

Studies on water splitting reaction via electrochemical and photoelectrochemical methods

Instruction:

Society concern about global energy crisis and environmental pollutions (CO₂ emission) due to utilization of fossil fuels as energy, new advance tools must be bring to bear on green and clean energy which can exhibit the novel properties require under a real-world environment. Triggered by the development of new technologies and the consequent decrease cost of the application devices, the use of renewable energies, and wind power, has rapidly evolved during the last years. Nevertheless, both technologies suffer from the disadvantage of the intermittency, which limits their usage as primary feed for the grid, requiring the use of mediating systems to buffer their output. A number of methods for storage are proposed hydroelectric, compressed air, thermal energy and batteries. Of course, the energy that can be produce in the chemical bonds of small molecules represents a very attractive approach. Inspired by this process, much effort is currently being devoted to the production of environmentally friendly hydrogen. Hydrogen is considered as an ideal fuel for the future. Hydrogen fuel can be produced from clean and renewable energy sources and, thus, its life cycle becomes clean and renewable.

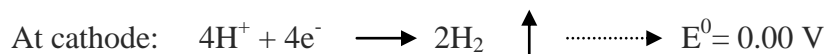
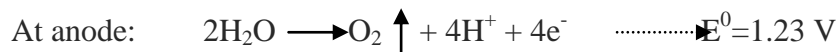
The advantages of using hydrogen as a fuel are:

- Harmless combustion product (H₂O) for the environment
- Hydrogen has the potential to run a fuel-cell engine with greater efficiency over an internal combustion engine.
- A key advantage of hydrogen is that when burned, carbon dioxide (CO₂) is not produced.

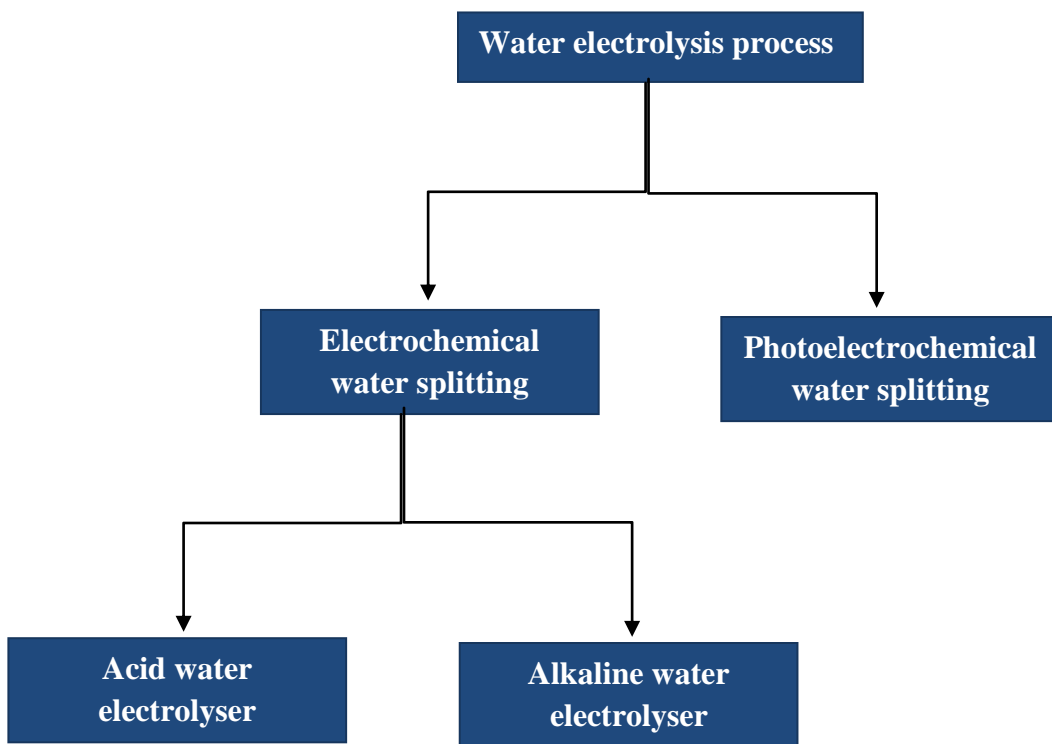
Further, the increasing interest in generation of hydrogen as an energy carrier, hydrogen can produce using several methods such as, Pyrolysis technology [1], Algae method [2], Steam reforming method [3], Gasification method [4] and water electrolysis process [5]. Among the all methods, the water electrolysis is best and easy method to produce hydrogen.

