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NANOMATERIALS: A GLOBAL SOLUTION TO THE ADVANCEMENT AND SUSTAINABILITY OF PHOTOVOLTAIC SOLAR CELLS – A REVIEW

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Abstract: With rising cost of energy, increased energy consumption, population growth, global industrialization, along with other challenges associated with the management of oil spillage and greenhouse gas emissions, scientists and researchers are faced with the responsibility of discovering energies that are renewable, reliable, sustainable, and eco–friendly. Over the years, solar photovoltaics (PV) has been the leading technology in renewable energy when compared with other technologies such as wind, biomass, geothermal and tidal. The energy from the sun is abundant and limitless around the world but the amount that is converted to electricity is small when compared to energy from fossil, gas, and coal. The performance and cost of photovoltaic cells are determined by the materials used in their manufacturing. The development of photovoltaic cells has advanced from first generation to third generation which are easy to manufacture, thin film, flexible and lightweight. Recently, nanomaterials have drawn attention in photovoltaic solar cells due to their nanosized and high conductivity; these properties enhance the performance of photovoltaic cells. This study reviews the effect of nanomaterials on the performance of the different generations of photovoltaic cells and the mechanisms behind the enhancement or deterioration of the solar cells.
Keywords: energy; photovoltaic solar cell; nanomaterials; performance; mechanism

1. INTRODUCTION

Natural gas, fossil fuels, and nuclear energy are the main non–renewable energy sources utilized worldwide to generate electricity. According to U.S Energy Information Administration (EIA) 2022 report, 60.2 percent of the electricity used in the United States for cooling, heating, cooking, lighting, and powering of electronic and energy systems is derived from fossil fuels, while 18.2 percent is gotten from nuclear sources [1]. The continuous burning of fossil fuels for electricity generation is not sustainable because of the depletion of fossil fuel reserves, greenhouse gas emissions, climatic change, energy insecurity, and the negative impact of oil spillage on land and aquatic environments [2, 3]. With the challenges associated with the use of fossil fuels, management of nuclear radioactive wastes and oil spillage, scientists and researchers are faced with the responsibility of discovering energies that are renewable, reliable, sustainable, and eco–friendly. Renewable energy from hydropower, wind, tidal, solar, and biomass provides a more environmentally and sustainably friendly alternative to energy derived from conventional sources and its deployment for electricity generation would reduce reliance on imported fuel in countries that lack fossil fuel reservoirs, thereby improving their energy security. However, the low efficiency and high initial development and installation costs of renewable energy systems are a significant barrier to their widespread deployment. [4].

The energy from the sun is renewable, clean, inexhaustible, sustainable and its utilization has the potential to address the energy and environmental crises associated with the use of fossil fuel. Some of the technologies used in harnessing the sun's radiant light include photovoltaic (PV) cells, solar heating, solar thermal, and molten salt power plants. Although solar energy is abundant and limitless around the world, it only accounts for 3.4 percent of the energy generated in the United States while Africa which has 40 percent of the world's potential for solar power, has a total capacity of 1.4% [5]. In photovoltaic cells, the photons from the sun irradiate on the PV cells' surface, the light is absorbed and converted into electrons; at a particular frequency, the electrons totally escape from the PV cells, producing electricity [6]. The solar PV cell has a lower power conversion efficiency (PCE) and high cost of production for large–scale electricity generation when compared with energy from fossil, gas, nuclear, and coal. Over time, research in materials development and photovoltaic cells performance has been carried out to address the challenges confronting the solar PV cell industries and advance the technology. The various generations of solar manufacturing technologies are shown in Fig. 1. First–generation photovoltaic cells are thick crystalline cells, whereas second–generation PV cells are thin crystalline cells intended to be a less expensive substitute to crystalline silicon cells. Emerging technologies based on novel chemical compounds constitute the third generation consisting of inventive inorganic nanostructures that combine the stability of organic nanostructures with the affordability and flexibility

of polymer thin films. Due to the high PCE (approximately 42.3% for some multijunction solar cells (SCs)), the silicon–based photovoltaic cells are mostly used in commercial applications [7]. However, comparing with other conventional energy sources like nuclear, fossil, coal–fired, hydropower and natural gas power plants, their high production costs, difficulties disposing of discarded silicon panels, and intricate fabrication procedures make them uncompetitive.

Nanotechnology is growing rapidly due to its potential to revolutionize the energy sector. The properties of materials are altered when they change from macro–/micro–size to nano–size (1 – 100 nm).

Figure 1: Generations of photovoltaic manufacturing technologies.

The change in material property and high surface area of the nanoparticles increases the performance of energy systems when they are deployed into the energy system. [8]. Nanostructures are used as anode material in sodium–ion and lithium batteries to enhance their performance [9]. Metal nanoparticles (NPs) are used as scattering centres in SCs because of their unique optical characteristics. The use of nanomaterials has received remarkable attention and proposed to be a future replacement to silicon because of their nanosized and high conductivity [10]. As a result of the excellent scattering properties, ease of preparation and integration of nanoparticles into the solar cell fabrication process, nanostructures in PVCs are becoming more popular without substantially raising production costs [11]. The solar device's PCE is a crucial factor to consider when evaluating different solar energy technologies with reference to other factors like manufacturing costs, weight, energy costs, durability, adaptability, and waste material disposal. Research have been conducted to demonstrate how organic and inorganic nanomaterials can address some of challenges identified with solar energy, thereby, boosting its performance and deployment for commercial use. Some of the nanotechnologies that have been incorporated into solar energy technology for better cost–effectiveness and higher efficiency includes the use of nano–enhanced phase change material for photovoltaic cells and photovoltaic thermal panels [12], nanofluids for photovoltaic thermal panels [13] and addition of nanoparticles in the photovoltaic cells [14]. Studies have shown that the addition of metallic nanoparticles to various photovoltaic technologies influences the performance of SCs but the mechanism behind the enhancement or deterioration of the performance of the PV cells have not been comprehensively reviewed. This study gives a comprehensive review of the effect of nanomaterials on the performance of first, and third generations of photovoltaic SCs while considering the mechanisms behind the systems performance.

