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1 2.6 % cm⁻² single-pass CO₂-to-CO conversion
2 using Ni single-atoms supported on ultra-thin
3 carbon nanosheets in a flow electrolyzer

4 *Yang Zhang^{1,2}, Kun Qi², Ji Li³, Bonito A. Karamoko², Luc Lajaunie^{4,5}, Franck*
5 *Godiard⁶, Erwan Oliviero⁶, Xiaoqiang Cui⁷, Ying Wang⁷, Yupeng Zhang¹, Huali Wu²,*
6 *Wensen Wang², Damien Voiry^{2*}*

7 ¹ Key Laboratory of Optoelectronic Devices and Systems of Ministry of Education and
8 Guangdong Province, College of Optoelectronic Engineering, Shenzhen University,
9 Shenzhen, 518000, China

10 ² Institut Européen des Membranes, IEM, UMR 5635, Université Montpellier,
11 ENSCM, CNRS, Montpellier, 34090, France

12 ³ College of Bioresources Chemical and Materials Engineering, Shaanxi University of
13 Science and Technology, Xi'an, 710000, China

14 ^{4,5} Departamento de Ciencia de los Materiales e Ingeniería Metalúrgica y Química
15 Inorgánica, Instituto Universitario de Investigación de Microscopía Electrónica y
16 Materiales (IMEYMAT), Facultad de Ciencias, Universidad de Cádiz, Campus Río San
17 Pedro S/N, Puerto Real, Cádiz, 11510, Spain

18 ⁶ MEA Platform, University of Montpellier, Montpellier, 34090, France.

1 ⁷ State Key Laboratory of Automotive Simulation and Control, Department of Materials
2 Science, Key Laboratory of Automobile Materials of MOE, Jilin University,
3 Changchun, 130000, China.

4

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6 phase interface, single pass conversions.

7

8 ABSTRACT

9 The CO₂ reduction reaction using a renewable energy source is a promising strategy for
10 its utilization. Such a technology however requires the development of catalysts with
11 optimized activity and selectivity that can be integrated into the device architectures.
12 Flow electrolyzers have recently been proposed for facilitating the electrochemical CO₂
13 reduction reaction thanks to their unique ability to perform electroreduction at high
14 reaction rates *via* the creation of three-phase interface. While some examples of flow
15 electrolyzers for the conversion of CO₂ has recently been reported, the influence of the
16 CO₂ and electrolyte streams on the overall catalytic mechanism is remained ambiguous.
17 Here, we synthesized single-atom nickel on two-dimensional nitrogen-doped carbon
18 nanosheets (SA Ni-NC) for the CO₂-to-CO conversion. Taking advantage of this model
19 catalyst, we explored the correlation between the applied potential and the feeds in both

1 electrolyte and CO₂ on the one hand, and the performance metrics on the other hand.
2 By regulating the feed stream's conditions, the SA Ni-NC achieves energy efficiencies
3 as high as 85% at $j_{CO} = 7.2 \text{ mA cm}^{-2}$ and 56% at $j_{CO} = 170 \text{ mA cm}^{-2}$ whereas the single-
4 pass CO₂-to-CO conversion efficiency (SPCC) reaches 2.6% cm⁻². We finally
5 demonstrated the scalability of the flow electrolyzers by stacking three 1-cm² reactors
6 and reached a record-high CO yield rate of 31.5 L min⁻¹ m⁻² with near-unity CO
7 selectivity and an SPCC of 8.9% from three.

8

9 **1. Introduction**

10 The intensive consumption of fossil fuels along with excessive emission of carbon
11 dioxide (CO₂) exacerbate global environmental problems, which severely limits the
12 potential of sustainable growth.¹ The CO₂ capture and utilization technologies are being
13 investigated to mitigate the release of CO₂ into the atmosphere.² Among the various
14 strategies, the electrochemical CO₂ reduction reaction (CO₂RR) under ambient
15 conditions, which can be coupled with renewable electricity sources, represents a
16 promising approach to reuse the CO₂ emissions, while generating value-added fuels
17 and chemicals.^{3,4} In this context, a vast amount of efforts are currently being devoted
18 to the development of novel electrocatalysts with optimum selectivity and activity
19 towards the production of various C₁-C₃ molecules.^{5,6} The discovery of single-atom
20 catalysts has extended new directions for the rational design of heterogeneous catalysts

1 with well-defined structure and maximum exposure of the active sites.⁷ Single-atom
2 catalysts have been demonstrated with outstanding electrochemical CO₂RR selectivity
3 and high current densities thanks to the peculiar coordination environment of the single
4 metal atom and the local electronic structures that differs from those of the nanoparticle
5 counterparts.⁸⁻¹⁰ Specifically, nitrogen-doped carbon with the inclusions of metal single
6 atoms (M-N-C) has been investigated for several key electrochemical reactions
7 including the hydrogen evolution reaction (HER), the oxygen reduction reaction (ORR)
8 and also the CO₂RR.¹¹⁻¹³

9 The search for highly active CO₂RR catalysts is typically carried out using traditional
10 “H-cell” reactors. The performance is however severely limited by the relatively low
11 CO₂ dissolvability in the liquid electrolyte. H-cell designs also face mass transport
12 limitation and high proton transfer resistance, thus leading to the current densities
13 typically lower than 100 mA cm⁻² which precluding its industrial applications.¹² To
14 unlock these bottlenecks, novel device architectures have recently been reported using
15 solid-state electrolytes or flow reactors. Specifically, mass transport limitations can
16 efficiently be overcome thanks to the continuously feed in the electrolyte and CO₂ and
17 current densities up to 1 A cm⁻² have recently been reported.¹⁴⁻¹⁶ In flow electrolyzers,
18 the reduction of CO₂ occurs at the three-phase interface, which is formed by CO₂ (gas),
19 the electrolyte (liquid) and the catalyst (solid) respectively. This strategy ensures an
20 efficient supply of CO₂ meanwhile electrons and protons for the successive electron-
21 proton coupled transfers associated with the reaction pathway.¹⁷ Two main strategies

1 are usually adopted in order to enhance the CO₂RR activity and selectivity using flow
2 electrolyzers: *i*) improve the intrinsic activity of the catalysts and *ii*) engineer the
3 structure of the gas diffusion electrodes (GDE). For example, by changing the structure
4 of catalysts, the porosity of the carbon support, or the hydrophilic/hydrophobic
5 properties of the electrode, the CO₂ diffusion length can be greatly reduced and the
6 mass transport will be significantly accelerated.¹⁸⁻²²

7 In addition to the design of the catalyst and the manipulation of electrode those all
8 focus on the optimizing of the solid phase for three-phase interface, the feed stream's
9 conditions of both the electrolyte (liquid) and CO₂ (gas) are therefore expected to play
10 a central role in the kinetics of the CO₂RR and the final CO₂-to-product conversion
11 efficiency.²³ For example, by tuning the gas flow rates, the transport of CO₂ to the
12 surface of the catalyst as well as its local concentration can be directly controlled to
13 optimize the equilibrium between the adsorption of CO₂ and the desorption of the
14 products on the active sites.²⁴⁻²⁶ This is particularly crucial concerning the reaction
15 processes at high conversion rates – *i.e.* at high current densities. For example, if we
16 consider the conversion of CO₂ to carbon monoxide (CO), a current density of 100 mA
17 cm⁻² – considered to be a threshold value for any industrial application – involves a
18 turnover of $\approx 6.2 \times 10^{17}$ cm⁻² molecules of CO₂ and protons per second. To date, the
19 understanding of the influence of electrolyte and CO₂ feeds on the overall CO₂RR
20 performance – notably the energy efficiency of the reaction – in flow electrolyzers has
21 remained elusive.