Water electrolysis process for hydrogen production

The principle of water electrolysis is the water split into oxygen at anode side (Oxygen Evolution Reaction) and hydrogen at cathode side (Hydrogen Evolution Reaction) using electricity. The equation is (1) and (2),



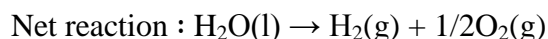
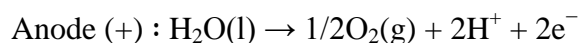
The water splitting process can be divided into two types as explain below.



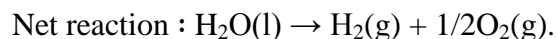
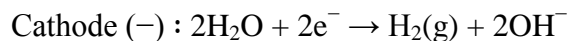
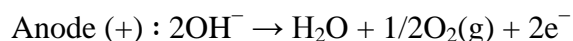
a. Electrochemical water splitting

Thermodynamics reactions explain that the water splitting reaction is a non-spontaneous transformation. However, it can be work out externally by providing energy to the system, for example, electricity. This is a so-called endergonic transformation and the device used for the process is an electrolyser. In water electrolysis cells, electrical work is provided to the cell to split water molecules into gaseous hydrogen and oxygen.

In acidic media,



In alkaline media,



Metal/metal oxides (Ni, Fe, Co etc...) [6-8] are interesting from fundamental research perspective as well as application point of view, for example it has been identified as a unique material in various electrochemical applications such as fuel cell catalysts and electrodes, electrodes in water electrolyzer etc. These electrochemical conversion systems are actively being considered for recent research activities for enhancing their modern energy technology. Moreover, nickel compounds are of great interest to build fuel cell/water electrolyzer using carbon-based materials due to the availability of various crystalline forms of carbon with relatively high conductivity and surface area with high electrode stability.

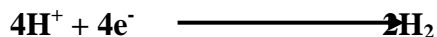
b. Photoelectrochemical water splitting

Photoelectrochemical (PEC) cells are special classes of electrochemical cells, wherein at least one of the electrodes is photo responsive. More broadly, PEC cell is defined as an electrochemical cell that can convert light energy into a more useful energy product through light-induced electrochemical processes. In PEC cells, water splits into hydrogen and oxygen with the aid of photocatalyst, which absorbs the photon energy and converts it to electrochemical energy (in the form of chemical bonds of hydrogen and oxygen) [9-11]. This is one of the most prominent ways of producing clean and cost-effective hydrogen by taking into account all photons that continuously strike the earth's surface. The process of splitting water with the aid of electrical energy is called electrolysis of water and if it is aided by photon energy of sunlight it is called photocatalysis of water splitting. PEC water splitting utilizes both solar and electrical energy to split water into H₂ and O₂.

At Anode:



At Cathode:



Overall Reaction:



PEC water splitting to hydrogen is an attractive method for capturing and storing the solar energy in the form of chemical energy. Metal oxides are promising as photoanode materials due to their low-cost synthetic routes and higher stability than other semiconductors. A recent renewal in solar hydrogen production by water splitting research has resulted in the exploration of new semiconductor materials electrodes. The nanostructure titanium dioxide (TiO₂) is an excellent semiconductor material in technological applications such as hydrogen production by water electrolysis, photocatalyst, photovoltaic material, and dye-sensitized solar cell etc. with the exceptional properties of high efficiency, chemical inertness, photostability, and low cost [12]. A major challenge of water splitting is the large overpotential to oxygen evolution at TiO₂

semiconductor electrode. In recent research on transition metal oxides, carbon based semiconductors and composite alloys to the promising approach of enhance the photo and electro catalytic efficiency of TiO_2 . In this contemporary context, this proposal aims at addressing particular issues related to reduce the band gap, surprising recombination of photogenerated electron-hole pairs in TiO_2 electrode material via applying a variety of fabrication strategies to metal oxide photoelectrode including (i) size and morphology-control, (ii) metal oxide heterostructuring, (iii) dopant incorporation (carbon and nitrogen based materials), (iv) attachments of quantum dots as sensitizer, and (v) co-catalyst coupling. Each strategy highlights the underlying principles and mechanisms for the performance enhancements. Moreover, the heteroatom (Nitrogen, Carbon etc...) doped TiO_2 nanostructure shows great result in the photoelectrochemical water splitting for hydrogen generation.

