GRAPHENE-BASED CATHODE MATERIALS FOR DYE-SENSITIZED SOLAR CELLS: A REVIEW

B. EMDADI [2], A. ASIMOV [1,2], F. TATARDAR [1,2]
[1] Institute of Physic of Azerbaijan National Academy of Science, AZ-1143, 131, H. Javid ave., Baku, Azerbaijan
[2]Institute of Physics & Electronic of Khazar University (Neftchilar Campus), AZ-1096, Khazar University 41 Mahsati Str., Baku, Azerbaijan
Corresponding author: emdadi.babak2021@khazar.org

In recent years, color-sensitive solar cells (DSSCs) have gained widespread attention for serving as potentially low-cost alternatives to silicon-based solar cells. In DSSCs, platinum-based materials (Pt) used as counter-electrodes (CEs) show superior catalytic ability than triiodide ion reduction reactions, which are attributed to their excellent catalytic activity and high electrical conductivity. However, in order to achieve cost-effective DSSCs, reasonable efforts have been made to discover alternatives without Pt. Recently, a large number of ground-based catalysts, especially carbon-based materials, have shown high activity, low cost, and good stability, making them attractive candidates for platinum replacement in DSSCs. Recently, inexpensive graphene-based counter (CE) electrodes have been developed that could serve as a potential alternative to expensive platinum-based CEs. In this review article, the development of DSSCs and the properties of graphene are briefly described. Then, the application of graphene-based materials for photo electrodes (transparent electrode, semiconductor layer, and color sensitizer) in DSSCs is discussed in depth. Finally, we have a comprehensive perspective on graphene materials in DSSCs is presented.

Keywords: Dye-Sensitized Solar Cells, Ghraphene, Graphene Molecules, Graphene-Carbon Nanotube Components, Solar Cells, Renewable energy.
PACS: 65.80 Ck, 61.48 Gh, 63.37 Hk

1. DYE-SENSITIZED SOLAR CELLS

Energy is one of the very crucial public difficulties which this generation confronts now because we demand energy in each direction of our routine life. Hence, copious several sources of energy, containing fossil, thermic, atomic, hydroelectric, wind, natural gas, and solar [1–5] are used to comply with our increasing plea. Solar energy is one of the excellent concerns because it provides pure energy harvested from the Sun [6]. The increase in energy demand and rising concern for the environment, brought solar cells into the limelight, as it is one of the best sources of sustainable, cleaner, and Renewable energy [7]. The dye-sensitized solar cell can prove itself as a suitable alternative to silicon solar cells. Systems based on intercrossing networks of mesoscopic semiconductors have displayed significantly great transformation efficiencies, which challenge those of conventional devices.

The archetype of this family of devices is the dye-sensitized solar cell, which figures out the optical attraction and the charge segregation processes by the association of a sensitizer as light-absorbing material with a vast bandgap semiconductor of Nano crystalline morphology [8]. Dye-sensitized solar cells (DSSCs) have got up as a technologically and economically reliable alternative to the p-n linkage photovoltaic systems [9]. Meanwhile, DSCs are as well as very economical to the scope that their price-to-performance proportion, which governs the economics of solar cells, exceeds “grid-parity” status. For instance, their value-to-efficiency ratio exceeds that of fossil fuels, which gives them competitive with customary energy technologies [10].

DSSCs are devices that convert solar to electric energy by light sensitization established on wide energy band semiconductors. DSSC shows a very promising future in the field of photovoltaic cells [11]. Dye-sensitized solar cells (DSCs) are typical third-generation photovoltaic devices with a mesoporous architecture and some attractive features, such as cost-effectiveness, environment friendliness, easy processing, and relatively high power conversion efficiency (PCE).

Dye-sensitized solar cells (DSSCs) are one potential alternative to silicon solar cells. DSSCs separate the light absorption and charge transfer processes, unlike Si-based cells. With the expansion of dye-sensitized solar cells (DSCs), 2 conventional solid-state photovoltaic technologies are now challenged by systems functioning at a molecular and Nano level [11]. DSCs suggest the probability of layout solar cells with huge flexibility in shape, hue, and transparency. Integration into diverse products opens up new commercial chances. Besides the exciting possibilities of using DSCs for solar energy application, the riddles of the device are as thrilling [12]. Dye Solar Cells were designed on a large internal interface prepared in a simple laboratory surrounding with no hard requests on the purity of the materials [12]. Dye sensitizer imbibes the incident sunlight and exploits the light vigor to persuade a vectorial electron transition response. Hence, DSSCs have the following privileges compared with Si-based photovoltaic [11].

