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Atomically Monodisperse Nickel Nanoclusters as Highly Active Electrocatalysts for Water Oxidation

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Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Achieving water splitting at low overpotential with high oxygen evolution efficiency and stability is important for realizing solar to chemical energy conversion devices. Herein we report the synthesis, characterization and electrochemical evaluation of highly active nickel nanoclusters (Ni NCs) for water oxidation at low overpotential. These atomically precise and monodisperse Ni NCs are characterized by using UV-visible absorption spectroscopy, single crystal X-ray diffraction and mass spectrometry. The molecular formulae of these Ni NCs are found to be Ni₄(PET)₈ and Ni₆(PET)₁₂ and are highly active electrocatalysts for oxygen evolution without any pre-conditioning. Ni₄(PET)₈ are slightly better catalysts than Ni₆(PET)₁₂ and initiate the oxygen evolution at an amazingly low overpotential of ~1.51 V (vs RHE; η ≈ 280 mV). The peak oxygen evolution current density (J) of ~150 mA cm⁻² at 2.0 V (vs. RHE) with a Tafel slope of 38 mV dec⁻¹ is observed using Ni₄(PET)₈. These results are comparable to the state-of-the-art RuO₂ electrocatalyst, which is highly expensive and rare compared to Ni-based materials. Sustained oxygen generation for several hours with an applied current density of 20 mA cm⁻² demonstrates the long-term stability and activity of these Ni NCs towards electrocatalytic water oxidation. This unique approach provides a facile method to prepare cost-effective, nanoscale and highly efficient electrocatalysts for water oxidation.

Introduction

Scientific and political communities have recently been prompted by the demand to develop technologies for alternative fuel generation and greener energy supplies.^{1, 2} Catalytic water oxidation processes driven by electrochemical or photoelectrochemical approaches to produce hydrogen and oxygen, with high efficiency and at a moderate overpotential, are attractive options in the pursuit of alternative fuels and solar to chemical energy conversion systems.³⁻⁵ The electrons and protons released from water oxidation reaction can also be combined with CO₂ to reduce it directly into liquid fuels like methanol or formic acid.^{6, 7} Therefore, this concept provides a route to renewable and alternative energy supplies to be obtained from abundant water and enormous sunlight available on earth.^{6, 8} But water oxidation is

an energy intensive reaction and requires a minimum of 1.23 V (vs RHE) for its initiation. Thus, the development of efficient water oxidation electrocatalysts (WOEC) is considered as a formidable challenge.⁹ Recently, many molecular complexes, transition metals oxides and inorganic materials have been explored for water oxidation under electrochemical conditions.⁹⁻¹³ Owing to the difficulties in the abstraction of four electrons from two water molecules and subsequent formation of an O–O bond, this process poses a great challenge to find a state of the art water splitting system.^{14, 15} Therefore, there is a continuous effort to develop stable and robust catalytic material for water splitting that could be produced from economical and earth abundant materials, while operating at a modest overpotential and with a high oxygen evolution current density.^{16, 17}

Noble metals based electrocatalysts such as ruthenium oxide (RuO₂) and iridium oxide (IrO₂) are benchmark materials for water splitting reaction.¹⁸⁻²⁰ However, due to limited supply and high cost, these precious metal oxides are not feasible to be implemented in water electrolysis setup for large scale industrial applications. Several efforts have been made to demonstrate the use of first row transition metal oxides that are cheaper and easily available for developing WOEC.²¹ Several Co-oxide and Ni-oxide based water splitting electrocatalysts are generated *via* electrodeposition from neutral and near-neutral phosphate, carbonate and borate buffers.^{22, 23} But these catalytic materials show higher onset potential for oxygen evolution reaction (OER), exhibit low stability under electrochemical conditions and slow catalytic rates.²⁴ Moreover, these catalytic materials have bulk structure and require a continuous presence of metal ions in the electrolyte during the

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† Footnotes relating to the title and/or authors should appear here. Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

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electrodeposition phase and catalytic run for sustained water oxidation.^{22, 25} Designing the catalytic materials of sub-nanometer dimensions may facilitate both mass transport and charge transfer during the catalysis process due to shorter electron-transfer distances and offer a high surface-to-volume ratio, enabling a fast kinetics for oxygen evolution mechanism.²⁶ Nanosizing is also projected to impose a cathodic shift in the oxygen evolution onset potential and improving catalytic material performance for electrochemical water oxidation.^{26, 27} Therefore, the development of cost-effective and earth-abundant nanoscale catalytic materials is highly desired, which can perform well for water electrooxidation in metal ions free electrolyte system.

