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REVIEW

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Recent Advances in Photo-supercapacitor: A Mini Review

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Abstract: Radiant energy (solar energy) plays a vital role due to its continuous power supply and environmentally friendly in meeting the people's energy demand. The need for an endless supply of energy, majorly through solar energy exploitation has driven the expansion and diversification of a device for proper energy storage. This review summarizes a photo-supercapacitor's working mechanism. The classification of a supercapacitor was discussed and the advancements of the active components that makeup a photo-supercapacitor and the improvements on photo-supercapacitor in energy storage were highlighted. For the constant generation of electricity, dye-sensitized solar cells (DSSCs) and supercapacitor are incorporated. The invention of hybridized dye-sensitized solar cell (DSSC)-capacitors and DSSC-supercapacitors are crucial in energy storage processes, and the advancement in technology has triggered the creation of a photo-supercapacitor for efficient harvesting of energy and proper storage mechanisms. The intent of pairing a DSSC with a supercapacitor for conversion of energy and proper energy storage arose when dye molecules absorb radiant energy and the absorbed energy is transformed to electrical energy. The use of active components of a photo-supercapacitor will determine its conversion efficiency. The performance of active components of photo-supercapacitors such as dye, electrolyte, photoanode, and the counter electrode are the main factors that contribute to efficient conversion of energy to improve the photo-supercapacitor's storage life.

Keywords: DSSCs; Supercapacitor; Counter electrode; Photoanode; Sensitizers; Photo-supercapacitor

1. Introduction

Energy is the most crucial and basic aspects of life after food and shelter, it is a daily need of life. The increasing population and rapid industrial growth have resulted in a dramatic rise in energy demand over the years. Presently, the non-renewable energy source such as fossil fuel, coal and so on are the major energy sources in use and it supply over 80% of energy but initiates environmental problems[1]. Due to the environmental risk of fossil fuels, the world is in search of sustainable, clean, and green forms of energy for instance geothermal, wind and solar energy[2,3] to replace the non-renewable energy sources.

Solar energy is considered to be a viable alternative among the various renewable energy available because the solar energy received is estimated to be much more than the energy required or the human rate of consumption[4]. This has driven researchers to the discovery of solar cells as the principal contrivance for the production of energy, in connection with fossil fuel‘s depletion and mineral resources[5].

In 1941, the first monocrystalline silicon solar cell was constructed when Jan Czochralski discovered that solar cells can be produced from monocrystalline silicon and had an energy conversion efficiency that is less than 1%. In 2010, a silicon photovoltaic cell had a 25% energy conversion efficiency[6,7]. This record efficiency increased to 25.6% in 2014 and 26.7% in 2017. Polymer solar cells, quantum dot solar cells, perovskite solar cells, and dye-sensitized solar cells (DSSCs) are examples of outstanding third-generation solar cells[8]. The low cost of production in DSSCs, higher efficiency, easy fabrication and better stability are the edges of DSSCs over conventional solar cells[4,9]. A photo-electrochemical device that generates electrons by sensitizers upon light absorption between a hole conducting electrolyte and a dye adhered metal oxide surface compartment is known as DSSC[10].

DSSCs is one part of thin-film solar cells. In 1988, DSSCs were brought to existence by Brian O'Regan and Michael Gratzel while searching for enhanced performance electrodes for electrochemical cells. DSSC's structure is sandwich-like that is majorly composed of a photoanode, electrolyte, and counter electrode[9,11]. DSSCs have gained popularity because of their excellent efficiency, flexibility, uncomplicated synthesis, low cost, and being environmentally friendly. Its drawbacks also include the low stability of the dye, small amount of dye molecules on TiO_2 surface, and low absorption of light[12].

Although there is a high conversion efficiency of energy in DSSCs, Zhang *et al*.[11] obtained 12.3% power conversion efficiency (PCE) of DSSCs with cobalt (II/III)-based redox electrolytes and platinum-based counter electrodes but it cannot store the converted energy. For this reason, a supplementary energy storage device for instance a supercapacitor is required for easy storage of converted energy and to serve as the primary power delivery output for most optoelectronic device applications. In this regard, a photo-supercapacitor is a device that combines a solar cell, commonly a DSSC, and an energy storage device like capacitors, batteries, or recently a supercapacitor could be used for the development of future energy storage. The combination of DSSC together with supercapacitor offer about 43% internal resistance reduction that elevates and smoothens the power delivering systems[13].

Because of higher power density and long battery life in supercapacitor, it has a wide range of applications in portable supplies, emergency backup power, and memory backup systems. Supercapacitors offer low-temperature charge and discharge performance which makes the work better compared to batteries in high degree temperature, also supercapacitor offers excellent specific power when compared with batteries or other storage devices as shown in **Figure 1**. Supercapacitors are high-power energy storage devices with higher capacitance output than conventional capacitors[14]. The main point for a supercapacitor to reach great performance with an improved specific capacitance are large surface area, layer stacking, controlled pore size, and electrode materials distribution. Electrochemical supercapacitors which is a high-frequency energy storage device shows a long life cycle, but a low energy density[15-17].