131, H.Javid ave, AZ-1143, Baku
ANAS, Institute of Physics
E-mail: jophphysics@gmail.com

2. STRUCTURE AND WORKING PRINCIPLES OF DYE-SENSITIZED SOLAR CELLS

Dye-sensitized solar cell (DSSC) is the just solar cell that is able to propose both flexibility and transparency [13]. DSSCs were found to be very helpful, exclusively in the applications of wireless detector networks (clever cities, smart homes, and smart buildings), sports and officinal systems, cameras, safety sensors, and wearable electronics. The structure of DSSCs is comprised of various sheets as compared to the conventional solar cells based on silicon. Each layer of DSSCs has various chemical matters that do a special act in the electricity generation from solar vigor. The fundamental assembly of the ingredients is presented in Fig. 1 [14].

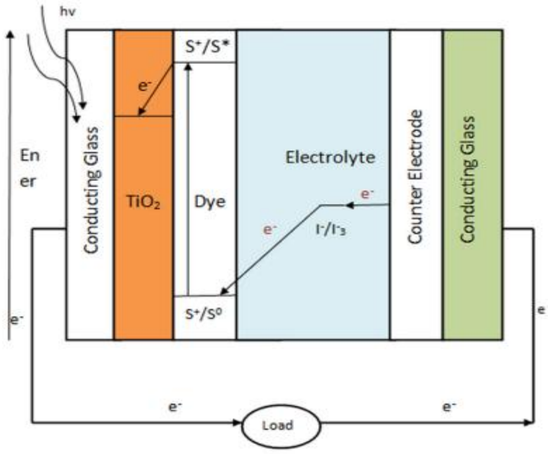

Fig. 1. Adjustment of ingredients and working principle of DSSCs. [9].

A DSSC includes three primary ingredients: the organic dye, the Nano crystalline semiconductor, and the redox couple in the electrolyte [15-22].

DSSC is composed of five elements: two transparent conductive substrates, titanium dioxide layer, dye molecules, electrolyte, and counter electrode (Carbon or Pt). The typical construction of DSSC is shown in Figure 1. The basic operating principle for any solar cell consists of absorption, separation, and collection. Different types optimize these parameters accordingly to attain better efficiency. Thus, absorption occurs in the first step of the reactions occurring in DSSC. The following steps are involved in the conversion of photons into current (as shown in Fig. 2):

1. Firstly, under illumination (photon) is absorbed by a photosensitizer, and thus, due to the photon absorption, electrons get promoted from the ground state (TiO_2/S) to the excited state (TiO_2 /S*) of the dye (Eq. 1).
2. After having been excited (S*) by a photon of light, the dye-usually a transition metal complex whose molecular properties are specifically for the task is able to transfer an electron to the semiconductor (TiO_2) by the injection process (Eq. (II))
3. The injected electron is transported between the TiO_2 nanoparticles and then extracted to a load where the work done is delivered as electrical energy (Equation III).
4. Electrolytes containing I^-/I_3^- redox ions are used as an electron mediator between the TiO2 photoelectrode and the carbon-coated counter electrode. Therefore, the oxidized dye molecules (photosensitizer) are regenerated by receiving electrons from the I^- ion redox mediator that get oxidized to I_3^- (Tri-iodide ions). This process is represented by Eq. 4
5. The I_3^- substitutes the internally donated with that from the external load and reduced back to I^- ion, (Eq. 6) [22]. The movement of electrons in the conduction band of the wide bandgap nanostructured semiconductor is accompanied by the diffusion of charge-compensating captions in the electrolyte layer close to the nanoparticle surface. Therefore, the generation of electric power in DSSC causes no permanent chemical change or transformation.

$$S + h\nu \rightarrow S^*$$
(I) Excitation process

$$S^* + TiO_2 \rightarrow e^-_{(TiO2)} + S^+$$
(II) Injection process

$$e^-_{(TiO2)} + C.E. \rightarrow TiO_2 + e^-_{(C.E)}$$
(III) Energy generation

$$S^+ + (3/2)I^- \rightarrow S + (1/2)I^-$$
(IV) Regeneration of dye

$$(1/2)I_3^- + e^-_{(C.E.)} \rightarrow (3/2)I^- + C.E.$$
(V) e- Recapture reaction

In a DSSC, the sunlight harvesting procedure is accomplished by the photosensitizing dye. It is so significant that the dye has a higher spectral attraction span so that it can attract as much sunlight as probable.

