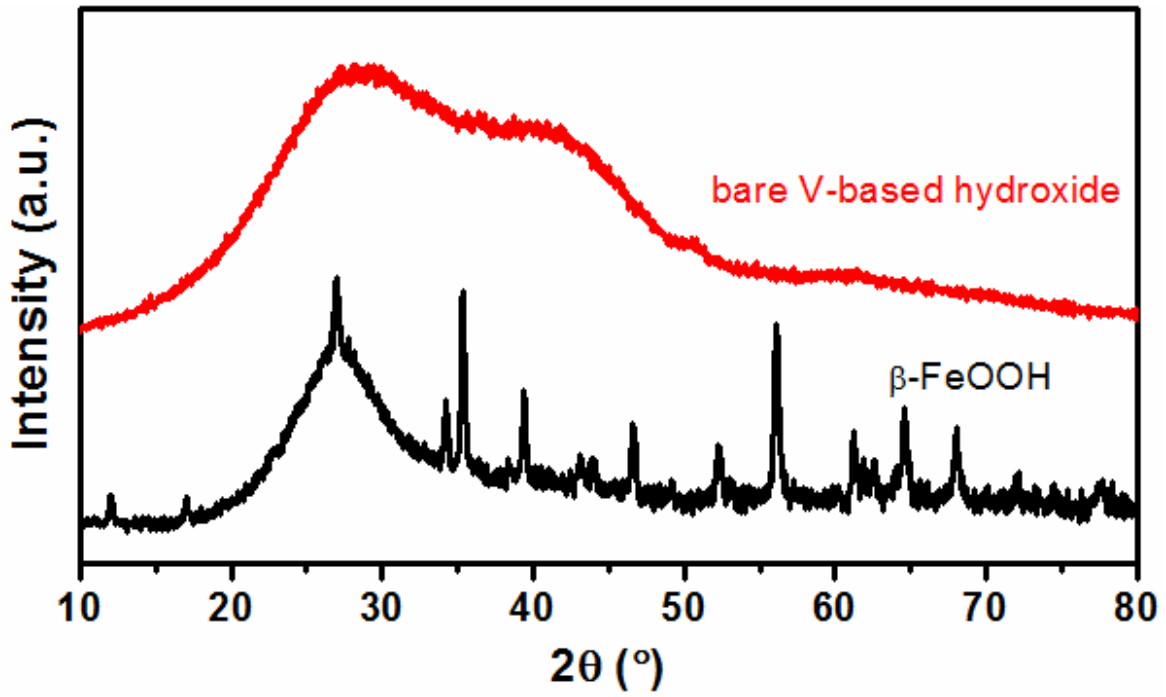
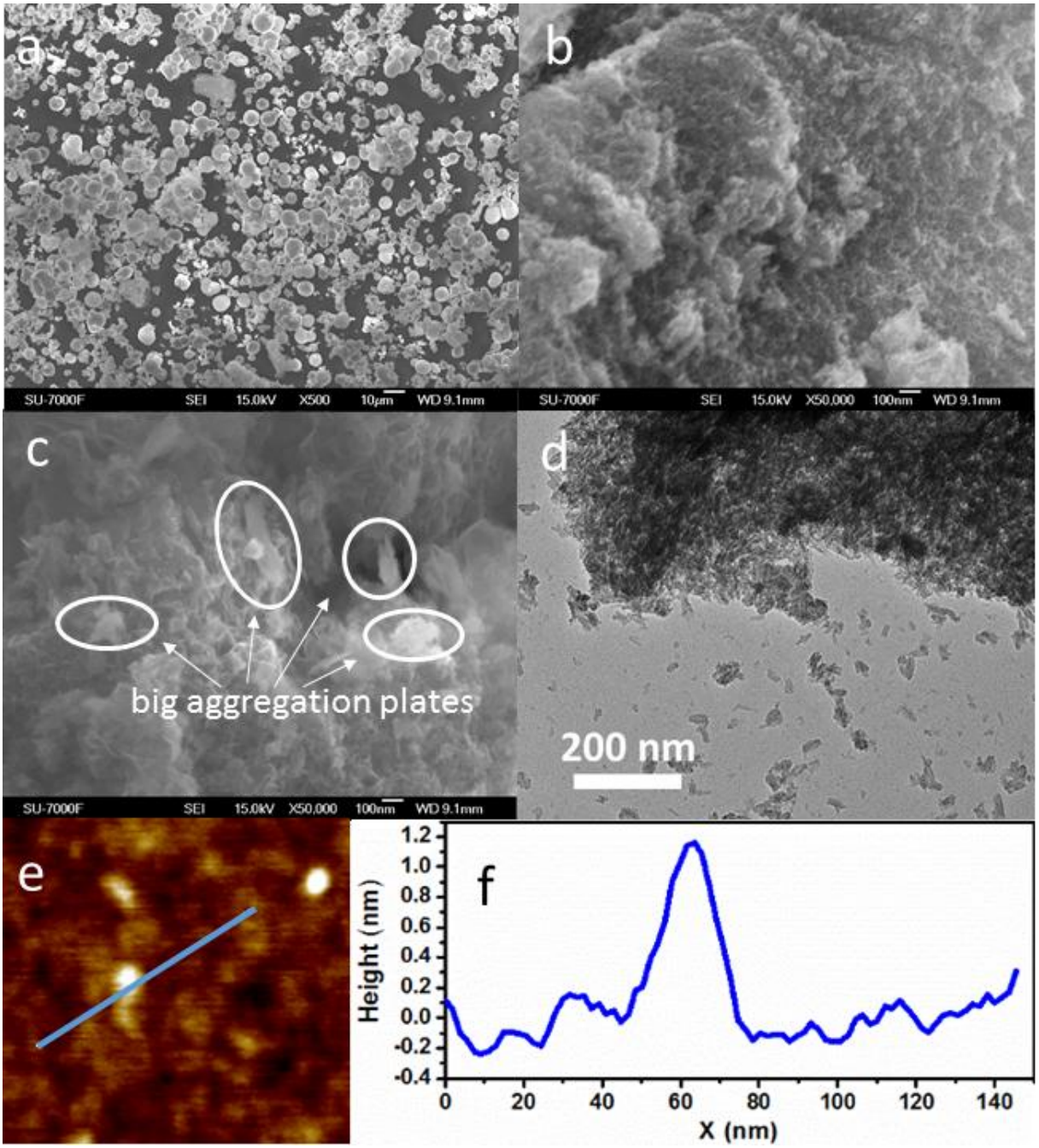
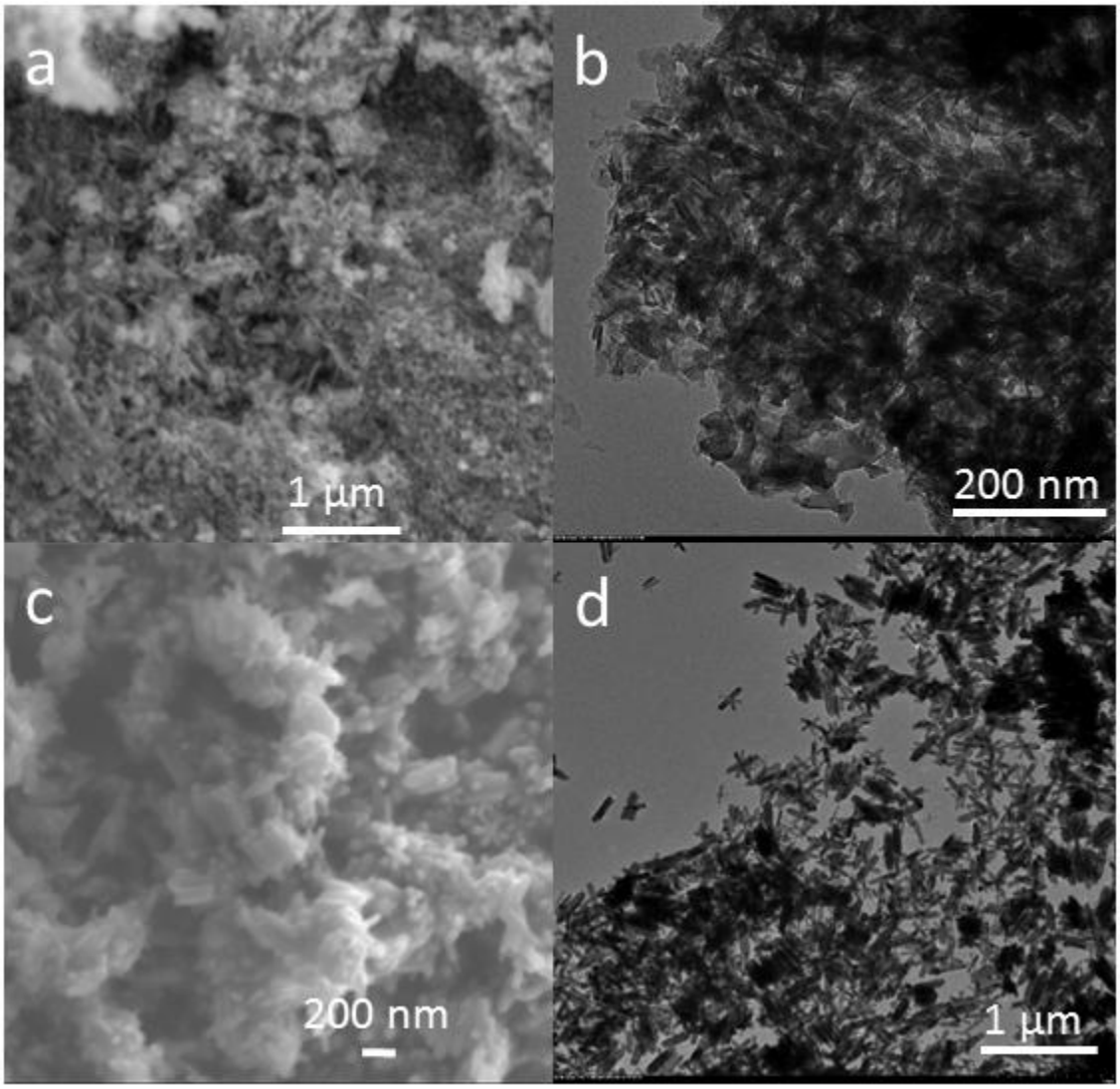


