Grave-to-cradle upcycling of Ni from electroplating wastewater to photothermal CO$_2$ catalysis

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Treating hazardous waste Ni from the electroplating industry is mandated world-wide, is exceptionally expensive, and carries a very high CO$_2$ footprint. Rather than regarding Ni as a disposable waste, the chemicals and petrochemicals industries could instead consider it a huge resource. In the work described herein, we present a strategy for upcycling waste Ni from electroplating wastewater into a photothermal catalyst for converting CO$_2$ to CO. Specifically, magnetic nanoparticles encapsulated in amine functionalized porous SiO$_2$, is demonstrated to efficiently scavenge Ni from electroplating wastewater for utilization in photothermal CO$_2$ catalysis. The core-shell catalyst architecture produces CO at a rate of $1.9 \text{ mol·g}_{\text{Ni}}^{-1} \cdot \text{h}^{-1}$ ($44.1 \text{ mmol·g}_{\text{cat}}^{-1} \cdot \text{h}^{-1}$), a selectivity close to 100%, and notable long-term stability. This strategy of upcycling metal waste into functional, catalytic materials offers a multi-pronged approach for clean and renewable energy technologies.

The annual discharge of heavy metal wastewater produced by the electroplating industry has exceeded 4 billion tons just in China$^1$. Ni electroplating is particularly widely practiced and allowed to enter natural water systems, causing serious lung, kidney, stomach, intestine, and skin diseases in humans$^2$. While Ni is less costly than precious metals, it has more health and safety regulatory standards by authorities like the EPA$^3$–$^5$. The discharged Ni has been commonly regarded as waste or hazard that needs to be treated via remediation methods, like chemical precipitation and electrodeposition$^6$, $^7$. The require preconcentration, post-treatment of sludge, and electricity input, which are often accompanied by high energy costs and a large CO$_2$ footprint$^6$–$^9$. In the meantime, other industries like chemicals and petrochemicals, as well as electroplating itself that requires an excessive amount of Ni are stimulating mining of more Ni from minerals and paying the added price of reagent-grade Ni chemicals, leaving the waste Ni from electroplating buried underground. This bleak situation is worrisome in the climate-challenged world, where the greenhouse effect is looming, and the transition towards sustainable energy and a green economy is of great urgency$^{10}$–$^{16}$. Fortunately, emerging wastewater techniques, including adsorption$^{17}$–$^{19}$ and ion exchange$^{20}$, many coupled with magnetic separation$^{21}$–$^{24}$, provide energy-saving solutions to scavenge and recycle Ni from the wastewater, but the big question is: what happens next to the adsorbents and exchangers? Landfilling them causes further environmental and health issues, whereas regenerating them and retrieving Ni costs more reagents and energy.

Richard Buckminster-Fuller in Life Magazine said, “Pollution is nothing but resources we’re not harvesting”. Today we are not unfamiliar with the concept of “recycling” waste, but industries’ bottom

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lines often demand that the resulting product of recycling must be better or even higher value than the original item. This paradigm of so-called “upcycling” has become a keyword in the new world of technologies being eco-friendly\(^22\). In this context, an economically and environmentally viable strategy should be to directly transform the scavenged Ni from electroplating wastewater to a valuable product that avoids energy- and CO\(_2\)-intensive mining and rather stores energy in chemicals and fuels made from CO\(_2\). Although nickel has been widely accepted as an excellent catalyst for CO\(_2\) reduction\(^22\)-\(^30\), this vision is challenging because electroplating wastewater has a complex composition containing Ni salts with multiple anions, including sulfate, chloride, and amino-sulphonate, which may hinder the recovery of pure Ni chemical feedstocks, and even if an adsorbent is used to retrieve Ni regardless of the anion mix, the adsorbing components can be redundant or even detrimental to the new product. For example, Mikhail et al.’s work suggests that the presence of Na and K impurities in Ni/CeZrO\(_x\) catalysts resulted in decreased CO\(_2\) conversions, lower selectivity, and upcycling strategy to scavenge the majority of the Ni from electroplating wastewater can be redundant or even detrimental to the new product. For example, Mikhail et al.’s work suggests that the presence of Na and K impurities in Ni/CeZrO\(_x\) catalysts resulted in decreased CO\(_2\) conversions, lower selectivity, and increased power consumption in DBD plasma-catalytic CO\(_2\) methanation\(^4\). In contrast, the impurities can also function as promoters rather than inhibitors. In many cases, different from Maria’s case, the introduction of alkali metals (e.g., Na and K) could instead improve the catalytic performance\(^32\). Nevertheless, the existence of impurities in wastewater still brings complications and uncertainties, so the judicious design of the upcycling process, materials, and catalysts are critical and must be validated.

Targeting this challenge, we demonstrate a two-fold direct recycling and upcycling strategy to scavenge the majority of the Ni from zero-cost and abundant electroplating wastewater and utilize it as a heterogeneous photothermal catalyst for converting CO\(_2\) to chemicals and fuels. A carefully designed adsorbent comprised of a sphere-shaped, multifunctional ternary heterostructure Fe\(_2\)O\(_3\)@SiO\(_2\)@mSiO\(_2\)-NH\(_2\) was utilized to capture high dispersions of Ni in real electroplating tailings, employing the chemical tethering property of –NH\(_2\) enhanced by the large surface area of mesopores in SiO\(_2\). The ternary nanocomposite Fe\(_2\)O\(_3\)@SiO\(_2\)@mSiO\(_2\)-NH\(_2\)@Ni is comprised of earth-abundant elements. It displays a remarkable 100% selectivity and high stability towards the reverse water-gas shift reaction CO\(_2\) + H\(_2\) \rightarrow \text{H}_2\text{O} + \text{CO}\). Qualities not enjoyed by traditional Ni-sourced heterogeneous catalysts. The Fe core provides additional benefits that include straightforward magnetic separation of the Fe\(_2\)O\(_3\)@SiO\(_2\)@mSiO\(_2\)-NH\(_2\)@Ni catalyst from the electroplating wastewater, a light-activated broadband nano heater to drive the photothermal reverse water-gas shift reaction at higher efficiency, milder conditions, and a lower CO\(_2\) footprint than the thermochemical reverse water-gas shift reaction.

