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# Recent advances in nanostructured metal chalcogenides for energy conversion and storage

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Energy requirement is increasing no matter what is the energy source. With the world's population projected to grow by around two billion people over the next twenty years, and with rising living standards, energy generation is estimated to rise by 49% by 2040. The major sources of energy are non-renewable, and their consumption leads to the deterioration of environment. In order to deal with the growing energy and environmental issues, energy conversion and storage (ECS) systems are predicted to be instrumental in the advancement of renewable technology. Lithium-ion batteries (LIBs), solar cells, water splitting photoelectrochemical cells, fuel cells and supercapacitors are important examples of ECS systems. The efficient use of ECS systems crucially relies on the synthesis of novel nanomaterials having superior performance, exceptional properties and are relatively cheaper. To meet the upcoming high demand of ECS, heterogeneous nanostructured metal chalcogenide materials are of immense interest due to their synergic properties and promising applications. This review is focused on providing an insight into the nanostructured metal chalcogenides, their different synthesis techniques, properties and ECS device applications including LIBs, solar cells and supercapacitors. This review will serve as a comprehensive guide for beginners as well as established researchers.

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*Keywords:* Nanostructures, Energy conversion, Energy storage, Batteries, Supercapacitors

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## 1. Introduction

With the increasing population, the demand for energy resources is rising. So, the ECS has globally become a crucial topic of concern in the 21st century. Extreme use of non-renewable fossil fuels produces a lot of $CO_2$, greenhouse gases into the air, causing not only major environmental problems but also substantial long-term economic and social implications. Energy-demanding regions, going from versatile gadgets (for example, mobile devices, digital cameras, PCs) to transportation (for example, electric motor cars, hybrid electric powered cars), require less burden, minimal effort, high-effectiveness and are harmless to the ecosystem ECS devices. Solar cells [1-3], fuel cells [4-7], LIBs [8-11], photo-electrochemical water splitting cells [12, 13], and supercapacitors [14-18] are examples of ECS devices. The interest in field of ECS has been increasing day by day in the present time. As per the data of Scopus till 22-04-2021, number of publications related to ECS devices are increasing very quickly. As seen in Fig. 1, in 2012 it is nearly around 1000 which is increasing every year and in 2020, it has increased to around 3000, which shows that there is huge scope of research in the domain of ECS devices. The characteristics of the nanostructured materials used in these energy devices play a big role in their performance. Nanostructured materials have pulled the attention of researchers because of their electrical, optical as well as their mechanical properties provided, the segment of these materials is restricted and also the overall behaviour of nanostructured materials exhibit a mixture of surface and bulk characteristics [19]. Low-dimensional nanostructures have attracted the attention of many scientists, due to their critical roles in determining quantum size's impact and their wide range of applications in gas sensors, piezoelectric nanogenerators, light-emitting diodes, nanothermometers, fuel cells, and LIBs, solar cells [20]. One-dimensional nanostructures are suitable for studying the effects of size and dimensionality on electrical, optical, transport, and mechanical properties. Numerous extraordinary and excellent properties, for example, higher proficiency for solar powered cells, superior mechanical durability, an improvement in thermoelectric value and improved electrochemical production for LIBs [21, 22], have already undergone a proposal or demonstration over the past few years. Two-dimensional nanostructures, for example, nano-sheets, nanowalls, nanoplates, etc are proposed to be complete segments for nanoscale gadgets utilized in natural sensors, data storage, and nano switches because of their large surface-to-volume proportion, entrancing optical and photocatalytic activities [23], and nanometre-scale thickness. Nanostructured materials have the ability to convert and store renewable energy. The advantages involves (a) the expanded lifespan with greater adaptability, (b) offering more reactive sites and catalytic activity and (c) transportation of electrons with short path [24].

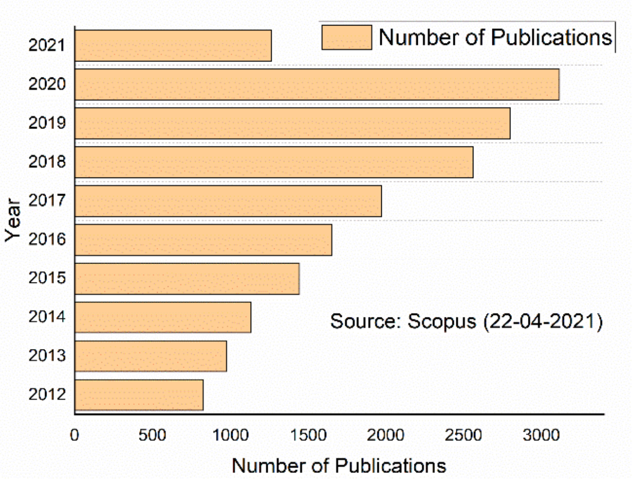


*Fig. 1. Publications on energy conversion and storage devices per year since 2012 (Scopus data extracted on 22-04-2021 with search keyword, Energy Conversion and Storage (color online)*

Nanostructured Metal Chalcogenides (MCs) have attracted a lot of interest in a variety of energy devices over the last couple of years due to their complex crystalline structures, redox activity and exceptional electrochemical activity [25]. These qualities have led to significant achievements in energy storage systems, such as LIBs, lithium-sulfur batteries (LiSBs) sodium-ion batteries (SIBs) batteries and supercapacitors, fuel cells, LED's, solar cells, sensors etc [26-30]. Rechargeable sodium-ion batteries (SIBs) have lately gathered a lot of research attention around the world, and they are thought to be promising options in contrast to LIBs [31]. Because of the abundance of sodium, SIBs have a lot of potential for grid energy storage.

Considering the current energy problem and pollution, society requires high-efficiency clean energy to completely replace fossil fuels. Hydrogen energy, which has the features of being pure (zero carbon emissions), having a large energy content (approximately 140 MJ kg$^{-1}$), and being easily renewable, has grabbed researchers' interest. Water electrolysis ($2H_2O \rightarrow O_2 + 2H_2$) is the cleanest method for creating hydrogen among the various methods available. Hydrogen evolution reaction (HER) [32, 33], Oxygen Evolution Reaction (OER) [34, 35], and Oxygen Reduction Reaction (ORR) [36] are electrocatalytic reactions that have received the most attention until now. HER is a conventional two-electron transfer reaction including one catalytic intermediate that has the potential to generate hydrogen, a crucial chemical reagent. Using the HER with renewable energy can result in a long-term supply of hydrogen fuel which can be stored, and utilized in a zero-emission fuel cell. Platinum is the most well-known HER catalyst, requiring quite small overpotentials even at large reaction rates in acidic solutions. OER is a far more complicated of the two half reactions, involving four protons as well as electron transfers per $O_2$ molecule, and is thus accountable for the most of inefficiency in electrolyzer systems. ORR is a critical step in several electrochemical energy conversion & storage techniques, such as fuel cells. ORR and OER are both critical components in the manufacture of rechargeable metal–air batteries [37]. The advancement in the synthesis of latest nanostructured substances of numerous sizes and morphologies has benefited broad range of applications of MCs. Owing to their peculiar physico-chemical properties (for example, huge electrical conductivity, earth abundance, strong thermal stability etc) [36], metal chalcogenides, just as metal selenides and metal sulfides, have pulled in a lot of consideration for different applications. In contrast to conventional intercalation electrode materials[38], MCs have better hypothetical essential capacities with regards to LIBs/SIBs. When examined as cathode materials for LIBs, Iron sulfide ($FeS_2$) can give a hypothetical explicit capacity of 894 mAh g$^{-1}$, which is essentially higher than $LiMO_2$ intercalation cathodes (M = manganese, nickel, cobalt, or a combination of them) under 200 mAh g$^{-1}$. Because of their quicker charge transfer kinetics, metal chalcogenides are more electrochemically reversible than metal oxide counterparts [39]. Then again, different metal chalcogenides, for example, Molybdenum disulfide ($MoS_2$) [37], Cobalt sulfide ($CoS_2$) [40], cobalt diselenide ($CoSe_2$) [41], Iron selenide ($FeSe_2$) [42], etc. have appeared as the potential electrocatalysts for hydrogen evolution reaction, oxygen evolution reaction, and oxygen reduction reaction with low overpotentials and little Tafel inclines. Despite these advantages, MCs face a variety of serious challenges, including few available dynamic destinations, obstructed particle and mass transmission channels, bad electrical conductivity, the knotty transport impact of Li/Na polysulfides, and critical volume difference during the charge or discharge

