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Silk & Ni Ion Derived Highly Dispersed Nickel-Nitrogen-Doped Carbon toward Enhanced Electrochemical CO_2 Reduction Reaction

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Statement of Originality

The research process and results of this team are conducted and derived under the guidance of the instructor. Other than the referenced content and the acknowledged sources, this paper does not include any published findings by this group or any other researchers. If there is any inaccuracy, this team is accountable for all liabilities.

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Table of Contents

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Author: *Shicheng Hu*

Abstract

Carbon dioxide is accumulating in our atmosphere as a result of increasing human activity dependent on fossil fuels. We now face the environmental problems caused by excessive atmospheric CO_2, and a near future without known efficient source of energy, as we are running out of fossil fuels. The coupling of **renewable resources** and electrochemical carbon dioxide reduction reaction (**CO_2RR**) into C-based **chemical fuels** and **industrial precursors** is becoming increasingly important as solution to environmental problems. Here we report a **novel synthesis** of highly dispersed nickel-nitrogen-doped carbon (**Ni/N-C**) from silkworm **silk** and **nickel ion**. Compared with other previous reports on highly dispersed Ni catalyst for CO_2RR, our synthetic method is obviously much more **facile**, **economic**, and **environmental friendly**. The Ni/N-C catalyst demonstrates **high selectivity for CO_2RR** over competing Hydrogen Evolution Reaction (HER), as the **Faradaic Efficiency** (FE) for CO_2 reduction towards CO reaches 74.6% at -0.95 V vs. RHE. The catalyst **maintained** a **current density** of about -4.5 mA cm^{-2} and a **Faradaic Efficiency** (FE) for CO of over 70% for **over 10 hours**. The comparison tests evidently shows that the excellent CO_2RR performance attribute to **highly dispersed nickel**, and the **massive nitrogen coordination sites** with nickel ion which helps create the highly dispersed catalyst upon **carbonisation**. We believe that our novel synthesis of Ni/N-C catalysts point out the possibility of **more facile method** to design and fabricate novel electrocatalysts for CO_2RR.

Keywords: Silk, highly dispersed nickel, catalyst, carbon dioxide reduction reaction, Faradaic Efficiency

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Introduction

Coal, petroleum and natural gas have been vastly used as the main source of energy and industrial organic chemicals since the 19th century. The combustion of fossil fuels has led to accumulating level of CO_2 in our atmosphere, which has caused a variety of environmental problems. Moreover, with growing human population and increasing quest for better life quality, global energy demand has reached an unprecedented level and is expected to rise further. Currently **renewable methods** only manage to supplement 10.3% of global summed demand for energy [1]. It becomes evident that the combination of **renewable energies** and the **carbon conversion technologies** is required to restore the normal levels of **atmospheric CO_2** and provide us with **fuels** and **chemical precursors**[2], which were conventionally provided by fossil fuels that will be in shortage in the near future.

The CO_2 electrochemical reduction reaction (**CO_2RR**), using **electricity** generated from **renewable resources**, enables the **conversion of CO_2** into **C-based fuels and chemicals**, which are in great and increasing demand.

The electrochemical CO_2 reduction reaction has the unique advantage of taking place under **room temperature and pressure**, compared with other CO_2 conversion methods. Its coupling with renewable resources allows the storage of excess electricity, generated during the peaks of production, in the form of **easily-transportable energy-dense fuel**. The electrolyte for CO_2RR can be organic solvents (i.e. DMF)[3], ionic liquids[4], or simply aqueous solution. **Aqueous electrolyte** is electro-conductive, able to provide the protons needed for CO_2 reduction[5,6], and has the prospect of being industrially used.

1. Reaction mechanism of CO_2RR

Aqueous electrolyte has the unique advantage of being cheap, easily accessible and environmental friendly, and has industrial application prospect.