In the pursuit of cheaper and abundant materials, transition metals, especially nickel based electrocatalysts, have been a subject of a lot of studies on WOEC due to their high stability and good OER activities.²⁸⁻³⁵ Meanwhile, nanostructuring of such catalysts has also emerged as an important strategy to improve their catalytic performance.³⁵ While many studies are focusing on the Ni based nanoparticles, there are no reports on using very small and atomically precise nickel based electrocatalyst known as *metal nanoclusters (NCs)*. Here, metal NCs refers to the nanocrystals with diameter/size typically less than 2 nm. Metal NCs are composed of discrete number of metal atoms in the core and surrounded with specific number of ligand molecules.³⁶ Due to their very small size, unique composition and atomic arrangement, NCs have shown unique optical, electronic and chemical properties different from their counterpart (nanoparticles or bulk material).³⁷ For example, thiol protected gold NCs [Au₂₅(SCH₂CH₂Ph)₁₈]⁻. They compose of 25 atoms of Au in icosahedral structure protected with 18 molecules of 2-Phenylethanethiol have shown unique discrete energy level of electrons, which make them catalytically active for CO oxidation.³⁸ Atomically precise metal nanoclusters (NCs) protected with organic ligands have emerged as interesting materials for optoelectronics, magnetic materials and catalysis.^{39, 40} Lately, Au, Ag and Pt NCs with different sizes also have been synthesized and used for photocatalytic applications.^{41, 42} However, there are very limited reports on the use of metals NCs immobilized on conducting surfaces for electro- and photocatalysis.⁴³

Herein we report the use of well characterized Ni NCs, Ni₄(PET)₈ and Ni₆(PET)₁₂ for anodic oxygen evolution reactions, demonstrating an example of efficient nanocrystals based electrocatalytic system for water oxidation. Exploitation of synthesized Ni NCs involves coating their thin film over electrode surface *via* simple drop casting that was later evaluated for oxygen evolution performance. Under electrochemical and catalytic water oxidation condition, the electrode surfaces modified with Ni₄(PET)₈ and Ni₆(PET)₁₂ showed remarkably low overpotential for oxygen generation onset. These Ni NCs coated electrode surfaces were also found to be very stable in alkaline conditions sustaining high current density for long-term water electrooxidation experiments under catalytic conditions. To activate the catalytic layer on anode, no annealing, pre-conditioning or electrochemical-treatment is required.

Experimental Section

Materials and methods. Nickel (II) Acetylacetonate [Ni(acac)₂; (Ni(C₅H₇O₂)₂), ≥95%, Sigma-Aldrich], Nickel (II) Chloride Hexahydrate (NiCl₂·6H₂O, 99.999%, Acros Organics), Tetraoctylammonium bromide/TOABr ([CH₃(CH₂)₇)₄NBr, 98%, Aldrich), L-Glutathione

(GSH) (C₁₀H₁₇N₃O₆S, reduced, 97%, Alfa Aesar), Sodium borohydride (NaBH₄, ≥98.0%, Sigma-Aldrich), and 2-Phenylethanethiol (PET; C₆H₅CH₂CH₂SH, 98%, Sigma-Aldrich) were used as received without further purification. Toluene (HPLC grade, Fisher Scientific), Tetrahydrofuran (THF), Dichloromethane (DCM), acetone, methanol, and ethanol absolute (≥99.8%, Sigma-Aldrich) were also used as received for cleaning and preparing the solution. Nanopure water (18.2 MΩ cm) was used in all experiments that involve water.

Synthesis of Ni₄(PET)₈. Synthesis of Ni₄(PET)₈ NCs was done using size-focusing method which was developed for Au₃₈(PET)₂₄ nanoclusters⁴⁴ with slight modification. In a typical synthesis procedure, 0.5 mmol of nickel(II) acetylacetonate and 2.0 mmol of glutathione (GSH) were mixed with 20 mL of acetone in a 40 mL glass vial under vigorous stirring. After 20 min of stirring, the glass vial was cooled to 0 °C using ice bath. After 20 min, 5 mmol of aqueous NaBH₄ (~6 mL) as reducing agent was added rapidly to the cooled reaction mixture under vigorous stirring that produced a dark-brown suspension, possibly nickel-glutathione (Ni-GSH) complex. Ni-GSH suspension was observed sticking on the wall of the glass vial in a few seconds after reduction. After 30 min, the clear acetone supernatant was removed from the glass vial and replaced with 6 mL of water to dissolve the Ni-GSH which was sticking on the glass vial.

The obtained 6 mL of aqueous Ni-GSH complex was mixed with 2 mL of ethanol, 2 mL of toluene, and 2 mL of PET in a glass vial under stirring at 1000 rpm and heating at 80°C. After several minutes, phase transfer of Ni-GSH from aqueous phase into toluene can be observed. This indicates the replacement of glutathione with the incoming ligand PET. The reaction was kept stirred overnight to ensure a complete transfer and formation of stable Ni₄(PET)₈ NCs. After stopping the reaction, the color of the upper solution (toluene) becoming dark-reddish solution and the color of the lower solution (water/ethanol) becoming more transparent brownish solution. (See Figure S1 in the supporting information). The obtained Ni₄(PET)₈ clusters were washed with methanol to remove the reaction by-products and excess thiol. Pure Ni₄(PET)₈ NCs, ~50 mg, were then extracted with 5 mL of toluene or DCM as required for further use.