1 Herein, we investigate the behavior of single atom nickel supported on ultrathin
2 nitrogen-doped carbon nanosheets (SA Ni-NC) in a flow electrolyzer for the
3 electrocatalytic conversion of CO₂-to-CO. The SA Ni-NC demonstrates excellent
4 CO₂RR stability together with a near-unity CO₂-to-CO selectivity; making it an ideal
5 platform to investigate the feedstock parameters in a flow electrolyzer. By tuning the
6 electrolyte or CO₂ flow rates, we explored the role of the CO₂ and electrolyte feeds on
7 the electrochemical CO₂RR properties and the reaction rates at the three-phase
8 interface. The optimum flow allowed achieving current densities as high as 170 mA
9 cm⁻² with an ultra-high energy efficiency ranging up to 85%. We finally demonstrate
10 the scalability of our catalyst by connecting up to three flow electrolyzers in series to
11 reach a single-pass CO₂-to-CO conversion of 8.9 % and a yield rate of $\approx 31.5 \text{ L min}^{-1}$
12 m⁻² while maintaining a near-unity CO₂-to-CO selectivity. Our work highlights the
13 importance of the understanding of the flow dynamics in CO₂RR to optimize the energy
14 efficiency, the single-pass conversion as well as the yield rate of the reaction, which are
15 key parameters for the development of industrial-scale processes towards the
16 conversion of CO₂-to-CO.

17 **2. Results and discussion**

18 **2.1. Density functional theory calculations and catalyst selection**

19 We first performed density functional theory (DFT) calculations to identify a model
20 CO₂RR catalyst for the conversion of CO₂-to-CO with high efficiency and selectivity.

21 **Figure 1a** shows the successive steps associated with the CO₂ electrochemical

1 reduction pathways on the optimized structures of atomic nickel coordinated by four
2 pyrrolic nitrogen: NiN₄ supported on a carbon nanosheet. The reaction pathways for the
3 CO₂ electroreduction to CO is known to proceed *via* two successive proton-coupled
4 electron transfer (PCET) associated with the formation of *COOH and *CO
5 intermediates.^{27,28} The energy profile associated with the CO₂-to-CO conversion has
6 been calculated for the NiN₄ and Ni (111) for comparison (**Figure 1b**). We first note
7 that the barrier energy associated with CO₂-to-CO reaction on the NiN₄ is 0.1 eV
8 smaller than that on Ni (111). The corresponding Gibbs free energy plot for the above-
9 mentioned Ni-based catalysts suggests that the free energy change of Ni (111) for the
10 formation of the *COOH intermediate is lower compared with that of NiN₄ at 0.09 eV
11 and 1.56 eV respectively. The formation of *COOH on NiN₄ is endergonic and
12 corresponds to the common rate-determining step for the CO₂RR on the single-atom
13 sites. This first PCET process is followed by the formation of *CO for both catalysts.
14 The *CO desorption from NiN₄ is then exothermic with a free energy change of 0.75
15 eV contrary to Ni (111), for which the desorption is endergonic with an associated free
16 energy change of 1.65 eV. We examined the influence of the applied potential on the
17 electrochemical CO₂RR performance for NiN₄ and Ni (111), respectively. As shown in
18 **Figure 1c** and **1d**, the free energy change of the rate-determining step for NiN₄
19 decreases with the applied potential increasing, while it remains virtually constant in
20 the case of Ni (111). The predictions therefore suggest that the increase of the
21 overpotential does not yield to an improved catalytic activity towards the production of

1 CO for Ni (111). In addition, the DFT calculations of HER show that the first
2 protonation step for Ni (111) is spontaneous, and the energy barrier for the formation
3 of $1/2 \text{ H}_2$ is estimated to be 0.36 eV – much smaller than the *CO desorption energy
4 barrier of 1.63 eV (**Figure S1**). Our results indicate that the NiN₄ sites supported on
5 carbon are promising to deliver high CO₂-to-CO selectively thanks to an efficient
6 desorption step, and a reduced barrier energy of rate-determining step at increasing
7 overpotentials. Conversely the Ni (111) sites are likely to be poisoned due to the rate-
8 determining step associated with the desorption of *CO. To further understand the
9 nature of binding of CO on NiN₄ and Ni (111), the projected density of states (PDOS)
10 was calculated in the presence and absence of CO, respectively. After the geometry
11 optimization, we found that the 3d orbitals of the active sites on Ni (111) hybridize with
12 the 5 σ and 2 π^* orbitals of CO, presenting strong chemisorption of CO molecules on
13 Ni (111) (**Figure 1e**). However, in the case of the NiN₄ sites, CO spontaneously desorbs
14 and no obvious orbital hybridization of CO and activate sites was observed. The
15 distance between the nickel atoms of NiN₄ and the carbon atoms of CO was estimated
16 to be larger than 3 Å, suggesting weak Van der Waals' interactions and confirming
17 facile desorption of the produced CO molecules. Our results thus predict again that the
18 rapid desorption of CO on NiN₄ plays a key role in the selectivity of the CO₂RR towards
19 the production of CO.

20 **2.2. Catalyst characterization and electrode preparation**

1 In the light of the DFT results, single-atom nickel with well-defined catalytically
2 active sites on ultrathin supported on two-dimensional (2D) nitrogen-doped carbon
3 nanosheets (SA Ni-NC) was prepared. The as-prepared catalyst exhibits a two-
4 dimensional structure with a smooth surface as confirmed by scanning electron
5 microscopy and atomic force microscopy characterizations (**Figure 2a, Figure S2**). To
6 provide compelling evidence of the uniform distribution of the nickel atoms on the
7 nitrogen-doped carbon nanosheets, we performed energy dispersive X-ray (EDX)
8 mapping on the SA Ni-NC nanosheets. EDX analyses revealed that the Ni, C, and N
9 elements are homogeneously distributed at the scale of the flake without noticeable
10 metal aggregation or formation of the Ni nanoparticles (**Figure 2b-2e**). The nature of
11 the Ni atoms in SA Ni-NC was further characterized by aberration-corrected high-angle
12 annular dark-field scanning transmission electron microscopy (HAADF-STEM). Ni
13 atoms are observed as brighter spots due to their larger atomic number compared with
14 those of carbon and nitrogen. Ultra-small bright dots from the nickel single-atoms are
15 found on SA Ni-NC confirming the uniform dispersion of the nickel with an average
16 size of 0.15 ± 0.04 nm as confirmed by the HAADF-STEM and electron energy-loss
17 spectroscopy (EELS) mapping (**Figure 2f, Figure S3**). To investigate the chemical
18 composition and oxidation state of Ni, X-ray photoelectron spectroscopy (XPS) was
19 performed on the SA Ni-NC (**Figure S4**). The Ni 2p spectrum of SA Ni-NC appears as
20 doublets corresponding to Ni 2p_{3/2} (855.5 eV) and Ni 2p_{1/2} (873.5 eV) respectively.
21 We observe a positive shift of the binding energy compared with that of bulk Ni –

1 expected at 852.4 eV and 869.6 eV for Ni 2p_{3/2} and Ni 2p_{1/2} respectively, which
2 reveals a higher oxidation state for Ni as expected for the NiN_x sites of the single
3 atoms.^{9,29} The high-resolution N 1s XPS spectrum of SA Ni-NC exhibits four peaks
4 located at 398.0, 400.5 and 401.2 eV, which are assigned to the pyridinic N, pyrrolic N
5 and graphitic N, respectively.⁸ Besides, the peak at a binding energy of 399.3 eV is
6 attributed to the presence of N atoms coordinated by metal and points out the presence
7 of Ni-N bonds in the case of SA Ni-NC. According to the XPS data, the atomic ratio of
8 N to Ni was estimated to be 2.7, which can be ascribed to the presence of a trace amount
9 of encapsulated Ni aggregates in the carbon layer. The atomic C : N ratio on the carbon
10 flakes was estimated by XPS and EELS to be between 9.2% and 11.5% respectively
11 (**Figure S5**). The oxidation state of the Ni atoms in SA Ni-NC was further determined
12 from the position of the rising edge of the Ni K-edge X-ray absorption near edge
13 structure (XANES). A positive peak offset is observed with respect to the position of
14 the K-edge of the reference nickel foil; in qualitative agreement with the shift observed
15 from the Ni 2p region in XPS (**Figure S6a**). The final evidence of the single-atomic
16 nature of the SA Ni-NC was provided by the extended X-ray absorption fine structure
17 (EXAFS) measurements. We obtained a good agreement between the Fourier
18 transformed EXAFS spectrum of SA Ni-NC in k-space and the simulated spectrum of
19 Ni-N₄, which indicates the presence of Ni-N₄ sites on SA Ni-NC (Inset **Figure 2g**,
20 **Figure S6b and Table S1**). And the Fourier transform of the phase uncorrected EXAFS
21 spectra of SA Ni-NC displayed a prominent peak at 1.42 Å (**Figure 2g**). Such a value

1 is shorter than the Ni-Ni interactions in Ni foil at 2.15 Å and attributed to the presence
2 of Ni-N interactions, in perfect agreement with the presence of isolated nickel atoms on
3 the nitrogen-doped carbon nanosheet for SA Ni-NC.

