Efficiency Improvement of Photoelectrochemical Solar Cell Applications by Using Ternary Hybrid $MoS_2/g - C_3N_4/Cu_2O$

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ABSTRACT

In this paper, molybdenum disulfide (MoS_2) was hybridized with graphene carbon nitrite ($g - C_3N_4$) and Cu_2O in consideration to heighten the photoelectrochemical (PEC) action and increase the light absorption range of Cu_2O thin film. The melamine powder was poured in an empty container and then heated in a furnace to attain the$g - C_3N_4$ powder. The ternary hetero-epitaxial growth was achieved by *growing* of $MoS_2/g - C_3N_4$ on the Cu_2O hybrid by a partial thermal oxidation process. The characteristics of $MoS_2/g - C_3N_4/Cu_2O$ hybrid film were investigated through XRD, FT-IR and photoelectronchemistry-related measurements. The PEC performance of the treble amalgam electrode was *investigated* by means of current-voltage test under illumination. The efficiency calculated from current-voltage test under illumination exhibited that the incidence of graphene carbon nitrite and molybdenum disulphide inside the coating networks, regardless of its low down content, may perhaps stimulate substantial improvement in maximum photoconversion effectiveness from 0.036% to 0.33%. This bettering is deducible to the enrichment of the electron-reassign proficiency au courant the incorporation of $g - C_3N_4$ and MoS_2, as corroborate by X-Ray Diffraction Analysis (XRD). The PEC investigation results signify that the photoelectrochemical action of the $MoS_2/g - C_3N_4/Cu_2O$ ternary hybrid is much higher than that of Cu_2O subtrate. The mechanisms accountable for the enhanced PEC behavior of the $MoS_2/g - C_3N_4/Cu_2O$ triplex hybrid are deliberated in detail.

I. Introduction

The Industrial rebellion has brought about a fabulous increase in the authentic terrestrial planet subpopulation, and the ultimatum for active energy is increasing [1]. It is anticipated that about nine (9) billion populaces will exist on the globe by the year 2050, and about thirty (30) TW of free energy will be requisite to sustain this populaces [2, 4]. On the other hand, more than 70% of our free energy needs are currently come across by finite black gold, which will soon be exhausted [3-5]. Therefore, using a green backup energy source has turn out to be a big challenge for populace. As a nearly limitless source of green free energy, solar free energy has received substantial consideration in recent period of time. To this closing stages, photoelectrochemical (PEC) cells are considered to be efficient devices for converting solar free energy into hydrogen compound energy by water dissever [6,7]. Photoelectrodes, typically organized of semiconducting material, play the largest part

important roles in luminosity absorption, electron-hole pairing and charge transport in PEC cells [8,9]. However, due to their large bandgaps, most semiconducting materials be able to only engrossed a small portion of daylight in the UV range, which severely limits their potential applications [10].

In order to improve the PEC effectiveness of photoelectrodes, doping by means of compounds or elements and fabrication of semiconductors with heterostructures has been painstakingly on account to the different interactions between different semiconducting materials [11-12]. The progressive or modern candidate of photocathode cuprous oxide (Cu_2O) has been well thought-out as one them, [13,14]. Cu_2O is a usual p-type semiconductor accompanying with a band gap of ~ 2 eV, in the company of which it may possibly accomplish a theoretical photocurrent of -14.7 $mAcm^{-2}$ for water split and a solar to hydrogen translation effectiveness of 18.1 % on the AM 1.5 continuum [14]. Furthermore, it is accessible, globe-copious, ecologically benevolent and companionable with inexpensive fabrication processes that are main necessities requirements to placate the terawatt-scale global free energy demand [15]. The pragmatic applications of Cu_2O in the PEC process is still restricted by two major negative aspect despite the aforementioned advantages: (1) sky-scraping reunification tempo of photogenerated electron-hole carriers, partially endorsed to its inequitable electron diffusion length (usually 20–100 nm) with the light assimilation depth (about 10 µm) [16]; (2) Deprived photostability by way of self-photocorrosion in electrolyte solution [17]. Configuration engineering has existed stated to efficiently address the above restrictions of Cu_2O. Currently, on account of the plain readiness process, most of Cu_2O-based photocathode for PEC water splitting is built basing on Cu_2O film, frequently displaying a low photoelectric translation effectiveness [18,19]. On the converse, its Cu_2O nanowire/nanorod-based counterparts show appreciably enhanced effectiveness. This is principally attributed to extra proficient light harvesting, more resourceful severance and transport of photogenerated charge carriers, larger exterior area for fast interfacial charge transport, and electrochemical reactions [20- 21]. In addition to structure engineering, heterojunction engineering is widely considered as another effective strategy to improve PEC water splitting performance of Cu_2O through efficient separation of photogenerated charge carriers. [22-23]. The Cu_2O-bound semiconductor is not only a key element in forming the pn junction, but in some cases also acts as a protective layer that slows down the corrosion of the latter [24-25].

