

# RECENT ADVANCEMENTS IN STRUCTURAL DESIGN OF NANOMATERIALS FOR ENERGY STORAGE DEVICES AND PHOTOCATALYSIS

## Abstract

One of the primary areas of concern in recent years has been the conversion and storage of renewable energy. An entirely new potential has emerged to address energy conversion and electrochemical energy storage. Nanomaterials have been employed for storage devices such solar cells, supercapacitors, and batteries as well as for the generation of hydrogen, CO<sub>2</sub> reduction, water splitting, oxygen reduction via electro catalysis, and photocatalysis. nonmaterial's such as graphitic carbon nitride, single walled CNT, nanostructured polymers and metal oxides (TiO<sub>2</sub> and ZnO nanowires) has prominent contribution. Keeping in mind the obvious characteristic of the nonmaterial's (surface to volume ratio, porosity, high conductivity, nanoscale dimensions). Herein recent trends electrochemical, photo electrochemical, photocatalytic area the fabrication advanced techniques and application in the field of renewable energy production and storage is discussed.

**Keyword:** Nanostructures, Energy storage, Energy conversion

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## I. INTRODUCTION

In the area of renewable energy, photocatalytic energy conversion and electrochemical energy storage both represent significant importance that helps to create clean and sustainable energy systems[1–3]. Utilising light energy to catalyse chemical reactions that transform solar energy into more usable forms, such as electricity or chemical fuels, is known as photo catalytic energy conversion[4,5]. A photocatalyst that absorbs light and starts a photochemical reaction, is commonly used in this method. The process of transforming electrical energy into chemical energy and storing it for later use is referred to as electrochemical energy storage[6]. With current research focused at increasing efficiency, extending functionality, and promoting scalability, the future of photocatalytic energy conversion seems bright. These developments could make a substantial contribution to the creation of renewable and sustainable energy systems. To increase the effectiveness of photo catalytic devices, researchers are always experimenting with new materials and engineering methods. This includes creating innovative photocatalyst with improved charge separation, band gap optimisation, and low recombination rates. In addition to converting solar energy, photocatalyst might be made to filter out impurities from water or air, which would have a combined positive impact on environmental sustainability and energy production. While lithium-ion batteries dominate the current energy storage landscape, future electrocatalysis energy storage systems will likely explore alternative chemistries[7–9]. Researchers have been working diligently on developing new electrocatalst with enhanced activity, selectivity, and stability. This involves the exploration of novel catalyst materials, such as transition metal oxides, carbon-based materials, and metal-organic frameworks. The development of photocatalytic energy conversion and electrochemical energy storage technologies[10] is significantly aided by nonmaterial's [11–14]. The performance of energy storage devices and energy conversion is improved by the high surface area-to-volume ratio that nonmaterial's provide as electrode materials[14–18]. Nanoscale catalysts improve the overall efficiency and kinetics of energy storage devices. Advanced electrolytes with enhanced ionic conductivity and stability can be created using nonmaterial's.

## II. ELECTRO CHMICAL ENERGY STORAGE

Today, photovoltaic cells have the greatest potential for contributing towards sustainable energy sector. The two-electrode battery, (PES) devices can efficiently convert and store solar energy, simplifying the arrangement and reducing external energy loss[20–22]. The electrode material is the primary determinant of the devices' ability to store energy and provide electricity. Graphite and other carbon-based materials, such as activated carbons, are frequently employed as electrodes in conjunction with other NPs.