2. PHOTOVOLTAIC CELLS

Photovoltaic (PV) cells are semiconductor electrons that use the photovoltaic effect of sunlight to directly convert its energy into electrical power. Some common examples of PV cells are crystalline silicon, perovskite, dye–sensitized, quantum dots and organic. The PV cell comprises of the p–type and n–type regions also known as the substrate and emitter respectively. Fig. 2 shows the diagram of the photovoltaic cell with n–type and p–type layers [1]. The unpolished p–type wafer, or substrate, is created by doping silicon with trivalent impurities like aluminium, gallium, indium, and boron while the pentavalent impurities like phosphorus are doped into silicon to form the emitter (n–type) region. One free electron in the emitter functions as a negative charge carrier, whereas one free space is left out, acting as a positive charge carrier, and creating a hole in the substrate during combination [15]. Due to the shiny nature of silicon, 30% of sunlight incident on them are reflected. To increase the amount of radiation that reaches the semiconductor film layer and reduce the surface reflection of desirable wavelength, the silicon surface is coated with antireflective coating. The application of antireflective coating increases the solar cell efficiency [7]. Another major component in the solar cell is the electrical contact that connects the semiconductor material with the external electrical load. Recent findings indicate that the crystalline size of the nanostructure is like the carrier scattering length [11]. This
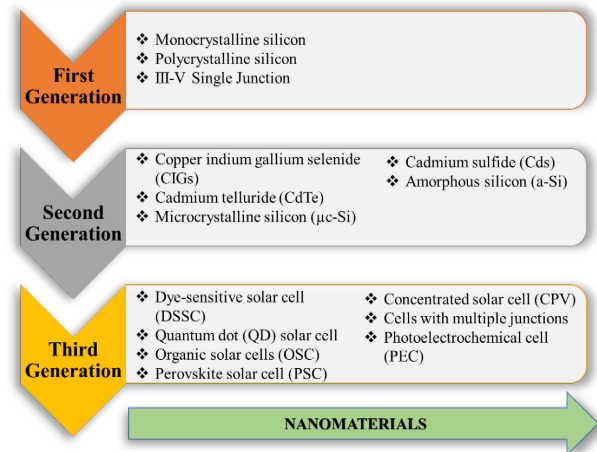
significantly lowers the scattering rate, enhances the cell's capacity to trap light within [16], strengthening the electric field inside the cell and lowering the front surface reflectance; all these enhances the PCE of the solar cells.

Crystalline silicon solar cells

Silicon is used extensively in the fabrication of SCs because of its appropriate bandgap, non–toxic nature, and it is the second most abundant element on Earth. In crystalline silicon cells, the silicon atoms are joined to form a crystal lattice, which offers an ordered structure that facilitates the effective conversion of light into electricity. Crystalline silicon SC are categorised into polycrystalline, monocrystalline amorphous [17]. Crystalline silicon solar cells have an advantage over other solar cells because of their stable power output [18]. Nevertheless, the reduced
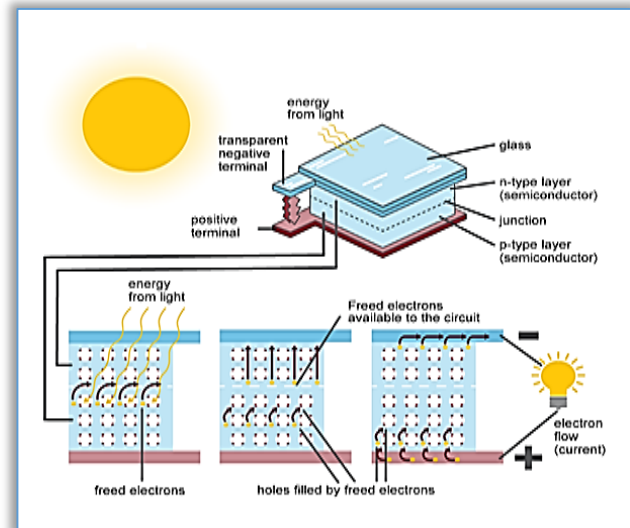

Figure 2: Schematic diagram of a PV cell, illustrating the p–type and n–type layers [1]

recombination rate of the additional carrier initiated by the crystalline silicon's indirect bandgap results in the decrease of the overall efficiency and output open circuit voltage (V_{oc}) of the SCs [19]. Several technologies such as application of antireflection coating layers, wafer size increase, addition of NPs to the structure of the solar cells, introduction of advanced assembly techniques and materials have the potential to enhance the wavelength range and solar absorption of the cells and surface textured structure to decrease the front surface reflectivity of the cells have been considered to enhance the efficiency of the crystalline silicon SCs [20, 21].

