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Review Article

NANOSCALE GRAPHENE OXIDE COUNTER ELECTRODE DOPING ENHANCES CURRENT CONVERSION EFFICIENCY IN DSSC: AN OVERVIEW

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ABSTRACT

To fulfill the energy requirements all the countries in the world are wondering for the new sources of energy generation. Extraction of fossil fuel from the earth crust is one of the most common practice in the today's world. But, one day these sources will be depleted and thus different ways need to be designed by which we can grow.

Renewable sources can be the better option to generate such energy requirements, tremendous work is also going to be done in this sector. This work is also deals with the generation of energy from the renewable source by the technique used for the extraction of energy from sunlight and convert it to electrical energy.

Present work reviles the importance of doping while using graphene oxide counter electrode. It was found that, the current conversion efficiency has been improved enormously with the addition of various dopant material instead of only graphene oxide used, as compared to platinum electrode under the same condition.

This review deals with, the components of graphene oxide counter electrode in a detailed manner, their uplifting concepts and conquer barriers.

Keywords: DSSC, Graphene Oxide, Counter electrode.

1. INTRODUCTION

DSSC's cheap cost, easy fabrication method and moderate photon to current conversion capacity (10.4%) attracts more attention. In the bidding days of development in the field of DSSC's, monolayer of platinum were used as counter electrode by the researchers [1, 2], but as the work fluoresced, various trial and error experiments were performed to get better results. The graphene based anode heated at nearly 400°C temperature will enhances efficiency of cell up to 6.81 % under the full sunlight performance compared with the platinized anode. Although platinum increases the cost of device prepared [3]. Even the efficiency can be enhanced by doping graphene oxide with Fe_20_3. Triiodide to iodide reduction easily facilitated with hierarchical Fe_3O_4- reduce graphene oxide couple which shows efficiency of 6.65% in DSSC, superior to platinized anode (6.37%) [4]. Reduced Graphene Oxide with Nanosize Polypyrrole counter electrode shows good conversion efficiency of 2.21% which is approximately equal to platinum electrode 2.19% made by sputtering method over FTO Conductive glass. But, low cost, simple fabrication makes this anode viable contender compared platinum electrode [5]. The synergetic effect between Nano-hybrid of Graphene-Carbon, Zinc, Nickel, Sulphur and a WO_3 nanorod influences the electro-catalytic activity for the reduction of tri-iodide to iodide, it enhances efficiency of the cell up to 12.16% which is higher compared to corresponding Pt-electrode under similar condition [6]. Present review, focused on the components of the photo anode used for DSSC, also discuss possible advancement in the material used for the cell development as well as the difficulties arises to achieve maximum efficiency with the device [7]. Anode prepared by sputtering method by FTO glass coated with black carbon required time 15 min [8]. First of all FTO glass was cleaned with ethanol, followed by coating of graphite pencil carbon, ensure that there are no space remain left covered graphite carbon [9]. Anode plays a key role in reduction of redox electrolyte used in DSSC, which helps to fasten the process of conduction of electrons in to the circuit. Graphene two dimensional structure shows the high current conduction capacity as compared to corresponding metallic materials, high transparency to light radiation (~97.9%), good thermal conductivity [10], and impermeability nature for the incoming gases, large surface area, anti-corrosiveness

etc. all these properties of nanoscale graphene catches more attention towards use in DSSC's. There is a need of corrections by adding dopant materials of carbon, metal oxide, transition metal carbide, conductive polymer, and quaternary chalcogenides which preferably enhances the efficiency of the cell. Efficiency of the cell is directly related to rate of transfer of electron from electrode to electrolyte. Aim of the review to update the technology to give the better results with stable device [11].

1.1. Structure and Working Process of DSSC

The exact working of the DSSC goes with the following steps,

i) Incident photon from the light radiation make the excitation of the electrons of the dye molecule.
ii) After the excitation of electron, it will get injected in to the semiconductor material coated on the surface of counter electrode glass of FTO/ITO.
iii) Injected electron will initiate the flow of electron from counter electrode semiconductor through circuit.
iv) This flowing electron through circuit will be accepted by the counter electrode (made up of graphene and along with various experimental dopant materials).
v) Which is further accepted by I^-/I^{3-} Pair of electrolyte solution by the reduction of triiodide to iodide.
vi) Again dye molecule who initially loss the electron by the attack of photon, it will then recovered from the redox process of the electrolyte solution. The process called as regeneration of the dye.