The chapters are reported that synthesized and characterized $\text{TC@WO}_3\text{@g-C}_3\text{N}_4\text{@Ni-NiO}$ composite matrix, $\text{Cu}_2\text{O-NiO}$ composite, defect rich TiO_2 and N-doped TiO_2 nanotubes nanocomposite materials using hydrothermal, thermal treatment, chemical and electrochemical anodization methods and it is studies on water oxidation via electrochemical and PEC methods to produce hydrogen.

Methods

(a) Synthesis of $\text{g-C}_3\text{N}_4\text{@Ni-NiO}$ Matrix: The $\text{g-C}_3\text{N}_4\text{@Ni-NiO}$ was synthesized by hydrothermal and thermal treatment method using melamine and nickel nitrate as starting materials. Melamine (3.8 g) and nickel nitrate (8.92 g) were dissolved in 25 mL of deionized water by stirring and heated to 100 °C to remove water, then kept the resultant white solid residues in an incubator for 6 h. The resultant white solid residues were calcinated in a muffle oven at 500 °C for 2 h with the rate of 4 °C min⁻¹. The resultant $\text{g-C}_3\text{N}_4\text{@Ni-NiO}$ matrix powder was collected and used for further experiments. In order to synthesize pristine $\text{g-C}_3\text{N}_4$ (control sample), melamine was thermally reduced without nickel nitrate.

Preparation of WO_3 Coated Toray Carbon (TC): The TC (obtained from SGL carbon Germany) sheet was cleaned with acetone and ethanol for 30 min under the ultrasonication and dried it at room temperature for few hrs. After drying, 1 cm⁻² area of TC sheet was marked for further use. The WO_3 was coated on this marked surface of TC in an air atmosphere using tungsten rod (Sigma-Aldrich, 99.99%) by physical vapor deposition (thermal evaporation)

method. The WO_3 coated TC was annealed at $450\text{ }^\circ\text{C}$ for 40 min in air and the same electrode was used for further experiments.

Preparation of $\text{TC@WO}_3\text{@g-C}_3\text{N}_4\text{@Ni-NiO}$ Matrix: The WO_3 coated TC electrode was further modified with $\text{g-C}_3\text{N}_4\text{@Ni-NiO}$ by drop casting method. Typically, 50 mg $\text{g-C}_3\text{N}_4\text{@Ni-NiO}$ matrix was dispersed with 30 mL deionized water under ultrasonication for 1 h. The WO_3 coated TC electrode kept on a hot plate at $100\text{ }^\circ\text{C}$ onto which about 10 μL slurry was drop cast and dried at $200\text{ }^\circ\text{C}$ in a tubular furnace under an inert atmosphere for 1 h. After cooling to room temperature, the $\text{TC@WO}_3\text{@g-C}_3\text{N}_4\text{@Ni-NiO}$ electrode was ready for further characterization and electrochemical analysis.

(b) Simple chemical method: All chemicals used in the experiment are analytic reagent grade. The CuO and related nanocomposite were prepared by simple chemical method. In a typical procedure, 2.72g of 0.05M copper acetate ($\text{Cu}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$) in 300 mL of deionized water dissolved under stirrer and then 0.5g of PVP was added into the solution for control the particle growth. The solution was temperature was raised 90°C . Then 1 ml glacial acetic acid is added to above aqueous solution with the constant stirring. After few minutes, 1.5g of NaOH pellets were directly added into the above solution. Subsequently, black precipitates were obtained and repeatedly washed by deionized water and absolute ethanol for several times till pH reached. Then, the precipitates were dried at $80\text{ }^\circ\text{C}$ for 2hrs. Finally, the obtained powders were Calcined at $500\text{ }^\circ\text{C}$ for 4 hrs. For preparation of the CuO-NiO nanocomposites, 0.5M of nickel chloride was added after dissolved the copper acetate in di-ionized water.

