Nanoscale nickel oxide/nickel heterostructures for active hydrogen evolution electrocatalysis

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Background

Electrolysis of water is the decomposition of water (H_2O) into oxygen (O_2) and hydrogen gas (H_2) due to an electric current being passed through the water.

Anode (oxidation): $2\ H^2O(l) \rightarrow O_2(g) + 4\ H^+(aq) + 4e^-$ $E^o_{ox} = -1.23\ V$ ($E^o_{red} = 1.23$)
Cathode (reduction): $2\ H^+(aq) + 2e^- \rightarrow H_2(g)$ $E^o_{red} = 0.00\ V$

The thermodynamic standard cell potential can be obtained from standard-state free energy calculations to find ΔG° and then using the equation: $\Delta G° = -nFE°$(where E° is the cell potential).

In practice when an electrochemical cell is "driven" toward completion by applying reasonable current, it is kinetically controlled. Therefore activation energy, ion mobility (diffusion) and concentration, wire resistance, surface hindrance including bubble formation (causes electrode area blockage) require a greater applied to potential to overcome these kinetic factors.

Real water electrolysers require higher voltages for the reaction to proceed. The part that exceeds 1.23 V is called overpotential or overvoltage, and represents any kind of loss and nonideality in the electrochemical process.

Introduction

Hydrogen, as a clean and renewable energy resource, has been intensely investigated as an alternative to the diminishing fossil fuel.

An effective way of producing high-purity hydrogen is to electrochemically split water into hydrogen and oxygen.

The state-of-art HER catalyst is platinum (Pt) and its alloys, but the scarcity and cost of Pt limit its large-scale application for electrolysis.

Here they report a nickel oxide/nickel (NiO/Ni) heterojunction-like structure attached to mildly oxidized carbon nanotube (NiO/Ni-CNT) exhibiting high HER catalytic activity close to commercial Pt/C catalysts in several types of basic solutions (pH=9.5–14).

The high catalytic activity of NiO/Ni-CNT towards HER enables a high-performance electrolyzer with around 20m Acm^{-2} at a voltage of 1.5 V.

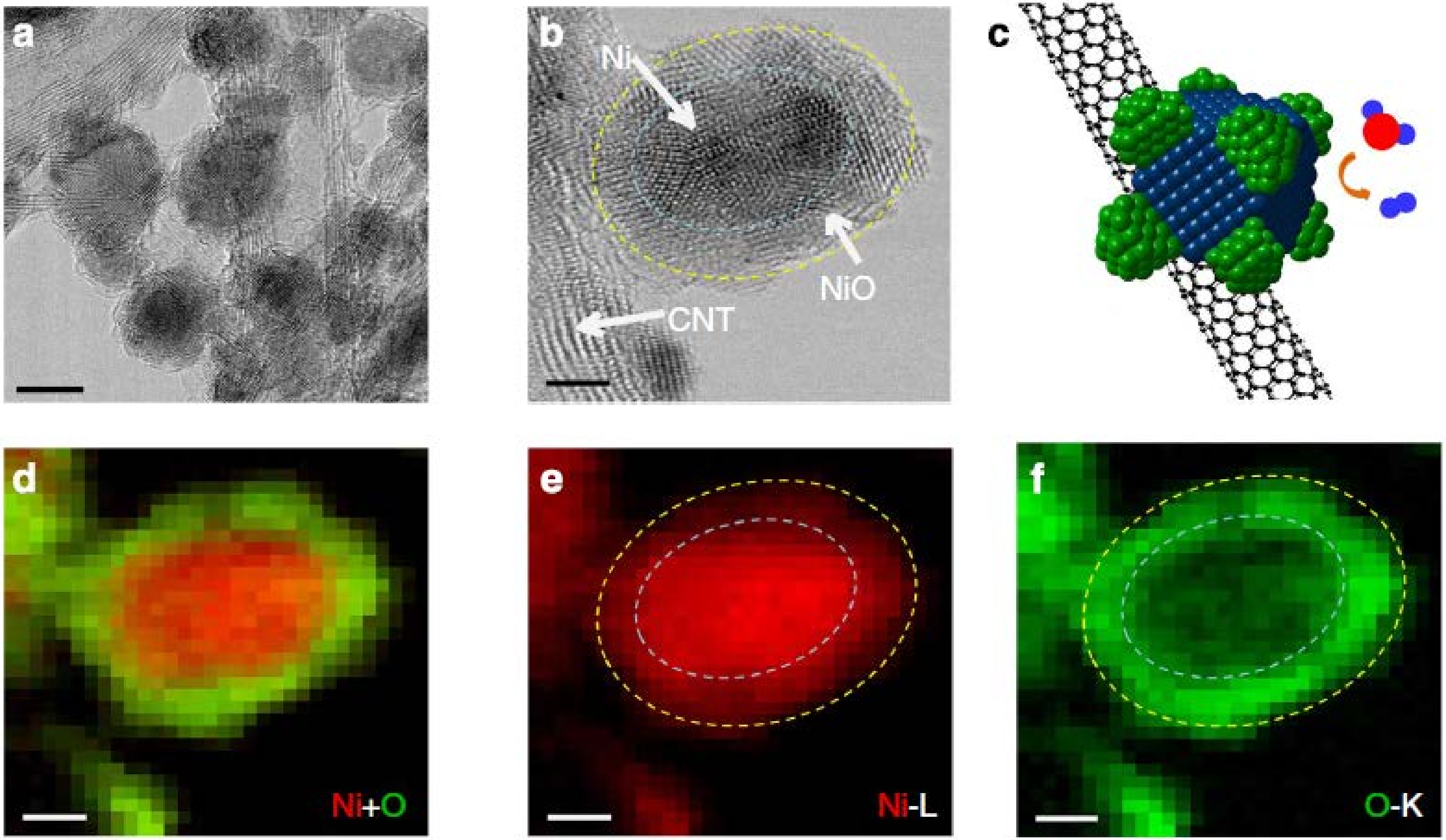
Sample preparation

NiO/Ni-CNT synthesis was done by low-temperature hydrolysis of Ni salts into Ni hydroxide on the sidewalls of mildly oxidized CNT [$Ni(OH)_2$/ox-CNT], followed by a low-pressure (around 1.5 torr) annealing at 300 C in an Ar flow.