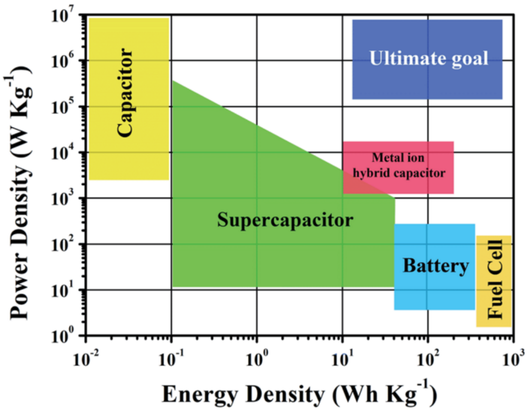

Figure 1. Plot that shows the comparison between various energy storage devices[18]

The attractive electrochemical characteristics of a supercapacitor like its fast charging, high power density (10 kw/kg), and long-life cycles have enticed enormous attention of researchers in the last few decades[19,20]. A supercapacitor also referred to as an ultracapacitor is a high-capacity device that can store and delivers energy with high current at a very fast rate, in a short time, and has higher capacitances and lower voltage limit compared to other capacitors and have caught the attention owing to high power density and their charge-discharge rate[16,21]. This review aims to present a current advancement in photo-supercapacitors, the working mechanism of a photo-supercapacitor, the classification of a supercapacitor, and the active component of a photo-supercapacitor.

2. Mechanisms of A Photo-supercapacitor

A photo-supercapacitor is a device assimilated for energy storage, it is composed of DSSCs (a primary electron contributor that causes the dye electron to move higher to an excited state in semiconductor's conduction band) and a supercapacitor[22]. In the photo-supercapacitor system, DSSCs take in radiant energy from the sun through dye molecules and converting it to a different form of energy like electrical energy that can be used during the supercapacitor charging process. A DSSCs device consists of a sensitizer, a photoactive metal oxide that is coated on a transparent photoanode substrate, a counter electrode, and an electrolyte[23]. The photogenerated electrons are separated and transferred from the dye sensitizer towards the collecting electrode by photoanode. For efficient photoanode materials exploration, numerous metal oxides such as titanium dioxide (TiO_2), tin (IV) oxide (SnO_2), zinc peroxide (ZnO_2) and niobium (V) oxide (Nb_2O_5) serve as photoanode. An optimal photoanode used in DSSCs should have quicker electronic transport, large specific surface area, and smaller amount of recombination of interfacial electron. For several years,TiO_2 nanostructured materials was the greatest operative photoanode products, subjugating the enormously efficient DSSCs[24].

Furthermore, for easy conversion of photons into the current, four basic steps of the DSSCs working principle are required, which include: absorption of light, carrier transportation, injection of electron, and current collection. when a photosensitizer absorbs the photon (sunlight), and due to this photon absorption, electrons will be promoted from the dye's ground state to its excited state, once there, the excited electrons are injected into the conduction band of nanoporous TiO_2 electrode and the dye molecules that lose an electron gets oxidized. The injected electrons pass through the TiO_2 layer to connect with counter electrode. These electrons are then pass to the electrolyte where the oxidized dye obtain an electron from the I^- ion to replace the lost electron, resulting in tri-iodide ions (I_3^-)[25]. Lastly, the I^- ion regeneration occurs at the counter electrode, and the electron migrates across the external load to give a complete circuit[24].

Active materials frequently used for DSSCs include TiO_2 as semiconductor, platinum (Pt) as a counter electrode, indium tin oxide (ITO) as a transparent photoanode substrate, a dye based on ruthenium and electrolyte enclosing I^-/I_3^- redox couple[26]. A sandwich supercapacitor is probably gotten from stacked current collectors and separated by the electrolytes. In order to complete the circuit, both devices share a mutual counter electrode. Photo-supercapacitor is designed to make use of the abundant and renewable solar energy resources to boost light to the conversion of electrical energy. DSSC behaves as an electron contributor when light is present and photons strikes the dye molecules.

For a photo-supercapacitor, irradiated electrons are moved from DSSCs and these electrons are stored in a supercapacitor reservoir. The supercapacitor's working principle imitates the photo-supercapacitors charging and discharging processes. The photo-electrons are created due to the utilization of solar energy in place of electrical energy by a power source which is the major attribute to distinguish the concept of a photo-supercapacitor from an ordinary supercapacitor. The photogenerated electrons are saved in a counter electrode, when light is not available, the solar energy is highly converted to electrical energy efficiently allowing for further electricity production to meet the energy-demanding application, this process is known as a discharging process[22].

The equations below show the precise working mechanisms of a photo-supercapacitor[27].

$$\mathrm{Dye}+h\nu \rightarrow \mathrm{Dye}^* \tag{1}$$

$$\mathrm{Dye}^*+\mathrm{TiO_2} \rightarrow \mathrm{TiO_2}\, e_{cb}^-+\mathrm{Dye}^+ \tag{2}$$

$$\mathrm{Dye}^* \rightarrow \mathrm{Dye} \tag{3}$$

$$2\mathrm{Dye}^+ + 3\mathrm{I}^- \rightarrow 2\mathrm{Dye}+\mathrm{I_3^-} \tag{4}$$

$$\mathrm{Dye}^+ + e_{cb}^-\, \mathrm{TiO_2} \rightarrow \mathrm{Dye}+\mathrm{TiO_2} \tag{5}$$

$$\mathrm{I_3^-}+2e^-\ (\mathrm{catalyst}) \rightarrow 3\mathrm{I}^- \tag{6}$$

$$\mathrm{I_3^-}+2e_{cb}^-\, \mathrm{TiO_2} \rightarrow 3\mathrm{I}^- + \mathrm{TiO_2} \tag{7}$$

Generally, supercapacitors can be categorized into three main types based on their mode of energy storage as shown in **Figure 2**. We have: electrostatic double-layer capacitors, pseudo-capacitors, and hybrid capacitors.