Synthesis of Ni₆(PET)₁₂. Synthesis of Ni₆(PET)₁₂ NCs was done following the previously reported method.⁴⁵ In a typical synthesis, 0.42 mmol of NiCl₂·6H₂O and 0.89 mmol of tetraoctylammonium bromide (TOAB) were dissolved in 100 mL of tetrahydrofuran (THF). Afterwards, 2.17 mmol of PET was added to the above solution with stirring, followed by the addition of freshly prepared aqueous NaBH₄ (4.23 mmol, 14 mL water) that produced a dark-brown mixture, indicating the formation of Ni NCs. The dark-brown mixture was allowed to stir for 24 h and then concentrated by removing THF using rotary evaporator. The concentrated product was washed thrice with methanol and finally extracted into 10 mL of DCM or toluene as required for further use. The final amount pure (PET)₁₂ NCs obtained was about 125 mg.

Crystallization of Ni NCs. Equal volume of ethanol and the obtained Ni NCs were placed in a small glass vial inside a fume hood for slow evaporation under ambient conditions. Needle-like crystals were formed within 1-5 days, which were carefully separated and washed before single-crystal X-ray diffraction measurement. In order to obtain a better crystal, the crystals obtained from the first attempt were cleaned and placed in a new vial and then re-dispersed in toluene or DCM. The same recrystallization process

was then repeated as mentioned above. The obtained crystals were selected for single crystal XRD measurement.

Characterization. UV-Vis absorbance spectra of Ni NCs were measured over the range 250–800 nm using Carry 6000i Spectrophotometry. Mass measurement of Ni NCs was carried out using Bruker MicroTOF-II and Bruker Ultraflex MALDI-TOF instruments. For ESI-MS, Ni NCs in toluene were mixed with 50 mM methanolic CsOAc solution in the ratio 1:1 (v/v) that was then injected into the ESI mass spectrometer at a flow rate of 300 $\mu\text{L/hr}$. Typical conditions for the data acquisition with the Bruker ESI microTOF under positive ionization mode are described below: Capillary voltage 4–4.5 kV, nebulizer gas 0.5 bar, and dry gas 5 L/min, mass range $m/z = 100$ –3000, and temperature 100 $^{\circ}\text{C}$. MALDI experiments were done in the reverse positive mode using Bruker Ultraflex MALDI-TOF instrument. Samples for MALDI were prepared by mixing matrix trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB, 10 mg/mL in toluene) with each purified Ni nanocluster in the ratio of 1:5 (v/v). Approx. 2 μL of this matrix-nanocluster mixture was then pipetted out and spotted on a MALDI target plate and allowed to dry under ambient conditions that was then used for the MALDI characterization. X-ray Single Crystal Diffraction data were collected using a Bruker APEX2 equipped with a Cu K α INCOATEC Imus micro-focus source ($\lambda = 1.54178$ Å). Indexing was performed using APEX2 (Difference Vectors method).⁴⁶ Data integration and reduction were performed using SaintPlus 6.01.⁴⁷ Absorption correction was performed by multi-scan method implemented in SADABS.⁴⁸ Space group were determined using XPREP implemented in APEX2. Using Olex2,⁴⁹ structure was solved using Direct Methods (SHELXS-97) and refined using SHELXL (full matrix least-squares minimisation on F2).⁵⁰ For XPS measurement, Ni₆(PET)₁₂ solution were drop-casted on Au film-coated glass slides. After that, cyclic voltammetry was performed to the catalyst on Au films-coated glass until reaching a stable current density. After cyclic voltammetry, the sample was cleaned with deionized water for several times. XPS measurement were carried out in a Kratos Axis Ultra DLD spectrometer equipped with a Mg K α x-ray source ($h\nu = 1253.6$ eV).

Electrochemical measurement. The two Ni NCs samples, Ni₄(PET)₈ and Ni₆(PET)₁₂ are functionalized on clean and polished glassy carbon (GC) electrode via drop casting from a 0.01 m mol stock solution in toluene. The so prepared electrode is dried in air under a cover and subjected to catalysis experiments. All the solutions for electrochemical measurements and electrodeposition were prepared in ultra-pure water (Millipore MilliQ®) and the electrochemical measurements were performed in deoxygenated aqueous solutions at room temperature. Prior to the water splitting investigations and before each measurement, the aqueous solutions were purged with high-purity argon (Linde Gas, 6.0) for at least 30 min to deoxygenate the solution. Cyclic voltammetry (CV) experiments were conducted in a three electrode configuration pyrex glass cell. The working electrodes (WE) in the CV's and catalytic water electrolysis experiments were a freshly mirror finished polished glassy carbon disc of 5.0 mm diameter, embedded in a PTFE shroud, and ITO coated glass substrates (1 cm x 2.5 cm, exposed surface area 1.0 cm²). The catalytic water electrolysis and oxygen evolution measurements were carried out in a three electrode double junction H-type glass cell where the counter electrode chamber was separated by a very fine porosity glass frit. Platinum wire (thickness: 1 mm), shaped into a spiral, was used as a counter electrode (CE). A silver-silver chloride reference electrode (SSCE: Ag/AgCl/KCl) was applied for the investigations in the neutral

