Inverse iron oxide/metal catalysts from galvanic replacement

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Key chemical transformations require metal and redox sites in proximity at interfaces; however, in traditional oxide-supported materials, this requirement is met only at the perimeters of metal nanoparticles. We report that galvanic replacement can produce inverse FeO\textsubscript{x}/metal nanostructures in which the concentration of oxide species adjoining metal domains is maximal. The synthesis involves reductive deposition of rhodium or platinum and oxidation of Fe\textsuperscript{2+} from magnetite (Fe\textsubscript{3}O\textsubscript{4}). We discovered a parallel dissolution and adsorption of Fe\textsuperscript{2+} onto the metal, yielding inverse FeO\textsubscript{x}-coated metal nanoparticles. This nanostructure exhibits the intrinsic activity in selective CO\textsubscript{2} reduction that simple metal nanoparticles have only at interfaces with the support. By enabling a simple way to control the surface functionality of metal particles, our approach is not only scalable but also enables a versatile palette for catalyst design.
Metal particles play a key role in chemical transformations that require activation of H₂ or hydrogenation/dehydrogenation of substrates. In many cases, the metal particles provide only one step in the catalytic cycle. For instance, metals have low activity in CO₂ reduction because of weak CO₂ adsorption, whereas the polar surface of oxides readily adsorbs CO₂ but suffers from low activity for H₂ activation. Thus, metal–oxide interfaces are much more effective because both the redox sites required to activate CO₂ and the metals providing active H₂ are in proximity. Challenges for maximizing such interfaces are stabilizing small metal particles on oxide supports or forcing migration of oxides onto metal particles while avoiding harsh synthesis conditions.

Inverse catalysts—oxides supported on metals—offer an attractive alternative to overcome the constraints of typical support metal catalysts because reactants can bind to sites in the oxide overlayer, onto the metal domains, or at their interface. Typically, surface science research selects only well-defined inverse catalysts to provide a basic understanding of their adsorption and catalytic properties; however, advancing from this approach into the more complex conditions relevant to technical applications is essential. In this regard, a major obstacle is encountered because typical surface science approaches for preparing inverse catalysts, such as reduction at high temperature, encountered because typical surface science approaches for preparing inverse catalysts, such as reduction at high temperature, deposition in ultrahigh vacuum, and deposition at atomic layers, are challenging to scale beyond certain models.

We report here a simple galvanic replacement approach for generating inverse FeOₓ/metal nanostructures. During galvanic replacement, one metal dissolves as a sacrificial species (Eq. (1)) and the solution is initially free of aqueous Fe²⁺ ions in the form of Fe₂O₃.727—suppresses electron equivalents in the form of Fe²⁺ enriched at the oxide surface, which reduce Rh³⁺ or Pt⁴⁺, thereby depositing metal nanostructures (Eqs. (1)–(3)).

\[
\begin{align*}
\text{Rh}^{3+} + 3e^- & \rightarrow \text{Rh}, \\
\text{Fe}^{2+} & \rightarrow \text{Fe}^{3+} + e^-, \\
\text{Rh}^{3+} + 3\text{Fe}^{2+} & \rightarrow \text{Rh} + 3\text{Fe}^{3+}.
\end{align*}
\]

We discovered that in addition to acting as sacrificial species, Fe²⁺ dissolves, and adsorbs onto the as-formed metal particles as Fe (II)-oxyhydroxide. The surface property of the metal is thus greatly changed by the FeOₓ overlayer, endowing the nanostructure with the high density of active sites for CO₂ reduction that well-dispersed Rh particles have only at the interface with FeO₃. This yields activity and selectivity for CO production significantly higher than well-dispersed Rh particles without FeOₓ overlayers. Our method demonstrates that the surface of metal nanoparticles can be manipulated by the sacrificial species during galvanic replacement, whereas galvanic replacement was previously thought to control only nanostructure morphologies.