This is a continuous process to generate the electricity.

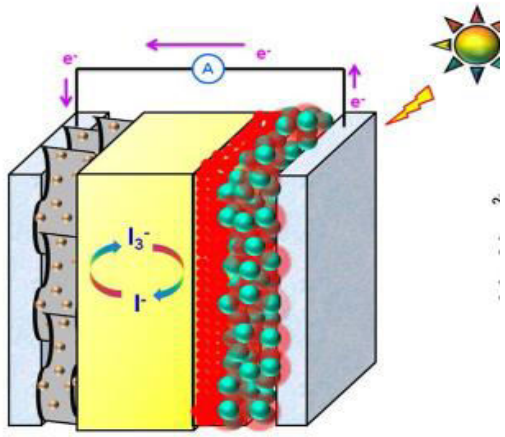

Fig. 1: Structure of DSSC [5]

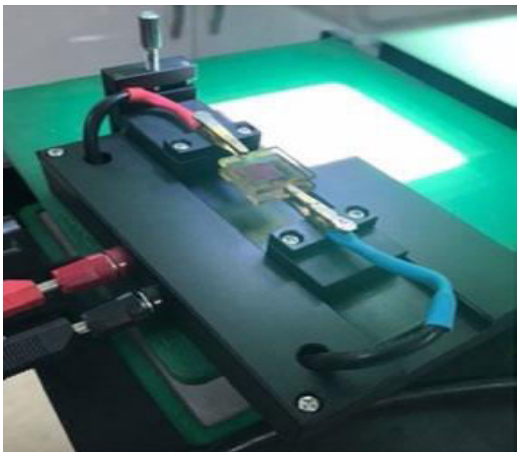

Fig. 2: Working process of DSSC [6]

1.2. Fabrication of DSSC

1. Weighed 1g of TiO_2 powder, mixed it with 5ml ethanol in to the mortar and pestle till homogeneous mixture obtained.
2. A slide fabricated by adding drop of TiO_2 paste over conducting FTO glass by doctor blade method.
3. Prepared film calcined at 450°C for 30 min. cooled to room temperature.
4. Film immersed into 0.5 mM ethanol with photosensitive dye for 1day for sensitization, Followed by washings with deionized water.
5. TiO_2 Photo anode kept over the counter electrode already prepared in such a way that faces of both the electrode covered with material, should be aligned towards each other.
6. Scotch-tape/Para film placed between this two electrodes with central hole.
7. Electrolyte solution added from the side of the plates taking care of no air gap will be present between electrode plates. The whole assembly seen as per fig.2.

Viyada Harnchana et al. fabricated photo anode for DSSC over FTO conducting glass (7Ω/ square) by adding 250µl nanohybrid material suspension of Fe_3O_4 - reduced graphene oxide grown over Sodium chloride (NaCl) crystals dissolved in acetone in the proportion of 1mg/ml. preparing a very thin film which was then dried at 80°C for 1hour followed by heating in air at 480°C for an hour for the reduction and subsequently improve adhesion with FTO surface of graphene oxide counter electrode [4].

Su Pei Lim et al. synthesized rGO@PPy (Reduced Graphene oxide with polypyrrole) nanocomposite material. Fabrication process was done by catalytic in-

situ electrochemical polymerization. Pyrrole (0.1 M), Graphene Oxide (1mg/ml), NapTS-catalyst (0.1 M), Ferric Chloride (0.1M) were mixed in the electro-chemical cell, stirred vigorously for 5 minutes gave polypyrrole nanoparticles. Potentiostat- galvanostat (Elchemamodel EQCN-502 Faraday cage) was employed for the electrodeposition of the formed rGO@PPy nanocomposite over the ITO (Indium doped Titanium Oxide) conducting glass with the constant applied potential of 10.8 V at room temperature for varied time interval of (10, 50,100,250 & 500 sec.). To remove excess impurity of iron salt, electrode plates were thoroughly rinsed with highly purified deionized water several time [5].