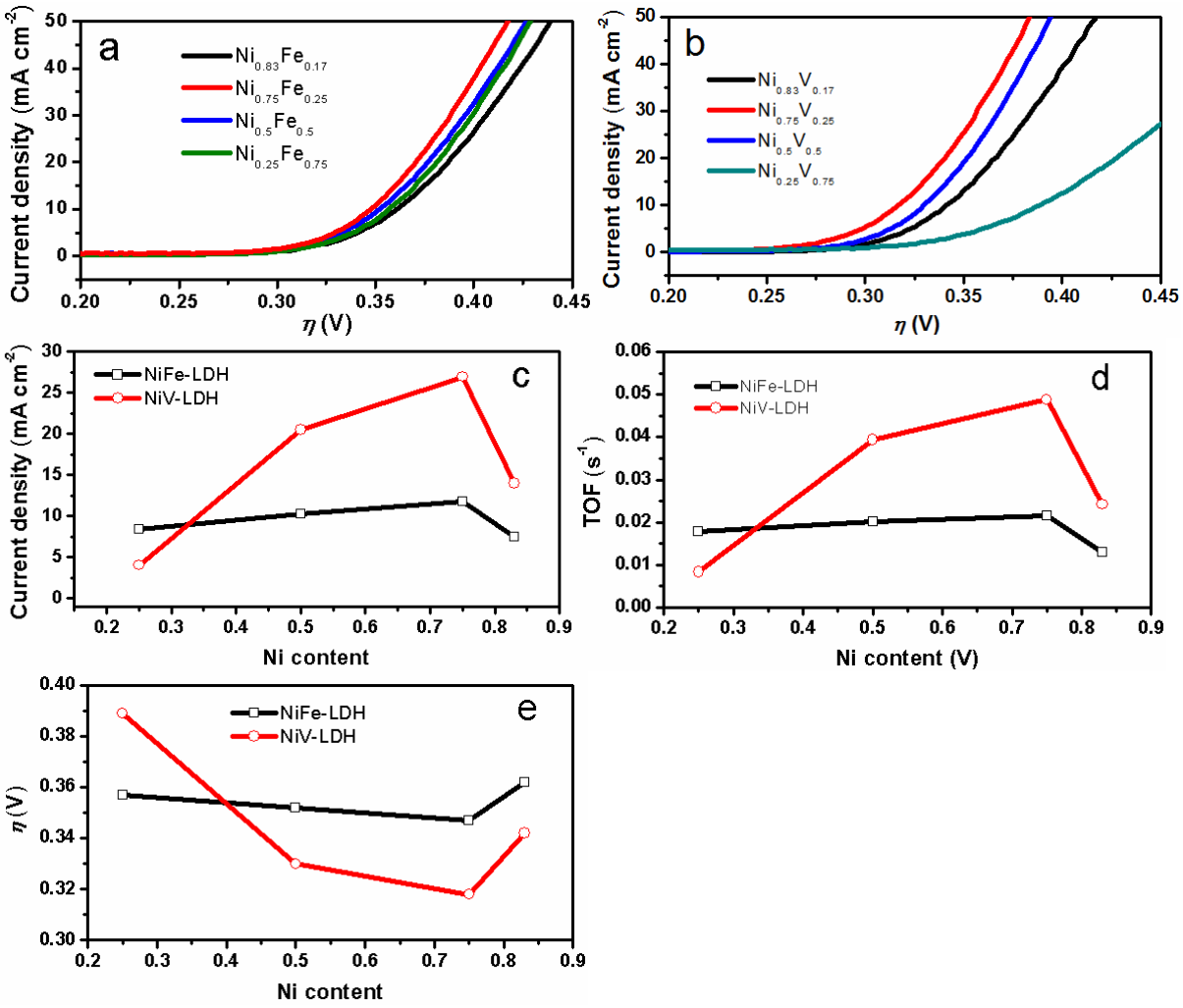
Supplementary Figure 1 | XRD pattern of as-synthesized bare V-based hydroxide and bare Fe-based hydroxide. The bare V-based hydroxide shows very low crystallinity and the XRD of bare Fe-based hydroxide indicates it is β-FeOOH.



