18] |
| Nanoporous Au | 0.1 M $NaHCO_3$ | 10 h | -0.60 V *vs.* RHE | $^{m}$-15 | 95.9% | [19] |
| Nanoporous Au leaf | 0.5 M $KHCO_3$ | 2.5 h | -1.2 V *vs.* Ag/AgCl | -20.51 A $g^{-1}$ | 90% | [20] |
| Nanoporous Au | 0.5 M $KHCO_3$ | 10 h | -0.6 V *vs.* RHE | $^{m}$-17 (pcd) | 94% | [21] |
| Hierarchically porous Au | 0.2 M $KHCO_3$ | - | -0.374 V *vs.* RHE | - | 85.8% | [22] |
| Oxide-derived nanoporous Au | 0.1 M $KHCO_3$ | 12 h | 0.3 V *vs.* RHE | $^{m}$-2.5 (pcd) | >90% | [23] |
| Nano-folded Au | 0.1 M $KHCO_3$ | - | 0.5V *vs.* RHE | -2.4 | 87.4% | [24] |
| Pore-like RA-Au | 0.2 M $KHCO_3$ | - | -0.39 V *vs.* RHE | $^{m}$-0.25 (pcd) | >90% | [25] |
| Nano-Au | 0.5 M $KHCO_3$ | 10000s | -0.57 V *vs.* RHE | $^{m}$-80 | ~92% | [26] |

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|---|---|---|---|---|---|---|
| Au/CNT | 0.5 M $NaHCO_3$ | 12 h | -0.50 V *vs.* RHE | -13 A $g^{-1}$ | 94% | 27 |
| Au NPs/GNR | 0.5 M $KHCO_3$ | >24 h | -0.66 V *vs.* RHE | $^{m}$-34 A $g^{-1}$ | 92% | 28 |
| Au/$CeO_x$-C | 0.1 M $KHCO_3$ | - | -0.89 V *vs.* RHE | -12.9 (pcd) | 89.1% | 29 |
| Au/$C_3N_4$ | 0.5 M $KHCO_3$ | 15h | -0.45 V *vs.* RHE | -2.48 | 90% | 30 |
| Au/Py-CNTs-O | 0.1 M $KHCO_3$ | 10 h | -0.58 *vs.* RHE | -69 A $g^{-1}{}_{Au}$ | 93% | 31 |
| CTAB-Au/$SnO_2$ | 0.5 M $KHCO_3$ | - | -0.5 *vs.* RHE | -0.26(pcd) | 96% | 32 |
| AuFe core-shell | 0.5 M $KHCO_3$ | 90 h | -0.4 V *vs.* RHE | -48.2 | 97.3% | 33 |
| Ordered AuCu NPs | 0.1 M $KHCO_3$ | 12 h | -0.77 V *vs.* RHE | -1.39 (pcd) | 80% | 34 |
| Ag@Au nanowires | 0.1 M $KHCO_3$+ 0.1 M KCl | 12 h | -1.14 V *vs.* RHE | -5.61 | 99.65% | 35 |
| $AuCu_3$@Au electrode | 0.1 M $KHCO_3$ | 100 h | -0.6 V *vs.* RHE | -5.3 (pcd) | 97.27% | 36 |
| $Au_{94}Pd_6$ nanoparticles | 0.5 M $KHCO_3$ | 12 h | -0.6 V *vs.* RHE | -156.1 A $g_{Pd+Au}{}^{-1}$ | 96.7% | 37 |
| Dealloyed $Au_3Cu$ | 0.5 M $KHCO_3$ | 5 h | -0.38 V *vs.* RHE | -3 | >90% | 38 |
| 4%Au-Cdots-$C_3N_4$ | 0.5 M $KHCO_3$ | 8 h, 60 d | -0.4 V *vs.* RHE | $^{m}$-0.05 | 79.8% | 39 |
| Cl modified Au | 0.2 M $KHCO_3$ | - | -0.39 V *vs.* RHE | $^{m}$-0.04 (pcd) | 79% | 40 |
| Porphyrin functionalized Au NPs | 0.5 M $KHCO_3$ | 72 h | -0.45 V *vs.* RHE | -2 | 93% | 41 |
| Au-OLA | 0.1 M $KHCO_3$ | 10 h | -0.65 V *vs.* RHE | -102 A $g^{-1}$ | 59% | 42 |
| PEG-modified Au | 0.5 M $KHCO_3$ | - | -0.57 V *vs.* RHE | $^{m}$-3 (pcd) | 100% | 43 |
| PVA- Au-C | 0.5 M $KHCO_3$ | 24 h | -0.77 V *vs.* RHE | -98.6 (pcd) | >90% | 44 |

m: evaluated from the figures, pcd: partial current density

**Table 2.** Performance of Ag-related materials for $CO_2$RR with CO as the main product

| Catalysts | Electrolyte | Durability test | Potential | Current density/ mA $cm^{-2}$ | CO FE | Reference |
|---|---|---|---|---|---|---|
| Ag electrode | 0.1 M $CsHCO_3$ | - | -1.0 V *vs.* RHE | $^{m}$-5.8 | 80.3% | [45] |
| Ag nanoparticles(>100nm) | 18 mol% EMIM $BF_4$ in $H_2O$ | 7 h | 1.5 V | - | 96% | [46] |
| Ag metal | EMIMBF$_4$+BMIM NO$_3$+0.25mg CoCl | - | -2.0 V *vs.* SCE | -5.4±0.1 | 98% | [47] |
| L25-Ag nanocubes | 0.1 M $KHCO_3$ | 18 h | -0.856 V *vs.* RHE | $^{m}$-1.7 | 99% | [48] |
| Ag NWs (35 nm) | 0.5 M $KHCO_3$ | 12 h | -0.9 V *vs.* RHE | $^{m}$-7 | 80% | [49] |
| D-25 Ag NWs (diameter less than 25 nm) | 0.1 M $KHCO_3$ | 24 h | -0.956V *vs.* RHE | $^{m}$-3.2 | 99.3% | [50] |
| Ag NWs (200 nm) | 0.5 M $KHCO_3$ | 24 h | -0.7V *vs.* RHE | -12.22 | 84% | [51] |
| Ag nanoporous | 0.5 M $KHCO_3$ | 2 h | -0.6 V *vs.* RHE | -18 | 92% | [52] |
| 6 μm thick highly porous Ag | 0.5 M $KHCO_3$ | 3 h | -0.5V *vs.* RHE | -10.5 (pcd) | 82% | [53] |
| porous Ag | 0.5 M $KHCO_3$ | 4 h | -1.7 V *vs.* SCE | -14 | 93% | [54] |
| Sponge-like porous Ag | 0.1 M $KHCO_3$ | 24 h | -0.9 V *vs.* RHE | $^{m}$-7 | 93% | [55] |
| Ag nanosheets | 0.5 M $KHCO_3$ | - | -0.6 V *vs.* RHE | -1.6 | >90% | [56] |
| Ag-IO | 0.1 M $KHCO_3$ | - | -0.7 V *vs.* RHE | $^{m}$-0.015 ($s_{CO}$) | 80% | [57] |
| oxide-derived Ag | 0.1 M $KHCO_3$ | 2 h | -0.8 V *vs.* RHE | -1.15 | 89% | [58] |
| $Ag_2CO_3$-derived Ag | 0.1 M $KHCO_3$ | 100 h | -0.55 V *vs.* RHE | $^{m}$-1.5 | >90% | [59] |
| $Ag_2CO_3$-derived Ag nanoparticles | 0.5 M $KHCO_3$ | - | -0.67 V *vs.* RHE | $^{m}$-4.2(pcd) | 96.7% | [60] |
| Carbonate-derived Ag | 1 M KOH(flow reactor) | 24 h | -0.7 V *vs.* RHE | >150 | >90% | [61] |
| Iodide-derived Ag | 0.5 M $KHCO_3$ | 10 h | -0.7 V *vs.* RHE | -16.7 | 94.5% | [62] |
| $Ag_3PO_4$-derived Ag | 0.5 M $KHCO_3$ | 10 h | -0.7 V *vs.* RHE | -2.93 | 97.3% | [63] |
| AgCl-derived Ag | NaCl(3.5%) | 24 h | -1.1 V *vs.* RHE | $^{m}$-7.5 | ~90% | [64] |

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|---|---|---|---|---|---|---|
| rough surface Ag | 0.1 M $KHCO_3$ | - | -1.1 V *vs.* RHE | -5.73 (pcd) | 88.87% | 65 |
| Cl modified Ag nonocorals | 0.1 M $KHCO_3$ | 72 h | -0.48 V *vs.* RHE | -2 | ca.98% | 66 |
| Cl modified Ag nanoparticles | 0.5 M $KHCO_3$ | 20 h | -0.8 V *vs.* RHE | -9.40 (pcd) | 98% | 67 |
| Amine modified Ag | 0.1 M $KHCO_3$ | - | -0.75 V *vs.* RHE | - | 94.20% | 68 |
| cysteamine Ag 5 nm nanoparticles | 0.5 M $KHCO_3$ | - | -0.75 V *vs.* RHE | -3.8 (pcd) | 84.40% | 69 |
| SCN modified Ag Foam | 0.5 M $KHCO_3$ | 10 h | -1.3 V *vs.* RHE | -32.4 | 94.8 ± 2.9% | 70 |
| Sodium dodecyl sulfate modified Ag Nps | 0.1 M $KHCO_3$ | 8 h | -0.79V *vs.* RHE | -8.23 | 92.2% | 71 |
| Protein modified Ag NR | 0.5 M $KHCO_3$ | 12 h | -1.128 V *vs.* RHE | -7.51 | 95% | 72 |
| mixed layer-Ag-MWCNT | 1M KOH | - | -3 V | -350 | >95% | 73 |
| $[PMo_{12}O_{40}]^{3-}$ modified Ag | DMF (0.1M $[n\text{-}Bu_4N]PF_6$ and 0.5% (v/v) $H_2O$) | - | -1.7 V vs. $Fc^{0/+}$ | $^{m}$-2.5 | 90±5% | 74 |
| Benzenethiolate-modified porous Ag | 0.1 M $KHCO_3$ | - | -1.03 *vs.* RHE | 502 A/g | 96% | 75 |
| Ag film/aminosilane deposited substrate | 0.5 M $KHCO_3$ | - | -0.3 V *vs.* RHE | - | 75.7% | 76 |
| plasma-activated Ag | 0.1 M $KHCO_3$ | 0.5 h | -0.6 V *vs.* RHE | $^{m}$-2.25 (pcd) | >90% | 77 |
| p-Ag:5 | 0.5 M $KHCO_3$ | 5 h | -1.04 V *vs.* RHE | $^{m}$-14 | 83.50% | 78 |
| anodized Ag | 0.1 M $KHCO_3$ | 2 h | -0.61 V *vs.* RHE | - | 92.80% | 79 |
| 3-D Ag foam | 0.1 M $KHCO_3$ | 12 h | -0.99 V *vs.* RHE | -10.8 | 94.70% | 80 |
| Ag foam | 0.5 M $KHCO_3$ | 72 h | --0.80 V *vs.* RHE | | >90% | 81 |
| Air-annealed Ag | 0.1 M $KHCO_3$ | 2.66 h | -0.97 V *vs.* RHE | -21.2 | 91.70% | 82 |
| 40% Ag/$TiO_2$ | 1 M KOH (flow reactor) | - | -1.8 V *vs.* Ag/AgCl | -101 (pcd) | 93% | 83 |

| | | | | | | |
|---|---|---|---|---|---|---|
| SnO$_x$/Ag | 0.5 M KHCO$_3$ | 12 h | -0.6 V *vs.* RHE | [m]-1 | 85% | [84] |
| Ag/(A-Sn(IV)) NPs | 0.5 M NaHCO$_3$ | 12 h | -0.7 V *vs.* RHE | -7.9 | 88% | [85] |
| Ag$_2$P nano crystals | 0.5 M KHCO$_3$ | 12 h | -0.8 V *vs.* RHE | [m]-7.5 | 82% | [86] |
| De-sulfidated Ag NWs | 0.5 M KHCO$_3$ | 18 h | -0.75 V *vs.* RHE | -1.3 | ~81% | [87] |

m: evaluated from the figures; pcd: partial current density; $s_{CO}$:specific current density of CO

