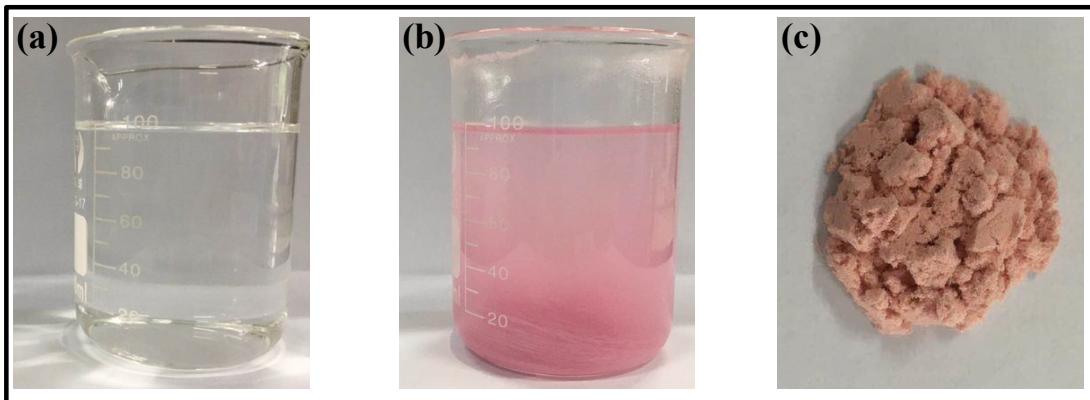


## **Tuning the activity of N-doped carbon for CO<sub>2</sub> reduction via in-situ encapsulation of nickel nanoparticles into- nano- hybrid carbon substrates**

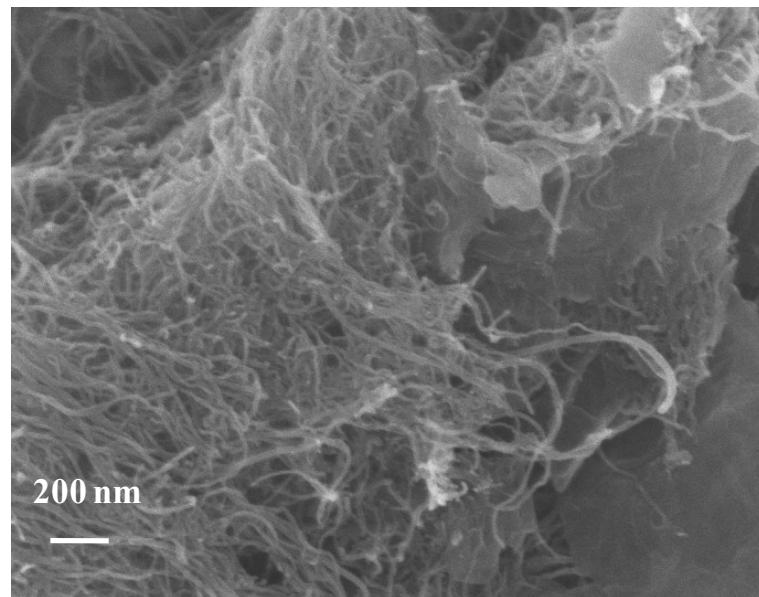
*Cheng-Zong Yuan,<sup>†a</sup> Hong-Bao Li,<sup>†a,b\*</sup> Yi-Fan Jiang,<sup>a</sup> Kuang Liang,<sup>a</sup>  
Sheng-Jie Zhao,<sup>a</sup> Xiao-Xiang Fang,<sup>a</sup> Liu-Bo Ma,<sup>a</sup> Tan Zhao,<sup>a</sup> Cong Lin<sup>a</sup>  
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<sup>a</sup> Division of Nanomaterials and Chemistry, Hefei National Laboratory  
for Physical Sciences at the Microscale, University of Science and  
Technology of China, Hefei 230026, China.