(c) Electrochemical studies:

Anodization:

The sonicated Ti plates were then subjected for anodisation process in 0.5 M sulphuric acid electrolyte. The cathode used here is pt. while the plate acts as anode. A Voltage of 10 is applied using potentiometer. The process is carried out for 1,3,5,7 minutes using several plates. At this stage the titanium plates are transformed into a defect rich titania which is a vibrant electro catalyst employed for water splitting.

Cathodization:

Once the anodization process has been completed the samples were subsequently subjected for cathodization process under same conditions as the anodization was carried out. This process was carried out to improve the surface of the sample for more electronic conductivity.

Polarization:

Electrochemical tests were performed using a Bio-Logic instrument with the conventional three electrode systems for OER and HER in alkaline and acid solution. Linear sweep voltammograms (LSVs) was recorded at 10 mV s^{-1} to minimize the capacitive current which is directly proportional to the scan rate and chronoamperometry was used to analyse the stability test of samples.

Electrochemical Impedance spectra (EIS):

The EIS were carried out using a Potentiostat / Galvanostat (Solartron analytical) impedance analyser at the DC amplitude of 10 mV and the frequency range of from 100 KHz to 1 mHz.

Characterizations techniques

The prepared N-doped TiO_2 nanotubes were analyzed using different characterization tools for their structural, compositional and morphological features. The XRD pattern was carried out using Bruker X-ray powder diffractometer with Cu-K_α radiation ($\lambda=0.154 \text{ nm}$) in the 2θ range of 10-100 degree for identifying the crystalline phase. The UV-visible spectrum was recorded by Varian spectrophotometer (Model: Cary5000 scan) to calculate the band-gap. The surface morphology of TiO_2 nanotubes was observed using a field emission scanning electron microscope (SEM) (Carl Zesis; SUPRA 55VPFEI; Germany), atomic force microscope (AFM) (Agilent tech; 5500) and transmission electron microscope (TEM) (TecnaiTM; G2, F20; FEI) instruments. The chemical and elemental composition of N-doped TiO_2 nanotubes were analysed by X-ray photoelectron spectrometer (PHI 5000 VersaProbe; ULVAC) instrument. Raman spectra were carried out using Raman microscope (Renishaw, UK) with laser light at incident wavelength of 632.8 nm. The presence of functional groups in N-doped TiO_2 nanotubes were observed using FTIR spectrometer (SENSOR27; BRUKER OPTIK GMBH, Germany). The EPR studies were carried out using Bruker bio-spin (EMX Plus; Xband). Photo-electrochemical

tests were performed using solar simulator (Solar simulator AM 1.5G, Photo emission tech., SS80AAA) with a light intensity of 1000 W/m^2 , and the light intensity was calibrated using a standard silicon solar cell before the PEC measurements. Photocurrents were recorded using a Potentiostat / Galvanostat (Solartron analytical).

Incident Photon to Charge carrier generation Efficiency (IPCE) measurement:

Photoconversion efficiency data was collected by Opto-solar instrument (GmbH SR300/300) from 200-800 nm using two electrodes system (N-doped TiO_2 nanotubes as Photoanode and Pt wire as cathode) in 1 M NaOH (14 pH).

Intensity Modulated Photovoltage Spectroscopy (IMVS) measurement:

IMVS measurement was performed by two electrode configuration in 1 M NaOH (14 pH) and the spectra were recorded under light intensity of 50% at 455 nm wavelength using Solartron 1260 frequency response analyzer (FRA) combined with a Thor labs DC2100 analytical instrument (bandwidth 100 kHz) driven by the dc and sine wave output of the FRA (Modulab XM Photochem).

Photoelectrochemical experiment

a. Photocurrent measurement

PEC measurement was performed in aqueous solution of 1 M NaOH (14 pH) with three electrodes (working, counter and ref.) system using Solar simulator AM 1.5G, Photo emission tech., SS80AAA with a light intensity of 1000 W/m^2 . The photocurrent was collected by potentiostat solartron analysis under xenon lamp light with two electrodes (N-doped TiO_2 nanotubes as a working electrode, platinum as a counter electrode and Hg/HgO as a reference electrode).

b. Outdoor Photoelectrochemical measurement

PEC (Photoelectrochemical cell) analysis for N-doped TiO_2 nanotubes was carried out under direct sunlight (1000 lux intensity) with two electrode system in 1 M NaOH (14 pH) / 1 M H_2SO_4 (1 pH) solutions and the potential and current data were collected by multimeter for each 1 hour. The N-doped TiO_2 nanotubes photoanode was kept in 1 M NaOH (14 pH) and Pt coated titanium (as cathode) was kept in 1 M H_2SO_4 (1 pH) solution.

