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1 Cyclic Voltammetry Driven Bi–Ag Single-Atom Alloy Electrocatalysts for Enhanced CO₂-to- 2 Formate Conversion

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10

11 Abstract

12 Single-atom alloy (SAA) catalysts offer synergistic electronic interactions, optimized adsorption
13 environments, and maximized atomic utilization. Here, we report an electrochemical strategy to
14 synthesize Bi single atoms dispersed on Ag (Bi–Ag SAAs), which serve as a promising catalyst
15 platform for CO₂-to-formate conversion. HAADF-STEM/EDS, XPS, and XRD collectively
16 demonstrate that cyclic voltammetry treatment reconstructs a thermally evaporated Bi layer on Ag
17 nanoparticles supported on a carbon electrode into atomically dispersed Bi sites on Ag. The resulting
18 Bi–Ag SAAs catalyst derived from a 15 nm Bi layer exhibited 1.9-fold higher formate Faradaic
19 efficiency and 3.5-fold higher formate selectivity than non-CV-treated samples, despite a substantially
20 lower Bi loading. Electrochemical impedance spectroscopy reveals a charge-transfer-resistance
21 hierarchy of Bi > AgBi > CV–AgBi under both N₂ and CO₂ saturated conditions, indicating enhanced
22 interfacial charge transfer for CO₂ reduction at atomically dispersed Bi sites. This work provides key
23 insight into how CV-driven reconstruction can be leveraged to create atomically dispersed single-atom
24 alloys for advanced CO₂-reduction catalyst design.

25

26 Keyword

27 Silver; Bismuth; Formate production; Single atom alloy; Cyclic voltammetry; CO₂ reduction;

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1 1. Introduction

2 The alarming rise in atmospheric carbon dioxide (CO₂) levels has emerged as one of the most critical
3 contributors to global warming. In response, the electrochemical CO₂ reduction reaction (CO₂RR) has
4 attracted growing interest as a promising route to not only mitigate CO₂ emissions but also convert it
5 into value-added chemicals such as methanol, ethanol, and formic acid^{1–3}. Among these, formic acid
6 stands out due to its high volumetric hydrogen content, non-toxicity, and capability to release hydrogen
7 under ambient conditions, making it a potential candidate for hydrogen storage applications^{4–7}. In
8 pursuit of selective CO₂-to-formate conversion, p-block metals such as Bi, Sn, and In have demonstrated
9 excellent catalytic activity^{8,9}, especially Bi exhibits the highest selectivity and lowest cost among
10 them^{10–14}. While monometallic Bi catalysts show high performance for formate production, recent
11 studies suggest that heterometallic systems can offer additional advantages such as synergistic
12 electronic interactions, optimized adsorption sites, and enhanced atomic utilization^{15–20}. Our previous
13 work²¹ on the micro Bi–nano Ni hierarchical system demonstrated that while full wetting significantly
14 enhanced formate production by increasing the surface area, hydrogen evolution reactions are not
15 completely suppressed due to the bulk-like characteristics of the Ni nanoparticles. On the other hand,
16 single-atom alloys (SAAs) are free from such concerns, enabling the precise tailoring of reaction
17 pathways toward the target product.

18 Despite extensive research on SAAs, reports on Bi-based catalysts remain scarcely explored^{14,22–27}, with
19 only a few reports on Bi SAAs involving Fe²⁵, Pd²⁶, and SnO₂²⁷. This lack of studies is primarily
20 attributed to the synthetic challenges associated with incorporating Bi as a single atom. Bi metal adopts
21 a rhombohedral lattice ($a = 0.454$ nm), which is distinct from the crystal structures of most other metals
22 and typically exhibits lattice mismatches exceeding 10%. This structural mismatch can promote the
23 formation of Janus-type architectures during wet-chemical synthesis, hindering uniform Bi atom
24 dispersion over the core surface and complicating SAAs fabrication^{28–30}. Lattice mismatch alone cannot
25 account for the synthetic challenges of Bi SAAs. Instead, surface and interfacial energies, cohesive and
26 segregation energetics, and growth kinetics—including precursor injection and reduction rates—
27 collectively determine whether Bi atoms remain as dispersed single atoms or phase-separate into Janus-
28 type architectures^{16,31–34}. Given the interplay of these multiple variables, the synthesis of Bi SAAs
29 demands a highly refined and precisely controlled process to achieve the desired atomic configuration.

30 Notably, another fundamental limitation is the intrinsic oxophilicity of Bi. Even ultrathin Bi coatings
31 on metallic cores oxidize rapidly to Bi₂O₃ upon brief air exposure³⁵. Once oxidized, Bi layers undergo
32 solid-state dewetting and islanding, yielding Bi aggregates rather than thin layers with conformal
33 coverage^{35–38}. The pronounced oxophilicity of Bi inherently undermines stable Bi structures unless Bi
34 is directly synthesized as a single atom dispersion and firmly anchored to the metal substrate via robust
35 Bi-M metallic bonding. As mentioned above, the synthesis of Bi SAAs is fundamentally hindered by a



1 combination of intrinsic limitations stemming from unique properties of Bi. These physicochemical
2 constraints severely impede synthesis via conventional approaches, necessitating the development of
3 new synthetic strategy that can effectively overcome these hurdles to stabilize atomically dispersed Bi
4 SAAs.

5 In this work, we introduce a voltammetry-regulated strategy that enables the formation of Bi SSAs on
6 Ag nanoparticles through selective redox cycling in chloride electrolytes. By combining thermal
7 evaporation of conformal Bi overlayers with controlled cyclic voltammetry, Bi is selectively oxidized
8 and subsequently reduced onto Ag, producing atomically isolated Bi sites without forming extended Bi
9 domains. Comprehensive structural and electrochemical analyses reveal that this process induces Bi
10 incorporation into the Ag lattice, establishes a thin AgCl/BiOCl passivation that is reductively removed
11 during CO₂RR, and ultimately yields stable Bi–Ag SAA catalytic centers. This synthetic method not
12 only maximizes Bi atom utilization but also enhances formate production and selectivity relative to
13 thick Bi layers, demonstrating the unique reactivity of Bi single-atom sites in CO₂ electroreduction.
14 Accordingly, this work establishes a robust and generalizable electrochemical route for constructing Bi
15 SAAs and elucidates the critical role of selective Bi redox processes in tailoring active sites for CO₂RR.

16

17 2. Experiments

18 2.1 Materials and Chemicals

19 AgNO₃ (99.8%), ethylene glycol (C₂H₆O₂, 99.9%) and isopropyl alcohol anhydrous (C₃H₈O, 99.9%)
20 were supplied by Samchun Chemicals. Polyvinylpyrrolidone (Mw ≈ 55 000) and NaSH·xH₂O were
21 purchased by Sigma-Aldrich. The Nafion NR211 membrane was obtained from Ion Power, Inc., a
22 Nafion solution (5 weight %, DuPont) from NanoHoldings (Korea), and carbon paper (Sigracet 28 BC)
23 from Fuel Cell Store. Bi shot (99.999%) was purchased by ITASCO.