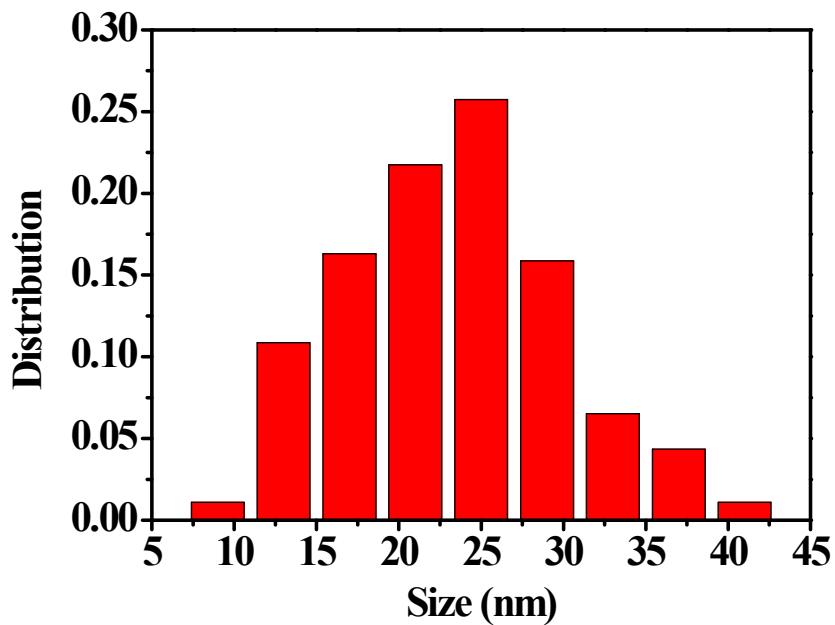
<sup>b</sup> Institute of Physical Science and Information Technology, Anhui  
University, Hefei 230601, China



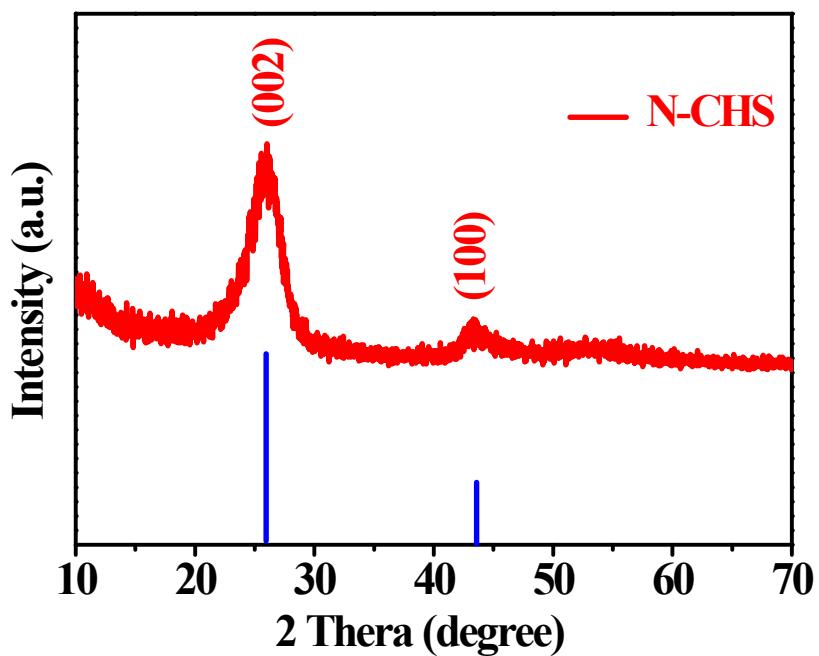
**Fig. S1** The corresponding optical photographs of (a) Phen solution, (b) Ni-Phen in acetone solution and (c) Ni-Phen complex powder.