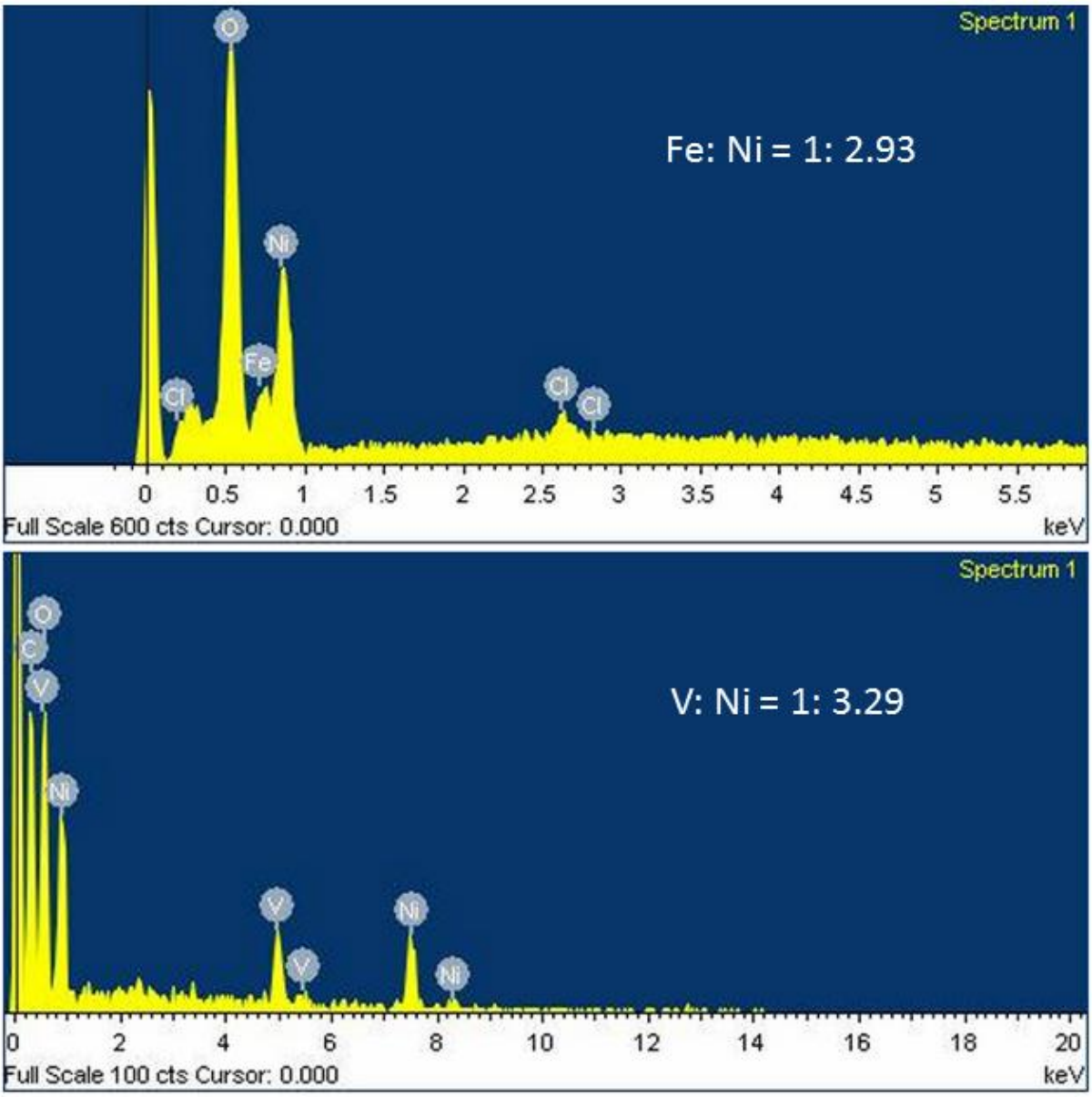
Supplementary Figure 2 | SEM, TEM and AFM of LDHs. (**a**) SEM images of as-synthesized pure α-$Ni(OH)_2$ spheres, (**b**) $Ni_{0.75}V_{0.25}$-LDH and (**c**) $Ni_{0.75}Fe_{0.25}$-LDH; (**d**) TEM (**e**) AFM and (**f**) height profile of $Ni_{0.75}Fe_{0.25}$-LDH.



