Graphene Derivatives As Photoanodes With Natural Photo-Sensitizer In Dye-Sensitized Solar Cells: An Insight

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Abstract: **Graphene a wonder material is a single layer of graphite and a carbon allotrope is a plentiful mineral on Earth. Graphene and its derivatives such as rGO, GO and pristine graphene, etc., when used as composites with TiO_2 semi-oxide material exhibited an improvement in PCE in Michael Grätzel and Brian O'Regans DSSCs from ~ 0.13% to above 12%. Graphene has unique properties, which make it more reliable than silicon solar cells and thin film solar cells, with the advantage of low cost, low toxicity, simple manufacturing techniques, flexibility, and extremely lightweight. They have a large specific surface area, transparency, electron mobility, and superior stability. Nature supplies a huge variety of putative structures for photosensitizers and combination may enhance stability, efficiencies, and sustainability. This review paper discusses a recent development reported in DSSCs when Anthocyanin Sensitizers with Graphene derivatives are used as photoanodes. Anthocyanin pigment is water-soluble and highly dependent on its pH value. If its pH value changes, then its appearance also changes. They have an absorption range between visible and ultraviolet spectra. Composites absorbed in Anthocyanin natural dyes show a favorable increase in charge transfer or conductivity of the cell. Moreover, the incorporation of Anthocyanin-based DSSCs has shown a much better power conversion efficiency (PCE) than the chlorophyll-based DSSCs.**

Keywords: Graphene, Reduced graphene oxide, Graphene oxide, Photoanodes, Photosensitizer, Anthocyanin dye, etc.

1.0 Introduction

The world is searching for a future in which all technological developments are environmentally responsible and reliable. Bioremediation technology or decontamination technology utilizes chemical, physical, and biological processes to reduce contaminants are also in rigorous advancement. Up to the recent history, some strategies carried out for the characterization and monitoring of these issues are Fiber Optic Chemical Sensors (FOCS), Gas Chromatography (GC), High- Resolution Site Characterization (HRSC), Immunoassay, Infrared Spectroscopy, Mass discharge and flux, Mass Spectroscopy, Test Kits, Direct-Push Platforms, Direct-Push Geotechnical Sensors, Open Path Technologies (Raman Spectroscopy), and Open Path Technologies (Tunable Diode Lasers or TDLS), etc. [1]. Approximately 84% of the world's energy consumption needs are met by fossil fuels like coal, crude oil, and natural gas. They liberate greenhouse gases and are extinguishable, which leads to a drastic effect on the environment. So, there is a need for an alternative renewable source to accomplish this issue. This directs the researchers to the use of solar energy which is free, renewable, and the cause of our existence. It creates two main types of energy- light, and heat- that we can harness to fulfill the current energy demands. The solar photovoltaic system is installed to generate electricity to power all electronic devices, and also for commercial and industrial applications. Solar heating and cooling (SHC) and concentrating solar power (CSP) are primarily used for household utilities. Traditionally, silicon is the most commonly used semiconductor material for the manufacture of first-generation solar cells, representing approximately 90% of the modules sold today. They are Fragile, rigid, expensive, and not ideal for transportation. Also, are heavily reliant on the weather, their installation cost is higher than those of electrical systems, and require enormous room for their accommodation. These were later overcome by the introduction of a thin film solar cell which is a second-generation solar cell that is made by depositing one or more thin layers of photovoltaic material on the substrate, such as glass, plastic, or metal. Film thickness varies from a few nanometers to micrometers. These thin film solar cells were flexible, cheap, and lower in weight. It can be used in building integrated photovoltaics and can be laminated onto windows. They have a better temperature coefficient than silicon solar panels [2-4]. They have been cheaper than the standard silicon solar cells, but less efficient than conventional c-Si technology. Thin film solar cells most often use CIGS (Copper Indium gallium(di)selenide) technology or Amorphous Silicon, which are much cheaper and easier to manufacture than the standard crystalline panel.

CIGS thin-film solar cells have reached 21.7% efficiency in laboratory settings and 18.7% in the field. Gallium arsenide (GaAs) thin-film solar cells have reached nearly 30% efficiency in laboratory environments, but they are very expensive to manufacture. The cost factor can be reduced by the use of Amorphous silicon thin-film solar cells which are nontoxic and abundant in nature but outperform due to low efficiency of about 10%. Unlike scientists, engineers are also not free to select the problems that interest them. They must solve some of the engineering problems like efficiency, cost, performance, safety, the weight of the device, environmental issues, etc. To overcome the issues of efficient utilization of resources and bio-friendly materials, the most desirable methods are developed and the optimum solution can be the development of natural material-based Dye Sensitized solar cells.