### Results
Our strategy to upcycle Ni from real electroplating wastewater can be divided into several steps (Fig. 1). First, a designed adsorbent is suspended in real Ni(II)-containing electroplating wastewater (step 1). After reaching adsorption equilibrium, the adsorbed Ni(II), together with the adsorbent, is collected via a magnet (step 2) and then directly calcined to be transformed into an active catalyst with a nanoreactor-type architecture (step 3). The obtained catalyst is then used in photothermal catalytic CO\(_2\) hydrogenation reactions (step 4). The architecture of the nanoreactor catalyst was carefully designed to realize the following functionalities: the Fe core of our nanoreactor supplies sustainable photothermal heat, and the Ni within the silicon oxide synthesizes solar fuel.

### Characterization of the catalysts
The adsorbent used in this work was designed to have a core-mantle-crust structure, with a magnetic core (Fe\(_2\)O\(_3\) colloidal nanocrystal clusters, denoted as CNC) and two layers of silica (Supplementary Fig. 1), employing the first and second most abundant element in the Earth’s crust: O and Si. The strong magnetism of the CNC core ensured easy separation of adsorbents from solution\(^25\)-\(^26\). The dense silica in the middle mantle layer prevented the CNC core from being etched in the acidic wastewater. The outmost crust of mesoporous silica serves to enlarge the specific surface area (SSA) to benefit adsorption and further catalytic reaction. Besides, the adsorbent particles (denoted as CNC@SiO\(_2\)(mSiO\(_2\))) were also grafted with amino groups (denoted as CNC@mSiO\(_2\)) to facilitate the capture of Ni(II). The Brunauer-Emmett-Teller (BET) surface areas of the amino-grafted adsorbents with and without the mesoporous silica layer were calculated to be 301.7 and 16.3 m\(^2\)g\(^{-1}\), respectively, demonstrating the function of mesoporous silica in increasing SSA (Supplementary Fig. 2). A sample prepared by coating CNC with only a mesoporous SiO\(_2\) layer (without the middle mantle protecting layer, denoted as CNC@mSiO\(_2\)) was used as a control sample to verify the acid resistance of the dense mantle SiO\(_2\) layer in CNC@SiO\(_2\)(mSiO\(_2\)) (Supplementary Fig. 3). The sample size distributions of CNC@SiO\(_2\)(mSiO\(_2\)) and CNC@SiO\(_2\) suggest that the thickness of SiO\(_2\) for these two samples are the same, making the comparison fair. The concentration of Fe in the etching solution for CNC@SiO\(_2\)(mSiO\(_2\)) is much lower than that for CNC@SiO\(_2\) under various etching conditions. These results indicate that the dense silica in the middle layer of CNC@SiO\(_2\)(mSiO\(_2\)) has strong resistance against acid.

After the treatment of the electroplating wastewater, the recycled Ni\(^{\text{II}}\) together with the adsorbents was directly calcined in air and H\(_2\) sequentially (denoted as S\(_{\text{Fe-Ni}}\)), which completed the assembly of the nanoreactor catalyst. Figure 2 shows the morphology and composition of the obtained catalyst. The overall core-shell structure was retained, while the CNC core was cracked (Fig. 2b and Supplementary Fig. 1). Notably, no apparent Ni nanoparticles could be observed, suggesting that Ni should be highly dispersed in S\(_{\text{Fe-Ni}}\). This was further corroborated by the X-ray diffraction (XRD) results (Supplementary Fig. 4). The patterns for S\(_{\text{Fe-Ni}}\) showed no characteristic peaks of Ni crystals, excluding the generation of large particles and aggregates. Whereas, the characteristic peaks of Fe were clearly observed in the patterns, suggesting that the CNC core had been reduced in the calcination process. The high dispersion of Ni in S\(_{\text{Fe-Ni}}\) was ultimately confirmed by the aberration-corrected high-angle annular darkfield-scanning transmission electron microscopy (HAADF-STEM) images (Fig. 2c), in which no nanoparticles but only bright dots could be observed. Energy Dispersive Spectrometer (EDS) mappings further demonstrated the core-mantle-crust structure (CNC@SiO\(_2\)(mSiO\(_2\))) in which Ni was successfully loaded (Fig. 2d–h).
To identify the chemical environment in the sub-nano dimension and the electronic structure of Ni in SFe-Ni, X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) spectra at the Ni K-edge for SFe-Ni were obtained (Fig. 3 and Supplementary Table 1). In the Ni K-edge XANES spectrum, the near-edge absorption energy of SFe-Ni is located between the Ni foil and NiO, indicating the partially oxidized state of Ni in SFe-Ni. The FT-EXAFS curve for SFe-Ni shows a main peak at ~1.6 Å, which could be attributed to Ni–Os scattering. A very small peak attributed to the Ni–Ni scattering signal (located at ~2.1 Å) for SFe-Ni demonstrates the existence of aggregated Ni is rare. Fitting the peak of the first shell of Ni–O shows the average coordination number (CN) of oxygen atoms around a Ni atom (CN (Ni–O)) in SFe-Ni is 3.8, indicating that Ni is unconventionally coordinated in comparison to NiO, which has a CN (Ni–O) of 6. The decreased CN (Ni–O) of SFe-Ni should be ascribed to the highly dispersed adsorbed state of Ni on the surface of SiO2 without NiO nanoparticles. The second coordinative shell can be assigned to Ni–Ni coordination, of which the CN (Ni–Ni) is 4.8. The much lower CN (Ni–Ni) of SFe-Ni than that of Ni foil (CN (Ni–Ni) = 12), combined with the aberration-corrected HAADF-STEM results, suggests that our catalyst preparation strategy ensured that Ni existed as highly dispersed atoms and ultrasmall clusters, rather than aggregated nanoparticles.