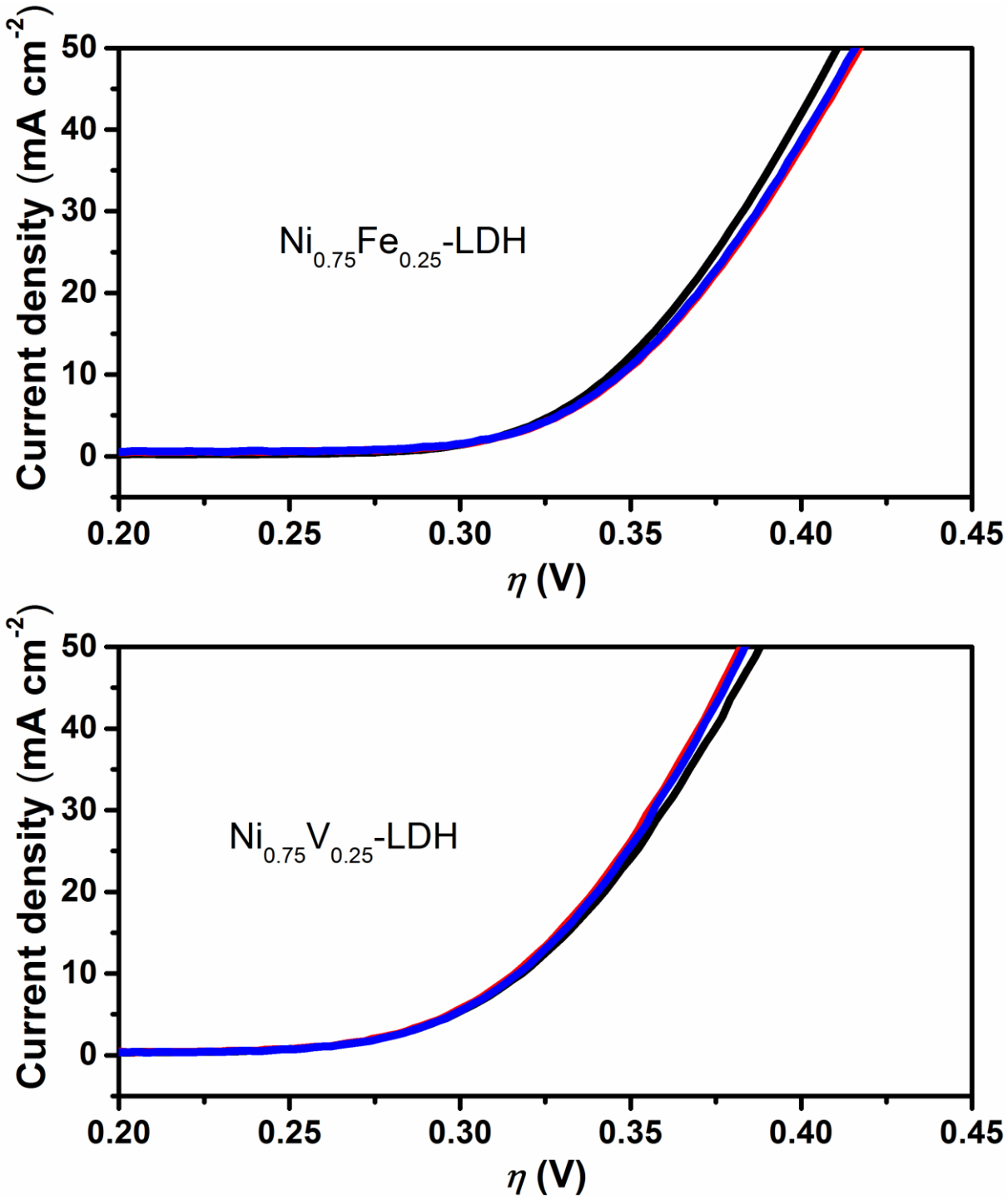
Supplementary Figure 3 | SEM and TEM of V- and Fe-based hydroxides. (**a**) SEM and (**b**)TEM images of as-synthesized bare V-based hydroxide; (**c**) SEM and (**d**)TEM images of bare Fe-based hydroxide (β-FeOOH).