Metallic NPs have been used to enhance the performance of SCs due to its local surface plasmon resonance (LSPR) effect. The LSPR effect of metallic NPs is an excitation occurring on the metal surface initiated by near ultraviolet, visible light, and infrared waves. Application of metallic NPs on the surface of SCs increases light absorption, thereby making them attractive for use in crystalline silicon SCs [22 – 24]. The LSPR effect is influenced by the surrounding medium and the NPs' shape, size, and composition [25]. Noble metals such as Au and Ag NPs were significantly investigated in the initial stages of plasmonic SCs research due to its ability to tune to the visible spectral region, which increased light scattering into the solar cell's region. Additionally, their enhanced radiative efficiency revealed that they effectively capture near–bandgap energy. However, the high cost of these noble metals prevented them from being used in large–scale applications. Aluminium nanoparticles were explored as a potential substitute to noble metals because of their earthy abundance, distinctive ultraviolet plasmonic resonances, affordability, and excellent compatibility with the complementary metal–oxide semiconductor production technique. The effect of the native Al oxide (Al_2O_3) layer that builds on Al nanoparticles on the effectiveness of a flat c–Si SC was investigated by Parashar et al. [26]. The efficiency increased from 8.80% without NPs to 9.17% with NPs without an oxide layer and finally to 10.42% with NPs with a 2.17 nm thick oxide layer in the simplified system utilizing c–Si SCs without anti–reflection coating. To examine the light incoupling properties, Zhang et al. [24] compared the absorption and scattering characteristics of aluminium (Al) nanoparticles with those of Ag and Au. The surface plasmon resonances of Al NPs showed ultraviolet resonance at about 300 nm while that of Au and Ag lay within the visible range of 550 nm and 400 nm respectively. Thin film aluminium nanoparticles surface layer was used to improve the performance of SC [27]. The light transmission increased by 3.3% using the optimal parameter of 140 nm for the nanoparticle diameter, 42 nm for the oxide layer thickness, 21.0% surface coverage, and 80 nm for the ARC thickness. The improvement was attributed to the nanoparticles' optical dual behaviour, showing both thin–film and particle properties. Gribov et al. [28] investigated the impact of silicon NPs on the efficiency of SCs. The outcome showed that the deposition of the films consisting of silicon NPs increases the SCs efficiency by 12%. The increase in efficiency was because of the passivation of defeats at the surface of the SCs and the lowering of the optical reflectance of the cell. Elrashidi and

Elleithy [29] employed graphene between the back reflector layer and silicon and TiO_2 texture layer on top of the system to investigate the PCE of silicon SC. The enhancement of the crystalline silicon solar cell's light absorption, PCE, and short circuit density were achieved by scattering plasmonic nanoparticles over the TiO_2 surface. Optimizing the width of grating, height and periodicity, the absorption of the SC was enhanced when the graphene layer was employed to cover the Al black reflector's grating period structure while high light harvesting performance was achieved through the scattering of light from the textured surface. Plasmonic nanoparticles with different nominal diameters were applied to the TiO_2 texturing surface to further improve light absorption. The crystalline silicon solar cell's performance was then optimized by simulating and comparing the light energy absorbed by each nanoparticle. The result revealed that the graphene layer improved absorption and hence the overall performance of the SC, while the grating structure in the Al back reflector had a significant impact on absorption and, thus, the PCE. The plasmonic nanoparticles size affected the maximum peak absorption wavelength. After the light was absorbed by the NPs and retransmitted into the solar cell's active layer, the rear reflector was used to reflect the light that was transmitted. Short circuit current density and PCE improved by 89% and 34% respectively for the proposed crystalline silicon SC. The structure of the silicon NPs also influences the absorption of the SC. The amorphous silicon–based cells have weak carrier mobilities despite their high absorption, which results in low conversion efficiencies [30]. In the study conducted by Mirnaziry et. al. [31], crystalline silicon (Si) nanoparticles stacked as light trapping absorber were used in the design and investigation of the light absorption behaviour of multi–layer ultrathin photovoltaics. The light absorber of the ultrathin solar cells is at least an order thinner than that of the standard solar cells, and they are bendable and flexible in addition to using fewer materials during production [32, 33]. When the number of layers in ultrathin solar cells is considered, it was found that the number of layers is inversely proportional to the absorption efficiency and that, in the case of dense silicon nanoparticles, the periodicity of the Si NPs has no effect on the improvement of absorption. The optical absorption behaviour was enhanced through the cell configurations in an essentially textured structure, but an existing contact layer can marginally decrease this advantage. Kang et al. [34] enhanced the PCE of silicon SCs using titanium oxide (TiO_2) nanomaterial layer as the electron–selection layer. Thermal evaporator alongside with oxidation process were used to deposit the titanium metal on the silicon cells to form titanium oxide. The amorphous phase of titanium oxide shows excellent passivation properties but deteriorates when there is phase change in the layer. The electric property, structure, and passivation property of the TiO_2 electron–selection layer were investigated [35]. The study revealed that the annealing time and layer phase affected the passivation property while the pseudo–efficiency of the cell–like structure using the oxidized layer demonstrated a 9.5% enhancement. Solar cells' surface reflectance can also be improved through surface roughening. This process improves the fill factor and current density at varying degrees, and this directly affects the reduction in series resistance and trapping of the broadband light [36]. The roughen of the top surfaces of optoelectronic devices such as solar cells are achieved through nanostructures, nanoimprint lithography and chemical wet etching process [37, 38]. Tu et. al [36], improved the conversion efficiency and light trapping efficiency of crystalline silicon based solar cell using cost–effective surface roughening scheme by employing silicon oxynitride (SiON) and zinc oxide (ZnO) nanotube. The ZnO was used for surface roughening because of its high transmittance of approximately 85% in visible region, high exciton binding energy and wide direct band gap. The results obtained for the optoelectronic behaviour of the designed SiON/ZnO arrays convention, ZnO nanowire, and ZnO nanotube arrays were evaluated with that of regular solar cells. The ZnO nanowire arrays had a reflectance of approximately 14% while SiON/ZnO nanotube had the most excellent antireflective properties of about 10% in the visible–light spectrum. Light trapping in the structures of SCs can be effectively enhanced through the texturing nature of nanoparticles but this benefit can decrease slightly by the existing contact layer. To overcome this challenge Mirnaziry et al [39] considered improving the light trapping by deploying SiO_2 nanoparticles as the absorber of an ultrathin SC. The result showed that the cell's photocurrent was enhanced by the addition of SiO_2 nanoparticles. For smaller nanoparticles radius of less than 300 nm, the current enhancement was insignificant but at higher radius of 500 nm, the enhancement of the

photocurrent reaches about 10%. The interaction between the different Mie resonances in SiO_2 and Si nanoparticles is the mechanism that causes the sensitivity of enhancement to particle size.