**Results and discussion**

**Identification of FeOₓ overlayer on Rh.** We performed the synthesis by simply suspending FeOₓ₅₇ (“Methods” section and Supplementary Fig. 1 for synthesis) in aqueous RhCl₃ solution (Fig. 1a), yielding the as-prepared material (FeOₓ/Rh/FeO₄-fresh). High-angle annular dark-field scanning tunneling electron microscopy (HAADF-STEM) imaging of FeOₓ/Rh/FeO₄-fresh (Fig. 1b and Supplementary Figs. 2–5) showed that the deposited nanostructures distribute along the whole surface of FeO₄ with the average size of 6.6 nm. These nanostructures seem to be composed by smaller Rh nanoparticles of around 2 nm. The nanosized structures were further examined by electron energy-loss spectroscopy (EELS) while manipulating the sample to avoid overlapping with the support along z-axis. Maps of Rh L₂,₃ and Fe L₂,₃ edges (Fig. 1b and Supplementary Figs. 3–5) show Fe signals in regions of the Rh domains. The line profile indicates that significant amounts of Fe coincide with Rh particles. The Fe spectra from the Rh domains give a lower loss energy (by 0.7 eV) than the signal from FeO₄ (Supplementary Fig. 3). This indicates that the Fe on Rh nanostructures have a lower average oxidation state (i.e., +2) than in FeO₄ (+3/4).

**Mechanism for the formation of FeOₓ overlayer.** We used the ferrozine method to monitor changes of Fe³⁺ and Fe²⁺ concentrations during synthesis of FeOₓ/Rh/FeO₄-fresh (Fig. 1c). Fe²⁺ was released immediately after FeO₄ was dispersed in the solution of Rh³⁺, which is consistent with the acidic FeO₄ oxidation chemistry (Eq. (4)). Because Fe²⁺ is much more soluble than Fe³⁺, and the solution is initially free of aqueous Fe²⁺ upon first contact the Rh³⁺ solution. The pH was observed to initially drift upwards from ~4 to 5, which is consistent with consumption of protons during the release (see section of methods for pH changes).

\[
[\text{Fe}^{3+}]_2[\text{Fe}^{2+}]\text{O}_{3.7}(s) + 2\text{H}^+(aq) + \frac{3}{4}\{[\text{Fe}^{3+}]_3[/\text{Vacancy}]\} \text{O}_{3.7}(s) + \text{H}_2\text{O} + \text{Fe}^{2+}(aq).
\]

The particle surface will be enriched in Fe²⁺ during the Fe²⁺ release into solution, thereby maintaining a dynamic equilibrium. In parallel, Rh³⁺ was reduced and deposited as the nanostructures that adsorb and bind Fe(II)-oxyhydroxide during the progressive Fe²⁺ accumulation on the FeO₄ surface (see below). This leads to a gradual reversal of the reaction in Eq. (4), detectable by a pH decrease from ~5 to 2.5 and an increase in Fe³⁺ in solution, reaching equilibrium after 3 h synthesis time. Note that if Rh³⁺ and Fe²⁺ (Rh³⁺/Fe²⁺ = 1:3) were mixed at the conditions of the galvanic replacement, neither Rh nor FeOₓ particles are observed by HAADF-STEM. Thus, Rh nucleation and growth requires the FeO₄ surface and productions of Fe²⁺ and Fe³⁺ in solution follow different mechanisms.

Because formation of metallic Rh is accompanied by increasing detectable aqueous Fe²⁺ (Eq. (3)) and consumption of Fe²⁺ (Fig. 1c), we attribute the Fe(II)-oxyhydroxide coating on Rh particles to the dynamic equilibrium of the Fe²⁺ release process (i.e., the reverse of Eq. (4)). To confirm the selective interaction of Fe²⁺ with Rh, we contacted pre-formed Rh...
nanoparticles with solutions containing either Fe\(^{2+}\) or Fe\(^{3+}\) cations and analyzed the recovered particles (Fig. 1d). The syntheses of these reference materials are described in the section of methods. The EELS images showed that Fe\(^{2+}\) species adsorb on the Rh surface to form a core-shell-like nanostructure (Fig. 1e), whereas Fe\(^{3+}\) species precipitate as a segregated phase with only weak association with Rh (Fig. 1f).

Overall, the charge transfer of galvanic replacement consumes Fe\(^{2+}\) supplied by Fe\(_3\)O\(_4\) for Rh\(^{3+}\) reduction yielding Rh particles (Fig. 2a). In parallel, Fe\(^{2+}\) released from the solid (Fig. 2b) adsorbs selectively on Rh (Fig. 2c). In order to verify the generality of our methodology to prepare inverse nanostructures, we also performed the galvanic replacement between the Pt\(^{4+}\) cations and Fe\(_3\)O\(_3\). The HAADF-STEM-EELS showed that Fe\(_O^x\) species coat the Pt nanoparticles (Supplementary Fig. 7). Hence, during the synthesis of Fe\(_O^x\)/metal nanostructures, the Fe\(^{2+}\) is not only a sacrificial species as one expects from the galvanic replacement alone, but a key constituent for tuning the surface of the metal nanoparticles.