- 1. Batteries:** An approach to build an anode material which is sustainable, cost effective Antonio Vázquez-López et al. [23] and his team worked on tin oxide ( $\text{SnO}_2$ ) doped with Lithium and nickel where innickel incorporation reduced the conductivity compared to that of lithium incorporation. This increase in the conductivity resulted due to higher doped Li acceptor sites are exposed and oxygen vacancies which are high oncomparing with  $\text{SnO}_2$  which not doped  $\text{SnO}_2:\text{Li}_{0.2}$  made them more stable. Kostiantyn V. Kravchyk et al. has compared the efficiency of bulk and nano antimony sulphidematerials for both sodium and lithium batteries[24]. For 1200 cycles, the capacities of the anodes made of small and big  $\text{Sb}_2\text{S}_3$  NPs remained steady. The charge storage capacities for nano- $\text{Sb}_2\text{S}_3$

were consistently higher than those for bulk  $\text{Sb}_2\text{S}_3$ , and the anode made of small  $\text{Sb}_2\text{S}_3$  NPs consistently demonstrated at least a 5% higher capacity than the anode composed of big NPs. They found that even though is not cost effective with respect to the bulk, nano- $\text{Sb}_2\text{S}_3$  showed stability in recyclability, higher retention capacity and higher charge storage capacity. Ni-rich  $\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$  nanomaterials[25] with a unique nanobrick NCM morphology (NB-NCM) has aimed for long term cycling electrode with high stability. Where in SEM image have showed cracking in cathode materials which can be attributed to decrease in capacity when cycling experiments for Ni-rich  $\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}(\text{C-NCM})$  and Ni-rich  $\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$  nanomaterials with a unique nanobrick NCM morphology (NB-NCM), showed no crack along with fast charging ability. Copper phosphide ( $\text{Cu}_3\text{P}$ ) has proved to be low cost and environmental friendly approach for sodium and lithium ion batteries by Ping Xu and Kaibin Dai et al.[26] t  $\text{Cu}_3\text{P}$  nanoparticles were uniformly distributed in the N-CN matrix. This porous textured have contributed for easy movement of Li/Na ions which enhanced the reversible capacity thus stability.

- 2. Super Capacitors:** The hydrothermal synthesis of the  $\text{NiCo}_2\text{O}_4/\text{NF}$  electrode by Zhe Lu et al. [27] showed that this material has shown 75% capacitance after 1000 cycle, where uniformly grown as Nanoneedle like structure over NF collector have enhanced the remarkable performance and stability. ASC study shown that power density, recycling ability and 97.1% after retention time after 1000 cycle. Jibo Jiang et al. [28] has prepared  $\text{CuCo}_2\text{S}_4/\text{Co-MOF}$  for symmetric Supercapacitors. The porous nanostructure of 2D like –  $\text{CuCo}_2\text{S}_4$ -45 played major role in electron transport and storage. The electrochemical impedance spectroscopy showed that good conductivity and electrochemical conductance because of the unique 2D layer which are interconnected.  $\text{CuCo}_2\text{S}_4$ -45 nanoparticles have high rate performance, which reached 80.3%, and have ordered porosity stable nanostructures and good synergy properties between the binary metals that make them superior to other materials in terms of specific capacitance and rate performance. Kannadasan Thiagarajan et al. [29] has developed  $\text{NiMO}_4/\text{g-C}_3\text{N}_4$  electrode for pseudocapacitor application. Where CV and GCD result showed that the columbic efficiency is 100% and there was a notable increase in anodic and cathodic peak current. lower  $R_{ct}$  value of  $\text{NiMO}_4/\text{g-C}_3\text{N}_4$  by EIS study proved the same. The higher density value of the materials made suitable for electrode materials for Supercapacitors.  $\text{ZnCo}_2\text{O}_4$  (ZC-UAH) urea (UA), ammonium fluoride (AF), and hexamethylenetetramine (HT) has been compared for super capacitors application by Yedluri Anil Kumar et al.[30]the resultant materials had highly porous region for redox reaction where ESI ,GCD and CV data have proved that cyclic stability, storage density along with faradic reaction were also carried out check for the capacity behaviour of electrode and  $\text{ZnCo}_2\text{O}_4$  (ZC-UAH) has higher significant values.
- 3. Fuel cell:** High-performance anode made of nickel foam (NF) modified with magnesium cobalt oxide ( $\text{MgCoO}_2$ ) and poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) as active components and among which  $\text{MgCoO}_2/\text{PEDOT:PSS}@NF$ [31] anode showed better compatibility for microbial fuel cell and also generation of bio electricity. The unique porous structure has resulted in easy electron transport system and charge transfer resistance also electrochemical studies such as ESI and CV have shown high anodic peak current with respect to the biofilm that has formed. Graphene-supported PdCa ( $\text{PdCa}/\text{rGO}$ ) [32]electrocatalst, where Rgo act as supporting sheet and even