In this Review, the exploration progress of the effectively examined MC's ($MS_x$ or $MSe_y$, where M = iron (Fe), cobalt (Co), nickel (Ni), tin (Sn), molybdenum (Mo), tungsten (W), antimony (Sb), manganese (Mn), zinc (Zn), Copper (Cu), titanium (Ti), tantalum (Ta), vanadium (V), bismuth (Bi), or a combination of them) for LIBs or SIBs. The numerous synthesis techniques are addressed and illustrated. The properties and applications of MCs for LIBs/SIBs, solar cells and supercapacitors [43], in the field of energy research are addressed. Finally, the challenges and future scope are discussed.

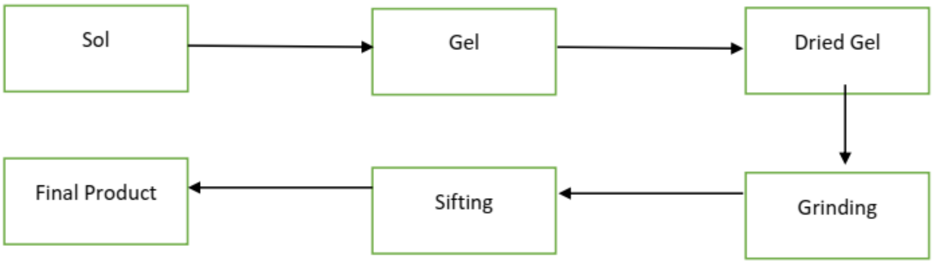
## 2. Synthesis techniques

### 2.1. Thin film synthesis

In order to prepare the bulk Chalcogenide Glasses, melt-quench process is the oldest and most commonly used. It is a glassmaking procedure that involves mixing components, heating to a temperature often more than 1300 degrees Celsius, and quenching the glass melt to generate glass frit [44]. For this procedure two things are necessary, one is quartz ampoules and the other is high-temperature furnace. Place the materials in ampoules that have been washed and sealed at a pressure of $10^{-3}$ to $10^{-4}$ Pa. The sealed ampoules are put in a furnace in which the temperature is steadily increased to approximately 50 degrees Celsius higher than the melting point of the constituent with a greater melting temperature. The temperature is then expanded at the warming rate of 2 to 5 degrees Celsius per minute. Ampoules are held at the maximum temperature for 6–12 hours. Ampoules must be rocked regularly during heating to ensure that the melt is homogeneous and also must be quenched in the ice-cold water. For certain situations, if we quench the glass with air, it would be sufficient. Thermal evaporation is the most basic method for producing thin chalcogenide glass films. The deposition material as well as the substrate are stored in direct line of vision under vacuum, usually separated by just few tens of centimetres. The material is heated till it gets evaporates, and when this evaporated material gets in touch with the substrate, it condenses to make a thin film. The source material can be heated in two ways: first, by sending a significant electric current across a filament, and second, by directing a beam of electrons onto it. E-beam evaporation is most commonly used to vaporise materials having high melting temperature. This technique produces thin films using standard coating units, which are widely available [45]. The resistive heating method can be used to create thin films of bulk glasses. The material is heated till it gets evaporates, and when this evaporated material gets in touch with the substrate, it condenses to make a thin film. In this method, firstly a filament, a boat or strip is cleaned in advance by flowing the current through it which makes it white hot, eliminating any kind of impurities from surface of the filament or a strip. After the vacuum chamber is properly cleaned, then the material is inserted into the filament or strip, keeping the chamber closed. The chamber is allowed to attain a pressure greater than $10^{-4}$ Pa. Whenever the proper deposition conditions, such as the vacuum temperature and the substrate temperature are met, the current is passed gently across the strip or filament and steadily increased until the melt creates a layer. The vapours are enabled to condense on the substrate by rising the current. The major downside of this approach is that it is difficult to determine the exact composition of any component because different components have different vapour pressures. Flash evaporation can be used to solve the difficulties of resistive heating. This technique is much like resistive heating technique however the most effective distinction in this technique is that, the tiny quantity of charge in the form of powder is delivered at the time whenever the filament or strip is white hot, allowing for the immediate evaporation of the overall charges without leaving any kind of traces. Sputtering is another significant technique. The benefit of this technique is that the sputtered film would have the same composition as the sputtered content.

### 2.2. Sol-gel technique

Since the late 1800s, the sol-gel method is quite well-known. The flexibility of this method was recreated within the early seventies once glasses were made without using the melting processes of high-temperature. It is a chemical solution method for producing the glass samples in the form of films, fibers and fine powders. A sol is basically a colloid in which the size of the dispersed particles is so minute that only Vander Waals forces and surface charges are present while the gravitational forces are absent. Once the solvent starts evaporating, a semi-rigid material is obtained, which is called ‘gel’, in which the particles or ions start to form a cross-linked structure.



*Scheme 1. Sol-Gel process (color online)*

The sol-gel process is a wet chemical approach of developing an interconnected network (gel) using either a chemical solution or colloidal particles. It includes a few stages, for example, hydrolysis, polycondensation, drying, maturing, calcination and warm disintegration.

According to the hydrolysis mechanism, precursors of the metal alkoxides $M(OR)_n$ or nonmetal alkoxides hydrolyse with water.

$$M(OR)_n + mH_2O \rightarrow M(OR)_{n-x}(OH)_x + xROH \quad (1)$$

$$2M(OR)_{n-x}(OH)_x \rightarrow (OH)_{x-1}(OR)_{n-x}\text{-M-O-M}(OR)_{n-x}(OH)_{x-1} + H_2O \quad (2)$$

where, if x is up to n, the reaction is completely hydrolysis, led either by a water condensation or by an alcohol condensation

$$2M(OR)_{n-x}(OH)_x \rightarrow (OH)_{x-1}(OR)_{n-x}\text{-M-O-M}(OR)_{n-x-1} + ROH \quad (3)$$

Overall reaction will be written as

$$M(OR)_n + n/2H_2O \rightarrow MO_{n/2} + nHOR \qquad (4)$$

The size of the particles can be adjusted by manipulating these variables. Metal oxide nanostructures such as Titanium dioxide ($TiO_2$) [46, 47], Silicon dioxide ($SiO_2$) [48], Tin dioxide ($SnO_2$) [49], Zinc oxide (ZnO) [50], Scandium(III) oxide ($Sc_2O_3$) [51], Zinc titanate ($ZnTiO_3$) [52], Barium zirconate ($BaZrO_3$) [53], Calcium tin oxide ($CaSnO_3$) [54] etc. have been synthesised using this method.

Sol gel technique has a lot of advantages, such as: (1) It is a low-cost and low-temperature method for fine-tuning the chemical composition of a component (2) Tiny amounts of dopants can be inserted into the sol and distributed equally throughout the final product (3) In this method, temperature regulation is an easy way to control the rate of reaction.

