Supporting Information

Ultrasmall and Atomically Monodisperse Nickel Nanoclusters as Highly Active Electrocatalysts for Water Oxidation

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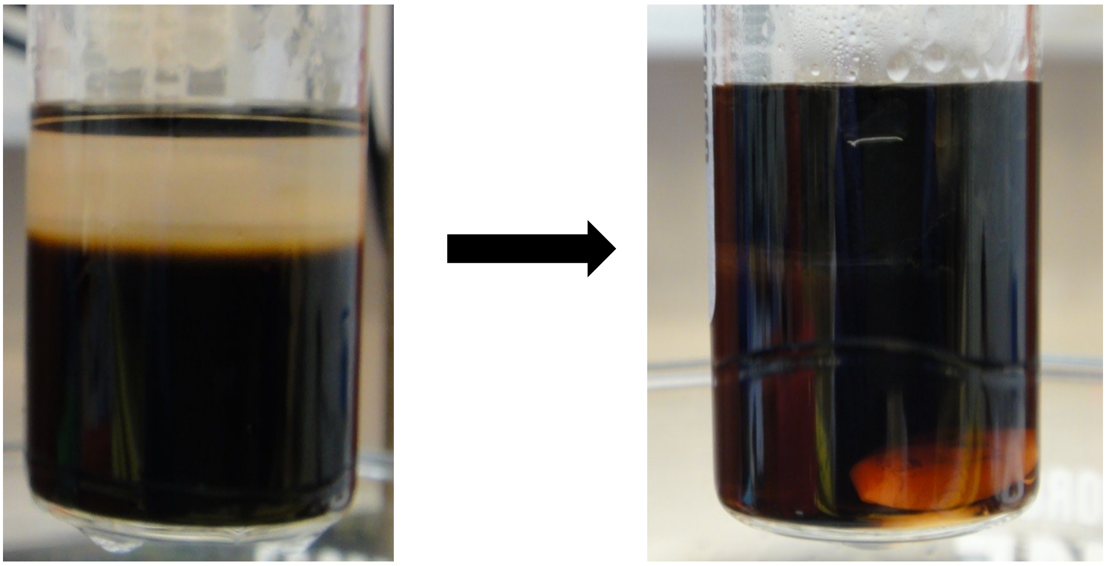

Figure S1. Color change of the solution after phase transfer from Ni-GSH into Ni_4PET_8.