**Table 3.** Performance of Pd-related materials for $CO_2$RR with CO as the main product

| Catalysts | Electrolyte | Durability test | Potential | Current density | CO FE | References |
|---|---|---|---|---|---|---|
| Pd icosahedra/C | 0.1 M $KHCO_3$ | 10 h | -0.8 V *vs.* RHE | [m]-2 mA cm$^{-2}$ | 91.1% | [88] |
| Pd octahedra/C | 0.1 M $KHCO_3$ | 10 h | -0.7 V *vs.* RHE | [m]-0.5 mA cm$^{-2}$ | 53.60% | [88] |
| Pd octahedra NPs | 0.5 M $NaHCO_3$ | - | -0.7 V *vs.* RHE | [m]-16 mA cm$^{-2}$(pcd) | 94% | [89] |
| Pd NPs (3.7nm) | 0.1 M $KHCO_3$ | - | -0.89 V *vs.* RHE | -23.9A g$^{-1}$ | 91.20% | [90] |
| Pd NPs | 1 M $KHCO_3$ |  | -0.7 V *vs.* RHE | -22.9 mA cm$^{-2}$ (pcd) | 93.4% | [91] |
| Pd/C | 0.5 M $NaHCO_3$ | - | -0.6 V *vs.* RHE | [m]-0.3 mA cm$^{-2}$ | ca.48% | [92] |
| Ultra-small Pd NPs | 0.5 M $KHCO_3$ | 12 h | -0.6V *vs.* RHE | [m]-2 mA cm$^{-2}$ | 92.6% | [93] |
| $Pd_3Cu$ nanocrystal | 0.1 M $KHCO_3$ | - | -0.9 V *vs.* RHE | -4.5 mA cm$^{-2}$ (pcd) | 82.10% | [94] |
| $Pd_{85}Cu_{15}$/C | 0.1 M $KHCO_3$ | - | -0.89 V *vs.* RHE | -6.9 mA cm$^{-2}$ (pcd) | 86% | [95] |
| PdCu | 0.1 M $KHCO_3$ | 5 h | -0.9 V *vs.* RHE | -47 mA mg$_{Pd}^{-1}$ | 87% | [96] |
| $Pd_{0.8}$ Au | 0.5 M $KHCO_3$ | 20 h | -0.6 V *vs.* RHE | -2.77 mA cm$^{-2}$ | 94.3% | [97] |
| Te-doped Pd | 0.1 M $KHCO_3$ | 5 h | -0.8 V *vs.* RHE | -4.4 mA cm$^{-2}$ (pcd) | 90.00% | [98] |
| Pd nanosheets(5.1 nm) | 0.1 M $KHCO_3$ | 8 h | -0.6 V *vs.* RHE | -3.0 mA cm$^{-2}$ | > 90% | [99] |

m: evaluated from the figures; pcd: partial current density

**Table 4.** Performance of Zn related materials for $CO_2$RR with CO as the main product

| Catalysts | Electrolyte | Durability test | Potential | Current density/ mA $cm^{-2}$ | CO FE | References |
|---|---|---|---|---|---|---|
| Anodized Zn | 0.5 M NaCl | 10h | -1.6 *vs.* SCE | $^{m}$-2 | 93% | [100] |
| Dendried Zn | 0.5 M $NaHCO_3$ | 3h | -0.9V *vs.* RHE | -4( pcd) | 62% | [101] |
| Porous Zn | 0.1 M $KHCO_3$ | | -0.95 V *vs.* RHE | -27 | 95% | [102] |
| h-Zn | 0.5 M $KHCO_3$ | 30h | -0.9V *vs.* RHE | -11.7 | 84% | [103] |
| RE-Zn-$CO_2$ | 0.5 M $KHCO_3$ | - | -0.9V *vs.* RHE | -6.6 | 78% | [104] |
| RE-Zn-$CO_2$/KCl | 0.5 M KCl | - | -1.05V *vs.* RHE | -4.3 | 95.3% | [202] |
| LiET-Zn/GCE | 0.1 M $KHCO_3$ | 4h | -1.17V *vs.* RHE | -26.5 | 91.1% | [105] |
| LiET-Zn/CPF | 0.1 M $KHCO_3$ | - | -0.8 V *vs.* RHE | $^{m}$-5.9 (pcd) | 71.0% | [207] |
| Zn foil | PC/TBAP +6.8%$H_2O$ | 4h | -2.3V *vs.* Fc/$Fc^+$ | -6.72 | 83% | [106] |
| Oxygen vacancies riched ZnO | 0.1 M $KHCO_3$ | 8h | -1.1 V *vs.* RHE | -16.1 | 83% | [107] |
| rZnO@G | EMIM-$BF_4$/$H_2O$ (V/V=7/1) | - | -0.813 V *vs.* RHE | -5.2 | 83% | [108] |
| Zn/ZnS | 0.1 M $KHCO_3$ | 15 h | -0.8 V *vs.* RHE | -4.28 (pcd) | 94.2% | [109] |
| Multilayered Zn nanosheets | 0.5 M $NaHCO_3$ | 7 h | -1.13 V *vs.* RHE | -14 | 86% | [110] |
| Porous Zn nanosheets | 0.1 M $KHCO_3$ | 12 h | -1.0V *vs.* RHE | -8.5 | >88% | [111] |
| $ZnGa_2O_4$ | 0.1 M $KHCO_3$ | 10 h | -0.8 V *vs.* RHE | $^{m}$-0.5 | 96% | [112] |

m: evaluated from the figures; pcd: partial current density

**Table 5.** Performance of other metals and metal compounds for $CO_2$RR with CO as the main product

| Catalysts | Electrolyte | Durability test | Potential | Current density/ mA $cm^{-2}$ | CO FE | Reference |
|---|---|---|---|---|---|---|
| CuO-derived Cu NWs | 0.1 M $KHCO_3$ | - | -0.60 V *vs.*RHE | $^{m}$-0.6 | ~50% | [113] |
| ECR Cu NWs | 0.5 M $KHCO_3$ | - | -0.41 V *vs.* RHE | -1 | ~60% | [114] |
| ECR-Cu NWs | 0.1 M $KHCO_3$ | - | -0.40 V *vs.* RHE | $^{m}$0.45 | ~62% | [115] |
| Cu nanopillar (5h) | 0.1 M $KHCO_3$ | 6 h | -0.5 V *vs.* RHE | $^{m}$-1.23 | 28.67% | [116] |
| Cu hollow fibers | 0.3 M $KHCO_3$ | 24 h | -0.4 V *vs.* RHE | $^{m}$-9 | 75% | [117] |
| Cu-IOs | 0.1 M $KHCO_3$ | 10 h | -0.6 V *vs.* RHE | -1.2 | 45.3% | [118] |
| CuO-IO | 0.1 M $KHCO_3$ | 24 h | -0.6 V *vs.* RHE | $^{m}$-2.5 | 72.5±1.8 % | [119] |
| Cu nanosheets | 0.5 M $KHCO_3$ | 20 h | -1.0 V *vs.* RHE | -23 (pcd) | 74.1% | [120] |
| Sn-modified $Cu_2O$ | 0.1 M $KHCO_3$ | 12 h | -0.6 V *vs.* RHE | $^{m}$-8.0 (pcd) | (CE) 75% | [121] |
| Sn-decorated $Cu_xO$ NWs | 0.1 M $KHCO_3$ | 12 h | -0.80 V *vs.* RHE | -4.5 (pcd) | 90% | [122] |
| Cu/$SnO_2$ core-shell | 0.5 M $KHCO_3$ | - | -0.7 V *vs.* RHE | -4.6 | 93% | [123] |
| Cu-Sn alloy | 0.1 M $KHCO_3$ | 14 h | -0.6 V *vs.* RHE | -1 | >90% | [124] |
| $Cu_{22}Sn$ | 0.1 M $KHCO_3$ | 6 h | -0.81 V *vs.* RHE | $^{m}$-2 | 92% | [125] |
| $Cu_2Cd$/Cd/Cu | 0.1 M $KHCO_3$ | 12 h | -0.80 V *vs.* RHE | -8 | 84% | [126] |
| Sn catalysts | MeCN (100 mM [MEMIM]OTf) | 1 h | -1.95 V *vs.* SCE | -5 | 77% | [127] |
| Cu/Ni(OH) nanosheets | 0.5 M $NaHCO_3$ | 22 h | -0.5 V *vs.* RHE | -4.3 | 92% | [128] |
| $Cu_xNi_y$/N-C | 0.5 M $KHCO_3$ | 38 h | -0.6 V *vs.* RHE | -18.8 | 94.5% | [129] |
| $Co_{0.75}Ni_{0.25}$/N-C NFs | 0.5 M $NaHCO_3$ | 20 h | -0.9 V *vs.* RHE | -13.4 | 85% | [130] |
| $Cu_2O$/CuO@Ni | 0.5 M $KHCO_3$ | 25 h | -1.2 V *vs.* RHE | $^{m}$-27 | 95% | [131] |
| Cu-In alloy | 0.1 M $KHCO_3$ | 7 h | -0.5 V *vs.* RHE | $^{m}$-0.5 | 90% | [132] |
| Cu-In alloy ($CuInO_2$) | 0.1 M $KHCO_3$ | 5 h | -0.80 V *vs.* RHE | $^{m}$-2.0 | 70% | [133] |
| CuIn alloy NWs | 0.5 M $KHCO_3$ | 15 h | -0.60 V *vs.* RHE | -2.66(pcd) | >68.2% | [134] |
| InCuO-0.92 | 0.5 M $KHCO_3$ | 24 h | -0.80 V *vs.* RHE | -11.2 | 92.1% | [135] |

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|---|---|---|---|---|---|---|
| In/Cu NWs | 0.1 M $KHCO_3$ | 60 h | -0.60 V *vs.* RHE | -1.7 | >90% | 136 |
| Nanoporous Cu-In | 0.1 M $KHCO_3$ | 7 h | -0.95 V *vs.* RHE | -4.5 | 91% | 137 |
| CuO-$In_2O_3$/NCNTs | 0.1 M $KHCO_3$ | 10 h | -0.70 V *vs.* RHE | -4.3(pcd) | 93% | 138 |
| CuIn-ESP25min | 1 M KOH (flow cell) | - | -1.17 V *vs.* RHE | -200 | ~90% | 139 |
| In-doped Cu@$Cu_2O$ | 0.1 M $KHCO_3$ | 4 h | -0.80 V *vs.* RHE | -(11.1 ± 0.85) | 87.6 ± 2.2% | 140 |
| $Ag_{91}Cu_9$ | 0.1 M $KHCO_3$ | 10 h | -0.70 V *vs.* RHE | -5.6 | 80.6% | 141 |
| h-CuS MCs | 0.5 M $KHCO_3$ | 10 h | -0.16 V *vs.* RHE | $^{m}$ -0.01 | 32.7% | 142 |
| 3D Cu-Ag | 0.5 M $KHCO_3$ (flow cell) | 15 h | -0.80 V *vs.* RHE | $^{m}$ -9 | 95.7% | 143 |
| Cu/CA | 0.1 M $KHCO_3$ | 10 h | -0.60 V *vs.* RHE | $^{m}$ -3 | 75.6% | 144 |
| $Cu_3P$/C | 0.1 M $NaHCO_3$ | 2000 s | -0.30 V *vs.* RHE | -0.05 | 47% | 145 |
| CuO-Cu@BC | 0.5 M $KHCO_3$ | 40 h | -0.60 V *vs.* RHE | $^{m}$-4.8 | 53% | 146 |
| $Ag_{0.66}In_{0.34}$ | 0.5 M $KHCO_3$ | - | -1.3 V *vs.* SCE | $^{m}$-0.5 | 68.8% | 147 |
| *In situ* reduced-$In_2O_3$ | 0.1 M $Na_2SO_4$ | - | -1.0 V *vs.* Ag/AgCl | $^{m}$-0.25 | ~100% | 148 |
| $Co_3O_4$ nanofibers | 0.1 M $TBAPF_6$ in acetonitrile + 0.1%$_{vol}$ $H_2O$ | 8 h | -1.56 V *vs.* NHE | -0.5 | 65% | 149 |
| Ga gel/C | 0.1 M $KHCO_3$ | 2000 s | -0.70 V *vs.* RHE | $^{m}$-5 | 77.0% | 150 |
| $MoS_2$ | 4 mol% EMIM-$BF_4$ in water | 10 h | -0.764 V *vs.* RHE | -65 | 98% | 151 |
| $Mo_{0.95}Nb_{0.05}S_2$ | 50 vol% EMIM-$BF_4$ in water | - | -0.8 V *vs.* RHE | -237 | 82% | 152 |
| $WSe_2$ | 50/50 vol% IL (EMIM-$BF_4$)/water | - | -0.164 V *vs.* RHE | -18.95 | 24% | 153 |
| $MoS_2$-PEI-modified graphene oxide | 0.5 M $NaHCO_3$ | 3 h | -0.65 V *vs.* RHE | $^{m}$-4 | 85% | 154 |
| $TiO_2$@$MoS_2$ | 0.1 M $NaHCO_3$ | 14 h | -0.7 V *vs.* RHE | -83 | 82% | 155 |
| Fluorosilance-decorated | 6 mol% EMIM-$BF_4$ in | 10 h | -0.92 V *vs.* RHE | $^{m}$-25 | 81.2% | 156 |

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|---|---|---|---|---|---|---|
| $MoS_2$ | water | | | | | |
| N-$MoS_2$@NCDs-180 | EMIM-$BF_4$ solutions (94 mol% $H_2O$) | 10 h | -0.9 V *vs.* RHE | -36.2 | 90.2% | 157 |
| $Ag_2S$ NWs | 50 vol% EMIM-$BF_4$ + 50 vol% $H_2O$ | 19 h | -0.864 V *vs.* RHE | [m]-10.2 (pcd) | 92% | 158 |
| MoSeS monolayer | 4 mol% EMIM $BF_4$ + 96% $H_2O$ | 10 h | -1.15 V *vs.* RHE | -43 | 45.2% | 159 |
| CdS | 0.1M $KHCO_3$ | 10 h | -1.2 V *vs.* RHE | -21.9 (pcd) | 81% | 160 |
| CdS nanoneedle arrays | 5 M KOH(flow cell) | 4 h | -1.2 V *vs.* RHE | -212 | ~95.5% | 161 |
| CdS-CNTs | 0.5 M $KHCO_3$ | 10 h | -1.2 V *vs.* RHE | -11.4 | 92% | 162 |
| F-γ-$In_2Se_3$/CP | 30wt%[Bmim]$PF_6$/65wt%MeCN/5 wt%$H_2O$ | 5 h | -2.0 V *vs.* SCE | -55.3 | 96.5% | 163 |
| Cd nanoparticles derived $Cd(OH)_2$ | [BMIM]$PF_6$ + MeCN | 10 h | -1.85 V *vs.* RHE | -59.0 (pcd) | 99.2% | 164 |
| Ga gel/C | 0.1M $KHCO_3$ | - | -0.71 V *vs.* RHE | -10.7 | 77% | 150 |
| $Fe_{4.5}Ni_{4.5}S_8$ | MeCN(24 ppm $H_2O$) | - | -1.8V *vs.* NHE | -3 | 87% | 165 |
| Pb/PbO@OMC-800 | [Bmim]$BF_4$(0.5 M)-MeCN | 10 h | -2.3 V *vs.* Ag/$Ag^+$ | -41.3 | 98.3% | 166 |
| Hierarchical $CoS_2$ nanocages-300 | 0.5 M $KHCO_3$ | 2000 s | -0.60 V *vs.* RHE | -2.8(pcd) | 85.7% | 167 |

m: evaluated from the figures; pcd: partial current density;CE: current efficiency.