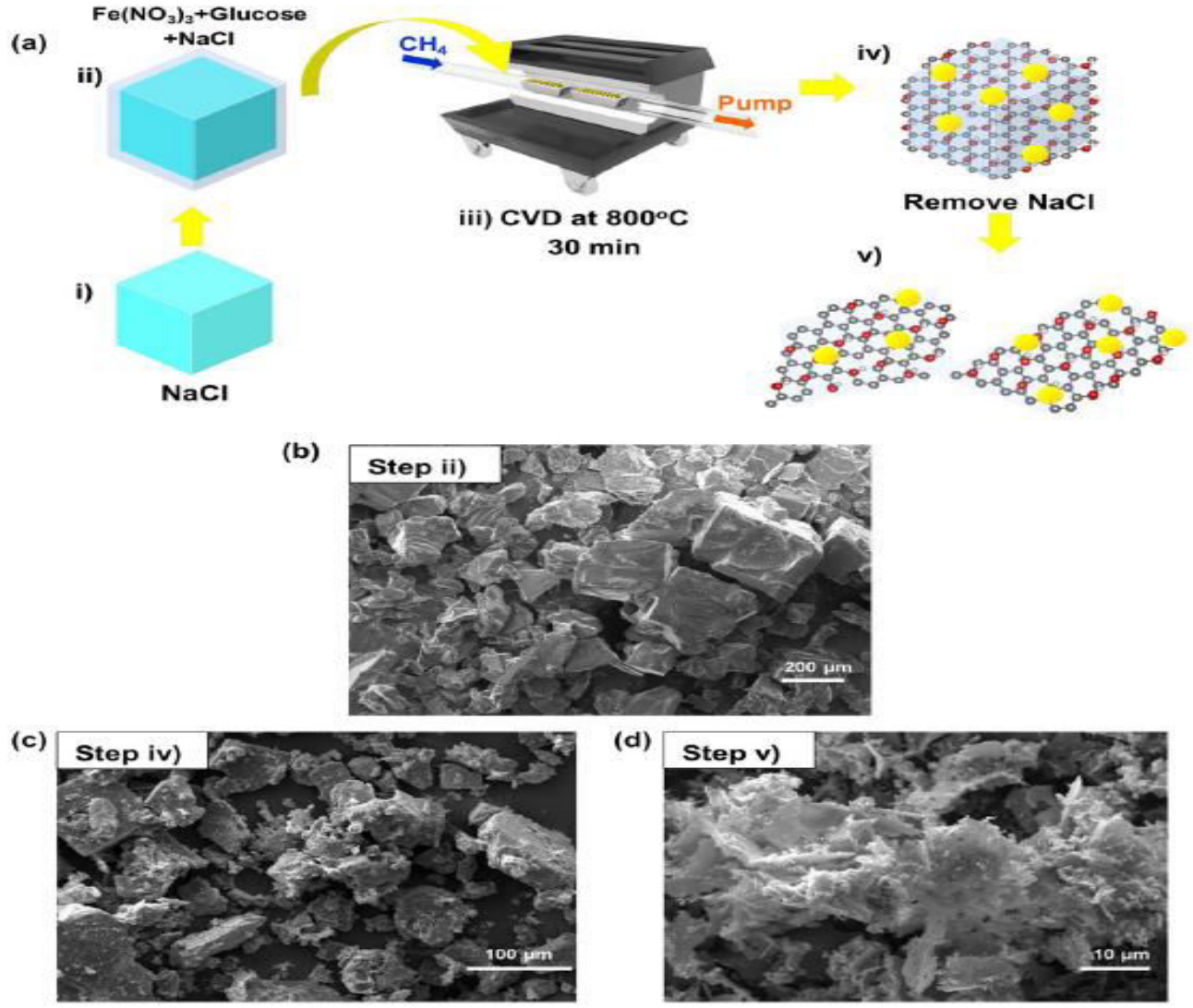

Fig. 3: (a) FGC sample preparation process (b) starting material SEM images of Fe(NO3)3, Glucose & NaCl (c) SEM images of Prepared Product by CVD method before removing NaCl-Crystal (d) SEM images of Prepared Product by CVD method after removing NaCl-Crystal [4]

Won Chun Oh et al. fabricated counter electrode with the nanocomposite of CZNS (C-Carbon, Z-Zinc, N-Nickel, S-Sulphur), WO_3 (Tungsten Oxide), G-CZNS @W (CZNS over Tungsten) over FTO (Fluorine doped Titanium Oxide) glass by simplest doctor blade method. Prepared film over FTO glass was annealed at 500°C for half an hour. Both the electrodes were coupled by keeping spacer of 25 µm thick parafilm of Surlyn (Solaronix). Electrolyte added from the side of the plates such that no air gap present. J-V measurement done by illuminating active area 0.25cm^2 [6].