As reported, small-sized Ni catalysts exhibit excellent catalytic performance in CO2 hydrogenation. Therefore, the unique structure of SFe-Ni should render it a potential candidate for this reaction. Meanwhile, the Fe core, as an active metal and a great photothermal material, could offer additional activity to the system. Therefore, we conducted systematic catalytic tests to evaluate the catalytic performance of this designed catalyst and identify the roles of the key components, under both thermal and photothermal conditions. For comparison, two primary control samples excluding either Fe or Ni were investigated to manifest the rationality of our catalyst design.
under the same testing conditions: a control sample prepared by annealing the bare Sn without Ni under the same condition as SnFeNi (denoted as SnFeNi, Supplementary Fig. 5), and another control sample substituting the CNC core with a SiO2 core (denoted as SnO2) by treating the SnO2@mSiO2 nanoparticles with the same amino functionalization, adsorption, and annealing procedure of SnFeNi (Supplementary Fig. 6). SnFeNi exhibited the same morphology of SnFeNi, while no Ni could be found from the EDX element maps. Meanwhile, a solid silica core was found for SnO2 with Ni uniformly dispersed in the outer silica layer, and no Fe was observed in the EDX element maps.

**Thermocatalytic performance**

Before pursuing the sustainable potential in light-driven CO2 reduction, we first evaluated the traditional thermocatalytic performances of the samples to provide fundamental insights into the catalytic sites, product selectivity, and thermal stability of our catalyst. It was found that the CO production rates of SnFeNi were much higher than those of SnFe at all testing temperatures (Supplementary Table 2). Below 400 °C, the control sample SnFe hardly even showed observable activity. This indicates that the loading of Ni led to pronounced improvement in catalytic performance for SnFe. Notably, the CO rate of SnFe was close to that of SnFeNi. This further demonstrates that the catalytic ability of our designed architecture under pure thermal conditions mainly comes from Ni rather than the Fe core. Only at the relatively high temperatures of 450 and 500 °C, when the diffusion of reactants was greatly enhanced, the Fe core could start to contribute to the yield of CO, indicated from the EDX element maps.

To examine whether the mesopores contribute to the small size of Ni and, in turn, the great selectivity, another control sample was prepared by using solid SiO2 spheres as the support to graft amino groups, followed by the adsorption and activation of Ni similar to other samples (denoted as S502-2NiO2). As Supplementary Fig. 9a-b shows, no large Ni particles, and no obvious crystalline Ni signals could be observed from the TEM and XRD results, respectively. Moreover, the thermocatalytic results suggest that CO was the only product for S502-2NiO2, which is characteristic of small-sized Ni (Supplementary Fig. 9c). The BET surface area of amino-grafted solid SiO2 (S502-2NiO2) is much lower than that of CNC@SiO2@mSiO2-NH2 (15.9 m²/g vs. 301.7 m²/g, Supplementary Fig. 9d). This leads to the much poorer catalytic activity of S502-2NiO2, only half of that of SnFeNi. These results indicate that the mesoporous SiO2 only act as effective support with a high specific surface area.

As Supplementary Table 3 shows, many other ions besides Ni exist in the electroplating wastewater. To verify the influence of these ions on the catalytic performance, a synthetic Ni solution made from reagent Ni(NO3)2·6H2O with only Ni2+ (the Ni2+ concentration is the same as that for the real electroplating wastewater) was used as the precursor to prepare the SnFeNi sample. Notably, Supplementary Fig. 10 shows that the CO rate for SnFeNi prepared from real electroplating wastewater is the same as that for SnFeNi prepared from the synthetic Ni solution at 400 °C, while only a slightly lower CO rate was found for the former than for the latter at 500 °C. Nevertheless, the overall discrepancy between these two SnFeNi samples is minimal. This should be attributed to the similar loading amount of Ni for these two samples and the trace amount of other ions therein (Supplementary Tables 4 and 5). These results suggest that the existence of the other ions besides Ni in the real electroplating wastewater does not deteriorate the upcycling efficiency of Ni for the CO2 catalysis reported herein. Overall, the above results preliminarily manifest that our designed solid support could successfully recycle Ni from the electroplating wastewater into a highly active and selective catalyst for CO2 hydrogenation reactions.

The stability of SnFeNi was evaluated through testing at the relatively high temperature of 500 °C, shown in Supplementary Fig. 7b. After a slight decrease, the CO rate began to increase slowly and tended to be stabilized above 5 mmol gcat⁻¹ h⁻¹. The mild decrease of yield in the initial stage should arise from the oxidation of Ni, demonstrated by the XAS results (Fig. 3 and Supplementary Table 1). The used catalyst, denoted as SnFeNi (after), showed a very similar Ni K-edge XANES spectrum with SnFeNi, but the pattern became slightly closer to that of NiO (Fig. 3a). In the Ni K-edge EXAFS spectrum, a small Ni–O–Ni hump (located at 2.6 Å) emerged while the small peak for Ni–Ni disappeared. This indicates that the Ni clusters had been oxidized after the reaction. Meanwhile, the intensity of the Ni–O with low CN was maintained after the stabilization test, which is in line with the preservation of high catalytic activity and selectivity towards CO production. Notably, more Ni atoms and clusters without serious aggregation could be seen in the used catalyst (Supplementary Fig. 11c) than in the fresh samples (Fig. 2c). The high dispersion of Ni in the used samples could also be evidenced by the XRD patterns which show no characteristic signals of crystalline Ni (Supplementary Fig. 12). The migration of Ni from the inner part of the mesopores to the more outer part was beneficial for the mass transfer of the reactants, leading to the gradual increase of production rate seen in Supplementary Fig 7b.