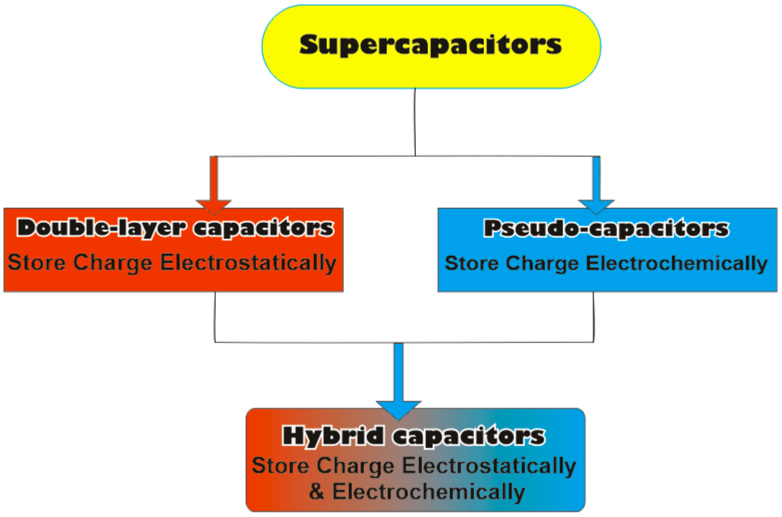

Figure 2. Classification of supercapacitor

Electrostatic double-layer capacitor (EDLC) contains two electrodes, a separator, and an electrolyte (usually use KOH) between the electrodes shown in **Figure 3**. The electrolyte is the mixture that constitutes positive and negative ions dissolved in water. Between an electrolyte and the conductive electrode, the Helmholtz double-layers are formed at interface causing fast adsorption of the electrolyte ions which leads to the provision of high-power density by a non-faradaic process. There is similarity between the double electric-layer formed and polarized charge produced under electric field's action through the dielectric in the traditional capacitor, causing effect in capacitance[17]. These supercapacitors use carbon electrodes which have higher electrostatic double-layer capacitance. The charge's separation of an EDLC ranges from 0.3 nm to 0.8 nm which is much lesser than a conventional capacitor.

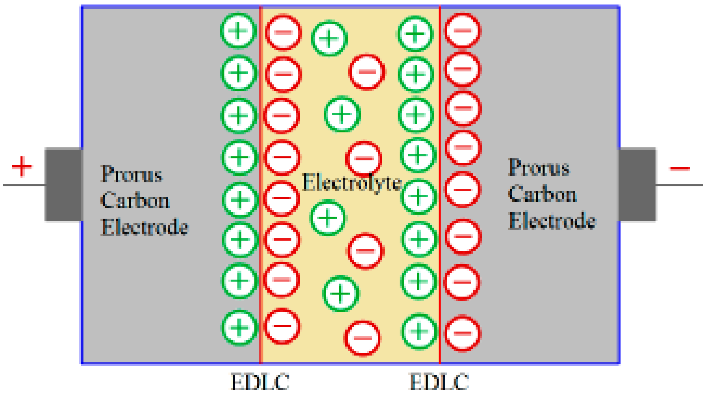

Figure 3. Schematic representation of an EDLC supercapacitor[28]

Pseudo capacitors make use of conducting polymer electrode with high electrochemical pseudo-capacitance as well as double-layer capacitance. It operates based on a faradaic electron charge transfer with a redox reaction occurring at the electrode. Like EDLCs, reactions take place at electrode's surface, which result in a high energy density, short life span and low-rate capability[17].

The hybrid capacitors are formed using the techniques of double-layer capacitors and pseudo-capacitors. Hybrid capacitors for instance lithium-ion capacitors, employ electrodes with different properties; the first exhibit electrostatic capacitance, and the second exhibit electrochemical capacitance. **Table 1** compares double-layer capacitor, pseudo capacitor, and hybrid capacitor.

Table 1. Differences between EDLC, pseudo-capacitor and hybrid capacitor[17,29]

	EDLC	Pseudo-capacitor	Hybrid capacitor
1	This makes use of carbon as electrode material	The electrode material used are conducting polymers or metal oxides.	They make used of carbon and metal oxides/conducting polymers, lithium-ion and Zn-ion
2	Charge is stored through non-faradaic process.	Electrical energy are stored by electron charge transfer between electrode and electrolyte.	Faradaic and non-faradaic processes are the method of their charge storage.

After solar energy is transformed into electrical energy, the next section of a photo-supercapacitor described how the energy is being stored. Rechargeable batteries are majorly used as energy storage units in an electronic gadget. Supercapacitors are capacitors that have high values of capacitance but low voltage. Low maintenance costs, high energy efficiency, long life cycle, and high performance are among the most important characteristics of a supercapacitor. The use of capacitors and supercapacitors have emerged for energy storage applications due to their high specific capacitance, long life cycle, and elevated energy transfer efficiency[30]. Supercapacitors have prominent power density and a few orders higher capacitances when compared to conventional capacitors. When compared to batteries, they also have low energy densities. Quick charging and cyclability are the main advantages of supercapacitors. Activated carbon, multi-walled carbon nanotubes, and single-walled carbon nanotubes are carbon-based materials that are part of the component that made up a supercapacitor[19,31].

Mensah-Darkwa *et al.*[28] worked on a sustainable approach to energy storage. They provided reports on the alternative development of supercapacitor energy storage devices using biowastes. They concluded that carbon-based materials are supercapacitor electrode material that offers high specific surface area, good conductivity, and excellent stability in harsh environments and that supercapacitor electrode material from biowaste helps in converting waste into a useful product and improve the supercapacitor technology[32].

Also, when transition metal oxides are added with conducting polymer it improves the specific capacitance of an energy storage system and the storage of a large capacitance per gram which is opposite to EDLC[22]. RuO_2, CO_3O_4, MnO_2, and NiO as transition metal oxides can achieve high specific capacitance and energy density on a current collector based on their capacity to exist in various oxidation states, promote efficient redox reactions[33]. The specific capacitance could be delivered by RuO_2-based materials in the range 1300-2200 F/g. Due to the low production cost, environmental friendliness, and high specific capacitance in MnO_2, it makes MnO_2 to be used in many energy storage systems[34]. ZnO is used as an active material mostly for a battery because of its high energy density which is 650 Wh/kg.

