Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information (S)

Scarify Ni-foam into nanocrystal growth of NiF_2 Nanorod-Arrays using hydrothermal process for Hydrogen Evolution Reaction Application

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Formulae S1

All potentials mentioned in this work measured verses Hg/HgO as a saturated calomel electrode (SCE) and converted in to a reversible hydrogen electrode (RHE) scale according to Nernst equationwithout iR-correction. Equation for conversion of potential as

$$E_{RHE} = E_{SCE} + 0.059 \times pH + E^0SCE \quad (1)$$

where, E_{RHE}, E_{SCE}, and $E^0{}_{SCE}$ are potential verses RHE, potential *vs.* SCE, and standard redox potential of SCE at 298 K.

The overpotential (η) at a current density of the prepared samples were calculated from linear sweep voltammetry (LSV) curves using following equation,

$$\eta = E_{RHE} - 1.23\ V \quad (2)$$

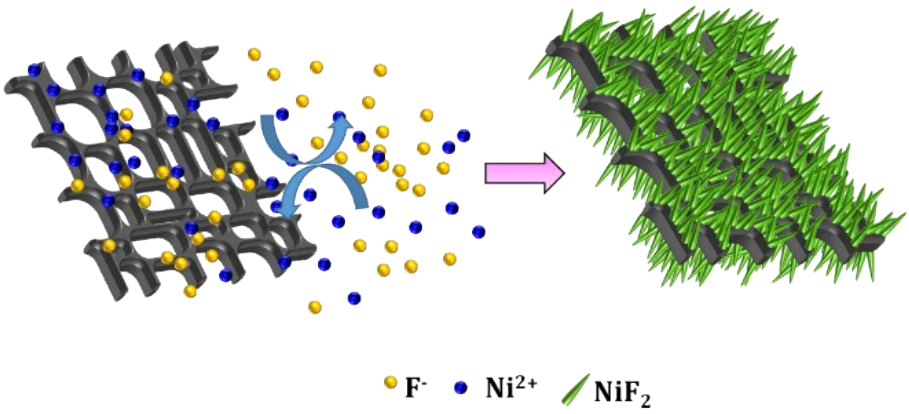
and Tafel slopes (b) were calculated by fitting linear portion of Tafelplot with Tafel equation as,

$$\eta = blogj + a - 1.23\ V \quad (3)$$

where, 'η', '*j*' and '*a*' are overpotential, current density and fitting parameter, respectively.

Reaction mechanism

The formation of NiF_2@Ni NAs in a 1:50 mL (v/v) HF solutionin ethanol occurs as follows under hydrothermal conditions. When ethanolic HF solution is hydrothermally heated it producesethoxy and fluorideion radicals and protons. At the same time, Ni foam in the solution oxidizes to provide nickel ions and electrons in to solution reducefluoride ionsto nucleate on the Ni foam surface as shown in Scheme S1. In this reaction, hydrothermal displacement occurs between Ni and F, causing deposition ofNiF_2@Ni.



Scheme S1. Schematic of the possible growth mechanism of the NiF_2@Ni nanorods during hydrothermal method. The black 3D network represents the Ni-foam surface, blue and yellow spheres are $Ni^{2+}$and F^{+} ions and on the right hand side we show a schematic sketch of the nanorod array (NA) of NiF_2.

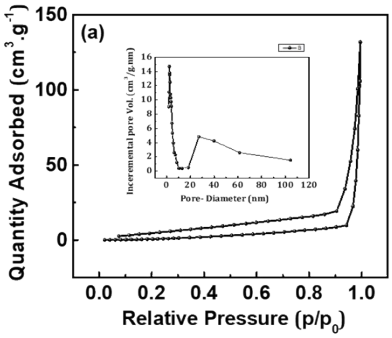


Figure S1.BET measurements (inset shows pore size distribution).