The catalytic pathway was studied through the in situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) experiments and kinetic studies (Supplementary Figs. 13–15). The in situ DRIFTS spectra of SnFeNi (Supplementary Fig. 13a) show weak signals of gaseous CO (2111 and 2174 cm⁻¹) and CH4 (3016 cm⁻¹) coinciding well with the products of the reverse water-gas shift reaction. No obvious signals of gaseous CH4 (3016 cm⁻¹) or other intermediate products were observed. The absence of peaks between 2800 and 2900 cm⁻¹ demonstrates the non-existence of formate species. Millet et al. also reported that only a weak formate signal could be observed for small-sized Ni, which favored the production of CO2 from hydrogenation of CO2 (a favorable route) at 500 °C, and this supports our small-sized Ni selectivity towards CO production. The lack of formate species and bridged CO (1800 cm⁻¹) or other intermediate products were observed. The absence of peaks between 2800 and 2900 cm⁻¹ demonstrates the non-existence of formate species. Millet et al. also reported that only a weak formate signal could be observed for small-sized Ni, which favored the production of CO2 from hydrogenation of CO2 (a favorable route) at 500 °C, and this supports our small-sized Ni selectivity towards CO production. Meanwhile, the intensity of the Ni–O with low CN was maintained after the stabilization test, which is in line with the presence of high catalytic activity and selectivity towards CO production. Notably, more Ni atoms and clusters without serious aggregation could be seen in the used catalyst (Supplementary Fig. 11c) than in the fresh samples (Fig. 2c). The high dispersion of Ni in the used samples could also be evidenced by the XRD patterns which show no characteristic signals of crystalline Ni (Supplementary Fig. 12). The migration of Ni from the inner part of the mesopores to the more outer part was beneficial for the mass transfer of the reactants, leading to the gradual increase of production rate seen in Supplementary Fig 7b.

The reverse water-gas shift reaction (RWGS) reaction commonly follows a direct dissociation route (CO2 → CO + O2) or a formate route28,43. Since the signal of ‘HCOO−’ is negligible, the RWGS reaction on the SnFeNi catalyst is more likely to follow a dissociation route. The overall weak signals in the in situ DRIFTS spectra for SnFeNi are ascribed to its excellent absorption in the infrared region (Supplementary Fig. 13b), but the relatively poor signal-to-noise ratio might cause difficulty for interpretation. Therefore, additionally, we obtained in situ DRIFTS spectra for S502-2NiO2-NH2. The S502-2NiO2-NH2 sample, which also has the characteristics of small-sized Ni but with more intense reflectance signals in the infrared light region (Supplementary Fig. 13b). It is a perfect substitute to verify the reaction route in this system. In the in situ DRIFTS spectra of S502-2NiO2-NH2 show distinct signals of gaseous CO and still no other obvious intermediates (Supplementary Fig. 13c). This again demonstrates the high possibility of a direct dissociation route for small-sized Ni in our catalysts as depicted above. Moreover, another control sample was prepared by
Impregnating Ni(NO₃)₂ • 6H₂O on solid SiO₂ spheres (Niim/SiO₂) to show the difference between the small-sized Ni and Ni nanoparticles. The characteristic signals of crystal Ni in the XRD pattern (Supplementary Fig. 13d) confirm the nanoparticle state of Ni in Niim/SiO₂, which showed low selectivity towards CO (only 35.8%, Supplementary Table 2). The in situ DRIFTS spectra of Niim/SiO₂ show obviously characteristic peaks of gaseous CH₄ and linearly absorbed CO (2030 cm⁻¹), which are not seen in the samples with small-sized Ni (Supplementary Fig. 13e). Therefore, the absence of intermediates verified from the in situ DRIFTS spectra of the samples with small-sized Ni can explain their much higher selectivity towards CO production, and accordingly insignificant production of CH₄. As to the kinetic studies, the results suggest that the CO production rate over the SFe-Ni catalyst exhibits higher dependence on CO₂ (0.8) than H₂ (0.08), as shown by Supplementary Figs. 14 and 15, respectively. This indicates that the Ni surface is mostly covered by hydrogen instead of carbon species, which is in good agreement with the in situ DRIFTS results. When the pressure of CO₂ increases, the dissociation of CO₂ becomes easier, leading to promoted CO production.

**Photothermal catalytic performance**

It was found that SFe-Ni and SFe appeared to be black while the color of S Ni is pale (Supplementary Fig. 16). The diffuse reflectance spectra of these samples show that SFe-Ni and SNi have similar reflectance, which is less than 15%, spanning the ultraviolet, visible-light, and part of the near-infrared region (Fig. 4a). Even in the further end with the longer wavelength, the reflectance of these two samples is not beyond 25%. In contrast, SNi exhibits much higher reflectance throughout the full solar spectrum from 200 to 2500 nm. These results manifest that the Fe core plays an important role in improving the light-harvesting ability of SFe-Ni. The strong light absorption of SFe-Ni should render it an excellent photothermal material, which allows the CO₂ hydrogenation reaction to be more sustainable with the aid of light.

The photothermal catalytic performances of the samples were first determined under illumination with a Xe arc lamp and without any heat supplied by the heating unit of the bulk reactor. Surprisingly, differently in the thermal test results, the yield of CO was only observed for SFe-Ni while the other two samples had no catalytic activity (Supplementary Fig. 17). With the further assistance of a light concentrator, the production of CO could finally be detected for SFe and SNi (Fig. 4b). However, their CO yields were still very low, in contrast to the pronounced rates for SFe-Ni under the same testing conditions. Typically, CO rates of 9.73, 3.59, and 1.35 mmol·g⁻¹·h⁻¹ were obtained for SFe-Ni, SFe, and SNi, respectively, under concentrated 210-W illumination.