Furthermore, transition metal dichalcogenides (TMDs) such as MoS_2, WS_2, $WoSe_2$, WSe_2 and so on, were also employed to improve the performance of supercapacitors. Among all the TMDs, molybdenum sulfide (MoS_2) is the most commonly used due to its unique properties like good electrical conductivity, light weight and intrinsic strength[16,35]. MoS_2 has an auspicious electrode material in energy storage application and offers a large surface area for double-layered charge storage.

Molybdenum sulfide is composed of S-Mo-S atoms bonded together covalently and are held by weak van der Waals forces. MoS_2 has been shown as a propitious electrode material for room-temperature gas sensing, nano-transistors, lubricants and hydrogen storage. MoS_2 nanosheet can be prepared in various ways like solvothermal, mechanical or liquid exfoliation, chemical vapour deposition and so on, and have shown excellent performance in their respective application[16].

Many researchers have delved on increasing their energy storage derivatives and capacity of their electrode material by means of molybdenum based supercapacitor. According to Gao *et al.*[36], molybdenum sulfide nanosheets of three-dimensional nanospheres was described through the synthesis of facile hydrothermal and a specific capacitance of 683 F/g was gotten at 1 A/g. $NiCo_2S_4$-C-MoS_4 composites with kelp-like layers were reported by Wang *et al.*[37] for application in supercapacitors. Using hydrothermal, solvothermal and electrochemical techniques to synthesize composites with a maximum specific capacitance of 1601 F/g at a current density of 0.5 A/g. High power and energy densities of 27.7 Wh/kg and 400 Wh/kg. In addition, Iqbal *et al.*[38] reported the potential of MoS_2 as an electrode material, two-dimensional MoS_2 nanostructure attaining a specific capacitance of 225 F/g at 0.25 A/g. Joseph *et al.*[39] reported that the preparation of sponge-like MoS_2 for energy storage application by Balasingam and others via hydrothermal synthesis demonstrate a specific capacitance of 128 F/g at 2 mV/s scan rate using 0.5 M H_2SO_4 electrolyte solution.

Recently, Bello *et al.*[40] reported from their work, that the non-modulated synthesis performance of cobalt-doped MoS_2 improves the performance of supercapacitor. This was accomplished through the use of Raman spectroscopy, Transmission electron microscopy analysis, and scanning electron microscopy (SEM) a specific capacitance of 164 F/g was gotten.

3. Advancements of the Active Components of A Photo-supercapacitor

The photon energy converter such as DSSCs and the external storage contrivances (a supercapacitor) are operated individually, consume some space and energy, thus reduces a supercapacitor's storage efficiency[30,41]. For this reason, a device that combines solar cells and supercapacitors by capturing energy from the sun and stored this energy in the same device is known as photo-supercapacitor. A photo-supercapacitors comprises solar cells technologies for the solar cell portion along with super-capacitors that serve as the energy storage part[30].

3.1 DSSCs

Solar energy is the most promising energy source owing to its abundance, constant power supply, and being environmentally friendly. The silicon-based solar cell is widely used because of its environmental stability and its efficiency of photo-conversion, but because of smooth fabrication, low cost, and higher conversion efficiency, DSSC is cheaper and is a promising replacement for silicon solar cell. The working principle of a DSSC is depicted in **Figure 4** below. There are four basic components of DSSCs, which include; working electrode, dye (sensitizer), electrolyte, and counter electrode.

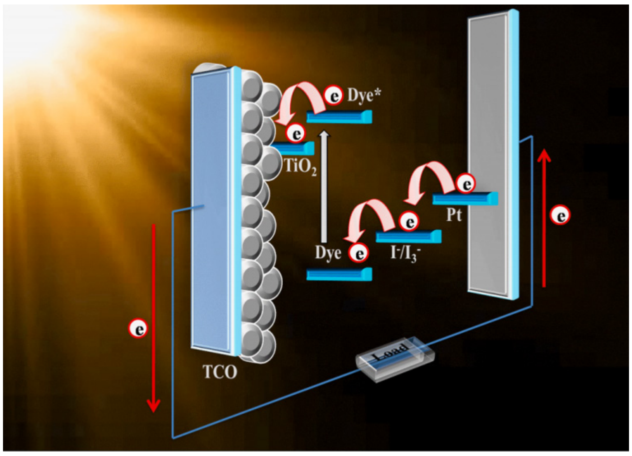

Figure 4. Schematic representation of the working mechanism of a DSSC[24]

3.1.1 Working electrode (photoanode)

Semiconducting metal oxides with broad bandgaps such as TiO_2, ZnO, SnO_2, or Nb_2O_5 deposited on transparent conducting oxide (TCO) are common materials used as photoanode. Among these semiconductors, TiO_2 nanoparticle-based photoanode is mostly used because it has good stability. Several studies have been concluded to improve TiO_2 based photo electrodes with improved interface quality, good stability, large light scattering effect, fast transportation of electrons, and high specific surface area[42].

TiO_2 has to be modified in order to enhance its photocatalytic capabilities. TiO_2 photocatalytic process is based on photoinduced interface charge transfer. Based on the type of surface modifiers, there are various methods by which TiO_2 can be modified such as polymer coating, metal loading, dye sensitization, impurity loading. Modifying TiO_2 in numerous ways not only change the mechanism and kinetics under UV irradiation but also introduce visible light activity that is absent with pure TiO_2[43]. **Figure 5** below depicts the three crystalline structures of TiO_2 which include: rutile, brookite, and anatase. Anatase has an energy band gap of 3.23 eV, brookite is 3.26 eV and that rutile is 3.05 eV. The most frequently used phase is anatase because its high conduction band edge energy of 3.2 eV which makes strong chemical stability[3,44].