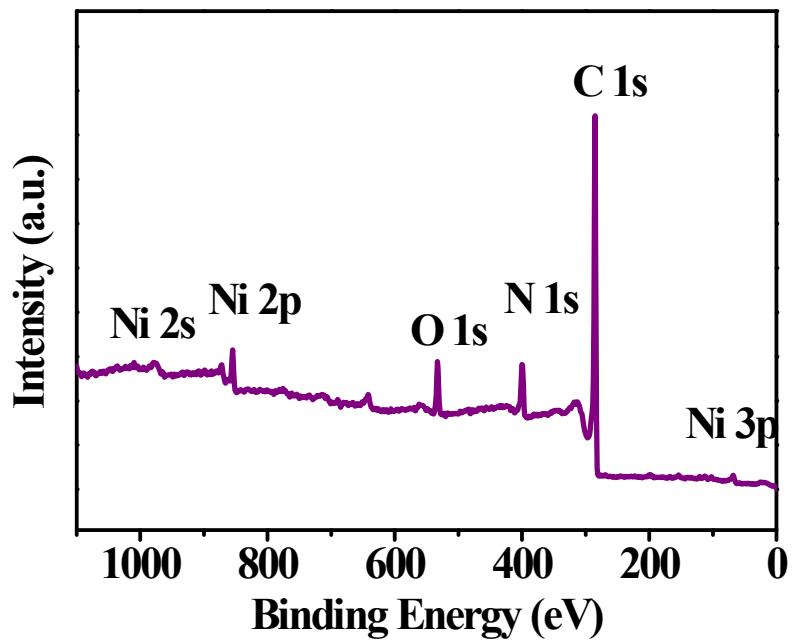
**Fig. S2** The scanning electron microscope (SEM) image of obtained N-CHS.



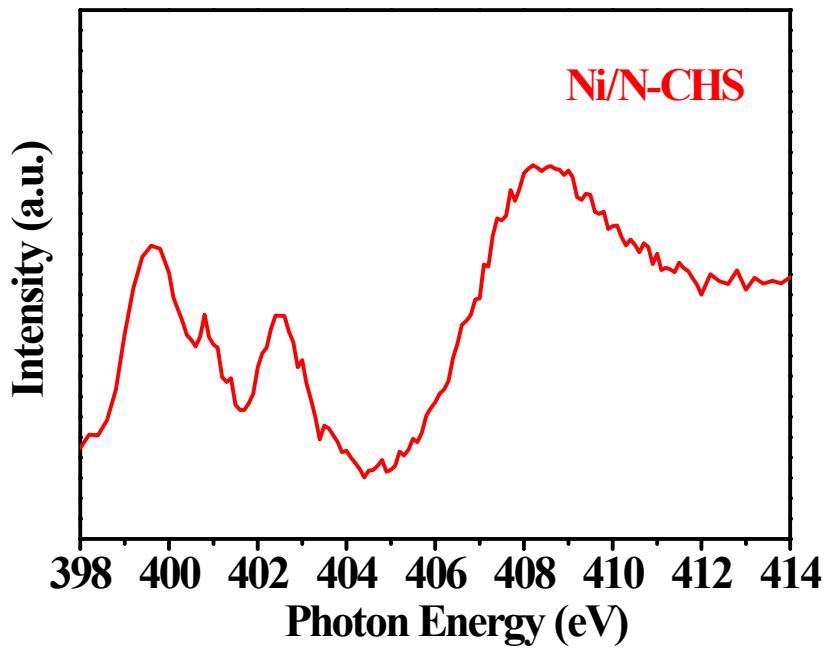
**Fig. S3** The particle size distribution of the Ni NPs on the Ni/N-CHS determined from the TEM analysis.