The half reaction at the **anode** of CO_2 RR in aqueous electrolyte is the **Oxygen**

Evolution Reaction (OER): $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$

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The half reaction at the **cathode** of CO_2RR in aqueous electrolyte can be:

(1) The **reduction of CO_2** into various carbon based products [7]

$2CO_2 + 12H^+ + 12e^- \rightarrow C_2H_4 + 4H_2O$	$E^o = +0.08$ V vs RHE
$CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O$	$E^o = +0.17$ V vs RHE
$2CO_2 + 12H^+ + 12e^- \rightarrow C_2H_5OH + 3H_2O$	$E^o = +0.08$ V vs RHE
$3CO_2 + 18H^+ + 18e \rightarrow C_3H_7OH + 5H_2O$	$E^o = +0.09$ V vs RHE
$CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O$	$E^o = -0.11$ V vs RHE
$CO_2 + 2H^+ + 2e^- \rightarrow HCOOH$	$E^o = -0.22$ V vs RHE
$CO_2 + 2H^+ + 2e^- \rightarrow HCOOH$	$E^o = -0.22$ V vs RHE

(2) or the Competitive **Reduction of H_2O** (its proton) into H_2

$H^+ + 2e^- \rightarrow H_2$	$E^o = 0$ V vs RHE

The reduction of H_2O to H_2 is kinetically favoured over the CO_2 reduction into C-based products. Also the **over-potentials** for the CO_2RR are high,as a result of the high kinetic barrier of the CO_2RR, and multiple proton/ electron transfer steps needed for hydrocarbon formation. **Good catalysts** are required to mitigate the energy lose due to high over-potentials. The optimal catalysts should have the following properties: (1) high **activity**; (2) high **selectivity** (i. selectivity of C-based products over H_2; ii. Selectivity of producing only the desired C-based product); (3) **stability** over long period of time; (4) **inexpensive**; (5) uncomplicated **synthesis**.

2. Catalysts for electrochemical CO_2 Reduction in Aqueous Electrolyte

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The reduction reaction **product distribution** is hugely dependent on the **cathode material**[8]. As a result, several researches have been conducted to find out the optimal catalyst[9].

2.1 Metals

Metals in general can be divided into the following groups according to the products [10,11]:

(1) Formic acid: Sn, Bi, Hg, Pb
(2) CO: Zn, Ag, Au
(3) A wide range of products: Cu

Noble metals such as Au and Ag are good catalysts for the electrochemical reduction of CO_2 to CO. It is unlikely that gold catalysts would be industrialised, given the metal's low abundance and high price. Lu et al. recently reported a highly active and selective nano porous silver catalyst for CO_2RR with a 92% FE to CO.[12]

However, the metal catalysts have many problems, including poor selectivity, poor stability and inactivation by CO.[13]

2.2 Carbon Based Electro-catalysts

Although **graphene** itself shows no activity toward the CO_2RR[14], **doping of heteroatom** such as B, N, or P can alter the electron distribution, and thus provides active sites for the CO_2RR[15, 16]. Moreover, graphene materials exhibit excellent stability during catalytic process[17, 18, 19]. Graphene is often used as support for metal nano catalysts, due to their ability to stabilise and anchor these particles, large surface area and high network conductivity.

2.3 Transition-Metal Single Atoms

Single Metal Atoms usually show different catalytic properties than their bulk counterparts, as the electronic structure is usually significantly changed. The CO_2-to-CO conversion is promoted, while the competing HER is drastically suppressed.

Wang et al. reported a graphene shell coordinated **nickel single atom catalyst** for CO_2RR in aqueous electrolyte. The maximum FE reached 90% while the current is up to 60 mA/mg. [20]

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There was report on atomic iron dispersed on nitrogen doped graphene as efficient catalyst for electrochemical CO_2RR to CO, with FE of 80%. The active sites were Fe surrounded by 4 nitrogen atoms. [21] Li et al. reported the adoption of metal organic frameworks (MOFs) to synthesize atomic Ni sites for efficient CO_2RR. The FE for CO is 71.9%.[22]

3. Silk & Ni^{2+} Derived Highly Dispersed Nichel-Nitrogen-Doped Carbon (Ni/N-C) toward Enhanced Electrochemical CO_2RR

We focus on the **design and synthesis** of high-efficiency **CO_2RR catalysts**, explores the promotion and regulation of electrocatalytic performance and selectivity. In Figure 1, a highly dispersed Ni supported by N-doped carbon (**Ni/N-C**) electrocatalyst was synthesized via a **facile method** from **silkworm silk and nickel ion**. The **massive nitrogen coordination sites** in silk help trap the nickel ions. The Ni/N-C electrocatalysts demonstrate **high selectivity for CO_2RR** over competing Hydrogen Evolution Reaction (HER), as the **Faradaic Efficiency** (FE) for CO_2 reduction towards CO reaches 74.6% at -1.6V. The **current density** of about -4.5 mA cm^{-2} and **Faradaic Efficiency** (FE) for CO of over 70% was **maintained for over 10 hours.**