4 **2.3. Investigations of the CO₂RR activity in an H-cell reactor**

5 To gauge the electrochemical CO₂RR performance, the SA Ni-NC catalyst was first
6 tested using a traditional H-cell equipped with a cation exchange membrane between
7 the anode and cathode chambers. A CO₂-saturated solution consisting of 0.1 M KOH +
8 0.5 M K₂SO₄ was used as the electrolyte and the catalyst was immobilized on a
9 mechanically polished glassy carbon electrode with a geometric loading of 0.044 mg
10 cm⁻² (See Experimental section for details). To observe the influence of the single-atom
11 nature of the Ni sites on the CO₂RR properties, we first compared the performance of
12 SA Ni-NC with that of Ni nanoparticles supported on reduced graphene oxide (Ni-
13 NPC) under the same conditions. The gas and liquid products were analyzed using gas
14 chromatography (GC) and nuclear magnetic resonance (NMR) respectively. Hydrogen
15 (H₂) and CO were found to be the only products of the reaction for both SA Ni-NC and
16 Ni-NPC catalysts. The linear scan voltammetry (LSV) curves demonstrate that Ni-NPC
17 has a larger reduction current at a large range of applied potential compared with that
18 of SA Ni-NC (**Figure 3a**), while most of the current works for hydrogen evolution. The
19 onset potential of SA Ni-NC for CO₂RR to occur is about -0.25 V *vs.* the reversible
20 hydrogen electrode (RHE), which compares favorably with the recently reported values
21 in the literature.^{9,16,30} Remarkably, the Faradaic efficiency of CO (FE_{CO}) for SA Ni-NC

1 is much larger than that for Ni-NPC and the FE_{CO} reaches the highest value of about
2 80% at an applied potential of -0.75 V vs. RHE (**Figure 3b**). At this applied potential,
3 the partial current density of CO (j_{CO}) reaches -1.87 mA cm^{-2} and -0.77 mA cm^{-2} for
4 the SA Ni-NC and Ni-NPC, respectively. We also observe that the reactions on Ni-NPC
5 are dominated by the HER process – i.e. the production of H_2 – and the Ni nanoparticles
6 are poorly selective towards CO_2RR (**Figure 3c**). The high selectivity of the NiN_4 sites
7 compared with Ni nanoparticles is in line with our numerical predictions and attributed
8 to the rapid desorption of $*CO$. To further assess the potential of SA Ni-NC as a CO_2RR
9 catalyst, we evaluated the electrochemical stability of the catalyst over 48 h at an
10 applied potential of -0.8 V vs. RHE (**Figure 3d**). The current was continuously
11 measured while the gas products were injected into the gas chromatograph every 3
12 hours. The SA Ni-NC catalyst exhibits a stable cathodic current density and negligible
13 drop of FE_{CO} as demonstrated by retentions of 92.5% and 95% respectively (Figure 3d).
14 We also measured the electrochemical double-layer capacity (C_{dl}) and the
15 electrochemical impedance spectroscopy (EIS) of the two catalysts (**Figure S7 and**
16 **Table S2**). The results show that SA Ni-NC catalyst exhibits a better interfacial charge
17 transfer and more electrochemical active sites for CO_2RR . All of the above results
18 indicate that SA Ni-NC holds promises as a CO_2RR catalyst with excellent selectivity
19 and stability towards the production of CO from CO_2 .

20 **2.4. Investigations of the CO_2RR activity in a flow electrolyzer**

1 The performance of SA Ni-NC was further evaluated in a liquid-electrolyte flow
2 electrolyzer using CO₂-saturated mixture of 0.1 M KOH+0.5 M K₂SO₄ solution as the
3 electrolyte for both the cathode and the anode chambers. The catalyst was loaded on a
4 GDE and the downstream products of the reaction were continuously analyzed using
5 gas chromatography. The model 1 cm² flow reactor allows for the continuous diffusion
6 of CO₂ to the catalyst layer thanks to the position of the supported catalyst directly at
7 the gas/liquid interface (**Figure S8**). To scrutinize the relationship between the CO₂RR
8 properties and the CO₂/electrolyte feedstocks, the flow rates for both the electrolyte and
9 CO₂ were controllably tuned from 20 to 100 mL min⁻¹ and 20 to 140 mL min⁻¹,
10 respectively. The specific current density and Faradaic efficiency were measured at
11 different potentials for each feed parameters, which allowed us to elucidate the behavior
12 of SA Ni-NC in the flow electrolyzer. The electrochemical CO₂RR properties of the
13 SA Ni-NC were first assessed at a fixed stream of 60 ml min⁻¹ CO₂ with the variation
14 of electrolyte flow rates (**Figure 4a**). The highest current reaches ≈ 170 mA cm⁻² at -
15 1.15 V vs. RHE for a 60 mL min⁻¹ electrolyte flow rate while the FE_{CO} shows near-
16 unity selectivity for all electrolyte flow rates – sharply improved compared with that
17 measured in H-cell (**Figure 4b and Figure 3b**). It should be noted that, due to the
18 experimental errors introduced by the GC analyzes, the measured CO selectivity could
19 sometimes be slightly higher than 100%, especially when H₂ was suppressed to below
20 1%.³¹ To further study the effects of the electrolyte flow rate on the CO₂RR
21 performance from the viewpoint of three-phase interface, we analyzed both the

1 electrochemical impedance spectra (EIS) of the catalyst and the double-layer
2 capacitance (C_{dl}) (**Figure 4c** and **4d**).³² As shown in Figure 4d, the C_{dl} values get larger
3 with the increase of the electrolyte flow rate and reaches a plateau for flow rates > 60
4 mL min⁻¹. We also found that the internal resistance (R_s) and the charge transfer
5 resistance (R_{ct}) simultaneously increase. In particular, the R_{ct} sharply increases at the
6 largest flow rates above 80 mL min⁻¹, suggesting an abrupt change in reaction kinetics
7 attributed to the modification of the three-phase interface. Below 80 mL min⁻¹, larger
8 flow rate may promote the penetration of the electrolyte inside the porous gas diffusion
9 electrode (GDE) and therefore improves the reaction interface between the catalyst
10 surface and the liquid electrolyte (**Figure 4e**). However, when further increasing the
11 flow of electrolyte, the gas-liquid interface moves deeper inside the GDE resulting in a
12 degraded three-phase interface and unfavorable conditions for the electrochemical
13 reactions.^{14, 33} Our experimental results highlight the critical role of interfaces for the
14 CO₂RR in a flow cell and the optimal electrolyte flow rate corresponds to the proper
15 balance between the surface of catalyst in contact with the electrolyte and the position
16 of the gas-liquid interface inside the GDE. To elucidate the influence of the CO₂ feed,
17 steady-state chronoamperometry was then recorded for different flow rates between 20
18 mL min⁻¹ and 140 mL min⁻¹ with a constant stream of electrolyte at 60 mL min⁻¹.
19 Remarkably, the selectivity of SA Ni-NC is not influenced by the gas flow and the
20 catalyst performs with nearly 100% selectivity towards the formation of CO over the
21 range of potential (**Figure 4f**). The onset potential for the production of CO reaches -