**Table 6.** $CO_2$RR performance of heteroatom-doped carbon materials with CO as the main product

| Catalysts | Electrolyte | Durability test | Potential | Current density/ mA cm$^{-2}$ | FE$_{CO}$ | Active sites |
|---|---|---|---|---|---|---|
| Fe-N-C(Fe$_{0.5}$d)[168] | 0.5 M $NaHCO_3$ | - | -0.6V *vs.* RHE | $^{m}$-7.5 | 80% | $FeN_4$ sites |
| Fe-N-C[169] | 0.1 M $NaHCO_3$ | - | -0.6V *vs.* RHE | $^{m}$-2.5 | 80% | N moieties |
| Fe-N-C[170] | 0.1 M $KHCO_3$ | - | -0.55 V *vs.* RHE | $^{m}$-2.5 | 65% | Fe-$N_x$ moieties |
| Fe-N-C-950[171] | 0.1 M $KHCO_3$ | 12 h | -0.6V *vs.* RHE | -1.2 | 74% | Fe-N sites |
| Ni-N-C[172] | 0.5 M $KHCO_3$ | 12 h | -0.67 V *vs.* RHE | -3.9 | 93% | Atomically dispersed Ni sites |
| NiASs/PTF[173] | 0.5 M $KHCO_3$ | 10 h | -0.8 V *vs.* RHE | -14.4 | 98% | Ni-$N_4$ |
| Ni-N-CNSs[174] | 0.5 M $KHCO_3$ | 25 h | -0.75 V *vs.* RHE | $^{m}$-5.5 | 95.3% | Ni-N |
| Fe/Ni-NC[175] | 0.5 M $KHCO_3$ | 50 h | -1.0 V *vs.* RHE | -10 | 96% | N-C and Fe/Ni nano-alloy |
| Ni-$N_3$-V/CC[176] | 0.5 M $KHCO_3$ | 14 h | -0.8 V *vs.* RHE | $^{m}$-50 | 94% | Ni-$N_3$-Vacancy |
| Fe-N-C[177] | 0.1 M $KHCO_3$ | - | -0.6 V *vs.* RHE | $^{m}$-4.5 | 85% | - |
| FexN@Fe-N-C[178] | 0.1 M $KHCO_3$ | 24 h | -0.53 V *vs.* RHE | -4.71 | 95% | Encased $Fe_xN$ |
| Fe/$Fe_3C$@NCNT-750[179] | 0.5 M $KHCO_3$ | - | -0.74 V *vs.* RHE | $^{m}$-11 | 50% | - |
| $Fe_3N_x$/C[180] | 0.1 M $Na_2SO_4$ | 5 h | -0.6 V *vs.* RHE | $^{m}$-2.5 | 85% | $Fe_xN$ and C-N-based centers |
| Fe-N-G/bC[181] | 0.1 M $KHCO_3$ | 12 h | -0.66 V *vs.* RHE | $^{m}$-7.5 | 95% | - |
| $Fe^{3+}$-N-C[182] | 0.5 M $KHCO_3$(flow cell) | 30 h | -0.45 V *vs.* RHE | -94(pcd) | >90% | $Fe^{3+}$ sites |
| Fe-NS-C[183] | 0.5 M $KHCO_3$ | 30 h | -0.56 *vs.* RHE | -11 | >90% | Doped S and Fe-$N_x$ |
| FeNPCN[184] | 0.1 M $KHCO_3$ | 12 h | -0.5 V *vs.* RHE | $^{m}$-0.7 | 94% | C,N coordinated atomic Fe |

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|---|---|---|---|---|---|---|
| Fe-SAs/N-C[185] | 0.5 M NaCl | - | -0.45 V *vs.* RHE | $^{m}$-7 | 99.6% | Single iron atoms |
| Fe-N/O-C(MZ)[186] | 0.1 M $KHCO_3$ | 22 h | -0.58 V *vs.* RHE | -5.4(pcd) | 96% | $Fe-N_4O$ sites |
| MPPCN-750[187] | 0.5 M $KHCO_3$ | 12 h | -0.7 V *vs.* RHE | $^{m}$-1.2 | 95.9% | $Fe-N_4$ |
| H-M-G[188] | 0.1 M $KHCO_3$ | 24 h | -0.46 V *vs.* RHE | $^{m}$-1.7 | 97% | $FeN_5$ |
| Fe-CNPs[189] | 1 M $KHCO_3$ | 8 h | -0.58 V *vs.* RHE | $^{m}$-7 | 98.8% | Fe-N |
| rGO-PVP-ZIFc[190] | 0.5 M $KHCO_3$ | 8 h | -0.62 V *vs.* RHE | $^{m}$-6.5 | 98.6% | Fe-N |
| Fe-SA/NCS-700[191] | 0.5 M $KHCO_3$ | 10 h | -0.45 V *vs.* RHE | $^{m}$-10 | 87% | $Fe-N_4$ |
| Ni-N-Gr[192] | 0.1 M $KHCO_3$ | 5 h | -0.7 V *vs.* RHE | $^{m}$-0.6 | >90% | Ni-N site |
| $Ni-N_4-C$[193] | 0.5 M $KHCO_3$ | 30 h | -0.81 V *vs.* RHE | -28.6 | 99% | $Ni-N_4$ sites |
| Ni-N-C[194] | 0.1 M $KHCO_3$ | 9 h | -0.75 V *vs.* RHE | -8.2 | 96% | Ni-N |
| Ni-N-MEGO[195] | 0.5 M $KHCO_3$ | 21 h | -0.7 V *vs.* RHE | 53.6 mA $mg^{-1}$ | 92.1% | Ni-N |
| Ni-SA-NCs[196] | 0.5 M $KHCO_3$ | 9 h | -1.0 V *vs.* RHE | ~-50 | 99% | $Ni-N_4$ |
| NiSA-NGA-900[197] | 0.5 M $KHCO_3$ | 6 h | -0.8 V *vs.* RHE | -5 | 90.2% | Unsaturated Ni-N sites |
| Ni-N-C[198] | 0.1 M $KHCO_3$ | 10 h | -0.75 V *vs.* RHE | -7.51(pcd) | 97% | Edge-hosted $Ni-N_{2+2}$ |
| Ni(NC)[199] | 0.5 M $KHCO_3$ | 20 h | -0.75 V *vs.* RHE | $^{m}$-9 | 99% | Low-valent Ni-N motifs |
| Ni-N-C[200] | 0.5 M $KHCO_3$ | 22 h | -0.9 V *vs.* RHE | $^{m}$-10 | 91.2% | Single Ni atoms |
| Ni/N-CHS[201] | 0.5 M $KHCO_3$ | 15 h | -0.9 V *vs.* RHE | -15 | 93.1% | N-C |
| NC-CNTs (Ni)[202] | 0.1 M $KHCO_3$ | 10 h | -0.8 V *vs.* RHE | $^{m}$-7 | >90% | $Ni@N_3$ (pyrrolic) sites |
| SANi-GO[203] | 0.5 M $KHCO_3$ | 50 h | -0.63 V *vs.* RHE | -8.3(pcd) | 96.6% | $Ni-N_4$ |
| NiSA-NWC[204] | 0.1 M $KHCO_3$ | 2 h | -1.6 V *vs.* Ag/AgCl | $^{m}$-5 | 95% | $Ni^+$ |
| Ni@NCNTs[205] | 0.5 M $KHCO_3$ | 20 h | -0.8 V *vs.* RHE | -8.01(pcd) | 99.1% | Confined Ni NPs |
| Ni@NC-900[206] | 0.1 M $KHCO_3$ | 50 h | -1.0 V *vs.* RHE | -17(pcd) | 96% | - |
| Ni-NPC/CMTs[207] | 0.5 M $KHCO_3$ | 48 h | -0.77 V *vs.* RHE | -11.2 | 94% | $Ni-N_x$ and |

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|---|---|---|---|---|---|---|
|  |  |  |  |  |  | pyridine N |
| Ni-N-OMMCs[208] | 0.1 M $KHCO_3$ | 25 h | -0.7 V *vs.* RHE | $^{m}$-1.5 | 98% | - |
| Ni SAC[209] | 0.5 M $KHCO_3$ | 8 h | -0.6 V *vs.* RHE | -15 | 95.2% | Atomic Ni-N sites |
| Ni-/N-C[210] | 0.5 M $KHCO_3$ | 36 h | -0.61 V *vs.* RHE | $^{m}$-9 | 97.5% | - |
| $NiN_xCNT$[211] | 0.5 M $KHCO_3$ | 44 h | -0.676 V *vs.* RHE | -9(pcd) | 98% | $Ni-N_x$ |
| Zn-N-C[212] | 0.5 M $KHCO_3$ | 15 h | -0.5 V *vs.* RHE | $^{m}$-3.9 | 90.8% | $Zn-N_x$ |
| ZIF-Fe-CNT-FA-p[213] | 0.1 M $NaHCO_3$ | - | -0.56 V *vs.* RHE | -1.9 (pcd) | 97% | pyridinic N and $Fe-N_x$ |
| C-AFC©ZIF-8[214] | 1.0 M $KHCO_3$ | - | -0.43 V *vs.* RHE | $^{m}$-4.8 | 93% | Fe-N |
| AD-Sn/N-C1000[215] | 0.1 M $KHCO_3$ | 24 h | -0.6 V *vs.* RHE | -1.75 (pcd) | 91% | Sn species and pyridinic N |
| Single Ni sites[216] | 0.5 M $KHCO_3$ | 60 h | -1.0 V *vs.* RHE | -7.37 (pcd) | ~71% | sigle Ni sites |
| $Co-N_2$[217] | 0.5 M $KHCO_3$ | 60 h | -0.63 *vs.* RHE | -18.1 | 93% | $Co-N_2$ site |
| $Co-N_5$/HNPCSs[218] | 0.2 M $KHCO_3$ | 10 h | -0.73 *vs.* RHE | -4.5 (pcd) | 99.2% | $Co-N_5$ site |
| $Co_1-N_4$[219] | 0.1 M $KHCO_3$ | 10 h | -0.8 *vs.* RHE | -15.7 | 82% | $Co_1-N_4$ |
| CoSA/HCNFs[220] | 0.1 M $KHCO_3$ | 50 h | -0.9 *vs.* RHE | -67(pcd) | 91% | Co single-atoms |
| A-Ni-NG[221] | 0.5 M $KHCO_3$ | 100 h | -0.61 *vs.* RHE | -22 (pcd) | 97% | Ni(I) atom center |
| Ni-NCB[222] | 0.5 M $KHCO_3$(flow cell) | 24 h | -0.66 *vs.* RHE | $^{m}$-25 | 99% | Ni SAs |
| NiSA-N-CNTs[223] | 0.5 M $KHCO_3$ | 12 h | -0.7 *vs.* RHE | -23.5 (pcd) | 91% | Ni single-atom |
| Unsaturated Ni-N doped porous carbon[224] | 1.0 M $KHCO_3$ | 12 h | -0.63 *vs.* RHE | $^{m}$-25 | 97.8% | Unsaturated Ni-N sites |
| NiSA/PCFM[225] | 0.5 M $KHCO_3$ | 120 h | -1.0 *vs.* RHE | -308.4(pcd) | 88% | Ni single atoms |
| $Cu-N_2$/GN[226] | 0.1 M $KHCO_3$ | 10 h | -0.5 *vs.* RHE | $^{m}$-1 | 81% | $Cu-N_2$ |
| $ZnN_4$-based single- | 0.5 M $KHCO_3$ | >75 h | -0.43 *vs.* RHE | -24.8 | 95% | $ZnN_4$ |

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|---|---|---|---|---|---|---|
| atom[227] |  |  |  |  |  |  |
| ZIF-8[228] | 0.25 M $K_2SO_4$ |  | -1.1 V *vs.* RHE | -6.9 (pcd) | 81% | imidazolate ligands coordinated Zn(II) center |
| $Ni^{2+}$@NG[229] | 0.5 M $KHCO_3$ | - | -0.68 V *vs.* RHE | -10.2 | 92% | $Ni^{2+}$@NG |
| CNT@f-NiNC[230] | 0.5 M $KHCO_3$ | 10 h | -0.6V *vs.* RHE | ~-(4.5±0.5) | 80±3% | - |
| Ni-NC SAC[231] | 0.5 M $KHCO_3$ | - | -0.85V *vs.* RHE | -30(pcd) | 89% | Ni-based active sites |
| Ni/NC_950[232] | 0.1 M $KHCO_3$ | 9 h | -0.8 V *vs.* RHE | [m]-4 | 92.3% | Ni sites |
| Ni-PACN[233] | 0.1 M $KHCO_3$ | - | -0.8 V *vs.* RHE | -14(pcd) | >95% | Pyrrolic coordinated-Ni atoms |
| Ni-TAPc[234] | 0.5 M $KHCO_3$ | 100 h | -0.65V *vs.* RHE | -17.5 | 99% | $Ni^{+}$ |
| Sb-NC[235] | 0.1 M $KHCO_3$ | 24 h | -0.9 V *vs.* RHE | -2.9 | 82% | Site sites and pyridinic N |
| SE-Ni SAS@PNC[236] | 0.5 M $KHCO_3$ | 60 h | -1.0 V *vs.* RHE | -18.3 | 87.8% | single Ni sites and porous NC |
| (Cl, N)-Mn/G[237] | 0.5 M $KHCO_3$ | 12 h | -0.6 V *vs.* RHE | -10 | 97% | Modified Mn sites |
| $Bi-N_4$[238] | 0.1 M $NaHCO_3$ | 4 h | -0.5 V *vs.* RHE | -5.1 | 97% | $Bi-N_4$ |
| Pd-NC[239] | 0.5 M $NaHCO_3$ | 3.5 h | -0.5 V *vs.* RHE | [m]-0.55 | 55% | $Pd-N_4$ |
| $Y_1$/NC[240] | 0.5 M $KHCO_3$ | 12 h | -0.68 V *vs.* RHE | [m]-0.2 | 88.3% | Y SACs |
| $Sc_1$/NC[240] | 0.5 M $KHCO_3$ | 12 h | -0.68 V *vs.* RHE | [m]-0.18 | 81.3% | Sc SACs |
| $Ag_2$/G[241] | 0.5 M $KHCO_3$ | > 36 h | -0.7 V *vs.* RHE | -11.87 | 93.4% | $AgN_3$- $AgN_3$ |
| Cu-APC/$Pd_{10}Te_3$[242] | 0.2 M $KHCO_3$ | 3 h | -0.78 V *vs.* RHE | -8.6 (pcd) | 92% | $Cu_1^{0}$-$Cu_1^{x+}$ |
| $ZrO_2$/N-C[243] | 0.5 M $KHCO_3$ | 5 h | -0.4 V *vs.* RHE | -2.6 | 64% | $ZrO_2$ NPs |
| $Co_3O_4$-CDots-$C_3N_4$[244] | 0.5 M $KHCO_3$ | 30 h | -0.6 V *vs.* RHE | [m]-1.3 | 89% | $C_3N_4$ |
| CoPc/CNT(3.5%)[245] | 0.1 M $KHCO_3$ | 1 h | -0.63 V *vs.* RHE | -10 | 92% | - |
| Ni-NC_ATPA@C[246] | 0.5 M $KHCO_3$ | 24 h | -0.7 V *vs.* RHE | -6 | ~93% | Ni nanoparticles |