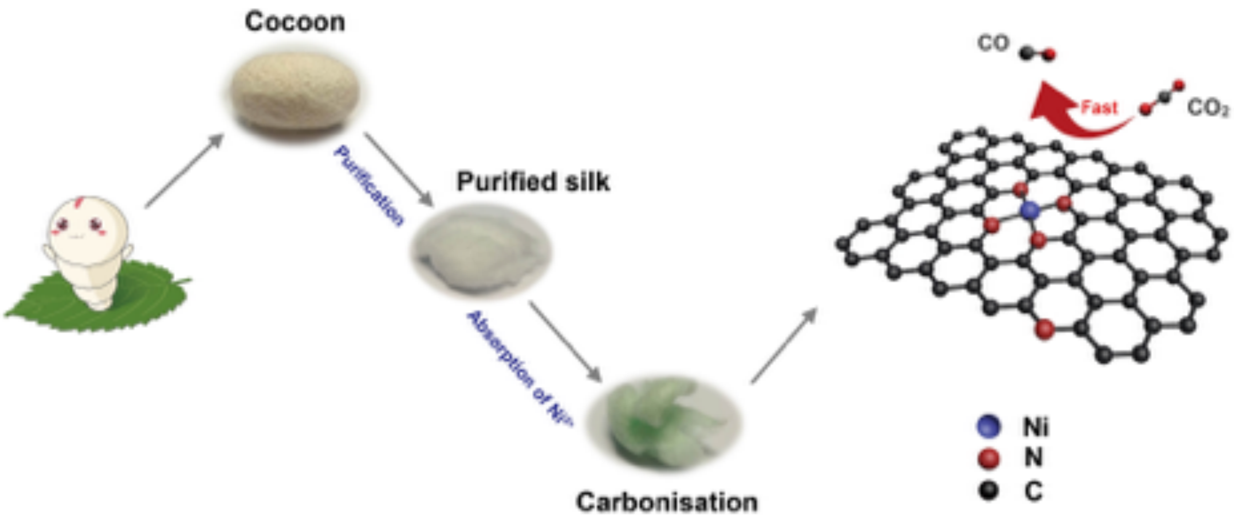

Figure 1. Scheme of experimental procedure and demonstration of electrochemical CO_2RR reaction mechanism.

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Experimental section

Cocoons from B. mori silkworms were dipped in 0.02 M Na_2CO_3 boiled aqueous solution for 30 minutes, and then rinsed three times with deionized water to get **pure fibroin**. After drying in an oven (temperature maintained at 60 °C) for 24 hours, the resulting **fibrous material** was used in further experiments.

$Ni(NO_3)_2$, Dimethylformamide (DMF) and hydrochloric acid were purchased from Sinopharm Chemical Reagent Co., Ltd.

1. Synthesis of Ni/N-C from silk and nickel ion

The processed silk (fibroin) was dipped in 0.044M $Ni(NO_3)_2$ (DMF) for 12 h. In an oven with temperature maintained at 60 °C, the sample was dried for 12 h until DMF was all evaporated. It was annealed in a furnace tube. The temperature rised at 5 °C/min, and maintained at 900 °C for 2 h under Ar atmosphere, then cooled to room temperature. The resultant sample has preserved the fibre-like structure and was dipped in 1M HCl (aq) to remove excess bulk nickel. It was rinsed by deionized water and ethanol for three times, respectively. Then it is dried in the oven (maintained at 60 °C) overnight.

2. Synthesis of N-C from silk

The silk was annealed in a furnace tube. It was annealed in a furnace tube. The temperature rised at 5 °C/min, and maintained at 900 °C for 2 hours under Ar atmosphere, then cooled to room temperature.

3. Synthesis of Ni/C form cotton fibre and nickel ion

The same exact procedures as experiment 1, except that the silk is substituted by cotton.