1 0.35 V vs. RHE in the flow reactor – slightly more negative than that in the H-cell
2 (**Figure 4a** and **4g**). This can be attributed to the fact that the instantaneous
3 concentration of CO at low potentials is below the detection limit of our instrument
4 (See Experimental section for details). At an applied potential of -0.35 V vs. RHE, the
5 SA Ni-NC shows similar current densities for all flow rates; therefore indicating similar
6 levels of CO₂RR activity (Figure 4g). At larger applied potentials, the current density
7 increases as the CO₂ flow rates increases from 20 to 60 mL min⁻¹ due to the local
8 depletion of CO₂ near the site active at low flow rates.³² The lower current density for
9 the CO₂ flow rates higher than 60 mL min⁻¹ points out a possible local decrease of the
10 pH, which perturbs the CO₂ activation and the free-energy barriers in CO₂RR, in
11 agreement with the endergonic nature of the first step. Indeed, a high feed in CO₂ will
12 result in a large excess of CO₂ molecules not involved in the CO₂RR, which will likely
13 induce a reduction of the local pH as previously been identified.^{35,36} Overall, we
14 identified optimal ranges for the electrolyte and CO₂ flow rates to be 40-80 mL min⁻¹
15 and 60 mL min⁻¹ respectively depending on the applied potentials (**Figure 5a**). Our
16 results demonstrate that the potential-dependent nature of the electrocatalytic reaction
17 rate is also controlled by the supply of CO₂ and electrolytes for the successive PCET
18 steps.³⁷ Remarkably, the FE_{CO} remains ≈100% even at current densities larger than
19 100 mA cm⁻² and the CO₂RR properties of SA Ni-NC in the flow electrolyzer are
20 superior to those measured in the H-Cell (**Figure 5b, c**). For example, the j_{mass} , j_{total}
21 and j_{CO} values at -0.75 V vs. RHE in flow electrolyzer are 2.2 A cm⁻², 111 mA cm⁻² and

1 109.18 mA cm⁻², respectively. However, the values in H-cell are 0.05 A cm⁻², 2.31 mA
2 cm⁻² and 1.87 mA cm⁻², respectively, which are all significantly smaller than those in
3 the flow electrolyzer. This is attributed to the *i*) better exposure of the active sites, *ii*)
4 larger local concentration of CO₂ and *iii*) reduced amount of hydrated proton which is
5 involved in the competitive HER.³⁸ To better evaluate the performance of SA Ni-NC,
6 we calculated the evaluative parameters of the system as a function of the CO₂ flow
7 rates at different applied potentials. The energy efficiency is found to be larger than 55
8 % for all the range of potentials. It reaches to 85% at -0.35 V vs. RHE with a current
9 density of 7.2 mA cm⁻² (**Figure 5d**). When considering the two important metrics, the
10 specific current density and the energy efficiency, the SA Ni-NC catalysts in a flow
11 reactor can achieve a current density larger than 170 mA cm⁻² while maintaining a high
12 energy efficiency of 56%. To gain some insight into the behavior of SA Ni-NC in the
13 flow reactor, we also explored the role of the CO₂ feed on the yield rate of CO (**Figure**
14 **5e**). The yield rate increases with the applied potential and reached values as high as
15 28.4 mL min⁻¹ mg_{catalyst}⁻¹ at an applied potential of -1.15 V vs. RHE and CO₂ flux of
16 60 mL min⁻¹ – equivalent to a continuous CO production of 12.6 L min⁻¹ m⁻² of the
17 electrode.

18 We further examined the single-pass CO₂-to-CO conversion, which represents the
19 percentage of CO₂-to-CO conversion after one pass in the reactor which is the key
20 parameter to assess the scalability of the CO₂RR system. For example, a single-pass
21 CO₂-to-CO conversion of 10% is associated with a separation cost of 23% of the total

1 operation cost for the production of CO.³⁹ Such a value is generally considered to be a
2 threshold target to demonstrate the industrial viability of the process. According to
3 **Figure 5f**, it can be observed that the single-pass CO₂-to-CO conversion obeys the same
4 trend as for j_{CO} and the largest values are obtained for electrolyte flow rates around 60
5 mL min⁻¹. At this specific electrolyte flow rate, the highest single-pass CO₂-to-CO
6 conversion for the flow reactor reaches $\approx 3\%$ at a potential of -1.15 V vs. RHE for a
7 CO₂ flow rate of 20 mL min⁻¹ (**Figure 5g**). We also note the tendency that for a constant
8 feed in CO₂, the single-pass CO₂-to-CO conversion values increase with the applied
9 potential, but decreases with the CO₂ flow rate. Overall, reducing the CO₂ flow rate
10 results in larger single-pass CO₂-to-CO conversion performance and improves the CO₂
11 conversion efficiency but lower the CO yield rate. Trade-offs between single-pass CO₂-
12 to-CO conversion and CO yield rate must therefore be chosen to meet the specific
13 industrial recommendations.

14 To finally demonstrate the potential of our approach, we stacked three identical flow
15 electrolyzer using the SA Ni-NC as a CO₂RR catalyst (**Figure 6a**). The anolyte and
16 catholyte were recycled using a peristaltic pump with a constant flow rate. The first
17 flow electrolyzer was continuously fed with pure CO₂ and the gas outlet was
18 successively injected in the second and third flow electrolyzer, while the downstream
19 gas products were continuously detected *via* GC analyses. The CO₂-to-CO
20 performances of each reactor were first examined and the specific current reached 160
21 ± 20 mA cm⁻² for each electrolyzer (**Figure 6b**). After the first two reactors, we

1 measured a single-pass CO₂-to-CO conversion and a CO yield rate of 4.4% and 35.3
2 mL min⁻¹ mg_{catalyst}⁻¹, respectively. These values were further improved after passing
3 through the third reactor and reached 8.9% and 71.2 mL min⁻¹ mg_{catalyst}⁻¹ – equivalent
4 to a continuous CO production of 31.5 L min⁻¹ m⁻², respectively – pointing out the
5 remarkable CO₂RR properties of SA Ni-NC in a diluted CO₂ environment (**Figure 6c**).
6 These results allowed the identification of a quasi-linear increase of the CO₂-to-CO
7 conversion and validated the scalability of our strategy towards higher single-pass CO₂-
8 to-CO conversion by rationally designing the electrolyzer and the feedstock parameters.
9 According to the linear fitting, the SA Ni-NC in a flow reactor demonstrates a single-
10 pass conversion of 2.6% per cm² of the electrode for the production from CO₂-to-CO,
11 which compares favorably to the best reports in the literature using flow electrolyzer
12 (**Table S3**).

13 **3. Conclusion**

14 In summary, we have prepared single-atom nickel supported on two-dimensional
15 nitrogen-doped carbon nanosheets using a salt template strategy. The controlled design
16 of the single-atom Ni sites translates into high selectivity and high efficiency towards
17 the conversion of CO₂-to-CO. When implemented in a flow electrolyzer, SA Ni-NC
18 exhibits near-unity selectivity towards the production of CO with a specific current
19 density as high as 170 mA cm⁻². Importantly, our study reveals the influence of feed-in
20 electrolytes and CO₂ on the catalytic performance in a flow electrolyzer system. Using
21 a model 1 cm² reactor, we determined the optimum flow rates for the electrolyte and

1 CO₂ at 40-80 mL min⁻¹ and 60 mL min⁻¹, respectively – corresponding to flow speeds
2 of 8.3-16.6 cm s⁻¹ and 12.5 cm s⁻¹. The feed parameters are found to modulate the
3 catalyst behavior in the reactor by tuning the equilibrium of the three-phase interface
4 between the electrolyte, the CO₂ atmosphere and the surface of the electrocatalyst. This
5 translates into a single-pass CO₂-to-CO conversion of 2.6% cm⁻², corresponding to a
6 total conversion efficiency of 8.9% when stacking three 1-cm² reactors without a
7 notifiable drop of the catalyst performance when operating under diluted CO₂
8 atmosphere. Our approach provides insight into the scalability of flow electrolyzers
9 toward the mass production of CO from CO₂ with high Faradaic efficiency using single-
10 atom electrocatalysts. Future developments require the further optimization of the size
11 of the electrodes and the number of stacks for optimizing the tradeoff between the
12 single-pass conversion and the yield rate .