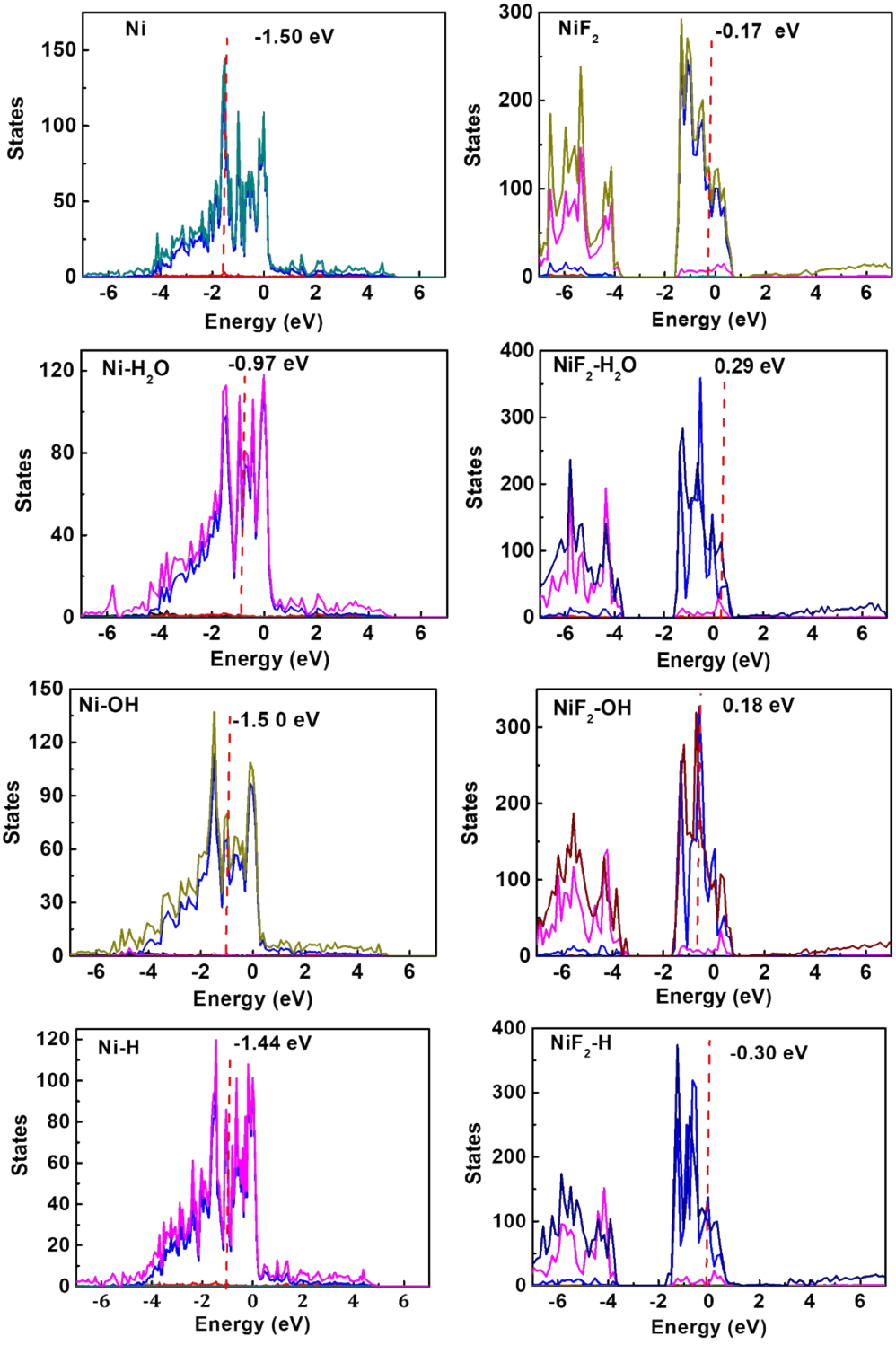


Figure S2. Comparison of total density of states (DOS) and projected DOS on to different atomic orbital's for Ni (111) and NiF_2 (110) surfaces following adsorption of H_2O, OH and H.

The Fermi level has been indicated with dashed line.Color codes:Ni= black- Ni-S, red- Ni-P, blue-Ni-D and dark cyan- total, NiF_2= black- Ni-S, red- Ni-P, blue-Ni-D and dark cyan- F-S, mangenta-F-P, dark yellow-total, Ni-H_2O= black- Ni-S, red- Ni-P, blue-Ni-D, dark cyan- O-S, mangenta-total, NiF_2-H_2O = black- Ni-S, red- Ni-P, blue-Ni-D, dark cyan- F-S, mangenta-F-T, dark yellow-O-S, navy-total, Ni-OH= black-Ni-S, red-Ni-P, blue-Ni-D, dark cyan-O-S, mangenta-O-P, dark yellow-total, NiF_2-OH= black-Ni-S, red-Ni-P, blue-Ni-D, dark cyan-F-S, mangenta-F-P, dark yellow-O-S, navy-O-P, wine-total, Ni-H= black-Ni-S, red-Ni-P, blue-Ni-D, dark cyan-H-S, mangenta-total, NiF_2-H = black-Ni-S, red-Ni-P, blue-Ni-D, dark cyan-F-S, mangenta-F-P, dark yellow-H-S, navy-total.