Chapter-1

NiWO₃ Nanoparticles Grown on Graphitic Carbon Nitride (g-C₃N₄) Supported Toray Carbon as an Efficient Bifunctional Electrocatalyst for Oxygen and Hydrogen Evolution Reactions

Catalysts for oxygen evolution reaction (OER) and hydrogen evolution reaction (HER) are at the heart of water oxidation reactions. Despite continuous efforts, the development of OER/HER electrocatalysts with high activity at low cost remains a big challenge. Herein, a composite material consisting of TC@WO₃@g-C₃N₄@Ni-NiO composite matrix as a bifunctional electrocatalyst for the OER and HER is described. Though the catalyst has modest activity for HER, it exhibits high OER activity thereby making it a better nonprecious bifunctional electrocatalyst and is further improved by g-C₃N₄. The catalytic activity arises from the synergetic effects between WO₃, Ni-NiO, and g-C₃N₄. A Ni-NiO alloy and WO₃ nanoparticles decorated on the g-C₃N₄ surface supported toray carbon (TC) matrix (TC@WO₃@g-C₃N₄@Ni-NiO) by a facile route that show an excellent and durable bifunctional catalytic activity for OER and HER in the alkaline medium are developed. This carbon nitride with binary metal/metal-oxide matrix supported with TC exhibit an overpotential of 0.385 and 0.535 V versus RHE at a current density of 10 mA cm⁻² (Tafel slopes of 0.057 and 0.246 V dec⁻¹ for OER and HER, respectively), in 0.1 M NaOH. The catalyst is stable for 17hrs on continuous electrolysis.

Chapter-2

Synthesis of Cu₂O-NiO heterostructure via simple chemical method: as a highly active electrocatalyst for oxygen evolution reaction

The chapter 2 represents the synthesis of Cu₂O-NiO binary metal oxide via simple chemical method. The Cu₂O-NiO heterostructure was characterized using XRD and Raman spectroscopy which is confirmed the formation monoclinic structure in the composite materials. XPS spectrum exhibits the oxidation state of Cu, Ni and O elements in Cu₂O-NiO heterostructure. TEM and SEM images shows pellet like morphology of Cu₂O-NiO heterostructure. The Electrochemical studies investigate that oxygen evolution reaction of Cu₂O-NiO heterostructure in 1 M KOH solution. It shows lower onset potential of 1.38 V with Tafel slope value of 0.250 V dec⁻¹. The Cu₂O-NiO heterostructure exhibits higher activity compare to

bare Ni metal in alkaline medium. The composite was highly stable for 2 hrs in 1 M KOH solution.

Chapter-3

Design of non-noble electrocatalyst for hydrogen evolution reaction

This chapter presented a feasible electrochemical cathodization method to prepare highly efficient HER electrocatalyst Titania with an excellent attributes in terms of onset potential, Tafel slope and stability. XRD pattern was confirmed the formation of crystalline TiO_2 on the titanium substrate. FE-SEM images reflect the porous surface morphology of TiO_2 for various time. The oxygen vacancies were represents by high resolution O1s XPS spectra. The prepared electrocatalyst exhibits a lower onset potential of 0.17 V Vs RHE and current density of 150 mA cm^{-2} to drive a HER which. In addition, the stability studies carried out in full cell characterizations showed that the titania is an extremely stable electrocatalytic electrode material for HER in high acidic conditions. This is mainly attributed to the high corrosion resistance .The encouraging and highly positive results of the overall study implied that the Titania can be chosen as the cost-efficient and stable electrocatalytic electrode material for bulk water electrolysis in future hydrogen production and at the same time it can be swapped with the precious and expensive materials like, Pt, Ir and Ru used in current water electrolyzers to reduce the cost of hydrogen production.

