

Trace Ni-dispersed Ag Catalyst Promotes Proton-transfer-mediated CO₂ Reduction to CO

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ABSTRACT Strongly acidic electrocatalytic CO₂ reduction holds great promise to address carbonate generation and substantial energy loss, but suffers from poor selectivity due to the dominant hydrogen evolution reaction (HER). It is still challenging to achieve highly selective CO production on Ag-based catalysts in strong acid. Herein, a trace Ni-dispersed Ag catalyst (NiAg₄₀₀, 0.13 wt% Ni) is synthesized via a polyol method, exhibiting a CO Faradaic efficiency of up to 95% at 100 mA cm⁻² in a membrane electrode assembly (MEA) with a strongly acidic electrolyte. Experimental results indicate that Trace Ni-dispersed Ag promotes proton-transfer-mediated CO₂ reduction and suppresses HER.

Keywords: electrocatalytic CO₂ reduction, CO, Ag-based catalysts

INTRODUCTION

The widespread combustion of fossil fuels has driven a persistent rise in atmospheric CO₂ concentrations, thereby intensifying climate change and a range of associated environmental challenges[1, 2]. Electrochemical CO₂ reduction reaction (CO₂RR), when powered by renewable electricity, offers a promising pathway for mitigating CO₂ emissions and reducing dependence on conventional fossil fuels. Within this context, CO stands out as one of the most economically competitive products of CO₂ reduction in terms of both value and performance metrics[3]. Furthermore, it serves as an essential feedstock for the Fischer-Tropsch synthesis[4] and the production of high-value chemicals[5].

During electrocatalytic CO₂ reduction to CO in neutral or alkaline electrolytes, hydroxide ions (OH⁻) generated at the cathode surface rapidly react with dissolved CO₂ to form carbonates/ bicarbonates. These species further combine with alkali metal cations in the electrolyte, leading to carbonate precipitation within the gas diffusion electrode (GDE). This results in substantial CO₂ loss and low single-pass conversion efficiency[6, 7]. Moreover, the instability of the anion exchange membrane, along with the rapid accumula-

tion and precipitation of carbonates, further exacerbates the flooding issue of the cathodic GDE[8, 9]. From a theoretical perspective, employing strongly acidic electrolytes can effectively address the aforementioned problem, the presence of a high concentration of H⁺ significantly enhances the competing HER, leading to poor selectivity for CO₂ reduction[10, 11].

Ag is one of the most widely used catalysts for CO₂RR to CO[12], however, Ag catalysts exhibit weak inhibition of HER under acidic conditions, resulting in decreased CO selectivity[13]. Surface-adsorbed active hydrogen (*H), serving as the protonating agent, is crucial for the hydrogenation of CO₂. Studies have shown that on nanostructured Ag surfaces, the protonation of the *COOH intermediate constitutes the kinetic rate-limiting step for the electroreduction reaction of CO₂ to CO[14]. Recent strategies to enhance CO₂ reduction activity have focused on promoting proton transfer, for instance, through the construction of specific adsorption and catalytic sites (such as the employment of transition metal nanoparticles or heteroatom dispersing with sulfur and phosphorus) as well as the functional modification of the catalyst surface[15, 16]. While promoting proton transfer can provide an adequate supply of active hydrogen (*H) species for CO₂ reduction, it may also simultaneously increase HER activity.

Previous literature has reported that the transition metal Ni is an effective catalyst for CO₂RR to CO due to its moderate CO₂ adsorption strength and CO desorption energy[17]. However, its intrinsic activity is poor; dispersing Ni into specific supports has proven to be an effective strategy to address this limitation[18]. It is worth noting that the size of Ni particles, which determines the surface state of Ni, is capable of regulating the reaction pathway toward either HER or CO₂RR. Ni particles at the atomic level demonstrate excellent carbon reduction capability, whereas the HER becomes predominant with the increase in particle size. Consequently, rational design of the size of Ni NPs is essential[19, 20]. Given the ability of Ni to effectively regulate active hydrogen (*H) in various electrocatalytic systems[21-24], this study introduces this general

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mechanism into Ag-based CO₂RR catalysis. Consequently, we synthesized a NiAg catalyst comprising an Ag matrix dispersed with 0.13 wt% Ni via a polyol process, which promotes proton-transfer-mediated CO₂ reduction and suppresses HER. This catalyst achieves a CO selectivity of approximately 95% faradaic efficiency (FE) at a current density of 100 mA cm⁻² in the strongly acidic electrolyte (pH = 1).