1.1 Dye-sensitized solar cells

In the last few decades, dye-sensitized solar cells (DSSC, DSC, DYSC, or Grätzel Cells) have received much attention as a thin film photovoltaic technology. They are considered third-generation solar cells. DSSC is a photochemical solar cell that is a promising alternative to traditional solar cells as they use natural dyes for energy manipulation. They perform better under diffused light and higher temperature conditions. It is composed of two conductive glasses, a photoanode sandwiched with an interim electrolyte solution [5]. To improve the efficiency of dye-sensitized solar cells, third-generation DSSCs are fabricated using graphene and its various derivatives. A graphene is an allotropic form of carbon atoms that are bonded together in a repeating pattern of the hexagon. It is made up of a single layer of carbon atoms and is an abundant mineral on earth. It is more reliable with the advantage of low cost, low toxicity, simple manufacturing techniques, flexibility, and ultra-lightweight, also they have a large specific surface area, transparency, electron mobility, and superior stability.

To improve the efficiency of graphene-based DSSCs, alternate components like graphene oxide (GO), reduced graphene oxide (rGO), or pristine graphene is also used. The efficiency of these cells depends upon the electrodes and the electrolytic solution. The use of natural dye enhances the absorption of photoelectrons and thus increases the power conversion efficiency.

1.1.1 Working of DSSC

DSSC is a photoelectrochemical solar cell, which consists of dye-sensitized mesoporous TiO_2/ZnO/SnO_2/graphene oxide (GO) or reduced graphene oxide (rGO) as a working electrode (WE), a redox electrolyte (I^-/I_3^-), and a counter electrode (Pt/carbon/carbonyl sulfide (CoS)/Au-GNP, an alloy of CEs like FeSe and CoNi $_{0.25,}$ etc.). Both WE and CE can be (semi) transparent to illuminate the cell from either side. The dye molecule absorbed by mesoporous oxide forms a monolayer.

A photon of a light particle when absorbed by the dye is excited from the highest occupied molecular orbit (HOMO) to that of the lowest unoccupied molecular orbit (LUMU) which injects electrons into the conduction band of semiconductor oxide material (absorption range~700nm, photon energy~1.72 eV), which lies below the excited state of the dye. Semiconducting oxide absorbs a small fraction of the solar photons from the UV region; thus, the dye gets oxidized. Through the external circuit, the electrons reach the counter electrode. Regeneration of the dye takes place due to the acceptance of electrons from the I^- redox electrolyte, later I^- gets oxidized to I_3^-. Again, the oxidized mediator diffuses towards the counter electrode and reduces to an iodide Figure.1 (webserver)

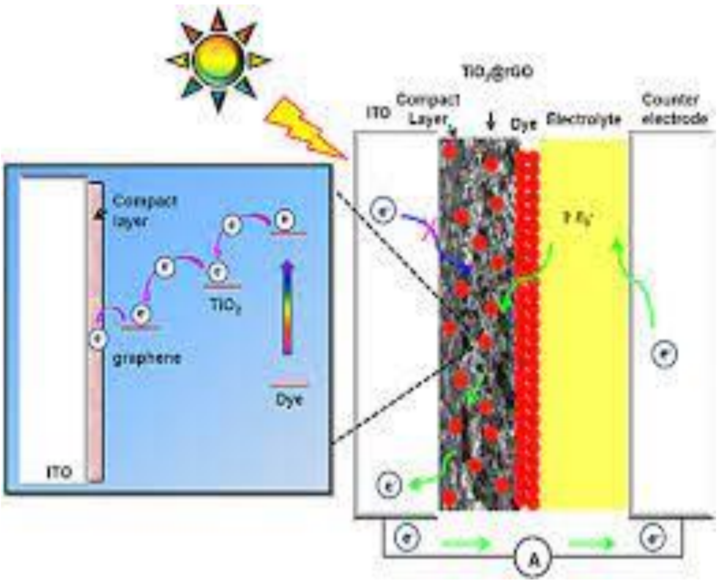

Fig.1 Dye-sensitized solar cell.