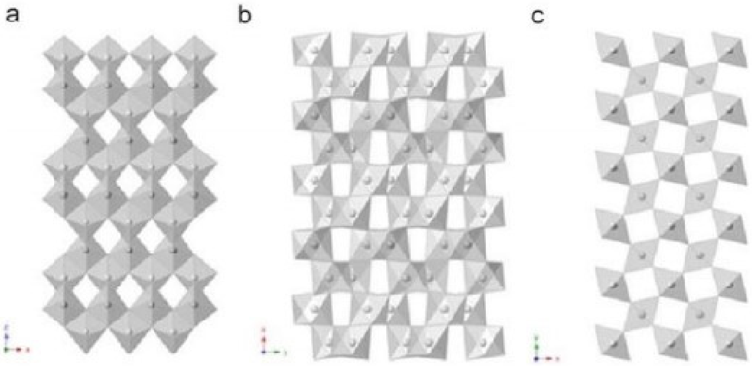

Figure 5. Structures of TiO_2: (a)anatase; (b) brookite; (c) rutile[3]

Over the years of development, several TiO_2 enhancements have been made to improve the overall performance of the DSSCs. Jun *et al.*[45] reported that Au nanoparticles having an average diameter of 5 nm were mixed with commercial TiO_2 powders in the fabrication of photoanode, and the PCE for Au nanoparticles doped with TiO_2 is plotted for different weight percentage as shown in **Figure 6**. The plot shows the 0.03% weight percentage of Au (5 nm) with TiO_2 exhibiting superior performance with the PCE of 3.12%.

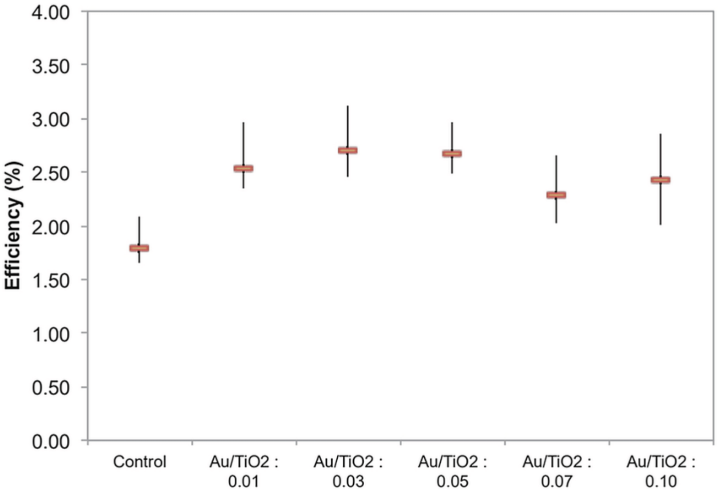

Figure 6. Efficiency range of Au/TiO_2[45]

In a study, sulphur-doped TiO_2 nanofiber-based anode was fabricated by Dakka and Barakat and it was reported that the doped anode demonstrates efficiency of 4.27% and the undoped anode has a 1.54% efficiency[46]. This showed improved performance with the addition of sulphur. Also, Gayathri and colleagues[47] reported a 5% efficiency for chromium (Cr) doped TiO_2 photoanode. Cr-doped TiO_2 nanoparticles of varying thicknesses used as blocking layers on the surface of the FTO substrate result in more efficient transfer of charge at the FTO/TiO_2 interface. They observed that pure and Cr-doped TiO_2 nanoparticles show tetragonal structures with anatase and rutile phases and that SEM analysis reveals a spherical shape morphology.

Nguyen *et al.*[48] used the sol-gel method to create the scattering layer in a photoanode by doping of nickel (Ni) with TiO_2. The DSSCs exhibited a conversion efficiency of 2.78% in the doping of Nickel with TiO_2. They fabricate DSSC using multi-walled carbon nanotubes as a counter electrode in place of a platinum electrodes.

In 2019, Ünlü and Özacar[49] in their application of photoanode in DSSC doped TiO_2 with copper (Cu) and manganese (Mn). The doped TiO_2 with 0.5%-1% of copper or manganese anode shows higher efficiency more than undoped anode. This doping constitutes a change in recombination and charge transportation. **Table 2** gives the performance parameters of the modified photoanode. Owino *et al.*[50] reported that TiO_2/Nb_2O_5 has an efficiency of 3.40. Furthermore, Adedokun *et al.*[51] reported that ZnO preparation is highly efficient in photon capturing and electron transportation. They obtained low conversion efficiency of ZnO-based DSSCs of 1.45 and is low compared to the TiO_2-based system.

Table 2. Parameters obtained by photoanode modification

Device	V_{oc} (mV)	J_{sc} (mA/cm^2)	ŋ (%)	Reference
TiO_2/Nb_2O_5	0.720	8.200	3.40	[50]
Z[NH_3OH]	0.663	5.063	1.45	[51]
SiO_2@Au@TiO_2	-	17.700	7.75	[52]
TiO_2-Nb_2O_5	-	5.700	1.48	[53]
TiO_2/C106	19.200	0.757	10.30	[54]

V_{oc}: open circuit voltage; J_{sc}: short circuit current; ŋ: conversion efficiency

3.1.2 Photo-sensitizer

Sensitizer plays a relevant role in DSSCs by absorbing sunlight and initiating the electrical current in solar cells[55]. DSSCs has their basis on single sensitizers like ruthenium dyes[56], porphyrin dyes[57] have achieved a maximum PCE and under standard illumination metal-free organic dyes exhibit a PCE of about 14%[58]. The common disadvantages of metal-based sensitizer in DSSCs application are environmental hazards, difficulty in purification, and low molar extinction coefficients[56]. As a result of their low toxicity, simple synthesis methods, environmentally friendly nature, high molar extinction coefficient, and high structural flexibility, metal-free organic sensitizers have gained popularity over metal-based organic sensitizers[59].