Notwithstanding marvelous efforts, Cu_2O-based photocathode contests still remain, and the combination of the above two strategies will lead to the development of a novel and efficient Cu_2O-based photocathode with potential applications in PEC water splitting. It indicates that the continuing need to further explore the photocathode could go further. This work deals with his PEC investigation of his Cu_2O films produced by thermal oxidation. Copper exhibits two dissimilar oxides, Cu_2O, with an unswerving bandgap of 2.1 eV [26,27], so it strongly absorbs barely at wavelengths underneath 600 nm, although CuO with a bandgap of 1.21–1.51 eV [28,29] absorbs the entire visible range. In addition, other reasons for choosing Cu_2O as a substance in this analysis are (a) its in large quantity in nature, (b) non-toxicity, (c) low cost of production, and (d) stability and (e) fairly good electrical properties. The effects of ternary hybrid deposition of $\boldsymbol{MoS_2/g-C_3N_4/Cu_2O}$ film's PEC behavior were investigated. In addition, the films were also characterized in terms of structure and phase analysis using XRD, I-V characteristic curve and FTIR, respectively.

II. Research Method

II.1 Synthesis of Cu_2O thin film

Commercial pure copper (99.98%) in foil form (0.1 mm thick) was censored into standard size wafers of 2 cm x 2 cm. The sample was pickled on the rim of the bud vase to make it smooth, wrapped up in dilute nitric acid, rinse off thoroughly via distilled water a number of times, and then desiccated to get rid of impurities on the film resurface. After cleaning, the copper film was thermally oxidized by furnace annealing in air. The oxidation temperature was controlled over a wide range beginning from room temperature (RT) to 450 °C. The heating tempo was about 10° C./min, and once the preferred maximum temperature was reached, it was held for 30 minutes to allow copper oxide to form. After oxide formation, the furnace was allowed to cool for 2 hours. Slow cooling was maintained to minimize possible thermal stress and film cracking.

II.2 Preparation of g-C3N4

In a usual synthesis, the g- C_3N_4 photocatalyst was analyzed disjointedly from melamine [30]. 3.0 g of melamine was naive alumina crucibles with cover and heat up at 500 °C by means of a heating rate of 3 °C min^{-1}. It is supplementary heated up to 520 °C for 2 h at a heating rate of 2 °C min and permissible to simmer down to room temperature. A yellow merchandise was gathered and ground into fine particles. The model was named as CN.

II.3 Synthesis of $MoS_2/g-C_3N_4/Cu_2O$ hybrid film

The technique used to evolve MoS_2 was chemical vapor deposition (CVD) [31, 32]. The substratum was to be set up under specific temperature and pressure conditions and single or a number of precursors were chemically respond on the outer surface of the substratum to fabricate a unsurpassed large-area thin coating. The appliance of CVD in the readying of single-layer TMDs starts with MoS_2 escalation. The heating system tempo was set to 10 °C for each min, the escalation high temperature was 650 °C, and the high temperature was well-kept for 30 min. Once the high temperature was descending to 400 °C, the closure was unlock. The MoS_2 configuration was acquired when the high temperature decreases to room temperature. The investigational procedure was shown in Figure 1.0. CVD can effectively produce monolayer and multilayer $MoS_2/g-C_3N_4$. It was able to grow up first-rate single-crystal material and produce thin films consistently distributed over large areas, which were useful in later fabrication of optoelectronic components.

Figure 1. Schematic of a growing $MoS_2/g-C_3N_4/Cu_2O$ film.