24

25 2.2. Sample preparation

26 Silver nanoparticles were synthesized by a polyol method³⁹ with minor modifications. Reactions were
27 carried out in a 50 mL round-bottom flask immersed in a silicone-oil bath. Ethylene glycol (EG, 6.0
28 mL) was heated to 150 °C under stirring (320 rpm), and all reagents were added as rapid, single-shot
29 pipette injections. A solution of NaSH·1.5H₂O in EG (3.0 mM; 70 μL) was injected, followed by PVP
30 (Mw ≈ 55,000) in EG (20 mg mL⁻¹; 1.5 mL). After 8 minutes at 150 °C, AgNO₃ in EG (282 mM; 0.50
31 mL) was injected and the reaction was continued for 20 minutes until the dispersion turned green–ochre,
32 then quenched in an ice bath. The dispersion was diluted with acetone (1:4, v/v), divided into two



1 conical tubes, and centrifuged (2,000 g, 25–30 minutes). Pellets were redispersed in deionized water (6
2 mL), transferred to microcentrifuge tubes, and centrifuged at 8,000 g for 10 minutes with isopropanol
3 (IPA) washing; this step was repeated three times. Purified Ag nanoparticles were finally dispersed in
4 EG (8.0 mL) containing PVP (20 mg mL⁻¹) for subsequent processing.

5 To remove residual PVP/EG prior to electrode fabrication, 80 μL of the prepared Ag dispersion in EG
6 was diluted in 1.5 mL IPA and centrifuged twice. The Ag was resuspended in IPA containing 10 μL of
7 Nafion solution (5 weight %) and drop-cast onto 1 × 1 cm² carbon paper pre-cleaned by O₂ plasma for
8 5 minutes. This Ag-loaded electrode is hereafter denoted “Ag.” Bi was subsequently deposited onto Ag
9 by thermal evaporator (REP-5004, SNTTEK, Korea). The deposition was carried out at a chamber
10 pressure of 6 × 10⁻⁶ Torr and a constant deposition rate of 0.5 Å s⁻¹, with the substrate maintained at an
11 ambient temperature of 20°C. The nominal thicknesses of 2, 5, 15, 25, 35, and 45 nm, yielding Bi-
12 overcoated Ag electrodes denoted “AgBi_t” (t = nominal Bi thickness in nm).

13 Cyclic voltammetry was performed in N₂-purged 0.1 M HCl using a three-electrode configuration. The
14 AgBi electrodes prepared above were used as the working electrode with an Ag/AgCl (3 M KCl)
15 reference electrode and a graphite rod counter electrode. The potential range was between -0.08 and
16 +0.08 V vs Ag/AgCl at a scan rate of 50 mV s⁻¹. After CV treatment, the electrodes were rinsed several
17 times with anhydrous IPA and dried under vacuum. Samples subjected to cyclic voltammetry in 0.1 M
18 HCl are labeled “CV-AgBi_t” (where t is the nominal Bi thickness in nm).

20 2.3. Characterization

21 The samples were analyzed by field-emission scanning electron microscopy (FE-SEM, JSM-7100F,
22 JEOL), energy-dispersive spectroscopy (EDS, attachment for SEM, Oxford), X-ray diffraction (XRD,
23 Rigaku SmartLab SE diffractometer) with Cu-Kα radiation (λ = 1.5405 Å), and field-emission gun
24 (FEG) TEM operating at 300 keV (Thermo Fisher Scientific Inc. Spectra 300 TEM) with STEM unit.
25 X-ray photoelectron spectroscopy (XPS) was performed using a concentric hemispherical analyzer
26 (PHOIBOS 150 1D-DLD, SPECS, Germany) with a monochromatic Al Kα source (hν = 1486.6 eV).
27 Nuclear magnetic resonance (FT-NMR 500 MHz, Unity Inova, Varian), gas chromatography (GC,
28 6890N, Agilent) was used to determine the H₂ and CO contents of the electrochemical CO₂ reduction
29 reaction.

31 2.4. Electrochemical Measurements

32 Chronoamperometry was performed using a PGSTAT128N (Autolab) at -1.5 V (vs. Ag/AgCl, 3 M
33 KCl). All electrochemical measurements were carried out in an H-cell with a Nafion NR211 membrane



1 using a 0.5 M KHCO_3 solution at room temperature. Prepared samples were used as the working
2 electrodes, whereas a graphite rod and Ag/AgCl (3 M KCl) served as the counter and reference
3 electrodes, respectively. In addition, CO_2 was bubbled into a 0.5 M KHCO_3 solution in the cathode
4 compartment.

5 Electrochemical impedance spectroscopy (EIS) was performed using a CompactStat spectrometer
6 (Ivium Technologies). The counter and reference electrodes were a graphite rod and Ag/AgCl (3 M
7 KCl), respectively. Bi, AgBi, and CV-AgBi samples measured in 0.5 M KHCO_3 electrolyte with N_2
8 and CO_2 saturated condition. The AC amplitude was 5 mV and the frequency range was from 100 MHz
9 to 0.1 Hz.

11 3. Results and Discussion

12 The strategy for synthesizing Bi SAAs on Ag nanoparticles is illustrated in Fig. 1a. Ag nanoparticles
13 (~50 nm) were first prepared via a conventional solution-based method and deposited onto carbon paper
14 by drop-casting. Subsequently, Bi thin layers were deposited by thermal evaporation to achieve
15 conformal coverage over the Ag surface, which is critical for enabling uniform electrochemical
16 modification during the following CV treatment, performed in 0.1 M HCl to induce the formation of
17 atomically dispersed Bi on the Ag surface (CV-AgBi) (Fig. 1b-e). Silver was selected as the core metal
18 owing to its established CO_2RR activity and broad applicability in bimetallic SAAs systems^{40–42}.

19 SEM images (Fig. S1) reveal the morphologies of Ag nanoparticles and the Bi overlayer as a function
20 of Bi-layer thickness (denoted as $\text{AgBi}_{2\text{nm}}$, $\text{AgBi}_{5\text{nm}}$, $\text{AgBi}_{15\text{nm}}$, $\text{AgBi}_{25\text{nm}}$, $\text{AgBi}_{35\text{nm}}$, and $\text{AgBi}_{45\text{nm}}$), as
21 well as the effect of the CV treatment. The Ag nanoparticle without Bi layer showed essentially
22 unchanged shape, but AgBi samples exhibited edge dissolution by CV. This morphological change
23 arises from the CV-induced redeposition of Bi onto Ag rather than from the direct effect of CV on Ag
24 itself. Furthermore, SEM images taken after 1 hour of the CO_2RR (Fig. S2) show no significant
25 morphological changes compared to the initial state, confirming the structural stability of the CV-
26 $\text{AgBi}_{15\text{nm}}$ during the early stage of the reaction.

