

Supporting Information

Atomically monodisperse nickel nanoclusters as highly active electrocatalysts for water oxidation

*Khurram S. Joya,^{[a] ‡ *} Lutfan Sinatra,^{[b] ‡} Lina G. AbdulHalim,^[b] Chakra P. Joshi,^[b] Mohamed N. Hedhili,^[b] Osman M. Bakr^[b] and Irshad Hussain^{*,[c]}*

^a a. Department of Chemistry, University of Engineering and Technology, GT Road 54890, Lahore, Pakistan. E-mail: khurram_joya@uet.edu.pk

^b Solar and Photovoltaics Engineering Research Center, Division of Physical Sciences and Engineering, King Abdullah University of Science and Technology (KAUST), Thuwal 23955-6900, Saudi Arabia.

^c Department of Chemistry, SBA School of Science & Engineering (SBASSE), Lahore University of Management Sciences (LUMS), DHA, Lahore-54792, Pakistan.

‡ These authors have equal contribution

* Corresponding authors:

Irshad Hussain (ihussain@lums.edu.pk)

Khurram S. Joya (khurram_joya@uet.edu.pk)

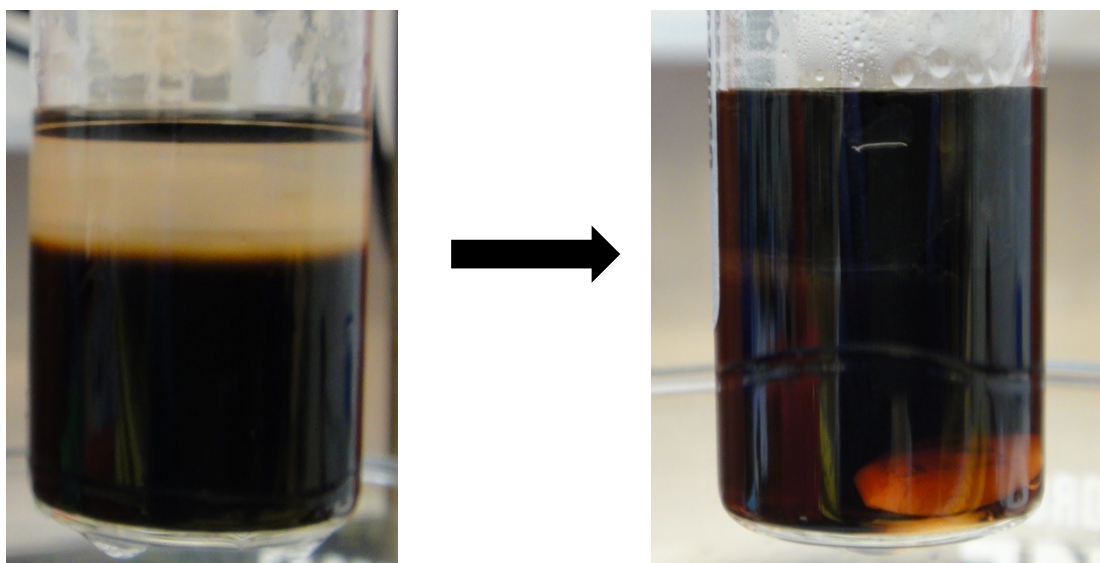


Figure S1. Color change of the solution after phase transfer from Ni-GSH into Ni₄PET₈.