4. Electrochemical CO_2 reduction reaction (CO_2RR) measurement

The CO_2RR was conducted in 0.1 M $KHCO_3$ (pH 6.8) solution with a common three-electrode system, using an Autolab electrochemical workstation. A saturated Ag/AgCl electrode and a platinum foil were applied as reference and counter electrodes, respectively. All potentials were referred to the reversible hydrogen electrode by adding a value of $(0.21 + 0.059 \times \text{pH})$ V. For the preparation of the working electrode, the sample was ground into powder, dispersed into Nafion/

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ethanol, and then ultra-sonicated for 45 min to create a fine suspension. Finally the suspension was drop-casted onto carbon paper to make the electrode. The electrolyte was 0.1 M $KHCO_3$ aqueous solution purged with CO_2 for at least 0.5 h before use. The gas products were analyzed using Shanghai Ramiin GC 2060 gas chromatograph equipped with a flame ionization detector (FID) and a thermal conductivity detector (TCD).

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Results and Discussion

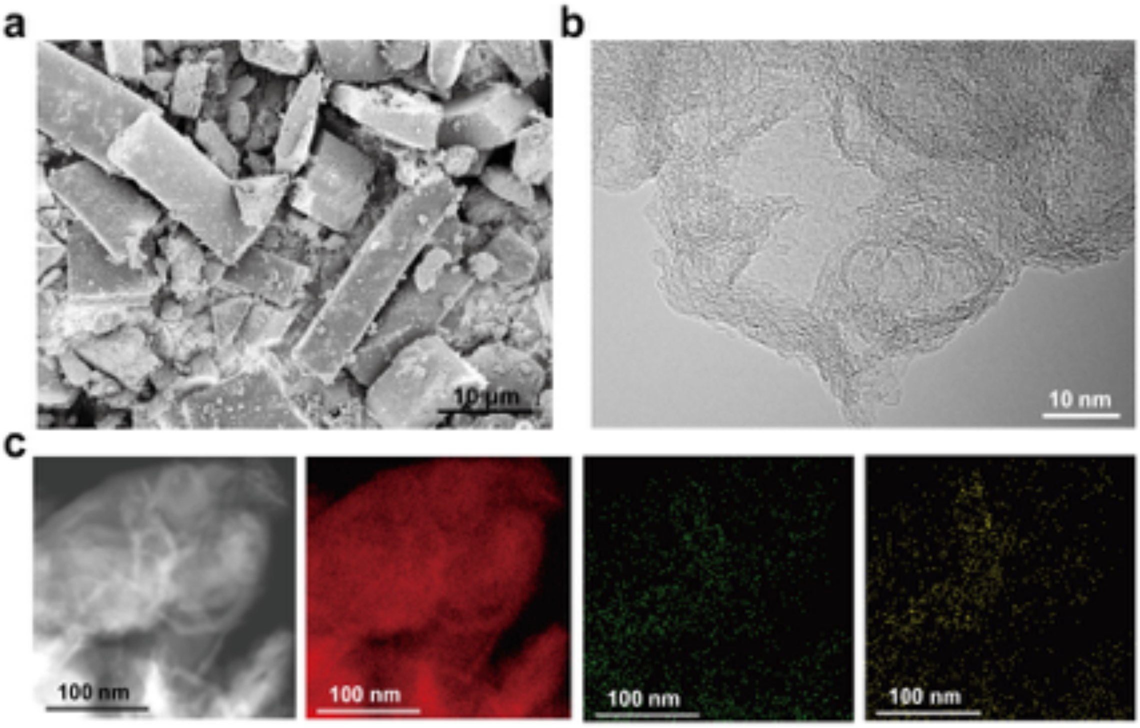

Figure 2. Structural Characterisation. (a) Scanning Electron Microscopy (SEM) of Carbonised $Ni(NO_3)_2$ (DMF) Dipped Silk (Ni/N-C). (b) Transmission Electron Microscopy (TEM) of Ni/N-C. (c) Energy Dispersive Spectroscopy (EDS) elemental mapping of Ni/N-C. The red, green and yellow colours were denoted for C, N and Ni, respectively.

In Figure 2a, the Scanning Electron Microscopy (SEM) showed the surface characteristics of ground Ni/N-C, which were fine particles. The catalyst preserved the fibre-like structure of the silk precursor. In Figure 2b, the Transition Electron Microscopy (TEM) demonstrated that **graphitic carbon** exists, and that there wasn't bulk nickel left. In Figure 2c, the Energy Dispersive Spectroscopy (EDS) elemental mapping demonstrated that **nitrogen** and **nickel** were **uniformly dispersed** on the carbon support.