RESULTS AND DISCUSSION

Synthesis and characterization

Ag/Ni nanoparticles with different ratios were prepared using a polyol method[25]. Sodium hydroxide and hydrazine solutions in excess act cooperatively to ensure the kinetic reduction and dispersion of Ni into Ag[26]. The preparation process is illustrated in Figure 1a. Samples with different ratios were obtained by controlling the Ag and Ni feed amounts and were named NiAg₄₀₀ (0.13 wt% Ni), NiAg₂₀₀ (0.25 wt% Ni), NiAg₇₀ (0.71 wt% Ni), and NiAg₂₀ (2.4 wt% Ni) (Figure S2, Table S1). Ag nanoparticles synthesized by the exact same polyol method without Ni; physical mixture of Ag nanoparticles and trace Ni species (0.13 wt%) ;

Ni-only; NiAg catalysts prepared by merely varying the PVP addition amount to 0.5 g and 1.5 g; Ag treated with NaOH/hydrazine but without Ni. These samples are designated as Ag-only, physical Ag/Ni mixture, Ni-only, NiAg PVP-0.5 g, NiAg PVP-1.5 g, and Ag PVP-0 g, respectively. Commercial Ag was also used as a reference sample.

The as-prepared NiAg₄₀₀ nanoparticles exhibit a homogeneous and spherical morphology with an approximate diameter of 50 nm, as demonstrated by the TEM images (Figure 1b and Figure S3) and the SEM images (Figure S2). High-resolution TEM (HRTEM) characterization (Figure 1c) demonstrates distinct lattice fringes, with an interplanar spacing of 0.241 nm that matches the (111) plane of Ag. The Ag (111) plane is the most densely packed atomic plane, possessing low surface energy and thermodynamic stability[27], which favors the adsorption and activation of CO₂ molecules and carbon-containing intermediates, directing the reaction along the desired pathway. Energy-dispersive X-ray spectroscopy (EDS) mappings (Figure 1d, e and Figure S4) confirm the presence and uniform distribution of Ag and Ni within NiAg₄₀₀.