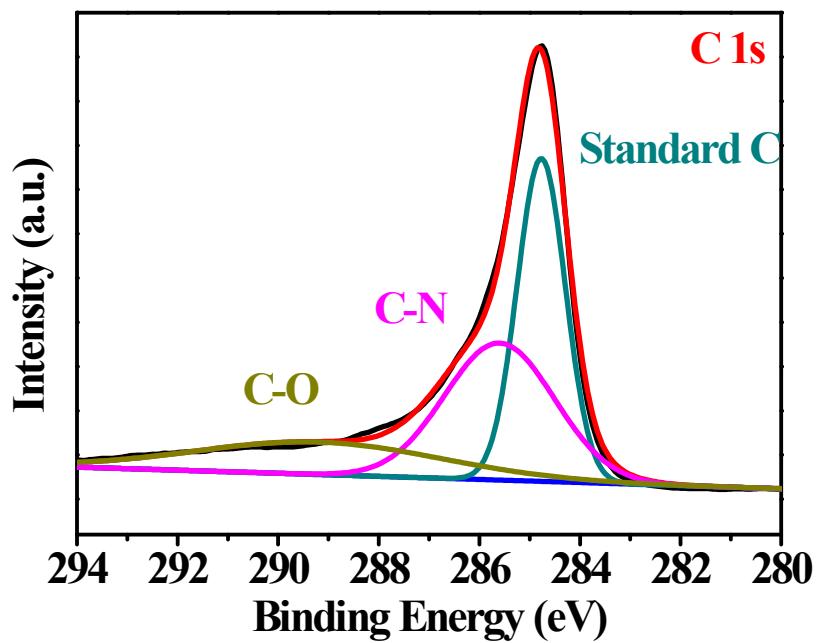
**Fig. S4** X-ray diffraction (XRD) characterization of the as-synthesized N-CHS.



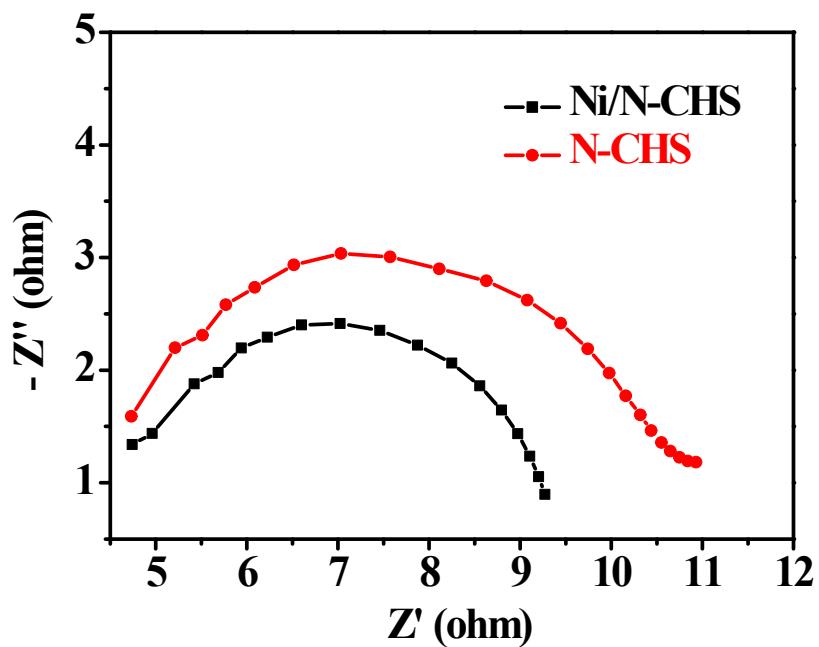
**Fig. S5** The XPS survey spectrum of Ni/N-CHS sample.