### 2.3. Hydrothermal/solvothermal synthesis

The hydrothermal or solvothermal method has had enormous success in the formation of various types of nanomaterials having different shapes and sizes. Its ground-breaking work in the 1960s and 1980s has been summarised in many excellent review papers [55-59]. In a hydrothermal reaction phase, water is the only solvent and the synthesis is carried out in an autoclave with Teflon liners at a regulated temperature or pressure. The temperature is mostly elevated over 100 °C to achieve vapour saturation pressure. This process is used to make a variety of nanoparticles, such as $TiO_2$ [60], Barium titanate ($BaTiO_3$) [61], Strontium titanate ($SrTiO_3$) [62], Lead(II) sulfide (PbS) [63], and Tin sulfide ($SnS_2$) nanotubes [64], Bismuth sulfide ($Bi_2S_3$) nanorods [65] and Silicon Carbide (SiC) nanowires [66]. The solvent is just not only confined to water but it may also consist of other polar and nonpolar solvents including $C_6H_6$ [67]. That's why this method is popularly known as the solvothermal synthesis. Organic solvents are preferred over water because the temperature can be raised significantly for the hydrothermal reaction and a lot of organic solvents are available with high boiling points to choose from. Recent research has shown that the modern approach focused on the hydrothermal synthesis, known as, "mixed solvent processes," can indeed be successful in generating nanomaterials which has a lot of specific morphologies.[68-70]. In this method, a mixed solvent made up of water and various organic solvents can be chosen, and the characteristics of the mixed solvent can be adjusted by modifying the materials, resulting in some favourable circumstances for the required nanostructures.

There are a lot of advantages of hydrothermal synthesis, such as: (1) It has the ability to synthesize nanomaterials that are unstable at high temperatures. (2) The processing of nanomaterials with high vapour pressures can be achieved with minimal material loss. (3) These approaches are more environment friendly.

## 3. Properties of nanostructured metal chalcogenides

### 3.1. Optical properties

Several metallic sulfides optical properties in their natural form are extremely significant. 1-D nanostructured zinc sulfide (ZnS) and cadmium sulfide (CdS) have gained a lot of interest for different optoelectronic purposes, which includes Field Effect Transistors (FET), solar cells, Light Emitting Diodes (LED) and also lasers [71, 72]. Fabrication of nanomaterials with continuously controllable physical properties is critical. Band gap engineering has been achieved with materials from the II–VI group, such as superlattices, heterostructures, QDs etc**.** For optoelectronic applications, till now, major issues have hindered the growth of II–VI group materials. One of the issues is the inability to achieve the desirable electrical conductivity by the reproducible doping. A shortage of high-standard single-crystalline II–VI semiconductors suitable for use as substrates [73, 74] is also one of the important issues that have hindered the growth of II–VI group materials. The use of nanomaterials in a ‘‘bottom-up" method could help to solve these big issues. Recent research shows that managing the constituent stoichiometry seems to be a more easy and convenient way to tune band gap in II–VI semiconducting nanomaterials.

Recently, Lu et al. and Fan et al. have published the morphological studies of ZnO-ZnS heterostructures [75, 76]. These findings show that maximum-quality crystalline heterostructures at the level of nanoscale can be synthesised by two different kind of materials which have a significant mismatch of lattice, which is difficult to achieve in bulk counterparts. At nanoscale, tiny interfaces and surface effects can have a big impact on the creation of nanostructured heterojunctions which are high-quality and dislocation-free. The synthesis of ZnO-ZnS heterojunction nano wire arrays, on the other hand, remains a problem. For the very first time, Lu et al. [77] successfully synthesised axial heterostructure ZnO-ZnS nanowire arrays using a method known as one-step thermal evaporation [78]. Fig. 2 shows the cathodoluminescence (CL) spectra of the ZnO-ZnS and ZnS nanowire arrays at room temperature. The CL peak for the ZnO-ZnS nanowire arrays appears at 509 nm and for Zn-S nanowire arrays is observed at 549 nm. In this paper [79], the presence of copper (Cu) or gold (Au) impurities was suggested as the cause of Zn-S luminescence at 509 nm. As a result, the blue-green emission could be due to Au. The maximum strength of the luminescence for ZnO–ZnS nanowire arrays (549 nm) is situated in the green field. Because of the asymmetric form of the peak, multipeak Gaussian fitting produces two Gaussian bands, as seen in Fig. 2b. The Gaussian curve matches the experimental curve quite well. As explained earlier, the blue-green peak is thought to be caused by ZnS. Another peak at 557 nm corresponds to zinc oxide. The green emission is caused by the recombination of electrons and holes trapped in oxygen vacancies and surface defects respectively [80]. The Scanning Electron Microscopy (SEM) representation of ZnO or ZnS nanowire arrays along with the corresponding cathodoluminescence image is shown in Fig. 2b. The luminescent positions are revealed in CL image's bright area, and the key light releasing regions match the locations of nanowire arrays. The results suggest a wide range of applications throughout the visible field for optoelectronic nanodevices. These unique types of part modulated nanomaterials not just allow for the design and manufacture of nanoscale devices without additional installation, but they also have innovative useful characteristics.

### 3.2. Electrical properties

Many metal sulfides, including nickel subsulfide ($Ni_3S_2$) and cobalt sulfide ($Co_9S_8$), are strong metallic conductors, but their value is limited due to magnetic instabilities and also due to electronic interactions [81, 82].

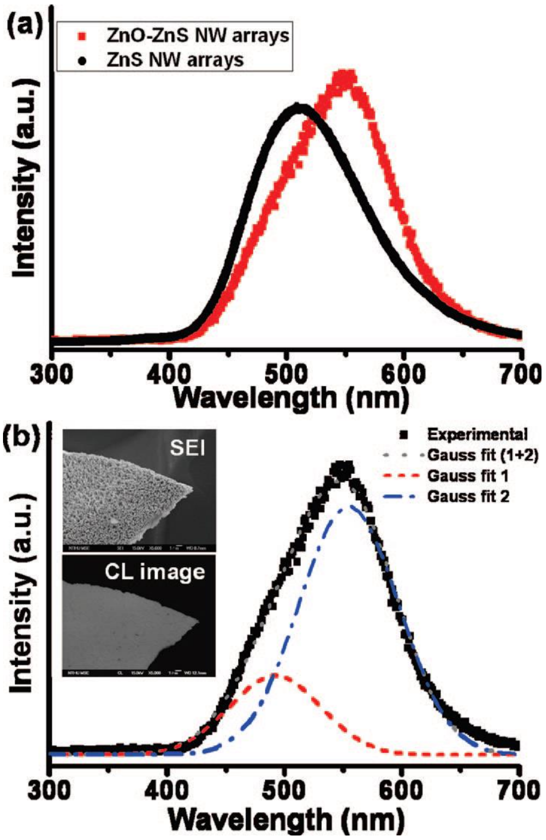


*Fig. 2 (a). At room temperature cathodoluminescence (CL) spectra of zinc oxide–zinc sulfide nanowire arrays; (b) The obtained CL spectra were fitted with a multipeak Gaussian model (color online) Zinc sulfide and zinc oxide contribute to the blue-green and green emission. The SEM and CL image of zinc oxide–zinc sulfide nanowire arrays are seen in the inset; reproduced from Ref. [78] with permission from American Chemical Society (color online)*

They have gained much attention due to their potential applications as cathode materials as well as anode materials. As a cathode material they have gained a lot interest for rechargeable LiBs, for interconnectors and also for supercapacitors. As an anode material, they have gained a lot of interest for SOFCs (Solid Oxide Fuel-Cells) [83-86]. Copper sulfide (CuS) is semi-conducting element of p-type. Its bandgap is 1.20 eV and it may be utilized as nano switche because of its mixed Cu-ionic/electronic conductivity [87]. ZnS is a II–VI group semiconductor which has a bandgap of 3.70 eV [88].

Doping is a common approach for fine-tuning the electrical properties and is commonly used in the semiconductor industry. Using a chemical vapour transport system, Lai, C.-H. et al. [77] was able to successfully synthesize Cobalt-doped ZnS nanowires. While replacing zinc with dopants, metal chloride plays a very crucial role. Lai, C.-H. et al. [77] show that various doping levels can be used to control the electrical properties of cobalt-doped ZnS nanowires [88]. The concentration dependency of conductivity in $Co_xZn_{1-x}S$ nanowires is shown in Fig. 3. Various concentration of dopants [89] are used to control the conductivity of nanowires. The presence of excess free carriers causes a rise in conductivity in several semiconductors because of an increase in doping concentration Transition metals in three dimensions have a much greater solubility of around 10 to 25 percent in II–VI group semiconductors as compared to III–V group semiconductors [90]. These findings suggest that cobalt-doped zinc sulfide nanowires may be used in a variety of practical applications, including magnetic and optical nanodevices.