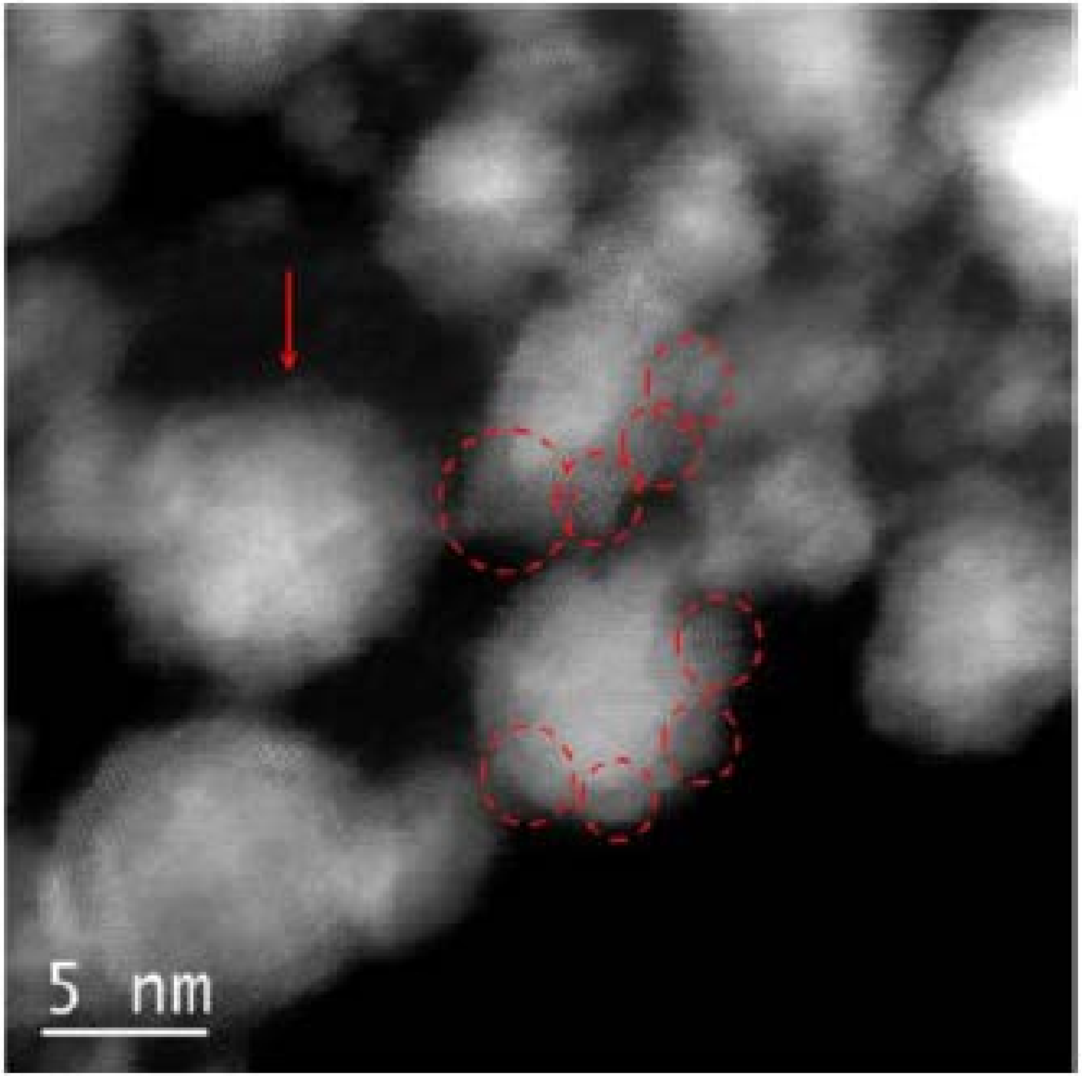
To prepare the NiO/Ni-CNT on RDE electrode, 1mg NiO/Ni-CNT hybrid was mixed with 190 ml water, 50 ml ethanol and 10 ml 5 wt% Nafion solution by at least 30 min sonication to form a homogeneous ink. Subsequently, 20 ml suspension was drop dried onto a glassy carbon electrode of 5mm in diameter (loading of 0.40 mg cm^{-2} including CNTs and loading of 0.28mg cm^{-2} for the active mass).

To prepare the NiO/Ni-CNT on Ni foam electrode, Ni(OH)2/ox-CNT was collected after 90 C oil bath process and washed with ethanol once. Ni(OH)2/ox-CNT was then redispersed in 2ml ethanol. After sonication for 10 min, all suspension was drop dried onto 1X1 cm Ni foam (1.6-mm thick, 100 p.p.i., 95% porosity, Marketech) at 90 C. The electrode was further heated at 120 C for 20 min till fully dry. The as-prepared electrode was annealed in a tube furnace at 300 C and constant pressure of 1.5 torr under Ar atmosphere (100 sccm) for 1 h, same as typical procedure.