To produce greater efficiency and performance of sensitizer for DSSCs, some important criteria have to be fulfilled. Firstly, during electron transfer, the excited state energy level should match the TiO_2's conduction band to minimize the loss of energy. Second, a dye's highest occupied molecular orbital (HOMO) must be lower than that of redox electrolytes[22]. Also, the bandgap between the dye's HOMO and the surface of the conduction band of the photoanode should be wider whereas the gap between the dye's lowest unoccupied molecular orbital (LUMO) and the surface of the photoanode should be narrow or close.

As shown in **Figure 7**, electrons are injected to the TiO_2 nanocrystal's conduction band and diffuse via multiple traps to the TiO_2/TCO contact, where a redox couple regenerates dye sensitizer. The dye cation or the redox couple are two electron loss pathways[60].

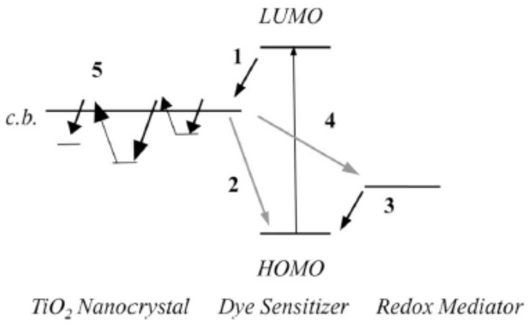

Figure 7. Illustration of process of electron transfer in a DSSC[60]

Ruthenium (II) polypyridyl is the most used dye in DSSCs due to its great performance. Ruthenium dyes RC-61 and RC-62 were created with acetyl electron acceptor auxiliary ligands, and the PCE of RC-62 is 9.10% which is higher than the conventional ruthenium dye (N3) of 8.23%[61]. In the mid-1990s, Ru (II) dye-based DSSC had an efficiency of 10.0% increasing to 11.2% in 2005 and reach 11.7% in 2010. Numerous reports have recently focused on the engineering of Ru (II) dyes with various ligands to ameliorate the overall efficiency and stability[62].

Apart from ruthenium complexes, organic dyes are important because of their high molar extinction coefficient and molecular structure. Although natural dyes have several advantages over ruthenium-based complexes due to its low cost, environmentally friendly and wide availability, but ruthenium complexes are considered as an attractive alternative to other metal oxide because of its stability and its highly efficient metal to ligand charge transfer[63]. The overall PCE of such organic dyes which have carbazoles as electron donor part, cyanoacrylic acid as acceptor part, thiophene as linker is 6.72%[64]. Other dyes with fascinating improvements include quantum dot sensitizers, metal-free organic dye, polymer dyes, black dyes, and perovskite-based sensitizers[65].

Sensitizers are gotten from natural sources in DSSCs for instance fruits, flower, and leaves. DSSCs were created with beetroot and Henna leaves as sensitizers, with efficiency rates of 1.3% and 1.08% respectively[66].

Table 3 compares the photovoltaic performance of sensitizers-based DSSCs of N-719, D358, and D149 dyes with N-719 had the highest efficiency and Fe chlorophyllin had the lowest efficiency. In addition, Adedokun *et al*.[67] reported from their study that ZnO based DSSCs coupled with the natural dyes from fruit peels of *Citrus paradise* give efficiency of 0.028% as showed in **Table 3** below.

Table 3. Comparison of photovoltaic performance of sensitizers-based DSSCs

Compound	V_{oc} (mV)	J_{sc} (mA/cm^2)	FF	ŋ (%)	Reference
D149	645	18.750	0.538	6.51	[22]
Fe chlorophyllin	500	0.620	0.520	0.16	[68]
D358	-	-	0.600	2.37	[69]
N-719	-	-	0.710	8.35	[70]
Citrus paradisi	323	0.299	0.291	0.028	[67]

FF: fill factor

3.1.3 Electrolyte

In DSSCs, redox electrolytes serve as a medium for electron transfer from counter electrode to the oxidized dye. Electrolytes type has a significant impacts on DSSCs efficiency and stability[71]. Tenacious investigations have been done on the various electrolyte's classifications, including liquid electrolytes, quasi-solid electrolytes, and solid-state electrolytes.

3.1.3.1 Liquid electrolyte

As shown some years ago, iodide–triiodide (I^-/I_3^-) electrolyte is the most commonly used redox shuttle due to its favourable kinetic properties, like the oxidation of I^-speedily at the electrolyte interface towards regeneration of dye efficiently and reduction of I_3^-slowly at the counter electrode interface for high carrier collection, relatively high stability, low cost and ease of preparation[71]. The PCE of I^-/I_3^- electrolyte-based DSSCs is about 11% according to the report of Yu *et al*.[72]. Despite this, I^-/I_3^- electrolyte has few limitations when it's been applied in DSSCs. Shortcomings like visible absorption light at 430 nm, and V_{oc} upper limit of 0.9 V, majorly limit DSSC's future development by means of this electrolyte system. Consequently, numerous substitute electrolytes such as Co (II/III) polypyridyl complex, Cu(I/II) complex, ferrocenium/ferrocene (Fc/Fc^+) couple, and thiolate/disulphide mediator have been explored[71]. A remarkable PCE of 12.3% was provided by Co (II/III) polypyridyl redox couple for liquid electrolyte-based DSSCs in 2011 and has a high V_{oc} of 0.935 V[73].