13 **4. Experimental Section**

14 **Materials:**

15 Nickel nitrate hexahydrate (Ni(NO₃)₂·6H₂O, ≥ 98.5%), 2-methylimidazole
16 (CH₃C₃H₂N₂H, 98%), methanol (CH₃OH, ≥ 99.9%), sodium chloride (NaCl, ≥
17 99.0%), ethylene glycol (HOCH₂CH₂OH, 99.8%), Nickel (II) acetate tetrahydrate
18 (Ni(CH₃COO)₂·4H₂O, 98%), graphene, urea (NH₂CONH₂, ≥ 99.5%), potassium
19 sulfate (K₂SO₄, ≥99.0%) and potassium hydroxide (KOH, 90%,) were purchased from
20 Sigma Aldrich. Nafion (5%) and hydrochloric acid (HCl, 37%) were purchased from
21 Alfa Aesar. All the chemicals in the experiment were used without further purification.

1 The gas diffusion electrode (GDE, Sigracet 29 BC) and cation exchange membrane
2 (CEM, Nafion 117) were both purchased from the Fuel Cell Store. The fresh cathode,
3 anode, and CEM were used for each electrolysis test to avoid contamination.

4 **Synthesis of SA Ni-NC:**

5 SA Ni-NC was synthesized from the graphitization of a zeolitic imidazolate metal-
6 organic framework (ZIF). In a typical synthesis of ultrathin ZIF-67 nanosheets, 200 mg
7 of 2-methylimidazole and 50 mg of nickel nitrate hexahydrate were dissolved in 2.5
8 mL of methanol, respectively.⁴⁰ After that, 20 g of the sodium chloride was mixed with
9 the two solutions into a flask under vigorous magnetic stirring overnight at room
10 temperature. The controlled ratio in MOF precursors and NaCl was adjusted to promote
11 a thin coating on the salt crystals and favor the lateral growth of ZIF-67s. Subsequently,
12 the NaCl@ZIF-67 nanosheets were obtained by the slow evaporation of the solvent at
13 35 °C followed by pyrolysis at 800 °C for 2 hours under argon (Ar). After cooling down
14 to room temperature, the product was soaked in 0.5 M HCl solution for 24 h at 60 °C
15 to remove the redundant nickel nanoparticles. Finally, the sample was washed with
16 deionized water for several times to remove the redundant NaCl, then centrifuged and
17 freeze-dried for further storage.

18 **Synthesis of Ni NPC:**

19 The Ni nanoparticles were prepared by a modified chemical reduction method.⁴¹ In a
20 typical synthesis process, 0.349 g Nickel (II) acetate tetrahydrate, 17.5 mg graphene,
21 and 1.394 g urea were mixed with 35 mL ethylene glycol through intense agitation for

1 0.5 h to form a homogeneous solution. Then the homogeneous solution was transferred
2 into a 50 mL Teflon-lined stainless-steel autoclave and kept at 200 ° C for 1 h. After
3 cooling down, the mixture was washed with ethanol for six times and dried at 80 ° C
4 in a vacuum oven. The Ni-NPC composite was obtained by annealing the above mixture
5 at 700 ° C in an Ar atmosphere for 10 h.

6 **Sample characterization:**

7 Transmission electron microscopy images (TEM) were obtained using a JEOL 1400
8 microscope with an emission gun operating at 120 kV. High-resolution transmission
9 electron microscopy images (HRTEM) were obtained using JEOL 2200 FS microscope
10 with an emission gun operating at 200 kV. The samples for electron microscopy were
11 prepared by dropping ethanol dispersions of the samples onto 300 mesh carbon-coated
12 copper grids and then evaporating the solvent. Aberration-corrected high-resolution
13 scanning transmission electron microscopy imaging (HR-STEM), and spatially-
14 resolved electron energy-loss spectroscopy (SR-EELS) were performed using an FEI
15 Titan Cubed Themis microscope which was operated at 80 kV. The Themis is equipped
16 with a double Cs aberration corrector, a monochromator, an X-FEG gun, and an ultra-
17 high resolution energy filter (Gatan Quantum ERS) which allows for working in Dual-
18 EELS mode. HR-STEM imaging was performed by using high-angle annular dark-field
19 (HAADF) and annular dark-field (ADF) detectors. SR-EELS spectra were acquired
20 with the monochromator excited allowing an energy resolution of 1.1 eV with an energy
21 dispersion of 0.4 eV/pixel. AFM images were obtained in Digital Instruments

1 Nanoscope IV in tapping mode with cantilevers with a spring constant of 40 N/m and
2 tip curvature < 10 nm and a frequency of 325 kHz (Dimension Icon, Veeco
3 Instruments/Bruker, Germany). X-ray photoelectron spectroscopy (XPS) was
4 performed using an ESCALAB-250 instrument (Thermo Fisher Scientific, USA),
5 performed with a monochromatic Al-K α (1486.6 eV) radiation source and a
6 hemisphere detector with an energy resolution of 0.1 eV. Peak positions were all
7 corrected by the C 1s spectrum at 284.8 eV. X-ray absorption spectra (XAS) were
8 measured at Beijing synchrotron radiation facility (BSRF) on beamline 1W1B. The
9 storage ring is operated at a beam current of 250 mA with an electron energy of
10 2.5 GeV. The beam size for the sample position was $\approx 900 \times 300 \mu\text{m}^2$. A Si (111)
11 double-crystal monochromator was applied. All of the experiments were conducted at
12 ambient temperature and applied in the transmission mode. The curve fitting and data
13 analysis were performed using the Artemis and IFEFFIT softwares.^{42,43} The energy
14 resolution ($\Delta E/E$) for the incident X-ray photons was estimated to be 2×10^{-4} .
15 Conventional transmission mode was adopted for the Ni K-edge EXAFS measurements.
16 To verify the reproducibility of the experimental data, at least two scans were collected
17 and analyzed for each sample.

18 **Electrode preparation for the H-Cell reactor:**

19 The SA Ni-NC catalyst ink was prepared by mixing 2.5 mg of SA Ni-NC powder
20 with 9.8 mL absolute ethanol and 200 μL of Nafion solution. Subsequently, 200 μL of

1 the ink was drop-casted on the mechanically polished glassy carbon electrode to obtain
2 a catalyst loading of 0.044 mg/cm² .

3 **H-Cell assembly:**

4 The H-Cell reactor was assembled using a Ag/AgCl reference electrode, a Pt plate
5 counter electrode (1.5 cm x 2 cm) and a glassy carbon working electrode (1.5 cm x 1
6 cm). The electrolyte consisted of 0.1 M KOH and 0.5 M K₂(SO)₄ mixture solution, the
7 pH value was 13.03. Before each time CO₂RR measurement, CO₂ is saturated for 30
8 min. The CO₂ flow is set to 5 mL min⁻¹ for the long-term stability tests. All data are
9 presented without iR-compensation.

10 **Electrode preparation for the flow reactor:**

11 The same amount of Ni catalyst (0.044 mg cm⁻²) was drop-casted on the surface of
12 GDE. The geometrical area was fixed to 1 cm² by the coverage of epoxy. A standard
13 cleaning procedure was used to clean the nickel foam anode by sonication in acetone
14 and then deionized water. The fresh cathode, anode, and CEM were used for each
15 electrolysis test to avoid contamination. The inner diameters for the inlet and outlet
16 tubes was 3.17 mm.

17 **Flow electrolyzer assembly:**

18 The model flow reactor was composed of a sandwich of flow frames, electrodes,
19 gaskets, and a membrane as illustrated in **Figure S8** forming a three-compartment
20 electrolyzer. One compartment delivered the CO₂ from the backside and through the
21 GDE (2.8 x 2.8 cm², fixed with a PTFE frame), while the second compartment

1 contained the catholyte solution (0.1 M KOH + 0.5 M K₂(SO)₄) between the GDE and
2 the CEM. The exposed area of the GDE was estimated to be 1 cm². A silver electrode
3 was used as a quasi reference electrode. Before the experiment, the electrode was
4 calibrated using a standard Ag/AgCl reference electrode. On the other side of the CEM,
5 the anolyte was injected between the CEM and the nickel foam anode. The flow frames
6 were made by PTFE, and the gaskets were made by rubber. Catholyte and anolyte were
7 recycled using the peristaltic pump (Heidolph PD 5201).