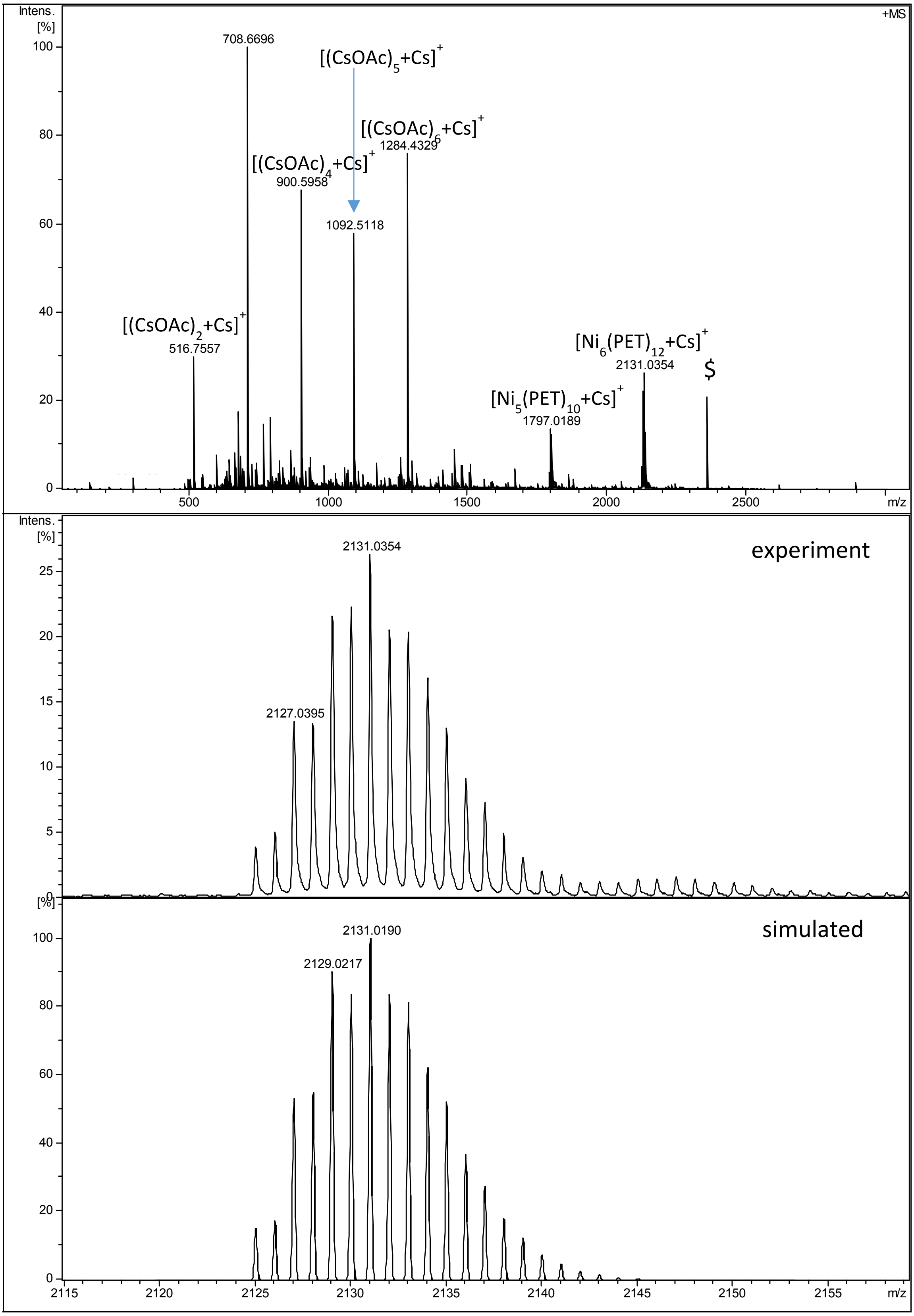

Figure S2. Electrospray mass spectrum of the synthesized PET ligated Ni nanoclusters. Several peaks were found to be due to polymerization of the cesium acetate used for charging clusters as labeled in the spectrum. The peak at *m/z* ~2131.03 assigned to Ni cluster with Cs adduct, i.e.,

$[Ni_6(PET)_{12} + Cs]^+$. Good agreement between the simulated mass spectrum for $[Ni_6(PET)_{12} + Cs]^+$ with the experimental data and the presence of another fragment peak$[Ni_5(PET)_{10} + Cs]^+$ confirming the cluster is indeed $[Ni_6(PET)_{12} + Cs]^+$.