Chapter-4

A photoelectrochemical system for unassisted high efficiency water splitting reaction using N-doped TiO_2 nanotubes

In chapter 4, a facile method to synthesis N-doped TiO_2 nanotubes by electrochemical anodization method and pH gradients effect in PEC water splitting reaction. N-doped TiO_2 nanotubes exhibited higher photoelectrochemical performance than bare TiO_2 nanotubes. This improved response is mainly attributed to enhanced light absorbtion at visible region, reduced electron-hole recombination and increased charge carriers in defect-rich N-doped TiO_2 nanotubes. The XPS confirmed the presence of nitrogen in TiO_2 lattice which occur as N-Ti-N and N-Ti-O bonding. FE-SEM, TEM and HR-TEM results shows morphology of nanotubes for bare and N-doped TiO_2 nanotubes. After doping of nitrogen into TiO_2 lattice, the band-gap values of bare TiO_2 nanotubes reduced from 3.2 to 2.7 eV. The Mott-Schottky plot indicated the increase in charge carrier density of $7.7728 \times 10^{22} \text{ m}^{-3}$ by nitrogen doping in TiO_2 lattice

compared with the charge carrier density of $1.462 \times 10^{22} \text{ m}^{-3}$ for bare TiO_2 nanotubes. The IPCE results showed the light-to-current conversion efficiency of nearly 70% for N-doped TiO_2 nanotubes which is one order higher than that of bare TiO_2 nanotubes. N-doped TiO_2 nanotubes exhibit the photo current density of 0.76 mA/cm^2 with long term stability of 120 hrs in the PEC water-splitting under direct sunlight. Moreover, the photoanode exhibited the solar-to-hydrogen conversion efficiency of 0.5% in aqueous electrolytes of 1 M NaOH (14 pH)/1 M H_2SO_4 (1 pH) solution. The porous, defect-rich and nitrogen doped TiO_2 nanotubes photoanode shows excellent performance and high stability for PEC water-splitting applications. Our findings may promote photoelectrode synthesis by electrochemical method with in-situ doping of non-metal especially under simple and environmentally benign conditions. An easy, inexpensive and efficient approach to introduce nitrogen atoms into the titania structure.

Conclusion:

The chapters represent design and developed the various nanomaterials as an electrocatalysts and photocatalysts using simple chemical and electrochemical methods for water oxidation process. The nanomaterials were investigated electrochemical and photoelectrochemical activities in acid and alkaline medium using LSV, chronoamperometry, impedance spectroscopy.

- a. In chapter 1, the $\text{TC@WO}_3\text{/g-C}_3\text{N}_4\text{/Ni-NiO}$ composite matrix shows good bifunctional electrocatalyst for OER and HER in alkaline medium. The complex matrix exhibits overpotential of 0.385 and 0.535 V versus RHE at a current density of 10 mA cm^{-2} (Tafel slopes of 0.057 and 0.246 V dec^{-1} for OER and HER, respectively), in 0.1 M NaOH.
- b. The chapter 2 represents $\text{Cu}_2\text{O-NiO}$ core-shell nanomaterial was prepared by simple chemical and thermal treatment method. A synthesized electrocatalyst has been tested for OER activity in 1 M KOH solution. The $\text{Cu}_2\text{O-NiO}$ core-shell electrode delivers the onset potential of 1.38 V at Current Density of 0.01 mA with Tafel slope value of 0.250 V dec^{-1} .
- c. The chapter 3 reported that the defect rich titania catalyst can be prepared via electrochemical cathodization method. The electrocatalyst has been delivered a lower onset potential of 0.17 V vs RHE and current density of 150 mA cm^{-2} for HER in 1M H_2SO_4 solution.

- d. In chapter 4, photoelectrochemical water splitting reaction was carried out for N-doped TiO₂ nanotubes. The N-doped TiO₂ nanotube was prepared via electrochemical anodization method. The photocatalyst shows good and highly stable in 1M NaOH/ 1M H₂SO₄ solution. N-doped TiO₂ nanotubes show the photo current density of 0.76 mA/cm² with long term stability of 120 hrs in the PEC water-splitting under direct sunlight. Moreover, the photoanode exhibited the solar-to-hydrogen conversion efficiency of 0.5%.

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