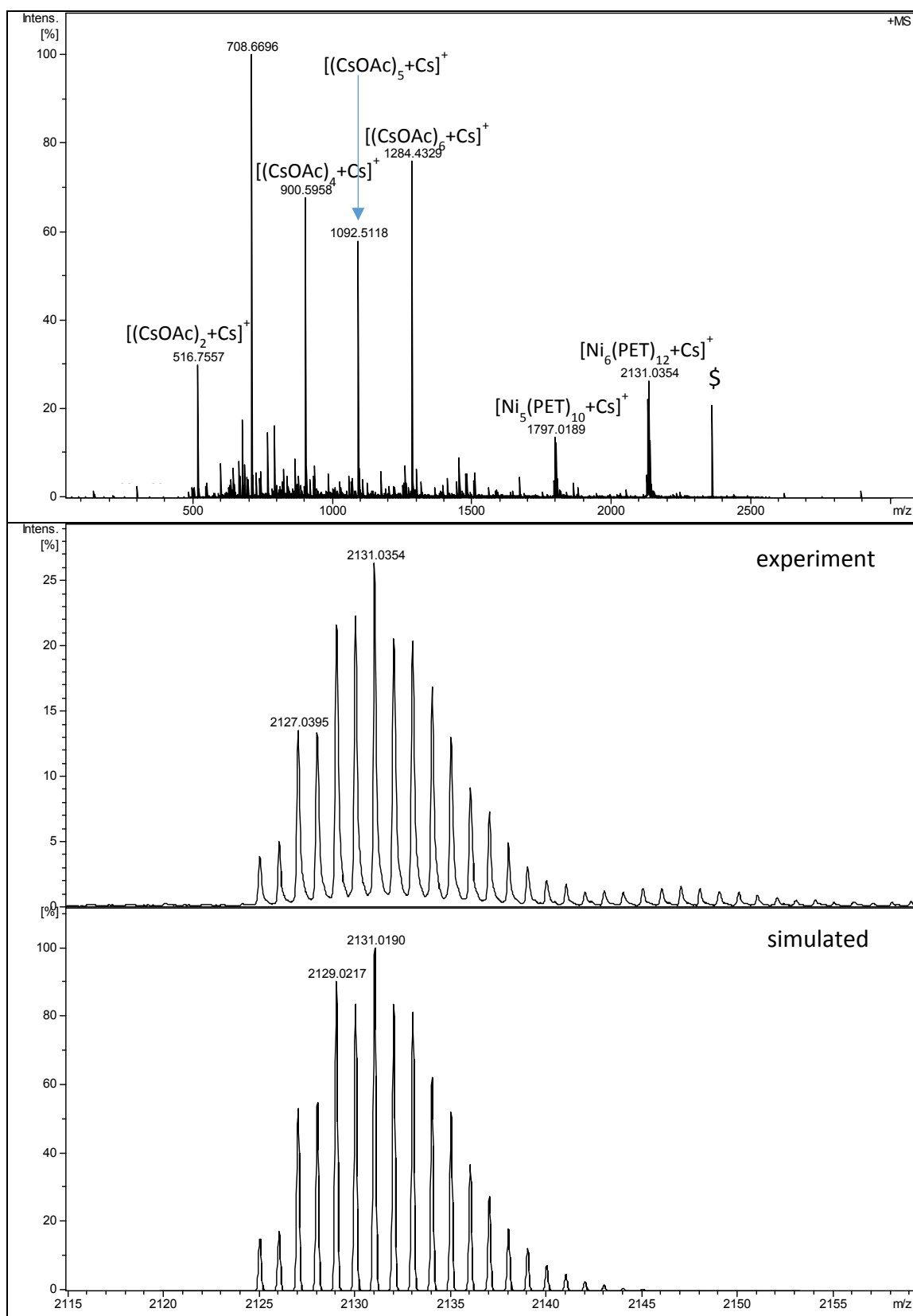


Figure S2. Electrospray mass spectrum of the synthesized PET ligated Ni nanoclusters. Several peaks were found to be due to polymerization of the cesium acetate used for charging clusters as labeled in the spectrum. The peak at $m/z \sim 2131.03$ assigned to Ni cluster with Cs adduct, i.e.,

$[\text{Ni}_6(\text{PET})_{12} + \text{Cs}]^+$. Good agreement between the simulated mass spectrum for $[\text{Ni}_6(\text{PET})_{12} + \text{Cs}]^+$ with the experimental data and the presence of another fragment peak $[\text{Ni}_5(\text{PET})_{10} + \text{Cs}]^+$ confirming the cluster is indeed $[\text{Ni}_6(\text{PET})_{12} + \text{Cs}]^+$.