II.4 Photoelectrochemical tests

For this purpose, $MoS_2/g-C_3N_4/Cu_2O$ and Cu electrode were arranged and dipped into transparent plastic container. To prepare the electrolyte, the 1g of NaCl powders were mixed with 25 ml of distilled water, stirrer gently until the electrolyte was dissolved completely. The PEC operation of the composite electrodes was evaluated by means of Current-Voltage measurements (Figure 2). The photoelectrochemical experiments were accomplished by means of a two-electrode electrochemical arrangement. A working electrode ($MoS_2/g-C_3N_4/Cu_2O$) and a copper coat were engaged as the counter electrodes, correspondingly. The multimeter was employed to accomplished electrical route of the photo-current density and photo-voltage of electrodes beneath the illumination (AM 1.5 G) within the potential window using 1g of NaCl electrolyte as a mediator between the two electrodes. The draw close described in this study provides a simple and novel method to produce thin coating materials, prepared for practical applications for instance the photoelectrochemical solar cell and hydrogen production.

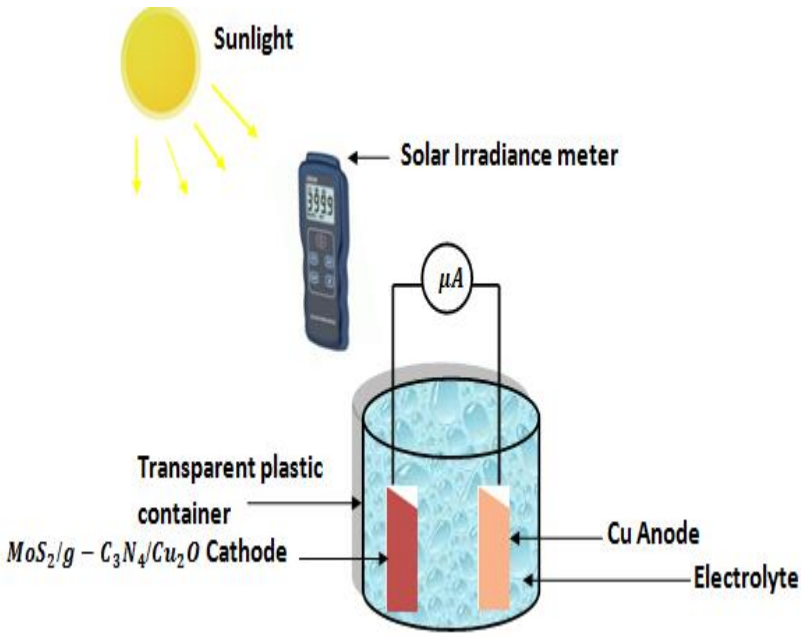

Figure 2: Illustration of the fabricated Cu – $MoS_2/g - C_3N_4/Cu_2O$ Photoelectrochemical solar cell.

II.5 Results and Discussion

The crystallized arrangement and the crystallized nature of the thermally oxidize $MoS_2/g - C_3N_4/Cu_2O$ coatings were examined by XRD investigation. Figure 3 displayed the XRD patterns of $MoS_2/g - C_3N_4/Cu_2O$ thin films deposited at different thermally oxidized temperature.

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XRD patterns show up that the sediment Cu_2O films are microcrystalline in nature and belong to cubic configuration. In addition, all slightly increasing characteristic peaks from the ternary samples were been examine entirely and their peaks are at 2θ numerical quantity of 29.01°, 36.52°, 42.11° and 61.11° matching to (110), (111), (200) and (220) diffraction plane of Cu_2O (JCPDS card no. 05-0667), correspondingly, were perceived [33,34,35]. Thermally oxidized MoS_2 the observed peaks at 33.6° correspond to (101) [36]. 37.158° displayed peak corresponding to (212) plane of $g - C_3N_4$, [37,38,39]. 38.9°, 43.8° and 52.2° corresponding to CuO (111), Cu (111) and Cu (200), [35]. MoS_2 also displays peaks that corresponded to (101) at 33.4°, (104) at 46.1° and (008) at 61.7° [40,41]. Table 1 displayed the qualitative analysis result of the triplex sample.

