Engineered Nickel Selenide based catalysts for Urea Oxidation Reaction

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Abstract :

The sustainable hydrogen economy has accelerated hydrogen production development, with urea-assisted hydrogen generation being a promising approach due to low voltage requirements and waste water remediation. Over time, significant focus has been placed on enhancing the performance of Ni-based catalysts in the urea oxidation reaction (UOR), a crucial factor in urea assisted hydrogen generation. Nickel selenides in recent years have proved to be a high performing nickel catalyst for UOR. In this review, we have discussed recent advances in nickel selenide-based catalyst for UOR and various strategy adopted for engineering the catalyst properties which resulted in enhancement of their catalytic activity for UOR.

Keywords: *Nickel selenides, Heterostructures, Interface engineering, UOR*

1. Introduction

Depleting fossil fuel and increasing climatic crisis have triggered a race in global energy and environment field to develop a reliable and sustainable energy source which with regard to meeting the global energy demands also generate least to zero carbon emission. With all the renewable energy options present like wind energy, solar energy, hydro energy and so on Hydrogen (H_2) is accepted as a promising sustainable energy candidate for meeting global energy demands because not only it possess high gravimetric energy density which is almost threefold higher than conventional gasoline but also generate lowest or zero carbon emission depending upon the process of production.[1]. Furthermore, hydrogen-based energy technology is recognised as a viable energy storage carrier for the reduction of greenhouse gases CO_2.[2]. Even though hydrogen generation from water electrolysis have various advantages but the sluggish kinetics associated with oxygen evolution reaction (half-cell reaction) results increase in energy input to drive the reaction process hence limiting the energy conversion efficiency of the system.[3]. Additionally, the commercial hydrogen generation through alkaline water-electrolysis relies on the clean or advanced water resources which in term increases the overall investment cost . Hence if anyway, we can use alternate source, such as organic waste water, it will be supported from the standpoint of both sustainable supplies and environmental management. Urea, a significant N-based fuel, is used in agriculture, drug, and adhesive industries. Untreated waste water poses a threat to ground water and air due to harmful products. However, urea is a good hydrogen carrier with a 6.67 wt.% hydrogen content, making it a potential energy carrier in fuel cell technology.[4, 5].

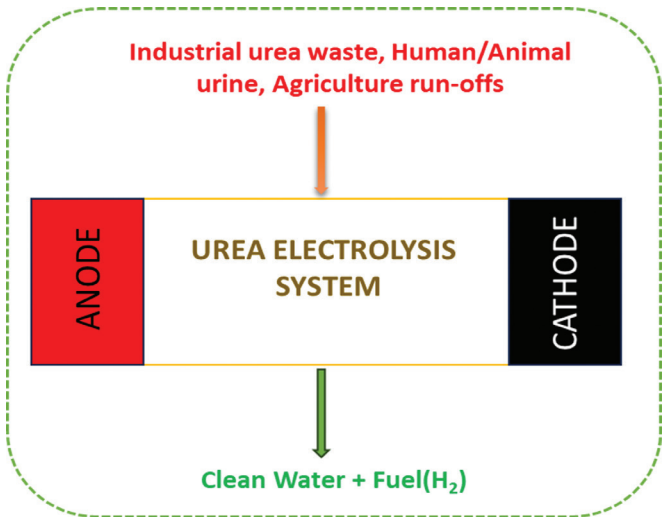


Fig.1. Schematic diagram of urea electrolysis and its applications

From all the available methods for the decomposition of urea, electrooxidation of urea is one of the cost effective and efficient method because along with decomposition of urea to non-toxic byproducts it as also helps generate hydrogen in alkaline medium (Fig.1). Overall urea electrolysis is depicted in the equation below (Fig. 2a):-

Anode:

$CO(NH_2)_2 + 6OH^- \rightarrow N_2 + 5H_2O + CO_2 + 6e^-$ E= - 0.46 V (1)

Cathode:

$6H_2O + 6e^- \rightarrow 3H_2 + 6OH^-$ E= - 0.83 V (2)

Overall:

$CO(NH_2)_2 + 6H2O \rightarrow N_2 + 3H_2 + CO_2$ E = 0.37 V (3)

In comparison to water electrolysis, the theoretical potential required to drive the urea electrolysis process is only 0.37 V, which is significantly lower than the 1.23 V necessary for water electrolysis.[6]. Nevertheless, as can be observed in above equation, the UOR undergoes $6e^-$ transfer process which is responsible for its relatively slower reaction kinetics along with that the byproducts that are produced CO_2,CO_x, etc during UOR make long term stability of catalyst challenging.[7]. Hence to overcome these challenges development of highly efficient catalyst were done and exclude the use of noble materials like ruthenium, platinum, etc since it will further increase the investment cost. The attention is mostly focused towards the nickel-based materials due to low cost and promising catalytic performance.[8-13].

UOR Mechanism

As previously stated, the majority of research into the production of UOR catalysts is centred on nickel and nickel-based compounds. The biocatalytic breakdown of urea in the active sites of urease enzymes, which contain hydroxide bridged Ni^{2+} centres, is thought to have inspired the use of nickel-based catalyst.[14, 15]. Later, it was experimentally discovered that Ni-based catalysts exhibits higher catalytic activity than other researched non-noble metal catalysts. Bottle's group have done extensive study on UOR and its mechanism, employing Raman spectroscopy, in-situ X-ray diffraction (XRD) and Density functional theory (DFT) calculations. Vedharathinam and Botte demonstrated via in-situ Raman spectroscopy that $Ni(OH)_2$ is surface oxidised to NiOOH, which serves as the real oxidation catalyst.[16]. Further, Bottle and group using in-situ XRD investigated Urea electrolysis on $Ni(OH)_2$ and according to their findings $Ni(OH)_2$ is oxidised to NiOOH at a potential between 1.2-1.6 V in 5.0 M KOH. The electrochemically produced NiOOH combines with urea and is reduced to $Ni(OH)_2$, while urea is oxidised to N_2 and CO_2. [17]. With all the findings and electrochemical results, they concluded NiOOH as the electroactive species for UOR and established it as the electro-chemical oxidation mechanism, shown below:-