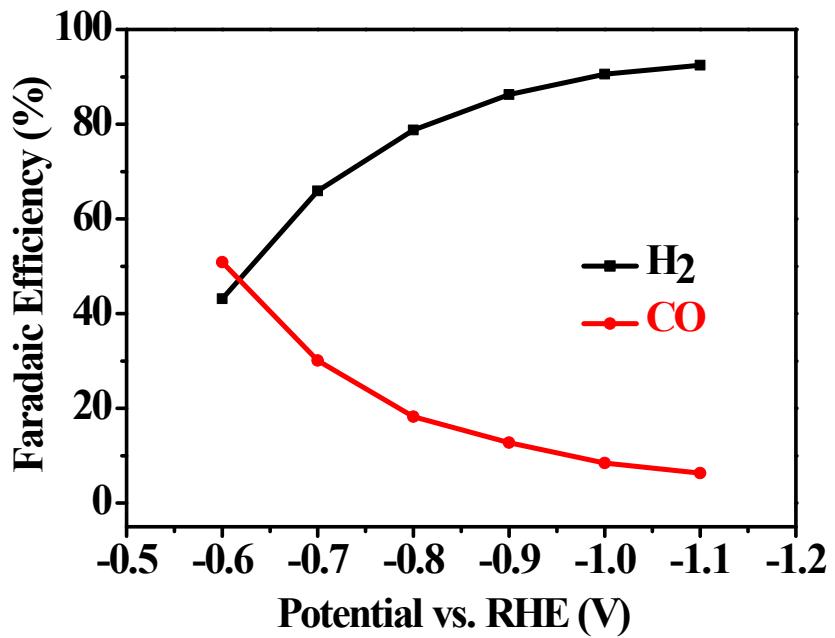
**Fig. S6** The N K-edge X-ray absorption near-edge structure (XANES) spectrum of Ni/N-CHS.



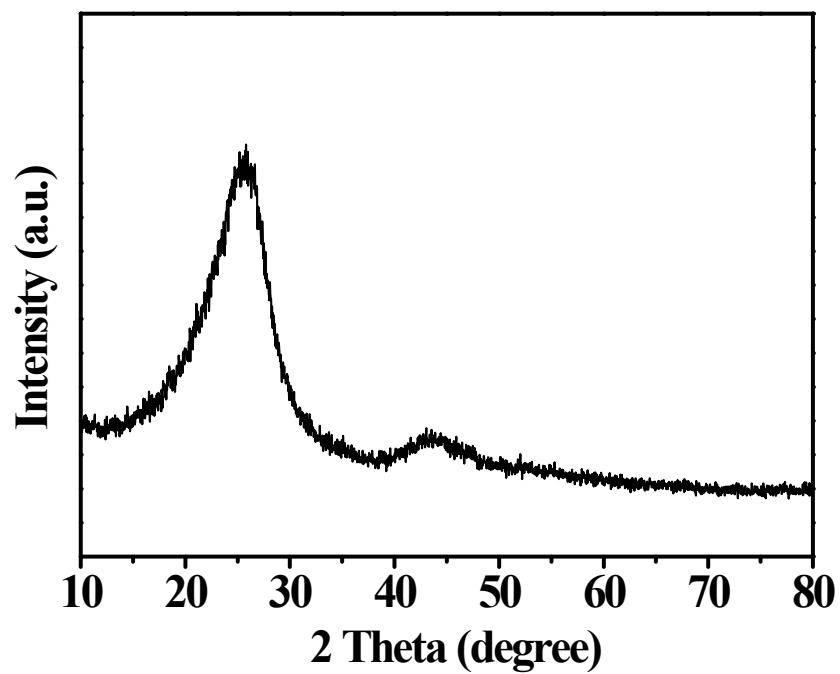
**Fig. S7** The high-resolution C 1s XPS spectrum of Ni/N-CHS.



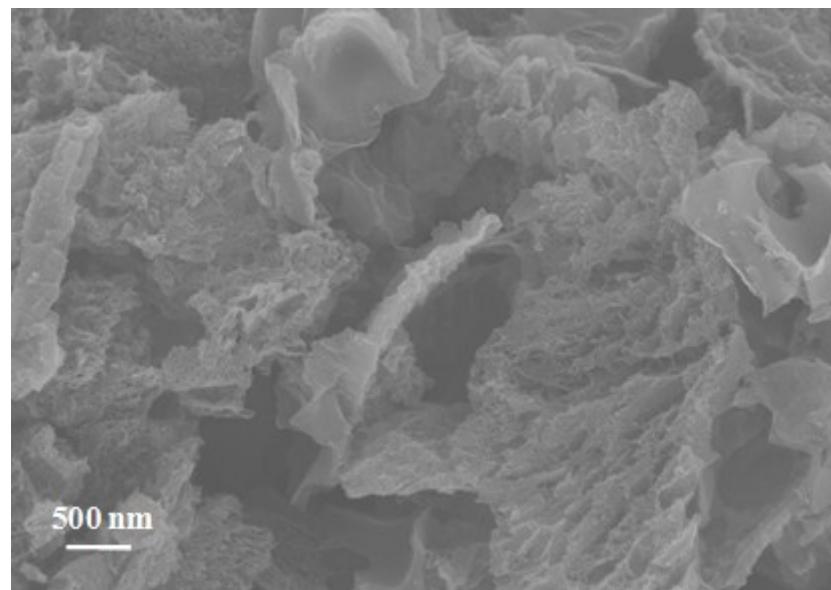
**Fig. S8** The Nyquist plots of Ni/N-CHS and N-CHS catalysts.