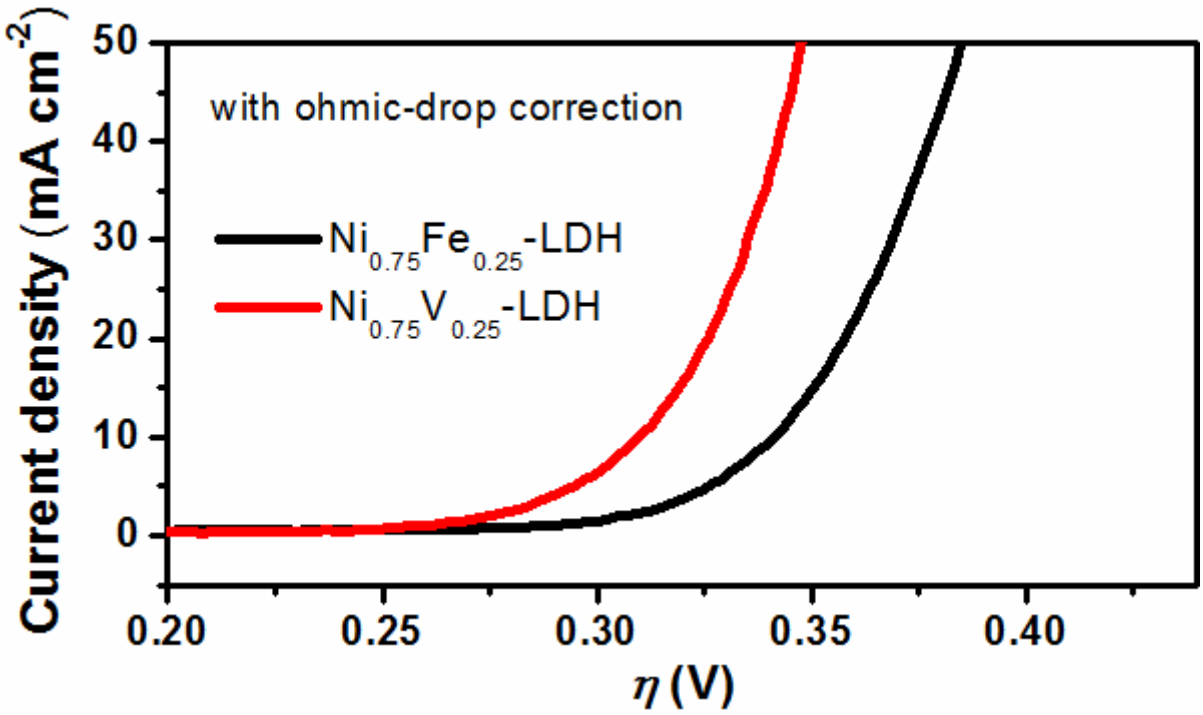
Supplementary Figure 4 | Catalytic properties of LDHs. (**a**) LSV curves of NiFe-LDHs and (**b**) NiV-LDHs with different Ni contents; (**c**) Current density and (**d**) TOF at 350 mV overpotential of NiFe-LDHs and NiV-LDHs with different Ni contents; (**e**) Overpotential required for 10 mA cm^{-2} current density of NiFe-LDHs and NiV-LDHs with different Ni contents. All the data were collected without ohmic-drop correction.