Meanwhile, the production of CH₄ was still negligible in photothermal catalytic reactions as well (Supplementary Fig. 18), ensuring ultrahigh selectivity towards CO (>99.99%). These results indicate that both the Fe core and Ni sites are indispensable components in the nanoreactor for achieving considerable CO rates in photothermal catalytic CO₂ hydrogenation. Compared with SNi that is devoid of Fe, the CO production rate of SFe-Ni was significantly boosted, around 7 times, which can be ascribed to the excellent light-harvesting ability...
and thereby high photo-thermal conversion efficiency of the Fe core. These are manifested by the fact that the equilibrium temperature of SFe-Ni could be achieved at the high value of 402 °C under the illumination of concentrated light (Fig. 4c). The surface temperature of SFe is close to that of SFe-Ni, which is far beyond 295 °C, the equilibrium temperature of Sn. This trend was also found under other illumination conditions (Supplementary Fig. 19). Therefore, the observed high rate is largely attributed to the heat provided by the Fe core under such light-only conditions. In comparison, Sn, which is with the Fe core but without Ni sites, could reach a similar high temperature under light but did not show a high reaction rate. This echoes with the thermocatalytic result that Ni was the major active site for the hydrogenation of CO2. Notably, SFe-Ni could achieve similar CO rates of \( \sim 5 \text{mmol·g}^{-1}\cdot\text{h}^{-1} \) in either the thermocatalytic process (500 °C) or the photothermal catalytic (190 W illumination assisted with a concentrator) process. This indicates the real local temperature of SFe-Ni under this illumination was much higher than the apparent surface temperature of 361 °C measured by the thermocouple, further demonstrating the excellent photothermal conversion property of SFe-Ni. The increased local temperature and its catalytic boosting effect induced by SiO2 encapsulation have also recently been discovered and discussed in detail by Cai et al.56,57. The heat insulation and infrared shielding effects of the SiO2 sheath were demonstrated by Cai et al.56,57, enabling a super-photothermal effect. The thermocouple could only reach the surface of the outer-layer mesoporous silica, the temperature of which was lower than that inside the catalyst. The fact that Sn only exhibited nearly 1/7 of the CO production rate of SFe-Ni under the same light illumination condition (33.3 suns) indicates that photochemical contribution if there was any, was trivial. The significant CO rate of SFe-Ni under light was still driven by the thermochemical reaction pathway, supported by the same product selectivity and similar activation energy as shown in thermal catalytic test results, shown in Supplementary Table 6 and Supplementary Fig. 20. Besides, the exponential dependence of the reaction rate on illumination intensity in Fig. 4b rather than a linear dependence, is a characteristic feature of thermally driven transformation6. The excellent phototherm catalytic performance of SFe-Ni was further demonstrated by using commercial Cu2ZnO·Al2O3 as a control sample which shows a lower CO rate than SFe-Ni under similar testing conditions (Supplementary Fig. 21). Another control experiment was also conducted by using only CO2 and Ni as the reactants, under which the production of CO is negligible in comparison to the H2existing atmosphere (Supplementary Fig. 22). This demonstrates that the production of CO originates from the reverse water-gas shift reaction rather than the Boudouard reaction (C + CO2 → 2CO).

Notably, the photothermal catalytic CO rate for SFe-Ni could be further improved to be 44.1 mmol·g·h\(^{-1}\) by using a batch reactor, which is about 9 times the rate in the flow reactor under the same light intensity (Fig. 4b, d). At the same time, the selectivity was maintained to be nearly 100%. This improvement can be attributed to the sealed environment and the catalyst bed geometry that can reduce loss of heat (reduced thermoconvection compared with the flow reactor) and enhance light absorption (larger absorption area due to the better dispersion of catalyst on the glass fiber filter). The photothermal catalytic activity of SFe-Ni was far beyond that of SFe (5.9 mmol·g·h\(^{-1}\)) in the batch reactor, again demonstrating that Ni is the major active component. This allows the CO production rate per weight of Ni to be calculated, which turned out to be as high as 1.9 mol·g·h\(^{-1}\). Meanwhile, the activity of the control sample Sn0 in the batch reactor was also improved compared to the flow reactor result, but only around half of the activity of SFe-Ni, due to the lack of the central Fe heating core. The photothermal activity of our catalyst was also compared with those of various reported photothermal catalysts (Supplementary Table 7). The SFe-Ni samples have higher or at least the same level of production rate compared with the listed catalysts. Overall, the intentionally designed architecture of our nanoreactor catalyst and control tests have pinpointed the functions of the Fe core and the well-distributed Ni sites, and exhibited extraordinarily high catalytic selectivity at a high production rate.

Cycle experiment

The concentration of Ni in the electroplating wastewater was 6576 mg L\(^{-1}\) according to the inductively coupled plasma mass spectrometry (ICP-MS) results. Obviously, the Ni resources in the wastewater were affluent. In this work, the Ni wastewater could be utilized as an abundant source for preparing large amounts and multiple batches of SFe-Ni Catalysts. To confirm this concept, a batch of wastewater was treated by Sn0 and repeated to determine how many times it could serve for the preparation of SFe-Ni. For each cycle of treatment, the fresh adsorbent was used, and the catalyst thus prepared was named as SFe-Ni\(n\), in which \(n\) represents the cycle number. Supplementary Fig. 23 shows the concentration of the remaining Ni in the wastewater after numerous typical cycles (abbreviated as CNi\(n\): \(n\) represents the cycle number). After 15 cycles, CNi15 was detected to be 224 mg L\(^{-1}\), about 3% of the original value (6676 mg L\(^{-1}\)). Namely, 97% of the Ni resources in the wastewater were upcycled to prepare 15 batches of the active catalyst SFe-Ni. The loading amounts of Ni onto SFe-Ni after these cycles were determined by ICP-MS (Supplementary Fig. 24). In the initial few cycles, the loading ratios of Ni for different SFe-Ni samples were similar: \(\sim 2\%\). After the 9th cycle, the Ni loading began to decrease, which is ascribed to the lower maximum adsorption capacity under equilibrium when CNi\(n\) drops. The loading ratio of Ni was 1% for SFe-Ni5, which is half of that for SFe-Ni15 (Supplementary Fig. 24 and Supplementary Table 4). The thermocatalytic property for three typical SFe-Ni\(n\) (\(n = 3, 9, 15\)) samples at 500 °C was evaluated (Supplementary Fig. 25). The CO production rates of SFe-Ni3 and SFe-Ni9 approached that of SFe-Ni15, which should be attributed to their similar loading amount of Ni and catalyst structure. In contrast, SFe-Ni15 showed a much lower CO production rate (3.12 mmol g\(^{-1}\)cat h\(^{-1}\)), which was expected since its Ni loading was only half that of SFe-Ni15. Nevertheless, this rate is still higher than that of Sn, again demonstrating the function of adsorbed Ni as the active sites. Besides, only a trace amount of CH4 could be detected for all these samples, marking good repeatability in achieving high product selectivity via this cycling approach. Overall, 97% of Ni in the electroplating wastewater could be recycled for the preparation of SFe-Ni catalysts through cycling adsorption and calcination, realizing the sustainable upcycling of waste Ni.

