A New in-situ Exsolution Supporting Framework for Metal Nanoparticle Growth

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Abstract

Catalysts made of in-situ exsolved metal nanoparticles often demonstrate promising activity and high stability in many applications. However, the design of these catalysts is greatly constrained by the classic exsolution mechanism, which occurs almost exclusively through substitutional metal-doping in perovskites. Here we show that metal nanoparticles can also be in-situ exsolved from interstitially doped metal cations in a NiOOH supporting framework with the guidance of theoretical calculation. The exsolution can be conducted swiftly at room temperature. A novel copper nanocatalyst prepared with this approach have a quasi-uniform size of 4 nm delivering an exceptional CO faradaic efficiency of 95.6% with a notable durability for the electrochemical reduction of CO₂. This design principle is further proven to be generally applicable to other metals and foregrounded for guiding the development of advanced catalytic materials.

Main Text

Catalysts based on supported metal nanoparticles (NPs) are broadly used in energy conversion and storage processes. The in situ exsolution with perovskites emerges as time-saving and cost-effective way to fabricate NPs catalysts, because of that this approach does not need multiple deposition steps or expensive precursors, while producing better-distributed and agglomeration-resistant metal NPs. However, the exsolution of NPs from perovskites (ABO₃) still faces several challenges. First of all, this process works with limited elements, as only the A/B sites with similar size can accommodate the formation of perovskite-type structure through a substitution mechanism. In addition, it is difficult to precisely control the composition of exsolved metal NPs due to the possibility of exsolution of both doping and doped metals. Moreover, the exsolution approach poses high energy consumption as it is typically conducted at high temperatures of 700-1200 °C in a H₂ atmosphere. High temperature may also cause uncontrolled growth and coarsening of the NPs. Lastly, the growth of NPs takes a relatively long time (10–30 hours) due to sluggish kinetics. These drawbacks largely originate from the perovskite supporting framework. Therefore, in order to tackle these challenges, a new in situ exsolution supporting framework is needed.

Copper (Cu) has been well studied as the electrocatalysts for electrochemical reduction of CO₂ (ERCO₂). In particular, Cu NPs with smaller diameters (<6 nm) can prevent the hydrogenation of CO and favors the formation of synthetic gas (CO and H₂). However, the Cu NPs catalysts prepared in the wet-chemical impregnation or even traditional exsolution are generally not stable for longer operation due to susceptible agglomeration.

Herein, we reported a new in situ exsolution of Cu NPs from nickel-based hydroxide (γ-NiOOH) with Cu cations confined in layer structures, denoted as CuₓNiOOH, where x represents molar ratio of Cu to Ni (Figure 1A). Ab initio constrained molecular dynamics calculations demonstrate that the γ-NiOOH framework offers spontaneous in situ exsolution of Cu NPs from interstitial doped Cu, as evidenced by a
negligible exsolution free energy barrier (~0.07 eV, Figure 1B). In comparison, a much higher free energy barrier of Cu exsolution from a typical LaSrFeO$_4$ perovskite$^{20}$ is found to be 4.54 eV, necessitating a high temperature for this process (Figure 1C). This result intrinsically underlines the advantage of exsolution of Cu$_x$NiOOH at mild condition, which is further corroborated by a comprehensive comparison with other perovskites in term of exsolution temperatures (Figure 1D).$^{20-27}$

With the guidance of molecular simulation, we synthesized Cu$_x$NiOOH, then applied the electrical activation, the obtained samples are denoted as Cu$_x$@NiOOH (Figure S1). The framework was proven to be predominantly γ-NiOOH with an intensive characteristic peak at 12.8° accompanied by tiny amount of β-Ni(OH)$_2$ and Ni(OH)$_2$·0.75H$_2$O in X-ray diffraction (XRD) patterns (Figure 2A). With the addition of copper, the peaks at 12.8° become sharpened and shift to lower angles, and no copper related peaks are observed when Cu/Ni ratio ≤ 1/2, which is due to an expansion of γ-NiOOH crystalline lattice with the doping of coppers.$^{28}$ While at Cu/Ni ratio ≥ 1/2, the peaks corresponding to Cu(OH)$_2$·2H$_2$O appear. This suggests that the 1:2 Cu/Ni ratio is the upper limit of Cu doping, beyond which copper will exist as Cu(OH)$_2$ outside of the γ-NiOOH framework.