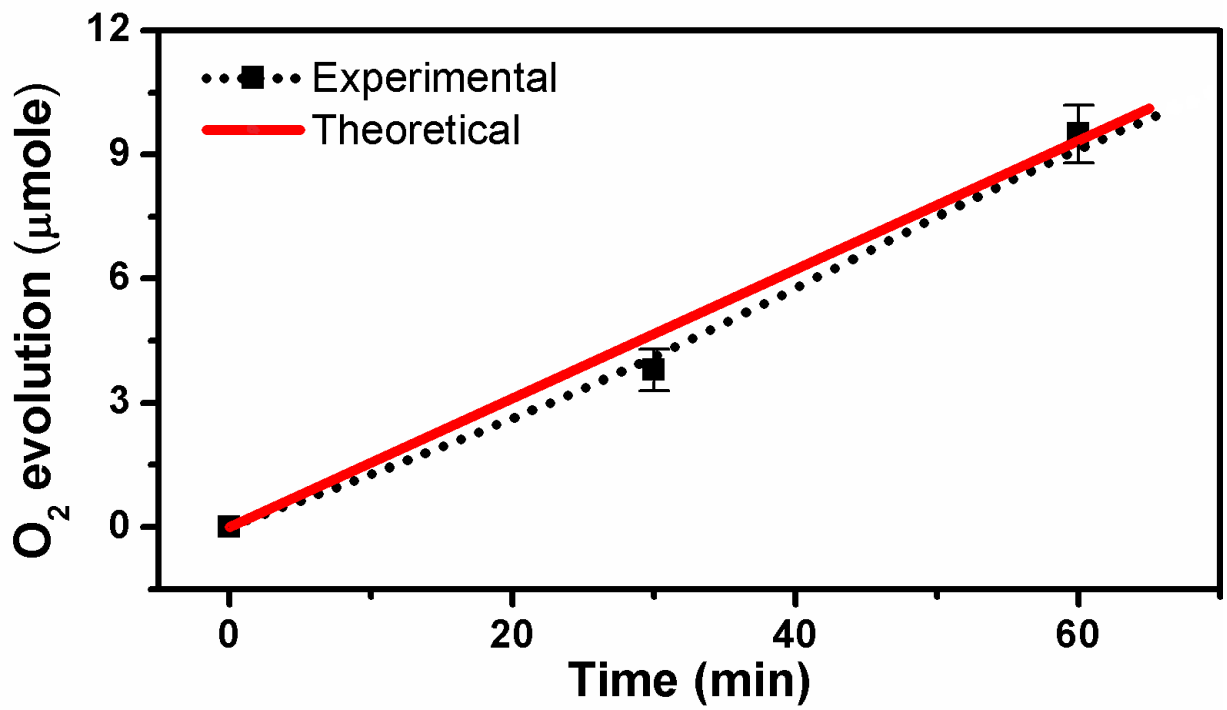
Supplementary Figure 5 | EDS. (**upper**) EDS of $Ni_{0.75}Fe_{0.25}$-LDH; (**bottom**) EDS of $Ni_{0.75}V_{0.25}$-LDH.