27 In the CV- $\text{AgBi}_{15\text{nm}}$ sample, HAADF-STEM and related EDS mapping (Fig. 1b–d) showed only trace
28 Bi localized on Ag, without evidence of extended Bi domains. High-resolution HAADF-STEM image
29 and corresponding EDS (Figs. 1e and S3) further revealed highly dispersed, isolated Bi atoms across
30 the Ag surface. The absence of continuous Bi phases together with the ultra-low Bi signal in elemental
31 maps demonstrated the single-atom nature of the Bi species after CV treatment.

32 The application of CV rests on two complementary properties (Figs. 2, S4–S7): (i) the standard
33 reduction potentials of the constituent elements and (ii) the electronic conductivities. These features



1 enabled the selective oxidation of Bi, which was subsequently re-reduced selectively on the Ag surface.
2 Fig. 2 presents the CV responses of bare carbon paper, Ag-deposited carbon paper (Ag), 2 nm-thick Bi
3 deposited on Ag (AgBi_{2nm}) and Ag-free 2 nm-thick Bi-coated carbon paper (Bi_{2nm}), enabling a
4 comparative analysis of electrochemical behavior. Within the potential window of -0.08 to 0.08 V,
5 carbon paper (Fig. 2a) and Ag (Fig. 2b) showed no discernible redox features attributable to silver
6 oxides or silver chloride (Figs. S4c and S6), confirming that Ag remained in the metallic state (Ag⁰)
7 within this potential window. By contrast, Bi_{2nm} (Fig. 2c) exhibited a distinct oxidation peak indicated
8 by the red dashed line. Notably, a corresponding reduction feature was absent for Bi_{2nm}, indicating that
9 Bi was not reduced within the applied potential range.

10 AgBi_{2nm} showed two additional peaks in the CV curves (Fig. 2d), which emerged in the oxidative scan
11 (blue box), following the oxidation of Bi (red box), and the other (green box) during the reductive scan.
12 The oxidation potentials for monolayer Bi are distinct from bulk Bi⁴³. The blue box is assigned to the
13 oxidation peak of Bi atoms on the Ag nanoparticle surface. The oxidation of Bi on Ag needs higher
14 energy than that of Bi on carbon. The reduction peak (green box) was observed exclusively in the
15 presence of Ag, suggesting that this process corresponds to the reduction of Bi onto Ag. A comparison
16 of AgBi_{1nm} and Bi_{1nm} in Fig. S4 demonstrated that the required potentials for overpotential deposition
17 (OPD) and underpotential deposition (UPD) are substrate-dependent^{44,45}, indicating that the reduction
18 peak in Fig. 2d corresponds to the UPD of Bi on Ag.

19 Notably, the Bi oxidation peak (red box in Fig. 2d) was observed only during the first CV cycle for the
20 Bi_{2nm} and AgBi_{2nm} samples, whereas the Ag-related peaks (blue box) persisted in the subsequent scans.
21 This behavior is consistent with the formation of BiOCl in the HCl electrolyte, whose reduction occurs
22 at more negative potential than that of free Bi ions (Fig. S5) and peak intensity is proportional to the
23 thickness of Bi layer. Chloride ion in HCl electrolyte scavenges Bi ion to form BiOCl, thereby depleting
24 free Bi ion and suppressing Bi reduction within the scanned potential window (-0.08 V to 0.08V). The
25 CV results strongly suggest that Bi was selectively retained on Ag sites, rather than on the carbon
26 substrate, following the initial oxidation scans.

27 The number of CV cycles required to remove Bi completely from the carbon electrode increases with
28 the thickness of the deposited Bi layer as shown in Fig. S7. For Bi thicknesses of 2 and 5 nm (AgBi_{2nm}
29 and AgBi_{5nm}), a single CV cycle is sufficient for complete removal. In contrast, the 15 and 25 nm layers
30 (AgBi_{15nm} and AgBi_{25nm}) required two cycles, while the 35 and 45 nm layers (AgBi_{35nm} and AgBi_{45nm})
31 necessitated three cycles. After the lifting-off cycles, all the AgBi samples demonstrated nearly identical
32 CV curves, indicating bismuth-selective redox behavior regardless of the initial Bi-layer thickness.
33 Quantitative analyses of reduced Bi on the electrodes were performed by integrating the Bi reduction
34 peaks in Fig. S7, where the reduced Bi quantity increased with Bi layer thickness (Figs. S8 and S9). For
35 Bi layers thicker than 35 nm, the amount of Bi incorporated into the Ag nanoparticles reached a plateau,



1 corresponding to the maximum electrochemically reducible Bi content.

2 The X-ray photoelectron spectroscopy (XPS) analysis revealed the oxidation states and atomic
3 compositions of AgBi_{15nm} and CV-AgBi_{15nm} (Fig. 3 and Table S1). The Bi 4f spectra indicates that the
4 surface of AgBi_{15nm} is predominantly composed of Bi³⁺ species, such as Bi₂O₃. A minor metallic Bi
5 component was also detected, which is attributed to the relatively thick Bi layer (15 nm) that likely
6 protected the underlying regions from oxidation. The CV-AgBi_{15nm} mostly has Bi³⁺ in the form of
7 BiOCl⁴⁶ since the CV has been done in 0.1 M HCl solution. AgBi_{15nm} showed exclusively metal state
8 of Ag (Ag⁰), whereas CV-AgBi_{15nm} exhibited both Ag⁰ and AgCl⁴⁷ components. The intensity of the Ag
9 3d peaks increased after CV, as the Bi overlayer was removed during the CV treatment. Notably, the
10 chlorine to bismuth atomic ratio was approximately 4.7 (Fig. S10), far exceeding the 1:1 stoichiometry
11 of BiOCl, corroborating the formation of an AgCl surface layer on Ag after CV.

12 The O 1s spectra also showed that AgBi_{15nm} has lower binding energy of both non-defective (O1) and
13 defective (O2) metal oxides⁴⁸, consistent with the presence of Bi₂O₃, along with C-O bonds peak
14 originating from oxygenated carbon electrode⁴⁹. In contrast, CV-AgBi_{15nm} exhibited the peaks with
15 higher binding energy, assigned to C-O bonds and Nafion⁵⁰. The absence of metal oxide related peaks
16 (O1 and O2) in CV-AgBi_{15nm} can be explained by the removal of most Bi species by CV, which exposed
17 the underlying substrates. This interpretation was corroborated by the emergence of Nafion-related
18 peaks in the C 1s (Fig. 3h) and S 2p (Fig. S10)⁵⁰.