Steps involved in the conversion of photon energy to electric current

1. Absorption: When a photon of energy (hν) falls on the photoelectrode, dye molecules (R) absorb energy and move to an excited state (R*).

$$R + h\nu \rightarrow R^*$$

2. Injection of electrons: These excited electrons of dye molecules jump to the conduction band (CB) of TiO_2 and then to the CB of rGO.

$$R^* \rightarrow R^+ + e^-(CB)$$

3. Regeneration of electrons: In the DSSC, the dye is oxidized and thus loses an electron. The oxidized dye receives an electron from an iodide ion, which reduces the dye back to its original form. In this process, the iodide ions undergo oxidation (Redox regeneration at the counter electrode).

$$3I^- \rightarrow I_3^- + 2e^- \text{ (oxidation)}$$

The electron that returns to the DSSC from the external circuit reduces the I_3^- ion back to iodide ions. This process is also called a Dye regeneration reduction reaction).

$$I_3^- + 2e^- \rightarrow 3I^- \text{ (reduction)}$$

Sunlight passes through the transparent conducting anodes and reaches dye-sensitized T_iO_2 nanoparticles. The use of nanoparticles coated with light-absorbing dye increases the effective surface area and allows more energy particles over a wider range of the visible spectrum to be absorbed. This allows the DSSC to absorb more light energy under cloudy conditions than silicon-based photovoltaic cells. [6,7]

1.1.2 Characterization of DSSC performance

The performance of DSSC is mainly dependent on the absorption of photons by the dye and charges collected at the electrodes per unit of time. PCE of the DSSC measures the efficiency of the conversion of incident light into electrical energy, which is calculated by the ratio of the power output (P_{out}) to the power input (P_{in}) and characterized by measuring the current density-voltage (J-V) characteristics.

$$PCE = \eta = \frac{Pout}{Pin} = \frac{Jsc\,Voc\,FF}{Pin}$$

Where V_{oc} →open-circuit voltage (maximum potential difference measured across a solar cell when no current flows). J_{sc}→ short-circuits current density (maximum current that flows through the cell when the potential difference across it is zero).

$$Jsc = \frac{measured\ short - circuit\ current}{active\ area\ of\ the\ cell}$$

FF →is a measure of solar cells quality as a power source and is defined as the ratio of maximum power output (P_m) to the product of the short-circuit photocurrent (I_{sc}) and open-circuit photovoltage (V_{oc}) [8].

Maximum power, $P_m = I_m \times V_m$ (I_m= photocurrent, V_m= photovoltage)

$$FF = \frac{Jmax \times Vmax}{Jsc \times Voc}$$

It is used to observe the closeness of the cell's J-V characteristics to ideality as shown in Figure.2 below.

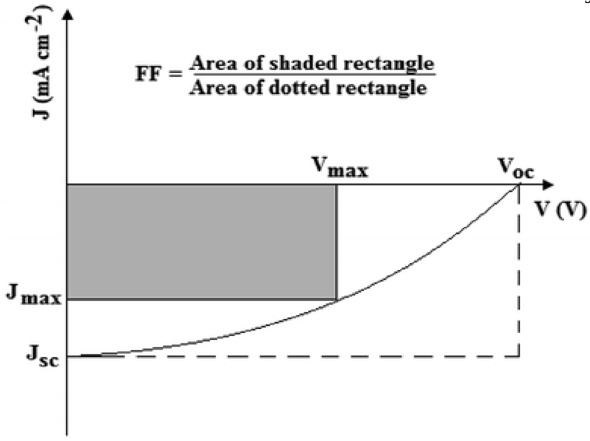

Fig.2 J-V characteristics. Reprinted from [2]

Incident photon to current conversion efficiency (IPCE) is the generation of electrons concerning the wavelength of incident light or photocurrent of a cell when illuminated by monochromatic light.

$$IPCE = \frac{1240 \times Jsc}{\lambda \times Pin}$$

1.2 Graphene in DSSC cells

Carbon-based material such as Graphene due to their unique properties have received considerable attention in DSSC solar cells. It is 200 times stronger than steel and basically a single layer of graphite. It is two-dimensional and just one atom thick and forms a hexagonal lattice. Graphene nanoparticles have a high surface area, excellent electrical conductivity, thermal conductivity, flexibility, wide absorption spectral range (UV-region to near-IR region), and chemical stability and they are hydrophobic [9]. Graphene exhibits a strong ambipolar electric field effect at room temperature with a minimum band gap between the valence and conduction bands. It enables ballistic electron transfer over long distances and with high that is only 300 times slower than the speed of light. This is 10 to 100 times greater than that in silicon chips [10]. All the components in the dye-sensitized solar cells must be optimized to obtain good PCE values.