Electrooxidation: $6Ni(OH)_2 + 6OH^- \rightarrow 6NiOOH + 6H_2O + 6e^-$ (4)

Chemical oxidation: $CO(NH_2)_2 + 6NiOOH + H_2O \rightarrow N_2 + CO_2 + 6Ni(OH)_2$ (5)

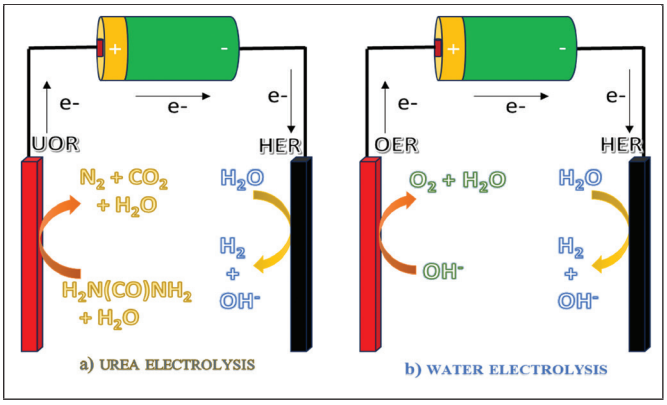


Fig.2 Schematic diagram of urea and water electrolysis

According to the mechanism, in the presence of OH-, $Ni(OH)_2$ was electrooxidized to NiOOH, and then urea molecules were adsorbed onto NiOOH via bridge coordination, in which the nickel atom interacts with the nitrogen and oxygen atoms, and the oxygen atom of nickel oxyhydroxide interacts with the carbon atom of urea. The dissociation of urea on NiOOH is a multistep process that generates a variety of intermediate species. Bottle et al. employed DFT to evaluate the products, catalytic mechanism, and relative rate-determining steps of urea degradation on NiOOH. [18]. The group put forward three possible reaction pathways and calculated the free energy of all the elementary steps. From the study they found out that desorption

of CO_2 is the rate limiting step due to highest Gibbs free energy change (1242.2 kJ mol^{-1}). The reaction pathway of the UOR can be described as follows:

$*CO(NH_2)_2$ → $*CO(NH_2.NH)$ → $*CO(NH_2.N)$ →$*CO(NH.N)$ → $*CO(N_2)$ → *CO(OH) →*COO, and the CO_2 desorption.

Over the years many nickel based catalysts have been designed in order to tackle the challenges associated with UOR and many reviews were published summerising based on various techniques of synthesis, strategy of modifying the catalyst surface for enhancedd adsorbtion and efficent breakdown of urea molecules for the generation of hydrogen. In this review the focus will be on the Nickel Selenide based catalyst which in recent years have drawn considerable attention and a peak in publications based on the same is observed as an electrocalyst for UOR.

2. Why Transition metal chalcogenides (TMCs)?

In brief, transition metal chalocogenides have shown prominent activity for UOR because of certain factors, first due to higher bulk conductivity than traditional nickel oxides and hydroxides which inturns provides a faster path for charge transfer across the electrocatalyst-electrolyte interfaces.[19]. Second, TMCs undergo surface reconstruction by partially exchanging anions with oxide/hydroxide which results in increasing the surface area, hence enhanching the catalytic performance. Third, presence of guest anions (undergo dissolution as oxianions due to formation of thermodynamically favorable metal oxide and hydroxides) causes alteration of the host metal's lattice structure and its electronic structure which according to reported literature is responsible for lower corndination number and longer bond length in transition metal chalocogrnides resulting in weakning of metal-metal bondstrength, enhancing the rate of surface oxidation process like UOR and OER.[20, 21]. Futher moderate abundance and lower cost can be the other factors for the increase in development of chalocogenides based catalyst for UOR (Fig.3).

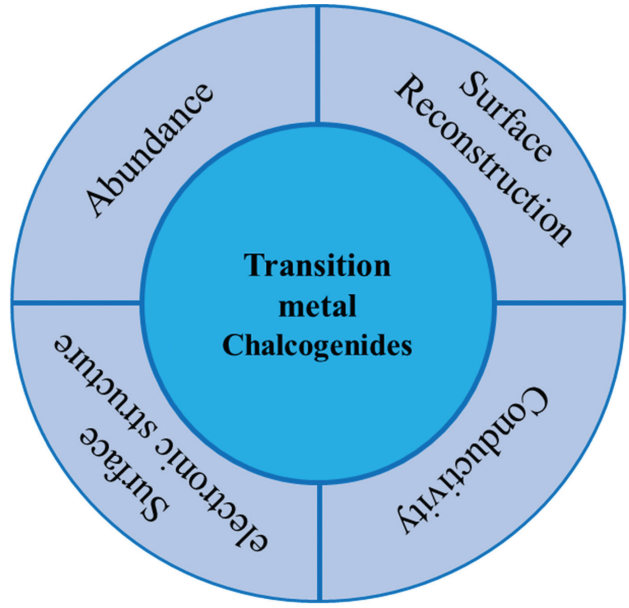


Fig.3. Shematic diagrams representing various factores reposible for implimentation of TMCs based catalyst for UOR

2.1 Nickel selenide and other Transition metal chalcogenides

The bulk conductivity of a catalyst has a substantial impact on its electrocatalytic activity. Increased conductivity is believed to aid in the transfer of charge across interfaces between electrolytes and electrocatalysts. Nickel selenides are semiconductors but oxides of nickel are insulating in nature. Therefore nickel selenides show better catalytic activity compare to its oxide counterpart. Despite tellurides having higher conductivity than selenides, nickel tellurides exhibit lower or comparable activity to nickel selenides. This can be attributed to factors such as the weaker tendency of nickel telluride to undergo surface reconstruction and the poor accessibility of Ni sites buried beneath the large anionic cloud of telluride. Conversely, nickel sulphide exhibits superior surface construction but has a relatively poor conductivity. Hence, nickel selenide was used for various electrocatalytic application like OER, HER, UOR,etc.[19, 22]. In case of UOR nickel based chalcogenides are intensively studied compared to other transition metal chalcogenides since NiOOH was proved to be the catalytic active site for oxidation of urea which was discussed earlier in above section.