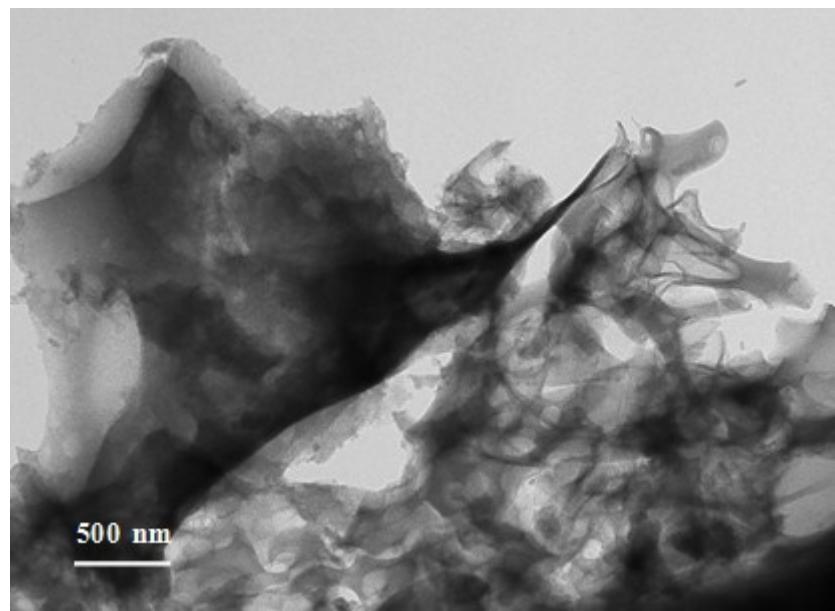
**Fig. S9** The CO<sub>2</sub>RR performances of N-C synthesized similarly without adding Ni source. The FE of CO production over N-C decreases from the potential -0.6 to -1.2 V, because the competing HER is dominant at high potential.



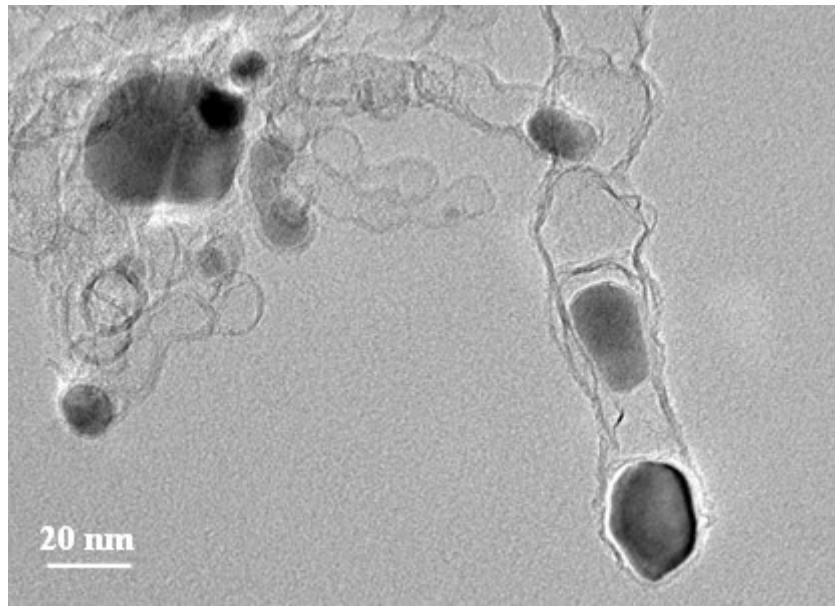
**Fig. S10** The XRD pattern of obtained N-C.