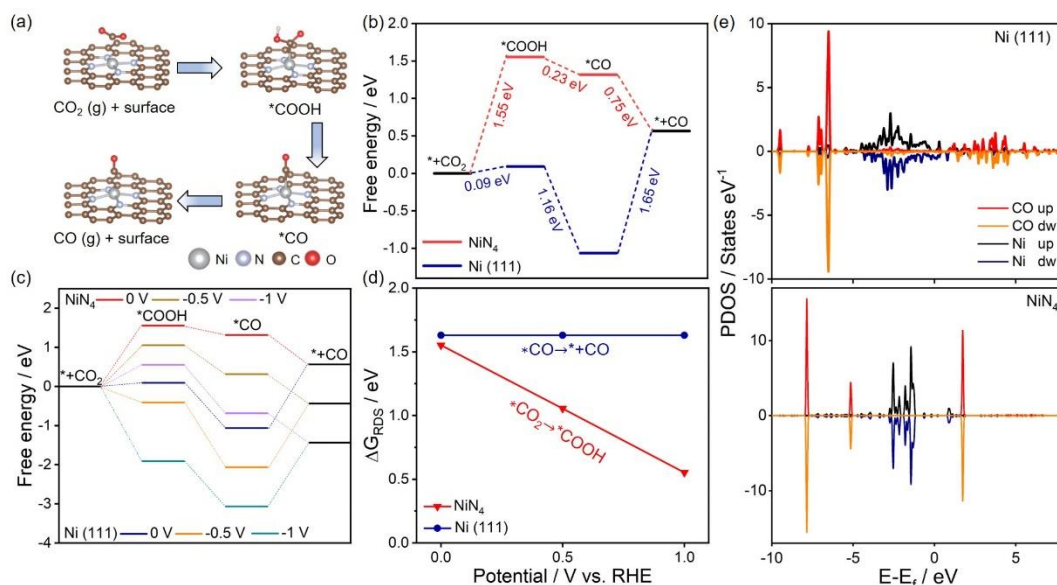
8 **Electrochemical measurements and gas-phase product analysis:**

9 All of the electrochemical measurements were measured with a VSP potentiostat (Bio-
10 Logic Science Instruments). All potentials were calibrated against the reversible
11 hydrogen electrode (RHE) by the equation: $E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.059 \text{ pH} + 0.197$. The
12 products of the reaction were detected using a micro gas chromatograph (Agilent 490)
13 and the micro-GC runs were initiated every 180 s. The GC was equipped with a packed
14 MolSieve 5 A column and a packed HaySep D column. Argon (Praxair, 99.999%) was
15 used as the carrier gas. A flame ionization detector with a mechanized was used to
16 quantify CO, CH₄, and C₂H₄ while a thermal conductivity detector (TCD) was used to
17 quantify hydrogen. The GC was calibrated by injecting a mixture calibration gas (2500
18 ppm CO, 2500 ppm CH₄, 2500 ppm, 2500 ppm C₂H₄, 2500 ppm C₂H₆ in CO₂, Linde).
19 In the H-cell system, the electrolyte was first saturated with CO₂ for 30 min and gas
20 products were detected after 30 min of reaction under potentiostat conditions. When
21 using the flow electrolyzer, the CO₂ flow rate was tuned between 20 and 140 standard
22 mL min⁻¹ using a calibrated flow controller. The electrolyte was circulated through the
23 anode and cathode compartments using a peristaltic pump. The gas outlet of the flow
24 cell was directed to a condenser before being vented directly into the gas-sampling loop
25 of the gas chromatograph. The EIS measurements were conducted at a constant
26 potential of 0.7 V vs. RHE with an AC voltage of 10 mV between 100 kHz to 100 mHz

1 in the flow cell. The C_{dl} was calculated from linear fit of the evolution of the cathodic
 2 and anodic current density with the potential scan rates.

3

4 FIGURES



5

6 **Figure 1. Theoretical and statistical predicational results on CO₂ reduction and**

7 **SA Ni-NC optimizing. a,** Proposed reaction pathways of SA Ni-NC for CO₂

8 electroreduction to CO. Silver, blue, grey and red balls represent Ni, N, C and O atoms,

9 respectively. **b,** DFT-based free energy profile for the optimized NiN₄ and Ni (111)

10 models during the CO₂ reduction process. **c,** Free energy diagram of the electrochemical

11 CO₂ reduction to CO for NiN₄ and Ni (111) at increasing applied potential (V vs. RHE)

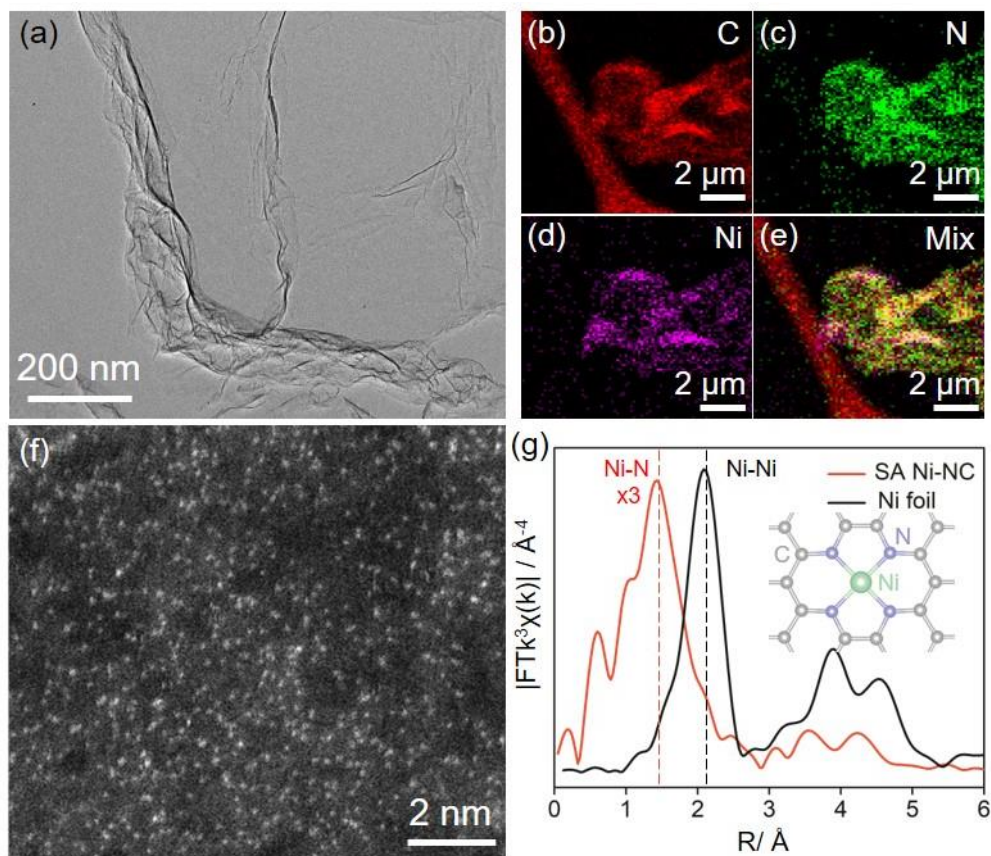
12 U = 0 V, U = -0.5 V and U = -1 V. **c,** Free energy change of the limiting step (ΔG_{RDS})

13 at different applied potential for NiN₄ and Ni (111), respectively. **d,** Free energy

14 diagram of hydrogen evolution for NiN₄ and Ni (111) without applied potential,