and higher pH aqueous solutions. All potentials are referred to reversible hydrogen electrode (RHE). Cyclic voltammetry (CV) experiments were performed with an Autolab PG-stat10 potentiostat controlled by GPES-4 software. Spiral platinum counter electrodes were flame annealed and washed with pure water before placing them into the cell.¹¹

Online oxygen measurements. Oxygen evolution during electrocatalysis was monitored with a calibrated oxygen electrode connected with a digital O₂ meter (YSI, Inc., Model 550A). Further oxygen evolution was characterized by online gas chromatographic (GC) measurements using micro-GC, T-3000 SRI instruments. The gas mixture from the cell was delivered directly to the sampling loop of a gas chromatograph. Sampling points were collected every 10 minutes, and the gaseous products were analyzed using a packed MolSieve 5A coupled with a thermal conductivity detector (TCD). Ar (99.9999%) was used as the carrier gas during the GC analysis.

Results and Discussion

For demonstrating metal clusters as efficient electrocatalyst for water splitting, we synthesized and well characterized two different Ni NCs, Ni₄(PET)₈ and Ni₆(PET)₁₂. After the synthesis, these Ni NCs were purified for further experiment. Both Ni NCs share many optical features such as intense absorption peaks at ~ 340 nm and 420 nm (Figure 1). Another broad absorption peak at ~ 550 nm was also observed in both Ni NCs. However, careful look may reveal a slight shift in peak features of Ni₄(PET)₈ compared to those of Ni₆(PET)₁₂. The multiple absorption features associated with these Ni NCs may have originated from the electronic transitions within a metal core that usually happens in metal nanoclusters in the size range of 1–2 nm.⁵¹ These multiple absorption features provided the first clue that the size of these synthesized Ni NCs are <2 nm in size.

Figure 1. UV-visible absorption spectra of the Ni₄(PET)₈ and Ni₆(PET)₁₂ NCs. Inset: photograph of the actual solution of these clusters dispersed in toluene.

Purified Ni NCs were characterized using mass spectrometry to establish their identity. The matrix assisted laser desorption ionization (MALDI) mass spectra of these Ni clusters using trans-2-[3-(4-tertbutylphenyl)-2-methyl-2-propenylidene] malononitrile

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(DCTB) matrix is shown in **Figure 2**. Clearly, MALDI peak at ~ 2000 m/z corresponds to $\text{Ni}_6(\text{PET})_{12}$ composition. This composition was further confirmed using high-resolution electrospray ionization mass spectrometry (ESI-MS) as described in **Figure S2** (see SI). The simulated mass spectrum for $[\text{Ni}_6(\text{PET})_{12} + \text{Cs}]^+$ was found to match with the experimental mass peak at $m/z \approx 2131$ confirming the NC composition as $\text{Ni}_6(\text{PET})_{12}$. Other ESI mass peak at $m/z \approx 1797$ was attributed to the loss of $\text{Ni}(\text{PET})_2$ fragments from the molecular ion peak. These information from the mass spectrometry measurement confirmed that the synthesized Ni NCs i.e., $\text{Ni}_6(\text{PET})_{12}$ are monodispersed and neutral. We used cesium acetate for ESI mass characterization of NCs in order to facilitate the ionization of neutral $\text{Ni}_6(\text{PET})_{12}$. The appearance of several intense mass peaks in the ESI spectrum was found to be due to the polymerization of the CsOAc as described in **Figure S2**.

Figure 2. MALDI spectra of the Ni NCs $\text{Ni}_4(\text{PET})_8$ and $\text{Ni}_6(\text{PET})_{12}$ using DCTB matrix.