19 Fig. S11 revealed that as the initial Bi thickness increases, the surface Bi concentration and the relative
20 proportion of metallic Bi⁰ significantly increase, with AgBi_{35nm} sample exhibiting a complete shielding
21 of the underlying Ag substrate as evidenced by the disappearance of Ag characteristic peaks.

22 This significant increase in metallic Bi⁰ intensity at 35 nm is related to our XRD observations, which
23 indicate a structural transition from a purely amorphous phase to a mixed amorphous-crystalline phase
24 at this thickness. These findings directly support the electrochemical results, where AgBi_{35nm} achieved
25 higher formate yield and selectivity compared to samples with lower thickness.

26 While the Ag/AgCl ratio varies with CV cycling (Fig. S12), it appears to have a negligible direct impact
27 on the steady-state activity since Ag/Cl is readily reduced to metallic Ag⁰ during the initial stage
28 of CO₂RR. The catalytic performance is primarily governed by the maximum density of active Bi
29 single-atom species integrated within the reconstructed Ag matrix, which increases proportionally with
30 the initial Bi loading.

31 The X-ray diffraction (XRD) patterns displayed the peaks corresponding to graphite ($2\theta \approx 37.6^\circ$) and
32 Ag(111) ($2\theta \approx 38.2^\circ$) within the 2θ range of 37.5° to 39.0° (Fig. 4), while the peaks from other species
33 were not observed in this region (Table S2). There was no noticeable peak shift of pure Ag before and



1 after the CV process (Fig. 4a). Upon Bi deposition, the Ag(111) peak exhibited a clear shift toward
2 lower angles compared to pure Ag, and the extent of this shift increased with increasing Bi layer
3 thickness, confirming that bismuth atoms were diffused into the Ag lattice, resulting in the lattice
4 expansion of Ag nanoparticles^{51–53}. Furthermore, after the CV process, the Ag(111) peak of AgBi
5 samples underwent an additional shift to lower angles, implying higher concentration of Bi in the Ag
6 lattice through electrochemical treatments.

7 Unlike the increasing shift of Ag (111) peaks in AgBi samples, the Ag(111) peaks of CV-AgBi samples
8 gave the similar diffraction angles ($38.16^\circ \sim 38.19^\circ$), regardless of the initial Bi thickness. Bi atoms
9 diffuse into the Ag lattice up to approximately 2.3 weight percentage⁵¹. We expect that the Bi content
10 in the AgBi samples reached an upper limit after the CV process, resulting in similar Ag(111) peak
11 positions for CV-AgBi samples, regardless of the thickness of the initial Bi deposition.

12 The intensity of the Ag(111) peak decreased in the CV-treated samples, and this decrease was closely
13 related to the number of CV cycles required to remove excess Bi. For instance, AgBi_{5nm} requires 1
14 cycle; AgBi_{15nm} and AgBi_{25nm} required 2 cycles; and AgBi_{35nm} and AgBi_{45nm} required 3 cycles, as
15 confirmed in Fig. S7. The variation of peak intensity is attributed to the partial transformation of surface
16 Ag into AgCl by CV treatments in the HCl electrolyte. For Bi, the Bi(104) peak was absent in the AgBi
17 samples with Bi thicknesses up to 25 nm, indicating that Bi predominantly existed as amorphous Bi₂O₃
18 under ambient conditions. Above 35 nm, a broad peak emerged and gradually increased in intensity
19 with increasing thickness, indicating the formation of a metallic Bi phase.

20 The CV, TEM, XPS, and XRD analyses indicated that Bi single atoms on Ag nanoparticles were
21 generated immediately after the CV treatment in 0.1 M HCl. During sample retrieval and washing, a
22 thin BiOCl/AgCl passivation layer formed on the Ag surface, in which BiOCl existed as isolated species
23 on AgCl (Fig. 1b–e). Upon applying a cathodic CO₂RR potential, AgCl and BiOCl were reduced to
24 Ag⁵⁴ and Bi^{55,56}, respectively. The resulting Bi atoms formed Bi–Ag SAAs rather than persistent Bi–O–
25 Ag or Bi–Cl–Ag coordination. Consistent with the coordination-stability hierarchy ($N > O \gg Cl$)^{57–60},
26 chloride coordination is far less robust than N- or lattice-O anchoring. Oxygen in robust oxide lattices
27 can persist under cathodic bias⁵⁶, whereas the oxygen associated with isolated BiOCl appeared only in
28 trace amounts and was readily removed, thereby facilitating Bi–Ag coordination. Thus, CV treatment
29 in HCl, followed by the application of a reducing potential, effectively removed Cl and O species and
30 promoted Bi–Ag coordination, thereby facilitating the formation of Bi–Ag SAAs.

31 The electrochemical CO₂RR measurements were conducted under identical conditions (–1.5 V vs
32 Ag/AgCl (3 M KCl), CO₂-saturated 0.5 M KHCO₃ solution in H-cell) to investigate the influence of Bi
33 single atoms on Ag via CV treatment (Figs. 5 and 6). As the Bi layer thickness increased in the Bi
34 catalysts without Ag nanoparticles, both the FE and the partial current density for formate increased,



1 whereas CO production showed only a modest rise to a thickness of 35 nm (Fig. 5a, d–e). As shown in
2 Fig. 4a, Bi crystallinity increased with thickness, and Bi transformed into mixed amorphous-crystalline
3 state. The mixed amorphous–crystalline Bi is reported to deliver higher formate production in CO₂RR
4 than either purely amorphous or purely crystalline Bi^{61,62}. Thus, CO₂RR performance shows the
5 dependence on deposited Bi layer thickness. The formate yield reached a plateau because the extent of
6 the amorphous–crystalline phase was similar for the 35 nm and 45 nm samples.

7 Meanwhile, both AgBi and CV-AgBi consistently exhibited higher FE_{CO} and *j*_{CO} values than Bi, which
8 is attributable to the presence of Ag (Fig. 5b–e). Notably, AgBi showed ~1.5-fold higher *j*_{CO} values than
9 CV-AgBi, even though the Ag surface was covered by a thick Bi overlayer. This suggests that the
10 contribution of Ag to CO₂RR remains more pronounced in AgBi with a thick Bi coating than in CV-
11 AgBi, where only Bi single atoms are present. Regarding formate production, both FE_{formate} and *j*_{formate}
12 for AgBi and CV-AgBi exhibited a clear dependence on Bi layer thickness and exceeded those of Bi
13 once the Bi thickness surpassed specific thresholds. In AgBi, FE_{formate} and *j*_{formate} became higher than
14 those of Bi only when the Bi overlayer was thicker than 35 nm, whereas in CV-AgBi this transition
15 occurred at a much lower thickness of 15 nm. This indicates that AgBi requires a substantially thicker
16 Bi layer (35 nm) to suppress the catalytic influence of Ag and to enable formate formation by Bi. In
17 contrast, CV-AgBi achieves comparable enhancement with only a 15 nm Bi layer, implying that Bi
18 single atoms in CV-AgBi are intrinsically more efficient for formate production. The CO₂RR activity
19 of the carbon electrode without metal catalysts and CV treated Bi 15 nm thickness samples showed only
20 hydrogen evolution reaction (Fig. S13). The presence of Ag nanoparticles played a crucial role in the
21 electrochemical reaction.