Despite the overall high upcycling efficiency through cycle adsorption, the drop of activity for the samples in the later cycles due to the lower loading of Ni might be a problem. We have clarified this in the revised manuscript, as the reviewer suggested. Moreover, we further propose a possible remedial strategy regarding this problem: performing adsorption in fresh wastewater again using the sample in the later cycles to achieve improved Ni loading. As a simple demonstration, we prepared a SFe-Ni Sample using diluted Ni wastewater (1 mL of wastewater diluted by 29 mL of milli-Q water) to simulate SFe-Ni in the later cycles. Next, a second adsorption process in the fresh Ni wastewater was operated on this sample. The CO rate of the treated sample achieved was 5.3 mmol g\(^{-1}\)cat h\(^{-1}\) which is similar to that of SFe-Ni prepared using fresh Ni wastewater under the same testing condition, demonstrating the feasibility of the remedial strategy. Nevertheless, the second adsorption also made the upcycling procedure more time-consuming. Simpler and more cost-effective upcycling strategies should be developed in future works.

\(\text{CO}_2\) footprint and cost evaluation

Carbon neutrality is an urgent goal in the current age59–65. Many technologies for producing value-added products claim using CO2 as the feedstock can reduce CO2 emission, but this may not be necessarily true, since the power consumed to run the facility, to produce H2, and
to drive the chemical reaction may generate an even larger CO2 footprint than the one the technology aims to reduce. Chen’s group has recently demonstrated that using CO2 to synthesize methanol either via thermocatalysis or electrocatalysis is still generating several mol of new CO2 when one mol of CO2 is consumed under the current US energy structure, far from reaching carbon neutrality. Inspired by his quantitative study, we recently developed a universal evaluation approach to compare the net CO2 emission rates between thermal and photothermal CO2 hydrogenation using typical small-scale fixed-bed reactors. As shown in Fig. 5, net CO2 emission rates (denoted as $dM/dt$) for SFe-Ni under the thermocatalytic and photothermal conditions were calculated based on the catalytic results from this work and the criterions built in our previous work. To be specific, the value of $M$ equals the amount of emitted CO2 after subtracting the consumed CO2 in a catalytic process. The derivatives of $M$ in terms of $t$ ($dM/dt$, representing net CO2 emission rate) for flow reactors are shown as follows:

$$dM_{1kp}/dt = x_1a + nx_2 - mc$$

$$dM_{2kp}/dt = (k_2T + b_2)x_1 + nx_3 - mc$$

in which, $a$, $c$, $m$, $n$, $x_1$, $x_2$, and $k_2T + b_2$ represent the power consumption of the lamp (kW), the conversion rate of CO2 (mol·g$^{-1}$·h$^{-1}$), the mass of the catalyst (g), the original feed amount of H$_2$ in a cycle (mol), CO2 emission per kWh of electricity according to the US 2014 energy structure (mol), CO2 produced per mol of H$_2$ (mol), and the electricity consumed to maintain the reactor at $T$ per hour (kW), respectively. The subscript ‘kp’ denotes that the H$_2$ feed is calculated based on the kinetic parameters. Detailed calculation and value assignment are listed in the supplementary notes.

Owing to the high photothermal activity of SFe-Ni, the net CO2 emission rates for the photothermal catalytic process (denoted as $dM_{1kp}/dt$) were obviously lower than that for the thermocatalytic process (denoted as $dM_{2kp}/dt$) when electricity was used to power the facilities (either the Xe arc lamp or the heating system), as shown in Fig. 5. For example, when considering the CO2 emission per kWh of electricity according to the reported US 2014 energy structure, the net CO2 emission rates of using 30 mg of the SFe-Ni catalyst was significantly reduced by 15% from 2.473 mol·h$^{-1}$ (500 °C) to 2.097 mol·h$^{-1}$ (190 W illumination supplemented with a light concentrator), while maintaining the same production rate of CO. Despite that these electricity-powered catalytic processes are still generating CO2 rather than reducing the amount of CO2, the values of $dM/dt$ for the photothermal catalytic process could be greatly reduced by increasing the usage of sustainable energy (sunlight, tide, wind, geothermal energy, etc.) to reduce $x_1$ (Fig. 5). When $x_1$ is 0.00079 mol·CO2·kWh$^{-1}$, the photothermal route can veritably achieve carbon neutrality, and at the same time produce fuel.

When it comes to practical utilization, the cost of Ni during catalyst preparation is also very important in addition to the CO2 footprint. The common Ni resources used in the preparation of Ni catalysts include Ni(NO$_3$)$_2$·6H$_2$O, NiCl$_2$·6H$_2$O, and NiSO$_4$·6H$_2$O. The prices of these Ni resources range from 1.7 to 9.84 USD·g$^{-1}$ (Supplementary Table 8). In contrast, the electroplating industries need to pay for the treatment of the Ni wastewater, contributing to a negative cost of Ni ($-$0.0019 g$^{-1}$ to $-$0.0028 g$^{-1}$) from it. This makes the wastewater from electroplating an ideal precursor for the preparation of the SFe-Ni catalysts.

**Discussion**

The essence of the work presented herein is inspired by the prescience of Buckminster-Fuller, who in a 1971 Life Magazine interview said, “There is no energy crisis, just a crisis of ignorance.” He imagined pollution as a feedstock to be harvested for its value rather than treated as the waste of a consumer society. This is the underpinning of our carefully designed adsorbent for the Ni tailings in electroplating wastewater. They can be given new life in a recycle-upcycle process that takes the Ni from a toxic grave to a sustainable cradle, a kind of inverse life cycle paradigm to create a cost-effective eco-friendly photothermal CO2 catalysis process. We envision many ‘pollution solutions’ that could benefit from the recycle-upcycle concepts and principles of the genre delineated herein, turning plastic, paper, mining, food, and electronic waste into sustainable consumer products.