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|---|---|---|---|---|---|---|
| | | | | | | and N doping |
| CoPc-CN/CNT (3.5%)[232] | 0.1 M KHCO$_3$ | 1 h | -0.63 V *vs.* RHE | -15 | 98% | CNT and cyano-group |
| CoFPC/C[247] | 0.5 M NaHCO$_3$ | - | -0.8 V *vs.* RHE | $^{m}$-4.3 | 93% | CoFPC |
| FeOx/FePc[248] | 0.5 M KHCO$_3$ | 2 h | -0.40 V *vs.* RHE | $^{m}$-4.0 | 93.0±4.8 % | in situ formed FeO$_X$/E-FePc |
| CoTPP-CNT[249] | 0.5 M KHCO$_3$ | 4 h | -1.35 V *vs.* SCE | -3.2 | 91% | CoTPP |
| FeTPP-WSCAT[250] | 0.1 M KCl + 0.5 M KHCO$_3$ | | -0.52V *vs.* RHE | $^{m}$-1.0 | ca.92% | - |
| FePGF/CFP[251] | 0.1 M KHCO$_3$ | 10 h | -0.54 V *vs.* RHE | -1.68 | 98.7% | FePGF |
| CATpyr[252] | 0.5 M KHCO$_3$ | 12 h | -0.59 V *vs.* RHE | $^{m}$-0.24 | 93% | - |
| [Co(qpy)]$^{2+}$/CNT[253] | 0.5 M NaHCO$_3$ | 4.5 h | -0.45 V *vs.* RHE | -19.9 | 100% | [Co(qpy)]$^{2+}$ |
| FePGH-H[254] | 0.1 M KHCO$_3$ | 20 h | -0.39 V *vs.* RHE | -0.42 | 96.2 | FeTMAP |
| NiPor-CTF[255] | 0.5 M KHCO$_3$ | 20 h | -0.9 V *vs.* RHE | ~-52.9 | 97% | NiN$_4$ |
| CoPc@Fe-N-C[256] | 0.5 M KOH(flow cell) | 20 h | -0.84 V *vs.* RHE | -(275.6 ± 27.0)(pcd) | >90% | CoPc |
| (CoPc+Phenol)GDE[257] | 0.5 M KHCO$_3$(flow cell) | 100 h | 2.52 V | 200 | 88% | CoPc and Phenol |
| Co$^{II}$Pc-tsGQwire[258] | 0.5 M [Bmim]Tf2N MeCN | - | -2.1 V *vs.* Ag/Ag$^{+}$ | -11.5 | 82.4% | - |
| Ni-CTF[259] | 0.1 M KHCO$_3$ | 3 h | -0.8 V *vs.* RHE | $^{m}$-1 | 90% | CTF |
| ZIF-A-LD[260] | 0.1 M KHCO$_3$ | 10 h | -1.0 V *vs.* RHE | $^{m}$-3 | 90.57 | sp$^2$ C atoms |
| CoPP@CNT[261] | 0.5 M NaHCO$_3$ | 12 h | -0.6 V *vs.* RHE | -25.1 | 98.3% | CoPP |
| CoPc-Pyr[262] | 0.05 K$_2$CO$_3$ | 5 h | -0.7 V *vs.* RHE | -2.5 | 95% | - |
| POM-MnL[263] | 0.5 M KHCO$_3$ | 12 h | -0.72 V *vs.* RHE | $^{m}$-16 | 95% | MnL |
| Co@Pc/C[264] | 0.5 M KHCO$_3$ | 20 h | -0.9 V *vs.* RHE | -28(pcd) | 84% | Pyridinic N and Co NPs |
| Co-TTCOF[265] | 0.5 M KHCO$_3$ | 40 h | -0.7 V *vs.* RHE | -1.84(pcd) | 91.3% | TTF and Co porphyrin |

m: evaluated from the figures; pcd: partial current density

**Table 7.** $CO_2$RR performance of non-metal carbons with CO as the main product

| Catalysts | Electrolyte | Durability test | Potential | Current density | $FE_{CO}$ | Active sites |
|---|---|---|---|---|---|---|
| CNFs[266] | EMIM-$BF_4$ | 9 h | -0.573 *vs.* SHE | $^{m}$-3.5 | 98% | reduced carbons |
| NCNT-3-700[267] | 0.5 M $NaHCO_3$ | 60 h | -0.9V *vs.* RHE | -5 (pcd) | 90% | quaternary N |
| 3-DN-doped graphene foam[268] | 0.1 M $KHCO_3$ | 5 h | -0.58V *vs.* RHE | -1.82 | 85% | pyridinic N |
| Nano N-doped CNT[269] | 0.1 M $KHCO_3$ | 10 h | -0.8 V *vs.* RHE | -0.75 | 80% | pyridinic N |
| NCNTs-ACN-850[270] | 0.1 M $KHCO_3$ | - | -1.05 V *vs.* RHE | - | 80% | pyridinic N |
| Nitrogen-doped carbon[271] | 1 M KCl | - | -1.46 V *vs.* Ag/AgCl | -29.2 A/g | 98% | doped-N |
| 2D-pg-$C_3N_4$[272] | 2 M $KHCO_3$ | 35000s | -1.1V *vs.* Ag/AgCl | -3 | 80% | Polarized melem subunits |
| NDC-700[273] | 0.5 M $NaHCO_3$ | 72 h | -0.82 V *vs.* RHE | -6.6 (pcd) | 83.70% | pyridinic N |
| ZIF-CNT-FA-p[213] | 0.1 M $NaHCO_3$ | - | -0.66 V *vs.* RHE | -1.8 (pcd) | 97% | pyridinic N |
| ZIF-CNT-FA-p[213] | 0.1 M $NaHCO_3$ | - | -0.86 V *vs.* RHE | -7.7 (pcd) | 100% | pyridinic N |
| H-CNT[274] | 0.1 M $KHCO_3$ | 24000s | -0.5 V *vs.* RHE | $^{m}$-0.5 | 88% | pyrrolic nitrogen |
| NC-900[275] | 0.1 M $KHCO_3$ | 2 h | -0.93 V *vs.* RHE | -1.1 (pcd) | 78% | pyridinic N and quaternary N |
| F interlayer doped carbon (FC)[276] | 0.1 M $NaClO_4$ | - | -0.62 *vs.* RHE | $^{m}$-0.2 (pcd) | 89.6% | doped F |
| NF-C-950[277] | 0.1 M $KHCO_3$ | 40 h | -0.6 *vs.* RHE | -1.9 | 90% | Co-doped F and N |
| F-CPC[278] | 0.5 M $KHCO_3$ | 12 h | -1.0 *vs.* RHE | -37.5 | 88.3% | Cagelike structure |
| N-GRW[279] | 0.5 M $KHCO_3$ | 10 h | -0.6 *vs.* RHE | -15.4 A $g_{catalyst}^{-1}$ | 87.6% | pyridinic N |
| thermally-treated | 0.5 M $KHCO_3$ | 12 h | -0.68 *vs.* RHE | -1.2 (pcd) | 82% | pyridinic N |

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|---|---|---|---|---|---|---|
| triazine-based framework[280] | | | | | | |
| MNC-D[281] | 0.1 M KHCO$_3$ | 16 h | -0.58 *vs.* RHE | -6.8 | 92% | Pyridinic N and defects |
| CNPC-1100[282] | 0.1 M KHCO$_3$ | 8 h | -0.6 *vs.* RHE | -1.0 | 92% | N defects |
| NCNTs[283] | 0.5 M NaHCO$_3$ | 40 h | -0.8 *vs.* RHE | -20.2 | 95% | Pyridinic N defects |
| OA-PCN[284] | 0.5 M NaHCO$_3$ | 24 h | -0.66 *vs.* RHE | $^{m}$-0.8 | 40.1% | -OH and –NH$_2$ |
| NS-C-900[285] | 0.1 M KHCO$_3$ | 20 h | -0.6 *vs.* RHE | -2.63 | 92% | Co-doped S and N |
| D-NC-1100[286] | 0.1 M KHCO$_3$ | 10 h | -0.6 *vs.* RHE | $^{m}$-0.8 | 94.5% | C defects |
| NC-900-HH[287] | 0.5 M NaHCO$_3$ | 10 h | -0.5 *vs.* RHE | -0.4 | 90% | Pyridinic N |
| WNCNs-1000[288] | 0.1 M KHCO$_3$ | 8 h | -0.49 *vs.* RHE | $^{m}$-0.5 | 84% | Pyridinic N |
| Se-CNs[289] | 0.1 M KHCO$_3$ | 19 h | -0.6 *vs.* RHE | $^{m}$-9 | 90% | Doped Se |
| NC1100[290] | 0.5 M KHCO$_3$ | 20 h | -0.5 *vs.* RHE | $^{m}$-1 | 95.4% | Pyridinic N |
| 1D/2D NR/CS-900[291] | 0.5 M KHCO$_3$ | 30 h | -0.45 *vs.* RHE | $^{m}$-1 | 94.2% | Pyridinic N |
| NSHCF900[292] | 0.1 M KHCO$_3$ | 36 h | -0.7 V *vs.* RHE | -103 | 94% | Co-doped N and S |
| CPSN[293] | 0.1 M KHCO$_3$ | 27 h | -0.99 V *vs.* RHE | $^{m}$-3.2 | 11.3% | pyridinic N |
| S, N, Cl doped C[294] | 0.1 M KHCO$_3$ | 18 h | -0.6 *vs.* RHE | -1.98(pcd) | 95.9% | Co-doped N and Cl |
| NSCNW-3[295] | 0.1 M KHCO$_3$ | 20 h | -0.6 *vs.* RHE | -5.93(pcd) | 93.4% | 3D structure and doped S |
| NS-CNSs[296] | 0.5 M KHCO$_3$ | 20 h | -0.55 *vs.* RHE | $^{m}$-2.4(pcd) | 85.4% | Co-doped N and S |
| NPCA[297] | 0.5 M [Bmim]PF$_6$/MeCN | 24 h | 2.4 V *vs.* Ag/Ag$^+$ | -143.6(pcd) | 99.1% | Co-doped P and N |
| Silkcocoon derived carbons[298] | 0.1 M KHCO$_3$ | 10 days | -1.09 *vs.* RHE | -0.8(pcd) | 89% | Pentagon-containing |

| | | | | | | |
|---|---|---|---|---|---|---|
| | | | | | | defects |
| NDC-4[299] | 0.1 M $KHCO_3$ | - | -1.1 *vs.* RHE | - | 82% | Doped N |
| DHPC[300] | 0.5 M $KHCO_3$ | 25 h | -0.5 *vs.* RHE | [m]-1.2 | 99.5% | Mesoporous and carbon defect structure |
| NPC[301] | 0.5 M $KHCO_3$ | 18 h | -0.55 *vs.* RHE | -3.01 | 98.4% | Pyridinic and graphitic N |

m: evaluated from the figures; pcd: partial current density

**Table 8.** $CO_2RR$ performance of catalysts with HCOOH/$HCOO^-$ as the main product

| Catalysts | Electrolyte | Durability test | Potential | Current density/ mA $cm^{-2}$ | FE | Reference |
|---|---|---|---|---|---|---|
| Sn NPs/GDL | 0.5 M $NaHCO_3$ | - | -1.6 V *vs.* NHE | -27 | 70% | [302] |
| Sn/GDE | 0.5 M $KHCO_3$ | - | -1.8 V *vs.* Ag/AgCl | -17.43±2.6 | 78.60±0.11% | [303] |
| Sn(100 nm)/GDE | 0.5 M $KHCO_3$ | - | -1.6 V *vs.* SCE | $^{m}$-7.5 | ~80% | [304] |
| Sn quantum sheets confined in graphene | 0.1 M $NaHCO_3$ | 50 h | -1.8 V *vs.* SCE | -21.1 | 89% | [305] |
| Sn metal electrodes | $[Bimim]PF_6$(30wt %)/acetonitrile/$H_2O$ (5wt%) | - | -2.3 V *vs.* $Ag/Ag^+$ | -32 | 92% | [306] |
| 5nm reduced $SnO_2$ NPs/graphene | 0.1 M $NaHCO_3$ | - | -1.8 V *vs.* SCE | -10.2 | 86.2% | [307] |
| 5nm $SnO_2$/C | 0.1 M $KHCO_3$ | 12 h | -0.9V *vs.* RHE | $^{m}$-4 | 54.2% | [308] |
| Ultra-small $SnO_2$ | 1 M $KHCO_3$ | - | -1.21V *vs.* RHE | -145 | 64% | [309] |
| Sn-OH-5.9 | 1 M $KHCO_3$ | 60 h | -1.8 V *vs.* Ag/AgCl | $^{m}$-17 | 82.5% | [310] |
| Ov-N-$SnO_2$ | 0.1 M $KHCO_3$ | 12 h | -1.7V *vs.* SCE | $^{m}$-4.2 | 88% | [311] |
| Sn@MJKTs | 0.5 M $KHCO_3$ | 5 h | -0.9 V *vs.* RHE | -19.9 | 94% | [312] |
| Sn/CNT-Agls/CC | 0.5 M $KHCO_3$ | 2000 s | -0.96 V *vs.* RHE | -26.7 | 82.7% | [313] |
| Sn/$SnS_2$/rGO | 0.5 M $NaHCO_3$ | 14h | -1.4 V *vs.* Ag/AgCl | -11.75 (pcd) | 84.5% | [314] |
| $SnO_2$@n-pc | 0.5 M $[Bmim]PF_6$ | 5 h | -2.2 V *vs.* $Ag/Ag^+$ | -28.4 | 94.1% | [315] |
| SL-NG@Sn foil | 0.5 M $KHCO_3$ | 5 h | -1.0 V *vs.* RHE | -21.3(pcd) | 92% | [316] |
| CNT#$SnO_2$ DSs | 0.1 M $KHCO_3$ | 10 h | -0.9 V *vs.* RHE | $^{m}$-4 | 70% | [317] |