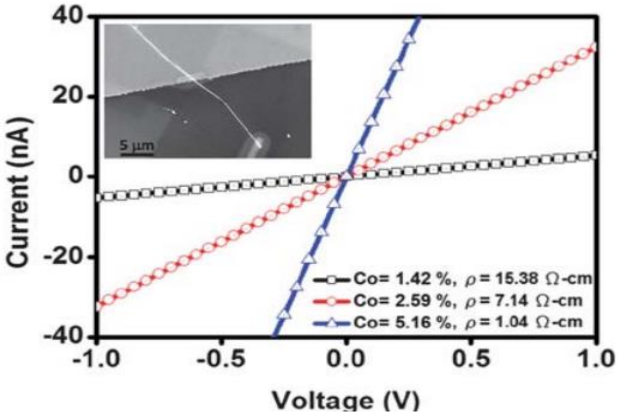


*Fig. 3. At room temperature, the cobalt content of $Co_xZn_{1-x}S$ nanowires were measured. The SEM image of the nanowire unit is seen in the inset. Reproduced from Ref. [91] with permission from AIP Publishing (color online)*

### 3.3. Photoelectric property

Till now, chemical sensors, biological sensors, optical sensors and nanomaterial-based gas sensors are fabricated and analysed w.r.t their optical as well as their electrical properties. Tin (II) sulfide (SnS) is one of the most essential IV-VI group semi-conductors with 1.330

electron volts bandgap. In general, SnS has received a lot of attention because of its diverse applications in high-efficiency photovoltaic materials, near-infrared detectors, and also in photoconductors [92]. ZnS and CdS nanostructures have received a lot of attention as an essential II–VI semiconductor materials because of their outstanding photoelectrical properties, which makes them promising nanomaterials not only for the photovoltaics but also for the photodetectors [71, 93]. It is noted that the thermal evaporation of mixed powders of ZnS and digallium trioxide through the self-catalysed formation method [23] produced inter-crossed sheet-like ZnS nanostructures with gallium dopant grown on silicon substrates. Because of the large region of surface and different morphology, zinc sulfide: gallium (ZnS: Ga) nanowalls have superior photoconductive properties, as seen Fig. 4 (a) and (b).

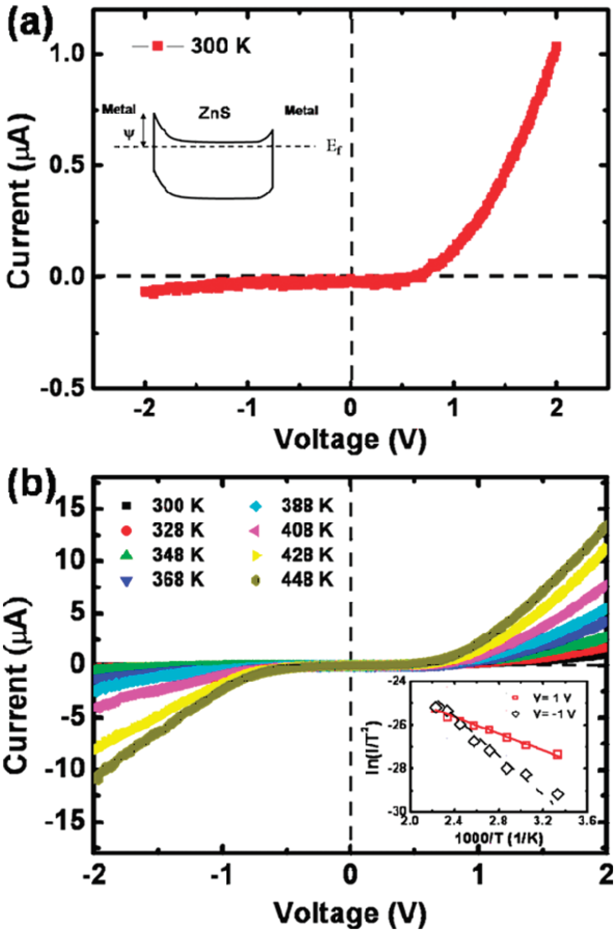


*Fig. 4 (a). At room temperature, curves of typical current to voltage in ZnS: Ga nanowall MSM photodetectors were tested. At the metal or zinc sulfide interface, ψ is the Schottky barrier height. (b). At temperatures ranging from 300 to 448 K, the temperature-dependent current to voltage characteristics of zinc sulfide: gallium nanowall MSM photodetectors were tested. The inset shows the graph of ln ($I/T^2$) vs 1/T at V = +1 and - 1 V, with effective Schottky barrier heights of 0.16 eV and 0.39 eV, respectively. Reproduced from Ref. [23] with permission from American Chemical Society (color online)*

The decrease in Schottky barrier height and the $O_2$ molecules desorption on the ZnS: Ga surface are the factors that contribute to the improved conductivity of metal–semiconductor–metal (MSM) Schottky photodetectors under visible light. Due to the fast response and high photosensitivity, ZnS nanostructures are favourable material structures for the optical switching, sensors etc.

### 3.4. Thermoelectric properties

It has been found that thermoelectric materials at nanoscale have a significantly higher thermoelectric figure of merit than their bulk counterparts. There is still a lot of work to be done in terms of creating nanostructures with the desired properties. Metal sulfide nanomaterials, for example, $Bi_2S_3$, $Sb_2S_3$, PbS and other nanostructures, had already created a lot of interest because of the potential applications based on thermoelectric region. Bismuth sulfide with bandgap of 1.30 electron volts is a semiconducting material. Antimony sulfide with bandgap of 1.780 electron volts is also a semiconducting material. They are the part of the $M_2X_3$ compounds family, in which M stands for Bi (bismuth), Pb (lead), Sb (tin), and X stands for S (sulfur), Se (selenium), and Te (tellurium), and have been proposed as possible thermoelectric materials for their possible applications [94, 95]. Theoretical results and corresponding experimental findings have shown that superlattices focused on Pb chalcogenide compounds [96] may have a significant rise in the thermoelectric ZT (where, ZT is called as figure of merit). These metal sulphide nanostructures have a higher thermoelectric power factor as compared their bulk counterparts. With these metal sulphide thermoelectric nanomaterials the capacity for producing solid-state energy from heating system is enormous [97].

### 3.5. Field-emission (FE) properties

Field-emission is among the most important property of nanomaterials. Also, it is an important property of nanostructures as well. Nanostructures have several advantages over traditional technologies. One of the advantages is faster system turn-on time, the other is sustainability, and also compactness [98]. Recent developments in the study of the field emission property and also the study of stimulated emission property of one-dimensional large bandgap semi conducting metal sulphide nanostructures have resulted in two things: (1) a substantial increase in current density (2) a reduction in turn-on voltage. Because of the increasing need for nanotechnologies and the high commercial value in flat panel displays, it has moved to the forefront of research. There are a lot of things which have been widely investigated including the consequences of various structural parameters, as well as morphology and field emission properties of semiconducting metal sulfides nanostructures [99, 100]. Different forms of metal sulfide semiconducting nanostructures with custom geometries can be used to investigate the complexity and size dependency of their properties for future applications. [101, 102].