distribution of Pd and Ca on the surface and with respect to methanol, ethanol, and formic acid, formic acid and showed better current density toward formic acid even distribution or synergic effect of Pd, Ca, rGO and has been attributed for electrocatalyst for fuel cell. Xuepeng Chen et al. [33] synthesised a novel poly(diallyldimethylammonium chloride) (PDDA) synergizing reduced graphene oxide (rGO) modified carbon cloth (CC-PDDA-rGO). CLSM measurements showed the viability towards biofilm formation. Also incorporation rGO resulted in good electrical conductivity. Because of its high electrochemical surface area and low charge transfer resistance, the CC-PDDA-rGO was excellent for microbial colonisation and increased EET, which enhanced the performance of the entire MFC.  $\text{LiCoO}_2$ - $\text{LiFeO}_2$  heterostructure is tested for semiconductor membrane layer in semiconductor-based fuel cells (SBFCs) by Yanyan Liu et al. [34]. As a step towards environmental energy conversion solid oxide fuel cell. With a larger  $\text{LiFeO}_2$  nanoparticle, this  $\text{LiCoO}_2$  nanoparticle is composited. The presence of electron conduction caused by the multivalent Co and Fe ions is responsible for the rising electrical conductivity. Ionic conduction and electrical assisted transportation make up the primary components of SBFCs in most cases.

### III. PHOTOCATALYTIC ENERGY CONVERSION

Coal and oil are the two main conventional fossil fuels that have been overused. The world now faces an imminent energy shortage. In order to guarantee a consistent supply of renewable energy, regardless of the duration, location, and intensity of natural sunshine, the current research issue is the development of efficient solar energy conversion and storage technologies [35]. A few of them include  $\text{CO}_2$  conversion to beneficial compounds [36,37], the hydrogen evolution reaction [38,39], and  $\text{N}_2$  reduction to  $\text{NH}_3$ .

**1.  $\text{CO}_2$  Reduction:** Apart from metal organic frame work (MOF) Metal organic monolayer (MOL) supported on graphene was prepared by Linghao Zhou et al. [40]. In contrast to samples for MOFs, Ni@C and Co@C nanoparticles generated from MOL are highly dispersive and attached to one another like pieces of paper. For the purpose of forming ultrathin carbon layers, the organic ligands (Graphene) in MOFs and MOLs serve as carbon suppliers. Due to the more efficient transfer of charge between Ru (photosensitizer) and L-Ni@C (or L-Co@C), MOL-derived L-Ni@C and L-Co@C samples are weaker than MOF-derived F-Ni@C and F-Co@C samples, proving that pyrolysis at high temperatures can increase conductivity and enhancing the CRR. Covalent metal organic frame work  $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$  were Ru nanoparticles (NPs) loaded ketoamine (TpPa-1) was developed by KeGuo et al. [41]. Ru based nanoparticles has boosted the overall photocatalytic activity towards  $\text{CO}_2$  reduction but the separation of the photo-generated charge carriers can be improved with the right amount of Ru NPs loaded on TpPa-1, but excessive Ru NPs on the COF surface the pores of the COF, which would lower TpPa-1's capacity for photoexcitation, thus the photocatalytic activity. Aiming at low cost, high stability, and cost effective approach Bifang Li et al. [42] focused on the synthesis of ternary transition metal tungstate mesoporous cobalt tungstate ( $\text{CoWO}_4$ ) for  $\text{CO}_2$  reduction reaction.  $\text{CoWO}_4$ -180 (180 is the calcining temperature) showed high rate in reduction of  $\text{CO}_2$  to CO.  $\text{CoWO}_4$ -180 has a well-dispersed, uniform nanoparticle structure. In addition to acting as an electron capturer to quicken the separation as well as transfer of photo induced charge carriers,  $\text{CoWO}_4$  can offer high surface area and a large number of active sites for  $\text{CO}_2$  adsorption. This significantly increased the  $\text{CO}_2$  reduction