The method offers many possibilities to tune the properties and structures of the final materials by controlling the rates of the individual processes taking place during the synthesis. Further

**Fig. 1 Synthesis of Fe\(_O^x\)/Rh/Fe\(_3\)O\(_4\) by galvanic replacement and reference experiments to elucidate the mechanism of Fe\(_O^x\) coating on Rh.** Synthesis of Fe\(_O^x\)/Rh/Fe\(_3\)O\(_4\)-fresh by galvanic replacement, where powder Fe\(_3\)O\(_3\) is contacted with a solution containing Rh\(^{3+}\) (a). Rh and Fe L-edges EELS images of the Fe\(_O^x\)/Rh/Fe\(_3\)O\(_4\)-fresh and the corresponding line-scan profile showing the Fe\(_O^x\) coating on Rh; the scale bar is 5 nm (b); more images can be found in Supplementary Figs. 2–5. Evolution of concentrations of aqueous Fe\(^{2+}\) and Fe\(^{3+}\) when Fe\(_3\)O\(_3\) is contacted with the Rh\(^{3+}\) solution (c). Scheme of the reference experiments, where pre-formed Rh nanoparticles were contacted with solutions containing Fe\(^{2+}\) or Fe\(^{3+}\) (d). HAADF-STEM-EELS images of the solids produced after contacting Rh nanoparticles with Fe\(^{2+}\) (e) or Fe\(^{3+}\) (f) in solution showing the selective adsorption of Fe\(^{2+}\) on Rh producing the Fe(II)-oxyhydroxide adlayers on Rh.

**Fig. 2 Mechanism for synthesis of inverse Fe\(_O^x\)/Rh/Fe\(_3\)O\(_4\).** Formation of Rh nanoparticles on Fe\(_3\)O\(_4\) and release of Fe\(^{3+}\) by galvanic replacement (a), dissolution of Fe\(^{2+}\) species (b), and selective deposition of Fe\(^{2+}\) on Rh particles (c).
work to control the metal particle size and FeOx coverage is ongoing.

Comparison of FeOx-covered and bare Rh particles supported on Fe3O4. We compared the inverse catalyst with Fe3O4-supported 1–2 nm Rh particles (Rh/Fe3O4) in CO2 hydrogenation. This reference was prepared by precipitating Rh3+ on Fe3O4 followed by treatment in air and reduction at 200 °C in H2 (Supplementary Fig. 8 for the Rh particle size distribution). To remove possible adsorbates remaining from synthesis and handling, the FeOx/Rh/Fe3O4-fresh material was treated at the same conditions as Rh/Fe3O4, yielding the material denoted as FeOx/Rh/Fe3O4. This material showed the same features of the parent FeOx/Rh/Fe3O4-fresh. That is, the dispersed FeOx species still decorated the metallic Rh particles (Fig. 3a–f and Supplementary Fig. 9). The inverse FeOx/Rh nanostructure was unaltered by the heat treatment, in agreement with the lower surface energy of iron oxide (Fig. 3h and Supplementary Table 3), which tends to wet the Rh surface13.

According to XANES (Fig. 3g) and EXAFS results (Fig. 4a), Rh in both FeOx/Rh/Fe3O4 and Rh/Fe3O4 are mainly metallic with a Rh–Rh distance of 2.68 Å. The Rh–Rh coordination number for FeOx/Rh/Fe3O4 is ~8.9 while for Rh/Fe3O4 it is 6.7 (Supplementary Tables 4 and 5 and Supplementary Figs. 10 and 11). This suggests that the Rh dispersion of FeOx/Rh/Fe3O4 was lower than Rh/Fe3O4 (i.e., 56% and 82%, respectively) (Supplementary Fig. 12). The difference in Rh dispersion was supported by time-of-flight secondary ion mass spectrometry (TOF-SIMS), which showed more abundant Rh2O+ fragments for FeOx/Rh/Fe3O4 than for Rh/Fe3O4 (Supplementary Fig. 13).