3. Nickel Selenides (NiSe)

3.1 Structural and elecronic properties of Nickel selenides

The suitability of a particular nickel chalcogenides for a specfic application is largerly depends upon the stiochiometric ratios and phases of the compound. [23, 24]. The involvement of d electrons in covalent bond formation in TMCs makes their properties dissimilar to their oxide counterparts, which helps in the development of metal-metal interactive bonds. This unique property associated with TMCs is one of the reasons for their enhanced electroactivity towards various application (ie, OER, HER, ORR, CORR, UOR,etc.). Nickel selenide, being one of the TMCs exists in the various polymorphs and its formation is influenced by certain factors, which are: a) multivalent states of nickel from +2 to +4 b) the smaller electronegativity difference between nickel and selenium. There are commonly 4 types of nickel selenides which are NiSe, $NiSe_2$, Ni_3Se_2 and Ni_3Se_4(Fig.4).[25]. The most common nickel selenides are non-stiochiometric in nature.

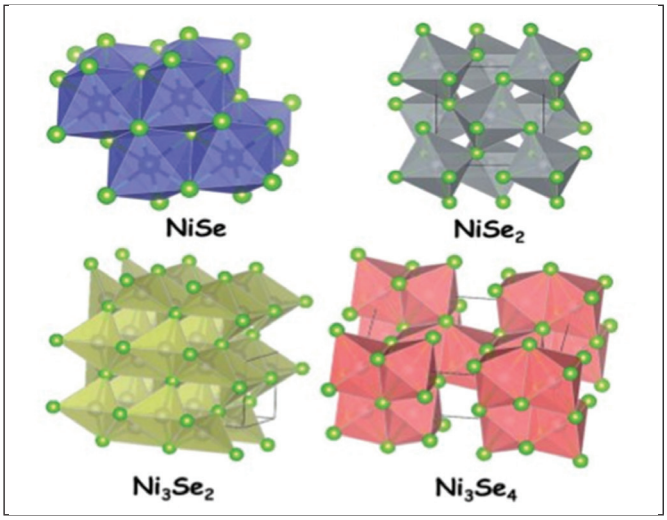


Fig.4. Different crystal structures of Nickel selenides[19](Reproduced from Ref. 19 with permission from the Royal Society of Chemistry)

By controlling the reaction conditions like time , temperature, and pH along with reactant ratio (Ni and Se) the desired nickel selenide can be synthesized, and intrestingly the excess selenium, nickel or both that can't be consumed during reaction can act as a template for obtaining the desired phase of nickel selenides. The impact of various parameters on the formation of different phases of nickel selenide was reported by Zhauang and group. For example, when the ratio of Ni:Se are kept equal at a high temperature (180^0C) for shorter duration of time, resulted in formation of hexagonal NiSe, but on extending the reaction time, the hexagonal NiSe gets transformed into rhombohedral NiSe. Futher, on adjusting the pH (~10) and increasing the percentage of Se resulted in formation of $NiSe_2$ with the cubic cyrstal structure . Lower pH (~10) plays a crucial role here because it results in the formation of both Se (elemental) and Se^{2-} which combine to form Se_2^{2-}, which is required for the formation $NiSe_2$, on incresing the pH to 14 leads to the formation of $Ni_{1-x}Se$ ($0<x\leq0.15$) due to lack of elemental Se. And by increasing nickel concentration (Ni:Se= 3:1) while holding the reaction at 180^0C for a longer period of time, produces pure Ni_3Se_2.[26].

Over the years, many unique synthetic procedures have been developed for the synthesis of nickel selenide phases, and in addition some other phases like monoclinic Ni_3Se_4 and orthorhombic Ni_6Se_5 have also been reported.[27, 28]. In general, nickel selenides synthesized are black in colour and are inslouble in water. The insolubility of nickel selenide acts as a boon for its application as an electrocalyst for urea splitting applications.

3.2 Synthesis strategies

Synthesis of nickel selenides are carried out employing various tehniques such as ele ctrodeposition, hydrothermal/solvothermal, reflux method, microwave irradiation and physical adsorption. In the upcoming section few of the well known, cost-effective and recently reported synthesis procedure is summerized.

3.2.1 Electrodeposition

The electrodeposition technique is one of the most attractive, cost-effective and oldest techniques for the fabrication of desired compounds via cathodic reduction in aqueous or organic solvents.[29]. While the growth of electrodeposited films is influenced by the applied potential, temperature of the reaction condition, time, and mobility of precursor ions, by

manipulating these parameters, films of the desired thickness, morphology, composition, etc. can be synthesized. Zhu and coworkers have synthesized different phases of nickel selenides by varying the applied potential using nickel foam as the cathodic substrate. They have reported that when the deposition is carried out at -0.35 V , -0.46 V and -0.60 V (vs SCE) it results in the formation of cubic $NiSe_2$, hexagonal NiSe and hexagonal Ni_2Se_3, respectively. [30]. Although, electrodeposition via chronoamperometry and CV cycling are very commom, but in recent years, pulse voltage technique have been employed for their synthesis. By adjusting the pulse time and duty cycle Ni-Se of the desired thickness and particle size can be achieved.[31]. Ahn and coworkers reported the use of pulsed voltage deposition to synthesize nickel selenide films with good uniformity and a thickness of 150 nm.[32].