efficiency. For the conversion of  $\text{CO}_2$  into  $\text{CO}$  and  $\text{CH}_4$ , a thiacalix[4]arene-based polymer is employed as a porous support with lots of docking sites for gold nanoparticles. In contrast to more sophisticated reported materials made of metal centres on polymer supports,  $\text{uNPs@SCX}_4^+$  was synthesised without undergoing substantial photosynthesis modifications to introduce MNPs docking sites. It demonstrated catalytic activity of a similar order of magnitude.  $\text{AuNPs@SCX}_4^+$  demonstrated strong photocatalytic conversion, with  $\text{CO}$  being the primary product produced by the Au metal centres [43].

- 2. Hydrogen Production:** Better visible light harvesting is made achievable by cobalt nanoparticles of variable size supported on nitrogen-deficient graphitic carbon nitride ( $\text{Co/g-C}_3\text{N}_{4-x}$ ) by Dan Zhang et al. [44]. By incorporating Co to the  $\text{g-C}_3\text{N}_{4-x}$ , the band gap of this photocatalyst was lowered. The efficiency of the electron-hole separation was substantially enhanced as the photogenerated electrons migrate from the CB of the  $\text{g-C}_3\text{N}_{4-x}$  to the metallic Co. The photoelectron separation from CN to metallic Co was accelerated by highly ordered metallic cobalt nanoparticles attached to the surface of the CN. Under visible light, the  $0.1\text{Co/CN}$  catalyst showed the greatest photocatalytic activity for  $\text{H}_2$  evolution, which was, respectively, 101.4 times higher than pure CN and 18.0 times higher than the  $0.1\text{Co/CN}$  catalyst. Four different conducting carbon nanomaterials (CNMs)—0D carbon nanohorns (CNHs), 1D single-walled carbon nanotubes (CNTs), 2D reduced graphene oxide (rGO), and 3D graphite (GP)—have been readily designed with Ru (0) nanoparticles (RuNPs). Additionally, carbon-based materials offer superb electrical conductivity between the Ru co-catalyst and mpg-CN. The performance of  $\text{RuNPs@CNT/mpg-CN}$  [45] was the highest. RuNPs the electron-transfer process was effective when CNMs used as nanotemplates to support them. Yttrium and cerium co-doped ZnO nanoparticles were synthesised using the combustion process. Both Y and Ce ions will interact with ZnO nanoparticles by charge transfer and that electron hole separation was aided by the addition of dopants to ZnO. 5% Y-3% Ce-ZnO demonstrated a high rate of hydrogen evolution [46]. This approach is regarded as a quick, simple, and affordable combustion method. It is also suggested that NiO nanoparticles dotted  $\text{TiO}_2$  nanotubes p-n heterojunction photocatalyst (NiO/TNs) used to promote spatial charge separation which in turn is a major concern with hydrogen evolution reactions.  $\text{TiO}_2$  and NiO exhibit an interface, where photogenerated electrons can travel through, considerably inhibiting photo generated electron-hole recombination. Number of nanosheets are evidently seen growing on the surface of the nanotubes were surface is exposed due to the assembly of nanosheets on the nanotubes which in turn helped in the development of an internal electric field between the TNs and NiO increases the separation efficiency of the photogenerated carriers [47].
- 3.  $\text{N}_2$  reduction:** A mesoporous  $\text{g-C}_3\text{N}_4$  that has been treated with a single calcium atom (Ca) to facilitate the photocatalytic  $\text{N}_2$  reduction process (pNRR). Systems for  $\text{N}_2$ -photofixation based on inexpensive s-block alkaline-earth metals. On the surface of m-g- $\text{C}_3\text{N}_4$ , the single Ca atoms were decorated as active sites to achieve high N<sub>2</sub> adsorption and activation while also enhancing the band gap structure and pNRRs. The  $0.5 \text{ Ca/m-g-C}_3\text{N}_4$  catalyst exhibits good pNRR activity as well as a high number of chemical adsorption sites for removing  $\text{N}_2$  from water.