**Methods**

**Materials and chemicals**

All the chemicals were used as received without further purification. Commercial Cu-ZnO-Al$_2$O$_3$ was purchased from Sichuan Shuitai Chemical Technology Co., Ltd. Tetraethyl orthosilicate (TEOS, ≥ 96%), N,N-diisopropylethylamine (≥99%), and hexadecyl trimethyl ammonium bromide (CTAB, ≥98%) were purchased from TCI. Ferric chloride hexahydrate (FeCl$_3$·6H$_2$O, reagent grade), nickel nitrate [Ni(NO$_3$)$_2$·6H$_2$O, ≥97%], and hexadecyl trimethyl ammonium bromide (CTAB, ≥98%) were purchased from TCI. Ferric chloride hexahydrate (FeCl$_3$·6H$_2$O, reagent grade), nickel nitrate hexahydrate (Ni(NO$_3$)$_2$·6H$_2$O, ≥97%), N,N,N-trimethylhexadecyl ammonium bromide (CTAB, ≥98%), and PSSMA [poly(4-styrenesulfonic acid-co-maleic acid) sodium salt] were purchased from Sigma-Aldrich. Sodium acetate anhydrous (99%), hydrochloric acid (36%–38%, analytical reagent), ethylene glycol (99.5%), ethanol (GR, ≥99.8%), and ammonium hydroxide solution (NH$_3$·H$_2$O, 28 wt %) were purchased from Energy Chemical, Enox, J&K scientific, Sinopharm Chemical Reagent Co., Ltd., and Macklin, respectively. Milli-Q water (Millipore, 18.2 Ω·cm at 25 °C) was used in all experiments.

**Synthesis of Fe$_3$O$_4$ colloidal nanocrystal clusters (CNC)**

Fe$_3$O$_4$ CNCs were synthesized according to a reported recipe. For a typical batch, 7.5 g of PSSMA was dissolved in 300 mL of ethylene glycol with magnetic stirring, 8.1 g of FeCl$_3$·6H$_2$O and 22.5 g of sodium acetate were then added to the mixture under continuous stirring until the solution turned homogeneously red-brown. The mixture was then sealed in a Teflon-lined stainless-steel autoclave and heated at 200 °C for 10 h. When cooled to room temperature, the dark precipitates were...
isolated from the solution by a magnet and washed with Milli-Q water and ethanol alternately six times, and finally dispersed in ethanol to form a suspension (concentration: 10 mg mL⁻¹).

**Synthesis of CNC@SiO₂@mSiO₂-NH₂**

The CNC nanoparticles were coated with a thin layer of dense silica via a modified Stöber method⁷¹,⁷². Briefly, 20 mL of the CNC suspension was diluted by ethanol (60 mL) and Milli-Q water (12 mL). The mixture was then sonicated for 30 min, followed by the addition of ammonium hydroxide solution (10 mL), and TEOS (500 μL) sequentially. The reaction vessel was then stirred in a shaking bed (400 rpm, 30 °C) for 1 h. The obtained nanoparticles (denoted as CNC@SiO₂) were washed twice with ethanol under centrifugation and redispersed in Milli-Q water to form a suspension (concentration: 40 mg mL⁻¹). 2.5 mL of the CNC@SiO₂ suspension was added to 20 mL of the prepared CTAB solution (0.9 g of CTAB dissolved in a mixture of 100 mL of ethanol and 300 mL of Milli-Q water). The suspension wassonicated and stirred, each for 20 min, followed by the sequential addition of ammonium hydroxide solution (125 μL), and TEOS (175 μL). The mixture was stirred for another 4 h in a shaking bed (400 rpm, 30 °C). The obtained nanoparticles were then separated and redispersed in acetone and refluxed at 80 °C for 48 h. The refluxing procedure was repeated 3 times. The obtained products (denoted as CNC@SiO₂@mSiO₂) were then washed with ethanol several times and dried in a vacuum oven. One hundred milligrams of the CNC@SiO₂@mSiO₂ powder was dispersed in ethanol (40 mL), followed by addition of N¹-(3-trimethoxysilylpropyl) diethylenetriamine (0.5 mL) and N,N-diisopropylethylamine (0.1 mL). The mixture was stirred in a shaking bed (400 rpm, 30 °C) for 1 h. The resulting nanoparticles were washed twice with ethanol and then washed with Milli-Q water and ethanol six times alternately. The obtained nanoparticles (S₅SiO₂-NH₂) were dried under vacuum.

**Preparation of the catalysts**

Two hundred milligrams of the dried Sad or SiO₂@mSiO₂-NH₂ or S₅SiO₂-NH₂ powder was mixed with 10 mL of the electroplating wastewater, the compositions of which are listed in Supplementary Table 3. The suspension was sonicated and then transferred to a shaking bed (400 rpm, 30 °C), subjected to stirring overnight. The adsorbents together with the adsorbed metal ions were collected via magnetic separation and then dried in a vacuum oven. The dried samples were calcined at 500 °C for 1 h in a muffle furnace to remove the organic pollutants, followed by reduction at 600 °C for 2 h in H₂ atmosphere. The reduction temperature, under which the metal precursors could be fully reduced, was determined by the TPR results (Supplementary Fig. 26). The final products were denoted as SFe-Ni, SNi, and S₅SiO₂-NH₂ corresponding to the Sad, SiO₂@mSiO₂-NH₂ and the S₅SiO₂-NH₂ support, respectively. The loading amounts of Ni and Fe for different samples are listed in Supplementary Table 4. A control sample was prepared by replacing the electroplating wastewater with manmade Ni²⁺ solution from reagent Ni(NO₃)₂·6H₂O. The compositions of the prepared catalysts are listed in Supplementary Tables 4 and 5.

In a cycle adsorption process, 10 mL of wastewater was mixed with Sad. After adsorption equilibrium, the spent Sad was separated from the solution for the following calcination process, and the same amounts of new Sad were put into the treated wastewater. The procedure was repeated multiple times.

