Highly Mismatched NiO$_2$-to-Pd Hetero-Structure as an Efficient Nanocatalyst for Hydrogen Evolution Reaction

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1. Quantitative XRD parameters of NiPd-CNT and Pd-CNT NCs.

Table S1. Quantitative XRD parameters of NiPd-CNT and Pd-CNT NCs.

NC	$d_{(111)}$ (Å)	$d_{(200)}$ (Å)	$d_{(220)}$ (Å)	$d_{NiPd3\ (20\text{-}2\text{-}2)}$ (Å)	$D_{(111)}$ (Å)	$D_{(200)}$ (Å)	$D_{(220)}$ (Å)	$D_{NiPd3\ (20\text{-}2\text{-}2)}$ (Å)
NiPd-CNT	2.276	1.991	1.395	1.528	75.6	52.3	31.7	27.5
Pd-CNT	2.278	1.984	1.392	N/A	86.6	64.4	61.1	N/A

2. XPS analysis of Ni-CNT and NiPd-CNT nanocatalyst at Ni-2p orbitals.

To further examine the structural changes in Ni-crystal, X-ray photoelectron spectroscopy (XPS) has been applied at Ni-2p orbitals of experimental NCs. **Figure S1** depicts the fitted XPS spectra in the Ni-2p region of the Ni-CNT and NiPd-CNT NCs. In a Ni-2p spectrum, apparently, two peaks around at 855.7 and 873.5 eV are corresponding to the binding energies of Ni^{2+}- $2p_{3/2}$ and Ni^{2+}- $2p_{1/2}$, respectively. Simultaneously, two satellite peaks nearly at 861 eV and 880 eV could be attributed to the oxidation products on the surface[1]. Meanwhile, a weak shake up peak centered nearly at 852.7 eV is corresponding to metallic state of Ni, which reveals that most of the Ni is present in form of NiO_2. The binding energies of Ni (0), Ni^{2+}- $2p_{3/2}$ and Ni^{2+}- $2p_{1/2}$ peaks for experimental NCs are summarized in **Table S2**. Accordingly, although the difference in binding energies of the Ni (0), Ni^{2+}- $2p_{3/2}$ and Ni^{2+}- $2p_{1/2}$ orbitals for Ni-CNT and NiPd-CNT NCs are not obvious. However, peaks are slightly shifted to lower energy values for NiPd-CNT NC as compared to that of Ni-CNT NC. This is acceptable because of increased index of electron relocation from Ni to Pd atoms in NiPd-CNT NC. Such a scenario is further confirmed by intensity difference of various peaks in both NCs. Intensity of emission peaks in a XPS spectrum is positively related to electron density of the target atoms. Therefore, the comparatively higher intensity in the XPS spectra of Ni-CNT reflects its most abundant Ni-2p electrons. Whereas, relatively decreased intensity observed in case of NiPd-CNT NC, which itself is a result of high index of electron relocation from Ni to Pd-atoms. Such characteristics are consistent with Pd-3d orbital XPS findings.
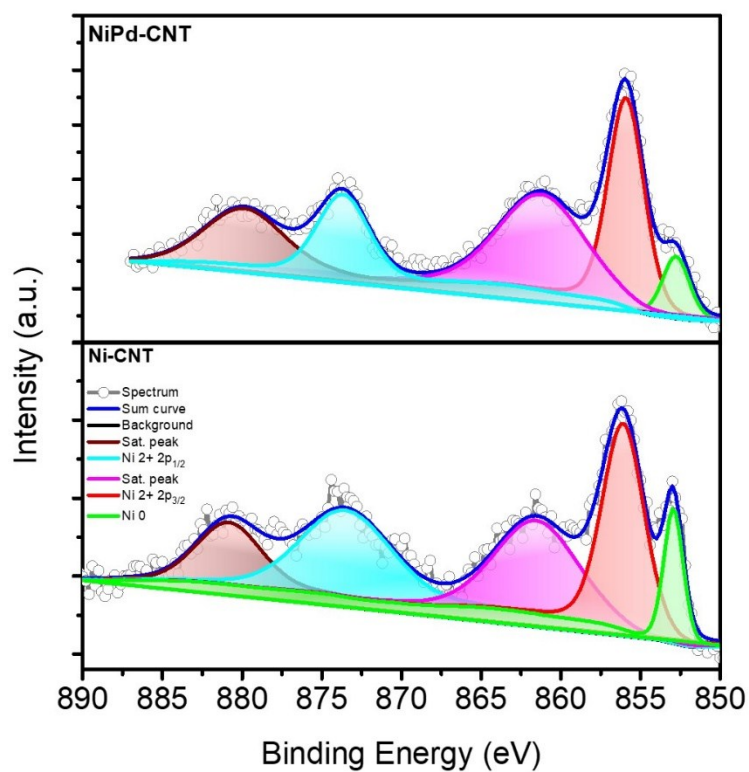
Figure S1. XPS spectra of Ni-CNT and NiPd-CNT nanocatalyst at Ni-2p orbitals.