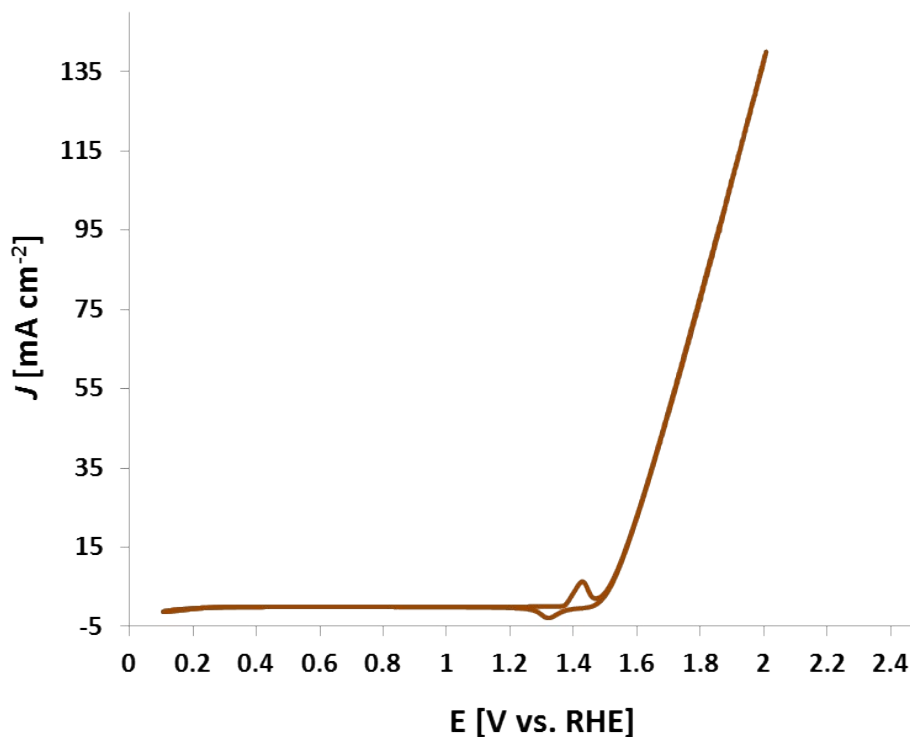


Figure S3. Full scale cyclic voltammetry (CV) curve for the $\text{Ni}_4(\text{PET})_8$ in 0.1 M KOH solution.