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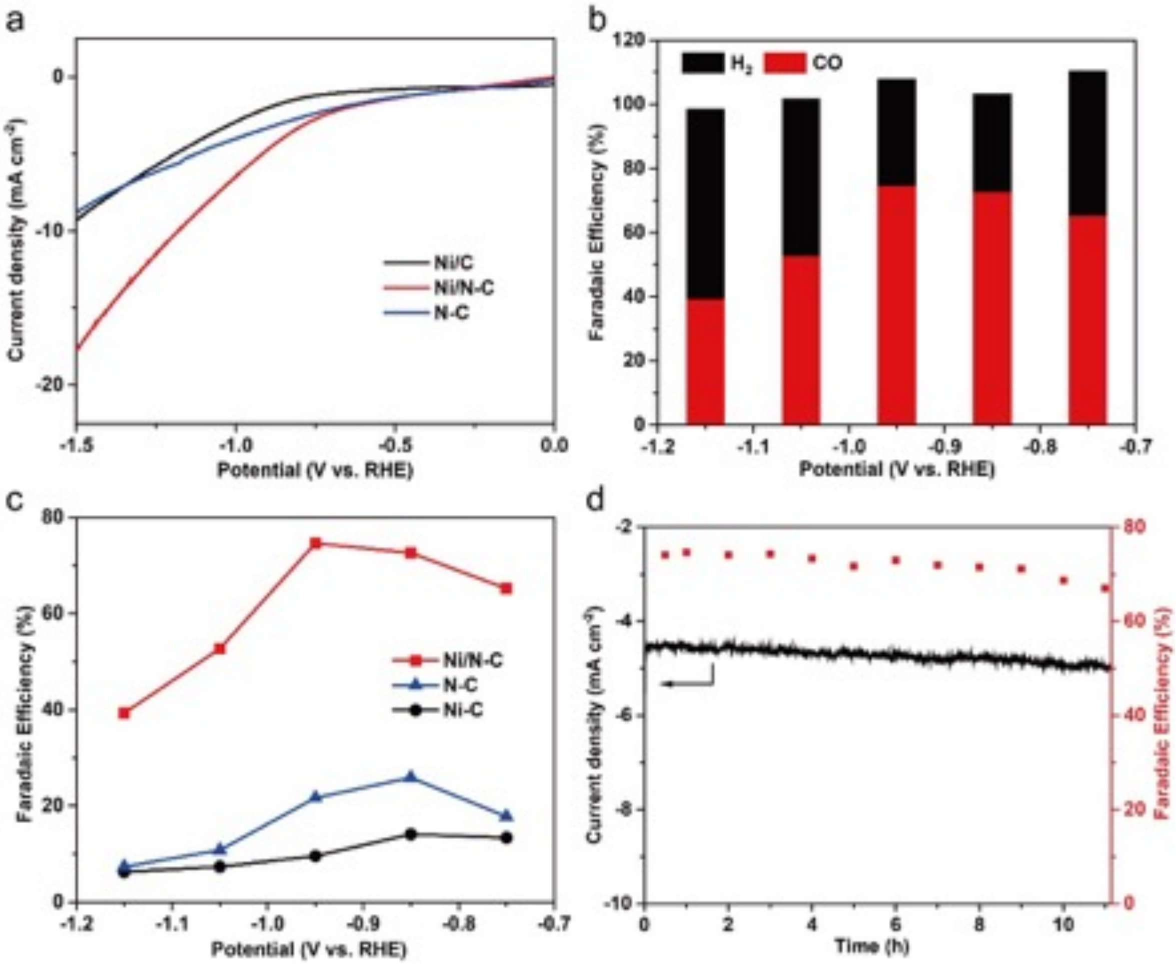

Figure 3. Electrochemical CO_2RR tests. (a) Linear sweep voltammetry (LSV) curves of Ni/C, N-C and Ni/N-C in CO_2-saturated 0.1 M $KHCO_3$ electrolyte. The scan rate was 20 mV s^{-1}. (b) Faradaic efficiencies to CO and H_2 of Ni/N-C. (c) Faradaic efficiencies to CO at different applied potentials on Ni/C, N-C and Ni/N-C, respectively. (d) i-t curve (left y-axis) and faradaic efficiency (right y-axis) for CO of Ni/N-C in CO_2-saturated 0.1 M $KHCO_3$ solution at an applied potential of –0.95 V vs. RHE for 11 h.