The doping process observed above is also supported by the X-ray photoelectron spectroscopy (XPS) results (Figure S2), which demonstrate the existence of Ni(II) and Ni(III) featured as the binding energies of the Ni 2p$_{3/2}$ spectra fall at 855.3 to 856.5 eV for γ-NiOOH,$^{29,30}$ whereas the Ni 2p$_{3/2}$ spectra for Cu-doped γ-NiOOH shift to a higher energy value caused by the interactions of copper-nickel d-d band.$^{31}$ And the peak areas for the Cu(OH)$_2$ species get higher with the increasing Cu doping level (Figure S3).

Moreover, Raman spectroscopy shows the existence of a wide peak located at 520–550 cm$^{-1}$ (Figure 2B). This is the $E_g$ Ni-O bending vibration and $A_{1g}$ Ni-O stretching vibration for γ-NiOOH.$^{32}$ Compared to pristine γ-NiOOH, copper doped samples have peaks slightly shifted towards higher wavenumber, which can be attributed to lattice distortion caused by the doping of copper ions into the γ-NiOOH structure.$^{33}$

X-ray absorption fine structure (XAFS) analysis shows that Cu was doped into the layered crystal structure of the γ-NiOOH with an interstitial mechanism instead of the substitution mechanism observed with perovskites. Extended XAFS (EXAFS) fitting data reveals that the bond distances for Cu-O and Cu-Ni (Cu) are 1.95 Å and 3.14 Å (Figure S4, Table S1), respectively, which are larger than the distances for Ni-O (1.81 Å) and Ni-Ni (2.82 Å) in γ-NiOOH, ruling out the possibility of copper replacing Ni sites or embedding in any layer, instead copper is doped into the interstitial space of the γ-NiOOH lattice. X-ray absorption near-edge structure (XANES) spectra further show that the doped Cu is in a +2 oxidation state as evidenced by the pre-edge intensity at 8970~8980 eV (Figure 2C). Further, no subnanometer Cu or CuO microcrystalline was observed because the absence of Cu-Cu scatterings (Figure S5).

The exsolution process of Cu from Cu$_{0.5}$NiOOH results are monitored by TEM and Raman after the electrochemical activation. TEM shows dark dots are formed on the surface of Cu$_{0.5}$@NiOOH, which are not present on Cu$_{0.5}$NiOOH (Figure 2D). These dots represent the interlayer spacings of 0.181, 0.198,
0.213, 0.203, and 0.273 nm, corresponding to the (1 1 0), (-1 1 1), and (1 1 1) planes of CuO, the (1 1 1) plane of Cu₂O, and the (2 0 0) plane of metallic Cu, respectively (Figure S6). We calculate the distribution of particle sizes based on Figure 2D, and the average size of exsolved Cu was ~4 nm (Figure S7A). Raman (Figure 2E) also confirms the existence of CuO (280, 321 cm⁻¹) and Cu₂O (623 cm⁻¹) in Cu₀.₅@NiOOH, which are absence in Cu₀.₅NiOOH.

To understand the exsolution at atomic level, we calculate the structure of γ-NiOOH with one doped or exsolved Cu as shown in Figure 2F. Initially, the Cu cation is confined in NiOOH layers, coordinating with four O atoms, with an average bond length of 1.94 Å as that of the typical copper oxides. With the cleavage of Cu-O mediated by electro-activation, Cu diffuses along the interlayers until stabilizing at the NiOOH (1 0 2) surface via a more weak Cu-O bonds with distance of ~ 2.10 Å. Figure 2G and Figure S8 further investigate the agglomeration with more Cu exsolved from bulk. It is interesting to find that less segregation energy is observed with the assembly of Cu, implying that a smaller size of copper would be expected which are consistent with TEM results. A bader charge analysis determines the oxidation state of exsolved Cu close to zero with more Cu exsolved (Figure S9). Alternatively, under the working circumstances of negative potential (-0.3~-1.5 V vs. RHE), Cu cations are easy to be reduced to metallic state as reported by other literature.