**Thermocatalytic tests**

Thermocatalytic CO₂ hydrogenation under atmospheric pressure was performed in a quartz tube flow reactor (CEL-GPPCM, BEIJING CHINA EDUCATION AU-LIGHT CO., LTD., Supplementary Fig. 27) at a certain temperature (300, 350, 400, 450, or 500 °C). Prior to the reaction, the powder catalysts (<80 mesh) were reduced under H₂ (20 mL min⁻¹) at 600 °C for 2 h. The flow rates of CO₂, H₂, and N₂ were set at ~2.5, 2.5, and 5 mL min⁻¹, respectively. The products at the reactor outlet were detected with an online gas chromatographer (Agilent 8650) equipped with a thermal conductivity detector (TCD) and a flame ionization detector (FID).

In-situ DRIFTS experiments were performed on a Bruker VERTEX 70 v Spectrometer with a mercury cadmium telluride detector cooled with liquid nitrogen. Approximately 20 mg of as-reduced SFe-Ni, S₅SiO₂-NH₂, or N₅SiO₂/Catalyst (<80 mesh) was packed into an in situ cell (BEIJING OPERANDO TECHNOLOGY CO., LTD.). Prior to the reaction, the catalyst was reduced in a H₂/N₂ mixture gas (2.5/17.5 mL/min) at 500 °C for 30 min. The inlet flow in the cell was then switched to N₂ (17.5 mL/min) for 30 min, and the temperature was kept at 500 °C. After obtaining the background spectra, the inlet flow was switched to a CO₂/H₂ mixture gas (2.5/2.5 mL/min). The adsorption species on the surface of catalysts were detected online.

Rate-order experiments were carried out with 30 mg of the SFe-Ni catalyst (<80 mesh) at 500 °C under a constant flow rate (40 mL/min). The internal and external diffusions were eliminated based on a reported recipe (see the details in the supplementary notes, Supplementary Figs. 28 and 29). To study the rate order for H₂, the concentration of feed CO₂ was kept at 12.5%, while the concentration of feed H₂ gradually decreased from 67.5% to 42.5% and then gradually increased back to 67.5%, and N₂ was used as the balance component. The CO rates in the downslope and uphil stages under the same conditions were averaged for the calculation of rate order for H₂. Similarly, to study the rate order for CO₂, the concentration of feed H₂...
was kept at 75%, while the concentration of feed CO₂ was gradually increased from 7.5 to 11.25% and then gradually decreased to 7.5%, and N₂ was used as the balance component. The CO rates in the up-slope and down-slope stages under the same conditions were averaged for the calculation of the rate order for CO₂. In all rate-order experiments, the conversions for H₂ and CO₂ were always kept below 5%.

Photothermal catalytic tests in the flow reactor
The photothermal tests were conducted similarly to the thermo-catalytic tests, except that a 300-W Xe arc lamp (PF300-TSE, BEIJING CHINA EDUCATION AU-LIGHT CO., LTD.) rather than heating modulate was used as the energy source. The light intensity was measured using an optical power meter (PL-MW2000, Beijing Perfectlight Technology Co., Ltd.). The relationship between the power of the lamp and light intensity is listed in Supplementary Fig. 30

Photothermal catalytic tests in the batch reactor
The gas-phase photothermal catalytic experiments were conducted in a batch reactor (CEL-HPR100T+) with an inner volume of 100 mL. A group of glass slides was put inside the reactor to support the catalyst. The final effective volume of the reactor was 57.77 mL. A 300 W Xe arc lamp was used to illuminate the catalysts with the assistance of a concentrator. For all the catalysts, Samples (9 mg) were dispersed in ethanol and then transferred into a glass fiber filter through drop-casting. The catalyst film was then dried under a vacuum. After the loading of the catalyst film, the reactor was degassed first. A mixture of CO₂ and H₂ (1:1) was used to purge the reactor three times. The reactor was sealed when the pressure reached 1 bar. The lamp was then turned on to initiate the photothermal catalytic reaction. After 10 min illumination, product gases were analyzed with a gas chromatograph (Agilent 8890E) equipped with a thermal conductivity detector (TCD) and a flame ionization detector (FID).

Characterization
STEM images and EDX mappings were obtained in a double aberration-corrected transmission electron microscope (FEI Titan Themis G2) operated at 300 kV with a HAADF detector (collection angle range of 48–200 mrad) and Super-X EDX detector. Transmission electron microscopy (TEM) images were obtained with an FEI-Tecnai F20 (200 kV) transmission electron microscope. The XAS experiments at the Ni K-edge were performed at the Shanghai Synchrotron Radiation Facility (SSRF,11B), and the intensities of the two SFe-Ni samples were measured by an Inductively coupled plasma optical emission spectrometer (ICP-OES) (i CAP Pro X, Thermo Fisher Scientific). The TPR results were recorded with an infrared spectrometer (Thermo, Nicolet iS 50). The intensities of the two SFe-Ni samples were measured by an Inductively coupled plasma source mass spectrometer (ICP-MS) (Agilent 8800) equipped with a thermal conductivity detector (TCD) and a flame ionization detector (FID).

Reporting summary
Further information on research design is available in the Nature Research Reporting Summary linked to this article.

Data availability
The datasets generated during and/or analyzed during the current study are available from the corresponding author on reasonable request. Source data are provided with this paper.

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Author contributions

W.S., S.W., D.Z., L.H., D.Y., and G.A.O. conceived and designed the experiments. S.W. and D.Z. carried out the synthesis and catalysis experiments. W.W. and J.H. carried out the HAADF-STEM experiments. J.Z. carried out and analyzed the XAS experiments. K.F. analyzed the XAS results. Z.W. carried out the TEM characterization. B.D. carried out the ICP experiments. Z.L. carried out part of the thermocatalytic experiments. W.S., G.A.O., and S.W. wrote the paper. All authors commented on the final manuscript.

Competing interests

The authors declare no competing interests.

Additional information

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