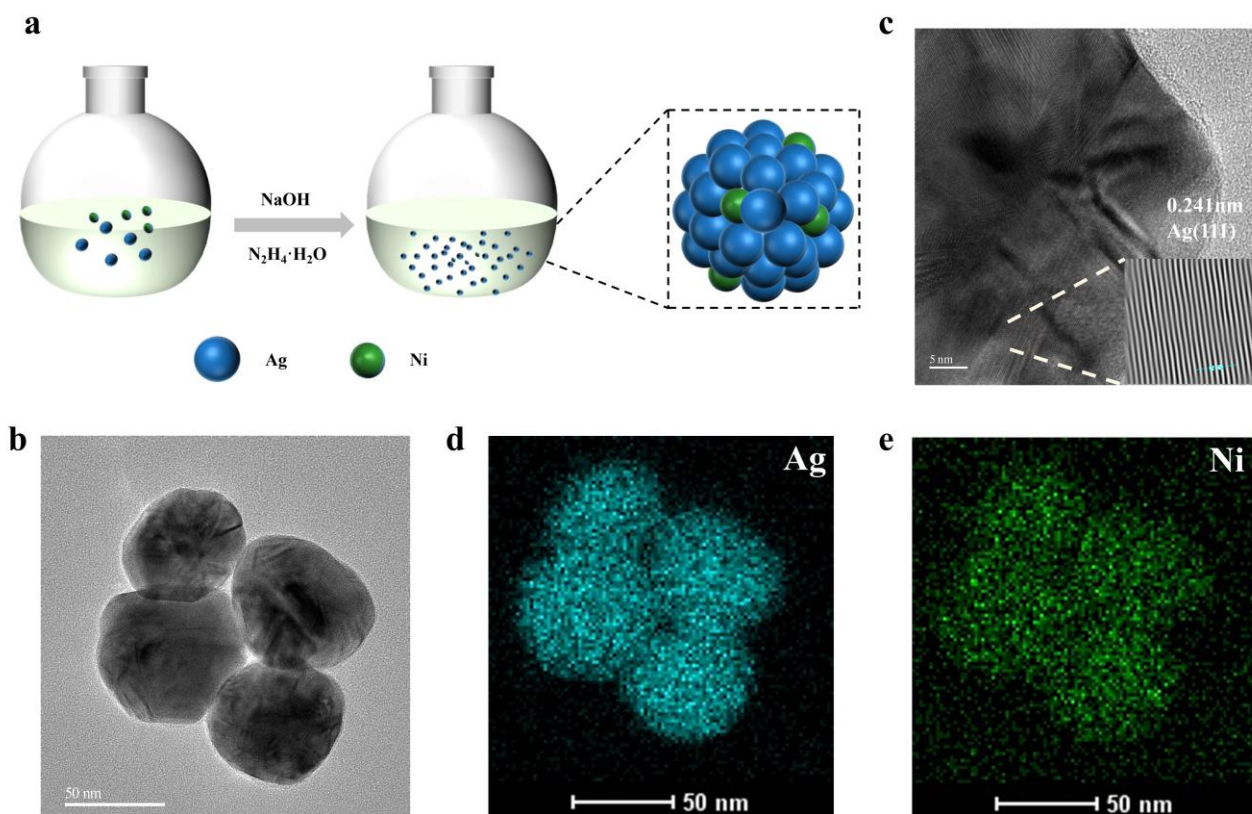


Fig. 1 (a) The scheme for the preparation of NiAg₄₀₀; (b) TEM of NiAg₄₀₀; (c) HRTEM of NiAg₄₀₀; (d) Ag and (e) Ni EDS mappings of NiAg₄₀₀

To determine the crystal phase of the catalysts, X-ray diffraction (XRD) analysis was performed on commercial Ag and NiAg₄₀₀. No characteristic peaks for Ni were

observed in the XRD patterns (Figure 2a), likely due to

its low dispersing level, which results in its signal being either masked or diluted within the Ag lattice. X-ray photoelectron spectroscopy (XPS) spectra of the NiAg₄₀₀ sample confirmed the presence of four elements: C, O, Ag, and Ni (Figure S5). As shown in Figure 2b, the Ag 3d XPS spectrum of the NiAg₄₀₀ catalyst exhibits characteristic peaks of metallic Ag⁰, with binding energies located at 368.2 eV for Ag 3d_{5/2} and 374.2 eV

for Ag 3d_{3/2}. [28] As illustrated in Figures 2b and 2c, the characteristic peaks in the Ag 3d and Ni 2p spectra correspond to the metallic states of Ag and Ni, respectively, confirming the successful dispersion of Ni within the Ag nanoparticles. Nevertheless, incomplete reduction during synthesis results in the coexistence of metallic Ni⁰ and oxidized Ni²⁺ species.

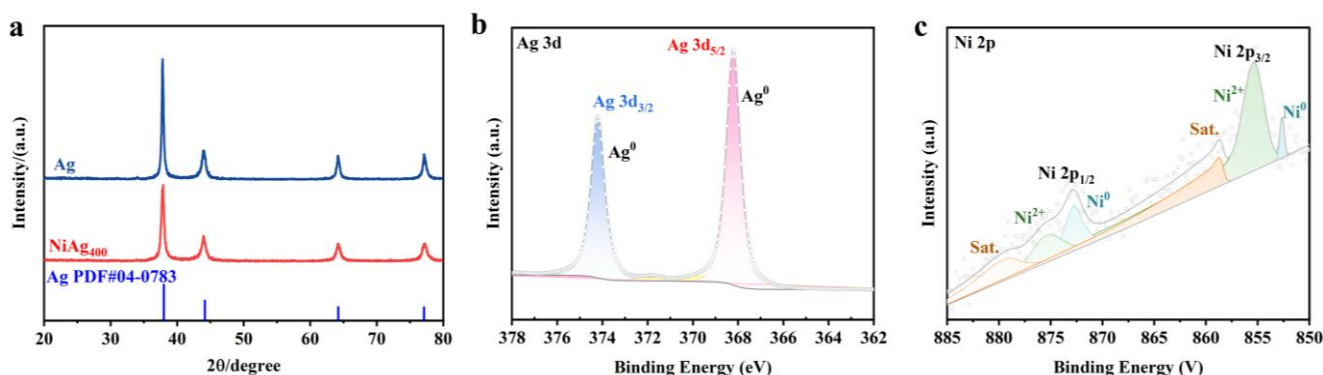


Fig. 2 (a) XRD of NiAg₄₀₀ and commercial Ag; (b) Ag 3d and (c) Ni 2p XPS spectrum of NiAg₄₀₀