In Figure 3a, the **Ni/N-C catalyst** derived from silk and Ni^{2+} ion demonstrated lowest over potential of approximately -0.6 V vs. RHE. Also it had significantly **higher current density** than **Ni-C** (from cotton and Ni^{2+}) and **N-C** (from silk) when the over potential was passed. While the current density (mA cm^{-2}) at -1.5 V vs RHE of Ni/C and N-C were approximately -9 mA cm^{-2}, that of Ni/N-C approached -20 mA cm^{-2}. We tested the **selectivity for CO** on **gas chromatography**, and observed the **highest efficiency for Ni/N-C**. In Figure 3b, Ni/N-C demonstrated **highest selectivity for CO** over H_2 at -0.95 V vs. RHE, with a **Faradaic Efficiency** for CO

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of 74.6%. At lower potential, the current density is small and the CO production wasn't optimal. At higher potential, the selectivity for CO decreased, as the competing HER became more favourable. Over a wide range of potentials, the Faradaic Efficiencies for CO were over 50%. As demonstrated in Figure 3c, **at all potentials** from -0.75 V to -1.15 V vs. RHE, **Ni/N-C** were better catalysts for CO_2RR than N-C and Ni-C. The highest Faradaic Efficiencies (~25% and 12%) of CO_2RR towards CO for N-C and Ni-C were achieved at -0.85 V vs. RHE. These were significantly lower than that of Ni/N-C. Finally, in Figure 3d, we conducted a **stability test** for Ni/N-C catalyst and showed that at -0.95 V, the catalyst **maintained** a **current density** of about -4.5 mA cm^{-2} and a **Faradaic Efficiency** for CO of over 70% for **over 10 hours**.

The fact that Ni/N-C demonstrated much better electrocatalytic performance than N-C and Ni-C indicates that it was the **highly dispersed nickel** that was the **active site for CO_2RR**, and the **nitrogen coordination** sites to nickel in silk, which were absent in cotton, help create such highly active sites. We propose that **application of coordination chemistry** can help design more highly dispersed metal catalytic system.

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Conclusion

In conclusion, we reported a **facile**, **economic** and **environmental friendly synthesis** of **highly dispersed nickel catalyst** supported by nitrogen doped carbon (**Ni/N-C**) derived from **silk**. The **stable** catalyst proved very efficient for the **selective** carbon dioxide reduction reaction (**CO_2RR**) to **CO** in **aqueous electrolyte**, as the highest **Faradaic Efficiency** (FE) for CO approached 75%. The **massive N coordination sites to nickel** in silk helped create **highly dispersed nickel** catalyst distributed in carbon. We concluded that the **active sites** for CO_2RR were the **highly dispersed nickel** through **comparison tests**. Our study will open a **new avenue** for the **facile synthesis** of **highly dispersed metal electrocatalysts** with **excellent performance**.

Prospect

It is possible to add nickel compounds to silkworms' diet and have them produce silk with nitrogen atoms coordinated with nickel ions, thus giving a highly dispersed system directly.

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Resume of Team Member

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*2017年12月，Rising Star China Chemistry Challenge Preliminary Round 2017 Gold Award
⁎2018年3月，Rising Star China Chemistry Challenge 2017-2018
Top 10 in Final Round
⁎2018年4月，China-US Local Chemistry Olympiad Competition China Section 2018 Gold Award
⁎2018年9月，第32届中国化学奥林匹克初赛上海市壹等奖

Biology
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⁎2018年4月，2018 BioOlympiad Initiative USA-China Silver Award

Math
⁎2017年2月，AMC （American Mathematics Competition） 10 Top 1%
⁎2018年2月，USAD（United States Academic Decathlon) Maths Gold Award
⁎2018年4月，ARML (American Regional Mathematics League) Regional Top 10

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Biography: Gengfeng Zheng obtained his bachelor degree (2000) at Fudan University in China, and his Ph.D. degree (2006) in chemistry at Harvard University in USA. He was a postdoctoral fellow at North-western University in USA (2007−2009). Since 2010, he has been a full professor at Laboratory of Advanced Materials and Department of Chemistry at Fudan University. His research interests include low-dimensional nanomaterial-based synthesis and surface chemistry, photoelectrochemical conversion, electrocatalysis and energy storage.