A review of the novelties of DSSCs is discussed below with description and utility to get an idea regarding the increase in performance of DSSCs due to the use of Anthocyanin pigment with graphene derivatives. Information regarding the dyes is manually retrieved from keyword searches on the web server. Thus, their performance parameters, co-absorbent material or semiconductor, and other information like PCE, Voc, Jsc, and FF are being retrieved from mentioned references.

1.2.1 Graphene derivatives as nanocomposites in photoanodes

Traditional DSSCs are fabricated by using TiO_2, ZnO, SnO_2, Nb_2O_5, etc., and obtained an efficiency of about 12%. But, encapsulation of Graphene derivatives such as Graphene oxide (GO), reduced Graphene oxide(rGO), etc. will enhance the efficiency of the solar cell with certain challenging factors.

Akbar Eshaghi et al. in his work describe that when TiO_2 -G nanocomposites are used to make photoanode, with the increase in the graphene content to 1.5 wt % the resultant dye adsorption will increase and obtains the 42% power conversion efficiency (TiO_2 -1.5 wt % Graphene). Further, an increase in graphene content will decrease the efficiency. [11, 12]

Syukur Daulay et al. prepared TiO_2 -rGO composites as the photoanode and found the best result with a 2 wt % addition of rGO into TiO_2 with the efficiency of 0.9% and with the increase in the concentration, the cell efficiency will decrease. [13,14]

Ghasem Habibi Jetani et al. have made photoanode using TiO_2 -GO composites, which also shows the increase in efficiency of the cell. The current density was increased from 10.18 mA cm^{-2} (TiO_2 based) to 10.79 mA cm^{-2} in the Graphene Oxide based cell, using 0.001 wt %. [15]

1.2.2 Graphene derivatives with Anthocyanin dye mixture as a photosensitizer for DSSCs: Results and discussion

Graphene belongs to a larger family comprising graphene oxide (GO), reduced graphene oxide (rGO), dots, graphene nanosheets, flakes, and a few layers of graphene and ribbons. All members have distinct chemical and physical characteristics of pure graphene.

Dye as a sensitizer plays a crucial role in assessing the performance of the DSSCs. Natural dyes have become a valuable and common substitute for scarce and costly inorganic sensitizers because of their cost-effectiveness, high availability, and biodegradability. To make DSSCs work eco-friendly, sensitizers used are obtained from plants and fruits. Common pigments present are: 1) Betalains 2) Carotenoids 3) Chlorophyll and 4) Flavonoids such as Anthocyanin. They are doped with semiconductor oxide to form a photoanode. These dye sensitizers must possess certain photophysical and electrochemical properties:

- Absorption spectra must be strong covering the ultraviolet-visible region to the near-infrared region.
- The absorption spectra of a dye must not overlap the spectra of an electrolyte. HOMO should lie below the redox electrolyte.
- The conduction band of semiconductor oxide must be closer to LUMO and far from the HOMO of the dye sensitizer.
- More electrons can be absorbed by adding suitable semiconducting oxide.
- The dyes used must be hydrophobic to increase the long-term stability of the cells as they decrease the direct contact between the electrolyte and photoanode.

  This work is performed to investigate the photovoltaic properties of graphene-based DSSCs sensitized with Anthocyanin natural pigments [16,17].

Anthocyanins derived from the Greek word 'Anthos' are water-soluble pigments, which appear red, purple, blue, or black due to their pH values. They are part of a larger group of antioxidants known as polyphenols. Anthocyanins give color to fruits and plant having photon absorbing range from 520nm to 550nm wavelength [18,19]. Food plants rich in anthocyanins include blueberry, raspberry, black rice, strawberries, grapes, cherries, purple rice, purple corn, purple sweet potatoes, black soybean, etc. [20].