A heterojunction of two-dimensional  $\text{Sb}_2\text{O}_3$  nanosheets and one-dimensional  $\text{W}_{18}\text{O}_{49}$  nanowires was created with the goal of synthesising  $\text{NH}_3$  in a clean and

sustainable manner[48]. The oxygen vacancies in unstructured  $W_{18}O_{49}$  nanowires made it easier for  $N_2$  molecules to bind and be activated, and the ultrafine nanowire structure with increased surface areas makes the way for solar energy harvesting from synthetic photosynthesis with reliable and affordable photocatalyst. Ultrathin  $Bi_{12}O_{17}Br_2$  nanosheets[49] are used in the chemical synthesis by Kaiyue Gao et al. to change  $N_2$  into  $NH_3$ . The HRTEM image of the UT  $VO-Bi_{12}O_{17}Br_2$  nanosheets revealed a significant number of irregular crystal edges and highly disorganised lattice stripes, pointing to the presence of a rich surface oxygen vacancy filled that can supply additional active sites for photocatalytic processes. The advantage of photocatalytic nitrogen reduction reactions (NRR) is that they are sustainable and clean. Considerable amounts of  $Bi_{12}O_{17}Br_2$  generated photogenerated electrons that are then used to directly reduce nitrogen molecules. Due to the large thickness of bulk  $Bi_{12}O_{17}Br_2$ , the electron-hole pair recombination rate may have an effect on the photocatalytic nitrogen fixation efficiency. DFT is used to conduct additional research on the  $N_2$  molecule's evolution on the catalyst surface. The nitrogen photofixation activity of UT  $VOBi_{12}O_{17}Br_2$  is found to substantially diminish when the electron scavenger ( $AgNO_3$ ) is added to the system, demonstrating the presence of active molecules. This shows that the main active species are photoexcited electrons. For the photocatalytic reduction of  $N_2$ , Ru-K catalysts supported by bulk carbon nitride (B-g- $C_3N_4$ ), exfoliated carbon nitride (E-g- $C_3N_4$ ), and graphite (g-C) were developed. These catalysts are denoted as Ru-K/B-g- $C_3N_4$ , Ru-K/E-g- $C_3N_4$ , and Ru-K/g-C, respectively[50]. Contrary to Ru nanoparticles at the edges of bulk g- $C_3N_4$ , which showed lower overall barriers for  $N_2$  activation and a significantly increased photocatalytic ammonia synthesis rate. Ru nanoparticles scattered uniformly over monolayer E-g- $C_3N_4$  gave lower surface reactivity to the  $N_2$  reduction with  $H_2$  than Ru nanoparticles at the edge steps over the multi-layered bulk support (B-g- $C_3N_4$ ). Over the Ru/B-g- $C_3N_4$  catalyst, the direct  $N_2$  dissociation approach was significantly more advantageous.

#### IV. CONCLUSION

Technologies like large-scale energy storage, electric vehicles (EVs), portable electronics, solar fuel production, environmental remediation, and photo catalytic energy conversion are expected to be crucial in addressing the world's energy and environmental challenges. Additionally, for these technologies to be widely adopted and have the greatest possible impact on our future energy landscape, improvements in materials science, catalyst design, and system integration will be essential.

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