22 We assume that these results closely correlate with both the crystallinity of Bi and the amount of Bi
23 incorporated into Ag. For AgBi samples with Bi layers thinner than 25 nm, the Bi phase is
24 predominantly amorphous (Fig. 4a), which is known to yield relatively poor CO₂RR performance^{61,62}.
25 *j*_{formate} for AgBi exceeds that of Bi only when the Bi thickness surpasses ~35 nm, where a mixed
26 amorphous–crystalline phase forms and enhances activity. For CV-AgBi samples within the 15–25 nm
27 range, sufficient Bi is reduced and anchored during CV to participate actively in CO₂RR (Fig. S8),
28 producing a pronounced performance enhancement through synergistic effects with Ag. However, at
29 very low thicknesses (2–5 nm), only a small amount of Bi is reduced during CV, leaving Ag to dominate
30 the surface (Fig. S8), and thus the improvement after CV is negligible. Beyond 35 nm, the Bi layer
31 existed in a mixed amorphous–crystalline phase, and the formate yield of Bi, AgBi, and CV-AgBi
32 reached an upper limit (Fig. 6a). Notably, over 35 nm, the formate yield of thick Bi layer in AgBi was
33 comparable to that of Bi single atoms in CV-AgBi, whereas the formate selectivity was substantially
34 higher for CV-AgBi (Fig. 6b).

35 Depending on the Bi layer thickness, three distinct regimes were observed (Fig. 6c). For Bi layers of



1 2–5 nm, the CO₂RR performance was similar with and without CV treatment. For Bi layers of 15–25
2 nm, the CV process markedly enhanced formate production and selectivity, by factors of ~1.8 and ~3.2,
3 respectively. For Bi layers of 35–45 nm, the catalysts exhibited comparable formate production
4 regardless of CV treatment, whereas the formate selectivity increased by ~1.7-fold after CV.

5 Electrochemical impedance spectroscopy (EIS) analysis was conducted to evaluate charge transfer
6 resistance (R_{ct}) under both N₂- and CO₂-saturated conditions (Fig. 7)⁶³. The bare carbon electrode
7 exhibited identical R_{ct} values regardless of the gas environment (Fig. 7a), indicating that only HER
8 occurred. Under N₂, Ag performed HER with a capability comparable to carbon paper, as evidenced by
9 an R_{ct} only ~1.5 Ω higher (Fig. 7b). In contrast, under CO₂-saturated conditions, Ag showed a higher
10 R_{ct} than under N₂, consistent with previous reports that the Nyquist semicircle reflects the charge-
11 transfer process associated with CO₂RR⁶³. Accordingly, the increased R_{ct} under CO₂ indicated the
12 engagement of the CO₂ reduction pathway.

13 Under N₂-saturated conditions, AgBi samples exhibited lower R_{ct} values than pure Bi, and CV-AgBi
14 samples showed an even further decrease in R_{ct} compared with AgBi (Fig. 7c–f). This result indicates
15 that the Ag-modified Bi catalysts enable more facile charge transfer for CO₂RR. Under N₂-saturated
16 conditions, the measured R_{ct} decreased in the order Bi > AgBi > CV-AgBi > Ag. The smaller R_{ct} under
17 N₂ indicates that protons can participate more readily in the interfacial process, thereby facilitating
18 hydrogen adsorption and evolution⁶⁴. The interfacial charge transfer process in CO₂RR also involves
19 protons or proton-containing reactants^{63,65}. Enhanced dissociation of H₂O and HCO₃⁻ can facilitate the
20 generation of sufficient protons and accelerate the hydrogenation of CO₂ to OCHO*, thereby improving
21 the formate yield⁶⁶. Based on the EIS results, we propose that AgBi and CV-AgBi enable more facile
22 charge transfer to CO₂RR intermediates, as well as increased proton availability at the interface, thereby
23 leading to higher rates of formate production. These electrochemical results demonstrated that the
24 presence of Ag particles boosted formate formation relative to Bi-only samples, highlighting the
25 superiority of the bimetallic configuration. Despite a substantially lower Bi loading, the single-atom
26 configuration can deliver formate yields comparable to those of thick Bi, underscoring its maximized
27 atom utilization of Bi in SAAs configuration.

28

29 4. Conclusion

30 We demonstrated a designed strategy for synthesizing Bi–Ag single-atom alloy catalysts (CV-AgBi)
31 by converting a thermally evaporated Bi overlayer on Ag nanoparticles into atomically dispersed Bi
32 species via cyclic voltammetry. Electrochemical measurements, together with structural and chemical
33 analyses, confirmed the formation of atomically dispersed Bi, while EIS results indicate that Bi single
34 atoms facilitate more efficient CO₂ activation through enhanced charge transfer and proton supply.



1 Catalytically, the Bi single-atom configuration (CV-AgBi_{15nm}) increases the formate yield by 1.9-fold
2 and boosts the formate selectivity ($FE_{\text{formate}}/FE_{\text{CO}}$) by 3.5-fold relative to the thick Bi overlayer
3 (AgBi_{15nm}), despite requiring substantially less Bi. These findings highlight that cyclic voltammetry
4 offers a simple and effective route for constructing Bi–Ag SAAs, and the concept is potentially
5 extendable to other metal systems.

7 **Author contributions**

8 Yongsu An: Conceptualization, Methodology, Formal analysis, Investigation, Visualization, Writing -
9 original draft. Sunlun Kwon: Validation. Chan Woo Lee: Writing - review & editing. Young Heon
10 Kim: Investigation, Writing - review & editing. Duk-Young Jung: Conceptualization, Supervision,
11 Project administration, Funding acquisition, Writing - review & editing.

13 **Conflicts of interest**

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

17 **Data availability**

18 Additional data supporting this article have been included as part of the ESI.† Numerical data can be
19 made available upon request.