Misha Patel et.al observed that when Anthocyanin dye is extracted from red Cabbage and is doped to T_iO_2 – GO photoanode and observed that, with the increase in graphene concentration the efficiency raises from 0.185% to 0.443%. The anthocyanin group bonding process with mesoporous GO is called Chelation [21]. In another work, Kyung Hee Park et al. studied the adsorption characteristics and electrochemical behavior of red cabbage without using Graphene derivatives. He investigated energy conversion efficiency by using a different solvent with different pH values. For pH 3.5, he obtained the highest PCE of 0.41% (Vcc =0.46V, Jsc= 1.60 mA/cm2, FF=0.55) which is lower than the graphene-based photoanode [22].

Anna Carissa et.al in their studies revealed that the incorporation of graphene into an anthocyanin dye mixture will increase the magnitude of absorption and thus increase the power conversion efficiency by 2.4 times Titania anode. She used Graphene Oxide with Malabar spinach (Basella alba) dye and observed short circuit current Jsc of 0.15-3mA/cm^2, open circuit voltage Voc ~ (0.40-0.60 V), and Power conversion efficiency PCE ~ 2% [23]. In a similar experiment, F. Kabir et al. fabricated DSSCs without using graphene derivatives and used co-sensitization of natural dyes extracted from Malabar spinach (Basella alba) and red spinach (Amaranthus dubius). The concentration of green dye was about 0.363 g/10 ml ethanol solution and red dye was approximately 0.314g mg/10 ml DI water solution. He performed experimental analysis for the different concentrations of green and red dye. Finally, concludes that the optimum combination of dyes (20%green + 80%red) exhibited the best efficiency. Thus, the cell efficiency was increased by 1.82 or 1.6 times more than the single individual green and red DSSCs Table.1 [24,25].

Table 1. Photoelectrical parameters for DSSC with Anthocyanin and Chlorophyll combination of dyes [19]

Dye / Combination of dyes	Voc (mV)	Isc(mA)	FF	η%
100% Green	0.347±0.003	2.875±0.011	0.468±0.003	0.466±0.008
100% Red	0.383±0.004	2.810±0.021	0.494±0.006	0.531±0.016
20% G + 80% R	0.385±0.009	4.273±0.017	0.515±0.011	0.847±0.041

R. Ramamoorthy et.al used anthocyanin from Nerium oleander, Ixora coccinea, and Erythrina variegate flowers with sol-gel routed Tio_2 - rGO nanocomposites proved the anatase phase titania. The influence of rGO oxide on the bandgap and lifetime of electron-hole pair in TiO_2- rGO nanocomposites was observed from UV-Visible and photoluminescence spectra. The solar cell exhibited enhanced efficiency of 0.47-0.57%. Reduced Graphene Oxide (rGO) is an intermediate stage of Graphene Oxide and Graphene and it has various types of oxygen-containing functional groups like -OH, =O, and -COOH and lattice surface defects which generate the electrocatalytic site in metal nanoparticles. This makes rGO better than fully reduced defect-free graphene [26].

Kwadwo Mensah- Darkwa et.al made a comparative study using chlorophyll dye and anthocyanin dye. Mimosa Pudica dye (chlorophyll dye) led to a 41% improvement in the efficiency for 0.71 wt. % GO double layer-based DSSC compared to the single layer nanoparticle-based DSSC. The highest efficiency was recorded for the double-layer (DL) photoanode with 0.71 wt.% GO composition (Voc = 0.284, Jsc= 16.085, FF=0.00035, η=0.1%). Whereas, single layer anthocyanin- sensitized photoanodes using Rhoeo spathacea and Hibiscus rosa-Sinensis dye extracts were obtained (Voc = 0.468, Jsc= 0.039, FF=0.485, η=0.55%) [27].

Bell et.al synthesized an rGO - Tio_2 composite by mixing suspensions of Tio_2 - GO at various concentrations. This nanocomposite paste was deposited on the FTO-coated glass using the doctor blade technique and annealed at 450˚C for 20min. This substrate is soaked in anthocyanin dye prepared from blackberries for 40min. Thus, the surface morphology of the nanocomposite film is improved when the rGO is less than or equal to 0.2 wt. %. If the rGO weight fraction increases, conductivity also increases, reaching a maximum of 8.04 S/cm for the thin film at 0.2 wt.% rGO. The following Table 2 shows the increase in conductivity at low rGO concentration, which enhances the charge transfer in the TiO_2-coated rGO [28].