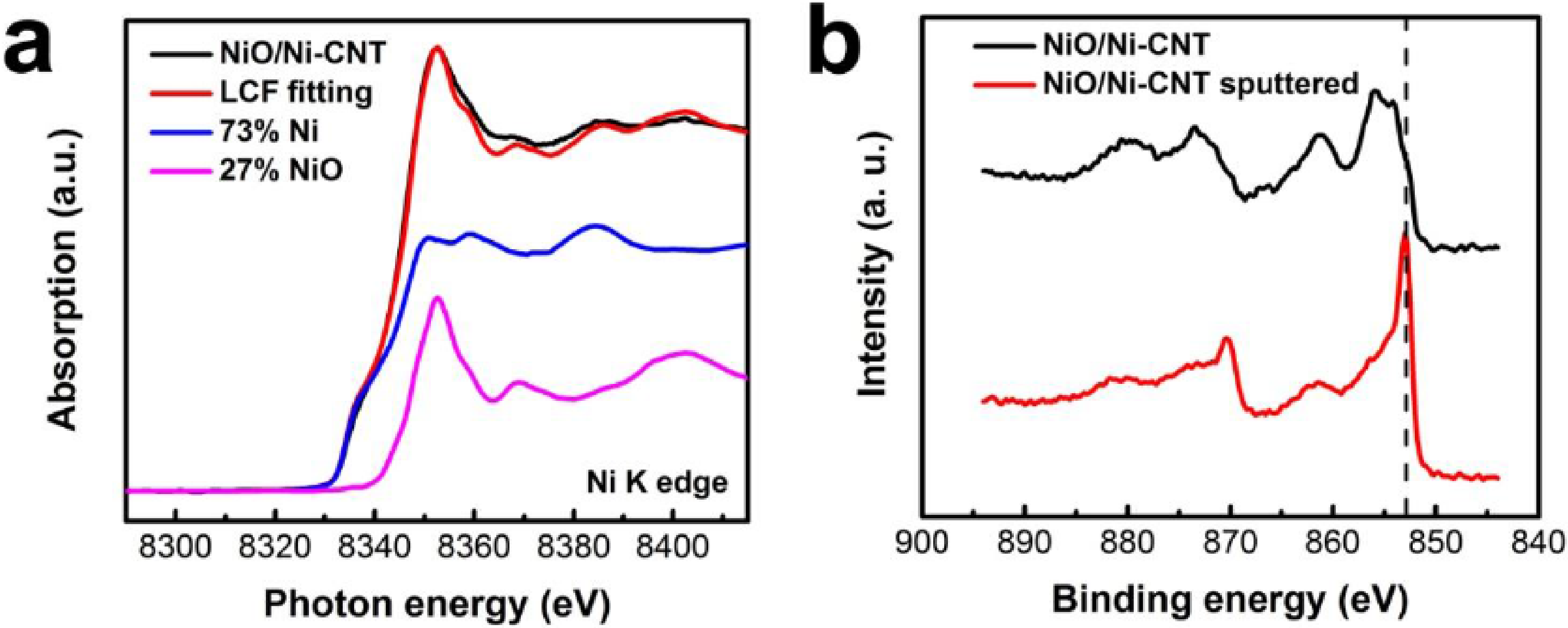
Characterization



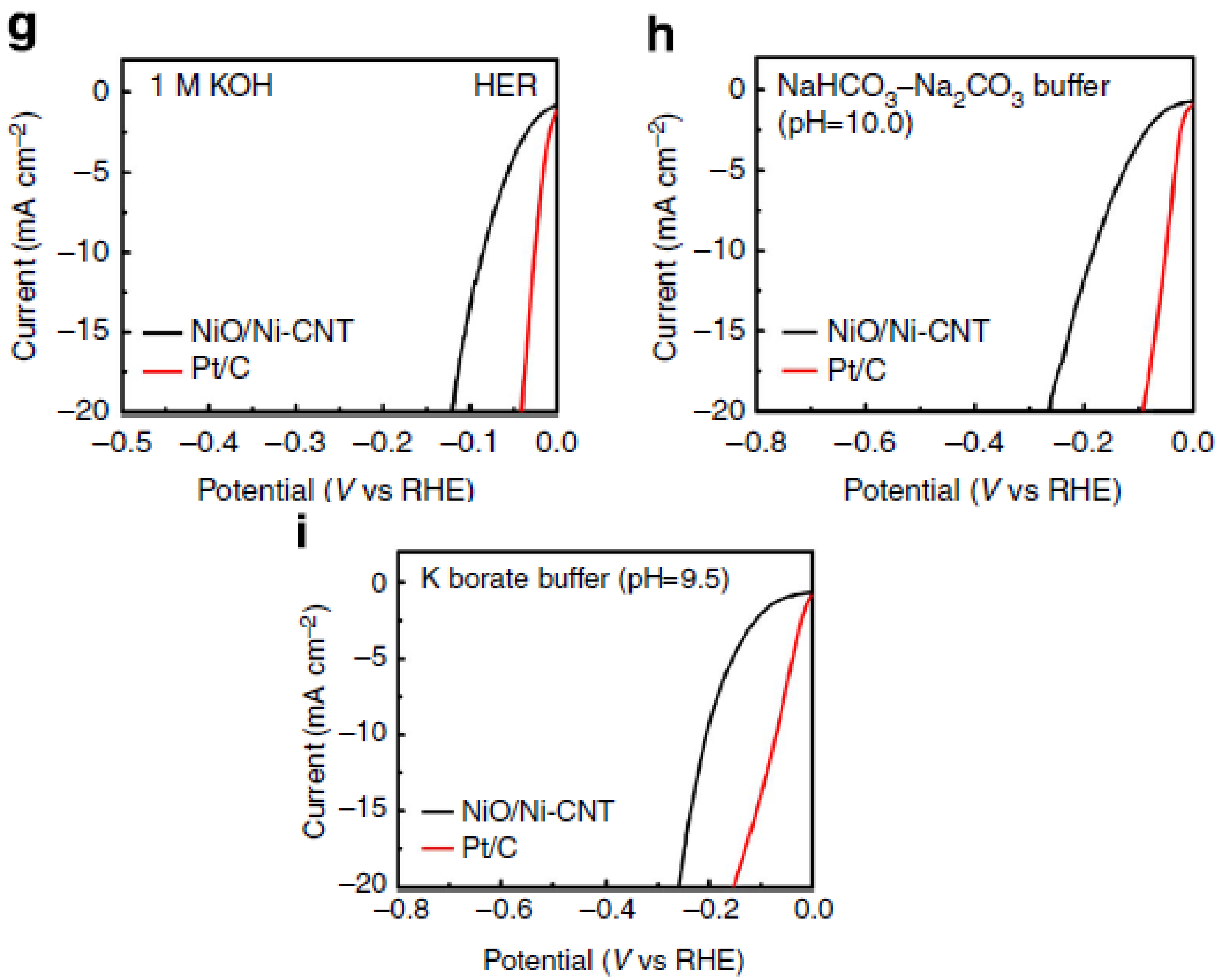
(a) Low-magnification STEM bright-field image showing the typical morphology of the NiO/Ni-CNT sample. (b) Atomic resolution STEM bright-field image showing the structure of a typical NiO/Ni particle on a CNT (small NiO nanoparticles over a larger Ni nanoparticle core). Scale bar, 2 nm. (c) A schematic illustration of the NiO/Ni-CNTstructure. (d–f) Chemical maps for the spatial distribution of Ni and O and their overlay, from the whole area shown in b. The two dashed circles highlight the NiO particle layer on the surface of the Ni core. Scale bar, 2 nm.



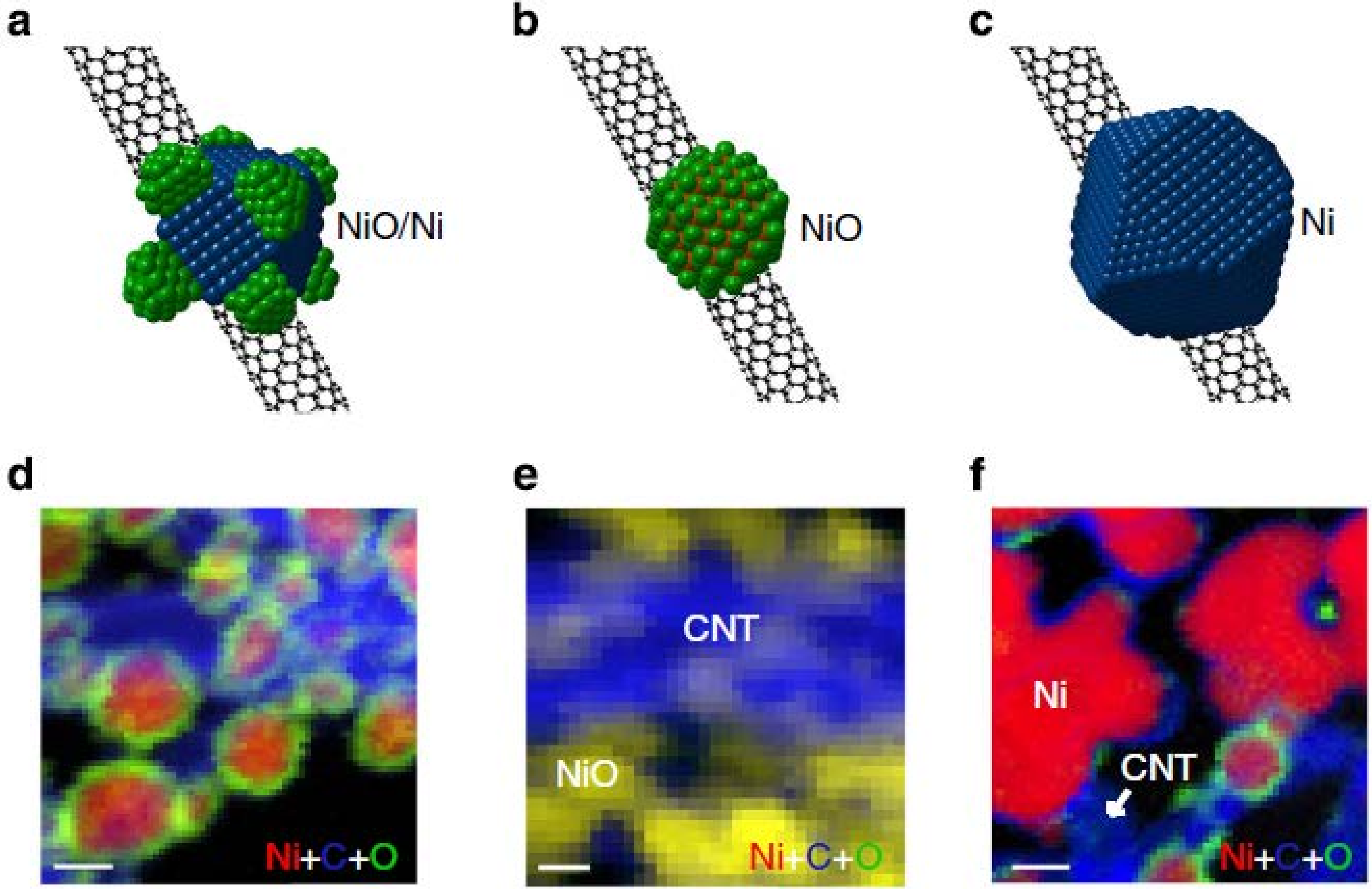
STEM annular dark field (ADF)image of NiO/Ni-CNT showing non-uniform coating of NiO nanoparticleson Ni cores (the red circles show individual NiO nanoparticles with different orientations, and the red arrow points out a NiO/Ni heterostructure with obvious morphology of Ni core non-uniformly coated with small NiO nanoparticles.