Electrochemical performance

The electrochemical CO₂RR performance of NiAg₄₀₀ was investigated in a MEA with an active area of 5.76 cm². Electrolysis was carried out in 0.5 M Cs₂SO₄ solution, with the pH adjusted to 1 using H₂SO₄. Gaseous products were quantified by online gas chromatography.

Linear sweep voltammetry (LSV) curves for Ni-dispersed Ag with different Ni loadings and commercial Ag are presented in Figure 3a. NiAg₄₀₀ shows a higher current density than other samples, suggesting its more favorable kinetics toward the CO₂ reduction reaction. The fluctuation observed around a cell voltage of −1 V in the LSV profiles can be ascribed to constraints imposed by H⁺ proton transport and CO₂ mass transfer within the system [29].

No liquid products but only CO and H₂ were detected during CO₂RR (Figure S6). To determine the optimal Ni dispersing ratio in the Ni-Ag catalyst, tests conducted at a current density of 100 mA cm^{−2} revealed that Ni dispersing significantly optimizes CO₂RR, with all Ni-Ag catalysts demonstrating a notable advantage in CO selectivity. Among them, NiAg₄₀₀ exhibited the best performance, achieving a CO FE of 95%, while samples with higher Ni content (e.g., 0.25 wt%, 0.71 wt%, 2.4 wt%) showed gradually decreasing CO selectivity and increased HER activity (Figure 3b). Control experiments further demonstrate that the appropriate PVP amount (1.0 g) in the current synthesis system, together with the synergistic effect of PVP, NaOH, and hydrazine, is the key to achieving uniform dispersing of trace Ni into the Ag matrix (Figure S7). The superior CO selectivity of NiAg₄₀₀ over commercial Ag was maintained across a current density range of 100–200 mA cm^{−2}, reaching a CO FE of about 80% at 200 mA

cm^{−2} (Figure 3c). The energy efficiency (EE) of NiAg₄₀₀ reaches 32.9% at 100 mA cm^{−2} (Figure S8). When the flow rate was decreased from 50 to 20 sccm, the CO FE of NiAg₄₀₀ remained above 90%, while that of Ag dropped to 55% at 20 sccm (Figure S9). NiAg₄₀₀ maintain higher FE_{CO} at low CO₂ flow rate may indicate improved CO₂RR selectivity or suppressed HER [30]. The long-term stability was assessed at 100 mA cm^{−2} in the MEA configuration, the catalyst exhibits limited durability in strongly acidic MEA operation. As shown in Figure 3d, the CO FE of NiAg₄₀₀ remained above 85% during the first 8 hours, then gradually decreased to 58% after 20 hours (Figure S10). The carbon paper after reaction was characterized by SEM, XRD, ICP and XPS. SEM images revealed partial agglomeration of nanoparticles on the carbon fibers (Figure S11), indicating some structural degradation of the catalyst. The XRD pattern (Figure S12) only showed diffraction peaks corresponding to the carbon cloth substrate and Ag, without detecting any new crystalline phases. To further probe possible catalyst degradation, the electrolyte was collected at different time intervals for ICP analysis (Table S2). The results reveal continuous leaching of both Ag and Ni. Ni exhibits a high leaching amount within 0–5 h, whereas significant Ag leaching occurs during 5–10 h. The total amount of leached Ni is essentially consistent with the nominal Ni loading on the electrode within experimental error, whereas Ag loss mainly originates from metal leaching into the electrolyte, with a small portion likely deposited on the membrane or GDL surface (Table S3). The results showed that Ag continuously leached out in the strongly acidic medium, while the trace Ni tended to stabilize after an initial leaching period. XPS characterization of the catalyst after 20 h of reaction (Figure

S13) showed that the characteristic peaks of metallic Ag⁰ could still be observed in the Ag 3d spectrum, but with a relatively lower intensity, corroborating the loss of Ag sites. Moreover, distinct Cs 3d and F 1s signals appeared in the XPS survey spectrum, which originate from Cs⁺ cations in the electrolyte and fluoride species from the membrane electrode assembly (e.g., Nafion membrane components), respectively. This indicates that inactive species adsorb/deposit on the catalyst surface during long-term operation, possibly covering some of the active sites and further reducing the effective active area. In summary, Ag leaching, nanoparticle agglomeration, and deposition of Cs/F-containing species contribute to performance decay.