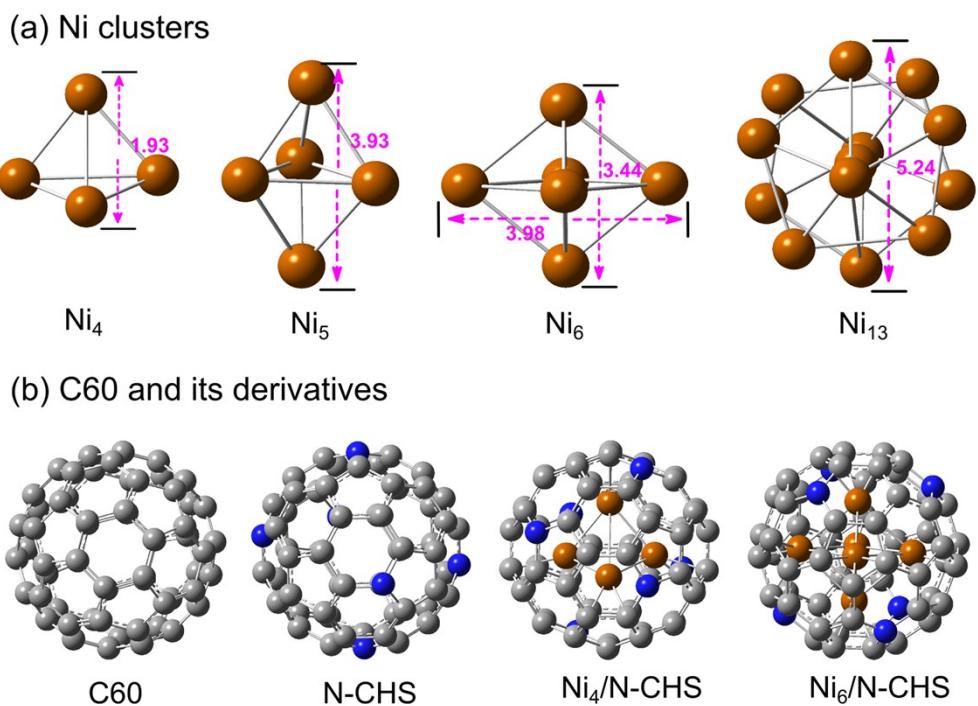
**Fig. S11** The SEM image of obtained N-C.



**Fig. S12** The TEM image of obtained N-C.



**Fig. S13** The TEM image of this catalyst after electrocatalysis.



**Fig. S14** (a) Structures and sizes of the optimized Ni<sub>n</sub> clusters (n = 4, 5, 6, 10, 13). The distorted structure Ni<sub>10</sub> was abandoned. (b) C<sub>60</sub> and its various derivatives: N-CHS, Ni<sub>4</sub>/N-CHS and Ni<sub>6</sub>/N-CHS.

**Table S1.** Comparison the performances of electrochemical reduction  $\text{CO}_2$  into CO production over some state-of-the-art materials.

Catalysts	Electrolyte	Potential (V vs. RHE)	FE <sub>CO</sub> (%)	Ref.
Ni-CHS	0.5 M $\text{KHCO}_3$	- 0.9	93	This work
Pd NPs	0.1 M $\text{KHCO}_3$	- 0.89	91.2	1
Pd/C	0.5 M $\text{KHCO}_3$	- 0.6	40	2
Au NPs	0.5 M $\text{KHCO}_3$	- 0.67	90	3
Zn dendrite	0.5 M $\text{KHCO}_3$	- 1.1	79	4
Ni–N–C	0.1 M $\text{KHCO}_3$	- 0.75	85	5
Graphene foam	0.1 M $\text{KHCO}_3$	- 0.58	85	6

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