To further confirm the structure/composition of these Ni NCs, we crystallized $\text{Ni}_6(\text{PET})_{12}$ and characterized *via* single crystal X-ray diffraction. The crystal structure proved our deduction from the mass measurement that the compound is $\text{Ni}_6(\text{PET})_{12}$. We could not detect counter-ions in the X-ray structure of $\text{Ni}_6(\text{PET})_{12}$, thus confirming our prediction that the cluster is neutral. Similar process was applied to another sample of Ni NCs, whose MALDI peak $m/z \sim 1350$ suggested a smaller size NCs than $\text{Ni}_6(\text{PET})_{12}$ cluster. The 2nd Ni NCs sample was assigned to be $\text{Ni}_4(\text{PET})_8$. Although there are high mass peaks, we suspect these peaks arise due to the rearrangement of fragments of Ni NCs in the gas phase. To ascertain our assignment, we also crystallized $\text{Ni}_4(\text{PET})_8$ and performed a single crystal X-ray measurement. The single-crystal structure shown in **Figure 3** unequivocally proved that the cluster composition is indeed $\text{Ni}_4(\text{PET})_8$. We could not detect any counter-ion in the X-ray structure confirming Ni_4 clusters are also neutral. **Figure 3** shows the molecular structure of Ni_4 and Ni_6 NCs resolved from single crystal XRD. These structures clearly indicate the presence of 4 and 6 nickel centers in the $\text{Ni}_4(\text{PET})_8$ and $\text{Ni}_6(\text{PET})_{12}$ samples. The deduced structures of the Ni NCs are in agreement with mass spectroscopy measurement and confirm that these synthesized Ni NCs are indeed $\text{Ni}_4(\text{PET})_8$ and $\text{Ni}_6(\text{PET})_{12}$.

Electrochemical cyclic voltammetry (CV) measurements for studying catalytic water oxidation performance of these Ni NCs samples $\text{Ni}_4(\text{PET})_8$ and $\text{Ni}_6(\text{PET})_{12}$ coated on a clean glassy carbon (GC) electrode are shown in **Figure 4a**. For a comparison, we also performed the same experiments for other well-known anodically prepared Ni-derived electrocatalysts such as Ni-Bi (electrodeposited from Ni^{2+} in borate electrolyte; pH=9.2),²² Ni-Ci (electrodeposited from $\text{HCO}_3^-/\text{CO}_2$ system containing Ni^{2+} ; pH $\approx$ 7)⁶ and anodically prepared NiO_x layer on a thin film Ni sample in alkaline solution (**Figure 4b**).⁵² The anodic potential sweep for electrocatalytic $\text{Ni}_6(\text{PET})_{12}$ system shows the oxidation pre-features at about 1.39–1.51 V (green line in **Figure 4a**). This oxidative current is indicative of the oxidation of Ni sites to nickel oxide species leading to active catalyst structure.⁵² Most probably the oxidation wave is due to the single electron oxidation of $\text{Ni}^{2+}/\text{Ni}^{3+}$.⁶ Furthermore, the Ni^{2+} oxidation state is assigned to the reversible $\text{Ni}(\text{OH})_2/\text{NiOOH}$ redox reaction that is observed previously within same potential range.^{53–55} The formation of NiOOH phase is considered as the active electrocatalyst for water oxidation. How quickly it is formed from NiO_x induce the overpotential change of the oxygen evolution reaction.

Figure 3. Molecular structure of (a) $\text{Ni}_4(\text{PET})_8$ and (b) $\text{Ni}_6(\text{PET})_{12}$ samples resolved from single crystal X-Ray Diffraction.

It is also notable that no pre-conditioning is required here to obtain the high oxidation state Ni-oxide as reported to be essential for many nickel based catalysts.⁵² This oxidative current wave, after a decline, is quickly followed by a large catalytic current rise, indicating oxygen onset current during water oxidation reaction, at just ~ 1.53 V (vs RHE; $\eta \approx 300$ mV) as presented in the enlarged view of CV (inset, **Figure 4a**). Notably, there is a very small potential interval between Ni oxidation and the generation of oxygen onset current which is observed for many Ni based materials under electrochemical conditions.^{21, 52} The catalytic current, after a sharp onset, reaches a value of > 75 mA cm^{-2} at just 1.88 V (vs RHE). The backward sweep produces a reduction wave below 1.41 V, and there were no major current hysteresis excluding the involvement of kinetic barriers during catalysis operation. Interestingly, the CV signatures of $\text{Ni}_4(\text{PET})_8$ NCs sample reveals the sharp rise in the oxidation current for oxygen onset at just ~ 1.51 V (vs RHE; $\eta \approx 280$ mV). This is very unique for $\text{Ni}_4(\text{PET})_8$ NCs and lowest for a nickel

based water oxidation electrocatalyst material. However, similar anodic oxidation features are observed for the tetra-atomic Ni-NCs between 1.39–1.50 V (black line in **Figure 4a**). In case of $\text{Ni}_4(\text{PET})_8$ NCs, there is a much smaller potential gap from Ni oxidation wave to the oxygen onset current relative to the $\text{Ni}_6(\text{PET})_{12}$. This might be associated with the faster electron-transfer in smaller sized $\text{Ni}_4(\text{PET})_8$ NCs compared to that of $\text{Ni}_6(\text{PET})_{12}$ based electrocatalytic system.

Figure 4. (a) Cyclic voltammetry (CV) curves for the two Ni NCs samples $\text{Ni}_4(\text{PET})_8$ and $\text{Ni}_6(\text{PET})_{12}$ on GC anode in 0.1 M KOH solution. (Inset shows the magnified view of the CVs showing anodic pre-features and onset of catalytic currents for $\text{Ni}_4(\text{PET})_8$ and $\text{Ni}_6(\text{PET})_{12}$ samples). (b) CVs for different Ni-derived water oxidation electrocatalysts and for the Ni nanocluster $\text{Ni}_6(\text{PET})_{12}$ sample in 0.1 M KOH solution. (CV's are conducted at a scan rate: 20 mV sec⁻¹).