| | | | | | | |
|---|---|---|---|---|---|---|
| electrodeposited Sn | 0.1 M $KHCO_3$ | - | -1.4 V *vs.* SCE | -0.75 | 91.7% | 318 |
| Sn/$SnO_x$ thin-film | 0.5 M $NaHCO_3$ | - | -0.7 V *vs.* RHE | -(0.4-0.6) | 19.0% | 319 |
| Commercial Sn NPs | Catholyte-free | 48 h | 2.2 V (cell voltage) | -51.7 | 93.3% | 320 |
| $SnO_x$/Sn | 0.1 M $KHCO_3$ | - | 1.2 V | $^{m}$-3.0 | 64.0% | 321 |
| Sn/$SnO_x$ | 0.1 M $KHCO_3$ | 12 h | -1.2 V *vs.* RHE | -11.2 | 89.6% | 322 |
| $SnO_2$/0.14@N-rGO | 0.5 M $NaHCO_3$ | 20 h | -0.8 *vs.* RHE | -21.3 | 78±2% | 323 |
| Sigle-atom $Sn^{\delta+}$ on N-doped graphene | 0.25 M $KHCO_3$ | 200 h | -1.0 *vs.* SCE | $^{m}$-11.8 | 74.3% | 324 |
| $V_O$-$SnO_x$/CF-40 | 0.1 M $KHCO_3$ | 12 h | -1.0 *vs.* RHE | -36 | 86% | 325 |
| Sn dendrites | 0.1 M $KHCO_3$ | - | -1.36 V *vs.* RHE | -17.1 | 71.60% | 326 |
| Dendritic Sn/Cu | 0.5 M $KHCO_3$ | 20 h | -0.95 V *vs.* RHE | $^{m}$-13 | 67.3% | 327 |
| Sn-pNWs | 0.1 M $KHCO_3$ | 15 h | -0.8 V *vs.* RHE | $^{m}$-5.5 | 80.0% | 328 |
| Mesoporous $SnO_2$ | 0.1 M $KHCO_3$ | - | -1.15 V *vs.* RHE | -10.8 | 75% | 329 |
| Porous Sn foam | 0.1 M $KHCO_3$ | 55 h | -1.6 V *vs.* Ag/AgCl | $^{m}$-6 | 95.6% | 330 |
| $SnO_x$-300 | 0.5 M $KHCO_3$ | 18 h | -0.98 V *vs.* RHE | -15(pcd) | 88.6% | 331 |
| mp-$SnO_2$ | 0.5 M $NaHCO_3$ | 12 h | -0.9 V *vs.* RHE | $^{m}$ -14(pcd) | 83% | 332 |
| $SnO_2$ QWs | 0.1 M $KHCO_3$ | 25000 s | -1.156 V *vs.* RHE | -13.7 | 87.3% | 333 |
| $SnO_2$-NFs | 0.5 M $KHCO_3$ | 12 h | -1.0 V *vs.* RHE | -9.4(pcd) | 82.1% | 334 |
| $SnO_2$/CC | 0.5 M $NaHCO_3$ | 24 h | -0.8 V *vs.* RHE | -45(pcd) | 87±2% | 335 |
| SnOx@MWCNT-COOH | 0.5 M $KHCO_3$ | 20 h | -1.25V *vs.* SHE | $^{m}$ -9.5 | 77% | 336 |
| $SnS_2$/Aminated-C | 0.5 M $KHCO_3$ | 15 h | -0.9 V *vs.* RHE | 41.1(pcd) | 92.6% | 337 |

| | | | | | | |
|---|---|---|---|---|---|---|
| SnO 2NC@EEG | 0.1 M $KHCO_3$ | 10 h | -1.2 V *vs.* RHE | -13.03 | 81.2% | [338] |
| WIT $SnO_2$ | 0.1 M $KHCO_3$ | 14 h | -0.99 V *vs.* RHE | [m] -6.1 | 63% | [339] |
| FSP-$SnO_2$-5 | 0.1 M $KHCO_3$ | - | -1.1V *vs.* RHE | -23.7 | 85% | [340] |
| 5%Ni-$SnS_2$ | 0.1 M $KHCO_3$ | 8 h | -0.9 V *vs.* RHE | -19.6 | 80% | [341] |
| $BiO_x$ modified 2D $SnO_x$ | 0.5 M $KHCO_3$ | 10 h | -1.37 V *vs.* RHE | -45 | 90.8% | [342] |
| $SrSnO_3$ NWs | 0.5 M $NaHCO_3$ | 10 h | -1.3 V *vs.* RHE | -21.6(pcd) | 77.6% | [343] |
| $SnSe_2$@CC | 0.1 M $KHCO_3$ | 10 h | -0.76 V *vs.* RHE | -12.0(pcd) | 88.4% | [344] |
| $SnO_2$/PC | 0.5 M $KHCO_3$ | 10 h | -0.86 V *vs.* RHE | -29.0(pcd) | 92% | [345] |
| SL-NG@Sn foil | 0.5 M $KHCO_3$ | 5 h | -10 V *vs.* RHE | -21.3(pcd) | 92% | [316] |
| Cu/SnOx-CNT (30.2%) | 0.1 M $KHCO_3$ | - | -0.99 V *vs.* RHE | -4.0(pcd) | 77% | [346] |
| Cu@Sn nanocones | 0.1 M $KHCO_3$ | 10 h | -1.1 V *vs.* RHE | -57.7 | 90.4% | [347] |
| Cu@Sn electrodes | 0.5 M $KHCO_3$ | 15 h | -0.93 V *vs.* RHE | 16.52 | 100% | [348] |
| $Cu_6Sn_5$ | 0.1 M $KHCO_3$ | 6 h | -1.17 V *vs.* RHE | [m]-6 | 73% | [125] |
| Sn-Cu | 0.1 $KHCO_3$ | 12 h | -0.95 V *vs.* RHE | [m]-7 | 92% | [349] |
| $Cu_3Sn/Cu_6Sn_5$ | 0.1 $NaHCO_3$ | 42 h | -1.0 V *vs.* RHE | -18.9 | 82% | [350] |
| CuSn NWs/C-Air | 0.5 $KHCO_3$ | 10 h | -1.0 V *vs.* RHE | -17.33(pcd) | 90.2% | [351] |
| $Cu_{(1)}Sn_{(4)}$-N-CC | 0.5 $KHCO_3$ | 20 h | -0.97 V *vs.* RHE | -15.56(pcd) | 90.24% | [352] |
| Mn-doped $SnO_2$ | 0.1 $KHCO_3$ | 28400 s | -1.03V *vs.* RHE | -21.2(pcd) | ~85% | [353] |
| $Cu_3$NiOCs | 0.5 $KHCO_3$ | 25 h | -0.57 V *vs.* RHE | -10.9(pcd) | 95.9% | [354] |
| $Cu_2O$/CuO/CuS | 0.1 $KHCO_3$ | 2.5 h | -0.7 V *vs.* RHE | -20(pcd) | 84% | [355] |
| SW-$Cu_2O$/Cu(60 atm) | 0.5 $KHCO_3$ | 20 h | -0.64 V *vs.* RHE | -5.7(pcd) | 98.2% | [356] |

| | | | | | | |
|---|---|---|---|---|---|---|
| AgSn/$SnO_x$ core-shell | 0.5 M $NaHCO_3$ | 25 h | -0.8 V *vs.* RHE | -16(pcd) | 87.2% | [357] |
| Ag-$SnS_2$ | 0.5 $KHCO_3$ | 10 h | -1.0 V *vs.* RHE | -23.3(pcd) | 60.0% | [358] |
| $SnO_x$/$AgO_x$ | 0.1 M $KHCO_3$ | 20 h | -0.8 V *vs.* RHE | $^{m}$-3.5(pcd) | 21.1% | [359] |
| Cu-Sn/rGO | 0.5 M $NaHCO_3$ | 6 h | -0.99 V *vs.* RHE | -23.6 | 87.4% | [360] |
| $CuSn_3$ | 0.1 M $KHCO_3$ | 50 h | -0.5V *vs.* RHE | -33 | 95% | [361] |
| Bi-Sn | 0.5 M $KHCO_3$ | 100 h | -1.14 V *vs.* RHE | $^{m}$-55(pcd) | 94±2% | [362] |
| CdCu@Cu | 0.5 M $NaHCO_3$ | 12 h | -1.05 V *vs.* RHE | -30.5(pcd) | 70.5% | [363] |
| TNS-2.0-$SnO_2$ | 0.1 M $KHCO_3$ | 18 h | -1.6 V *vs.* RHE | -22.5 | 73% | [364] |
| $SnO_x$/Ag | 0.1 M $KHCO_3$ | 12 h | -1.0 V *vs.* RHE | $^{m}$-7.5 | 83% | [84] |
| GDE-In/C | 0.1 M $Na_2SO_4$ | 15 h | -1.65 V *vs.* Ag/AgCl | $^{m}$-8.5 | 45% | [365] |
| Pb | 0.1 M $K_2CO_3$ | - | -1.5 V *vs.* SCE | -4.4 | 95% | [366] |
| Pb cubic | 0.1 M $KHCO_3$ | - | -1.7 V *vs.* Ag/AgCl | -25 | 94.1%(278K) | [367] |
| roughed Pb | 0.1 M $KHCO_3$ | - | -0.96 V *vs.* RHE | -1.17(pcd) | 88% | [368] |
| OD-Pb | 0.5 M $NaHCO_3$ | 4.5 h | -0.7 V *vs.* RHE | -4.6 | ~90 | [369] |
| Pb meltal electrodes | [Bimim]$PF_6$(30wt%)/acetonitrile/$H_2O$ (5wt%) | 6 h | -2.3 V *vs.* Ag/$Ag^+$ | -37 | 91.6 | [306] |
| Pb-PhyA | [Bzmim]$BF_6$(12.8wt%)/ $H_2O$(9.9wt%) | 5 h | -2.25 V *vs.* Ag/$Ag^+$ | -30.5 | 92.7% | [370] |
| Porous Pb | 1.0 M $KHCO_3$ | 6 h | -0.99 V *vs.* RHE | -7.5 (pcd) | 97% | [371] |
| Pb QDDCs | 0.5 M $KHCO_3$ | 80 h | -0.2 V *vs.* RHE | -16 | 95% | [10] |
| SD-Pb | 1.0 M $KHCO_3$ | 2 h | -1.08 V *vs.* RHE | -12 (pcd) | 88% | [372] |
| SELF-CAT-Pb | $KHCO_3$ | 6 h | -1.2 V *vs.* RHE | -22 (pcd) | 90.5% | [373] |
| FD-PbNP/MWCNT/CPE | 0.5 M $KHCO_3$ | 10 h | -1.7 V *vs.* Ag/AgCl | -28 | 84.6% | [374] |
| PbS-150/C | 0.1 M $KHCO_3$ | 10 h | -1.2 V *vs.* RHE | -( 52.2 ± 5.2) mA $mg^{-1}$ | 97.6 ± 5.3% | [375] |

| | | | | | | |
|---|---|---|---|---|---|---|
| $Pb_{2.25}Pd_{3.75}$ | 0.5 M HCOOK | - | -1.5 V *vs.* Ag/AgCl | -5.6 (pcd) | 85% | [376] |
| 4-aminomethylbenzene modified Pb | 1 M $KHCO_3$ | 11 h | -1.09 V *vs.* RHE | -9.0 | >90% | [375] |
| Bi dendrite | 0.5 M $KHCO_3$ | 12 h | -0.74 V *vs.* RHE | -2.7 | 89% | [377] |
| Bi dendrite | 0.5 M $KHCO_3$ | - | -1.26 V *vs.* RHE | -68.51 ±4.04 (pcd) | ~100% | [378] |
| Bi nanoflack | 0.1 M $KHCO_3$ | 10 h | -0.60 V *vs.* RHE | $^{m}$-1.0 | ~100% | [379] |
| $BiO_x$/C | 0.5 M $NaHCO_3$/0.5 M $NaClO_4$ | - | -1.37 V *vs.* Ag/AgCl | $^{m}$-1.3 | 93.4% | [380] |
| Bi/GDE | 0.5M $KHCO_3$ | 20 h | -1.45 V *vs.* SCE | -1.5 (pcd) | 90% | [381] |
| BiOI derived Bi nanosheets | 0.5M $NaHCO_3$ | 10 h | -1.5 V *vs.* SCE | -15~16 | ~95% | [382] |
| $Bi_5O_7I$ | 0.5 M $KHCO_3$ | 18 h | -0.89 *vs.* RHE | -13.2 (pcd) | 89% | [383] |
| BiOBr derived 2D Bi | 0.1 M $KHCO_3$ | 65 h | -0.9 *vs.* RHE | $^{m}$-70 | >90% | [384] |
| BiOBr derived 2D Bi | 2.0 M $KHCO_3$ | - | - | -200 | 90% | [384] |
| Bi nanosheets(~10nm) | 0.5M $NaHCO_3$ | 5 h | -1.0 V *vs.* RHE | $^{m}$-13 | >90% | [385] |
| Defect-rich Bi derived from $Bi_2S_3$ | 0.5M $NaHCO_3$ | 24 h | -0.75 V *vs.* RHE | $^{m}$-5 | 84% | [386] |
| $Bi_2O_2CO_3$ nanosheets | 0.5M $NaHCO_3$ | 12 h | -0.7 V *vs.* RHE | -11 | 85% | [387] |
| $Bi_2O_2CO_3$ derived Bi | 0.1 M $KHCO_3$ | 100 h | -0.8 V *vs.* RHE | $^{m}$-6 | 95% | [388] |