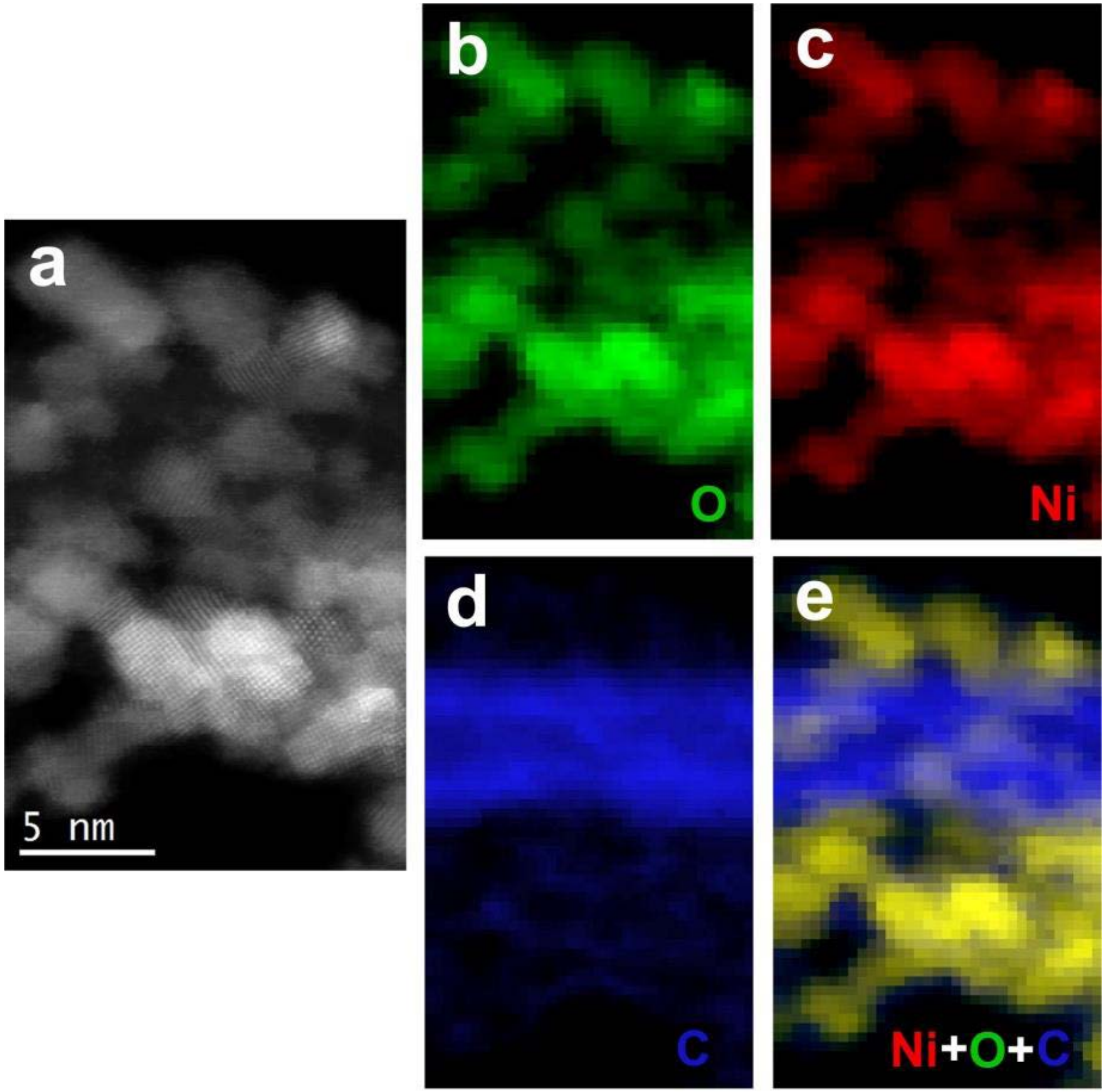
a) Ni K edge XANES spectrum of NiO/Ni-CNT (black), standard pattern of Ni (blue) and NiO (purple), linear fitting spectrum (red). b) XPS survey spectrum of NiO/Ni-CNT and sputtered NiO/Ni-CNT by Ar ion gun.