▦ Thin film solar cells

The thin film solar cells are categorised as third generation and are produced by depositing one or more layers of thin photovoltaic materials onto a substrate like glass, metal, or plastic. The normal thickness of these solar cells ranges from a few nanometers to several micrometers, making them thinner than traditional silicon SCs. The thin film SCs consist of a protective sheet, conductive layer, and photovoltaic materials.

— Dye–sensitized solar cells

Recently, dye–sensitized solar cells (DSSCs) have gained popularity and are a viable alternative to single–junction silicon–based SCs for sustainable electricity generation. DSSCs are inexpensive, lightweight, flexible, thin–film, easy to manufacture, and absorb more sunlight per surface area than crystalline silicon solar cells. [40, 41]. The photosensitiser, a crucial part of DSSCs, is responsible for injecting electrons into a semiconductor's conduction band as well as absorbing light. The dye–sensitizer molecules are often derived from synthetic and natural sources and absorbs photons with energy up to or more than their own molecules' energy gap while transforming them into electrical energy, thereby, increasing the efficiency of dye–sensitized solar cells [42]. DSSCs are referred to as green energy photovoltaic cells because most of the dyes employed in the DSSCs' photosensitiser are derived from plants. Dye–sensitized solar cells show a noteworthy power–generating capacity throughout the day, even at low–intensity light, regardless of the light's angle of incidence [43]. In diffuse light conditions, the dye–sensitive solar cell (photoelectrochemical cell) uses a mechanism like natural photosynthesis to effectively separate charges and improve the performance of SCs [44]. The basic components of a typical DSSC are the redox mediator or the electrolyte usually made of triiodide/iodide solution; the working electrode which is a transparent conductive substrate (photoanode) usually covered in a layer of transparent conductive oxide (TCO) made of indium tin oxide or fluorine–doped tin oxide. The photoanode is coated with a thin film of materials, such as zinc oxide (ZnO), tungsten trioxide (WO_3), titanium oxide (TiO_2), tin dioxide (SnO_2), and niobium pentoxide (Nb_2O_5). TiO_2 is the most widely used material because of its large specific surface area, stability, non–toxicity, and high transmittance in the visible spectrum [45]; the photosensitiser also known as the dye makes the photoanodes more sensitive to light. The dye solution is applied to the anode to bond the TiO_2. The dyes commonly used in DSSC are organic (synthetic/natural) such as free compounds or ruthenium complex (N3 or cis–bis (iso–thiocyanato) bis (2,2'–bipyridyl–4,4'–dicarboxylato) ruthenium (II) (N719) dye) and plain fruit juice from pomegranates and blackberries and the inorganic dyes with various metals like osmium, ruthenium, platinum, copper, and Iridium [46]. These dyes contain pigment which converts light energy into electrical energy; counter electrode which acts as a cathode with carbon (C), and platinum (Pt) deposited as conducting materials that function as catalysts [47 – 49].

The effectiveness of each component in the DSSCs determines its photoconversion efficiency, while the photoanode is essential to the processes of charge generation and transfer. Nevertheless, as compared to silicon–based solar cells, the DSSCs' lower PCE and lesser long–term operational stability are restricting their commercial deployment. The PCE of conventional DSSCs is about 20%, as theoretically predicted. This is still less than that of commercial Si–based SCs, but higher efficiency can be attained by adding nanomaterials during the DSSC production process. To maximize the efficiency of the solar cells and optimize the DSSC components, most studies focused on the dye–sensitized TiO_2 photoanode on a fluorine–doped tin oxide (FTO) glass. This component is crucial to the DSSCs' overall PCE and absorption of solar radiation. The TiO_2 photoanodes' surface treatment increases the dye loading, which improves the interaction between the dyes and the TiO_2 surface [50]. The light harvesting efficiency is dependent on the thickness of the photoanode, the quantity of dye molecules adsorbed on the photoanode, and the type of responsive dye molecules [51 – 52]. The titanium oxide (TiO_2) nanoparticles are frequently used in the development of DSSCs because they are semiconductors that are cheap with high electronic mobility, good physical characteristics with broadband gap. The characteristics of TiO_2 are crucial for electron transport, and its large surface area allows it to hold a significant amount of the

dye molecules needed to capture the photons [53]. The fundamental challenge with using TiO_2–based photoanodes in DSSCs is random electron transport, which leads to electron–hole recombination and affects efficiency. This challenge was handled by doping the TiO_2–based photoanode with carbon compounds, semiconductors, non–metals, and metal NPs [54].

The performance of DSSC using a photoanode made of TiO_2 fused with gold nanoparticles was studied by Kabir et al [55]. Gold (Au) nanoparticles have a high surface–to–size ratio and the capacity to cling to other materials due to their surface chemistry. The gold nanoparticles were synthesised using the Frens/Turkevich method and had nanoparticle sizes within 10 to 30 nm. The photoanode of the DSSC structure was modified using gold nanoparticles and the artificial dye N719; it was shown that the plasmonic effect of the gold nanoparticles improved the DSSC's performance. The solar cells with gold nanoparticles had a solar–to–electric power efficiency that was almost 50% greater than those without. Photoactive TiO_2 hierarchical nanoforest TiO_2 structure and surface plasmonic resonance of silver (Ag) NPs were used to increase the photoanode solar radiation absorption [56]. The photoanode's branched structure filled the spaces between the nanowires, thereby, increasing the dye loading. The plasmonic Ag nanoparticles were deposited on the TiO_2 photoanode using the photoreduction method to improve the dye absorption and light scattering characteristics of the photoanode. According to the results, the rate of conversion of light into current increased, thereby increasing the DSSC's efficiency. Figure 3 illustrates how green–produced Ag NPs were added to TiO_2 photoanodes to investigate the impact of the plasmonic effect on the power efficiency conversion (57). Greenly synthesised Ag NPs (about 20–30 nm in size) with 1, 2, and 3 wt.% concentration was used to form the plasmonic nanocomposite materials. Titanium dioxide (P25) – TiO_2 NPs were combined with silver nitrate to create the photoanodes that were used in dye–sensitized SCs. The plasmonic effect of the 2 wt per cent Ag doping in TiO_2 significantly enhanced the efficiency of DSSCs by 28%. The electromagnetic field associated with the near field plasmonic effect decreased at decreasing weight concentrations due to the larger distance between the dye molecules and the Ag NPs. The open circuit voltage (V_{OC}) and fill factor (FF) increased with the doping concentration up to 2 weight percent of Ag NPs, reaching a maximum of around 12.1% and 7.2%, respectively, comparing the result with the non–doped sample it was revealed that the PCE of the TiO_2 was improved by the inclusion of silver nanoparticles. These nanoparticles served as a scattering element for plasmonic scattering, which captures light and near–field interactions with dye molecules, and as an electron sink for photo–induced charge carriers.