3.2.2 Hydrothermal

Hydrothermal methodology is widely used for the synthesis of compounds of desired morphology, particle shapes, sizes and different phases of desired compound.[33, 34]. Engineering the parameters of the reaction, like time, temperature, solvent volume and type, etc affect the properties of synthesized product. Few advantages associated with hydrothermal method are high crystallinity, phase purity, fast reaction kinetics, etc.[35]. Nickel selenides with different morphology has been reported by changing the selenium precursor, like selenourea ($SeC(NH_2)_2$),selenium dioxide (SeO_2) and potassium slenocyanate (KSeCN) which resulted in production of nickel selenide with wires, spheres and hexagons morphology respectively. [36]. Hydrothermally produced $Ni(OH)_2$ is followed by a hydrothermal anion exchange reaction of nickel hydroxide with chalcogen ions created by using a reducing agent to produce nickel selenide nanosheets. Reduction by $NaBH_4$ causes a rapid exchange of OH- from $Ni(OH)_2$ with Se ions, resulting in the formation of a thin layer of $NiSe_2$. The reaction mention below provides a possible mechanism for anion-exchange reaction.[37].

$$Ni(OH)_2 + 2Se + NaBH_4 \rightarrow NiSe_2 + B(OH)_2^- Na^+ + 2H_2 \quad (1)$$

Advancement in direct selenization of metallic substrate like Ni foil and Ni foam are also observed in recent years. Various techniques other than hydrothermal used for direct selenization of metallic substrate are like thermal deposition[38], Physical vapour deposition[39], chemical vapor deosition[40] and others are employed to obtain desired nickel selenides. The superiority of direct selenization of metallic substrates is envisaged due to the metallic substrate's predominant conductivity and binder-free approach. Tang et. al. synthesized NiSe nanowires on the surface of Ni foam by simple hydrothermal approach in which Ni foam is placed in a solution containing NaHSe as Se source.[41].

3.2.3 Microwave-assisted (MW) synthesis

A rapid growth is observed in MW- assisted synthesis of inorganic nanomaterials since it is considered as one of the fast synthesis practice. It is also postulated that the efficient and controlled heating conditions that can be achieved by microwave irradiation prove to be highly beneficial for the synthesis of nanomaterials and nanostructures, whose growth is highly sensitive towards reaction conditions. Anantharaj and group have reported successful synthesis of Ni_3Se_4 nanoassemblies for the application of water splitting in neutral and alkaline media. In their work, they have fabricated Ni_3Se_4 on the surface of nickel foam (NF) using NaHSe as selenium precursor. The reaction mixture containing NF and NaHSe is irradiated with microwave radiation of power 300 W continuously for 3 minutes for the successful formation of Ni_3Se_4. [42].

4. Engineering Nickel selenides for UOR

In recent years a peak in nickel selenide based catalysts for the application of UOR has been observed, in which various strategies were implemented in order to ehance the structural, electronic and morphological properties of the catalyst for the boost in UOR activity, and those developments are discussed in the upcoming session of the paper.

4.1 Incorporation of Heteroatom

Heteroatom doping is a widely studied area and is being employed to enhance catalyst performance, and it is widely used in the field of UOR to improve catalytic performance by regulating the electronic structure of Ni active sites. Based on this strategy, Yu and coworkers synthesised iron-doped nickel diselenide. Three different Fe doped $NiSe_2$ are produced, which vary with respect to the percentage of iron used for the synthesis. Among the three catalysts with different Fe doping percentages, the one with 1.68 at% iron showed superior activity by achieving a current density of 125.8 mA/cm^2 at a potential of 1.54 V vs. RHE. Iron with a certain concentration can affect Ni valence, as demonstrated in the Fe doped NiO system, where Fe^{3+} ions act as lewis acid, promoting Ni^{4+} formation.[20]. On comparing with $NiSe_2$, in Fe-$NiSe_2$ due to doping of iron resulted in an increase in precentage of high valent Ni^{3+} but also optimized the adsorption capacity of nickel to urea molecules as revealed through DFT analysis. Compared to $NiSe_2$ (-1.12 eV), Fe doped $NiSe_2$ (-1.68 eV) showed a higher adsorption energy of urea molecules on the Ni sites. This enchancement witnessed was caused by the electronic structure regulation induced by doping resulting in increment of electron abundance around Ni atom in Fe-$NiSe_2$. Trimetallic selenide $NiFeCoSe_2$ with superior catalytic activity, owing to the synergy existed between the three metals has been reported for UOR. XPS analysis revealed that, compared to its bimetallic counterpart, the Co 2p XPS spectra showed a shift towards lower binding energy, implying an increase in electron transfer and a stronger interaction between the metals, proving existance of synergy between metals.[43]. Incorporating non-metals like sulphur in nickel selenide (Ni-S-Se/NF) showed a great improvement in the activity for UOR, which can be assigned to the following reasons; a) increase in amorphicity due to sulphur incorporation and higher active site genration, b) Ni-S-Se/NF showed higher hydrophilicity and aerophobicity. Increase in amorphicity of the catalyst compared to its NiSe and NiS counterparts provides Ni-S-Se compound and in-situ generated NiOOH with higher active sites and improvement in hydrophilicity and aerophiolicity of the catalyst aid its long-term performance.[44].

4.2 Nickel selenide integrated Carbon based substarte

Carbon-based materials are cost-effective and environmentally friendly materials, owing to their good conductivity, fast charge transfer, stability, high surface area, & ease of modification have drawn considerable attention of researchers to incorporate various carbon based materials like rGO, CNTs, amorphous carbon with nickel based compounds for the enhancement of catalytic activity.[45]. $Ni_{0.85}Se$ nanocrystals grown on the surface of rGO ($Ni_{0.85}Se$@ rGO) reported to achieve superior catalytic activity in comparison to their non-rGO couterpart. The enhancement is ascribed to the unique cluster structure, which provides higher surface area and exposure to higher catalytic sites and in addition rGO as a carrier improves conductivity and electron transfer rate, thereby boosting UOR activity.[46]. Khalafallah et. al. has synthesised muti-walled CNT supported nickel cobalt selenide composite (Ni-Co-Se/CNT) via one pot hydrothermal method. The synthesised catalyst shows a remarkable activity for UOR (0.29 V vs. Hg/Hgo @10 mA/cm^2). The incorporation of tubular CNTs amended the rate of mass transfer ascribed to their porous network architectures, while presence of Co active sites along with electrochemically active NiOOH layer helped boost the catalytic activity. Morphological analysis revealed the twisted atomic arrangements on the hybrid surface, suggesting disordered selenide formation due to defects. These defects contribute to the enhancement of electroactivity by promoting active edge sites and improving reaction kinetics.[47]. Nitrogen doping in carbon-based substrates enhances composite porosity, surface composition, and interlayer spacing, thereby improving electrochemical performance. Qiuhan and coworkers successfully coupled dual phase nickel selenide ($Ni_{0.85}Se/NiSe_2$) with N-doped carbon through hydrothermal and calcination, revealing higher active sites in the dual phase. Furthermore, interfacial charge transfer existed