| | | | | | | |
|---|---|---|---|---|---|---|
| nanosheets | | | | | | |
| Bi-based catalysts | 0.5 M $KHCO_3$ | 7 h | -1.0 V *vs.* RHE | -40 | >90% | 389 |
| Oxide containing Bi nanosheets | 0.5M $NaHCO_3$ | 10 h | -0.86 V *vs.* RHE | -30 (pcd) | 93 ± 2% | 390 |
| $Bi_2S_3$ derived Bi | 0.5M $NaHCO_3$ | 24 h | -0.75 V *vs.* RHE | -5 | 84% | 386 |
| Bi nanotubes | 0.5M $KHCO_3$ | 10 h | -1.0 V *vs.* RHE | -24 | ~95% | 5 |
| $Bi_2O_3$ derived nanotubes | 0.1M $KHCO_3$ | 48 h | -0.82V *vs.* RHE | ~-36 | ~98-100% | 391 |
| $Bi_2O_3$ NSs@MCCM | 0.1M $KHCO_3$ | 12 h | -0.956 V *vs.* RHE | ~-6 | ~76.3% | 392 |
| Bi nanostructure | 0.5M $KHCO_3$ | 30 h | -0.9 V *vs.* RHE | ~-13 | 90.74% | 393 |
| $Bi_2O_3$-NGQDs | 0.5M $KHCO_3$ | 15 h | -1.2 V *vs.* RHE | -29.4 (pcd) | >90% | 394 |
| $Bi_2O_3$/NCF | 0.5M $KHCO_3$ | 24 h | -1.0 V *vs.* RHE | $^{m}$-15 | 94% | 395 |
| f-$Bi_2O_3$/CNF | 0.1 M $KHCO_3$ | - | -1.2 V *vs.* RHE | -20.9 | 87% | 396 |
| $Bi_2O_3$@C-800 | 1M KOH(flow cell) | 6 h | -0.9 V *vs.* RHE | ~-150 | >93% | 397 |
| $Bi_2S_3$-$Bi_2O_3$@rGO | 0.1M $KHCO_3$ | 24 h | -0.9 V *vs.* RHE | $^{m}$-3.5 | >90% | 398 |
| Bi spheres | 0.5M $KHCO_3$ | 24 h | -0.9 V *vs.* RHE | ~-8 | 91% | 399 |
| Bi nanosheets | 0.5M $KHCO_3$ | 17 h | -0.97 V *vs.* RHE | -25 | 92.5% | 400 |
| Bismuthene@BP | 0.5M $KHCO_3$ | >75 h | -0.58 V *vs.* RHE | $^{m}$-16 | ~99% | 401 |
| Bi/rGO | 0.1 M $KHCO_3$ | 15 h | -0.8 V *vs.* RHE | $^{m}$-2 | 98% | 402 |
| Bi/Gr | 0.5M $KHCO_3$ | 30 h | -0.97 V *vs.* RHE | $^{m}$-20 | 92.1% | 403 |
| Bi@NPC | 0.1 M $KHCO_3$ | 20 h | -1.5 V *vs.* SCE | -14.4 (pcd) | 92% | 404 |
| Cu foam@BiNW | 0.5M $NaHCO_3$ | 12 h | -0.69 V *vs.* RHE | -~15 (pcd) | 95% | 405 |
| CuBi | 0.5M $KHCO_3$ | 10 h | -1.0 V *vs.* RHE | $^{m}$-20 | >80% | 406 |

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|---|---|---|---|---|---|---|
| Cu-Bi | 0.5M $NaHCO_3$ | 6 h | -0.93 V *vs.* RHE | $^{m}$-4.5 | 95% | [407] |
| Ag-Bi-S-O decorated Bi | 0.1 M $KHCO_3$ | 12 h | -0.7 V *vs.* RHE | -12.52 (pcd) | 94.3% | [408] |
| Bi decorated Sn nanosheets | 0.5M $KHCO_3$ | 100 h | -1.1 V *vs.* RHE | $^{m}$-55(pcd) | 96% | [362] |
| Bi doped SnO nanosheets | 0.1 M $KHCO_3$ | | -1.7 V *vs.* Ag/AgCl | -12 | 93% | [409] |
| Bi-MWCNT-COOH/Cu | 0.5 M $KHCO_3$ | 12 h | -0.76 V *vs.* RHE | -6~7 | 91.7% | [410] |
| Bi(btb) | 0.5 M $KHCO_3$ | 32 h | -0.97 V *vs.* RHE | -5.44 | 95.3% | [411] |
| $Pd_{70}Pt_{30}/C$ | 0.1 M $KH_2PO_4$/0.1 M $K_2HPO_4$ | - | -0.4 V *vs.* RHE | -5 | 88% | [412] |
| branched Pd NPs | 0.5 M $KHCO_3$ | - | -0.2 V *vs.* RHE | -22 | 97% | [413] |
| Pd interconnected nanosheets | 0.1 M NaCl | - | -0.31 V *vs.* RHE | -15 | 89% | [414] |
| Pd-B/C | 0.1 M $KHCO_3$ | 5 h | -0.5 V *vs.* RHE | $^{m}$-10 | 70% | [415] |
| Pd@Au (10nm thick Pd shells) | 0.1 M $Na_2SO_4$ | - | -0.5 V *vs.* RHE | $^{m}$-0.2 | 25% | [416] |
| $Pd/Cu_2O$-Cu NPs | 0.5 M $NaHCO_3$ | 3 h | -0.25 V *vs.* RHE | -4.2(pcd) | 92% | [417] |
| $Co_3O_4$ | 0.1 M $KHCO_3$ | 20 h | -0.88 V *vs.* SCE | -0.68 | 64.30% | [418] |
| $CoO_x/Co$ | 0.1 M $Na_2SO_4$ | 40 h | -0.85 V *vs.* SCE | -10.59 | 90.1% | [419] |
| Vo-rich $Co_3O_4$ | 0.1 M $KHCO_3$ | 40 h | -0.87 V *vs.* SCE | -2.7 | 87.6% | [420] |
| $CoO_x/ZrO_2$-graphite | 0.1 M $KHCO_3$ | 60 h | -0.35 V *vs.* RHE | -8.2 | 98.4% | [421] |
| Dendritic In foam | 0.5 M $KHCO_3$ | - | -0.86 V *vs.* SCE | -5.8 | 86% | [422] |

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|---|---|---|---|---|---|---|
| 3D hierarchical porous In | 0.1 M $KHCO_3$ | 24 h | -1.2 V *vs.* RHE | -33 | ~90% | [423] |
| O-$InO_x$ | 0.5 M $NaHCO_3$ | 20 h | -0.8 V *vs.* RHE | -7.8 | 90.2% | [424] |
| S doped In | 0.5 M $KHCO_3$ | 10 h | -0.98 V *vs.* RHE | $^{m}$-60 | 93% | [425] |
| Flowerlike $In_2S_3$ | ([Bmim][$PF_6$])/meCN-$H_2O$ | 10 h | -2.3 V *vs.* Ag/$Ag^+$ | -25.6(pcd) | 86% | [426] |
| In-$In_2S_3$ | 0.1 M $KHCO_3$ | 8 h | -1.0 V *vs.* RHE | $^{m}$-51 | 76% | [427] |
| $In_2O_3$-rGO | 0.1 M $KHCO_3$ | 10 h | -1.2 V *vs.* RHE | $^{m}$-22.5(pcd) | 84.6% | [428] |
| In-$TiO_2$ | 0.1 M KCl | - | -1.6 V *vs.* SCE | - | 86% | [429] |
| Sb nanosheets | 0.5 M $NaHCO_3$ | 12 h | -1.06 V *vs.* RHE | $^{m}$ -8 | ~84% | [430] |
| Cu-Zn alloys | 0.1 M $KHCO_3$ | - | -1.0 V *vs.* Ag/AgCl | $^{m}$-0.5 | 71.1% | [431] |
| In-Sn alloy NPs | 0.1 M $KHCO_3$ | 12 h | -1.1 V *vs.* SCE | $^{m}$-7 | 78.6% | [432] |
| $Sn_{56.3}Pb_{43.7}$ | 0.5M $KHCO_3$ | 2 h | -2.0 V *vs.* Ag/AgCl | -45.7(pcd) | 79.8% | [433] |
| Cu-In(80 at% In) | 0.1 M $KHCO_3$ | - | -1.0 V *vs.* RHE | $^{m}$-0.52(pcd) | 62% | [434] |
| $In(OH)_3$-$Cu_2O$ | 0.1 M $KHCO_3$ | 12 h | -0.8 V *vs.* RHE | $^{m}$-6.8(pcd) | 90.37% | [435] |
| In-Zn NCs | 0.5M $KHCO_3$ | 2 h | -1.2 V *vs.* RHE | -22 | 95% | [436] |
| Coralline $Ag_{65}Cu_{35}$ | 0.1 M $KHCO_3$ | 10 h | -1.0 V *vs.* RHE | 18.3 | 91.8% | [141] |
| Amorphous Cu NPs | 0.1 M $KHCO_3$ | 12 h | -1.4 V *vs.* Ag/AgCl | $^{m}$-12 | 37% | [437] |
| Cu fiber felt | 0.1 M $KHCO_3$ | 390 min | -1.1 V *vs.* RHE | $^{m}$-5 | 71.1±3.1% | [438] |
| Cu, Cd/Cu (300 nm) | 0.5 M $KHCO_3$ | 20000 s | -1.8 V *vs.* Ag/AgCl | -10.6 | 76.2% | [439] |
| S-modified Cu | 0.1 M $KHCO_3$ | - | -0.8 V *vs.* RHE | -28 | 80% | [440] |
| $CuS_x$ | 0.1 M $KHCO_3$ | - | -0.9 V *vs.* RHE | -9 | 75% | [441] |
| S-doped $Cu_2O$-derived Cu | 0.1 M $KHCO_3$ | 12 h | -0.8 V *vs.* RHE | $^{m}$-11(pcd) | ~75% | [442] |
| S-doped Cu | 0.1 M $KHCO_3$ | 12 h | -0.9 V *vs.* RHE | -12.3(pcd) | 76.5% | [443] |

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|---|---|---|---|---|---|---|
| based catalyst | | | | | | |
| $Cu_2S$ | 0.1 M $NaHCO_3$ | 9 h | -0.9 V *vs.* RHE | -19.1(pcd) | 87.3% | 444 |
| MOF-derived Cu dendrites | $[Bmim]PF_6$(0.5 M)/MeCN/$H_2O$(1 M) | - | -1.85 V *vs.* $Ag/Ag^+$ | -102.1 | 98.2% | 445 |
| Cu/Au | 0.5 M $KHCO_3$ | 4 h | -0.6 V *vs.* RHE | -10.4(pcd) | 81% | 446 |
| G-$Cu_xO$-2h | 0.5 M $KHCO_3$ | 9 h | -0.8 V *vs.* RHE | -19.3 | 81% | 447 |
| MoP@In-PC | $[Bmim]PF_6$(30 wt%)/MeCN/$H_2O$(5 wt%) | 6 h | -2.2 V *vs.* $Ag/Ag^+$ | -43.8 | 96.5% | 448 |
| Dendritic Cu foam | $[Bimim]BF_6/H_2O$ (8wt%) | - | -1.55 V *vs.* $Fc^+/Fc$ | -6.5 | 83% | 449 |
| Cu foam(60 s) | 0.5 M $NaHCO_3$ | - | -1.5 V *vs.* Ag/AgCl | -10 | 37% | 450 |
| $Cu_xO$/Cu | 0.5 M $KHCO_3$ | 20 h | -1.1 V *vs.* SCE | -10 | ~62% | 451 |
| Cu nanoflower | 0.1 M $KHCO_3$ | 9 h | -1.0 V *vs.* RHE | -21 | 26% | 452 |
| $Cu_2O$/Cu@NC-800 | 1 M $KHCO_3$ | 30 h | -0.68 V *vs.* RHE | -4.4 | 70.5% | 453 |
| CuO STNW | 0.5 M $KHCO_3$ | 7200 s | -1.2 V *vs.* Ag/AgCl | -6 | $^m$55% | 454 |
| (7nm)Cu/p-NG | 0.5 M $KHCO_3$ | 12 h | -0.90 V *vs.* RHE | -7.7A/g | 65% | 455 |
| Pt-NPs@NCNFs@CC | 0.1 M $KHCO_3$ | 30 h | -0.50 V *vs.* RHE | -40 | 91% | 456 |
| HNCM/CNT | 0.1 M $KHCO_3$ | 35 h | -0.80 V *vs.* RHE | $^m$-2.15 | 81% | 457 |
| PEI-NCNT | 0.1 M $KHCO_3$ | 24 h | -1.8 V *vs.* SCE | -7.2 | 85% | 458 |
| Nitrogen-doped graphenes | 0.5 M $KHCO_3$ | 12 h | -0.84 V *vs.* RHE | -7.5 | 73% | 459 |
| Boron-doped graphene | 0.1 M $KHCO_3$ | - | -1.4 V *vs.* SCE | $^m$-2.25 | 66% | 460 |
| Boron-doped | 0.5 M KCl | 24 h | $^m$-2.3 V *vs.* Ag/AgCl | -2 | 94.7% | 461 |

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| diamond (BDD) | | | | | | |
| BCN-40 | 0.1 M $KHCO_3$ | - | -0.3 V *vs*. RHE | [m]-0.36 | 83.5% | [462] |
| N-C61-800 | 0.5 M $KHCO_3$ | | -0.9 V *vs*. RHE | [m]-11(pcd) | 91.2% | [463] |
| Activated wood | 0.5 M $KHCO_3$ | 24 h | -1.8 V *vs*. SCE | -53.8 | 70.8% | [464] |