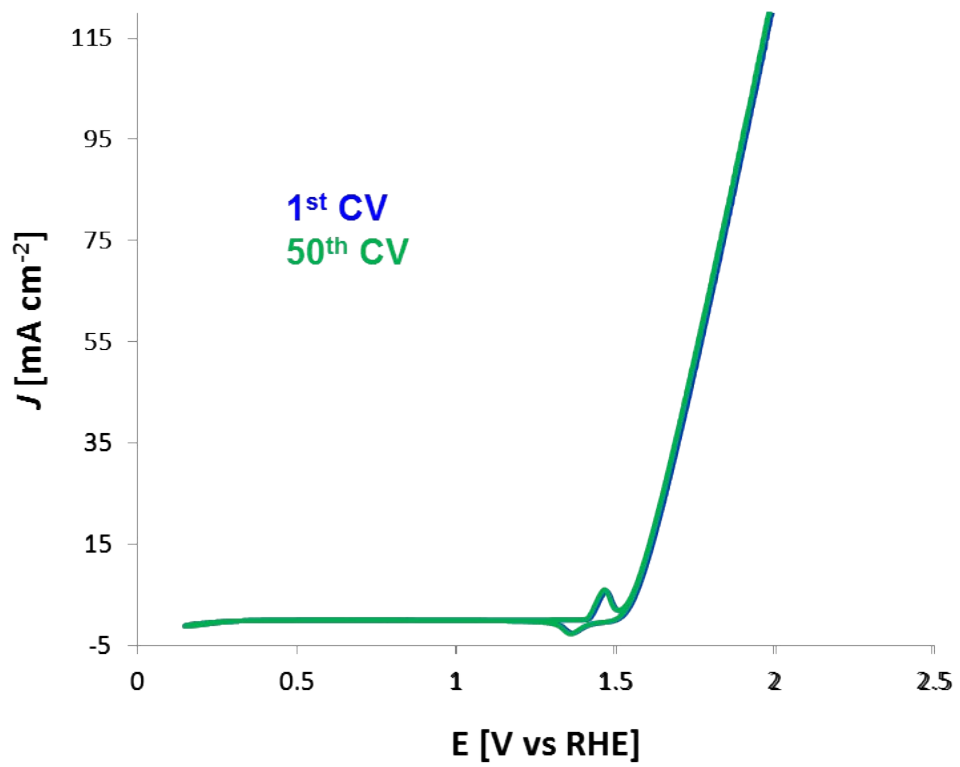


Figure S4. Concurrent 1st and 50th cyclic voltammetry sweeps for the $\text{Ni}_4(\text{PET})_8$ in aqueous 0.1 M KOH.

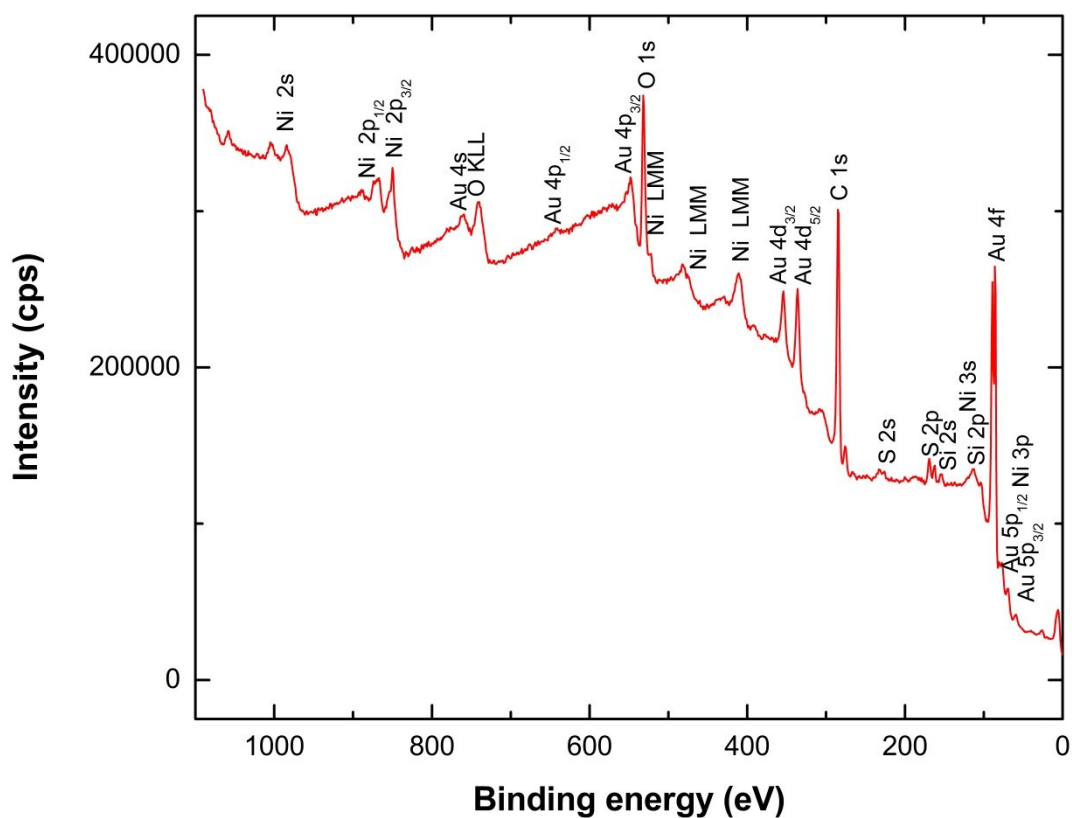


Figure S5. XPS Survey spectra of $\text{Ni}_6(\text{PET})_{12}$ NCs after 30 cycles of cyclic voltammetry.