from Ni/Se and N/C atoms will generate strong electronic contacts between $Ni_{0.85}Se$, $NiSe_2$, and the NC matrix, allowing charge transfer and electronic modulation, resulting in an increase in catalytic performance. The composite $Ni_{0.85}Se/NiSe_2$@NC demonstrated superior COx poisoning resistance compared to the non-composite counterpart (i.e, $Ni_{0.85}Se/NiSe_2$), attributed to the doped nitrogen element's ability to facilitate COx desorption.[48]. To summerize, combining carbon substrate to nickel selenide revelead to possess advantages of pure nickel selenide. The combination of carbon substrate with nickel selenide demonstrated numerous advantages compared to pure nickel selenide. Top of the list incorporating carbon substrate limits the growth of nickel selenide nanoparticles to prevent agglomeration, which reduces electrical conductivity and the availability of active sites. The direct interaction between carbonaceous platforms and metallic atoms shortens diffusion pathways for electrolyte ions and electrons, enhancing catalytic activity by providing higher electroactive sites and modulating electronic configuration, resulting in superior electrochemical characteristics. CNT with its 3D tubular structure and porous network architecture, improves structural stability and facilitates interaction between the active material and electrolyte ions. This helps prevent connectivity issues, aggregation, and phase separation, ultimately enhancing catalytic performance compared to pure nickel selenide.

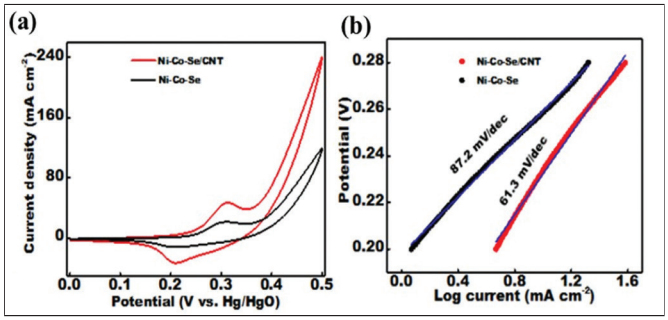


Fig.5. a) CVs of the catalysts recorded at a scan rate of 10 mVs -1 at room temperature in 1 M KOH + 0.5 M urea and b) Tafel plots of Ni-Co-Se and Ni-Co-Se/CNT catalysts in 1 M KOH with 0.5 M urea. [47] (Reproduced from Ref. 47 with permission from the John Wiley and Sons, Inc.)

4.3 Hetrostructuring

Nickel selenides, with their unique electronic configuration and high conductivity, have potential as electrocatalysts for hydrogen production. But their efficacy, is hampered by fewer exposed active areas and poor structural stability. Construction of heterostructures by hybridization of suitable components can substantially improve the percentage of active sites and structural stability , based on that various papers have reported strategies for constructing heterostructures to enhance catalytic performance for UOR, which are discussed in the following section.

4.3.1 Metal oxide-Nickel selenide heterostructures

As for the published literature, NiO shows inferior activity compared to nickel selenide, but when NiO is incorporated with Nickel selenide, the heterostructure generated shows comparably higher activity for UOR (1.33 V vs RHE @10 mA/cm^2). HR-TEM analysis of NiO-$NiSe_2$ edge regions revealed an interface between NiO nanosheets and $NiSe_2$ nanoparticles, generating higher active sites and facilitating faster reactant and electrolyte diffusion. Moreover, the concomitant bonds of Ni-$_O$ and Ni-Se bond induce the high valence state of Ni, which acts as the active site for UOR.[49] Doping CeO_2 onto $Ni_{0.85}Se$ on the surface of N-doped carbon showed superior performance with respect to its non-CeO_2 counterpart since CeO_2-$Ni_{0.85}Se$-NC required a potential of 1.294 V vs RHE to achieve a current density of 10 mA/cm^2 which is about 28 mV lower than $Ni_{0.85}Se$-NC. XPS analysis revealed, CeO_2 incorporation resulted in an alteration of chemical state and electronic structure, as suggested by the Ni 2p spectrum, where a negative shift in peak is observed w.r.t its non-CeO_2 counterpart. Moreover, the Ce 3d spectrum showed increased Ce^{3+} in the catalyst, indicating oxygen vacancies and defect sites, resulting in enhanced catalytic activity due to the generated metal and oxygen defects.[50].

4.3.2 Metal hydroxide-Nickel selenide heterostructures

Chun et.al. produced Se-$Ni(OH)_2$@NiSe/NF via in-situ electroxidation of NiSe/NF, which showed a shift

towards lower potential to achieve a current density of 100 mA/cm^2 i.e. 0.366 V vs. SCE, compared to NiSe/NF nanowires (0.384 V vs. SCE) and $Ni(OH)_2$/NF (0.486 vs. SCE) respectively. The electroxidation of NiSe/NF led to a decrease in crystallinity and the formation of core shell hetrostructure nanowires and abundant nanosheets, as observed through HR-TEM images while a new peak near 857.1 eV is observed ascirbed to NiOOH formation. Generation of core shell heterostructure and higher valent Ni^{3+}(NiOOH) responsible for improved catalytic activity for UOR. [51]. The catalyst core-shell structure consisting of a NiSe core with intrinsic semiconductor properties that facilitate rapid electron transport along the nanowire. The shell, made of Se-$Ni(OH)_2$, offers numerous active catalytic sites and reduces the adsorption/desorption barrier to promote fast reaction kinetics. The synergistic effect of these two features is responsible for the increased activity observed in Se-$Ni(OH)_2$@NiSe/NF compared to NiSe and $Ni(OH)_2$ alone.