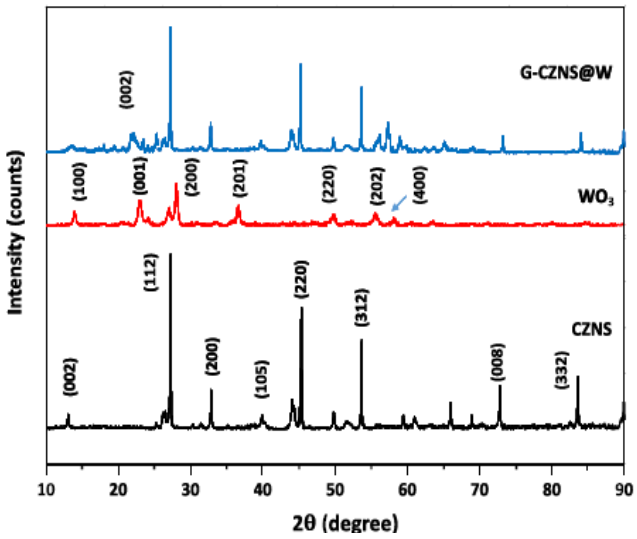

Fig. 4: X-ray diffraction spectra of CZNS, WO3, G-CZNS & G-CZNS@W

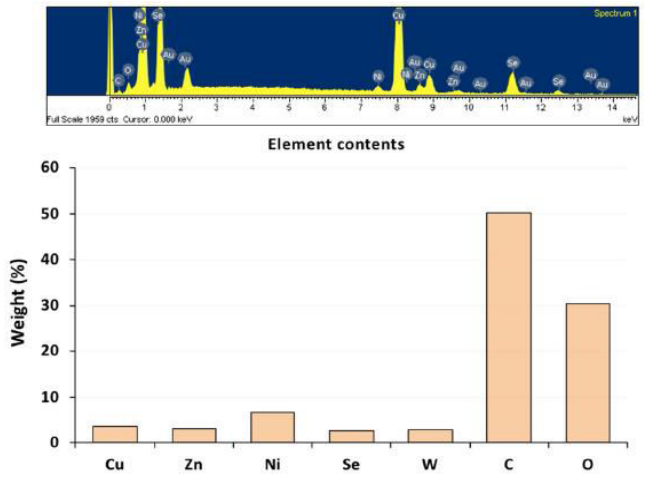

Fig. 5: EDX Spectrum of G-CZNS@W

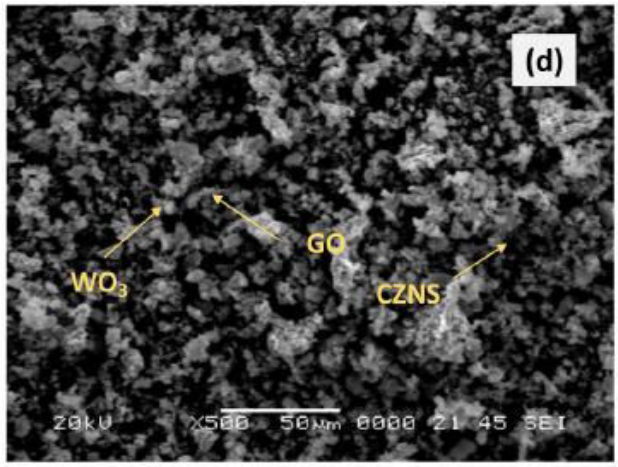

Fig. 6: Scanning Electron Micrograph of G-CZNS@W

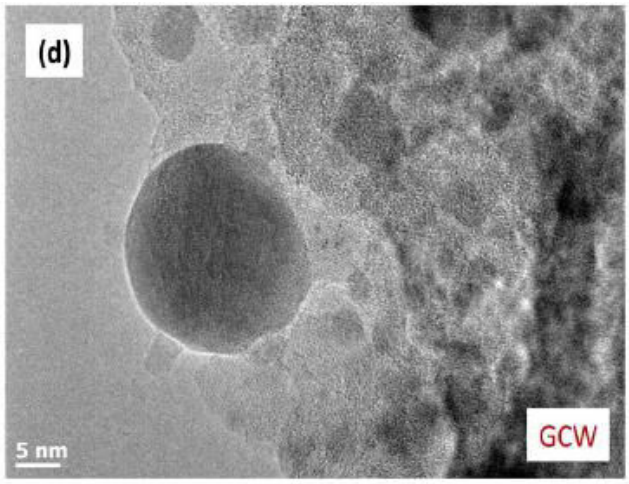

Fig. 7: Transmission Electron Micrograph of G-CZNS

S.A. Salleh et al. applied the procedure of Umar et.al. (2016) [12] called modified Hummer's method, for the synthesis of Graphene Oxide. Prepared 5ml solution of 0.01M $NiCl_2$ was added to GO powder dissolved in 10ml Distilled water and stirred ultrasonically for 1 hour. Thiourea was added to this solution again sonicated for half an hour and stirred for 3 hours. To obtain NiS-GO thin film, drop of solution was deposited over ITO glass thrice. Fixed the