3.1.3.2 Quasi-solid-state electrolytes

The act of incorporating liquid electrolytes and solid-state electrolytes results in quasi-solid-state electrolytes. Sealing issues and long-term durability for liquid electrolytes significantly limit DSSCs practical application. As a result, efforts have been made to get alternatives for liquid electrolytes, such as quasi-solid-state electrolytes and solid-state electrolytes[62]. To surmount the problems of volatilization and leakage associated with liquid electrolytes, ionic liquids and polymer gel which contains redox couples are frequently used as quasi-solid-state electrolytes. Presently, the corresponding PCE of DSSCs based on quasi-solid-state electrolytes is 8%-9%. Although, owing to their thermodynamic instability at high temperatures, quasi-solid-state electrolytes continue to leak solvent, and as a result, require careful sealing treatment when used in high-temperature environments[62]. Therefore, solid-state electrolytes will remain the main focus of future DSSC electrolyte research and industrialization.

3.1.3.3. Solid-state electrolytes

A solid-state electrolyte made of p-type semiconductor material is an alternative idea to deal effectively with the problem of liquid-electrolyte-based DSSCs. CuI, CuBr, $CsSnI_3$, and CuSCN are the common inorganic-based hole-transfer materials, which have good conductivities[22] and organic polymers like poly (3,4-ethylenedioxythiophene) have been used successfully in solid-state DSSCs[62]. Although, solid-state-based DSSCs had low efficiency because of the high rate of charge recombination between the semiconductor and hole-transfer material, it still provides better mechanical stability. CuI/CuSCN hole-transporting materials have high hole mobility, and their fast crystallization rates causing poor filling into photoanode films, resulting in a relatively low PCE of 3.8% for DSSCs. $CsSnI_3$ is a p-type semiconductor hole transporting material with high hole mobility, abundant raw materials, and low-cost processing. In 2012, electrolyte-based devices achieved a PCE of up to 10.2% for DSSC[62]. Thus, good diffusion of hole-transporting materials in photoanode films and high conductivity for transferring hole effectively is the main subject for solid-state electrolytes in high-performance DSSCs. When comparing liquid electrolyte with gel electrolyte as shown in **Table 4**, the liquid electrolyte has better performance efficiency than gel electrolyte.

Table 4. Comparison of liquid electrolyte and gel electrolyte[22]

Electrolyte	V_{oc} (mV)	J_{sc} (mA/cm^2)	FF	ŋ (%)
Liquid electrolyte	0.686	16.88	71	8.27
Gel electrolyte	0.712	16.78	68	8.18

3.1.4 Counter electrode (CE)

In an electrochemical cell, an anode or a cathode is an electrode. The electrode by which electrons exit the cell and oxidation transpires is known as anode while the cathode is an electrode through which electrons enter the cell and reduction takes place. In DSSCs, the electrode in which the metal oxide semiconductor is deposited is known as the anode and is often referred to as photoanode, because incident sunlight frequently emanates from it. The cathode also known as the counter electrode is the electrode in which platinum and other conducting materials are deposited. The counter electrode is also an important catalyst for reducing electrolytes in the DSSCs. Platinum-coated fluorine-doped tin oxide or Indium tin oxide substrates with high conductivity and good electrocatalytic activity are mostly used as counter electrodes in DSSCs[27,70].

Platinum (Pt) is commonly used as a counter electrode to catalyse the formation of triiodide ions in the electrolyte by iodide ions reduction. Using platinum as a counter electrode, it increases the efficiencies of energy conversion, but it has some limitations which are higher cost, resource scarcity, instability in redox electrolyte, and high-temperature sintering[74]. Due to platinum limitations, the development of a low cost, chemically stable counter electrode with good catalytic properties was required[74]. Also, DSSC is expensive because of the high cost of platinum and TCO, necessitating changes to the counter electrode. Carbon-based materials, among other counter electrode materials, carbon-based materials, are very promising for the replacement of expensive platinum materials as counter electrode materials in DSSCs because of their advantages such as low price, high thermal stability, high catalytic activity, high electrical conductivity, high triiodide reduction reactivity, large surface area, and strong iodine corrosion resistance[70].

Porous carbon from quince leaf was created, using fallen quince leaves (QLs) as counter electrode in DSSCs[75]. Chemical activation and carbonization of quince leaf powder occur via alkali treatment and pyrolysis cycle (at different temperatures), producing a honeycomb-like quince leaves derived porous carbon (QLPC) with abundant micro/mesopores and large surface area. The prepared QLPC-based counter electrode system shows a maximum PCE of 5.52%.

Also, Riaz *et al*.[76] reported an active spacer between reduced graphene oxide (rGO) sheets (activated charcoal) as a counter electrode in DSSCs. The counter electrode which has a concentration of 30% activated charcoal in reduced graphene oxide demonstrates high porosity, conductivity, and active sites concentration in the single composite structure and shows a PCE of 8.6%. Also, Yang *et al*.[77] reported that C60 CE with PCE of 0.76 which is the least compared to the other ones listed. Hussain *et al*.[78] reported that Pt has a PCE of 8.74. Pt CE shows better performance when compared to other counter electrodes, which has a suitable agreement with the power conversion efficiencies as showed in **Table 5**.

Table 5. Photovoltaic parameters of the DSSCs with different CEs

Ces	V_{oc} (V)	J_{sc} (mA/cm^2)	FF	PCE (%)	Reference
C60 CE	0.53	10.08	14.00	0.76	[77]
Pt	0.73	16.71	70.78	8.74	[78]
TiN	0.79	12.83	61.00	6.23	[79]
rGO	0.54	10.47	63.00	3.60	[80]
PtMo	0.69	15.48	62.00	6.75	[81]
Pt/C60 CE	0.72	12.47	64.00	5.78	[82]
Cu_2O	0.68	11.35	47.00	3.62	[83]

3.2 Recent Improvements on Photo-supercapacitor in Energy Storage

The energy produced from sunlight via DSSCs cannot be directly stored. For this reason, a device for energy storage needed to be introduced. If we expose a solar cell to solar radiation, the voltage rises, as the cell is being lighted. Nevertheless, when connecting solar cells to a supercapacitor, the voltage of the device does not drop to zero instantly. As a result, when there is no light, the power is not interrupted. Integrated devices deliver more reliable power output, because the power is not interrupted, allowing them to be used in a wider variety of applications. The **Figure 8** below shows the working mechanism of a photo-supercapacitor starting from absorption of solar radiation via solar cell to storage of the energy.