4.3.3 Metal sulphide – Nickel selenide heterostructures

Lin and coworkers via electrodeposition, synthesised Heazlewoodite-phased Ni_3Se_2 nanocrystals on a Cu_2S nanowire backbone. The as-generated hierarchical Cu_2S@Ni_3Se_2 exhibits improved catalytic activity for UOR, requiring a potential of 1.338 V vs RHE to obtain a current density of 10 mA/cm^2.The outstanding catalytic activity is attributed to an increase in geometric area achieved due to the vertically grown nanowire morphology of Cu_2S resulting in higher loading and exposure of catalytically active Ni_3Se_2 and a boost in charge transfer between electrode and electrolyte owing to the closely contacted interface between Cu_2S and Ni_3Se_2.[52]. Ultrathin MoS_2 nanosheets composited with NiSe nanowire arrays demonstrated an onset potential of 1.42 V vs RHE for UOR, which is 50 mV lower than its OER counterpart. The positive shift of 0.6 eV for the peak related to Mo^{3+} in Mo 3d of the concerned catalyst w.r.t MoS_2 and similarly, a 0.3 eV positive shift in S $2p_{1/2}$ peak w.r.t MoS_2 S $2p_{1/2}$ peak confirms a strong electronic interaction between NiSe and MoS_2 which is the reason for higher catalytic performance.[53]. The MoS_2 nanosheets can increase the active sites and provide a channel for electrolyte transport and gas release, then the interfacial interaction between NiSe and MoS_2 can promote electron transfer. Hence, NiSe@MoS_2/NF requires lowest onset potential for UOR compared to NiSe@NF and MoS_2@NF.

4.3.4 Metal selenide-Nickel selenide heterostructures

$NiSe_2$/$FeSe_2$ with p-p hetrojunction was developed by Shan and coworkers using a feasible solid-state selenization strategy using Fe-Ni PBA(Prussian blue analogues) as the precursor. Owing to the difference in energy levels between $NiSe_2$ and $FeSe_2$, a built-in electric field is generated at the heterointerface. The built-in electric field creates a space-charge region at the interface, enhancing electron transfer and adsorption of targeted reactants, leading to higher UOR activity.[54]. Xiujuan et al. reported controllable transition engineering from homogeneous $NiSe_2$ nanowrinkles (NWs) to heterogeneous Ni_3Se_4/$NiSe_2$ nanorods (NRs) for the first time by manipulating the selenization temperature, resulting in the development of interfaces. The self-supported nanorod arrays on the 3D nickel foam expose more catalytic sites and allow for unhindered transport of electrolyte ions and released gases. From the DFT study reported in the paper discloses that the redistribution of electrons in the interfacial region resulted in reformation of charge transfer efficiency and electron, which further helped in optimization in the adsorption & desorption of reactive intermediates for the reduction in Gibbs free energy associated with UOR. Owing to enhancements in structural and electronic properties, Ni_3Se_4/$NiSe_2$ NRs only require a potential of 1.296 V vs RHE to achieve a current density of 10 mA/cm^2 which in much lower compared to Ni_3Se_4/$NiSe_2$ NWs (1.339 V vs RHE) and $NiSe_2$ NWs (1.362 V vs RHE).[55] Mixed phased $CuSe_x$@Ni_3Se_2 with interconnected nanoflake morphology resulted in enhancement in UOR activity when compared with individual components owing to its hierarchical heterostructures.[56].

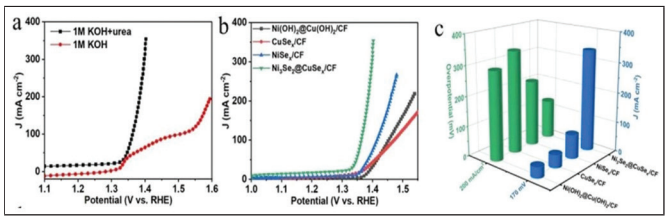
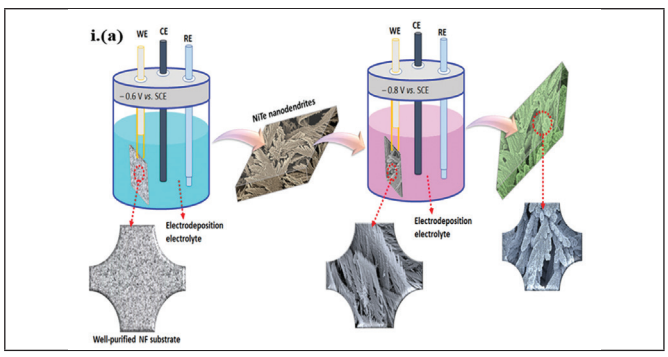
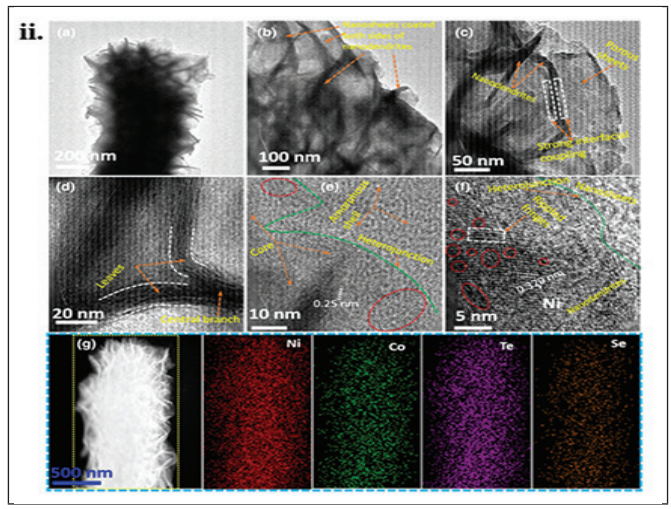


Fig.6. (a) iR-corrected polarization curves of Ni_3Se_2@$CuSe_x$/CF in 1m KOH electrolyte with and without 0.5 m urea. (b) iR-corrected UOR polarization curves and (c) comparison diagram of overpotential at 200 mAcm^2 and current density at 170 mV.[56]. (Reproduced from Ref. 56 with permission from the John Wiley and Sons, Inc.)