Almost half of the solar energy that reaches Earth are made up of infrared photons [58, 59] which most of the existing DSSCs cannot convert into electricity. The photon upconversion technique which involves the use of dye–sensitised upconversion nanoparticles (DSUCNPs) transforms unused sub–bandgap NIR photons into visible photons above the bandgap thereby reducing the transmission losses in DSSCs. By upconverting non–responsive NIR light in a broad spectral range (about 190 nm, 670–860 nm) to narrow visible emissions that respond

Figure 3: Diagrammatic representation of the Ag NPs-mixed TiO2-coated photoanode used in the DSSC [57]

to solar cells, Hao et al. [60] discovered that they could increase the solar cell efficiency of DSSC. The SC efficiency increased from 7.573 per cent to 8.568 per cent at the optimum treatment concentration and period of 20 mg ml^{-1} and 20 minutes respectively for DSUCNPs integrated into the TiO_2. This result presented a 13.1 per cent enhancement over the control cell without DSUCNPs. The combination of DSUCNPs' broadband upconversion and scattering effect was responsible for the increased efficiency. Another factor contributing to the DSSC's low efficiency is the recombination effect between the different interfaces inside the structure. The recombination effect happens when the redox electrolyte encounters the TCO electrons. To create a uniform and dense structure that restricts direct interactions between the FTO surface and electrolyte, blocking layers made of various materials were used [61]. Wu et al. [62], created mesoporous TiO_2 NPs layer using screen–printing, while the blocking layer was
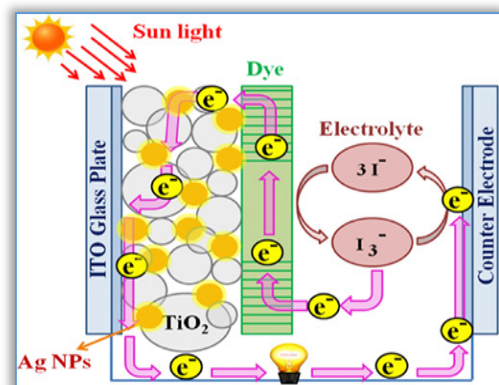
created via spin coating to create a compact TiO_2 thin film. The TiO_2 NPs layer was compressed using a hydraulic press to create a pressed layer of TiO_2 NPs. The DSSC photoanode was constructed by combining and assembling these three unique layers. The pressed TiO_2 NPs added to the DSSC photoanode significantly increased the photoanode's PCE. The mesoporous TiO_2 NPs layer in the DSSC had a PCE of 4.08%, whereas the pressed TiO_2 NPs layer had a PCE of 5.4%. The electron lifetime for DSSC with photoanodes using mesoporous TiO_2 NPs and pressed TiO_2 NPs layers was 6.287 and 8.217 ms, respectively. The pressed photoanodes showed a notable increase in power conversion efficiency of 36.16% when compared with the photoanodes based on the mesoporous TiO_2 NPs layer. Table 1 shows how these variables affect the performance of DSSCs.

Table 1: Summary of the performance and mechanism behind the enhancement of different DSSCs based on sensitisers and photoanode.

Photoanode/ Nanoparticles	Sensitizer	PCE (%)	Enhancement mechanism	Ref.
Modified TiO_2 with $TiCl_4$/Ag	N719	1.76	Improved absorption of light; introduction of $TiCl4$ improved swift charge transfer and dye adsorption.	[63]
TiO_2/Ag	N3	6.99	Visible light absorption was enhanced by the nanoparticles' surface plasmon effect.	[64]
TiO_2/TiO_2	Green natural dye (Spinach and Henna)	Spinach−0.24 Henna − 2.19	The pigments in the leaves (flavonoid, chlorophyll, lawsone) affected the light absorption.	[65]
Bio−Ca−doped TiO_2 nanofibres	Green natural dye (Syzygium cumini fruit and Malva verticillata leaves)	1.48	Improved electrolyte accessibility, dye loading, and directed electron transport on the semiconductor surface.	[66]
TiO_2/Au	N719	2.72	Enhanced light−harvesting capacity initiated by the LSPR effect; enhanced light absorption due to Au NPs modified photoanode.	[67]
Graphene/ZnO	N719	3.98	Strong light harvesting efficiency combined with strong dye absorption lowers the loss of electron recombination.	[68]
TiO_2/NiO	N719	8.39	Inhibiting electron transit and preventing electron recombination with the electrolyte due to the addition of NiO NPs.	[69]
Delafossite $KFeO_2$	N719	2.54	Reduced rate of charge recombination, enhanced charge−transfer efficiency, improved electron injection and high dye absorption efficiency and incident photon−to−current conversion efficiency of $KFeO_2$ NPs.	[70]