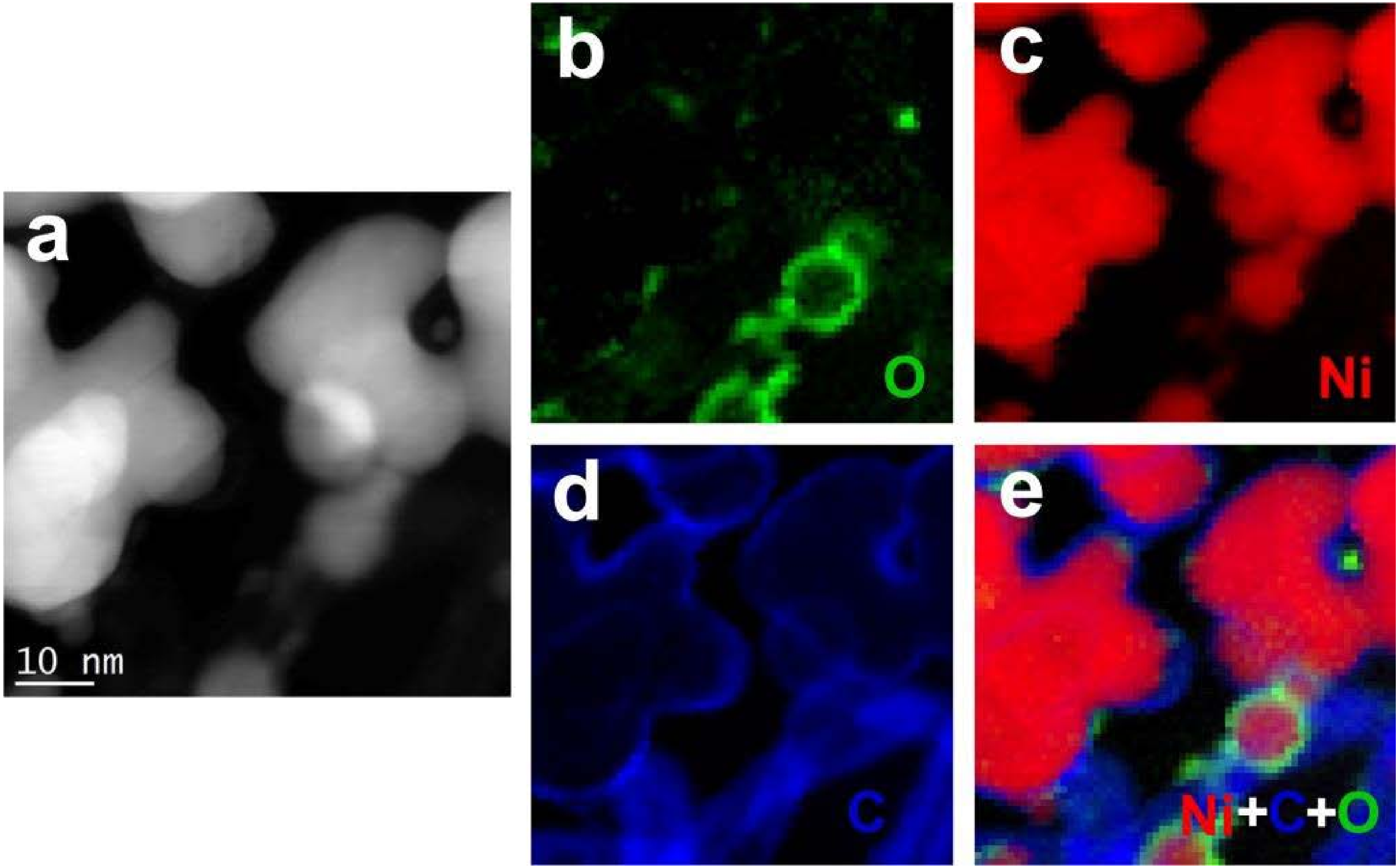
(g)Linear sweep voltametry of NiO/Ni-CNT and Pt/C in g 1M KOH (h) $NaHCO_3$-Na_2CO_3 buffer (pH=10.0) and (i) potasium borate buffer (pH=9.5) at a scan rate of $1mVs^{-1}$ under the loading of 0.28 $mgcm^2$ on RDE showing high HER catalytic activity of NiO/Ni-CNT.



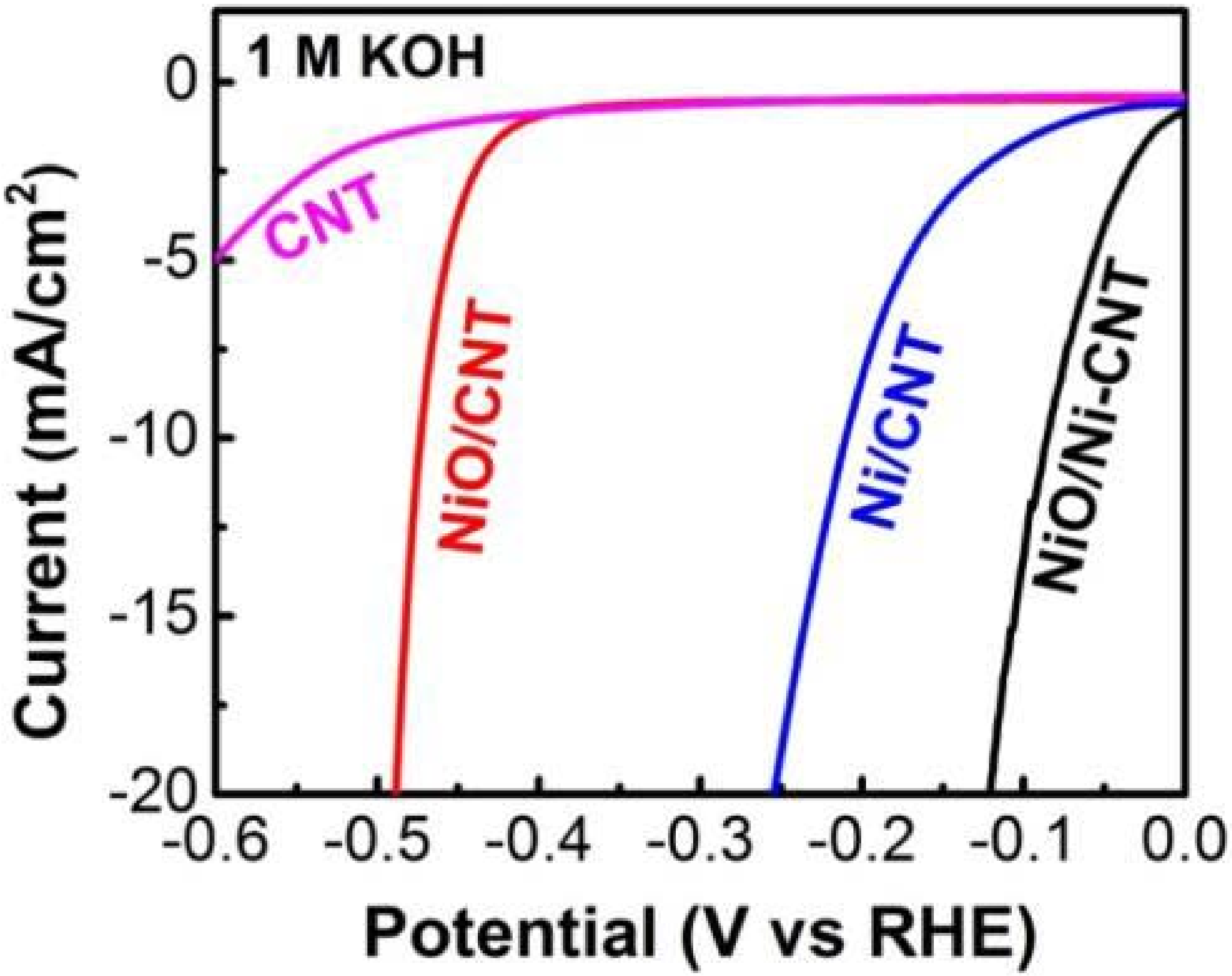
Structure and performance of NiO/Ni-CNT compared with NiO/CNT and Ni/CNT. (a–c) Schematic illustrations of (a) NiO/Ni-CNT, (b) NiO/CNTand (c) Ni/CNTstructure. (d–f) Reconstructed elemental maps with Ni in red, C in blue and O in green for (d) NiO/Ni-CNT, scale bar is 5 nm (e) NiO/CNT, scale bar is 2 nm and (f) Ni/CNT structure, scale bar is 10 nm.