4.3.5 Metal Telluride – Nickel selenide heterostructures

Both Te and Se belong to the chalcogen group, and with an increase in atomic number, the elctronegativity decreases; hence Te possess a lower electronegativity than Se. The ionocity and covalent strength of chemical bonds depend on the electronegativity of bonded particles, and as transition metals move from oxygen to Te, ionicity weakens while covelenity strengthens. According to prior research, the stronger the covalent character of the M-X bond, the more favourable the redox reaction at the transition metal center.[57]. The high degree of covalency and higher intrensic metallicity are resposible for the higher conductivity and mass transfer rate of the transition metal tellurides. Ting and coworkers employed interface engineering to integrate both selenide and telluride to take advantage of the benefits of both systems. The HRTEM analysis of Ni0.85Se/NiTe@NF showed nanorod thickening after electrodeposition of nickel selenide onto nickel telluride, justifying the formation of a core shell structure.





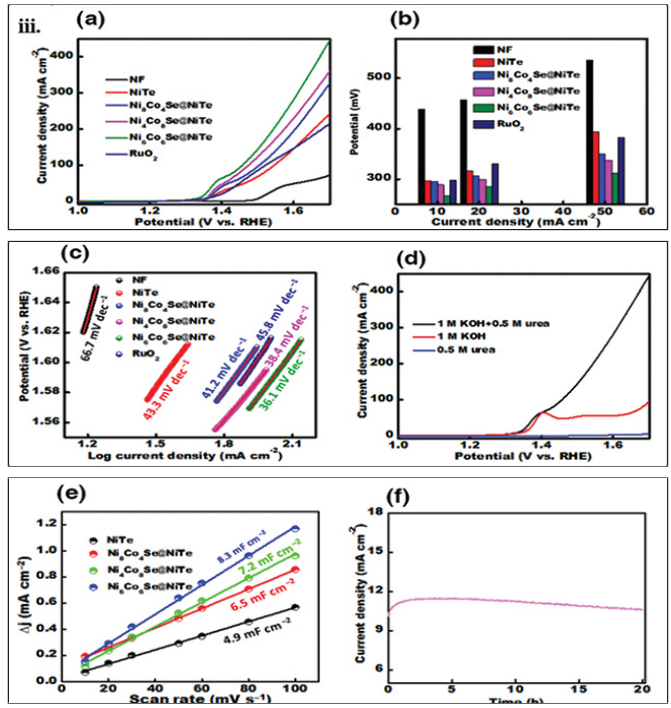


Fig.7. i) schematic diagram of Synthetic strategy ii) HRTEM images of $Ni_xCo_{12-x}Se$@NiTe iii) a. polarization curve of ifferent catalyts, b. comparison graph, c. Tafel plot , d. polarozation plot with and without the presence of urea, e. ECSA and f. stability graph.[58]. (Reproduced from Ref. 58 with permission from the John Wiley & Sons Australia, Ltd)

Further high angle annular dark field-scanning TEM (HAADF-STEM) results showed a uniform distribution of Ni throughout the catalyst surface, while Se and Te were present in the core of the structure. An enhancement in peak area of Ni^{2+} and Ni^{3+} after electrodeposition, while a positive shift

and negative shift in peaks concerned with Te 3d and Se 3d suggested the formation of an interface that favours electron transfer from Te to Se. All this enhancement resulted in achieving superior activity for UOR where it acquired a current density of 200 mA/cm^2 at a potential of just 1.324 mA/cm^2. [59]. Diab et.al. synthesised $Ni_xCo_{12-x}Se$@NiTe via the two stage electrodeposition process shown in (Fig.5.i.a). FESEM images display a greater and uniform coverage of squama-like architectures composed of a 2D $Ni_xCo_{12-x}Se$ nanosheet network on the surface of freestanding NiTe dendritic frameworks, whereas the HR-TEM picture shows interlacing between the 3D arrayed dendrites and the 2D nanosheet network, forming a hierarchical core-shell architecture (Fig.5.ii.a-f) while EDS-mapping reveals the presence of Ni,Co,Te, and Se on the catalyst's surface. Ni_6Co_6Se@NiTe electrode achieves the a current density of 10 mA/cm^2 at a potential of 1.33 V vs RHE while Ni_4Co_8Se@NiTe achieves same current density at 1.35 V vs RHE and Ni_8Co_4Se@NiTe at 1.36 V vs RHE. Similarly, Ni_6Co_6Se@NiTe shows the lowest tafel and highest ECSA due to their unique structure (Fig.5.iiia-f). [58]. In the above discussion we observed various examples of heterostructure engineering where by coupling the advantage of individual components and regulating the redistribution of electrons around metal active centers, resulted in the the optimal adsorption energies of reactive species for rapid reaction kinetics and generation of higher number of active sites compared to its unitary counterparts. Simply put, the Se-Ni(OH)$_2$@NiSe/NF structure combines the conductivity of the NiSe core with the high active sites provided by the Ni(OH)$_2$ shell. The polymetallic $NiSe_2$ and $FeSe_2$ create a p-p heterojunction that facilitates the adsorption of target molecules. By heterostructuring selenides and tellurides of nickel, the system benefits from the advantages of both components. The distinct morphologies and structure achieved through heterostructuring are responsible for the enhanced catalytic performance of heterostructured catalysts compared to their unstructured counterparts.