**Table 9.** $CO_2$RR performance over materials with alcohols as the main product

| Catalysts | Electrolyte | Durability test | Potential | Current density/ mA $cm^{-2}$ | Products | FE | Reference |
|---|---|---|---|---|---|---|---|
| Mo electrode | 0.2 M $Na_2SO_4$ | - | -0.8 V *vs.* SCE | -0.12 | $CH_3OH$ | 84% | 465 |
| $RuO_2$+$TiO_2$ (35+65 m/o) | 0.05 M $H_2SO_4$ | - | -0.9 V *vs.* $Hg_2SO_4$ | -0.52 | $CH_3OH$ | 24% | 466 |
| Ru | 0.5 M $NaHCO_3$ | 8 h | -0.8 V *vs.* SCE | $^{m}$-0.055 | $CH_3OH$ | 17.2 | 467 |
| Cu atom modified Ru | 0.5 M $NaHCO_3$ | 8 h | -0.8 V *vs.* SCE | $^{m}$-0.045 | $CH_3OH$ | 41.3% | 344 |
| $Cu_2O$ | 0.5 M $KHCO_3$ | - | -1.1 V *vs.* SCE | - | $CH_3OH$ | 38% | 468 |
| 20% Cu (3-60 nm)/CNT | 0.5 M $NaHCO_3$ | 6000 s | -1.7 V *vs.* SCE | $^{m}$-16 | $CH_3OH$ | 38.5% | 469 |
| Cd atom modified Ru | 0.5 M $NaHCO_3$ | 8 h | -0.8 V *vs.* SCE | $^{m}$-0.05 | $CH_3OH$ | 38.2% | 344 |
| $RuO_2$/B-doped diamond | 0.4 M Britton-Robinson solution | - | -0.8 V *vs.* SCE | $^{m}$ -0.65 | $CH_3OH$ | 8.12% | 470 |
| [PYD]@Cu-Pt | 0.5 KCl | 22 h | -0.6 V *vs.* SCE | -22 | $CH_3OH$ | 37% | 471 |
| V-doped $In_2O_3$ NCs | 0.1 M $KHCO_3$ |  | -0.83V *vs.* RHE | $^{m}$ -2 | $CH_3OH$ | 15.8% | 472 |
| $RuO_2$/$TiO_2$ NTs/Pt | 0.5 M $NaHCO_3$ | - | -0.8 V *vs.* SCE | $^{m}$-1.05 | $CH_3OH$ | 60.50% | 473 |
| $RuO_2$/$TiO_2$ NPs/Pt | 0.5 M $NaHCO_3$ | - | -0.8 V *vs.* SCE | -0.45 | $CH_3OH$ | 40.20% | 345 |
| [PYD]@Pd | 0.5 M KCl | 15 h | -0.6 V *vs.* SCE | $^{m}$-30 | $CH_3OH$ | 35% | 474 |
| Pd-Cu bimetallic aerogel | 25 mol% $[Bimim]BF_6$/ 75 mol % $H_2O$ | 24 h | -2.1 V *vs.* Ag/$Ag^+$ | $^{m}$-31.8 | $CH_3OH$ | 80.0% | 475 |
| Mo-Bi BMC/CP | 0.5 M | 5 h | -0.7 V *vs.* SHE | -12.1 | $CH_3OH$ | 71.2% | 476 |

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|---|---|---|---|---|---|---|---|
| | [Bimim]BF$_6$/MeCN | | | | | | |
| Cu$_2$O$_{(OL-MH)}$/Ppy LT paper | 0.5 M KHCO$_3$ | 15 h | -0.85 V *vs.* RHE | $^{m}$-0.14 | CH$_3$OH | 93±1.2% | 477 |
| Cu$_{1.63}$Se(1/3) | [Bimim]PF$_6$(30wt%)/MeCN/H$_2$O(5wt%) | | -2.1 V *vs.* Ag/Ag$^+$ | -41.5 | CH$_3$OH | 77.6% | 478 |
| 2-pyridinethiol@Pt-Au NPs | 0.1 M KNO$_3$ | 20 h | -0.2 V *vs.* Ag/AgCl | - | CH$_3$OH | 39% | 479 |
| PD-Zn/Ag | 0.1 M KHCO$_3$ | - | ~-1.4 V *vs.* RHE | -2.7(pcd) | CH$_3$OH | 10.5% | 480 |
| FeP NA/TM | 0.5 M KHCO$_3$ | 36 h | -0.2 V *vs.* RHE | $^{m}$-1.5 | CH$_3$OH | 80.2% | 481 |
| PD-Zn/Ag foam | 0.1 M KHCO$_3$ | 8 h | -1.38 V *vs.* RHE | -2.1(pcd) | CH$_3$OH | 8.1% | 481 |
| Pt$_x$Zn/C | 0.1 M NaHCO$_3$ | 16 h | -0.9 V *vs.* RHE | $^{m}$-0.4 | CH$_3$OH | 81.4% | 482 |
| Cu$_{63.9}$Au$_{36.1}$/NCF | 0.5 M KHCO$_3$ | - | -1.1 V *vs.* SCE | $^{m}$-0.025 | CH$_3$OH | 15.90% | 483 |
| CoPc-NH$_2$/CNT | 0.1 M KHCO$_3$ | 12 h | -1.0 V *vs.* RHE | -10.2(pcd) | CH$_3$OH | 32% | 484 |
| BP NPs | 0.1 M KHCO$_3$ | 18 h | -0.5 V *vs.* RHE | $^{m}$-0.16 | CH$_3$OH | 92% | 485 |
| Cu$_{0.8ML}$/THH Pd NCs | 0.1 M NaHCO$_3$ | - | -0.46 V *vs.* RHE | $^{m}$-0.08 | CH$_3$OH | 19.50% | 486 |
| CuSAs/TCNFs | 0.1 M KHCO$_3$ | 50 h | -0.9 V *vs.* RHE | $^{m}$-41(pcd) | CH$_3$OH | 44% | 487 |
| Cu/TiO$_2$/NG | 0.2 M KI | 20 h | -0.75V *vs.* RHE | -0.625 | C$_2$H$_5$OH | 43.6% | 488 |
| c-NC | 0.1 M KHCO$_3$ | 24 h | -0.56 V *vs.* RHE | $^{m}$-1.0 | C$_2$H$_5$OH | 77% | 489 |
| BND3 | 0.1 M NaHCO$_3$ | 48 h | -1.0 V *vs.* RHE | $^{m}$-0.7 | C$_2$H$_5$OH | 93.20% | 490 |
| Ag-G-NCF | 0.1 M KHCO$_3$ | 10 h | -0.6 V *vs.* RHE | $^{m}$-0.1 | C$_2$H$_5$OH | 85.2% | 491 |
| phase-blended Ag-Cu$_2$O | 0.2 M KCl | - | -1.2 V *vs.* RHE | $^{m}$-3.0 | C$_2$H$_5$OH | 34.15% | 492 |
| OD-Ag$_{15}$Cu$_{85}$ Foam | 0.5 M KHCO$_3$ | 100 h | -1.0 V *vs.* RHE | -8.67(pcd) | C$_2$H$_5$OH | 33.7% | 493 |
| Cu electrode | 0.1 M KCl | - | -1.44 V *vs.* NHE | -5 | C$_2$H$_5$OH | 21.9% | 494 |

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|---|---|---|---|---|---|---|---|
| Amorphous Cu NPs | 0.1 M $KHCO_3$ | 12 h | -1.4 V *vs.* Ag/AgCl | $^{m}$-12 | $C_2H_5OH$ | 22% | 437 |
| CuO-FC | 1 M KOH(flow cell) | - | -1.0 V *vs.* RHE | -127.2 | $C_2H_5OH$ | 35.7% | 495 |
| $Cu_4Zn$ | 0.1 M $KHCO_3$ | 5 h | -1.05 V *vs.* RHE | -8.2(pcd) | $C_2H_5OH$ | 29.1% | 496 |
| Ag/Cu | 1 M KOH(flow cell) | - | -0.67 V *vs.* RHE | -250 | $C_2H_5OH$ | 41% | 497 |
| $Ce(OH)_x$-doped-Cu | 1 M KOH(flow cell) | 6 h | -0.7 V *vs.* RHE | -128(pcd) | $C_2H_5OH$ | 43% | 498 |
| Cu/NPC-800 | 0.2 M $KHCO_3$ | 10 h | -1.05 V *vs.* RHE | $^{m}$-6(pcd) | $C_2H_5OH$ | 64.6% | 499 |
| Cu GNC-VL | 0.5 M $KHCO_3$ | 12 h | -0.87 V *vs.* RHE | -10.4 | $C_2H_5OH$ | 70.52% | 500 |
| GO-VB6-Cu | 0.1 M $KHCO_3$ | 24 h | -0.25 V *vs.* RHE | -4.571 | $C_2H_5OH$ | 56.3% | 501 |
| N-C/Cu | 1 M KOH | 15 h | -3.67 V | -(156±3)(pcd) | $C_2H_5OH$ | 52±1% | 502 |
| N-NC/Cu | 0.5 M $KHCO_3$ | 120 h | -0. 5 V *vs.* RHE | 84.9 A $g_{Cu}^{-1}$ | $C_2H_5OH$ | 28.9% | 503 |
| $Ni_2Al$ film | 0.1 M $K_2SO_4$ | 4-5 d | -1.38 V *vs.* Ag/AgCl | -2.1 | n-propanol | 1.9% | 504 |
| Cu electrode | 0.1 M KCl | - | -1.44 V *vs.* NHE | -5 | n-propanol | 3.6% | 494 |
| Cu electrode | 0.1 M $KClO_4$ | - | -1.40 V *vs.* NHE | -5 | n-propanol | 4.2% | 494 |
| Cu nanocrystal | 0.1 M $KHCO_3$ | 6h | -0.95 V *vs.* RHE | -1.74pcd | n-propanol | 8.8% | 505 |
| Plasma-oxidized Cu | 0.3 M KI +0.1 M $KHCO_3$ | - | -1.0 V *vs.* RHE | $^{m}$-59 | n-propanol | 7% | 506 |

**Table 10.** $CO_2$RR performance on Cu related materials with hydrocarbons as the main products

| Catalyst | Electrolyte | Durability test | Potential | Current density/ mA cm$^{-2}$ | FE/$CH_4$ | FE/$C_2H_4$ | FE/$C_2H_6$ |
|---|---|---|---|---|---|---|---|
| Cold-rolled Cu[507] (99.9%) | 0.5 M $KHCO_3$ | - | -2.29 V *vs.* SCE | -38 | 33% | - | - |
| In situ deposited Cu[508] | 0.5 M $KHCO_4$ + $5\times10^{-4}$ M $CuSO_4$ | - | - | -8.3 | 73% | 25% | - |
| Cu electrode[494] | 0.1 M $KHCO_3$ | - | -1.41 V *vs.* NHE | -5 | 29.4% | 30.1% | - |
| Cu electrode[494] | 0.1 M KCl | - | -1.44 V *vs.* NHE | -5 | 11.5% | 47.8% | - |
| Cu(100)[509] | 0.1 M $KHCO_3$ | - | -1.39V *vs.* SHE | -5 | CE: 19.8% | 40.7% | - |
| Cu(100)[510] | 0.1 M $KHCO_3$ | - | -1.4 V *vs.* SHE | -5 | CE: 30.4% | 40.4% | - |
| Electropolished Cu surface[511] | 0.1 M $KClO_4$ | - | -1.1 V *vs.* RHE | - | 5% | 14% | - |
| $Cu_2O$-derived Cu electrode[512] | 0.1 M $KHCO_3$ | - | -0.98 V *vs.* RHE | $^{m}$-10pcd |  | 32.4% |  |
| Oxide-derived Cu[513] | 0.1 M $KHCO_3$ | 5 h | -1.0 V *vs.* RHE | -10.9 |  | 34% |  |
| Cu foil[514] | 0.3 KI + 0.1 M $KHCO_3$ | - | -1.0 V *vs.* RHE | $^{m}$-12 | $^{m}$58% | $^{m}$22% | - |
| Polycrystalline Cu[515] | 0.1 M $KHCO_3$ | - | m-1.41 V *vs.* NHE | $^{m}$-14.5 | $^{m}$70% | $^{m}$15% | - |
| CuCl-confined Cu[516] | 4 M KCl | - | -1.8 V *vs.* Ag/AgCl | -(16.9~13.6) | - | 69.5% | - |
| CuCl derived Cu[517] | 0.1 M $KHCO_3$ | - | -1.06 V *vs.* RHE | -14.8 (pcd for $C_2H_4$) |  | 37% | - |
| CuBr-confined | 3 M KBr | - | -2.4 V *vs.* Ag/AgCl | -(46.1~39.2) | - | 79.5% | - |

|  |  |  |  |  |  |  |  |
|---|---|---|---|---|---|---|---|
| Cu mesh electrode[518] |  |  |  |  |  |  |  |
| Glycine-modified Cu foil[519] | 0.1 M $KHCO_3$ | - | -1.9 V *vs.* Ag/AgCl | -2.1(pcd) | 32.1% | 24.0% | - |
| Hydrophobic Cu dendrites[520] | 0.1 M $CsHCO_3$ | 5 h | -1.1~-1.5 V *vs.* RHE | -30 | - | 56% | - |
| Truncated-octahedral $Cu_2O$ NPs[521] | 0.5 M $KHCO_3$ | 2 h | -1.1 V *vs.* RHE | -23.1(pcd) | - | 59% | - |
| MOF-derived Cu clusters[522] | 1 M KOH | - | -1.07 V *vs.* RHE | -269 |  | 45% |  |
| B-doped Cu[523] | 0.1 M KCl | 40 h | -1.0 V *vs.* RHE | -70 |  | 53±1% |  |
| OFn-Cu[524] | 1 M $KHCO_3$ |  | -1.05 V *vs.* RHE | -36.24 | 60.6% | - | - |
| $Cu_2O$@Cu-MOF[525] | 0.1 M $KHCO_3$ | 1 h | -1.71 V *vs.* RHE | -8.4(pcd) | 63.2% | - | - |
| $Cu_2O$/Cu[526] | 0.1 M $KHCO_3$ | 24 h | -0.9 V *vs.* RHE | -26.2 | - | $^{m}$20% | $^{m}$30% |
| Cu-Ag[527] | 0.1 M $KHCO_3$ | 12 h | -1.05 V *vs.* RHE | -18.07 (pcd for $C_2H_4$) | - | 52% | - |
| Cu oxide/ZnO GDE[528] | 0.1 M $KHCO_3$ | - | -2.5 V *vs.* Ag/AgCl | -7.5 | - | 91.1% | - |
| Hydroxide-mediated Cu[529] | 10 M KOH | 150 h | -0.55 V *vs.* RHE | -275 |  | 70% |  |
| $Cu_2O$[530] | 0.5 M $KHCO_3$ | 2 h | -1.9 V *vs.* Ag/AgCl | -10 |  | 22% |  |
| Coral-like Cu NPs[531] | 0.1 M $KHCO_3$ | 15 h | -1.1 V *vs.* RHE | -25.2 | - | $^{m}$45% | - |
| $O_2$ plasma oxidized Cu[532] | 0.1 M $KHCO_3$ | - | -0.9 V *vs.* RHE | $^{m}$-14 |  | 60% |  |
| [110] oriented | 0.1 M $KHCO_3$ | 5 h | -1.1 V *vs.* RHE | $^{m}$-12.5 | - | $^{m}$32.5% | - |