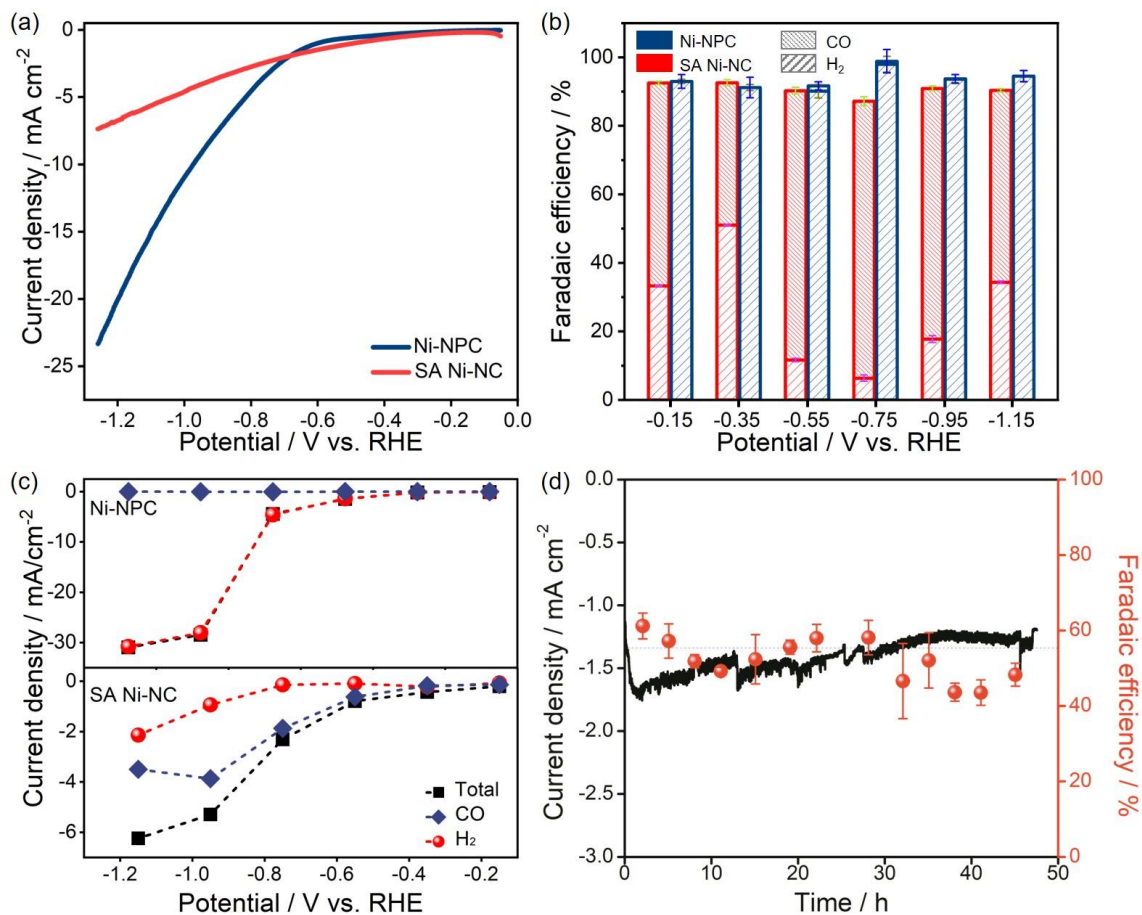
1 respectively. e, PDOS calculated by DFT for CO adsorbed on the active sites of the Ni
2 (111) and NiN₄.

3



4

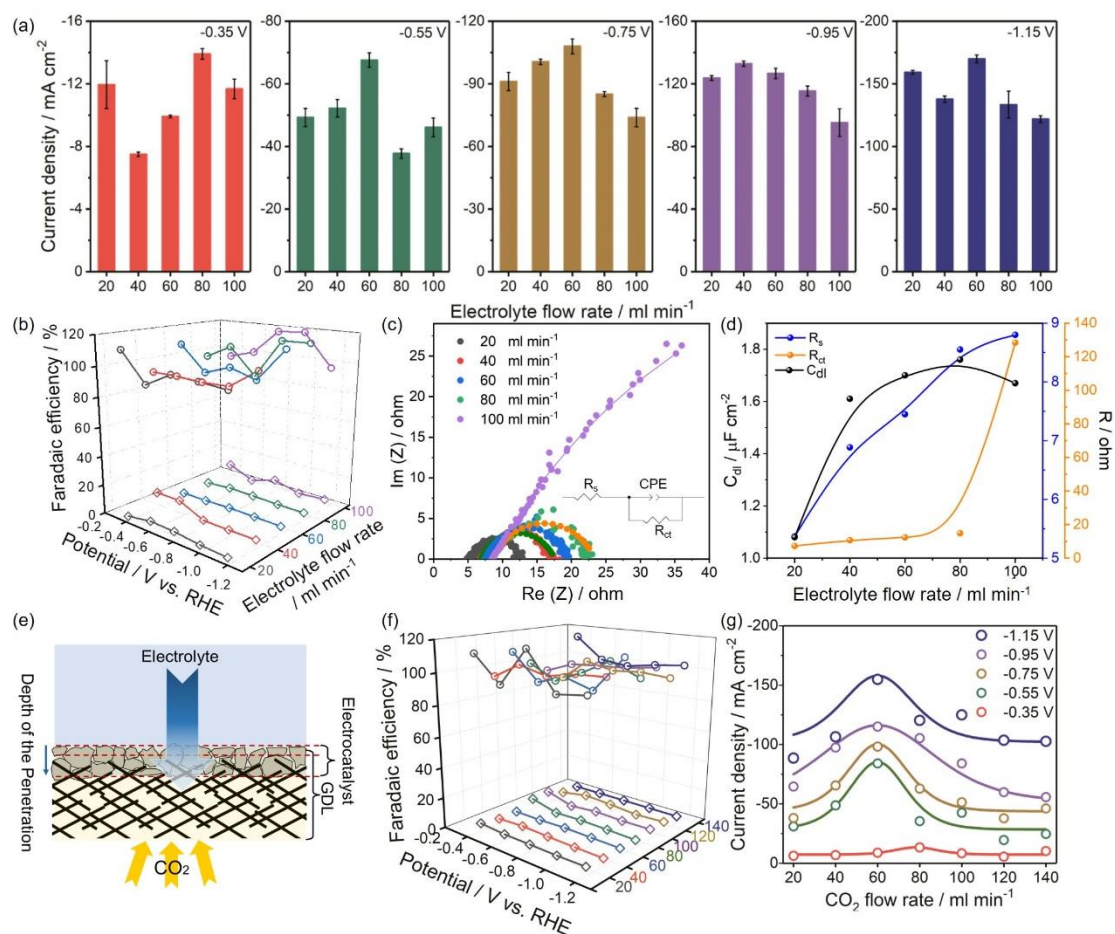
5 **Figure 2. Characterization of the SA Ni-NC catalyst.** a, Bright-field TEM image of
6 the SA Ni-NC. b-e, The EDX mapping of the SA Ni-NC, which demonstrates the
7 distribution of C, N, Ni. f, HAADF-STEM image of the SA Ni-NC. g, Fourier
8 transformed EXAFS spectrum for the SA Ni-NC and Ni foil. The SA Ni-NC spectrum
9 has been magnified 3 times.



1

2 **Figure 3. CO₂ electroreduction performance in the H-cell. a**, LSV curves measured
 3 in CO₂-saturated 0.1 M KOH + 0.5 M K₂SO₄ mixture electrolyte of SA Ni-NC and Ni-
 4 NPC modified glassy carbon electrodes. **b**, Faradaic efficiency and **c**, partial current
 5 density at various applied potentials of the SA Ni-NC and Ni-NPC electrodes. **d**,
 6 Evolution of the cathode current density and FE_{CO} of the SA Ni-NC catalyst obtained
 7 via potentiostatic measurement at -0.8 V vs. RHE.