Table 1: Qualitative Analysis Results of the sample

S.No.	Phase name	Formula	Figure of merit
1	Cuprite	Cu_2O	0.950
2	Molybdenite-2H	MoS_2	2.970
3	Copper	Cu	2.448
4	Iron	Fe	1.003

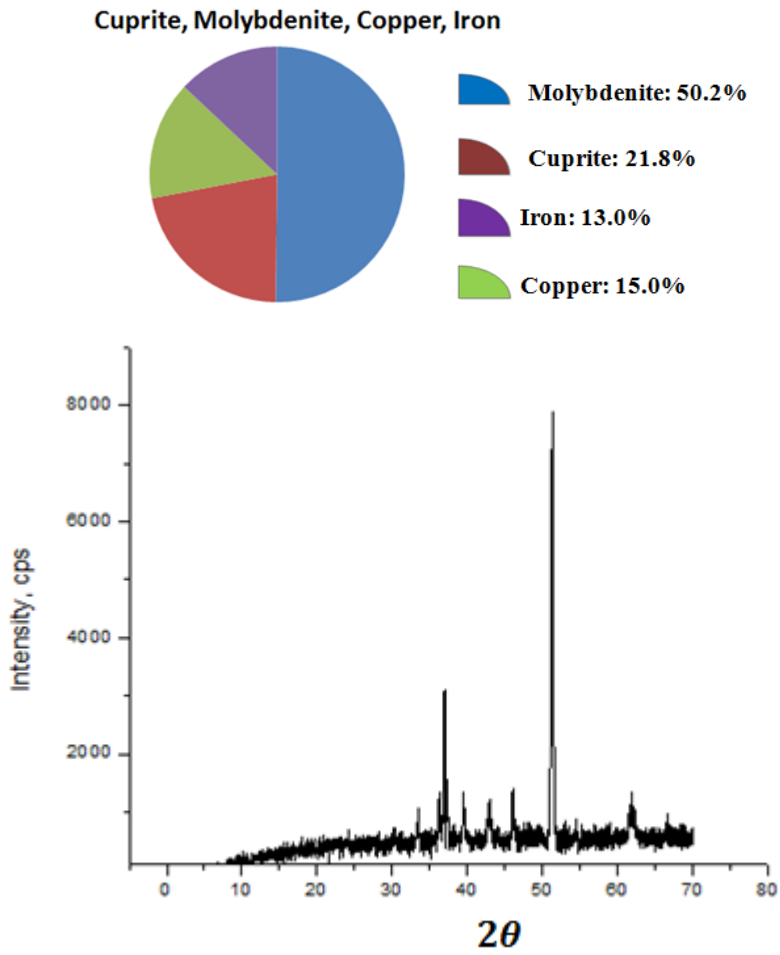

Figure 3. XRD pattern of MoS_2/g-C_3N_4/Cu_2O

II.6 FT-IR spectra analysis

FT-IR investigation (Figure 4.) was performed to analyze the compound and functional properties of mere g-C_3N_4, MoS_2, and Cu_2O thin films. Pure g-C_3N_4 exhibits a characteristic IR extremum at 1632 cm^1, whereas peaks at 1245, 1320 and 1417 cm^1 are imputed to the C-N heterocyclic stretch of g-C_3N_4 [42,43] . Broad shoulder bands in the regions of 3150, 3320 and 3350 cm^1 adhered to the elongated modes of the terminal NH groups at the aromatic ring defects [44, 45]. The existence of oxygen-correlated bonds was due to the occurrence of sharp bonds regarding 3620 cm^{-1} [44, 45]. The peak at 3405 cm^{-1} is ascribed to O-H groups [44, 45], and 839 cm^{-1} and 893.39 cm^{-1} are broad absorption bands attributed to MoS_2 [46, 47]. The peak at 3506 cm^{-1} is due to the oxygen correlated composite [44, 45]. An extremum of in relation to 1730 cm^{-1} bespeak the occurrence of C = O bonds in the model. The 2325-2425 cm^{-1} band represents the P-H stretch. 2998-2959 cm^{-1} is assigned to symmetric C-H stretch vibration. From Figure. 4 it is observed that, the attributed peaks for Cu_2O (630cm^1) shift (towards lower wavenumber) after the incorporation of g-C_3N_4 and MoS_2, which bespeak that there was an interface stuck between g-C_3N_4, Cu_2O and MoS_2. From the spectra, all the characteristic peaks of both g-C_3N_4, Cu_2O and MoS_2 appeared in the MoS_2/g-C_3N_4/Cu_2O, which is in compliance with the XPS spectrum.