It is noted that metallic Cu in Cu₀.₅@NiOOH are easily oxidized when unavoidable exposure to air. Considering that Cu₀.₅NiOOH are calcined in air but without copper oxides observed, the CuO and Cu₂O on Cu₀.₅@NiOOH are likely formed by the oxidation of metallic Cu exsolved.

This new exsolution method offers several major advantages over the conventional perovskite-based framework (Figure 1D). Our exsolution can be achieved in as little as ~20 minutes through electrochemical activation at room temperature due to much lower barrier of 0.07 eV. In comparison, the exsolution with perovskites typically takes 10-30 hours due to the much higher energy of 4.54 eV. Moreover, our approach produces smaller Cu NPs (~4 nm) (Figure S7A) than a typical perovskite-based approach (10—2000 nm). As predicted by DFT results, the well-control of Cu NPs size is determined by segregation energy, which declines with more Cu exsolved, indicating that the formation of smaller Cu NPs is energy-favorable.

The exsolved Cu NPs from the γ-NiOOH exhibit high catalytic activity for ERCO₂ to CO (Table S2), which showing a volcano dependence on the size of exsolved Cu NPs resulting from different loading of doped Cu (Figure 3A, Figure S7B and S10), while the γ-NiOOH is also confirmed to be no activity, as no CO was observed (Figures 3C, S11 and S12), proving that exsolved Cu NPs are active sites.

Among all the tested catalysts, Cu₀.₅@NiOOH with ~3.5 nm Cu NPs shows the highest activity for ERCO₂ (Figure 3A-3C), which can be explained by the availability of ultrafine Cu NPs exsolved from the framework. Specifically, at an applied potential of -0.7 V vs. RHE, the faradaic efficiency for CO (FE-CO) reached an unprecedented 95.6% with an acceptable CO current density (J_CO) of 10.6 mA cm⁻². In addition, The FE towards CO remains greater than 80% (Figure 3B) over a potential range between −0.5 V and −0.9 V.
To gain insight into the ERCO$_2$ performance of Cu$_{0.5}$@NiOOH, we investigated the electrochemical active surface area (ECSA). Larger ECSA indicates more active sites are available for the adsorption of reactants, thus facilitating CO evolution in ERCO$_2$. The ECSA of Cu$_{0.5}$@NiOOH (133.53 cm$^2$) is 1.38, 1.22, 1.03, and 1.61 times larger than that of Cu$_1$@NiOOH (96.69 cm$^2$), Cu$_{0.7}$@NiOOH (109.25 cm$^2$), Cu$_{0.3}$@NiOOH (129.70 cm$^2$), and NiOOH (82.86 cm$^2$), respectively (Figure S13 and Table S3). These results further suggest that exsolved Cu NPs expose a large number of active sites. CO$_2$ adsorption measurements for Cu$_{0.5}$@NiOOH exhibited an excellent CO$_2$ adsorption capacity of 99.8 mg g$^{-1}$, which facilitates ERCO$_2$ (Figure S14).

Electrochemical impedance spectroscopy (EIS) analysis of Cu$_{0.5}$@NiOOH demonstrates the extremely low charge transfer resistance ($R_{ct}$) at the interface of the dip-coated catalyst and electrolyte (Figure 3D). Furthermore, the kinetics of the CO evolution was evaluated by tafel analysis. The tafel slop of Cu$_{0.5}$@NiOOH was measured to be 103 mV dec$^{-1}$ (Figure 3E), suggesting fast kinetics for the CO formation, which is close to the theoretical value (118 mV dec$^{-1}$), indicating that the one electron transfer is the rate-determining step (RDS) for the generation of CO.