The electron transfer capacity of NiAg₄₀₀ and commercial Ag is determined by electrochemical impedance spectroscopy (EIS). The R_{ct} value of NiAg₄₀₀ is smaller than that of commercial Ag (Figure 4a), implying that NiAg₄₀₀ is more beneficial to promote the transfer of extrinsic charge, and thus improve CO₂RR activity and

selectivity. The enhanced electrochemically active surface area ECSA of NiAg₄₀₀ not only furnishes more abundant active sites but also enhances CO₂ adsorption capacity. The ECSA of commercial Ag and the as-synthesized NiAg₄₀₀ catalyst was measured using cyclic voltammetry (CV) (Figures 4b, c). The double-layer capacitance (C_{dl}) acquired from CV tests (Figure 4d) serves as an indicator of the catalysts' ECSA. The C_{dl} value of NiAg₄₀₀ was 0.48 mF cm⁻², which exceeds the value recorded for commercial Ag (0.38 mF cm⁻²). This suggests that the introduction of Ni increases the number of CO₂RR active sites on the Ag surface, resulting in a higher ECSA. The results in (Fig. S12, Figure. S14) show that the ECSA-normalized j_{CO} of NiAg₄₀₀ is higher than that of Ag, indicating that the intrinsic activity of NiAg₄₀₀ is superior to that of Ag, and the NiAg₄₀₀ sites contribute to a higher j_{CO} . The j_{CO} value of NiAg₄₀₀ under high current density is higher than that of Ag (108 mA cm⁻²) and reaches 188 mA cm⁻² (Figure. S15).