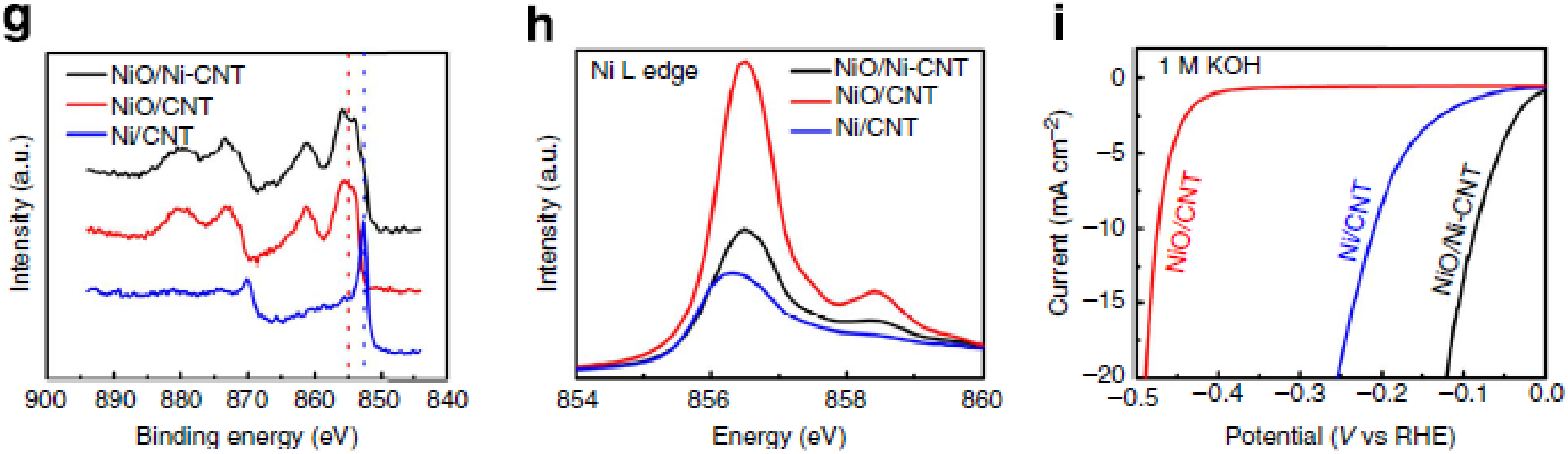


STEM ADF image of NiO/CNT hybrid.