The exsolved Cu NPs demonstrate a notable electrochemical stability. Both the current density and the corresponding FE-CO are stable during a 40 h electrolysis process (Figure 3F). Additionally, TEM and Raman show that the microstructure of NiOOH and exsolved Cu NPs are maintained (Figure 2E and S15).

To demonstrate general applicability of in situ exsolution from metal doped γ-NiOOH, we further examined the case of Mn and Zn. Raman shows three bands centered at 467, 571 and 624 cm$^{-1}$ in Mn$_{0.25}$@NiOOH correspond to the MnO$_2$, which are not present on Mn$_{0.25}$NiOOH (Figure 4A). TEM confirms the existence of MnO$_2$ and metallic Mn (Figure 4B). Compared to Zn$_{0.25}$@NiOOH, Zn$_{0.25}$@NiOOH has peaks shifted towards lower wavenumber in the Raman spectra, which revealing a contraction of the crystalline lattice due to the Zn NPs exsolution (Figure 4C). Figure 4D further confirms the phenomenon of Zn exsolution. Moreover, a more comprehensive comparison by the DFT simulation also shows that various metal components are thermodynamically more favorable to in situ exsolve from the γ-NiOOH as compared to their counterparts from perovskites.$^{[20, 36-38]}$ The segregation energy of in situ exsolving Cu and other transition metals (Mn, Fe, Co) from the γ-NiOOH framework (Figure 4E) is lower or on par with most exsolving atoms in perovskite frameworks. This suggests that similar exsolution approaches can be easily performed with a wide range of elements to form different NPs.

The results discussed herein showcase a new design principle for preparing stable metal nanoparticles for catalysis applications by in situ exsolution. This design principle may also be used to develop other alternative frameworks which can tackle the major challenges faced by conventional in situ exsolution technologies.
Catalysts based on supported metal nanoparticles (NPs) are broadly used in energy conversion and storage processes.\textsuperscript{1,2} The \textit{in situ} exsolution with perovskites emerges as a time-saving and cost-effective way to fabricate NPs catalysts,\textsuperscript{3-6} because of that this approach does not need multiple deposition steps or expensive precursors, while producing better-distributed and agglomeration-resistant metal NPs.\textsuperscript{7-10} However, the exsolution of NPs from perovskites (ABO$_3$) still faces several challenges. First of all, this process works with limited elements, as only the A/B sites with similar size can accommodate the formation of perovskite-type structure through a substitution mechanism. In addition, it is difficult to precisely control the composition of exsolved metal NPs due to the possibility of exsolution of both doping and doped metals.\textsuperscript{11} Moreover, the exsolution approach poses high energy consumption as it is typically conducted at high temperatures of 700-1200 °C in a H$_2$ atmosphere.\textsuperscript{12,13} High temperature may also cause uncontrolled growth and coarsening of the NPs. Lastly, the growth of NPs takes a relatively long time (10–30 hours) due to sluggish kinetics.\textsuperscript{14,15} These drawbacks largely originate from the perovskite supporting framework. Therefore, in order to tackle these challenges, a new \textit{in situ} exsolution supporting framework is needed.

Copper (Cu) has been well studied as the electrocatalysts for electrochemical reduction of CO$_2$ (ERCO$_2$).\textsuperscript{16,17} In particular, Cu NPs with smaller diameters (<6 nm) can prevent the hydrogenation of CO and favors the formation of synthetic gas (CO and H$_2$).\textsuperscript{18} However, the Cu NPs catalysts prepared in the wet-chemical impregnation or even traditional exsolution are generally not stable for longer operation due to susceptible agglomeration.\textsuperscript{19}