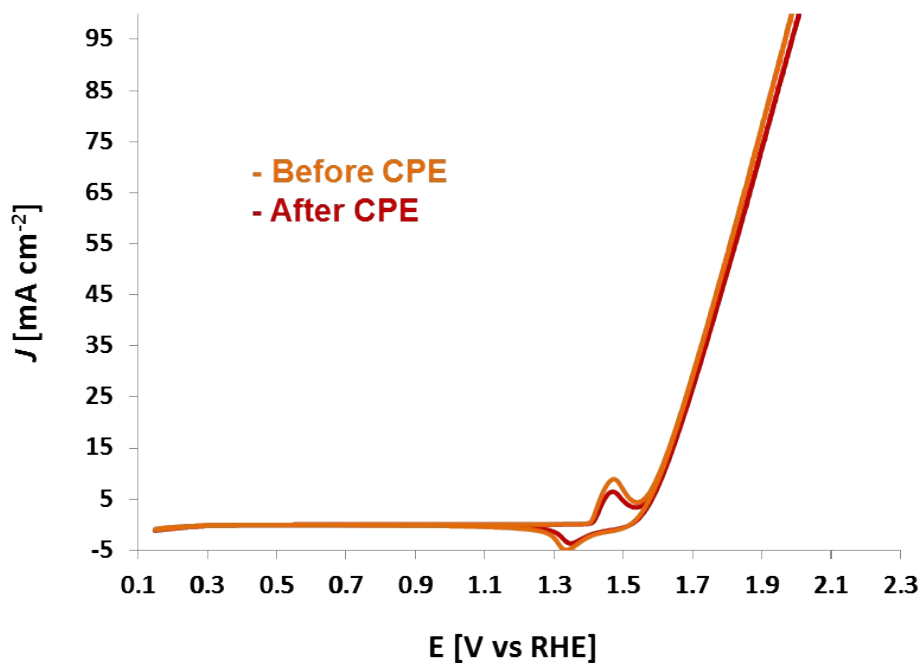


Figure S6. Cyclic voltammetry curves for $\text{Ni}_6(\text{PET})_{12}$ before and after long-term CPE operation in aqueous 0.1 M KOH.

Structural details for Ni₄(PET)₈ and Ni₆(PET)₁₂

Supplementary Table S1. Crystal data and structure refinement conditions for Ni ₄ (PET) ₈	
Identification code	Ni ₄ (PET) ₈
$D_{calc.}/\text{g cm}^{-3}$	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
$a/\text{\AA}$	12.9570(9)
$b/\text{\AA}$	15.3918(10)
$c/\text{\AA}$	16.9527(11)
$\alpha/^\circ$	86.571(2)
$\beta/^\circ$	70.541(2)
$\gamma/^\circ$	73.400(2)
$V/\text{\AA}^3$	3052.6(4)
Z	2
Z'	1
$\theta_{min}/^\circ$	3.771
$\theta_{max}/^\circ$	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 Ni₆(PET)₁₂

Identification code	Ni ₆ (PET) ₁₂
$D_{calc.}/\text{g cm}^{-3}$	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
$a/\text{\AA}$	11.1685(11)
$b/\text{\AA}$	12.4485(12)
$c/\text{\AA}$	18.1823(18)
$\alpha/^\circ$	77.032(4)
$\beta/^\circ$	82.429(4)
$\gamma/^\circ$	89.334(4)
$V/\text{\AA}^3$	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