For $\text{Ni}_4(\text{PET})_8$ NCs, a peak oxygen evolution current density of $\sim 150 \text{ mA cm}^{-2}$ is achieved at about 2.0 V (vs. RHE (**Figure S3**)). The enlarged view of CVs (inset, **Figure 4a**) clearly shows 20 mV difference in the onset potential for $\text{Ni}_6(\text{PET})_{12}$ @ 1.53 V and $\text{Ni}_4(\text{PET})_8$ @ 1.51 V (vs RHE). The lower oxygen evolution onset potential for $\text{Ni}_4(\text{PET})_8$ nanocluster is attributed to the small nanoscale size of the tetra-nickel cluster and unique atomic arrangement and crystal structure of the nanocluster (**Figure 3a**). The Ni-derived electrodeposited electrocatalysts (Ni-Bi, Ni-Ci and anodically prepared NiOx thin film) show oxygen onset above 1.60 V (vs RHE) in the presence of same electrolyte (**Figure 4b**). This

behaviour shows that Ni NCs derived electrocatalysts presented here are much superior in their performance and activity for water oxidation compared to other Ni-based materials. In addition, the repetitive potential sweeps (forward and backward) for the surface assembled Ni NCs catalyst regenerates the similar current signatures during the 1st and 50th CV's indicating excellent stability and robustness of the catalytic system, with no noticeable degradation or loss of performance of the catalytic system under anodic electrochemical condition (**Figure S4**). In order to further validate our data for superior water oxidation performance by surface assembled Ni NCs and to exclude any involvement of iron contamination in the catalytically active species that might be associated with high activities,^{56, 57} we performed X-ray photoelectron spectroscopic (XPS) measurement on the catalyst sample after water electrolysis experiment. The XPS survey spectrum of the catalyst sample using Mg K α x-ray source show that Ni, O, S, Si, Au and C elements are detected. (**Figure S5** in the SI) However the survey spectrum clearly show that there is no sign of Fe presence (the most intense peak Fe2p_{3/2} is expected to be around 710 eV binding energy) in the catalytic sample certifying the superior performance of pure Ni NCs for anodic water oxidation reaction.

Figure 5. Tafel plots (η vs $\log i$) obtained for electrocatalytic Ni NCs samples $\text{Ni}_4(\text{PET})_8$ and $\text{Ni}_6(\text{PET})_{12}$.

For 10% efficiency of the solar-to-fuel conversion system, a sustained current density of 10 mA cm^{-2} is a pre-requisite.⁵ The current density of 10 mA cm^{-2} for $\text{Ni}_6(\text{PET})_{12}$ sample is obtained at just 1.58 V (vs RHE). On the other hand, the $\text{Ni}_4(\text{PET})_8$ nanocluster reaches the 10 mA cm^{-2} current even at 1.56 V (vs RHE). Most of the activation barriers in water splitting and overpotential originate from slow kinetics of the oxygen evolution reaction. For a sustained and higher water oxidation rate, the electrocatalytic materials are required to operate over a narrow potential window with high current densities. Therefore we also measured the Tafel slope [Current – overpotential ($\log i$ vs η) plot] in oxygen evolution regime for the two Ni-NCs samples. Tafel slope of 60 mV dec^{-1} represents a proton-coupled electron transfer mechanism for water oxidation involving one electron oxidation coupled with one proton transfer simultaneously, but lower Tafel slope indicates a smaller potential window to acquire a current decade and it is more desirable in water oxidation catalysis. Both Ni NCs derived catalysts i.e.,

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$\text{Ni}_6(\text{PET})_{12}$ and $\text{Ni}_4(\text{PET})_8$ showed Tafel slopes around 40 mV dec^{-1} during OER in the current region of 0.1 mA cm^{-2} to 1 mA cm^{-2} (Figure 5). The small Tafel slope of 38 mV dec^{-1} for $\text{Ni}_4(\text{PET})_8$ derived water oxidation electrocatalyst, is quite comparable with that of RuO_2 , indicating excellent activity of the Ni NCs.⁵⁸