Herein, we reported a new \textit{in situ} exsolution of Cu NPs from nickel-based hydroxide ($\gamma$-NiOOH) with Cu cations confined in layer structures, denoted as Cu$_x$NiOOH, where $x$ represents molar ratio of Cu to Ni (Figure 1A). \textit{Ab initio} constrained molecular dynamics calculations demonstrate that the $\gamma$-NiOOH framework offers spontaneous \textit{in situ} exsolution of Cu NPs from interstitial doped Cu, as evidenced by a negligible exsolution free energy barrier (~0.07 eV, Figure 1B). In comparison, a much higher free energy barrier of Cu exsolution from a typical LaSrFeO$_4$ perovskite\textsuperscript{20} is found to be 4.54 eV, necessitating a high temperature for this process (Figure 1C). This result intrinsically underlines the advantage of exsolution of Cu$_x$NiOOH at mild condition, which is further corroborated by a comprehensive comparison with other perovskites in term of exsolution temperatures (Figure 1D).\textsuperscript{20-27}

With the guidance of molecular simulation, we synthesized Cu$_x$NiOOH, then applied the electrical activation, the obtained samples are denoted as Cu$_x$@NiOOH (Figure S1). The framework was proven to be predominantly $\gamma$-NiOOH with an intensive characteristic peak at 12.8° accompanied by tiny amount of $\beta$-Ni(OH)$_2$ and Ni(OH)$_2$·0.75H$_2$O in X-ray diffraction (XRD) patterns (Figure 2A). With the addition of copper, the peaks at 12.8° become sharpened and shift to lower angles, and no copper related peaks are observed when Cu/Ni ratio $\leq$1/2, which is due to an expansion of $\gamma$-NiOOH crystalline lattice with the doping of coppers.\textsuperscript{28} While at Cu/Ni ratio $\geq$1/2, the peaks corresponding to Cu(OH)$_2$·2H$_2$O appear. This
suggests that the 1:2 Cu/Ni ratio is the upper limit of Cu doping, beyond which copper will exist as Cu(OH)$_2$ outside of the γ-NiOOH framework.

The doping process observed above is also supported by the X-ray photoelectron spectroscopy (XPS) results (Figure S2), which demonstrate the existence of Ni(II) and Ni(III) featured as the binding energies of the Ni 2p$_{3/2}$ spectra fall at 855.3 to 856.5 eV for γ-NiOOH, whereas the Ni 2p$_{3/2}$ spectra for Cu-doped γ-NiOOH shift to a higher energy value caused by the interactions of copper-nickel d-d band. And the peak areas for the Cu(OH)$_2$ species get higher with the increasing Cu doping level (Figure S3).

Moreover, Raman spectroscopy shows the existence of a wide peak located at 520-550 cm$^{-1}$ (Figure 2B). This is the E$_g$ Ni-O bending vibration and A$_{1g}$ Ni-O stretching vibration for γ-NiOOH. Compared to pristine γ-NiOOH, copper doped samples have peaks slightly shifted towards higher wavenumber, which can be attributed to lattice distortion caused by the doping of copper ions into the γ-NiOOH structure.

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The exsolution process of Cu from Cu$_{0.5}$NiOOH results are monitored by TEM and Raman after the electrochemical activation. TEM shows dark dots are formed on the surface of Cu$_{0.5}$@NiOOH, which are not present on Cu$_{0.5}$NiOOH (Figure 2D). These dots represent the interlayer spacings of 0.181, 0.198, 0.213, 0.203, and 0.273 nm, corresponding to the (1 1 0), (-1 1 1), and (1 1 1) planes of CuO, the (1 1 1) plane of Cu$_2$O, and the (2 0 0) plane of metallic Cu, respectively (Figure S6). We calculate the distribution of particle sizes based on Figure 2D, and the average size of exsolved Cu was ~4 nm (Figure S7A). Raman (Figure 2E) also confirms the existence of CuO (280, 321 cm$^{-1}$) and Cu$_2$O (623 cm$^{-1}$) in Cu$_{0.5}$@NiOOH, which are absence in Cu$_{0.5}$NiOOH.