### 3.6. Photocatalytic activity

In the field of environmental nanotechnology, photocatalytic degradation of organic compounds using semiconductor nanomaterials is really an excellent approach. $TiO_2$ is one of the outstanding photocatalyst due to its minimal price, good consistency and also due to its environmentally friendly nature. Due to high band gap of 3.2 eV, $TiO_2$ exhibits photocatalytic activity only when exposed to UV light, which is really a major disadvantage. One of the most crucial aspects of photocatalysis research is the synthesis of various visible light-active photocatalysts. Some of the examples of metal sulphide semiconductors that are used as visible light photocatalysts include CdS, CuS, ZnS, $Bi_2S_3$ and $Sb_2S_3$ [103-105]. To make photocatalysts, metal ions were doped in metal sulphide semiconductor nanomaterials with a large band gap. The photocatalytic behaviour of ZnS: Ga nanowalls is shown in Fig. 5.

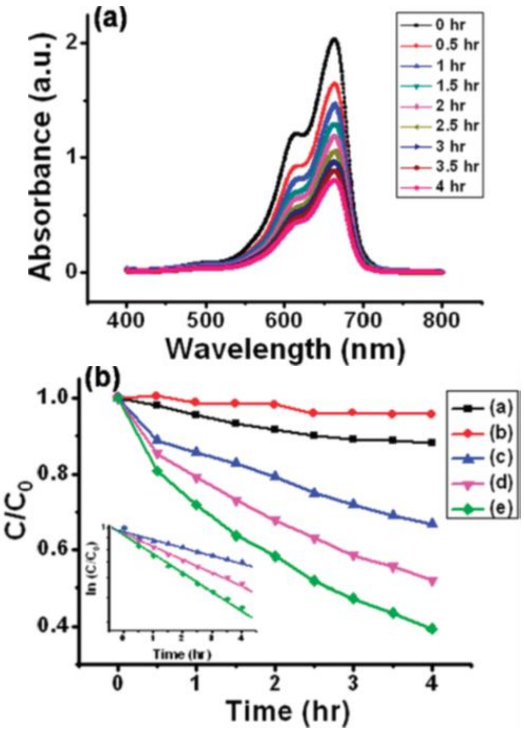


*Fig. 5 (a). Methylene blue (MB) solution absorption range in the presence of ZnS: Ga nanowalls exposed to ultra violet light for varying amounts of time. Decomposition of MB is responsible for the reduction in the intensity at 664 nm of absorbance peak. (b) Variation of photodegradation of MB over time under various conditions: (1) ZnS: Ga nanowalls: in dark and (2) without catalysts under ultra violet light (3) ZnS: Ga film, under ultra violet light (4) P25 $TiO_2$ film under ultra violet light and (5) ZnS: Ga nanowalls under ultra violet light. The data plotted on a logarithmic scale can be seen in the inset. The data is consistent with the 1st-order reaction kinetics equation. Reproduced from Ref. [23] with permission from American Chemical Society (color online)*

The results show that ZnS: Ga nanowalls may be excellent photocatalysts for the environment preservation techniques.

## 4. Applications

Considering the fact that the majority of energy already comes from the burning of fossil fuels and we know these are non-renewable in the coming years and can cause serious emissions in the atmosphere; it has become completely obvious that we are facing an increasingly serious energy shortage as well as environmental issues such as global heating and climatic changes. Under current circumstances of the energy crisis, conversion and utilization of clean and renewable energies are serious problems. Several alternative energy materials have been proposed to address these issues. Due to their distinct physical as well as chemical properties, nanostructured MCs have quite a vast variety of utilization in the advancement of ECS technologies. Besides that, MCs nanomaterials have many advantages, including low cost, abundance on earth and ease of acquisition, all of which are obviously important for their practical uses. In this part, we try to provide a more comprehensive summary of existing ECS applications of MCs, including LIBs/SIBs, supercapacitors and solar cells.

### 4.1. Lithium-ion batteries/sodium ion batteries (LIBs/SIBs)

Energy storage is one of the critical factors to consider when using various types of energy. As a type of secondary energy storage system, LIBs are already illustrated as one of the key examples since its last decade in commercial applications. Rechargeable LIBs do not have a very long history. The first rechargeable LIB was introduced by Armand in 1972 and in the late 1980s, Sony Energytec researchers produced the very first commercial LIB.

It is now the key source of energy for cell phones, PCs, telecommunications equipment and for various other things because it offers numerous advantages over other batteries such as lead acid batteries, nickel cadmium batteries etc. As compared to nickel cadmium batteries, LIBs four times the energy density and also double the power density. Also, LIBs are very environmental-friendly and consists of low density ($\rho$) of 0.534 g $cm^{-3}$ [106].

Using the traditional lithium-ion cell such as graphite or lithium cobalt oxide ($LiCoO_2$) as an example (as shown in Fig. 6), at the time of spontaneous discharge phase, graphite is often used as an anode and lithium cobalt oxide ($LiCoO_2$) as cathodes through the electrolyte by way of a redox reaction, whereas electrons travel by the same path via the external circuit, which converts the electrochemical energy into the electrical energy. The cell's potential is similar to the redox potential between the anode and cathode. During the charge phase, lithium ion has to move back from the cathode to the anode (i.e., from $LiCoO_2$ to graphite) due to an external electrical power supply, storing the electrical energy as electrochemical energy. All such electrode materials, however, have limitations. For example, graphite forms $LiC_6$ at the anode with the theoretical capacity of 372 mAh $g^{-1}$ and has a Li-ion diffusion rate of $10^{-8}$ $cm^2$ $s^{-1}$, resulting in a low power density and limited energy density of the battery [10, 107, 108]. To deal with these challenges, several new electrode materials have been created, including graphene, lithium manganese oxide ($LiMn_2O_4$), metal oxides, lithium iron phosphate ($LiFePO_4$) [10, 107, 108], metal phosphides, etc. Due to their high lithium storage ability, TMCs (Transition metal chalcogenides) are pronounced to be successful electrode material for use in LIBs [10, 109].

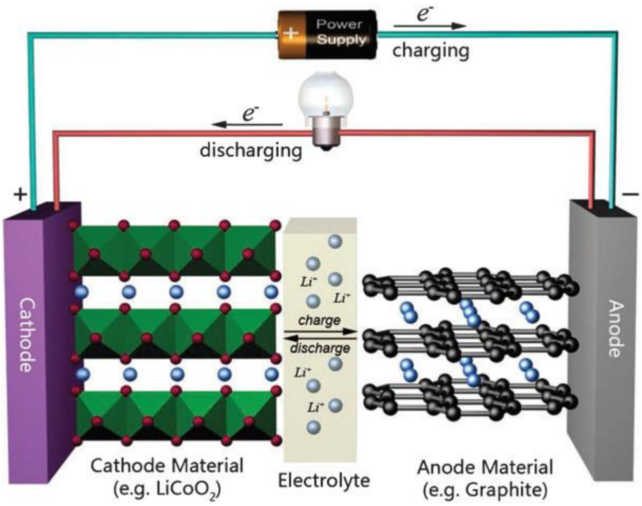


*Fig. 6. Working procedure of rechargeable LIBs; Reproduced from Ref. [110] with permission from The Royal Society of Chemistry (color online)*

As cathode material, a wide range of TMC nanostructures have been investigated including, copper sulfide (CuS) [111], $Cu_xS$/Cu [112], nickel sulfide (NiS) [113], nickel subsulfide ($Ni_3S_2$) [83, 84, 114, 115], titanium sulfide ($TiS_2$) [116] Vanadium sulfide ($VS_2$) [117] etc. Lai et al. [84] found that $Ni_3S_2$ nanowire arrays had excellent rate capability and at a 10C rate the power delivered is up to 2.5 times more than the commercially available $LiCoO_2$ (less than 145 mA h $g^{-1}$) cathode material. In later research, the researchers used CuS nanowire as the functioning cathode of LIBs. The CuS nanowire array's reversible capability was calculated around 230 mA h $g^{-1}$, which is 1.6 times higher than that of $LiCoO_2$ and can sustain over fifty percent at a rate of 2C after hundred cycles.