coat by heating in air for 10 min. at 100°C. Spin coating at 1500 rpm was done for 30s. To obtain NiS-rGO, film need to be heated over 350°C under inert atmosphere of argon gas. By varying Nickel chloride concentration of 0.02, 0.03, 0.04, 0.05 and 0.06 M, experiment was repeated. Pure r-GO was prepared without adding Nickel chloride and thiourea by the same method.

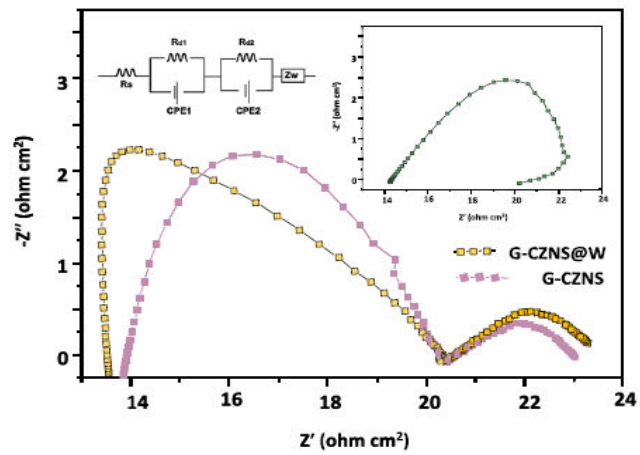

Fig. 8: Nyquist plots of CZNS, G-CZNS, & G-CZNS@W with Resistance [6]

The following data included table-1 clearly shows the Graphene based counter electrodes [3] are producing better results as compared to corresponding Platinum based electrodes, which able to produced even more better results with doped Graphene.

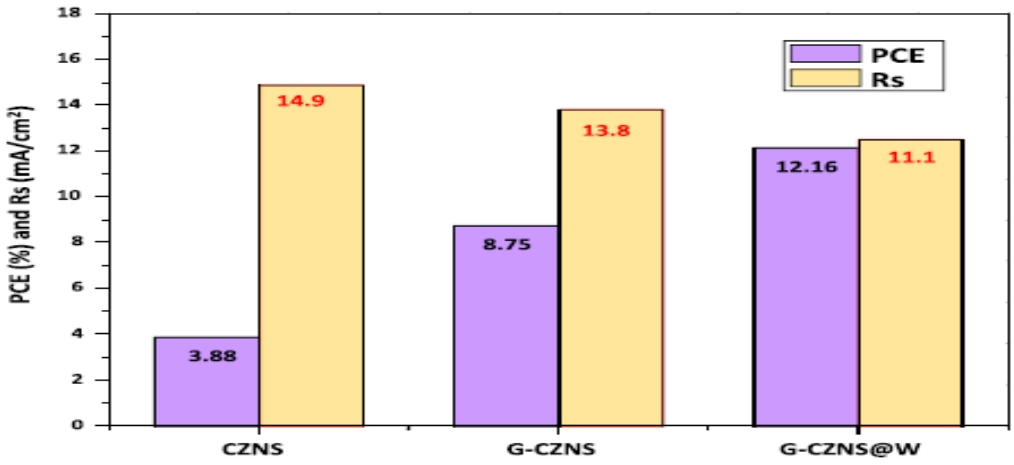

Fig. 9: Power Conversion Efficiency, Series of resistance [6]