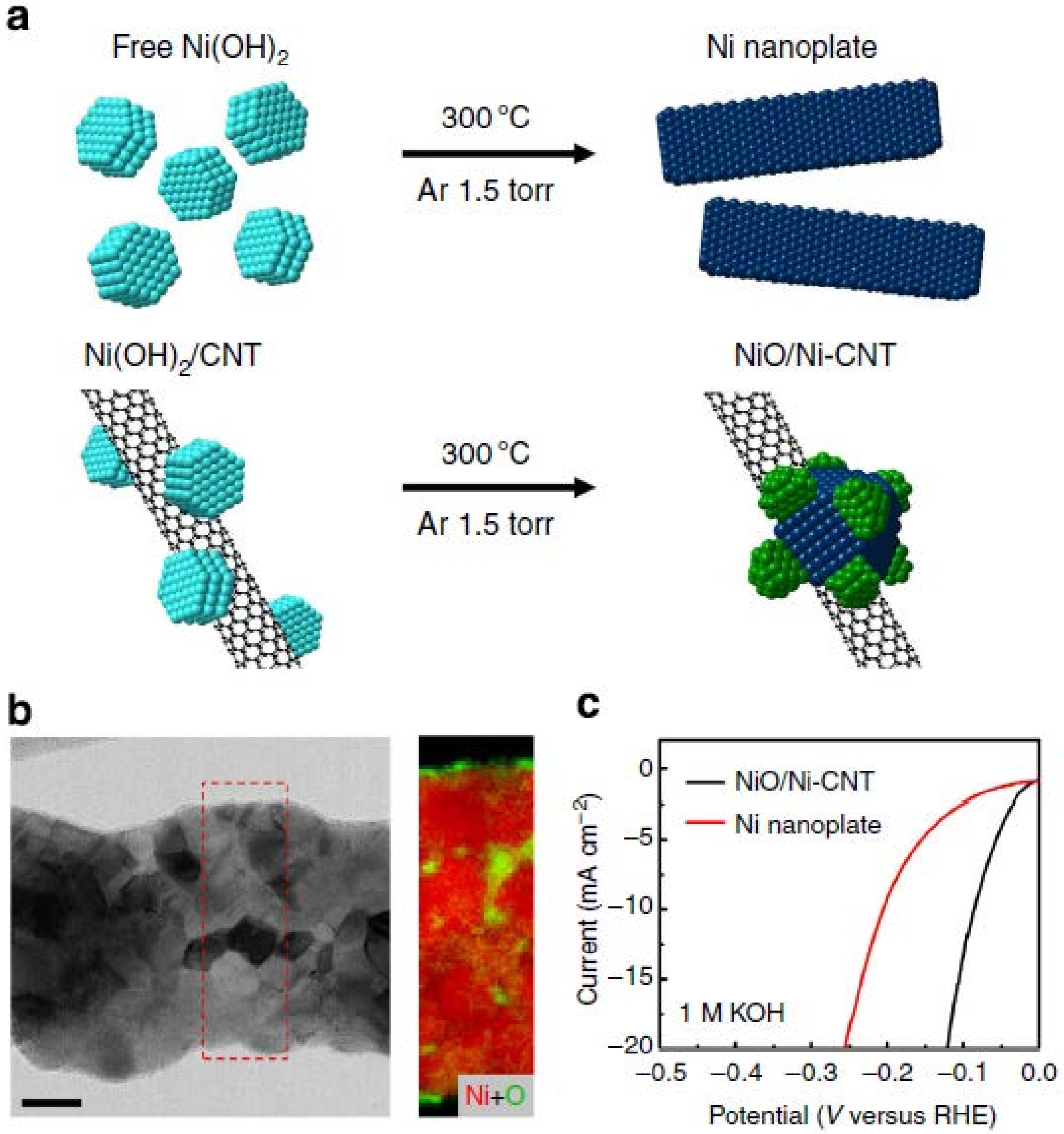


STEM ADF image of Ni/CNT hybrid. b

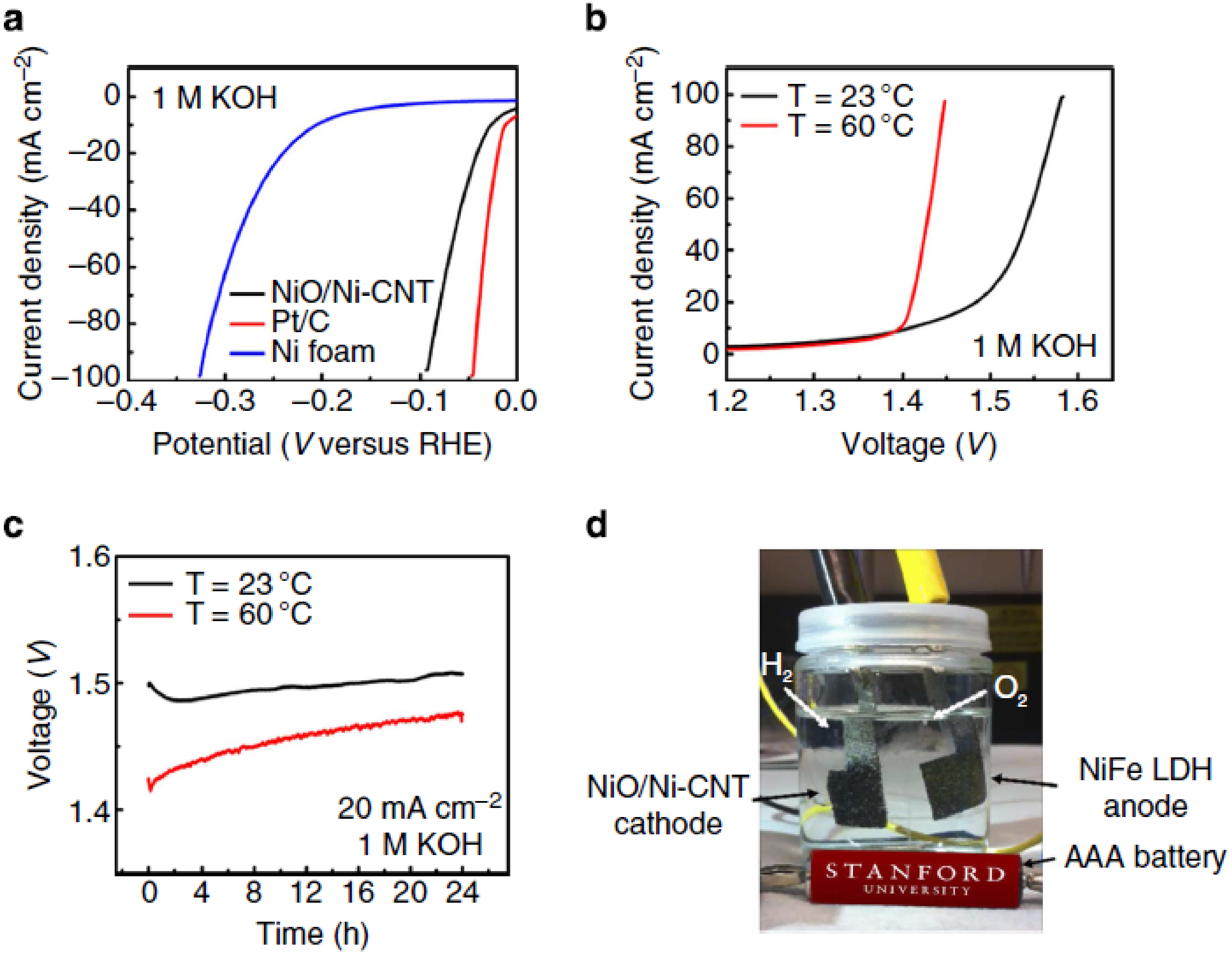

1 M KOH
CNT
NiO/CNT
Ni/CNT
NiO/Ni-CNT
0
-5
-10
-15
-20
-0.6
-0.5
-0.4
-0.3
-0.2
-0.1
0.0
Current (mA/cm^2)
Potential (V vs RHE)

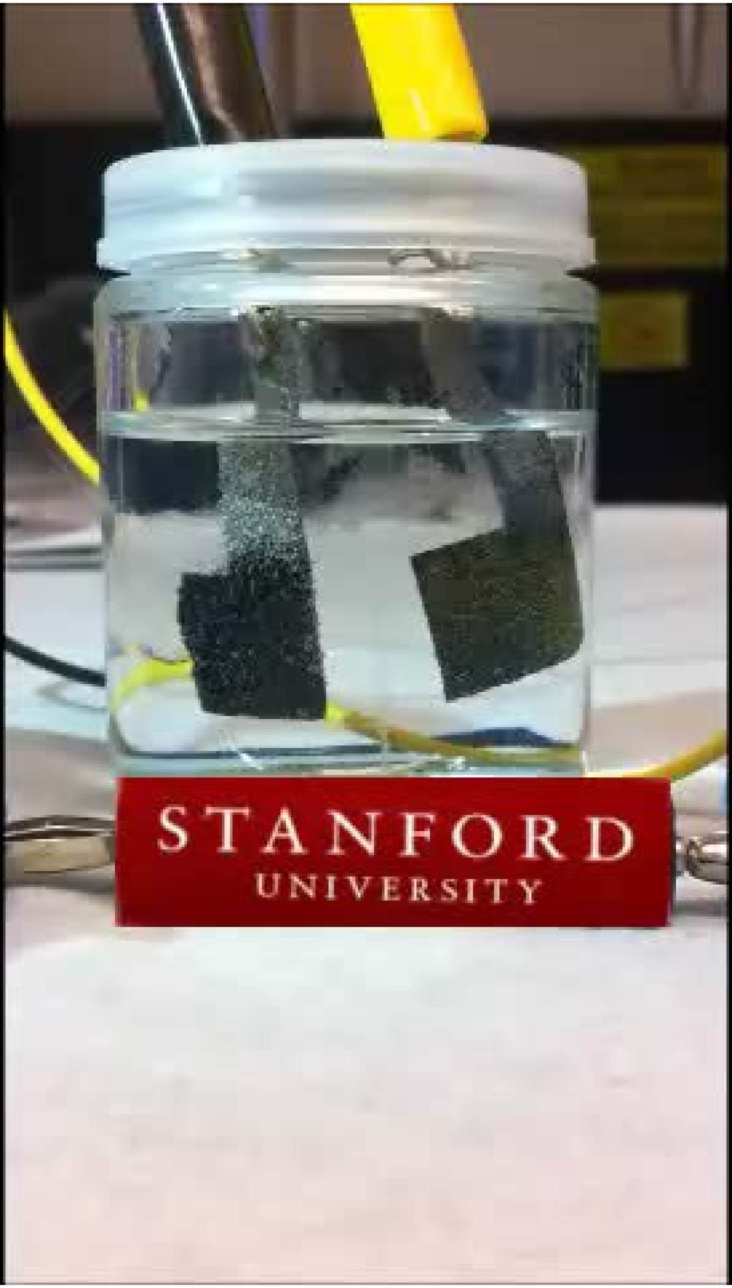


(g) High-resolution Ni XPS spectra of the three hybrid materials (the dotted line points out the binding energy of Ni$_{2p}$ (red) and metallic Ni (blue). (h) Ni L edge XANES spectra of the three hybrid materials. (i) Linear sweep voltametry of the three hybrid materials in 1M KOH at a scan rate of 1mVs$_1$ under the loading of 0.28mgcm$_2$ on RDE showing superior HER catalytic activity of NiO/Ni-CNT.