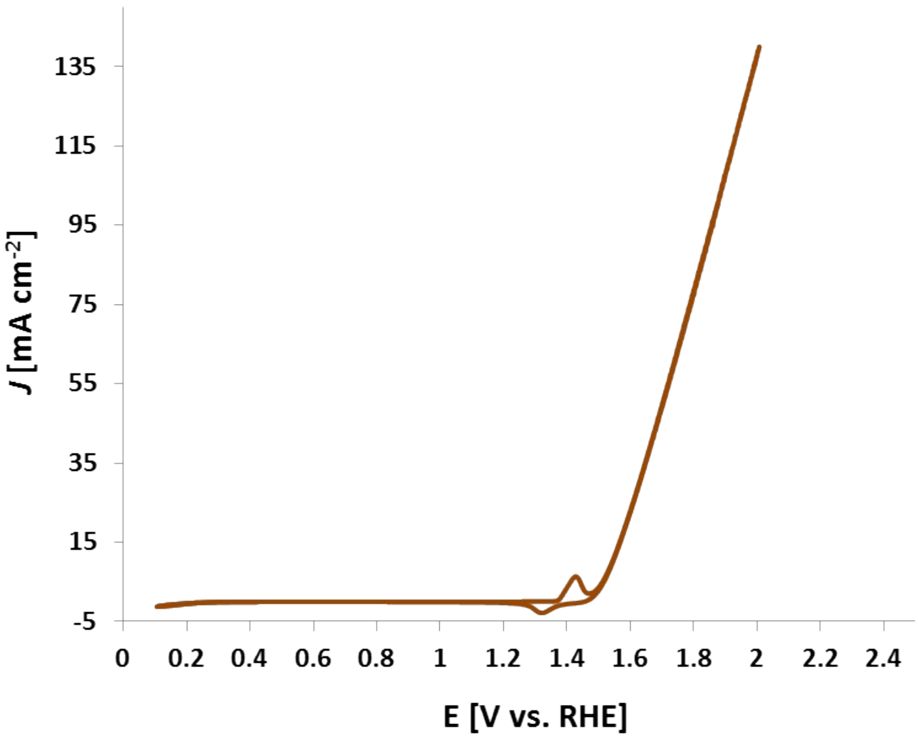

Figure S3. Full scale cyclic voltammetry (CV) curve for the $Ni_4(PET)_8$ in 0.1 M KOH solution.

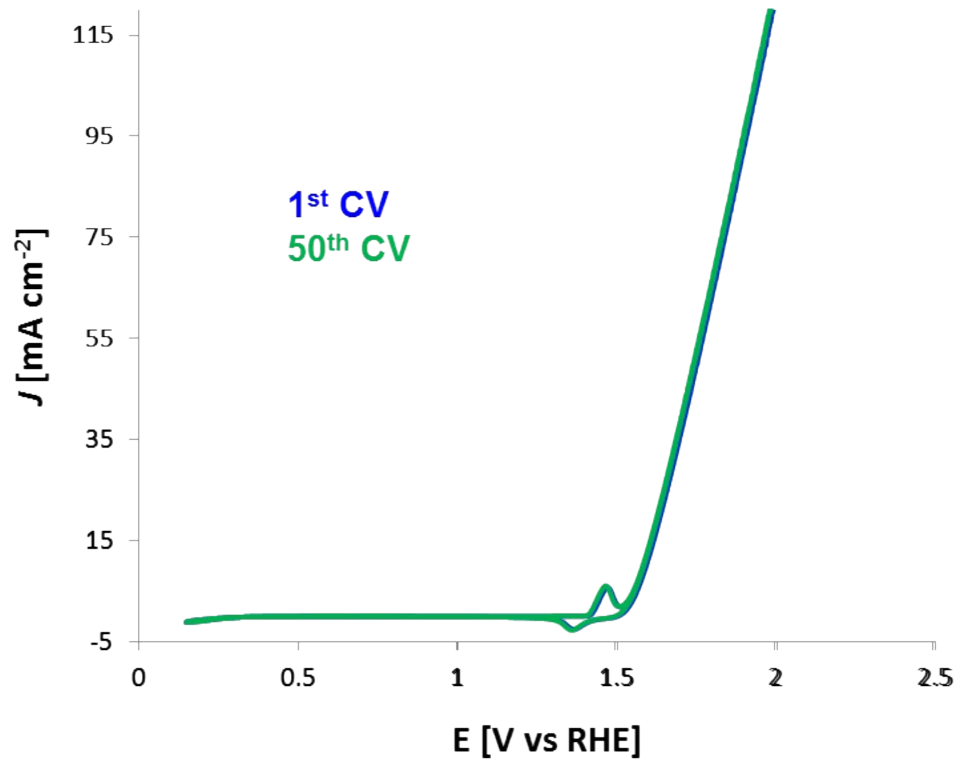

Figure S4. Concurrent 1st and 50th cyclic voltammetry sweeps for the $Ni_4(PET)_8$ in aqueous 0.1 M KOH.