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expected which are consistent with TEM results. A bader charge analysis determines the oxidation state of exsolved Cu close to zero with more Cu exsolved (Figure S9). Alternatively, under the working circumstances of negative potential (-0.3~1.5 V vs. RHE), Cu cations are easy to be reduced to metallic state as reported by other literature.\textsuperscript{35} It is noted that metallic Cu in Cu\textsubscript{x}@NiOOH are easily oxidized when unavoidable exposure to air. Considering that Cu\textsubscript{0.5}NiOOH are calcined in air but without copper oxides observed, the CuO and Cu\textsubscript{2}O on Cu\textsubscript{0.5}@NiOOH are likely formed by the oxidation of metallic Cu exsolved.

This new exsolution method offers several major advantages over the conventional perovskite-based framework (Figure 1D). Our exsolution can be achieved in as little as ~20 minutes through electrochemical activation at room temperature due to much lower barrier of 0.07 eV. In comparison, the exsolution with perovskites typically takes 10-30 hours due to the much higher energy of 4.54 eV. Moreover, our approach produces smaller Cu NPs (~4 nm) (Figure S7A) than a typical perovskite-based approach (10—2000 nm).\textsuperscript{20-27} As predicted by DFT results, the well-control of Cu NPs size is determined by segregation energy, which declines with more Cu exsolved, indicating that the formation of smaller Cu NPs is energy-favorable.

The exsolved Cu NPs from the γ-NiOOH exhibit high catalytic activity for ERCO\textsubscript{2} to CO (Table S2), which showing a volcano dependence on the size of exsolved Cu NPs resulting from different loading of doped Cu (Figure 3A, Figure S7B and S10), while the γ-NiOOH is also confirmed to be no activity, as no CO was observed (Figures 3C, S11 and S12), proving that exsolved Cu NPs are active sites.

Among all the tested catalysts, Cu\textsubscript{0.5}@NiOOH with ~3.5 nm Cu NPs shows the highest activity for ERCO\textsubscript{2} (Figure 3A-3C), which can be explained by the availability of ultrafine Cu NPs exsolved from the framework. Specifically, at an applied potential of -0.7 V vs. RHE, the faradaic efficiency for CO (FE-CO) reached an unprecedented 95.6% with an acceptable CO current density (J\textsubscript{CO}) of 10.6 mA cm\textsuperscript{-2}. In addition, The FE towards CO remains greater than 80% (Figure 3B) over a potential range between −0.5 V and −0.9 V.

To gain insight into the ERCO\textsubscript{2} performance of Cu\textsubscript{0.5}@NiOOH, we investigated the electrochemical active surface area (ECSA). Larger ECSA indicates more active sites are available for the adsorption of reactants, thus facilitating CO evolution in ERCO\textsubscript{2}. The ECSA of Cu\textsubscript{0.5}@NiOOH (133.53 cm\textsuperscript{2}) is 1.38, 1.22, 1.03, and 1.61 times larger than that of Cu\textsubscript{1}@NiOOH (96.69 cm\textsuperscript{2}), Cu\textsubscript{0.7}@NiOOH (109.25 cm\textsuperscript{2}), Cu\textsubscript{0.3}@NiOOH (129.70 cm\textsuperscript{2}), and NiOOH (82.86 cm\textsuperscript{2}), respectively (Figure S13 and Table S3). These results further suggest that exsolved Cu NPs expose a large number of active sites. CO\textsubscript{2} adsorption measurements for Cu\textsubscript{0.5}@NiOOH exhibited an excellent CO\textsubscript{2} adsorption capacity of 99.8 mg g\textsuperscript{-1}, which facilitates ERCO\textsubscript{2} (Figure S14).

Electrochemical impedance spectroscopy (EIS) analysis of Cu\textsubscript{0.5}@NiOOH demonstrates the extremely low charge transfer resistance (R\textsubscript{ct}) at the interface of the dip-coated catalyst and electrolyte (Figure 3D). Furthermore, the kinetics of the CO evolution was evaluated by tafel analysis. The tafel slop of
Cu$_{0.5}$@NiOOH was measured to be 103 mV dec$^{-1}$ (Figure 3E), suggesting fast kinetics for the CO formation, which is close to the theoretical value (118 mV dec$^{-1}$), indicating that the one electron transfer is the rate-determining step (RDS) for the generation of CO.