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23 Research Foundation of Korea (RS-2025-25442528). S. Kwon acknowledges Sejong Science
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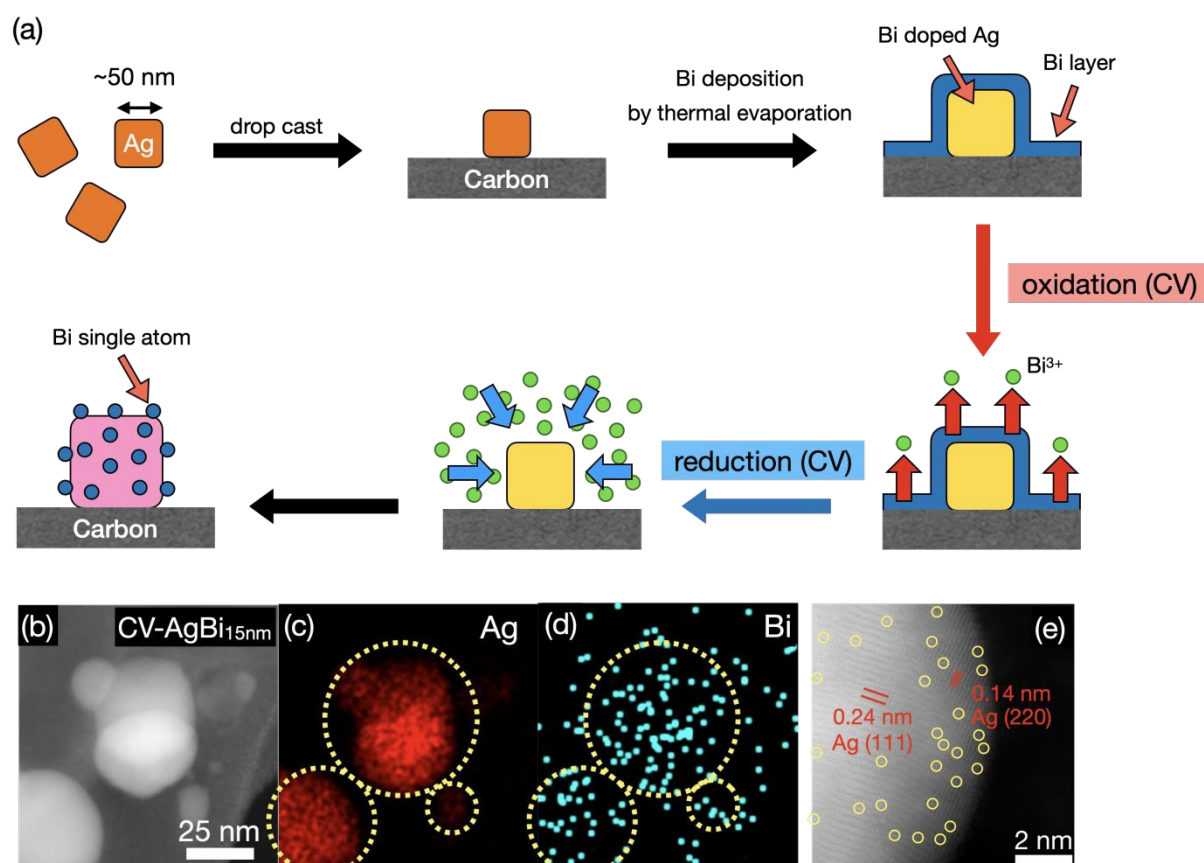
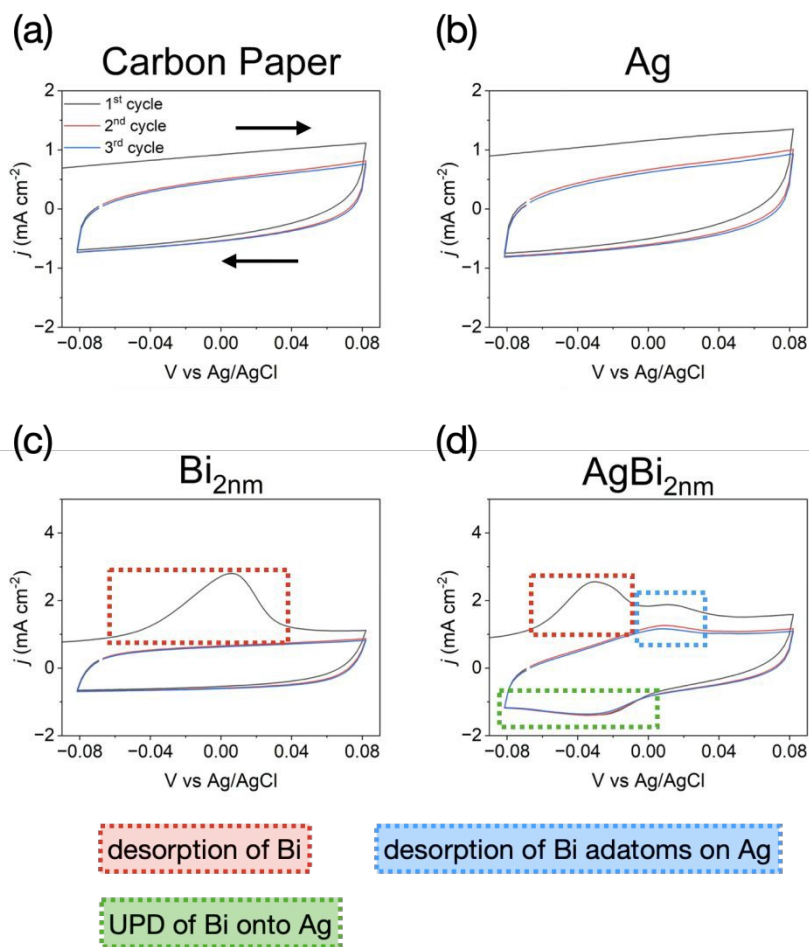


Fig. 1. (a) Schematic illustration of the synthesis of CV-AgBi, Bi deposition followed by cyclic voltammetry (CV) in 0.1 M HCl. (b) HAADF-STEM and related EDS-mapping results of (c) Ag, (d) Bi for CV-AgBi_{15nm}. The blue circles in (d) serve as graphical guides to highlight representative Bi single atom sites. (e) High-resolution HAADF-STEM image of CV-AgBi_{15nm}.





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Fig. 2. Cyclic voltammetry curves of (a) carbon paper, (b) Ag, (c) Bi_{2nm} and (d) AgBi_{2nm}.