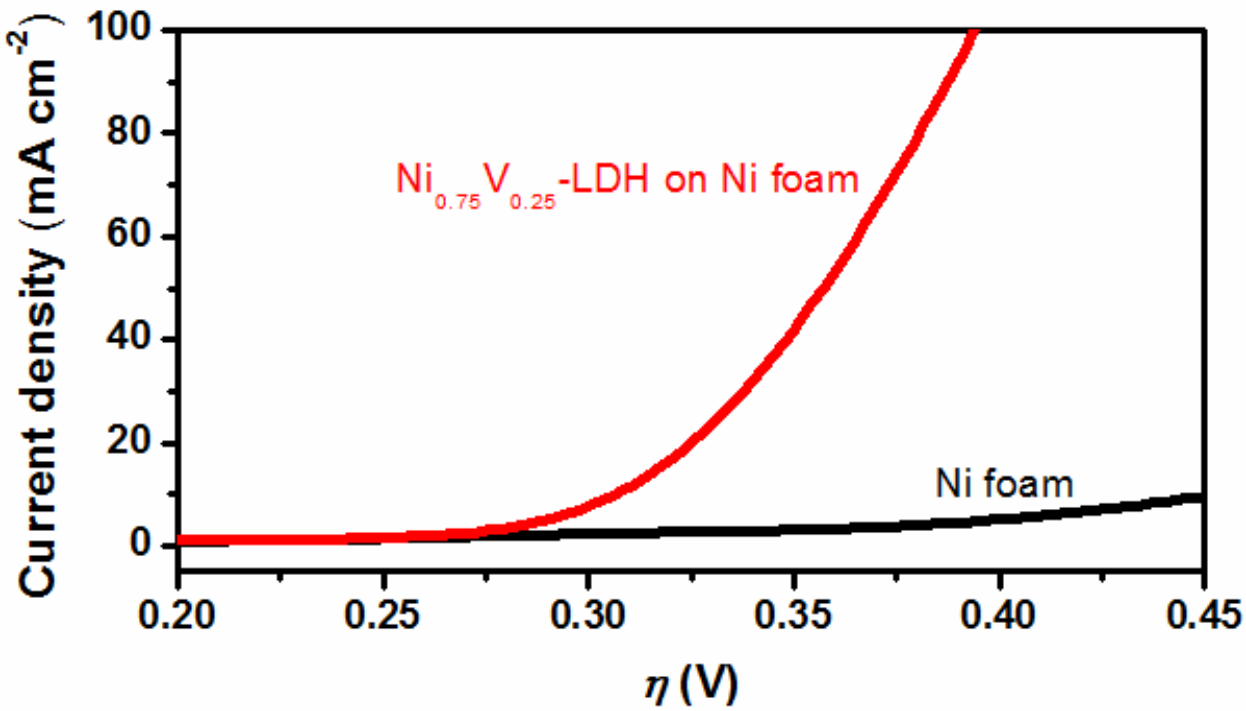
Supplementary Figure 6 | Reproducibility of water oxidation of LDH catalysts. (**upper**) Reproducibility of $Ni_{0.75}Fe_{0.25}$-LDH; (**bottom**) Reproducibility of $Ni_{0.75}V_{0.25}$-LDH. Every experiment was repeated 3 times.