The preliminary electrochemical data, suggesting remarkable performance of the electrocatalysts $\text{Ni}_6(\text{PET})_{12}$ and $\text{Ni}_4(\text{PET})_8$ for water oxidation, led us to perform long-term catalytic performance and stability tests. Controlled-potential water electrolysis (CPE) and controlled-current electrolysis (CCE) studies are conducted in clean electrolyte solution for surface assembled Ni NCs derived electrocatalysts. For $\text{Ni}_4(\text{PET})_8$ derived electrocatalytic system, the long-term CPE at a mere 1.65 V vs RHE ($\eta \approx 420 \text{ mV}$) generated an excellent oxygen evolution current density approaching 14.5 mA cm^{-2} right from the beginning of the CPE test (Figure 6a). The oxygen evolution current density remains very stable and sustained over extended period of time. During more than 24 h of water electrolysis, a rich stream of oxygen bubbles kept coming out of the catalytic surface and there was no decrease in the catalytic performance. On the other hand, the CPE run for $\text{Ni}_6(\text{PET})_{12}$ based catalyst produced about 9.5 mA cm^{-2} current density initially (Figure 6a). There is a slight reduction in the oxygen evolution current in the beginning, which is ascribed to the bubble accumulation on the anode surface. The current gets stable after a while and remained constant for many hours during water oxidation catalysis. The electrochemical response of the $\text{Ni}_6(\text{PET})_{12}$ based catalyst before and after long-term CPE operations reproduced the CVs signature well indicating the excellent stability of the Ni-nanocluster (Figure S6). Online GC (Gas chromatography) measurement has confirmed the gas coming out of the catalytic surface is molecular oxygen. This performance is very remarkable for single metal derived water oxidation electrocatalysts that exhibit high activities for water oxidation showing high anodic current densities for oxygen evolution. The current density remained below $40 \mu\text{A cm}^{-2}$ for the blank electrode without electrocatalysts (Figure 6a).

We also employed constant-current electrolysis (chronopotentiometry) experiments to investigate the performance and stability of the $\text{Ni}_6(\text{PET})_{12}$ and $\text{Ni}_4(\text{PET})_8$ electrocatalysts. Stable current densities of 10 mA cm^{-2} and 20 mA cm^{-2} were selected and maintained throughout the water oxidation test, while monitoring the voltage response of the system at the same time to maintain high current densities. The potential of tetra-atomic Ni cluster during CCE remained amazingly stable for water oxidation at 10 mA cm^{-2} . A steady potential of 1.63 V (vs RHE) was preserved for long-time water electrolysis operation (Figure 6b). This is a very low potential to maintain a stable current of 10 mA cm^{-2} for a nickel metal based water oxidation material. For the $\text{Ni}_6(\text{PET})_{12}$ electrocatalyst system, the 10 mA cm^{-2} benchmark is achieved at slightly more potential than that of $\text{Ni}_4(\text{PET})_8$. A steady-state potential of $\sim 1.66 \text{ V}$ (vs RHE) is obtained over 8 h after oxidation experiment. Furthermore, we stepped up the current density to a higher regime, i.e. 20 mA cm^{-2} and the current density of 20 mA cm^{-2} was maintained with a mere increment of 40 mV . For both $\text{Ni}_6(\text{PET})_{12}$ and $\text{Ni}_4(\text{PET})_8$ derived electrocatalyst systems, there is no noticeable change in the potential and no observable catalytic degradation over the 8 h CCE test, indicating the superior stability and high catalytic activity of the Ni NCs for anodic water oxidation.

Figure 6. Extended period anodic water oxidation tests during (a) controlled-potential electrolysis using surface assembled two Ni NCs catalysts $\text{Ni}_4(\text{PET})_8$ and $\text{Ni}_6(\text{PET})_{12}$ in 0.1 M KOH solution at 1.65 V vs RHE; and (b) Long-term constant-current electrolysis of water for the two Ni NCs electrocatalyst at stable current densities $J=10 \text{ mA cm}^{-2}$ for $\text{Ni}_4(\text{PET})_8$ and $J=10 \text{ mA cm}^{-2}$ and 20 mA cm^{-2} for $\text{Ni}_6(\text{PET})_{12}$. (BL represents the blank experiment without the catalyst loading on the electrode surface).

A comparative analysis of the electrochemical performance of the benchmark Ni-derived water oxidation electrocatalysts, recently evolved, is presented in Table 1. Top in the table, the Ni NCs described in this study exhibit the lowest potential (E/V)/overpotential (η) [$\text{Ni}_4(\text{PET})_8$; E/V 1.51 vs RHE ($\eta = 280 \text{ mV}$) and $\text{Ni}_6(\text{PET})_{12}$; E/V 1.53 vs RHE ($\eta = 300 \text{ mV}$)] for the anodic oxygen onset relative to other highly active water oxidation catalysts. The NiOx based catalytic film obtained from molecular precursor reveals a moderate potential, E/V approximately 1.63 vs RHE, for water oxidation, however it shows a large Tafel slope of greater than 100 mV dec^{-1} .⁵⁹ The NiOx thin film (obtained from drop casting of solution precursor following annealing) and NiOx/ $\text{Ni}(\text{OH})_2$ spheres type electrocatalyst (prepared by hydrothermal method) show Tafel slopes of just around 40 mV dec^{-1} but they also exhibit high oxygen evolution potentials relative to these ultrasmall Ni nanoclusters i.e., $\text{Ni}_4(\text{PET})_8$ and $\text{Ni}_6(\text{PET})_{12}$.^{52, 60} The electrodeposited Ni-Ci (in $\text{HCO}_3^-/\text{CO}_2$ system; $\text{pH} \approx 7$) catalytic layer shows a much higher oxygen onset potential of 1.67 V vs RHE, whereas Ni-Bi (in borate electrolyte; $\text{pH} \approx 9.2$)²² exhibits the highest in the list exceeding 1.70 V vs RHE. However, Ni-Ci and N-Bi show medium range Tafel slopes $\sim 59 \text{ mV dec}^{-1}$ representing one electron oxidation with simultaneous proton removal.