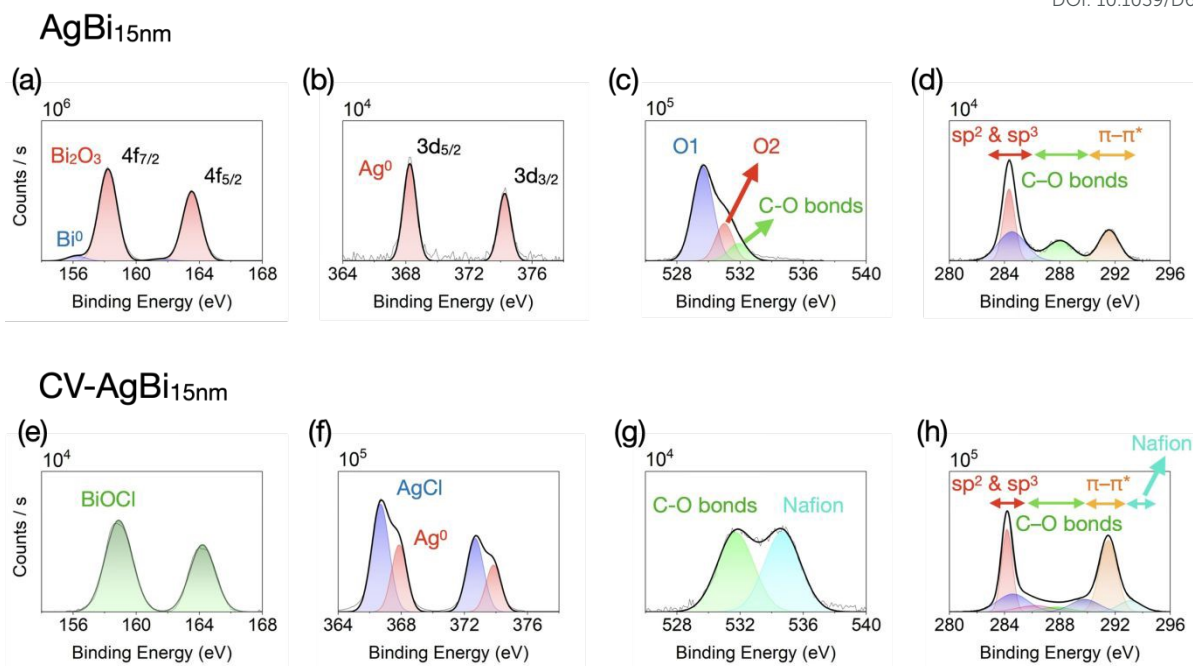


Fig. 3. XPS spectra of $\text{AgBi}_{15\text{nm}}$ (a–d) and $\text{CV-AgBi}_{15\text{nm}}$ (e–h). Spectra are shown for (a, e) Bi 4f, (b, f) Ag 3d, (c, g) O 1s, and (d, h) C 1s, respectively.

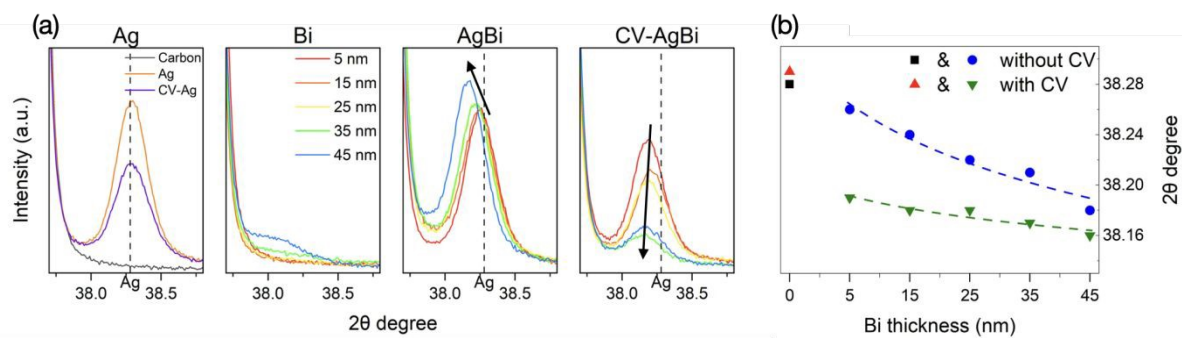
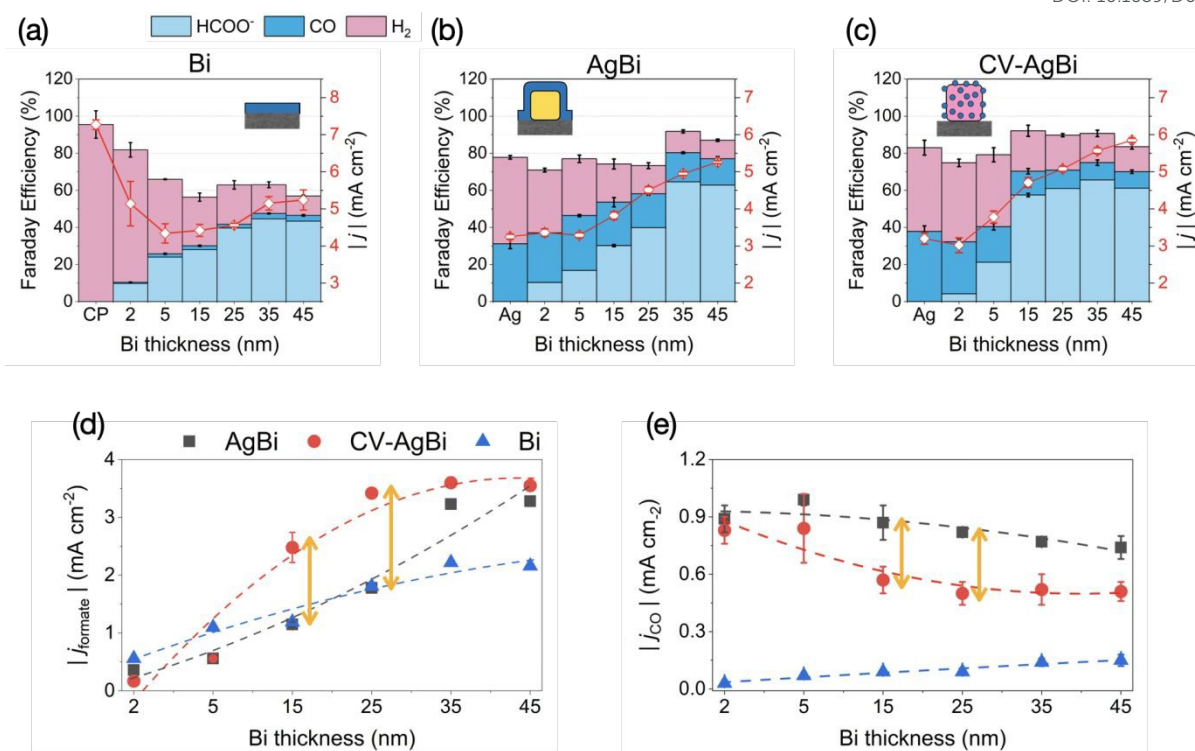