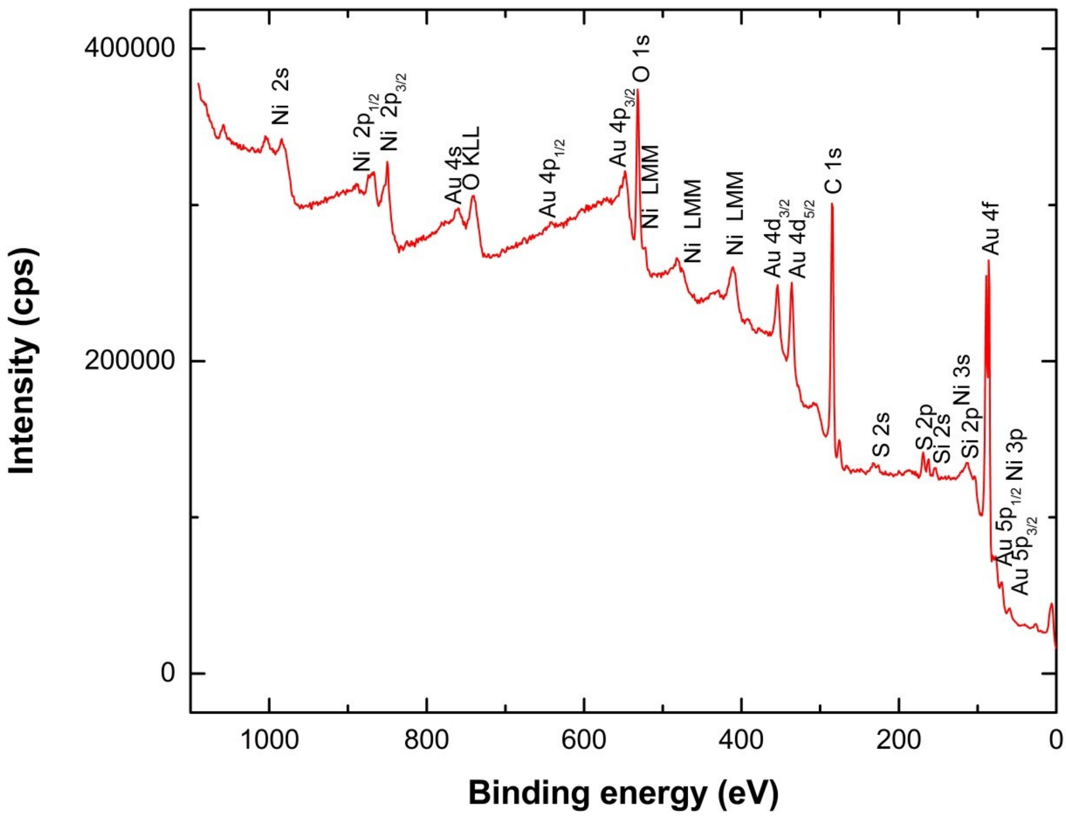

Figure S5. XPS Survey spectra of $Ni_6(PET)_{12}$ NCs after 30 cycles of cyclic voltammetry.