In comparison, several other TMCs, such as SnS [118], SnSe (tin selenide) [119], $In_2S_3$ (indium sulfide) and layered transition metal dichalcogenides (TMDCs) (i.e., $MS_2$, where M = molybdenum, tungsten, tin, cobalt, zirconium) [120-127] have been thoroughly investigated as LIBs anode materials. Layered $MS_2$ nanostructures are perhaps the most promising among these TMC nanomaterials since they can act as outstanding lithium intercalation hosts. A full charge conversion happens during lithium intercalation, which includes the reduction of $M^{4+}$ to $M^{3+}$. It has been noticed that anodes based on TMCs, have high power as well as high cycling stability.

At a rate of 1C and reversible capacity of 912 mA h $g^{-1}$ , Cho et al. [120] created different $MoS_2$ nanoplates. They also created the same nanoplates with super reversible capacity of 554 mA h $g^{-1}$ at the rate of 50C despite of twenty cycles. The enlarged interlayer distance in graphene-like $MoS_2$ nanoplates housed more $Li^+$ ions leading to the cycling stability. Seo and team [122] discovered that layered structure of $SnS_2$ nanoplates massively enhanced its host abilities as an LIB electrode. For first cycle, the experimentally determined discharge potential has a value of 1311 mA h $g^{-1}$, that was similar to sum of the theoretical irreversible potential and the theoretical reversible potential with the values of 587 mA h $g^{-1}$ and 645 mA h $g^{-1}$ respectively. More enhanced electrode materials based on TMCs for LIBs can be obtained by integrating them with several other famous LIB materials. For example, graphene-$In_2S_3$ composites which show improved discharge capacities and higher stability [128], FeS/C, $MoS_2$/graphene [129, 130], graphene-$SnS_2$ [131], $MoS_2$ nanosheets on the carbon nanotube (CNT) [132], etc. For example, Luo et al.[131] used a two-step method to successfully prepare porous graphene-$SnS_2$ nanohybrid materials, which resulted in greatly enhanced transport kinetics for lithium ions as well as for electrons in $SnS_2$. Chen and his team [130] recently created a simple solution-phase *in situ* reduced process of fabricating $MoS_2$/GNS (graphene nanosheets) which is an extremely developed anode material for LIBs. It can be noticed from Fig. 7 (b) that the very first charging and discharging capacities for the fabricating $MoS_2$/GNS electrode are 2200 mA h $g^{-1}$ and 1300 mA h $g^{-1}$, respectively, that are much larger than the number of the bare $MoS_2$ electrode as shown in Fig. 7 (a). Fig. 7c shows that after 50 cycles the $MoS_2$/GNS composites will sustain a reversible capability of 1290 mA h $g^{-1}$, which is around 2.2 times greater than the free $MoS_2$ electrodes having a value of 605 mA h $g^{-1}$, suggesting an exceptional cycling nature.

SIBs and LIBs have a common operating process. Despite their high-power density, long lifespan, and utilization in our everyday lives, lithium-ion battery (LIB) production for massive energy storage objectives is hampered by inadequate supplies and high costs of lithium resources on Earth [133, 134] . So, in this situation SIBs are being seen as a possible alternative to the current LIBs because of the inherent availability of sodium (Na) in the Earth's crust [135, 136]. Nonetheless, sodium-ion batteries yet face a number of difficulties: (1) SIBs have a smaller power density and also have a smaller energy density as compared to the LIBs as sodium has greater ionic size of 0.102 nanometers than $Li^+$ ion (0.076 nanometers) and smaller electrochemical potential of 2.71 volts which for $Li^+$ ion is 3.04 volts; (2) Li can be found either of the octahedral or tetrahedral coordination, but in case of Na, it exists in octahedral coordination as well as in prismatic coordination [135, 136]. This may result in a slow reaction mechanism and crucial sodium-ion diffusion situations, implying that certain electrodes desirable for LIBs would not be desirable for SIBs. Graphite, for example, a commonly used anode medium in LIBs, doesn't really work in SIBs because sodium plates on the carbon layer before creating graphite intercalation substances, result in low potential (less than 35 mA h g$^{-1}$) in carbon-ester electrolytes [137]. As a result, developing appropriate anode materials is critical for growing sodium-ion batteries.

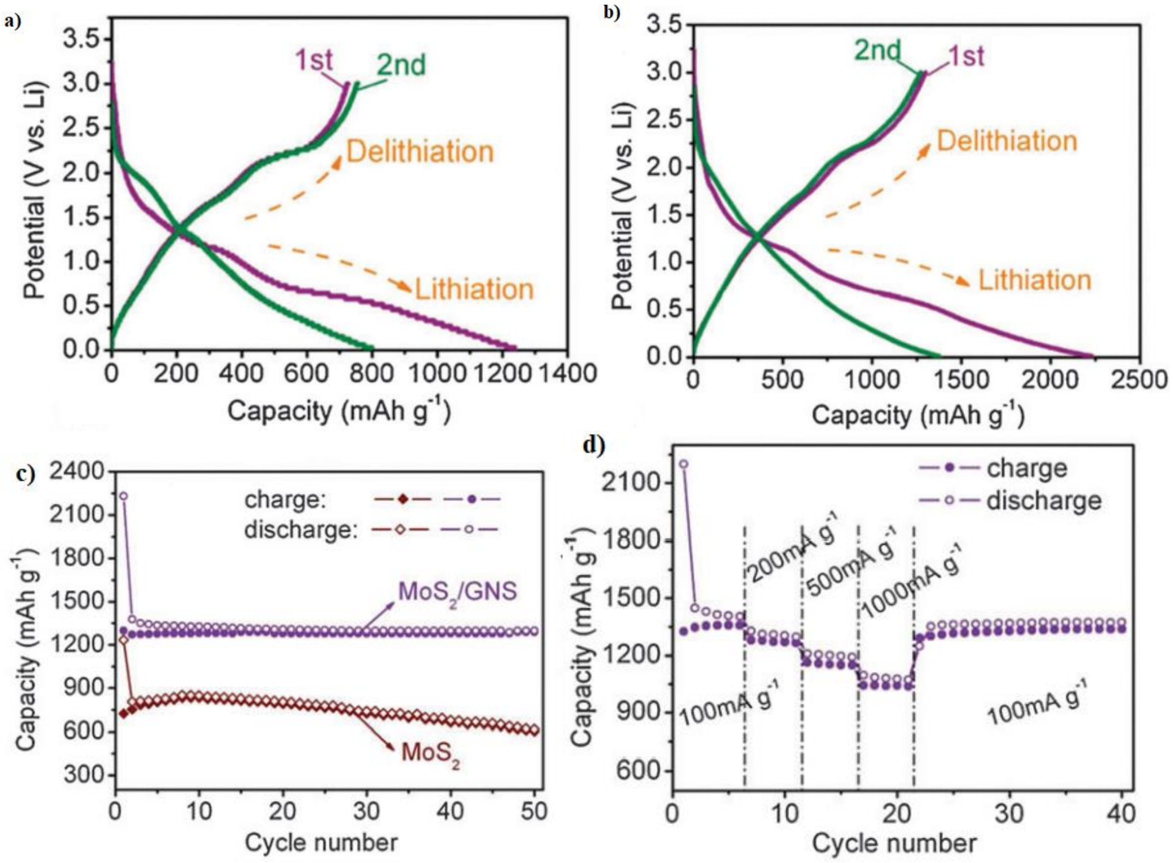


*Fig. 7. (a, b). Charge and discharge curves of the MoS$_2$ electrode and MoS$_2$/GNS electrode at 100 mA g$^{-1}$ current density for the first cycle and for the second cycle respectively. (c) Cycling performance of molybdenum disulfide electrode and molybdenum disulfide/graphene electrodes at 100 mA g$^{-1}$ current density. (d) Cycling performance of the molybdenum disulfide/graphene electrode at number of current densities. Reproduced from Ref. [130] with permission from The Royal Society of Chemistry (color online)*

### 4.2. Rechargeable magnesium batteries

Lithium-ion batteries (LIBs) have dominated the energy storage sector over many years due to their long lifespan, higher energy density, and cost-effectiveness. However, the worldwide demand of lithium is restricted, and our continued reliance on LIBs may face a significant danger in the coming years. As a result, new battery chemistries are always being developed on a regular basis, with the aim of boosting long-term energy storage devices. Rechargeable magnesium batteries (RMBs) are regarded as one of the rapidly developing batteries due to the number of benefits. Magnesium has relatively high volumetric capacity as compared to lithium (3833 mAh cm-3 for magnesium whereas 2046 mAh cm$^{-3}$ for lithium), low reduction potential (-2.37 V) as compared to SHE (Standard Hydrogen Electrode). Magnesium is easily available in the crust of the earth; its value is around 2.9 percent that is approximately 10$^{4}$ times that of lithium (0.002 percent), that results in decreasing RMB production costs. One more significant benefit is that the magnesium metal anode is less susceptible to dendritic deposition, in comparison to the lithium or sodium metal anodes, allowing for safe and secure battery operation [138]. As a result of these factors, RMBs are predicted to be a serious contender for massive-scale energy storage devices.