In contrast to the EXAFS of FeOx/Rh/Fe3O4 showing 56% Rh dispersion, H2 chemisorption indicates that only 5.6% of Rh is available to adsorb H2 (Fig. 4b and Supplementary Table 6). The discrepancy between EXAFS and H2 chemisorption is clearly due to the presence of FeOx overlayer. For Rh/Fe3O4, H2 chemisorption suggests a 70% dispersion, which is in good agreement with EXAFS results (i.e., most of the surface Rh atoms in the nanoparticles are available to adsorb H2). Both FeOx/Rh/Fe3O4 and Rh/Fe3O4 have the same adsorption equilibrium constant for H2 chemisorption (~7, Supplementary Table 6). Therefore, metallic Rh atoms are the sites for H2 activation on both materials.

Catalytic improvement by the FeOx overlayer. We targeted CO2 hydrogenation to test the activity of our inverse catalysts. Thus, we measured isotherms for CO2 adsorption (Fig. 4c), which showed that FeOx/Rh/Fe3O4 can adsorb more CO2 than Rh/Fe3O4 and pure Fe3O4 (Supplementary Table 6) (i.e., 7.2, 4.3, and 2.2 μmol CO2 g−1, respectively, at 33 kPa). The adsorption equilibrium constant for CO2/Rh/Fe3O4 is also higher than for Rh/Fe3O4 (i.e., 100 and 51, respectively) (Fig. 4c and Supplementary Table 6). Thus, the adsorption sites on the inverse FeOx/Rh catalyst have stronger interactions with CO2 than the sites in Rh/Fe3O4. The differences in adsorption capacity and strength have important consequences in the coverages of molecular species during the reaction (Supplementary Table 7 and Supplementary Figs. 14 and 15), and thus the catalytic performance described below.

The inverse FeOx/Rh/Fe3O4 catalyst showed high activity for CO2 reduction per mol of surface Rh (determined from the Rh–Rh coordination number from EXAFS analysis) compared to that of Rh/Fe3O4 (Fig. 4d). We used this normalization to reflect the surface of the catalysts that is potentially active, i.e., Rh with or without interactions with the support (note however, these trends are the same per mass of catalyst and mass of Rh). The selectivity to CO and the corresponding CO production rates are also higher on FeOx/Rh/Fe3O4 than on Rh/Fe3O4 (Fig. 4e, f). This highlights
the higher activity of the FeO\textsubscript{x}-coated particles than simple supported Rh particles. We analyzed the intrinsic activity of the materials not by normalizing rates to the fraction of exposed Rh (as determined from H\textsubscript{2} chemisorption) nor to the fraction of Rh covered by oxide species (Supplementary Table 8 and Supplementary Note). Instead, we considered that the uptake of CO\textsubscript{2} serves as titration of adsorption sites that can potentially produce CO (see the supporting information for more details). The rates of CO production normalized to the concentration of sites that dissociate H\textsubscript{2} but with limited capacity to produce methane.

Fig. 4 Characterizations and catalytic performance showing the impact of the FeO\textsubscript{x} overlayer on CO\textsubscript{2} reduction. Rh K-edge EXAFS spectra (a), isotherms of H\textsubscript{2} and CO\textsubscript{2} chemisorption (b, c), CO\textsubscript{2} conversion rates (d), and CO selectivity for CO\textsubscript{2} conversion (e), and the Arrhenius plots for CO\textsubscript{2} reduction to CO (f) for FeO\textsubscript{x}/Rh/Fe\textsubscript{3}O\textsubscript{4} and Rh/Fe\textsubscript{3}O\textsubscript{4}. Reaction conditions: 523–623 K, 101 kPa, CO\textsubscript{2}/H\textsubscript{2}/He = 7/28/105 mL min\textsuperscript{-1} (gas hourly space velocity of 7 × 10\textsuperscript{3} mL g\textsuperscript{-1} h\textsuperscript{-1}). The CO\textsubscript{2} and CO rates are normalized to the concentration of surface Rh as derived from EXAFS fitting.

The FeO\textsubscript{x}/Rh/Fe\textsubscript{3}O\textsubscript{4} inverse catalyst is also more productive than typical supported noble-metal nanoparticles and atomically dispersed Rh (Supplementary Table 10). Thus, leaving some exposed Rh on the surface of FeO\textsubscript{x}/Rh/Fe\textsubscript{3}O\textsubscript{4} does not lead to low activity because the surface behaves like Rh–Fe\textsubscript{3}O\textsubscript{4} interfaces.