Figure. 3 displays the chemic structures of a few commonly used redox electrolytes, solid-state electrolytes (HTMs), and photosensitizers in the construction of DSSCs.

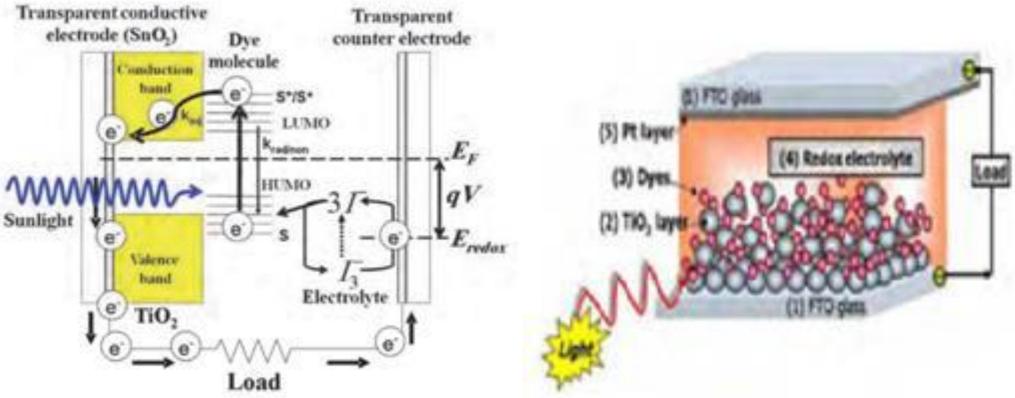

Fig. 2. Typical design of a dye-sensitized solar cell.

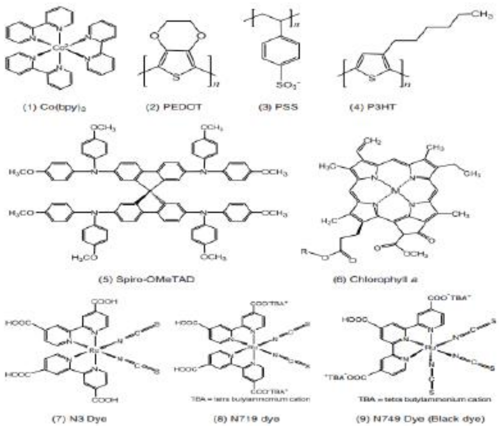

Fig. 3. Chemical structures of a few commonly used redox electrolytes, solid-state electrolytes (HTMs) and photosensitizers.

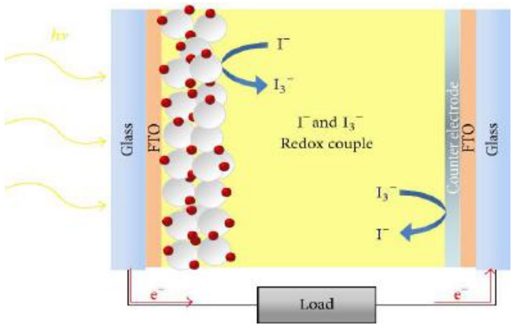

Fig. 4. Schematic illustration of the operation principle of a DSSC.

As displayed in Figure 4, a general DSSC fundamentally includes a nano crystalline semiconductor oxide, a dye sensitizer, an electrolyte redox pair, and a catalyst material as cathode, also named counter electrode (CE) [26].

To obtain high cell performance, the individual ingredients in DSSCs are incumbent to be optimized [27].

3. NEED OF GRAPHENE IN SOLAR INDUSTRY

A crucial origin of materials, critical to energy descendent, are irons found in our earth's scale. Prevalent semiconductor electronic industries are based on silicon tech. Even though these metals ((including platinum (Pt), gallium (Ga), germanium (Ge), selenium (Se), tellurium (Te), gold (Au), chromium (Cr), tungsten (W), and molybdenum (Mo)) are utilized in a very little amount, running and appearing great technology industries can face jeopardizes due to the unacceptable of these critically crucial minerals. Once fossil fuel-based energy resources become used up, high-tech industries and our routine life will be more related to other sources, containing renewable energy sources such as solar energy [6]. The necessities of 11 minerals, containing copper, gallium, indium, lithium, manganese, niobium, some platinum group metals, and some uncommon-earth origins, as assessed by a criticality matrix, are shown in Figure 5 [6].