Table 1. List summerizing catalytic performance of engineered Nickel selenide based catalysts for UOR

S.N.	Catalyst	Electrolyte	Catalytic activity	Tafel	Reference
1.	Fe-$NiSe_2$	1.0 M KOH + 0.33 M urea	1.367 V vs RHE @10 mA/cm^2 1.54 V vs RHE @ 125 mA/cm^2	22.9 mV dec^{-1}	[20]
2.	NiMoSe	1.0 M KOH + 0.33 M urea	1.39 V vs RHE @ 10mA/cm^2	43.3 mV dec^{-1}	[60]
3.	$NiCoFeSe_2$	1.0 M KOH + 0.33 M urea	1.37 V vs RHE @ 50 mA/cm^2 1.44 V vs RHE @ 100 mA/cm^2	149.0 mV dec^{-1}	[43]
4.	MoSe@NiSe & FeSe@NiSe	1.0 M KOH + 0.33 M urea	1.42 V vs RHE @ 100 mA/cm^2 (Both MS@NS & FS@NS)	(48.0 & 57.0) mV dec^{-1}	[61]
5.	$Cu_2S@Ni_3Se_2$	1.0 M KOH + 0.50 M urea	1.338 V vs RHE @ 10 mA/cm^2	76.0 mVdec^{-1}	[52]
6.	$Ni_{0.85}Se$@rGO	1.0 M KOH + 0.50 M urea	1.36 V vs RHE @ 10 mA/cm^2	152.08 mV dec^{-1}	[46]
7.	NiCoSe@CNT	1.0 M KOH + 0.50 M urea	0.29 V vs Hg/HgO	61.3 mV dec^{-1}	[47]
8.	Ni_3Se_2@CuSex/CF	1.0 M KOH + 0.50 M urea	~ 1.35 V vs RHE @ 100 mA/cm^2	45.0 mV dec^{-1}	[56]
9.	$NiSe_2$@NiO	1.0 M KOH + 0.33 M urea	1.33 V vs RHE @10 mA/c^{m}2	38.5 mV dec^{-1}	[49]
10.	$Ni_xCo_{12-x}Se$@NiTe	1.0 M KOH + 0.5 M urea	1.33 V vs RHE @ 10 mA/cm^2	36.1 mV dec^{-1}	[47]
11.	3D-$NiSe_2$@NC	1.0 M KOH + 0.5 M urea	1.32 V vs RHE @ 10 mA/cm^2	---	[62]
12.	Ni-S-Se	1.0 M KOH + 0.50 M urea	1.38 V vs RHE @10 mA/cm^2 1.42 V vs RHE @ 100 mA/cm^2	28.0 mV.dec^{-1}	[44]
13.	$Ni_3Se_4/NiSe_2$	1.0 M KOH + 0.50 M urea	1.296 V vs RHE @ 100 mA/cm^2	44.4 mV dec^{-1}	[55]
14.	Se-Ni(OH)2@ NiSe	1.0 M KOH + 0.33 M urea	0.366 V vs SCE @ 100 mA/cm^2	---	[51]
15.	$NiSe_2$ /$FeSe_2$	1.0 M KOH + 0.5 M urea	~ 1.33 V vs RHE @10 mA/cm^2	32.0 mVdec^{-1}	[54]
16.	$Ni_{0.85}Se/NiSe_2$@NC	1.0 M KOH + 0.33 M urea	252 mA/cm^2 @ 1.6 V vs RHE	64.4 mV dec^{-1}	[48]
17.	$Ni_{0.85}Se/CeO_2$@NC	1.0 M KOH + 0.33 M urea	1.294 V vs RHE @ 10 mA/cm^2	20.09 mV dec^{-1}	[50]
18.	$Ni_{0.85}Se$/NiTe	1.0 M KOH + 0.30 M urea	1.324 V vs RHE @ 200 mA/cm^2	3.66 mV dec^{-1}	[59]

5. Discussion

Catalysts towards urea oxidation reaction are subject to the multi-functionality which includes low overpotential, faster reaction kinetics, long-term stability (superior poising resistance) and high electrocatalytic activity. Unitary catalysts (e.g. NiO, $Ni(OH)_2$, and NiSe,etc.) which exhibit catalytic activity for UOR, may not excel in all the necessary parameters to be considered as a robust catalyst. In the previous sections, we explored how herostructure engineering has been advantageous in enhancing UOR activity. Through heterostructuring we can intergrate two or more components and get benifeted from each of their strength. Transition metal chalcogenides have been widely used in research for applications such as sensors and supercapacitors due to their ability to form diverse and distinct heterostructures, setting them apart from other compounds.[63]. Nickel selenide owing to this property along with its semiconducting nature and higher surface reconstruction ability w.r.t to other chalocogenides is the reason of its intesive use for UOR application. While significant progress has been achieved through heterostructuring, further attention and research are needed to fully utilise its untapped potential. DFT calculations are used to analyse the catalyst mechanism of hetero-structured catalysts, but they do not completely represent the actual working conditions of the catalyst system. Factors like variations in electrolyte, dynamics, and structural changes during catalysis are frequently overlooked. Additionally, a UOR specific mechanistic research is necessary to comprehensively grasp the interplay of heterostructures and their role in the UOR mechanism. Strategical improvements are necessary to fully achieve the potential of both systems. Despite the abundance of reported hetero-structured catalysts, there is still an inadequate understanding of aspects such as crystal planes, chemical bond types, interface position, and spacings between hetero-interfaces that are pertinent to the heterostructure.

6. Conclusion and Outlook

This review discusses about the electrochemical UOR and its cruical role in urea assisted hydrogen generation. Nickel selenides have been endorsed as an efficent materials to promote UOR due to their high abundance, intrinsic electrical conductivity and ability for surface reconstruction. Different strategies that were implemented for enhancement of properties of nickel selenides like incorporation/ doping of heteroatom, constructing heterostructures, synthesizing carbon based composites have been discussed in this review. Apart from these valuable progress there are still some challenges and problems which need to be addressed some of which are; a) UOR mechanism is still debatable and futher studies are required for proper understanding. b) compsites based on 2D materials like rGO, functionalized rGO are needed to be explored, c) Although nickel selenides possess tremendous potential but it also associated with toxicity since higher concentration of Se is harmful for enviroment, therfore proper mangement of waste is required for the success of these catalyst for the application of energy generation.

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