In the 1990s, Gregory et al. observed the initial idea of RMB, which comprised of Mg||0.25 mol L$^{-1}$ magnesium dibutyldiphenylborate (Mg[B(Bu$_2$Ph$_2$)]$_2$) in THF (tetrahydrofuran) and Co$_3$O$_4$ (cobalt tetraoxide) cathode [139]. In the 2000s, Aurbach et al. successfully developed a RMB that is highly reversible, that is comprised of Mg||0.25 m Mg (AlCl$_2$BuEt)$_2$) in THF and Mo$_6$S$_8$ using a Mg anode as well as a Mo$_6$S$_8$ cathode, that demonstrated a steady cycling over two thousand cycles, marking a significant landmark in RMB research and advancement [140]. RMBs have grown in popularity among the scientific community since then.

The Mg-battery research group, in recent times, has shifted its focus to MC's (it may be metal sulfides or it may be metal selenides) as potential cathode materials. Till now, the majority of studies on MC cathodes was focused on $Mo_6S_8$, that is broadly utilised as the basic cathode material for reviewing latest electrolyte systems or latest cathode materials. There are numerous benefits of using MC cathode materials like i) specific capacity is very large; ii) excellent compatibility with numerous electrolytes [141]; or iii) because of the creation of metal clusters throughout discharge, the conversion cathode has a greater electronic conductivity [142].

### 4.3. Supercapacitors

Supercapacitors are also known by the names of ultracapacitors or electrochemical capacitors. They have generated a lot of interest in research in recent decades because of their high-power density. They also have the fast charging and discharging, large thermal operating range, and environmentally friendly features. There are two types of supercapacitors based on the energy storage system namely: (1) Electrical Double Layer Supercapacitors (EDLS) (2) Pseudocapacitors. Electrical double layer supercapacitors at the electrode interface, collects the electrical energy by accumulating charges electrostatically, whereas, on the other hand pseudocapacitors collects the electrical energy from the fast surface redox reactions [16]. Pseudocapacitors have a higher capacitance and also higher energy density than EDLS, making them particularly promising for the upcoming era of electrochemical capacitors [143]. In order to accelerate its development, super-efficient electrode materials with a short electron pathway, a short ion transport pathway and a sufficient electroactive site are required. Due to the recent advancements in material science, conducting polymers, materials based on carbon, and metal oxides have been found to be very efficient electrode materials for the supercapacitors [16]. Despite this, massive efforts in supercapacitor technology continue to concentrate on developing new electrodes with increased energy capability or with lower costs in order to realise their widespread application in our lifetime. Because of exciting intrinsic properties and high performance, few MC nanomaterials are gaining popularity as an electrode material for supercapacitors [144-148]. Electrode materials containing NiS play a very significant role in helping to improve the electrochemical behaviour of supercapacitors. NiS are consider as the attractive materials for supercapacitors because of their small charge transfer resistances and multiple valance states [149, 150]. NiS is the most frequently studied phase in terms of ease of synthesis, large theoretical capacities, as well as various morphologies [151, 152].

Zhu et al.[153], described the preparation of NiS hollow spheres with an effective method which is known as template-engaged conversion. Due to their peculiar structural characteristics, NiS hollow spheres provide relatively high capacitances of 583 F $g^{-1}$ (farad per gram) to 927.0 F $g^{-1}$ (farad per gram) at varying current densities of 4.080 A $g^{-1}$ (ampere per gram) to10.2 A $g^{-1}$ (ampere per gram). Furthermore, despite of deep cycling of around 1000–3000 cycles, above 70 percent of the original capacitances can be maintained.

For HSC (Hybrid Supercapacitors), Yang-Tan et al. [154]. recently mentioned α-NiS particles as kind of a battery-type electrode. The morphological characteristics of NiS was adapted by varying the reaction time, that has an impact on their electrochemical properties. Annealing at high temperatures improves their structural stability as well as their electrochemical performance. At 1 $Ag^{-1}$, the specific capacity of approximately 235.9 mA $g^{-1}$ was attained with the retention of almost 87.1% at 5 $Ag^{-1}$ after two thousand cycles. Later, HSC was built with cabbage-like α-NiS as the +ve electrode whereas reduced graphene oxide (rGO) as the -ve electrode, resulting in an energy density of approximately 48.7 Wh $kg^{-1}$ (watt hour per kilograms).

Despite the above efforts, further research and development of metal chalcogenide substances through successful routes (for example, MC-based composite materials) is needed to achieve the top standard electrode materials for supercapacitor applications.

### 4.4. Solar cells

Solar energy plays a major role in green and clean renewable energy. It's a profitable and valuable substitute to traditional fossil fuels. Solar energy is the least harmful to the atmosphere and is technically the most advanced of the renewable energy sources. Researchers from a number of disciplines are interested in solar cells from a long time because of their ability to turn sunlight into electric power. Solar cells have the potential to replace fossil fuels in meeting rising energy demand in a clean and sustainable manner. Apart from conventional silicon-based solar cells, a number of newly developed solar cells which includes DSSCs (Dye Sensitized Solar Cells), QDSSCs (Quantum Dot Sensitized Solar Cells), organic solar cells, etc. have all received a lot of attention. DSSCs are perhaps the most impressive light to energy conversion systems because of their cheap price, simple fabrication, environmentally friendly nature, and excellent performance. Several MC nanocrystals have been found to be favourable alternatives for the solar absorber material and system architectures [155-162]. The utilization of rare or expensive platinum as counter electrode severely restricts the mass production of dye-sensitized solar cells. Few MC nanomaterials, including FeS (Pyrite) [163], $FeS_2$ (pyrrhotite) [163], CoS [157] and NiS [158], have been identified as effective and stable counter electrode materials. To achieve a high efficiency value, the easiest phase of NiS, can be synthesised using a variety of techniques. Yu et al. described use of certain nickel sulfide submicron cubes in DSSCs. Under the similar conditions, the material attained a PCE of approximately 6.4 percent, which was higher as compared to Pt that attained a PCE of around 5.3 percent [164]. Sarkar et al. merged NiS and graphene to create a hybrid structure with an impressive PCE of 9.5 percent, which is higher than Pt. It was noticed that graphene and NiS balance each other during phase formation. The appearance of graphene inhibits the progress of the $NiS_2$ phase and favours the progress of NiS, whereas the creation of NiS nanoparticles inhibits the restacking of graphene sheets. They noticed that the hydrothermal method outperformed the CVD process because functional groups that have been lacking in CVD are observed in the material that are prepared hydrothermally, and uniform allocation of NiS nanoparticles was also noticed. Wang and his team [159] have established a hydrothermal process with low-temperature for growing metal selenides *in situ* on clear conductive glass of FTO (Fluorine-Doped Tin Oxide). In case of $Co_{0.85}Se$, nano-sheets which have large crystallisation were deposited on fluorine-doped tin oxide (FTO), as shown in Fig. 8 (a-c). In the case of $Ni_{0.85}Se$, rather than nano-sheets spherical nanoparticles were developed [159]. Without even any kind of post-treatments, the $Co_{0.85}Se$ or the $Ni_{0.85}Se$ coated FTOs are used instantly as counter electrodes in the assembly of DSSCs.