In summary, this galvanic replacement approach to prepare inverse FeO\textsubscript{x}/metal nanostructures not only yields particularly compelling catalytic reactivity under real conditions but is versatile and easily scalable\textsuperscript{13,17,34}. The ability to control the surface functionality of metal nanoparticles enables a palette for catalyst design via galvanic replacement. The presence of the oxide overlayer makes the metal much more efficient for activating CO\textsubscript{2} while maintaining its hydrogenation ability. That is, the whole surface of the metal particle functions as metal/oxide interface with redox sites for adsorbing CO\textsubscript{2} near metal domains that dissociate H\textsubscript{2} but with limited capacity to produce methane.

Methods

Materials. The chemicals including magnetite (Fe\textsubscript{3}O\textsubscript{4}) nanoparticles (50–100 nm), RhCl\textsubscript{3} (37% Rh), rhodium (III) nitrate hydrate (Rh(NO\textsubscript{3})\textsubscript{3}·H\textsubscript{2}O), FeCl\textsubscript{3} (99.0%), FeCl\textsubscript{2} (99.5%), urea (99.0–100.5%), polyvinylpyrrolidone (PVP), and ethylene glycol were purchased from Sigma-Aldrich. The deionized water was obtained from a Milli-Q water system.

Synthesis of FeO\textsubscript{x}/Rh/Fe\textsubscript{3}O\textsubscript{4-fresh, FeO\textsubscript{x}/Rh/Fe\textsubscript{3}O\textsubscript{4 and FeO\textsubscript{x}/Pt/Fe\textsubscript{3}O\textsubscript{4-fresh. The FeO\textsubscript{x}/Rh/Fe\textsubscript{3}O\textsubscript{4-fresh with the pre-set Rh loading of 0.5 wt% was prepared by galvanic replacement between Rh\textsuperscript{3+} and partially reduced magnetite (Fe\textsubscript{3}O\textsubscript{4-x}). In a typical procedure, 9.95 g of Fe\textsubscript{3}O\textsubscript{4} was reacted in 5 vol.% H\textsubscript{2}/N\textsubscript{2} at 400 °C in a tube furnace to produce Fe\textsubscript{3}O\textsubscript{2-x}. The Fe\textsubscript{3}O\textsubscript{2} symmetry group remained for Fe\textsubscript{2}O\textsubscript{3} after this step (Supplementary Fig. 1). A 10 mL aqueous solution of RhCl\textsubscript{3} at a concentration of 5 mg\textsubscript{Rh} mL\textsuperscript{-1} was mixed with 90 mL deionized water at
room temperature. The Fe$_3$O$_3$ was then added to the solution and stirred for 7 h. The resulting material was separated, washed with water, and dried at 80 °C overnight. The as-prepared material was calcined in air at 450 °C with a ramping rate of 2 °C/min. The inductively coupled plasma (ICP) analysis showed that the effective Rh loading in the final material was 0.37 wt%. Prior to the catalytic test, the sample was treated at 200 °C in H$_2$. The purpose of heat treatments is to remove the possible surface ligands and surface-oxidized Rh species that remained during the synthesis. A material containing Pt (FeO$_x$Rh$_y$Pt$_z$O$_{1-x}$) was prepared by the same method with aqueous solution of H$_2$PtCl$_6$ as the precursor and a pre-set Pt loading of 0.5 wt%.

The dynamic changes of the Fe$_{2+}$ and Fe$_{3+}$ concentrations in the aqueous fraction during the galvanic replacement synthesis for Fe$_3$O$_4$/Rh$_x$Fe$_{2-x}$O$_3$(OH)$_n$ were analyzed by the ferrozine method. The suspension was centrifuged to isolate the aqueous fraction during the galvanic replacement (0, 0.1, 0.5, 1, 2, 3, 4, 5, 6, and 7 h). The pH values for the aqueous solutions increased slightly at first (from 4.0 to 5.0), and then decreased to 2.5. The resulting aqueous solutions were diluted in a 10$^{-2}$ M HCl solution and used for the analysis.