Table S2. XPS determined binding energy of experimental NC at Ni-2p orbital

Samples	Binding Energies		
	Ni (0)	Ni $^{2+}$ 2p $_{3/2}$	Ni $^{2+}$ 2p $_{1/2}$
NiPd-CNT	852.778	855.902	873.643
Ni-CNT	852.985	856.011	873.745

3. Cyclic voltammogram (CV) of NiPd-CNT NC compared with control samples (Ni-CNT and Pd-CNT) and commercial J.M.-Pt/C NC.
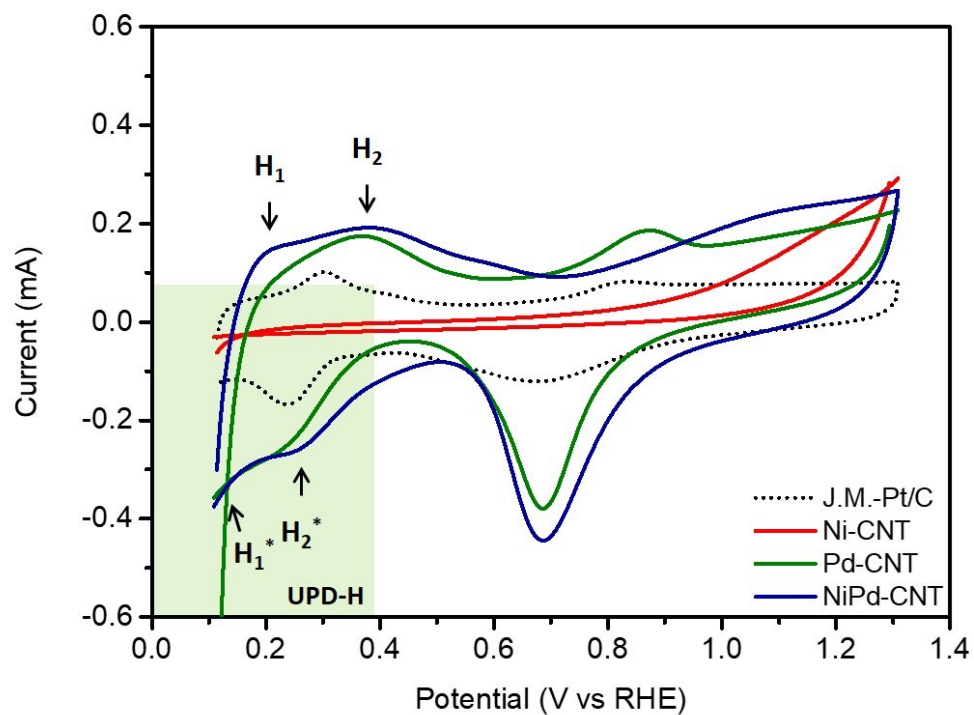

Figure S2. Cyclic voltammogram (CV) of NiPd-CNT NC compared with control samples (Ni-CNT and Pd-CNT) and commercial J.M.-Pt/C NC.

4. ICP-AES determined composition ratios of experimental nanocatalysts

Table S3. ICP-AES determined composition ratios of experimental nanocatalysts

Samples	Ni (wt.%)	Pd (wt.%)
NiPd-CNT	9.287	16.95

References

1.   D. Bin, B. Yang, F. Ren, K. Zhang, P. Yang and Y. Du, *Journal of Materials Chemistry A*, 2015, **3**, 14001-14006.