Table 2. The conductivity of rGO at different concentration

S. No	rGO	Isc (mA)	Voc (v)	PCE (%)	FF
1	0.000	4.601	0.4160	0.1760	0.3319
2	0.002	4.632	0.4130	0.2322	0.4382
3	0.003	5.516	0.4180	0.2371	0.3712
4	0.004	5.640	0.4170	0.2564	0.4062
5	0.100	2.855	0.4570	0.1209	0.3345
6	0.133	1.786	1.1770	0.0812	0.3983
7	0.200	1.185	0.2610	0.0261	0.3051

Thus, a 46% increase in PCE was achieved by incorporating 0.004% of the rGO weight fraction in the Tio_2 photoanode. Also, the electrical conductivity of the nanocomposite increases from 1.85 S/cm to 3.56 S/cm, increasing charge transfer from the nanocomposite to the FTO. Additionally, the rGO - Tio_2 solar cells yielded ten times the photogenerated current of Tio_2 solar cells [29,30].

Ismail et al. fabricated DSSCs by using Mangosteen natural dye with GO/ Tio_2 composites. He observed that the addition of graphene has improved the charge recombination and electron lifetime. This improved the PCE from 0.31% for the DSSCs with Tio_2 to 0.40% for the GO/ Tio_2 /Mangosteen-based devices (Voc = 0.61, Jsc= 1.00, FF=0.66) [31].

Ahmed A. Al-Ghamdi et al. in a paper evaluated that incorporating GO in photosensitizer doped on TiO_2 will increase the efficiency of the DSSCs. Under similar experimental conditions, he used N719 (commercial dye) and observed the efficiency of ~ (0.078 ± 0.002%) on the other hand used natural dye extracted from purple cabbage along with GO/ TiO_2 composites and obtained the efficiency from (0.150 ± 0.020%) to (0.361 ± 0.009 %) [32].

1.2.3 Improvements in the DSSC solar cells components with the addition of Graphene derivatives

Over the last few decades, much improvement in the efficiency of DSSCs based on natural dye has not been recorded compared to first-generation silicon solar cells. But the researchers are waiting for the breakthrough by which DSSCs can work more efficiently. In the present scenario, much effort has been taken to fabricate the DSSCs by modifying the various components with a variety of novel materials, among which graphene became the most attractive option.

Edigar Muchuweni et al. in their paper described the replacement materials for the transparent conducting electrode. Preferably, ITO/FTO are used as working electrodes due to high electrical conductivity and high optical transmittance in the visible range. But, the problem with ITO was that it is toxic, costly, and not available readily [33-36]. ITO is rigid and brittle, so cannot be used in flexible substrates. The next alternative material used was FTO, which was more economical but it has certain structural defects due to its rough surface, which leads to short circuits and leakage of current. This will drop the performance of the device. To overcome these disadvantages the other optional materials such as metal nanowires [37], conductive polymers [38,39], transparent conducting oxide [40,41], CNTS [42,43], and graphene [44,45] have been prepared as potential replacements to the conventional ITO or FTO electrodes.

Lung Chien Chen et al. studied the performance of DSSCs by taking the sandwich structure of TiO_2 /graphene/ TiO_2 and found a 60% improvement in cell efficiency. The characteristic study shows that the cell exhibited a Voc of 0.6 V, a high Jsc of 11.22 mA/cm^2 a fill factor (FF) of 0.58, and the calculated η of 3.93%. The absorption range was found to be 400-600nm. He made a remarkable point that the absorbance of light was improved due to the sandwich system, a wide range of absorption wavelength, shorter charge transportation distances, and due to the introduction of graphene, charge recombination can be minimized [46].

Simone Casaluci et al. fabricated graphene-based DSSC modules by spray coating graphene ink. By liquid phase exfoliation, the graphene ink can be obtained and spray-coated over the conductive oxide substrate for a large area (>90 cm^2). This type of graphene-based counter electrodes achieved a power conversion efficiency of 3.5% [47].