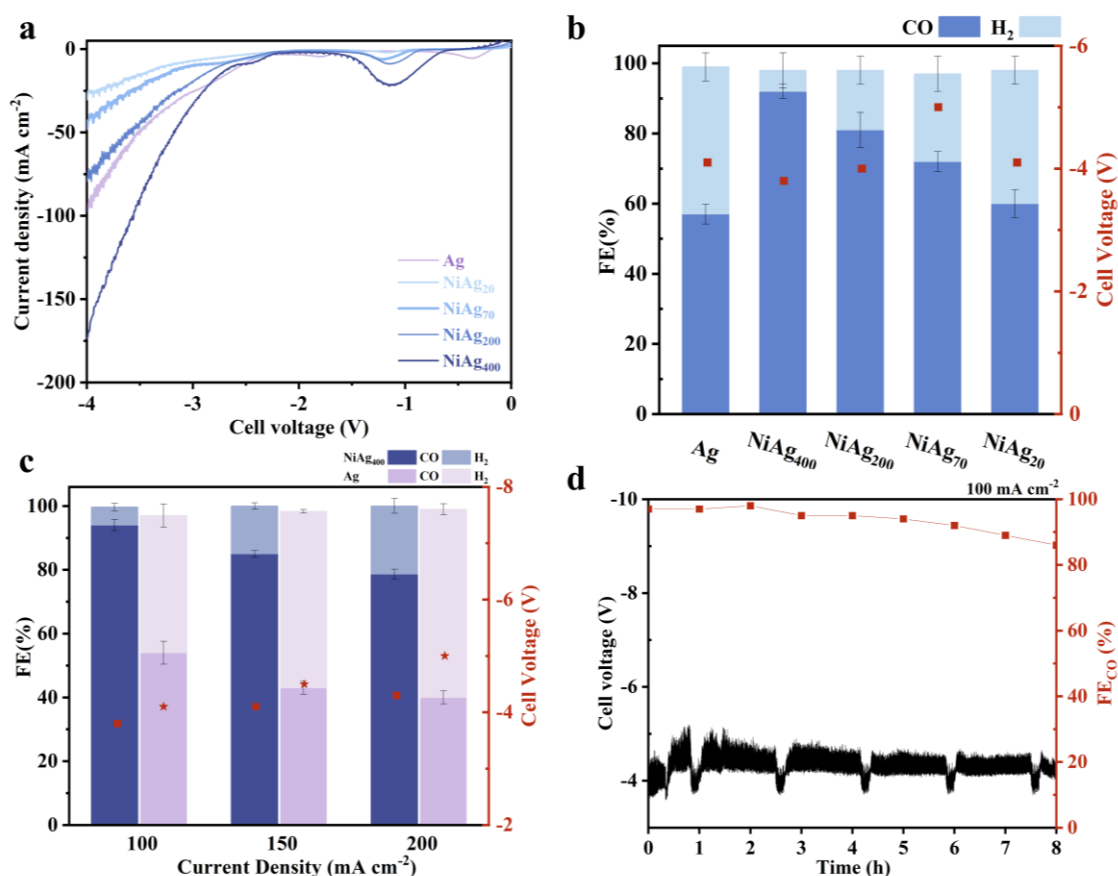


Fig. 3 (a) LSV curves of Ni-dispersed Ag with different Ni loadings and commercial Ag measured in CO₂ flow; (b) Comparison of samples with different Ni contents at 100 mA/cm²; (c) The FE of NiAg₄₀₀ and commercial Ag at applied current densities spanning from 100 to 200 mA cm⁻² (d) The long-term stability of NiAg₄₀₀/gas diffusion layer at 100 mA cm⁻². Every CO₂RR test performed here was carried out in 0.5 M Cs₂SO₄ (pH = 1, H₂SO₄) in MEA at a CO₂ flow rate of 40 sccm. The error bars represent the standard deviation based on three separate measure-

ments. All electrochemical data are presented without *iR*-correction.

Mechanism study

Electrochemical measurements show that NiAg₄₀₀ exhibits superior CO selectivity and weaker HER activity compared with pure Ag, achieving an optimal CO FE of 95% at a current density of 100 mA cm⁻². Comparison of the CO FE among samples with different Ni dispersion levels reveals that HER activity increases with Ni content. Based on these observations, it is speculated that the introduction of trace Ni-dispersed Ag promotes proton-transfer-mediated CO₂ reduction and suppresses HER. The hydrogenation of CO₂ is highly dependent on surface-adsorbed active hydrogen (*H), which serves as the protonating agent in the reaction. To more directly verify the influence of Ni species on the proton transfer process, we performed kinetic isotope effect (KIE) experiments comparing H₂O and D₂O (Figure S16). The results show that when the solvent was switched from H₂O to D₂O, the *j*_{CO} of pure Ag decreased significantly, with a KIE value of approximately 1.34, indicating that proton transfer is the rate-determining step for CO₂RR. In contrast, the FE_{CO} of NiAg₄₀₀ exhibited only a slight decrease, with a KIE value of about 1.09, suggesting that after Ni introduction, proton transfer becomes less rate-limiting [31, 32]. That is, Ni dispersing accelerates the proton transfer process, thereby reducing the dependence of CO₂RR on the proton source. Combined with the electrochemical performance of the NiAg₄₀₀ catalyst, which shows suppressed HER and enhanced CO selectivity, it can be inferred that an appropriate trace amount of Ni likely optimizes the balance between *H generation and consumption, promoting preferential *H utilization for CO₂ hydrogenation to form *COOH while inhibiting *H coupling to produce H₂. To recognize the reaction intermediates on the catalyst surface and clarify the catalytic mechanism, *In-situ* ATR-SEIRAS tests were carried out at different potentials in CO₂-saturated 0.5 M Cs₂SO₄ solution (pH = 1 adjusted by H₂SO₄). As shown in Figure 4f and 4g, several vibration peaks can be seen when the potential changes from -0.1 to -1.3 V. A clear peak at 1630 cm⁻¹ is ascribed to H₂O [33], while *COOH and *CO are the key reaction intermediates in the CO₂RR process, identified by characteristic peaks at 1445 cm⁻¹ [34, 35, 36] and 2086 cm⁻¹ [37], respectively. In the ATR-SEIRAS analysis, the peak near 1445 cm⁻¹ may be partially interfered by surface carbonate species (~1500, 1450