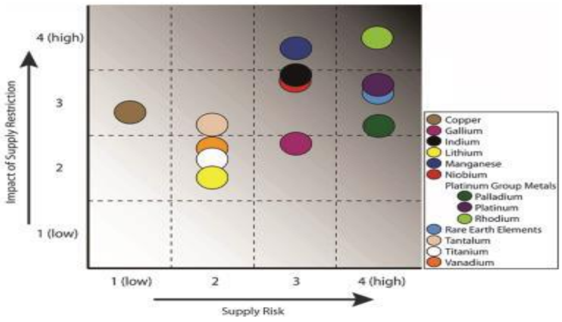

Fig. 5. Criticality assessments for 11 minerals or mineral-based materials.

Between these 11 critical minerals, traditionally used platinum and indium were found to be the most important minerals from the sight of their future accessibility due to likewise factors (some unpredictable) as use up of natural resources, economic and environmental tolerability, and geopolitical concerns. It has become a preference to detect fit low-value organic successors for solar energy industries as well as other appearing future technologies [6].

Alternative crucial metal is platinum, which is although more costly in comparison to gold but is worth for electronic ingredients manufacturing, catalytic technologies, and chemotherapy. In reality, indium and platinum are the main and significant metals currently used in solar energy investigation as electrode materials for dye-sensitized solar cells (DSSCs). Graphene and graphene-based materials suggest the flexibility to create systems over huge districts; Moreover, their low-value generation and low gravity are also absorbing characters for tapping their possible in organic solar cells.

Graphene has appeared as a possible novel material to substitute inorganic semiconductors in solar cell fabrication and hence, has drawn the consideration of the scientific association [6]. Novel materials display a significant duty in processing solar energy technologies. Graphene, one of the allotropes of plentifully exciting carbon, has appeared as one of the main promising materials for benefits in solar cells since its exploration in 2004 [23-25]. Scientists are exploring novel chemical and physical methods to create a feigned band gap in graphene, which is one of the demands for the construction of electronic systems [6]. In as much as graphene is an atom-thick substrate, it is a full-scale nano scale material and, therefore, has excellent potential in a very extensive span of applications in the field of nanotechnology.

Graphene is a 2D carbon-based material having a single layer of carbon atoms; hence, it is an ordinary nanostructured material. Because of this, graphene has been widely studied for nano technological applications in field-effect transistors, solar cells, fuel cells, super capacitors, rechargeable batteries, optical modulators, chemical sensors, medicine delivery, and biomedical applications, in addition to other areas [6]. Graphene has been evaluated as one of the undertaking Pt-free CE alternatives in DSSCs due to its particular attributes of great electrical conductance, perfect electro catalytic activity, supreme anti-corrosion opposition, and larger surface area [28, 29].

This review outlines details from easily accessible research articles on graphene-based DSSCs.

4. CONCLUSION

In this review article, we've tried to give a comprehensive view of Dye-Sensitized Solar Cells, and Structure and Working principles of that. Moreover, we've strived for giving some explanations about graphene in the solar industry, and graphene-Based Cathode Materials. As we've elucidated in this paper, energy is one of the very crucial public difficulties which this generation confronts now because we demand energy in each direction of our routine life. Hence, copious several sources of energy, containing fossil, thermic, atomic, hydroelectric, wind, natural gas, and solar are used to comply with our increasing plea. Solar energy is one of excellent concern because it provides pure energy harvested from the Sun. Last but not least, Novel materials display a significant duty in processing solar energy technologies. Graphene, one of the allotropes of plentifully exciting carbon, has appeared as one of the main promising materials for benefits in solar cells since its exploration, and this material is one of the demands for the construction of electronic systems.

[1] Energy Technology Perspectives 2015, International Energy Agency, Paris, France, 2015.
[2] *C. Philibert.* Solar energy perspectives 2011, Organizations for Economic Co-operation and Development and International Energy Agency, Paris, France 2011.
[3] International Technology Roadmap for Photovoltaic (ITRPV).
[4] *T. Bradford.* Solar Revolution: The Economic Transformation of the Global Energy Industry, MIT Press, Cambridge 2006.
[5] *V. Balzani and N. Armaroli.* Energy for a Sustainable World— From the Oil Age to a Sun-Powered Future, Wiley-VCH, Weinheim 2011.

[6] *Eric Singh, Hari Singh Nalwa.* "Graphene-Based Dye-Sensitized Solar Cells: A Review" Sci. Adv. Mater. 2015, Vol. 7, No. 10

[7] *K.L. Chopra, P.D. Paulson, & V. Dutta.* 2004. Thin-film solar cells: An overview, progress in photovoltaics. Res. Appl., 12, 69–92.