Table 1. Electrochemical and catalytic water oxidation/oxygen evolution data for different Ni-derived materials.

Catalyst materials ^[a]	Electrolyte (pH)	system	O ₂ onset E (E/V RHE) ^[b]	E vs	Tafel Slope (mV/dec) ^[c]	Ref.
Ni-NCs Ni ₄ (PET) ₈	0.1 M KOH (13)		1.51 V		38	This work
Ni-NCs Ni ₆ (PET) ₁₂	0.1 M KOH (13)		1.53 V		40	This work
NiOx thin film	1 M KOH (14)		1.57 V		39	34
Ni(OH) ₂ spheres	0.1 M KOH (~13)		~1.63 V		42	40
NiO _x (from molecular precursor)	0.1 M Na-borate (9.2)		1.63 V		>100	39
Ni-Ci/GC	0.2 M HCO ₃ ⁻ /CO ₂ (~6.9)		1.67 V		53	6
Ni-Bi/GC	0.1 M K-borate (9.2)		1.74 V		59/120 ^[d]	22

^[a]The Ni-based electrocatalysts in the list are prepared from different procedures, details are described in the respective references. ^[b]The oxygen onset is the calculated from the anodic current onset at $J > 0.1 \text{ mA cm}^{-2}$. ^[c]Tafel slope is taken from current – overpotential ($\log i$ vs η) plot in oxygen evolution regime from 0.1 to 1.0 mA cm^{-2} . ^[d]Tafel slopes of 59 and 120 mV dec^{-1} are taken with and without preconditioning respectively, for 12 h of pre-electrolysis at a current density of 1.0 mA cm^{-2} .

Conclusions

We have demonstrated the use of sub-nanometer and atomically monodisperse Ni NCs i.e., Ni₄(PET)₈ and Ni₆(PET)₁₂ as cost-effective, stable and low overpotential oxygen evolution electrocatalysts for water oxidation, which can be exploited to fabricate solar energy to chemical energy conversion devices. These NCs were found to be highly active water oxidation electrocatalysts under anodic conditions without any electrochemical pre-conditioning procedure or heat treatment. On electrode surface decorated with Ni₄(PET)₈ and Ni₆(PET)₁₂, the oxygen evolution onset occurred at a low overpotential of 1.51 V (vs RHE; $\eta \approx 280 \text{ mV}$) and 1.53 V (vs RHE; $\eta \approx 300 \text{ mV}$), respectively. These oxygen evolution potentials are the lowest for Ni-based electrocatalytic materials reported so far. The other nickel derived water oxidation catalysts have higher overpotential for O₂ evolution. For long-term stability and performance tests, there is no need to put metal ions in the electrolyte solution, which is essentially required for other electro-generated catalysts. For Ni₄(PET)₈, a peak oxygen evolution current density approaching 150 mA cm^{-2} at 2.0 V (vs RHE) and a Tafel slope of 38 mV dec^{-1} is observed for oxygen evolution which is comparable with the state-of-the art but expensive RuO₂ based catalysts. XPS data clearly exclude the presence or involvement of iron in the catalytically active sample that might be associated with the high performance of Ni NCs for anodic water oxidation. Long-term controlled-potential water electrolysis showed excellent oxygen evolution current density of above 14.0 mA cm^{-2} for Ni₄(PET)₈ and 9.0 mA cm^{-2} for Ni₆(PET)₁₂ at 1.65 V vs RHE. These results are very impressive for a simple metal based water oxidation

electrocatalyst. We have made a step forward in developing simple, cheap and efficient water oxidation electrocatalysts. It is anticipated that this investigation will further advance the knowledge and methods to prepare robust and high activity catalytic materials for anodic water splitting.⁶¹

Acknowledgements

This work was supported by KAUST. K.S.J. acknowledges the research support from Higher Education Commission (HEC), Government of Pakistan. I.H. also acknowledges KAUST and LUMS for financial support. All authors thank Prof. Mohamed Eddaoudi and his team for support with single crystal XRD measurements.

Notes and references

‡ The X-ray crystallographic data for Ni NCs have been deposited in the Cambridge Crystallographic Data Centre with CCDC number 1419754 and 1419731 for Ni₄(PET)₈ and Ni₆(PET)₁₂, respectively.

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