The Fe$_{3+}$ can react with ferrozine to form a stable magenta complex which gives a maximum absorbance at 562 nm on an ultraviolet–vis spectrophotometer. The Fe$_{3+}$ fraction can be detected by reducing with hydroxylamine hydrochloride solution, stabilized in a buffer, and followed by complexing with ferrozine.

Synthesis of Rh/Fe$_3$O$_4$. The Rh/Fe$_3$O$_4$ with a Rh loading of 0.5 wt% was prepared by a urea hydrolysis assisted deposition method. In a typical procedure, 9.95 g of Fe$_3$O$_4$ were dispersed in 100 mL deionized water. Then, a 10 mL aqueous solution of $9.95 \times 10^{-3}$ g Rh$_3$O$_4$ (0.05 M) was added to the suspension and stirred for 7 h. This procedure was performed in a N$_2$ glove box.

Synthesis of Rh nanoparticles (PVP method). In a typical procedure, Rh nanoparticles were synthesized following a polyol-based method. Rh nitrate (Rh$_3$O$_4$, 500 mg) was dissolved in 100 mL deionized water. Then, a 10 mL aqueous solution of H$_2$PtCl$_6$ (1 mg/mL) was added to the suspension and stirred for 7 h. The resulting suspension then was stirred for 7 h.

Mixing of Fe$_{3+}$ and Fe$_{2+}$ cations in solution in the absence of solid. In a typical procedure, 0.25 mL RhCl$_3$ aqueous solution (5 mg/mL) and 1 mL Fe$_3$Cl$_4$ aqueous solution (2 mg/mL) were added to deionized water at room temperature and stirred for 7 h. This procedure was performed in an N$_2$ glove box.

Reaction of Rh nanoparticle and Fe$^{2+}$ cations. After washing three times with deionized water, 1.25 mg Rh$_{30}$ nanoparticles were dispersed in 4 mL deionized water and mixed with 1 mL Fe$_3$Cl$_4$ aqueous solution (2 mg/mL) at room temperature. The resulting suspension then was stirred for 7 h. The Rh$_{30}$ nanoparticles immersed in Fe$^{2+}$ solution and parent Rh$_{30}$ nanoparticles were also dispersed in SiO$_2$ as the reference samples (Rh loading of 0.5%) for handling and catalytic testing.

Reaction of Rh$_{30}$ nanoparticles and Fe$^{3+}$ cations. After washing three times with deionized water, 1.25 mg Rh$_{30}$ nanoparticles were dispersed in 4 mL deionized water and mixed with 1 mL Fe$_3$Cl$_4$ aqueous solution (2 mg/mL) at room temperature. The resulting suspension then was stirred for 7 h.

Characterization. HAADF-STEM measurements were conducted with an aberration-corrected FEI Titan 80-300 STEM operated at 300 kV. EELS mapping and analysis were performed with aberration-corrected JEM-ARM200F instrument operated at 200 kV. The instrument (Quantum 965) is capable of performing dual EELS experiment. The EELS mapping was performed in the STEM mode in the range of ~50 to 500 eV for the zero-loss peak, 300 to 800 eV for the iron signal, and 2500 to 3500 eV for rhodium the signal maps. The zero-loss peak for zero-loss calibration was acquired in low loss spectrum images and aligned at 0 eV. The images of EELS were analyzed and processed using Gatan Digital Micrograph software. The EELS maps were constructed by analyzing the Fe L$_{3,2}$ (~708 eV), Rh L$_{3,2}$ (~3004 eV), and Pt M$_{4,5}$ (~2122 eV) edge peaks after the background subtraction.

X-ray absorption spectroscopy measurements were conducted in sector 20 of the Advanced Photon Source operated by Argonne National Laboratory. A rejection mirror was used to reduce the effects of harmonics. The metal foil was placed downstream of the sample cell, as a reference to calibrate the photon energy of each spectrum. The EXAFS spectra were analyzed with the ATHENA (g(k) oscillation background removal), FEFF9 (theoretical model calculation), and Artemis software packages. The fit to the Rh K-edge EXAFS (k$^2$) data was weighted by k$^2$ and windowed between 1.5 Å$^{-1}$ < k < 15.0 Å$^{-1}$ using a Hanning window with dk = 1.0 Å$^{-1}$.