— Perovskite solar cells

In 2009, the first widely recognised perovskite solar cell (PSC) was created by replacing the dye molecules in DSSCs with perovskite crystals. In recent years, the development of perovskite solar cells has grown significantly because of their unique properties such as the ability to capture the visible part of the solar spectrum, low production cost, low exciton binding energy, high optical absorption coefficient, excellent tolerance towards defects, long carrier diffusion length, and high hole and electron mobility [71 – 73]. The structure of PSC comprises of a thin film of perovskite that is sandwiched between two charge extraction layers which are the electron transport layer and hole transport layer. Even though PCE of PSC has considerably improved, the interaction of heat, oxygen, and moisture with the cells continues to produce instability in the system [74]. The intrinsic defects in the electron transport layers, the decrease in resistive losses, the PSC's commercial competitiveness and transition of individual small−size devices into large−area modules in comparison to other thin−film solar cells are other significant challenges faced in PSC technology [75]. Plasmonic is an essential element of the fascinating science of nano−photonics, which examines how electromagnetic fields behave in dimensions smaller than wavelength [76].

Plasmonic nanomaterials play a vital part in the development and commercialization of the PSC because of their role in charge transport layers and absorption of the active layer of the cell in the perovskite film [77, 78]. Zheng et al. [79] investigated the impact of plasmonic nanomaterials on the effectiveness of methylammonium lead iodide ($MAPbI_3$) PSC employing gold nanoparticles (Au NPs) and the underlying mechanism responsible for the enhancement of the PCF of the PSC. N−propylamine hydroiodide was applied as a post−treatment to the surface of the $MAPbI_3$ perovskite layer to further improve the performance of the PSCs. This created a barrier that restricted the degradation of the 3D perovskite film and prevented exciton recombination. The result showed that the $MAPbI_3$ perovskite solar cells' efficiency increased to 19.01% with the addition of Au NPs. The $MAPbI_3$ perovskite layer post−treatment increased the PSC's efficiency by an additional 20.44%. The results of the optical simulation explained the concentration−dependent augmentation of perovskite absorption caused by plasmonic phenomena. According to the results, Au NPs concentrations of 1% volume fraction and higher are

required to enhance light absorption through LSPR effects. In addition, the increased photovoltaic efficiency was hardly influenced by the possible potential differences in MAPbI₃ thickness caused by the Au NPs. The improvement of the intrinsic characteristics of the perovskite layer was credited with the improved performance. Omrani et al. [80] used electro–optical coupled simulation to evaluate the effect of interface energy alignment and incorporating plasmonic NPs on the efficiency of carbon–based PSCs. In this work, the mesoporous TiO_2 was removed, and plasmonic NPs of $Ag@SiO_2$ and $SiO_2@Ag@SiO_2$ at different concentrations were embedded in the working electrode within the surrounding area of the compact TiO_2 interface. The removal of mesoporous TiO_2 increased the PCE of the PSC from 14.83% to 16.50% and this increment was attributed to the increase in the exciton generation rate and mobility of the charge carrier in the vicinity of the $CH_3NH_3PbI_3$–compact TiO_2 interface while the embedded $Ag@SiO_2$ and $SiO_2@Ag@SiO_2$ increased the PCE from 16.50% to 19.72% and 18.92% respectively. The embedded nanoparticles produced strong plasmonic fields, light scattering, and trapping.

To address the high open–circuit voltage and high short–circuit current density encountered by PSC devices, Zhang et al. [81] combined insulating metal oxides and gold (Au) nanoparticles to improve PSC efficiency. The Au nanoparticles were incorporated into the mesoporous TiO_2 films while the pyrolysis of magnesium salt and wet spinning were used to deposit MgO passivation film on the Au NP–modified mesoporous titania. The result showed that the photovoltage performance of the PSC degraded from 12.0% to 10.7% when only Au NPs were incorporated between the perovskite capping layer and mesoporous TiO_2 layer while the use of only pure MgO nanolayer increased the PCE from 12.0% to 15.1%. The combination of the MgO in the passivation layer and Au NPs produces a higher PCE of 16.1%, having a high open–circuit voltage of 1.09 V and high short–circuit current density of 21.76 mA cm⁻². Compared to pure TiO_2–based PSC, the efficiency, photocurrent, and photovoltage were 34.2%, 11.6%, and 16.0% higher respectively. The enhancement was attributed to the effective management of photon in the presence of the MgO shell and Au NPs which caused a reduction in the energy and photonic losses for the generation of carriers, thereby, leading to high charge transport capability and low charge recombination losses of the PSC. Furthermore, the combination of MgO and Au NPs in the passivation layer greatly enhanced the stability of the PSC devices under UV light irradiation. To further understand the mechanism behind the performance of PSC embedded with nanoparticles, Bastianini et al, [82], integrated silver (Ag) nanoparticles (prepared using different synthesis method) into SnO_2 electron transport layers of $CH_3NH_3PbI_3$ in PSC. The Ag NPs were considered as suitable material for this research because of its plasmonic effect in the visible region of the spectrum, high conductivity at room temperature, its stability and facile growth in nanostructured forms [83].

Table 2: Summary on the performance and mechanism behind enhancement of different types of PSCs based on the photoanodes and nanoparticles.