Kaustubh Patil et al. we're exploring a new chemical and physical way to create an artificial bandgap in graphene which is one of the requirements for the fabrication of electronic devices. Zero-bandgap graphene can be transformed into a wide-bandgap semiconductor through hydrogenation via sp^3 C-H bond formation. DSSCs with TiO_2/graphene composites as photoelectrode have the highest efficiency of 9.3% than the 6.5% of TiO_2- ZnO photoelectrode. Further, he reported that when TiO_2- rGO composites are used to fabricate photoanode with 0.3% wt. of TiO_2 and rGO photoanode has a maximum of 7.2% (Voc = 0.54V, Jsc= 28.36 mA/ cm2, FF=0.47) [48,49].

Yan et al. constructed a DSSC solar cell and reported that Graphene can act as a photosensitizer because charge can flow from graphene to TiO_2. But these types of DSSCs were not efficient. Later he used black Graphene quantum dots (GQDs) as a photosensitizer which satisfies all the transformation and regeneration processes [50].

Another important component of DSSCs is transparent conducting oxide, basically a nanometer crystal array with mesoscopic pores that act as dye attachment area and electron transfer passage through the DSSCs. Some readily used semiconductor oxides are titanium dioxide (TiO_2), zinc oxide (ZnO), tin oxide (SnO_2), etc. But, now inorganic materials such as carbon nanotube, reduced graphene oxide, graphene oxide, quantum dots, graphene or graphite, etc. are used, codoping of these nanocomposites in the DSSCs have successfully shown good photon absorption and charge transport at the interface of semiconductor oxide/dye/electrolyte through different components. Certain combinations with different concentrations will bring change in device efficiency.

Recently, the Researchers at Switzerland's Ecole Polytechnique Federale de Lausanne (EPFL) fabricated DSSCs with a PCE of 15.2% in direct sunlight and up to 30.2% in diffused light conditions. Researchers used the method of co-sensitization, a chemical manufacturing approach that produces DSSCs with two or more dyes with complementary optical absorption i.e., sensitizers can absorb light from across the entire spectrum. They obtained a well-organized and densely packed sensitizing layer on the semiconductive oxide. In this technique monolayer of hydroxamic acid, the derivative is pre-adsorbed onto the surface of nanocrystalline mesoporous titanium dioxide. They also manufactured a perovskite-on-silicon-tandem solar cell, which sets the record of above 30% of efficiency. On the other hand, researchers from China, Australia, and Singapore fabricated the plasma-assisted atomic layer deposition (PEALD) method and obtained a power conversion efficiency of 22.8% in a 613-Watt tunnel oxide passivated contact module with 60 cells [51].

The next era of development in DSSC is the flexibility of solar modules. Huda Abdullah et al. recently developed flexible DSSCs in which stainless steel mesh was used and an efficiency of about 2.8% was obtained [52]. In a similar kind of work Haruna P Wante et al.[53] , Girija Nandan Arka et al. [54], Anupam Agrawal et al. [55], Marek Szindler et al. [56], Syamimi Noorasid et al. [57], and many others have done a lot to make flexible solar cells, but due to temperature limitations, the Polymer foils of PET and PEN are found to be unstable above 120^{o} C to 150^{o} C. Mostly, FTO coated glass is replaced by polymeric materials, such as polyethylene terephthalate or polyethylene naphthalate are used and reported 3.8% and 7.8% efficiency respectively. But are prohibited due to the inaccessibility of high temperatures. Other metals like Tungsten, Titanium, and stainless steel can also be used as substrates.

Natural dyes or dye sensitizers places an important role in the potential generation of DSSCs. They are responsible for the absorption of the visible light spectrum and sensitize large bandgap semiconductors.

Conclusion

There is a great deal of research going on to improve the effectiveness of DSSCs. Graphene as a newly born material has great potential in various fields. The usage of graphene in the coming years will give a tremendous difference to current technologies. Like any other newly risen phenomenon in the world, graphene has its downsides and dark side, but the advantages are greater than what these burred points could affect them. Graphene and its derivatives with Anthocyanin sensitizers significantly increase its effectiveness. They form an effective photoanode for the absorption of incoming light. Graphene photovoltaic cells, in solar cell technology, will provide many potential applications in renewable energy resources. Moreover, the commercial-scale development of Graphene-based DSSCs has gained remarkable progress. However, making and utilizing Graphene for useful purposes is still challenging, also the effect of acidic contents of the solution, light, and temperature is unsatisfactory for technological applications. Hence, more advanced technological development is required to fully furnish the proper application of Graphene and its derivatives in the photovoltaic industry.

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