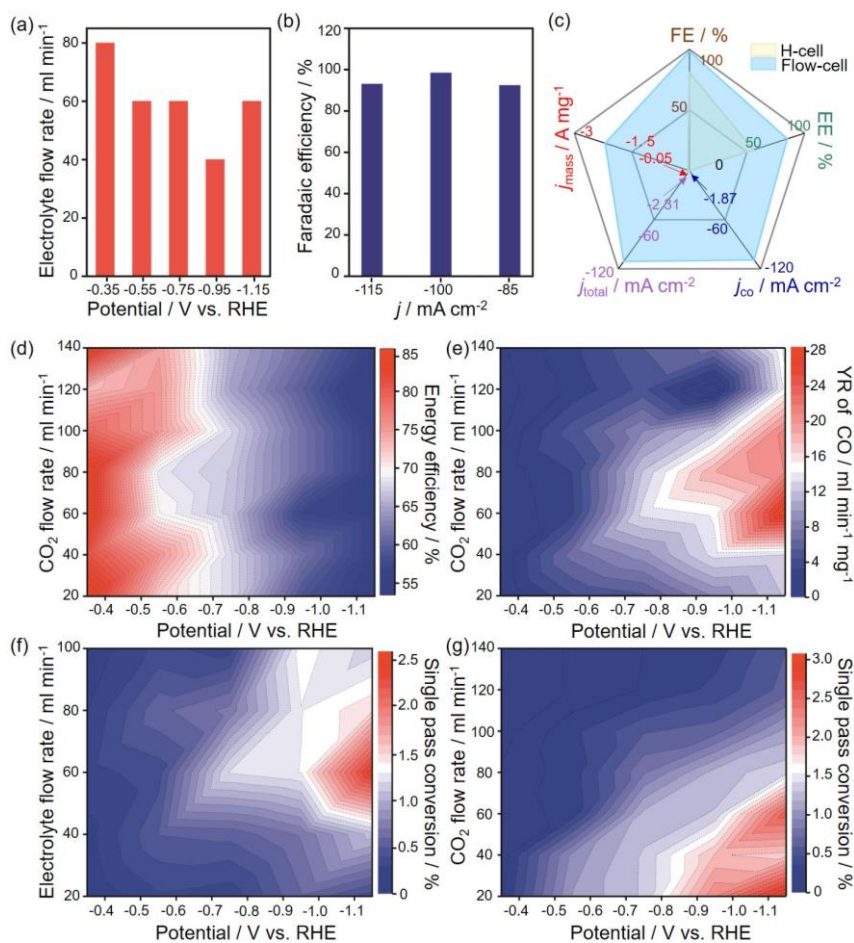
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1

2 **Figure 4. CO₂ electroreduction performance in the flow electrolyzer. a,** Current
 3 densities for the CO₂ reduction at various applied potentials and electrolyte flow rates
 4 on SA Ni-NC catalyst. **b,** FE_{CO} measured at different applied potentials with different
 5 electrolyte flow rates. **c,** Nyquist plots of Ni SA-NC catalyst with CO₂ flow of 60 mL
 6 min⁻¹ and electrolyte flow rates ranging from 20 mL min⁻¹ to 100 mL min⁻¹ (solid
 7 symbols are experimental results and solid lines are fitting results). **d,** C_{dl}, R_s and R_{ct} as
 8 a function of the flow rate of electrolyte for SA Ni-NC supported on the GDE in the
 9 flow cell reactor. R_s and R_{ct} are simulated based on the equivalent circuit (Insert in
 10 Figure 4c). **e,** Schematic illustration of the change of the three-phase interface with the
 11 electrolyte flow rate. **f,** FE_{CO} measured at different applied potentials with different CO₂
 12 flow rates. **g,** Evolution of the current density with the applied potentials for different
 13 CO₂ flow rates.

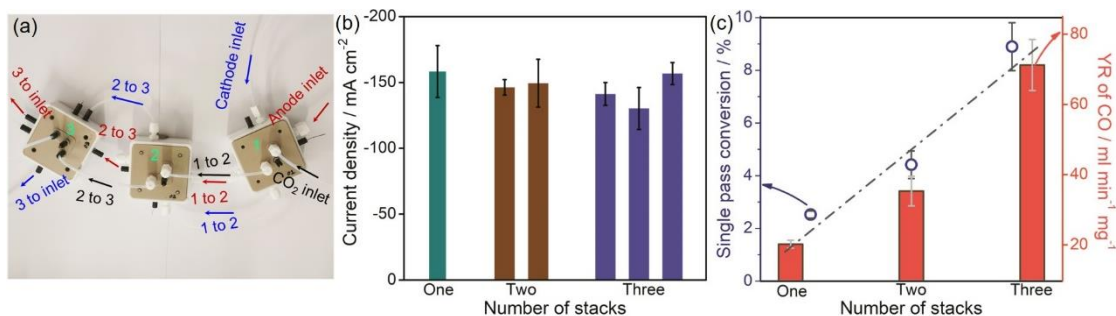
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2 **Figure 5. CO₂ electroreduction performance in the flow electrolyzer. a,** Optimum
 3 electrolyte flow rates determined for each potential with a constant CO₂ flow rate. **b,**
 4 FE_{CO} values from SA Ni-NC under different current densities. **c,** CO₂RR performance
 5 from SA Ni-NC measured in the H-cell and in the flow electrolyzer (The bold values
 6 with different colors labeled in the graph are corresponding to the j_{total} , j_{mass} and j_{CO}
 7 performance in H-cell, respectively). **d and e,** 2D map of the energy efficiency (**d**) and
 8 the yield rate of CO (YR of CO) (**e**) of electrochemical CO₂ reduction from SA Ni-NC
 9 catalyst with different CO₂ flow rates with a constant electrolyte flux of 60 mL min⁻¹ at
 10 different applied potentials. **f,** Single-pass CO₂ conversion for SA Ni-NC catalyst with
 11 different electrolyte flow rates at different applied potentials. **g,** Single-pass CO₂
 12 conversion for SA Ni-NC with different CO₂ flow rates at different applied potentials.

13



1

2 **Figure 6. CO₂ electroreduction performance in the stacked flow electrolyzers. a,**

3 **Scheme of the stack configuration consisting of three flow electrolyzers in series. b,**

4 **Current densities measured by implementing with one stack, two stacks and three stacks**

5 **of flow electrolyzers. c, Evolution of the single-pass CO₂ conversion and the yield rates**

6 **for SA Ni-NC catalyst with the flow electrolyzer stack.**

7 **ASSOCIATED CONTENT**

8 **Computational details, AFM image, SEM image, HRTEM images, STEM-ADF**

9 **micrographs, XPS spectra, XANES spectra, the expanded view of the flow electrolyzer**

10 **and the comparison of the single-pass CO₂-to-CO conversion performance (PDF).**

11 **AUTHOR INFORMATION**

12 **Corresponding Author**

13 *E-mail: damien.voiry@umontpellier.fr (D. Voiry).

14 **Author Contributions**

15 D.V., and Y. Z. designed and directed the research. Y. Z., K. Q., B. A. K., H. L. W.,

16 Y. P. Z, and W. S. W. synthesized the materials and performed the materials property

1 characterization. X. Q. C. and Y. W. performed the TEM, HAADF-STEM
2 characterization and XAS experiments. F.G., E.O., and L. L. performed the HRTEM
3 characterization. J. L. carried out and analyzed the theoretical results. Y. Z. and D. V.
4 wrote the manuscript. D. V. supervised the project and established the final version of
5 the paper. All authors discussed the results and commented on the manuscript. All
6 authors have approved the final version of the manuscript.

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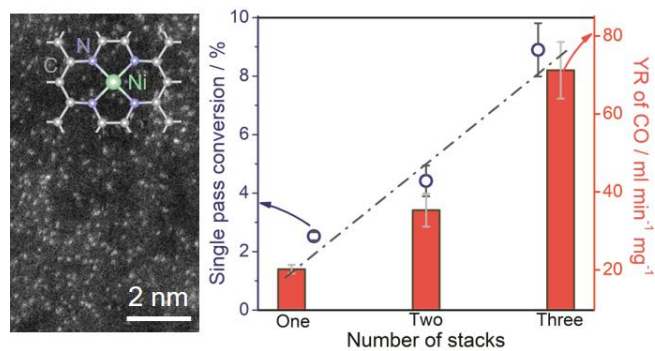
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