[8] *Michael Grätzel.* "Dye-sensitized solar cells" , Journal of Photochemistry and Photobiology C: Photochemistry Reviews, Volume 4, Issue 2, 2003, Pages 145-153.

[9] *Khushboo Sharma, Vinay Sharma, S.S. Sharma.* "Dye-Sensitized Solar Cells: Fundamentals and Current Status" Nanoscale Research Letters volume 13, 2018, Article number: 381.

[10] *Cole, M. Jacqueline, Pepe, Giulio, Al Bahri, K. Othman, B. Cooper, Christopher.* 2019. Cosensitization in Dye-Sensitized Solar Cells. Chemical Reviews, acs. chemrev.8b00632.

[11] *B. O'Regan, M. Gratzel.* 1991. A Low-cost highefficiency solar cell based on dye-sensitized colloidal TiO_2 films, Nature, 353: 737-740.

[12] *Anders Hagfeldt, Gerrit Boschloo, Licheng Sun, Lars Kloo, and Henrik Pettersson.* "Dye-Sensitized Solar Cells" Chem. Rev. 2010, 110, 6595–6663.

[13] *Di Wei.* "Dye Sensitized Solar Cells", Int. J. Mol. Sci. 2010, 11, 1103-1113.

[14] *Aslam, Asad; Mehmood, Umer; Arshad, Muhammad Hamza; Ishfaq, Abdulrehman; Zaheer, Junaid; Ul Haq Khan, Anwar; Sufyan, Muhammad.* 2020. Dye-sensitized solar cells (DSSCs) as a potential photovoltaic technology for the self-powered internet of things (IoTs) applications. Solar Energy, 207, 874–892.

[15] *M.-E. Ragoussi, T. Torres.* Chem. Commun. 51, 2015, 3957–3972.

[16] *N.S. Lewis, D.G. Nocera.* Proc. Natl. Acad. Sci. U.S.A. 103, 2006. 15729–15735.

[17] *M.A. Green.* Phil. Trans. R. Soc. A 371, 2013, 1–14.

[18] *M.A. Green, K. Emery, Y. Hishikawa, W. Warta, E.D. Dunlop.* Prog. Photovolt: Res. Appl. 21, 2013, 827–837.

[19] *L.M. Peter, Phil.* Trans. R. Soc. A 369, 2011, 1840–1856.

[20] *P.M. Beaujuge, J.M.J. Fréchet.* J. Am. Chem. Soc. 133, 2011, 20009–20029.

[21] *M. Urbani, M. Grätzel, M.K. Nazeeruddin, T. Torres.* Chem. Rev. 114, 2014, 12330–12396.

[22] *M. Grätzel.* Acc. Chem. Res. 42, 2009, 1788–1798.

[23] *K.S. Novoselov, A.K. Geim, S.V. Morozov, D. Jiang, M. I. Katsnelson, I. V. Grigorieva, S. V. Dubonos, and A. A. Firsov.* 2D gas of massless Dirac fermions in graphene. Nature 438, 197–200, 2005.

[24] *A.K. Geim and K. S. Novoselov.* The rise of graphene. Nature Mater. 6, 183–191, 2007.

[25] A.K. Geim. Graphene: Status and prospects. Science 324, 2009. 1530–1534.

[26] *Man-Ning Lu, Chin-Yu Chang,Tzu-Chien Wei, Jeng-Yu Lin.* "Recent Development of Graphene-Based Cathode Materials for Dye-Sensitized Solar Cells" Volume 2016, |Article ID 4742724.

[27] *G. Calogero, A. Bartolotta, G. Di Marco, A. Di Carlo, and F. Bonaccorso.* "Vegetable-based dye-sensitized solar cells," Chemical Society Reviews, vol. 44, no. 10, pp. 3244–3294, 2015.

[28] *J.D. Roy-Mayhew, D.J. Bozym, C. Punckt, and I.A. Aksay.* "Functionalized graphene as a catalytic counter electrode in dye-sensitized solar cells," ACS Nano, vol. 4, no. 10, pp. 6203–6211, 2010.

[29] *D.W. Zhang, X.D. Li, H.B. Li* et al., "Graphene-based counter electrode for dye-sensitized solar cells," Carbon 2011, vol. 49, No. 15, pp. 5382–5388.

Received:11.03.2022