Photoanodes	Nanoparticles	PCE (%)	Reason for enhancement	Ref.
TiO_2	2% Zn	13.76	Increase in layer conductivity and wettability.	[84]
TiO_2	Ag	5.69	Enhanced light absorption.	[85]
TiO_2	Au	17.72	Enhanced light absorption and suppressed charge.	[86]
TiO_2	Up–conversion nanoparticles (UCNPs) ($NaYF_4$:Yb^{3+}+Er^{3+} nanoparticles)	15.56	Collective influence of surface plasmon resonance (SPR) phenomenon and near infrared light utilization originating from the Au top electrode, which was interfacing the UCNPs.	[87]
TiO_2	Ag (30 nm radius)	16.20	The radius and location of NPs strongly influenced the performance of PSC. Over the planar structures, the NPs increased the active layer absorption.	[88]
Indium tin oxide (ITO)	Au	30.4	The perovskite layer's absorbance was influenced by the nanosphere array. The improvement in the absorption and photocurrent of the enhanced the PCE of PSC.	[89]
TiO_2 Microdot Arrays	Au	12.60	The addition of Au enhanced the formation of free carriers, charge separation, charge collection, and reduced exciton binding energy.	[90]
TiO_2 mesoporous layer	$NaEuF_4$	14.51	The $NaEuF_4$ NPs converted high–energy photons into low–energy photons, which enabled $CH_3NH_3PbI_3$ to absorb them and create more electron–hole pairs.	[91]

The result showed that the method used in the synthesising of the nanoparticle affected the performance of the PSC. The Ag NPS from thermally evaporated nanoparticles decreased the PCE while chemical synthesis co–deposited with SnO_2 increased the PCE by 7%. The electrochemical Impedance Spectroscopy (EIS) result revealed that the inclusion of the Ag NPs increases the recombination rate as the concentration increased (disadvantageous to PCE) while the extraction and charge carrier transfer were enhanced (advantageous to PCE). The nanoparticle concentration was optimized to an intermediate concentration to balance the occurrence for optimal performance of the PSC.

— Quantum dots solar cells

The visible and infrared portions of the sun spectrum cannot be captured by silicon–based solar cells, while perovskite solar cells are highly unstable, and the high efficiency observed in the laboratory is difficult to replicate when scaled up to mass production. Quantum dots, which are semiconductor nanocrystals with a size of 2 to 10 nm, are used in solar cell applications to capture the infrared portion of the spectrum and ultimately improve solar device performance. Copper indium, gallium selenide, cadmium–telluride, and silicon currently used in solar cells are rapidly being replaced by quantum dots due to their electrical and optical qualities. To improve its efficiency, lower its high manufacturing costs, address the light–absorbing range, and ensure environmental safety, the quantum dots are used to replace the synthetic dyes used in DSSC [92]. The quantum dots emit different wavelengths of light due to changes in particle size when light is illuminated on them [93]. Figure 4 illustrates how the energy bandgap increases as the quantum dot size decreases while the wavelength emitted increases with the quantum dot size [94]. In bulk materials, the energy bandgap and electronic characteristics are determined by the properties of the selected material [95]. The QDSCs has gained attention over the years due to its advantages over other solar cells as highlighted in Figure 5 [96, 97]. The structure of QDSCs is like dye–sensitized solar cells, consisting of a light–harvesting material–sensitized photoanode, an electrolyte, and a counter electrode but its efficiency is lower that that of DSSCs due narrow absorption ranges and charge recombination occurring at the QD–electrolyte and TiO_2–electrolyte interfaces. During the production QDSCs' photoanode, the quantum dots are directly deposited on the nanocrystallite metal oxide (mesoporous TiO_2). Chemical bath deposition (CBD) and successive ionic layer absorption and reaction (SILAR) are the methods that have been developed to immobilize QDs on

the mesoporous film electrode [98]. In the CBD, the generated QDs are fastened to the film electrode through direct adsorption, molecular linkers, or electrophoresis–assisted assembly [99] while the SILAR uses a solution containing the proper cationic and anionic precursors to form QDs in situ on a mesoporous TiO_2 film electrode [100].

The development of new type of electrolytes, counter electrodes, sensitizers and working electrode have the tendency to further enhance the efficiency of the QDSCs. Tian et al. [101] optimized the precursor solution and electrolytes to improve the performance of lead sulphate (PbS) QDSC. In this study, the SILAR method was used to deposit the PbS quantum dots directly on the mesoporous TiO_2 sheets. The concentration of the precursor solution affects both the quantum dot quantity and particle size. The PCE of the QDSC was further enhanced to 4.01% when methanol was used to replace the 30% deionized water of the polysulfide electrolyte. The addition of methanol improved the permeability and wettability of the electrolytes in the TiO_2 film, thereby accelerating the redox couple diffusion in the electrolyte solution and improving the charge transfer at the interfaces between electrolytes and photoanodes. Furthermore, the
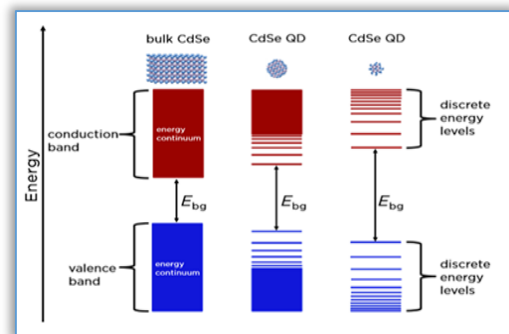

Figure 4: A schematic representation that shows how the transition from the bulk to the nanoscale changes the electronic energy levels and band gap (Ebg) in CdSe [94].

Figure 5: Properties of QDSC

addition of methanol improved the stability of the PbS quantum dots in the electrolyte, extending the electron's lifetime and lowering charge recombination. With respect to the quantity and size of synthesised QDs, the optimum concentration of precursor was observed to be 0.06M. The in–situ growth approach, which makes use of ionic precursors' practical penetration into the nanoscaled channels of the mesoporous film electrode, can effectively and highly cover QDs on the electrode

surface. However, this approach has drawbacks, including a high density of trap state defects and an uneven size distribution of the formed QDs [102]. To address this disadvantage, a transformative method that involves the brushing of solar paint QD composite and the TiO_2) on the FTO of the conductive glass was developed [114]. Sandwich–structured QDSCs were constructed using Cu_2S/brass as a counter electrode and polysulfide redox couple as an electrolyte. The result obtained from this study established that the film thickness of the QDSC affects the performance of the device. As the film thickness increased from 9 to 12 µm, the average photovoltaic performances improved as well. At 12 µm, the QDSC achieved excellent performance and device stability. At a higher film thickness, the solar paint easily falls off from the FTO glass substrates.