H$_2$ and CO$_2$ chemisorption experiments were conducted with a Micromeritics 2020 instrument. In a typical procedure, 100 to 200 mg of the sample was degassed at 100 °C for 30 min, followed by in situ treatment at 200 °C in H$_2$ and evacuation at 200 °C for 30 min. Then, the temperature was decreased to 35 °C under vacuum. Prior to the chemisorption experiments, the sample was further evacuated for 40 min. The adsorbates (H$_2$ or CO$_2$) were introduced into the system for 1 h. The resulting chemisorption isotherm was measured in the pressure range of 0–40 kPa at 35 °C. The sample was evacuated after the first adsorption cycle and a second chemisorption isotherm was recorded. The CO$_2$ uptake on the parent Fe$_3$O$_4$ has been subtracted for plotting and derivation of adsorption parameters.

N$_2$ physisorption experiments at −196 °C were performed on a Micromeritics 2020 instrument. The samples were degassed in vacuum at 200 °C before the measurements.

TOF-SIMS was applied with a TOF-SIMS V spectrometer (IONTOF GmbH, Münster, Germany) equipped with a 25 keV bismuth cluster ion source, a 20 keV Ar$^+$, and a 2 keV Cs$^+$ sputtering ion sources. Prior to the TOF-SIMS experiments, the samples were deposited on an Au(111) substrate and exposed to ultrahigh vacuum overnight.

X-ray diffraction experiments were performed in a Philips X-pert Multi-Purpose Diffractometer equipped with a Cu anode (30 kV and 40 mA).

The elemental composition of samples was measured by ICP optical emission spectroscopy (Perkin Elmer 7300DV). Prior to the ICP experiments, the samples were digested in a mixture of HNO$_3$/HCl/HF/H$_2$O followed by H$_2$BO$_3$ addition for extra HF treatment.

Reaction tests. The CO$_2$ reduction was performed in a flow reactor equipped with an online gas chromatograph (Agilent 7890B). In a typical procedure, prior to the catalytic test, 12 mg of 30–80 mesh catalyst (diluted with 50 mg SiC) was loaded into the reactor and treated at 200 °C in 20 vol.% H$_2$ with a ramping rate of 2 °C min$^{-1}$. After the reactor reached the target reaction temperature, a mixture of CO$_2$, H$_2$, and He with a total flow rate of 140 mL min$^{-1}$ was fed into the reactor (CO$_2$: H$_2$:He = 7:28:105).

Correlations of coordination number and metal dispersion. The correlation between coordination number and metal dispersion was derived from the data in the reference (Supplementary Fig. 12)$^{35}$. The relationship between the coordination number of metal–metal shell and the metal dispersion was based on two different shapes of metal particles (spherical and raft-like shapes).

Calculation of adsorption constant and monolayer coverage from isotherms. The adsorption constant and monolayer coverage were derived from the chemisorption isotherms where chemisorption is treated as a chemical reaction between the gas-phase molecule (A) and the site (n) for adsorption (Eq. (5)).

$$A + n \leftrightarrow A^n.$$  (5)

The adsorption can be fitted with a Langmuir adsorption model (Eq. (6)).

$$\theta_{\text{A}} = \frac{V_{\text{A}}}{V_{\text{M}}} = \frac{KP}{1 + KP}. \quad (6)$$

The adsorption parameters can be obtained from the linear form of Eq. (2) (Eq. (7)). In Eq. (7), $\theta_A$ is the fractional coverage of the adsorption sites, $P$ is the partial pressure of the adsorbate, $V_{\text{M}}$ is the volume of the monolayer, and $K$ is the equilibrium adsorption constant.

$$\frac{1}{\theta_{\text{A}}} = \frac{1}{V_{\text{M}}} \left( \frac{1}{P} \right) + 1. \quad (7)$$

Data availability

The source data underlying Figs. 1–4 are provided as a Source Data file. The other relevant data that support the findings of this study are available from the corresponding author upon request. Source Data are provided with this paper.

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Author contributions
Y.Z. and O.Y.G. led the project and conceived the experiments. Y.Z., X.Z., and K.K. performed the material synthesis. L.K. was responsible for the microscopy studies. J.L.F. was responsible for the X-ray absorption spectroscopy studies. K.M.R. contributed to the analysis of the mechanism and manuscript writing. Y.Z. and O.Y.G. wrote the manuscript with the inputs from all authors.

Competing interests
The authors declare no competing interests.

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