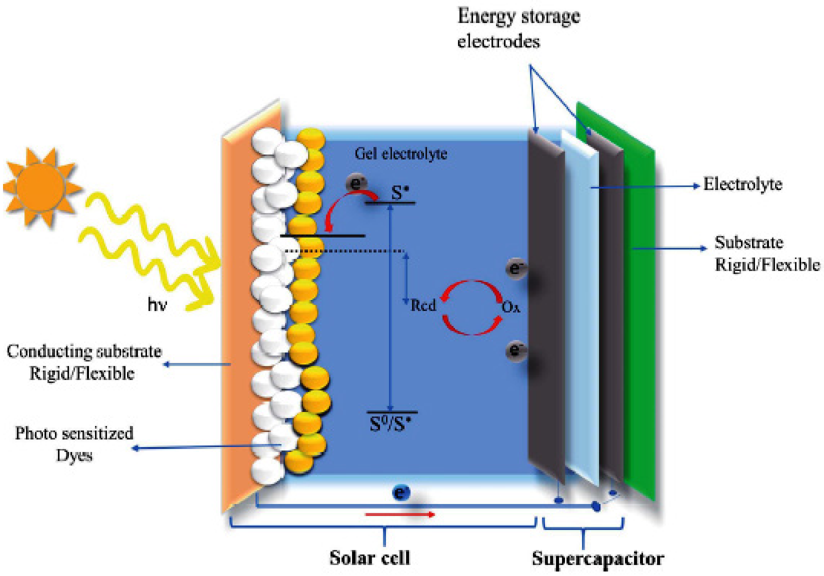

Figure 8. Schematic diagram of a photo-integrated supercapacitor[84]

Integrated photo-supercapacitors with three electrodes, was reported by Lau *et al.*[61] using a graphene-based intermediate bi-functional electrode. When a single PPy/rGO electrode is used at the interface of a supercapacitor, there is an increase in the lifespan of up to 50 charge/discharge cycles and the photo-supercapacitor exhibited a specific capacitance of 124.7 F/g as shown in **Table 6**. Cohn *et al.*[85] reported that Ionic polymer gives a capacitance of 3.5 mF/cm^2 as shown in **Table 6**. Liu *et al.*[86] reported from their study that a photocapacitor was integrated as the absorber and a PANI/CNT SC. This shows a large specific capacitance of 103.4 F/g as shown in **Table 6**.

In 2019, Song and colleague[87] reported that self-charging, light weight, and portable devices are used in collecting solar energy and convert it to electrical energy, which is then stored in a supercapacitor to power portable electronics sustainably.

Table 6. Specific capacitance of distinct supercapacitors

SC	Capacitance	Reference
Ionic polymer	3.5 mF/cm^2	[85]
CF/TiO_2/MOS_2	18.5 mF/cm^2	[88]
Al/graphene/ITO	2.5 mF/cm^2	[89]
PPy/rGO	124.7 F/g	[61]
Polypyrrole-based	572 mF/cm^2	[13]
PANI/CNT	103.4 F/g	[86]
PPy/Go/ZnO	123.8 F/g	[22]

4. Conclusion and Outlook

The improvement of a photo-supercapacitor was attributed to the incorporation of DSSCs along with supercapacitor which is a great ambition to ensure smooth uninterrupted power output delivery in many applications. The most relevant aspect is the compatibility of the active materials which is a great factor to obtain fabulous photons conversion efficiency, storage capacity, and delivering power efficiencies for a photo-supercapacitor. Several improvements had been made to various active materials such as photoanode, dye, electrolyte, the counter electrode of DSSCs, and carbon-based components of a supercapacitor to increase the overall performance of a photo-supercapacitor. Relentless efforts have been dedicated over the last few decades, to improve the DSSCs to obtain efficiencies comparable to solar cells. In DSSCs fabrication, TiO_2 has superior performance against ZnO-based and SnO_2-based DSSCs because it delivers high efficiency of solar energy to electricity conversion and ruthenium-based sensitizers have better PCE than organic dyes. The voltage does not reduce to zero instantly because of the supercapacitor that is alloyed with the DSSCs. So, even in the absence of light, the power is not interrupted. PPy/rGO material acted as a bi-functional intermediate electrode and there is an increase in the lifecycle by 50 charge or discharge cycles. The combination of a DSSCs and a supercapacitor produces a highly efficient photo-supercapacitor. This review demonstrates and discusses some of the recent advances in DSSC photoanodes, dyes, electrolytes, counter electrodes, and supercapacitors. If all the four sections of a DSSCs are given attention and a proper storage device such as a supercapacitor is alloyed with it, a photo-supercapacitor with high efficiency can be generated and it might be of great interest for commercial use. A photo-supercapacitor has shown its significance in multiple applications by powering the majority of the electronic systems that require electrical energy for their operation. However, there are great difficulties with photo-supercapacitor s, including technological issues, consistency testing and creating industrial standard. The development of a photo-supercapacitor has huge market requirement and long-term progress is needed for their successful advancement and commercialization. Future research should be focussed on enhancing the manufacturing process to discover the best materials to improve the performance of a photo-supercapacitor as well as lowering the cost of production.

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