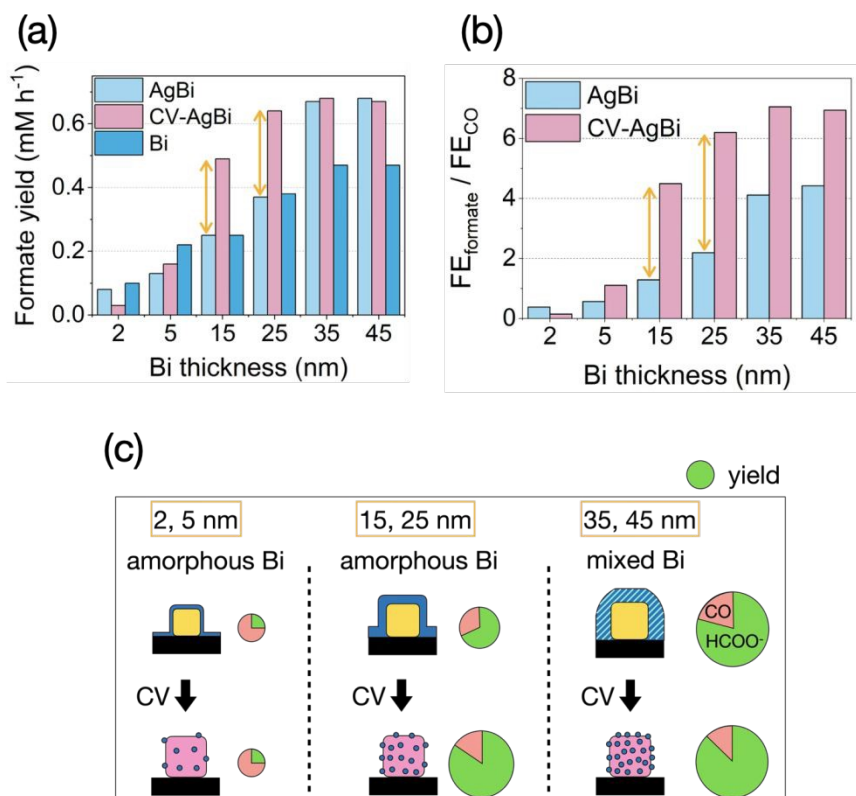
Fig. 4. XRD patterns of (a) Carbon paper, Ag, Bi, AgBi, and CV-AgBi. (b) 2θ values of the Ag (111) diffraction peak ($\sim 38.2^\circ$). The peak at $\sim 37.6^\circ$ corresponds to the carbon paper (CP) substrate.





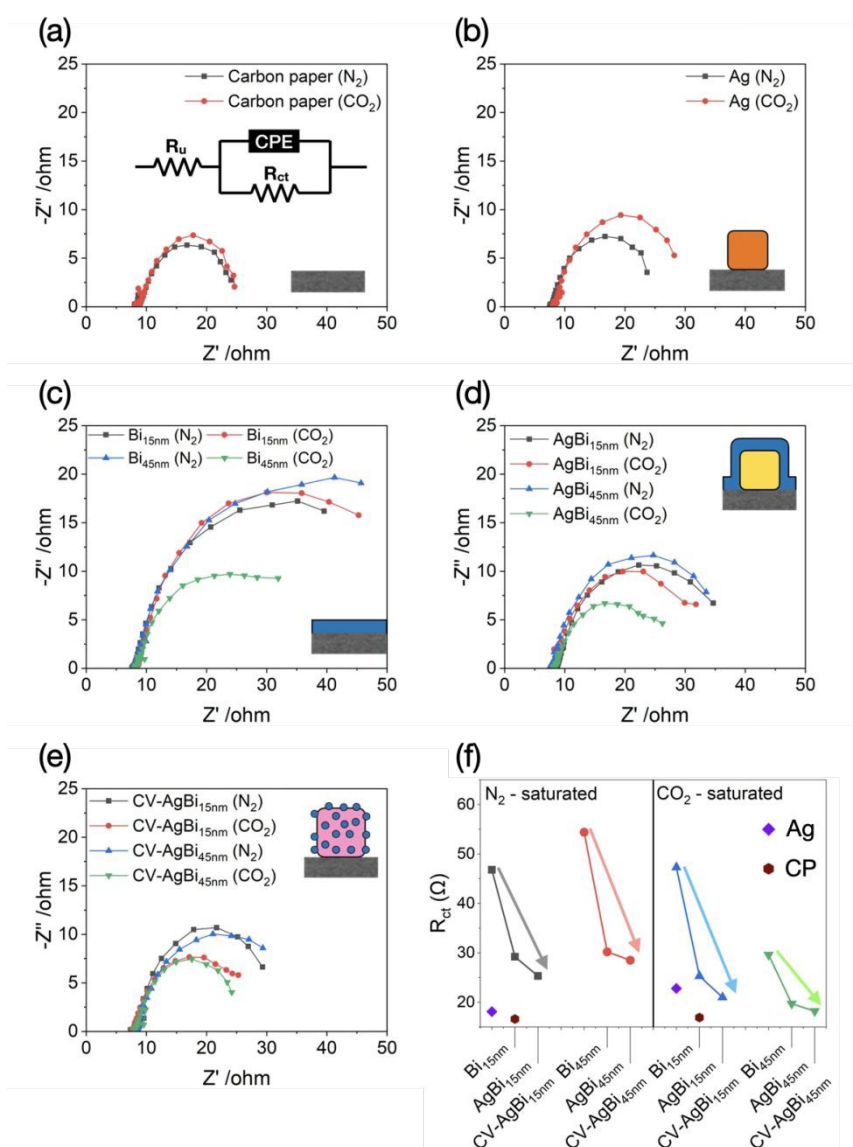
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2 Fig. 5. Faradaic efficiencies and total current densities of (a) Bi, (b) AgBi, and (c) CV-AgBi electrodes.
3 Partial current densities of each product for Bi, AgBi, and CV-AgBi: (d) formate (j_{formate}), (e) CO (j_{CO}).
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2 Fig. 6. Comparison of (a) formate yield and (b) Faradaic efficiency ratio of formate/CO for AgBi and
3 CV-AgBi as a function of Bi thickness, respectively. (c) Summary of catalytic performance change
4 depending on Bi thickness.





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2 Fig. 7. Electrochemical impedance spectroscopy (EIS) Nyquist plots of (a) carbon paper, (b) Ag, (c)
3 Bi_{15nm} and Bi_{45nm} , (d) $AgBi_{15nm}$ and $AgBi_{45nm}$, and (e) CV- $AgBi_{15nm}$ and CV- $AgBi_{45nm}$, measured in 0.5
4 M $KHCO_3$ under N_2 - and CO_2 -saturated conditions. (f) Comparison of charge transfer resistance (R_{ct})
5 values extracted from equivalent circuit fitting.

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Data availability

Additional data supporting this article have been included as part of the ESI.† Numerical data can be made available upon request.