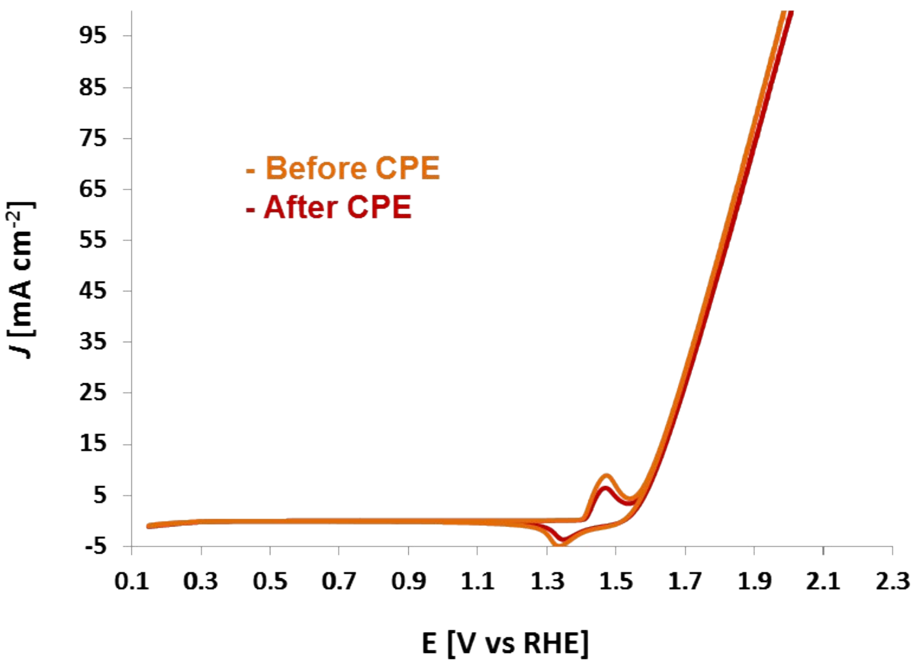

Figure S6. Cyclic voltammetry curves for $Ni_6(PET)_{12}$ before and after long-term CPE operation in aqueous 0.1 M KOH.

Structural details for $Ni_4(PET)_8$ and $Ni_6(PET)_{12}$

Supplementary Table S1. Crystal data and structure refinement conditions for $Ni_4(PET)_8$

Identification code	$Ni_4(PET)_8$
$D_{calc.}$/ g cm^{-3}	1.450
μ/mm^{-1}	4.233
Formula Weight	1332.53
Colour	black
Shape	irregular
Max Size/mm	0.25
Mid Size/mm	0.15
Min Size/mm	0.12
T/K	140(1)
Crystal System	triclinic
Space Group	P-1
a/Å	12.9570(9)
b/Å	15.3918(10)
c/Å	16.9527(11)
α/°	86.571(2)
β/°	70.541(2)
γ/°	73.400(2)
V/Å^3	3052.6(4)
Z	2
Z'	1
Θ_{min}/°	3.771
Θ_{max}/°	66.643
Measured Refl.	36951
Independent Refl.	10539
Reflections Used	9930
R_{int}	0.0264
Parameters	685
Restraints	0
Largest Peak	0.416
Deepest Hole	-0.370
GooF	1.025
wR_2 (all data)	0.0639
wR_2	0.0626
R_1 (all data)	0.0260
R_1	0.0244

Supplementary Table S2. Crystal data and structure refinement conditions for $Ni_6(PET)_{12}$	
Identification code	$Ni_6(PET)_{12}$
$D_{calc.}$/ g cm^{-3}	1.475
μ/mm^{-1}	4.999
Formula Weight	2168.65
Colour	black
Shape	irregular
Max Size/mm	0.18
Mid Size/mm	0.12
Min Size/mm	0.09
T/K	100(2)
Crystal System	triclinic
Space Group	P-1
a/Å	11.1685(11)
b/Å	12.4485(12)
c/Å	18.1823(18)
$\alpha/^{\circ}$	77.032(4)
$\beta/^{\circ}$	82.429(4)
$\gamma/^{\circ}$	89.334(4)
V/Å^3	2441.5(4)
Z	1
Z'	0.5
$\Theta_{min}/^{\circ}$	2.516
$\Theta_{max}/^{\circ}$	66.751
Measured Refl.	23227
Independent Refl.	8407
Reflections Used	7717
R_{int}	0.0304
Parameters	541
Restraints	15
Largest Peak	2.466
Deepest Hole	-2.985
GooF	1.063
wR_2 (all data)	0.1519
wR_2	0.1450
R_1 (all data)	0.0564
R_1	0.0520