The exsolved Cu NPs demonstrate a notable electrochemical stability. Both the current density and the corresponding FE-CO are stable during a 40 h electrolysis process (Figure 3F). Additionally, TEM and Raman show that the microstructure of NiOOH and exsolved Cu NPs are maintained (Figure 2E and S15).

To demonstrate general applicability of in situ exsolution from metal doped γ-NiOOH, we further examined the case of Mn and Zn. Raman shows three bands centered at 467, 571 and 624 cm$^{-1}$ in Mn$_{0.25}$@NiOOH correspond to the MnO$_2$, which are not present on Mn$_{0.25}$NiOOH (Figure 4A). TEM confirms the existence of MnO$_2$ and metallic Mn (Figure 4B). Compared to Zn$_{0.25}$NiOOH, Zn$_{0.25}$@NiOOH has peaks shifted towards lower wavenumber in the Raman spectra, which revealing a contraction of the crystalline lattice due to the Zn NPs exsolution (Figure 4C). Figure 4D further confirms the phenomenon of Zn exsolution. Moreover, a more comprehensive comparison by the DFT simulation also shows that various metal components are thermodynamically more favorable to in situ exsolve from the γ-NiOOH as compared to their counterparts from perovskites.$^{[20, 36-38]}$ The segregation energy of in situ exsolving Cu and other transition metals (Mn, Fe, Co) from the γ-NiOOH framework (Figure 4E) is lower or on par with most exsolving atoms in perovskite frameworks. This suggests that similar exsolution approaches can be easily performed with a wide range of elements to form different NPs.

The results discussed herein showcase a new design principle for preparing stable metal nanoparticles for catalysis applications by in situ exsolution. This design principle may also be used to develop other alternative frameworks which can tackle the major challenges faced by conventional in situ exsolution technologies.

Declarations

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Author contributions: M. C. W. and B. K. Z. performed the experiments. J. Q. D. performed the simulations. Y. H. designed the simulations and experiments. M. C. W. and P. F. X. analyzed the data. All authors discussed the results and wrote the manuscript.

Competing interests: Authors declare no competing interests.

Data and materials availability: All data is available in the main text or the supplementary materials.
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**Figures**
Figure 1

(A) Schematic diagram of exsolving metal nanoparticles from the interstitial spaces of γ-NiOOH. The relative free energy of Cu atoms along the exsolution processes for (B) γ-NiOOH and (C) LaSrFeO4 perovskite. (D) Exsolution temperature and exsolved Cu particle size of various comparative catalysts. The purple, cyan, blue, brown, and red spheres represent Cu, Sr, La, Fe, and O atoms, respectively.
Figure 2

(A) XRD patterns and (B) UV Raman spectroscopy of the CuxNiOOH catalysts. (C) Cu K-edge X-ray absorption near-edge structure (XANES) spectra of Cu foil, CuO, and Cu0.5NiOOH catalysts. (D) TEM micrograph of Cu0.5NiOOH and Cu0.5@NiOOH catalysts. (E) Raman patterns for Cu0.5NiOOH, Cu0.5@NiOOH and Cu0.5@NiOOH (used for 40 h). (F) Simulation models for Cu exsolution. (G) Segregation energy of exsolving more Cu atoms.
Figure 3

(A) Faraday efficiency with Cu NPs particle size. (B) Faradaic efficiency towards CO, H2, and CH4 at different potentials for Cu0.5@NiOOH. (C) CO current density at different potentials for NiOOH and exsolved-catalysts. (D) EIS nyquist analysis of NiOOH and Cu0.5@NiOOH. (E) Tafel plot and (F) Long-term stability testing of Cu0.5@NiOOH electrode over 40 h.

Figure 4

(A) Raman spectroscopy for Mn0.25NiOOH and Mn0.25@NiOOH. (B) TEM for Mn0.25@NiOOH. (C) Raman spectroscopy for Zn0.25NiOOH and Zn0.25@NiOOH. (D) TEM for Zn0.25@NiOOH. (E) Segregation energies of transition metal dopants in different hosts.

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