Under AM1.5G (where AM stands for air mass and G stands for global) simulated solar light of hundred milliwatts per centimetre square (i.e., 100 mW $cm^{-2}$), the $Co_{0.85}Se$ obtained power conversion efficiency (PCE) of 9.4 percent whereas under the same circumstances, platinum (Pt) obtained a PCE of 8.64 circumstances as shown in Fig. 8d. This is the maximum PCE for DSSCs based on $I^-$ or $I_3^-$ redox pairs with a Pt-free cathode. QDs (Quantum dots) as sensitizer provide different kind of advantages for dye sensitized solar cells which includes a tuneable absorption range, fast charge separation and a short Shockley-Queisser limit. Yu et al. [160] used $(NH_4)_3(N_2H_5)_4Sn_2Se_6$ as precursors to make tin (IV) selenide ($SnSe_2$) quantum dot-sensitized titanium dioxide ($TiO_2$) photoanodes in a recent study. The PCE of the assembled QDSSCs was 0.12 percent, which is significantly higher than the PCE bare titanium dioxide ($TiO_2$) solar cells which is 0.004 percent under the same circumstances. It has been proposed that the *in-situ* formation of $SnSe_2$ quantum dots on the surface of titanium dioxide is thought to improve the electron transition from tin diselenide to titanium dioxide, resulting in high-performance solar cells.

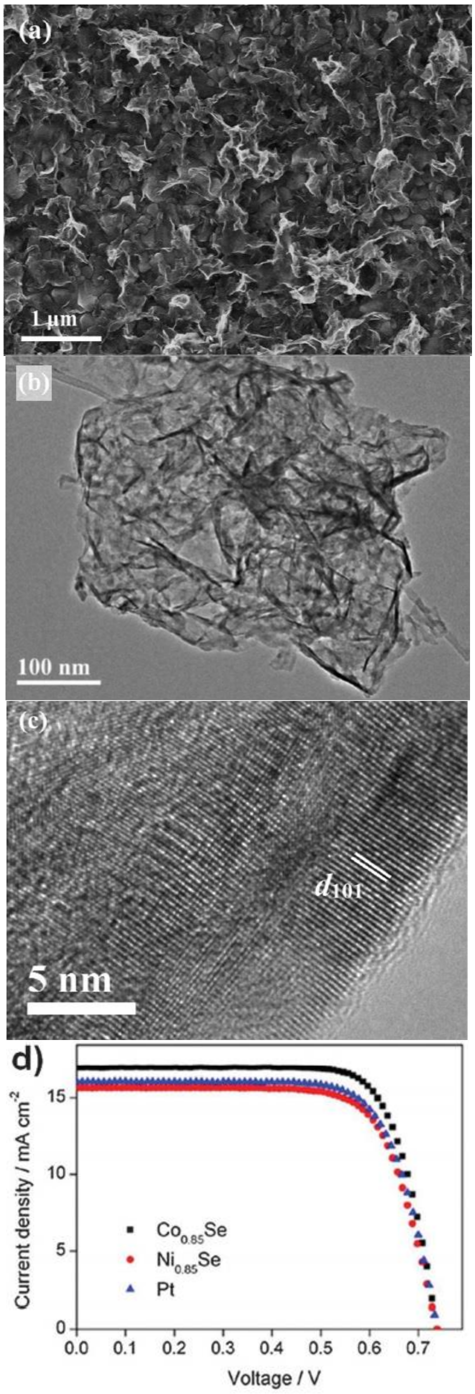


*Fig. 8. (a-c). SEM, TEM and HRTEM (High- Resolution Transmission Electron Microscopy) images of as-synthesized $Co_{0.85}Se$, respectively. (d) At AM 1.5G illumination, photocurrent density–voltage characteristics of dye sensitized solar cells with various CEs were tested (100 mW $cm^{-2}$). Reproduced from Ref. [159] with permission from American Chemical Society (color online)*

## 5. Summary

In the twenty-first century, global warming and scarcity of energy are the two major threats humans are facing. The need for effective and renewable green energy production has risen to the top of the priority study list. The world would need nearly thirty terawatts of new power [165] by 2050, according to estimates.

The tremendous energy demand and pollution caused by fossil fuels put immense pressure on researchers to establish clean and renewable technology that can offer sufficient resources in a cost-effective manner. ECS devices including Solar cells[1-3], fuel cells[4-7], LIBs [8-11], photo-electrochemical water splitting cells [12, 13], and supercapacitors [14-18] have the potential to provide the energy demanding regions, going from versatile gadgets (for example, mobile devices, digital cameras, PCs) to transportation (for example, electric motor cars, hybrid electric powered cars), and even stationary [3]. Nonetheless, the actual progress of ECS devices would rely heavily on the development of new practical materials that are of minimum-cost, high-efficiency, and have exceptional properties.

This review mainly concentrates on latest research advancement in the field of nanostructured chalcogenides, which covers everything from synthesis techniques to nanoscale properties to applications, especially in ECS, including LIBs (Lithium-Ion Batteries), supercapacitors, and solar cells. These new synthetic processes, as well as their excellent properties and wide range of applications, would be extremely useful in a variety of fields. High-overall performance and multi-feature systems for PCs, telecommunications, and electronic products are in massive requirements in today's information or media-rich culture. Besides improving performance, new doping strengths and the advancement of clean energy alternatives have the potential to be used in a wide variety of metal sulfide applications. They offer a variety of possibilities for scientists and researchers to gain experience in nanostructured material science and development. In order to resolve the major challenges of energy scarcity and global warming, nanodevices made of nanostructured metal sulphide structures have been demonstrated, especially for ECS. Commercial applications are expected to emerge rapidly, given the rapid development of nanotechnology and the growing interest from industry.

Apart from traditional secondary batteries such as lead-acid battery, nickel-cadmium battery, which provide a minimal energy capacity, limited lifespan, and heavy weight, LIBs have been preferred as the upcoming rechargeable batteries because of their significant benefits, including a comparatively high energy density of approximately 450 Wh $L^{-1}$, long lifespan of two to three years and lighter weight. In regards to energy density (Wh $L^{-1}$) as well as specific energy (Wh $kg^{-1}$), there has been a transformation in the battery sector over the past several decades, with significant achievements in battery performance. Even after the significant achievements, several challenges still remain in the development of upcoming generation batteries. The lithium or sodium storage characteristics of metal chalcogenides are currently insufficient to substitute widely used electrodes in accordance with the basic capacities, cycling reliability, price, and safety concerns. To compete with commercialised noble-based catalysts and lithium-ion batteries, more research is needed to produce high-efficiency, cost-effective, and durable battery electrodes. Furthermore, due to low yield morphologies, existing synthetic methodologies are restricted to the laboratory scale. As a result, it is critical to achieve both huge-scale and less-price synthesis of nanostructured metal chalcogenides. Furthermore, the most popular technique of integrating metal chalcogenides with carbonaceous substances decreases the volumetric capabilities of LIBs or SIBs due to the comparatively small tapping density of carbonaceous substances, which is often overlooked despite being a crucial parameter for practical applications. As a result, rather than that of carbonaceous substances, future work in nanostructured metal chalcogenides for lithium-ion batteries or sodium-ion batteries can concentrate on developing novel architectures for different high-capacity and conductive substances. Overall, creating nanostructured metal chalcogenides for ESC is encouraging yet difficult, and further advancements will lead to significant fundamental and technological breakthroughs in the energy sector in the upcoming years.

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