cm⁻¹) [38], bicarbonate (~1468 cm⁻¹) [39], and *OCCOH (~1550 cm⁻¹) [40]. However, since the Ag-based catalyst in this work produces CO as the major product, the contribution from the C-C coupling pathway is negligible. Meanwhile, *CO₂⁻ adsorption on Ag is weak. Therefore, combined with the potential-dependent enhancement of this peak upon negative shifting and its synergistic evolution with the CO peak (~2086 cm⁻¹), we assign the 1445 cm⁻¹ peak mainly to the *COOH intermediate. To eliminate possible variations in the ATR-SEIRAS measurements, we normalized the integrated peak area of *COOH using the water peak as a reference (Table. S4), thereby enabling a more reliable comparison of the potential-dependent trends in intermediate signal intensities across different samples. According to the normalized results, the *COOH signal of NiAg₄₀₀ exhibits an initial increase followed by a decrease as the applied potential becomes more negative. This suggests that at relatively low overpotentials, *COOH intermediates gradually form on the catalyst surface; at more negative potentials, they are rapidly converted into *CO and subsequently desorb as CO products [41]. Notably, under all tested potentials, the normalized *COOH peak area of NiAg₄₀₀ is higher than that of Ag, indicating that NiAg₄₀₀ can accumulate significantly more *COOH intermediates. This finding further confirms that NiAg₄₀₀ promotes accumulation or formation of CO₂RR intermediates under the tested conditions.

In the conventional preparation of CO₂RR electrodes, Nafion is one of the most widely used polymer binders owing to its excellent proton conductivity and chemical stability [42]; it is mainly employed to immobilize catalyst powders and maintain the structural integrity of the electrode. Previous studies have shown that modification of Nafion [43, 44] or changes in its loading [45], can enhance the selectivity of catalysts toward target products. However, in the present work, all samples were prepared using identical Nafion loading and the same fabrication procedures. Consequently, the effect of Nafion on proton transport and selectivity is consistent and systematic across all compared samples. Under this equitable comparison, any bias introduced by Nafion is mutually cancelled, and the observed differences in performance can be reliably attributed to the composition of the catalysts themselves (i.e., Ni dispersing) rather than to variations in Nafion loading.