a
Free Ni(OH)$_2$
300 °C
Ar 1.5 torr
Ni nanoplate
Ni(OH)$_2$/CNT
300 °C
Ar 1.5 torr
NiO/Ni-CNT
b
Ni+O
c
NiO/Ni-CNT
Ni nanoplate
1 M KOH
Current (mA cm^{-2})
0
−5
−10
−15
−20
−0.5
−0.4
−0.3
−0.2
−0.1
0.0
Potential (V versus RHE)

Water electrolysis by NiO/Ni-CNT and NiFe LDH

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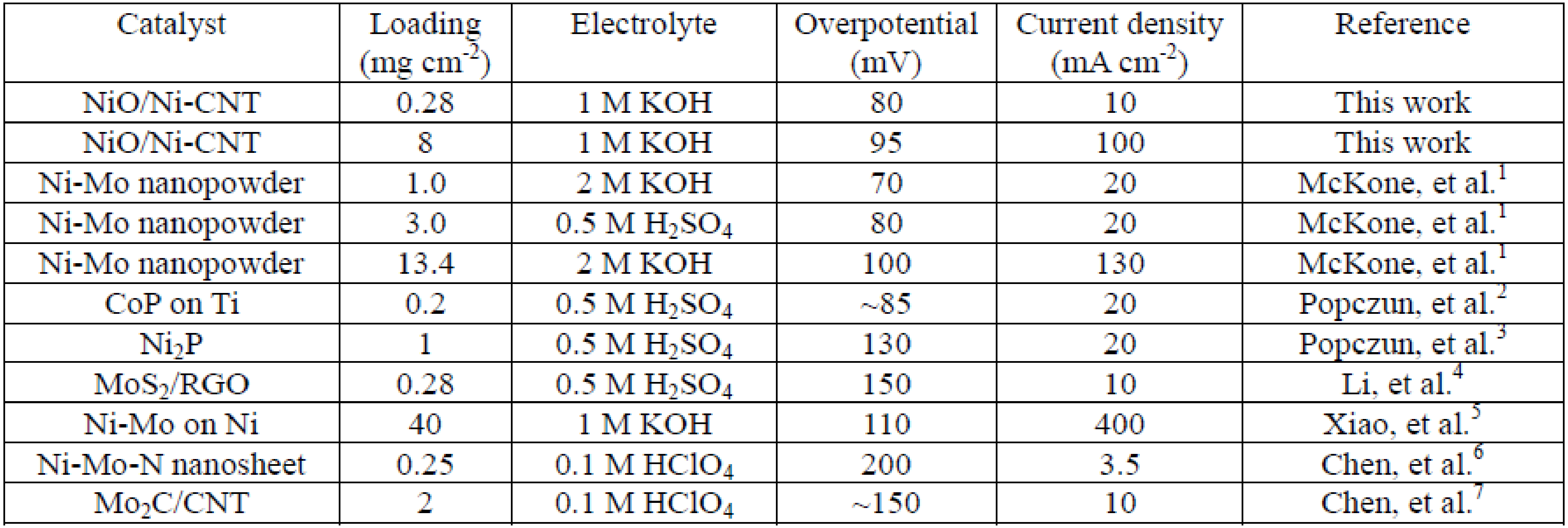
Due to the observation of gaps in the NiO shell and thus incomplete coverage of the Ni core by NiO, we proposed that the exposed NiO/Ni nano-interfaces might be synergistically active sites for HER catalysis. In alkaline media, the HER pathway could be through the Volmer–Heyrovsky process or Volmer–Tafel pathways.

$$H_2O + e \rightarrow H_{ads} + OH^- \ \text{(Volmer) and}$$
$$H_{ads} + H_{ads} \rightarrow H_2 \text{(Tafel)}$$

$$H_2O + e \rightarrow H_{ads} + OH^- \ \text{(Volmer) and}$$
$$H_2O + H_{ads} + e \rightarrow H_2 + OH^- \ \text{(Heyrovsky)}$$

The kinetics and thermodynamics were greatly improved at high temperature (around 60 C), showing lower voltage of around 1.42 V at 20 mAcm^{-2} and higher current increase, reaching 100 mAcm^{-2} at a voltage of around 1.45 V with good stability.

Summary of the HER catalytic activity of representative catalysts



Catalyst	Loading (mg cm^{-2})	Electrolyte	Overpotential (mV)	Current density (mA cm^{-2})	Reference
NiO/Ni-CNT	0.28	1 M KOH	80	10	This work
NiO/Ni-CNT	8	1 M KOH	95	100	This work
Ni-Mo nanopowder	1.0	2 M KOH	70	20	McKone, et al.[1]
Ni-Mo nanopowder	3.0	0.5 M H_2SO_4	80	20	McKone, et al.[1]
Ni-Mo nanopowder	13.4	2 M KOH	100	130	McKone, et al.[1]
CoP on Ti	0.2	0.5 M H_2SO_4	~85	20	Popczun, et al.[2]
Ni_2P	1	0.5 M H_2SO_4	130	20	Popczun, et al.[3]
MoS_2/RGO	0.28	0.5 M H_2SO_4	150	10	Li, et al.[4]
Ni-Mo on Ni	40	1 M KOH	110	400	Xiao, et al.[5]
Ni-Mo-N nanosheet	0.25	0.1 M $HClO_4$	200	3.5	Chen, et al.[6]
Mo_2C/CNT	2	0.1 M $HClO_4$	~150	10	Chen, et al.[7]

Summary and Conclusion

They discovered nanoscale NiO/Ni heterostructure attached to CNT network as a novel HER catalyst.

The structure of Ni cores partially covered with small NiO nanoparticles was created by a simple process of $Ni(OH)_2$ decomposition involving CNT substrate delaying the $Ni(OH)_2$ reduction and Ni aggregation.

An efficient electrolyzer achieving around 20 $mAcm^{-2}$ at a voltage of 1.5 V with good stability was demonstrated.

The high activity of NiO/Ni-CNT was possibly attributed to the nanoscopic NiO/Ni interfaces in the heterostructure.

The highly active NiO/ Ni heterostructure-based catalyst with low cost, earth abundance and environmental friendliness is promising for future watersplitting devices.


Thank You