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|---|---|---|---|---|---|---|---|
| $Cu_2O$-derived nanoparticles[533] | | | | | | | |
| Multihollow $Cu_2O$[534] | 2 M KOH (flow cell) | 3 h | -0.61 V *vs.* RHE | $^{m}$-360 | - | 38±1.4% | - |
| Multi-shelled CuO microboxes[535] | 0.1 M $K_2SO_4$ | 10 h | -1.05 V *vs.* RHE | -27.7 | - | 51.3% | - |
| Cu particles supported on glassy carbon n-Cu/C[536] | 0.1 M $NaHCO_3$ | - | -1.35 V *vs.* RHE | $^{m}$-9.5 | 76% | - | - |
| Cu catalysts[537] | 1 M $KHCO_3$(flow cell) | 22 h | $^{m}$-1.0 V *vs.* RHE | -108 ± 5(pcd) | 48 ± 2 | - | - |
| 44 nm Cu NCs[538] | 0.1 M $KHCO_3$ | - | -1.1 V *vs.* RHE | $^{m}$-5.6 | | 41% | |
| Cu nanocubes (70 nm)[539] | 10 M KOH (flow cell) | 3 h | -0.8 V *vs.* RHE | 144(pcd) | - | 60% | - |
| Cu cubes[540] | 1 M KOH (flow cell) | - | -0.75 V *vs.* RHE | -300 | - | 57% | - |
| Densily packed Cu NPs[541] | 0.1 M $KHCO_3$ | 10 h | -0.73 V *vs.* RHE | $^{m}$-20 | - | m26% | - |
| Prism shaped Cu[542] | 0.1 M $KHCO_3$ | 12h | -1.1 V *vs.* RHE | -28.6 | | 27.8% | |
| Cu NPs/N-doped carbon frameworks[543] | 0.1 M $KHCO_3$ | 24 h | -1.0 V *vs.* RHE | $^{m}$-50 | | 63.7±1.4% | |
| $Cu_2O$/NCS[544] | 0.1 M $KHCO_3$ | 4 h | -1.3 V *vs.* RHE | $^{m}$-10 | - | 24.7% | - |
| $Cu_2O$/NRGO[545] | 0.1 M $KHCO_3$ | 10000 s | -1.4 V *vs.* RHE | -12 | - | 19.7% | - |
| $Cu_2O$/ILGS-100[546] | 0.1 M $KHCO_3$ | 6000 s | -1.15 V *vs.* RHE | $^{m}$-12 | - | 31.1% | - |

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|---|---|---|---|---|---|---|---|
| Cu$_2$O NP/C[547] | 0.1 M KHCO$_3$ | 6 h | -1.1 V *vs.* RHE | $^{m}$-17.5 | 1.9% | 57.3% | - |
| Cu-N-C-900[548] | 0.1 M KHCO$_3$ | 10 h | -1.6 V *vs.* RHE | -14.8(pcd) | 38.6% | - | - |
| P-ED-Cu[549] | 0.5 M NaHCO$_3$ | 2.5 h | -2.8 V *vs.* SCE | -38(pcd) | 85% | | |
| Cu(2)GO/GC[550] | 0.1 M NaHCO$_3$ | 2 h | -1.3 V *vs.* RHE | -4.6 | 43.6% | | |
| Pd@Cu NCs[551] | 0.25 K$_2$CO$_3$ | 4000 s | -1.4 V *vs.* Ag/AgCl | -14.2 | $^{m}$45% | $^{m}$6% | |
| Pd@Cu NCs[551] | 0.25 K$_2$CO$_3$ | 4000 s | -1.4 V *vs.* Ag/AgCl | -33.6 | $^{m}$58% | $^{m}$16% | |
| Glycine-modified Cu NWs[519] | 0.1 M KHCO$_3$ | 14 h | -1.9 V *vs.* Ag/AgCl | -11 | | 6.7% | 13% |
| CTF-Cu-4.8% | 0.3 M KCl | 10 h | -1.51 V *vs.* SHE | -44.5 mA mg$^{-1}$ | $^{m}$60% | $^{m}$20% | - |
| Polycrystalline Cu[552] | 0.1 M KHCO$_3$+10 mM N-aryl pyridinium salt) | 43 h | -1.15 V *vs.* RHE | -6.4 | - | 40% | - |
| Cu NWs[553] | 0.1 M KHCO$_3$ | 6 h | -1.3 V *vs.* RHE | $^{m}$-12.5 | $^{m}$6.2% | 12% | |
| Cu NNs | 0.1 M KHCO$_3$ | 6 h | -1.2 V *vs.* RHE | $^{m}$-17 | 14.3% | $^{m}$6% | |
| Cu-DAT wire[554] | 1 M KOH(flow cell) | - | -0.5 V *vs.* RHE | $^{m}$-124 | - | 40% | |
| Cu-Ag alloy DAT wire[555] | 1 M KOH(flow cell) | - | -0.7 V *vs.* RHE | -300 | | 60% | |
| CuSn-DAT[556] | 1 M KOH(flow cell) | - | -0.8 V *vs.* RHE | -225 | - | 40% | |
| Ag/Cu[557] | 0.1 M KHCO$_3$ | 30 h | -1.1 V *vs.* RHE | -5.9 | - | 42% | - |
| Anodized Cu[558] | 0.1 M KHCO$_3$ | 40 h | -1.08 V *vs.* RHE | $^{m}$-7.3 (pcd) | | 38.1% | |
| Dendritic Cu[559] | 0.1 M KBr | 2.5 h | -1.9 V *vs.* Ag/AgCl | -170 | - | 57% | |
| Honeycomb Cu(VII)[560] | 0.1 M KHCO$_3$ | - | -1.9 V *vs.* Ag/AgCl | - | - | CE.m12% | CE.m2.5% |
| Oxide-derived foam Cu[561] | 0.5 M KHCO$_3$ | - | -0.9 V *vs.* RHE | $^{m}$-23 | - | $^{m}$15% | $^{m}$40% |

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|---|---|---|---|---|---|---|---|
| mesopore Cu[562] | 0.1 M KHCO$_3$ | - | -1.7V *vs.*NHE | -14.3 | - | - | 46% |
| CuO-derived Cu NRAs[563] | 0.1 M KHCO$_3$ | 5400 s | -0.816 V *vs.* RHE | [m]-12.5 | - | 23% | 7% |
| Nanopore modified Cu [564] | 0.1 M KHCO$_3$ | 8 h | -1.3 V *vs.* RHE | -45 | - | 35% | - |
| Plasma-oxidized Cu[506] | 0.3 KI + 0.1 M KHCO$_3$ | - | -1.0 V *vs.* RHE | [m]-59 | - | 47.6% | - |
| Cu$_2$O[565] | 0.1 M KHCO$_3$ | - | -0.99 V *vs.* RHE | -35 | - | 34.26% | - |
| Cu$_2$(OH)$_3$Cl[566] | 0.1 M KHCO$_3$ | - | -1.2 V *vs.* RHE | -22(pcd) (C$_2$H$_4$) | - | 38% | - |
| Cu based catalyst with Cu$_4$O$_3$ particles[567] | 0.5 M Cs$_2$SO$_4$ | 24 h | -0.64 V *vs.* RHE | -300 | - | 43% | - |
| CuCl-based electrode[517] | 0.1 M KHCO$_3$ | 6 h | -1.06 V *vs.* RHE | -14.8(pcd) (C$_2$H$_4$) | - | 37% | - |
| Cu-on Cu$_3$N[246] | 0.1 M KHCO$_3$ | 30 h | -0.95 V *vs.* RHE | -14(pcd) for C$_2$H$_4$, C$_2$H$_5$OH, and C3H$_7$OH | - | 39±2% | - |
| Cu$_3$N NCs[568] | 0.1 M KHCO$_3$ | 20 h | -1.6 V *vs.* RHE | -34 A/g | - | 60% | - |
| Cu$_3$N-derived Cu[569] | 0.1 M CsHCO$_3$ | - | -1.0 V *vs.* RHE | ~18.5 | - | 33% | ~20% |
| Cu$_3$Pd[94] | 0.1 M KHCO$_3$ | - | -1.2 V *vs.* RHE | -3.8(pcd) | 40.6% | - | - |
| PdCl/Cu$_2$O-Derived Cu[570] | 0.1 M KHCO$_3$ | 12 h | -1.0 V *vs.* RHE | [m]-17 | - | 3.4% | 30.1% |
| 3MLCu/ZnO[571] | 0.1 M KHCO$_3$ | - | -1.4 V *vs.* Ag/AgCl | [m]-12 | - | [m]10.2% | - |
| Cu$_{4.16}$CeO$_2$[572] | 0.1 M KHCO$_3$ | 6 h | -1.1 V *vs.* RHE | -3.2 | ~10% | 47.6% | |
| Cu-substituted | 0.1 M KHCO$_3$ | 8000s | -1.8 V *vs.* RHE | -70 | 58% | - | - |

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|---|---|---|---|---|---|---|---|
| $CeO_2$(4%)[227] | | | | | | | |
| Cu/$CeO_{2-x}$ hterodimers[573] | 0.1 M $KHCO_3$ | - | -1.2 V *vs.* RHE | - | 54% | - | - |
| $La_2CuO_4$[574] | 1 M KOH(flow cell) | - | -1.4 V *vs.* RHE | 117(pcd) | 56.3% | - | - |
| NGQDs[575] | 1 M KOH | - | -0.75 V *vs.* RHE | $^{m}$-13 ($C_2H_5OH$),<br>$^{m}$-28($C_2H_4$) | - | 31% | - |
| N-doped C/CP[576] | [Bmim]$BF_4$ | 5 h | -1.4 V *vs.* SHE | -1.42 | 93.5% | - | - |
| $MoTe_2$ layer[577] | 0.1 M $KHCO_3$ | 45 h | -1.0 V *vs.* RHE | -25.6 | 83±3 % | - | - |
| CuS@NF[578] | 0.1 M $KHCO_3$ | 60 h | -1.0 V *vs.* RHE | $^{m}$-7.3 | 73±5 % | | |
| CuPc/CNT | 0.5 M $KHCO_3$ | - | -1.06 V *vs.* RHE | -13(pcd) | 66% | - | - |

m: evaluated from the figures, pcd: partial current density, CE: current efficiency.

**Table 11.** $CO_2$RR performance on materials with acetate and oxalate formation

| Catalyst | Electrolyte | Durability test | Potential | Current density/ mA $cm^{-2}$ | Products | FE | Reference |
|---|---|---|---|---|---|---|---|
| Cu(110) | 0.1 M $KHCO_3$ | - | -1.58 V *vs.* SHE | -5 | acetate | CE.20.8% | [579] |
| NDD/Si RA | 0.5 M $NaHCO_3$ | 30 h | -1.0 V *vs.* RHE | $^{m}$-1.0 | acetate | 91.8% | [580] |
| Cu(I) complex /BN-C | 25 mol% [Emim]$BF_4$)-0.01M LiI-$H_2O$ | 5 h | -1.3 V *vs.* RHE | -13.9 | acetate | 80.3% | [581] |
| Cu(10)-CNT | 0.5 M $KHCO_3$ | 24 h | -1.4 V *vs.* Ag/AgCl | -100 | acetate | 56.3% | [582] |
| *Fh*-FeOOH/N-C | 0.05 M $KHCO_3$ | - | -0.5 V *vs.* Ag/AgCl | -0.36 | acetate | 60.9% | [583] |
| In sheet | 0.1 M $Na_2SO_4$+2mM $SiW_9V_3$ | - | -0.71 V *vs.* RHE | $^{m}$-0.5 | acetate | 96.5% | [584] |
| Cu-$Cu_2O$/Cu | 0.1 M KCl | 24 h | -0.4 V *vs.* RHE | -11.5 | acetate | 48% | [585] |
| N-NC/Cu | 0.5 M $KHCO_3$ | 120 h | -0.5 V *vs.* RHE | 102.2 A $g_{Cu}^{-1}$ | acetate | 34.7% | [503] |
| $MoO_2$ /Pb(-20 ° -) | 0.1 M $TBAPF_6$/MeCN | 5 h | -2.45 V *vs.* Fc/Fc+ | -20 | oxalate | 45% | [586] |
| Cr-Ga/GC | 0.1 M KCl | 10 days | -1.48 *vs.* Ag/AgCl | -(8~10) | oxalate | 59% | [587] |

m: evaluated from the figures, pcd: partial current density, CE: current efficiency

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