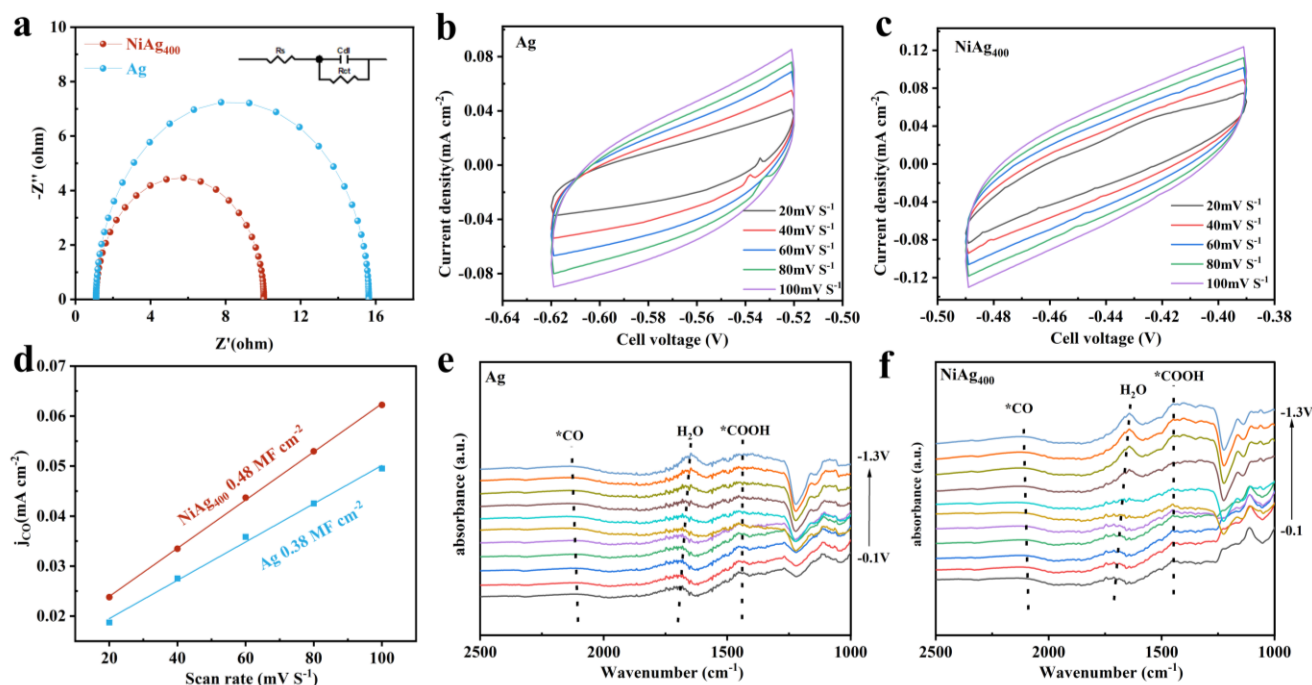


Fig. 4 (a) Nyquist plots of NiAg₄₀₀ and commercial Ag (the inset is the equivalent circuit diagram), CV curves of (b) commercial Ag and (c) NiAg₄₀₀ at various scan rates of 20, 40, 60, 80, and 100 mV s⁻¹ in CO₂-saturated 0.5 M Cs₂SO₄ (pH = 1, H₂SO₄) in MEA; (d) Half of the difference in capacitive current density at the midpoint of the selected potential window in CV curves is plotted against scan rate for NiAg₄₀₀ and commercial Ag; *In-situ* ATR-SEIRAS of commercial Ag (e) and NiAg₄₀₀ (f).

CONCLUSIONS

In summary, a trace Ni-dispersed Ag catalyst (NiAg₄₀₀, 0.13 wt% Ni) was synthesized via a polyol method for CO₂ electroreduction in strong acidic media (pH = 1). NiAg₄₀₀ catalyst exhibits uniform morphology and element distribution, and achieves a CO FE of 95% at 100 mA cm⁻² in the MEA system. Mechanistically, Trace Ni-dispersed Ag promotes proton-transfer-mediated CO₂ reduction and suppresses HER. This work provides an effective strategy for designing high-selectivity Ag-based catalysts for acidic CO₂RR.

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Author contributions Li Y. and Li C. guided the project and conceived the idea. Wang T. designed the experiments and analyzed the data. Yang Z., Sun R., Wang K., Sun Y., Lin J., Lu B. contributed to the experimental improvements. All authors contributed to the general discussion.

Conflict of interest The authors declare that they have no conflict of interest.

Supplementary information Experimental details and supporting data are available in the online version of the paper.



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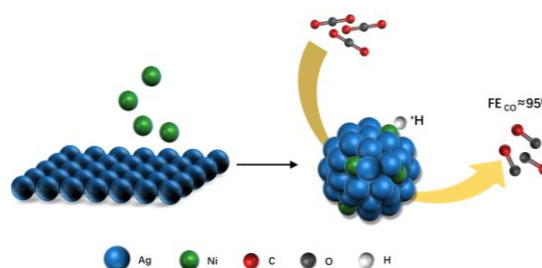


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痕量镍分散银催化剂促进质子转移介导的二氧化碳还原为一氧化碳

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摘要 强酸性体系下电催化CO₂还原在解决碳酸盐生成与大幅能量损耗方面极具应用潜力, 但受析氢反应(HER)占主导的影响, 其选择性较差。在强酸性环境中, 银基催化剂实现高选择性制备CO仍颇具挑战。本文采用多元醇法合成了一种痕量镍分散于银催化剂(NiAg₄₀₀, Ni含量0.13 wt%), 该催化剂在100 mA·cm⁻²电流密度下, 强酸性电解液的膜电极组件(MEA)中, 最大FE_{CO}可达95%。实验结果表明, 痕量镍分散的银能够促进质子转移介导的CO₂还原反应, 并抑制HER。



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Sincerely,
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Comments to the Author

The authors have substantially revised the manuscript and have adequately addressed my previous major concerns. In particular, the title and mechanistic interpretation have been appropriately softened, the Ni content and terminology have been clarified, the ICP leaching/mass-balance issue has been addressed, and the KIE/ATR-SEIRAS analyses have been improved. The manuscript is now scientifically more balanced and suitable for publication in Science China Materials. I recommend acceptance.

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Comments to the Author

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