The efficiencies of light harvesting, and electron injection are affected by the concentration, morphology, size and type of nanomaterials used in the production of QDSCs. In the research conducted by Kottayi et al. [103], zinc doped (0, 1, and 2 weight per cent) titania nanoparticles ($Zn–TiO_2$ NPs) were made by sol–gel, while the quaternary quantum dots (QDs) based on S, In, Ag, and Cu were synthesised using the hot–injection technique. Using a linker–based assembly technique, the produced QDs were fastened onto $Zn–TiO_2$ NPs film to create Cu_2AgInS_4 QDs/$Zn–TiO_2$ NPs, which were then used as the photoanodes for QDSCs. The purpose of this study was to address the issues of improper band alignment in the conduction bands of QDs, metal oxides in the sensitized photoanode, and high surface trap state defect of quantum dots. The light harvesting capacity of the Cu_2AgInS_4 quantum dots was enhanced by the Ag introduced into the Cu–In–S host. Consequently, compared to the Cu_2AgInS_4 QDs/TiO_2 NPs (3.92%) based QDSC, the photoconversion efficiency (5.43%) of the Cu_2AgInS_4 QDs/$Zn–TiO_2$ NPs photoanode– based QDSC is 36% higher. Quantum dots are advantageous in multi–junction solar cells due to their flexibility. Table 3 gives the summary of the performance of different type QDSCs and the mechanism behind the enhancement.

Table 3: Summary on the performance of different types of QDSCs based on the photoanodes

Photoanodes	Sensitizers	Reason for enhancement	PCE (%)	Ref.
ZnO	CdS/CdSe	The thickness of the film.	1.25	[104]
ZnO	CdS/CdSe	Recombination process restriction at the ZnO/electrolyte interface. The chemically active ZnO was protected from erosion by the CdS mid–layer	4.463	[105]
ZnO	CdS/CdSe	Electrons from ZnO's conduction band are kept from moving to the oxidized ions in the electrolyte, inhibiting charge recombination.	3.14	[106]
ZnO NP	CdS	Decrease in photoexcited electron recombination and an increase in the photoanode's specific area.	1.4	[107]
$ZnTiO_3$	CdS/CdSe	Enhanced material properties.	1.95	[108]
Graphene–ZnO	CdSe	The decreased series resistance inhibited interfacial carrier recombination and promoted electron transport.	1.72	[109]
Graphene	CdSe	As a surface coating layer, graphene quantum dots (GQDs) decreased the amount of charge recombination occurring at the interface between the QDs and electrolyte.	6.59	[110]
Graphene	CdSe	Rapid diffusion of the photo–generated minority carriers was caused by the reduction of recombination trap density brought about by the graphene nanoparticle coverage.	0.11	[112]
TiO_2/ZnO NR	CdS	By passivating the surface recombination sites in TiO_2 NAs, the ZnO layer inhibited the recombination of photogenerated carriers. and creating an energy barrier between ZnO and TiO_2, which facilitates the deposit of CdS QDs and improves light absorption in the visible light spectrum.	0.33	[113]
TiO_2	CdS	The technique used in the synthesis of TiO_2 nanostructure.	0.749	[114]
TiO_2	CdSeS	The electron transport process was enhanced by the combined effects of increased hydrophilicity, high surface roughness, and better conductivity.	5.01	[115]
TiO_2 NFs	CAISe	The exceptional charge transport characteristics of P–TiO_2 NPs and the broad absorption range of developed $Cu_2AgInSe_4$ QDs.	4.24	[116]

3. CONCLUSIONS

The global trend towards sustainable and renewable energy sources has seen a significant rise in the use of solar energy. Solar energy has become increasingly popular as the globe solution to the severe energy crises and environmental challenges caused using fossil–fuel–based electricity. Photovoltaic solar energy technology accounts for 24% of the overall electricity production from other renewable energy sources. The global adoption of solar energy in the energy mix is gradually being adopted despite its high initial cost of installation because they often generate energy bill savings over their lifetime due to their lower operating costs [1]. Solar technology has experienced significant expansion over the last few years, increasing the global energy source from renewable energy. It is projected that by 2030, the global solar PV technology will provide an estimate value of 500GW of electricity [1]. Increasing the PCE of the photovoltaic solar cells is very fundamental in achieving this goal and making the energy from

solar PV cost–effective and viable replacement for fossil–fuel–based technologies. The incorporation of nanomaterials in SC technology has enhanced the PCE of the cell while decreasing the cost of manufacturing, processing time and the use of less expensive materials. Several phenomena have been suggested as the potential mechanisms underlying the improved photovoltaic SC performance following the incorporation of nanomaterials. One such phenomenon is the beneficial optical effects that metal nanoparticles provide, which increases the light trapping within the active layer of the photovoltaic SC. An additional advantage of using nanomaterials in the development of photovoltaic solar cells is that the surface area and roughness of the transport layer are increased by the incorporated nanoparticles. This enhances charge carrier extraction and offers superior adhesion with the active layer on top. One possible explanation for this enhancement mechanism could be the high thermal conductivity of metallic nanoparticles, which leads to an increase in the conductivity of charge carriers through the transport layer. Additionally, the complete covering of the transport layer surrounding the nanoparticles' surface guarantees that the opposite charge carrier is blocked. As of right now, only 40% of the solar panels that are manufactured are deployed. Proper PV deployment might hasten the switch from fossil fuel to solar energy. Third–generation photovoltaic SCs, including dye–sensitized, , and quantum dot solar cells, are emerging photovoltaic technologies that have the potential to replace first– and second–generation solar cells due to their flexibility, low manufacturing costs, and lightweight nature. However, more research is needed to improve the device's performance and material stability when it is scaled up for commercial use.

Acknowledgement

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