Supplementary Figure 7 | LSV curves with ohmic-drop correction of $Ni_{0.75}Fe_{0.25}$-LDH and $Ni_{0.75}V_{0.25}$-LDH. The resistance used here is around 10 Ω.



Supplementary Figure 8 | O_2 evolution. The experimental and theoretical O_2 evolution amount by $Ni_{0.75}V_{0.25}$-LDH at a constant oxidative current of 1 mA. All the error bars represent the standard deviations of three replicate measurements.



Supplementary Figure 9 | LSV curves of bare Ni foam and $Ni_{0.75}V_{0.25}$-LDH on Ni foam.

The catalyst loading amount is 0.25 mg cm^{-2}.

Supplementary Table 1 | Comparison of LDH catalysts for water oxidation. All the LDHs were loaded on GC electrode unless noted otherwise.

LDH catalysts loaded on glassy carbon	Electrolyte	Current density (mA cm^{-2}) at η=350 mV	Mass activity (A g^{-1}) at η=350 mV	References
NiV	1 M KOH	~ 27	~ 190	This work
NiV*	1 M KOH	~ 57	~ 400	This work
NiFe*	1 M KOH	~ 11	~ 154	1
NiFe* (exfoliated)	1 M KOH	~ 17	~ 68	2
NiFe*	1 M KOH	~ 17	~ 85	3
NiFe*	0.1 M KOH	~ 10 (η=300 mV)	-	4
NiCo*	1 M KOH	~ 3.2	~ 44.8	1
NiCo double hydroxide nanocage*	1 M KOH	~ 10	~ 49	5
NiCo (exfoliated) [a]	1 M KOH	~ 5.8	-	6
ZnCo nanosheet	0.1 M KOH	~ 1.3	-	7
ZnCo nanoparticle	0.1 M KOH	~ 0	~ 0	7
ZnCo	0.1 M KOH	<1	<3.5	8
ZnCo [b]	0.1 M KOH	~ 0	~ 0	9
CoCo*	1 M KOH	~ 2.2	~ 30.8	1
CoCo * (exfoliated)	1 M KOH	~ 11	~ 154	1
CoMn*	1 M KOH	~ 43	~ 301	10
IrO_2*	1 M KOH	~ 16	~ 112	10

* Ohmic-drop correction, [a] loaded on carbon paper, [b] loaded on Ni foil

Supplementary references

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