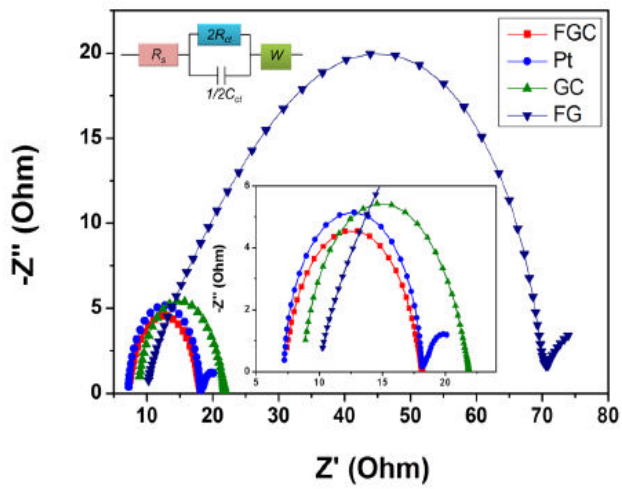

Fig. 10: Nyquist Plot of the FGC, FG, GC & Pt Counter Electrode [4]

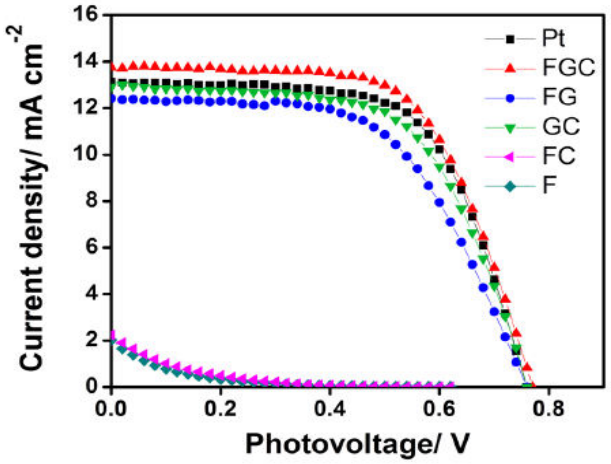

Fig. 11: Photocurrent density-Voltage (J-V) curve of the DSSC with FGC, FG, GC, FC & Pt Counter Electrode [4]

Table 1: DSSC performance using counter electrode doped materials

CE	Voc(V)	Jsc(mAcm^{-2})	FF (%)	PCE (%)	References
Pt.	0.66	7.80	70.01	4.07	[13]
CNSZ	0.68	17.50	32.60	3.88	[6]
G-CNSZ	0.86	21.21	47.97	8.75	
G-CNSZ@W	0.88	24.70	55.95	12.16	
Pt.	0.76	13.16	0.64	6.73	[4]
FGC	0.77	13.74	0.63	6.65	
GC	0.76	12.80	0.61	5.99	
FG	0.76	12.38	0.58	5.41	
FC	0.67	1.99	0.08	0.10	
F	0.64	2.30	0.07	0.07	

2. CONCLUSION

To satisfy global energy demand, needs maximum investment in the field of renewable energy sources. DSSC is a promising alternative to fulfil the global energy requirement. If each component of the DSSC is optimized and efficient to convert photon in to the electric current, more conversion can be possible. In this review focused on one of the component of DSSC, Counter Electrode, which also plays a very important role to enhance harvesting capacity of the cell. There is large scope in the area of development of the counter electrode by doping Graphene oxide with various ferromagnetic materials and by this to improve the efficiency of DSSC.

3. ACKNOWLEDGMENT

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Conflicts of Interest

The author declares that there is no conflicts of interest.

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