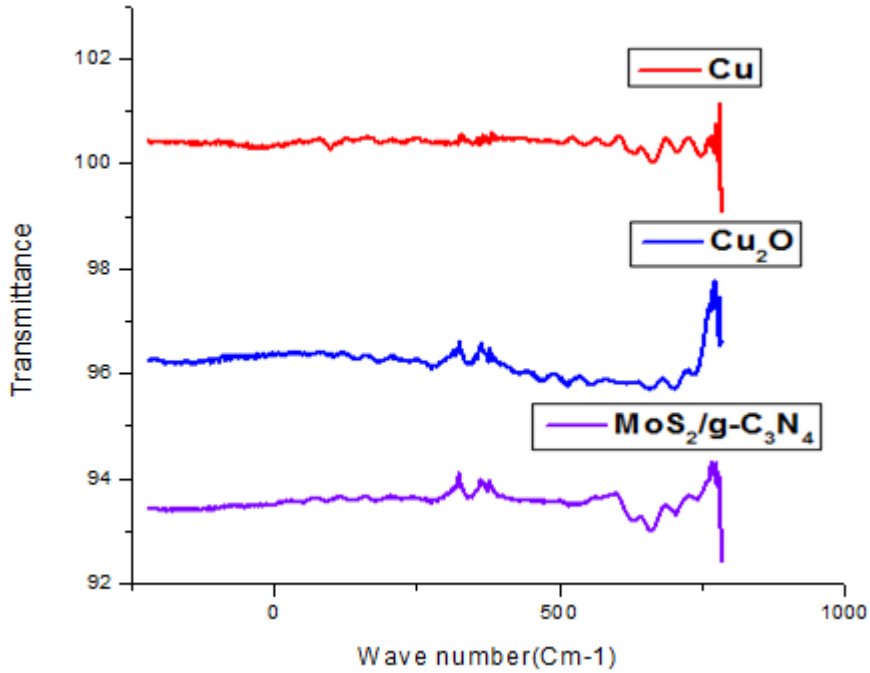

Figure 4. FTIR spectra of $MoS_2/g - C_3N_4/Cu_2O$

II.7 I-V Curve analysis

The effectiveness, utmost power, photo voltage and photo-current was acquired neath illumination as lineation in Table 2.0 and the Cu- $MoS_2/g - C_3N_4/Cu_2O$ PEC solar cell showed characteristic curves of a number of external parameters followed by transition power efficiency deduce from figure 4 and figure 5. When analyzing the trial product, the deliberate external parametric quantity of the organized samples Cu-Cu_2O and $MoS_2/g - C_3N_4/Cu_2O$ are avowed as revealed in table 2.0. Two dissimilar readings are recorded by means of a multimeter and frequent solar irradiances in sequence to study the solar cell parameters, two different graphical records are premeditated for two different samples for examining photo response and photo voltage of the electrode under illumination. In table 2.0 it can appear that for the synthesized $MoS_2/g - C_3N_4/Cu_2O$, the deposited of 2D materials increases the photo response at the equivalent time escalating the effectiveness of the model. It additional mechanism as an absorber stratum to produces charge carriers (electrons and holes) beneath solar light irradiation. A Comparison of some Findings of I_{sc}, V_{oc} and η with other Works in Literature displayed in table 3 below.

Table 2.0: The photocurrent, utmost power, effectiveness and photo voltage of dissimilar reading of Cu-Cu_2O and Cu- $MoS_2/g - C_3N_4/Cu_2O$ photoelectrochemical solar cell

S/N	Sample	$I_{sc}(mA)$	$V_{oc}(mV)$	$\eta(\%)$
1	Cu_2O	0.14	11.0	0.036
2	$MoS_2/g - C_3N_4$	1.20	60	0.33

The foremost row in table 2.0 is for Cu-Cu_2O synthesized using thermal oxidation method while the subsequent row is for - $MoS_2/g - C_3N_4/Cu_2O$ layer deposited by partially thermal oxidation method.

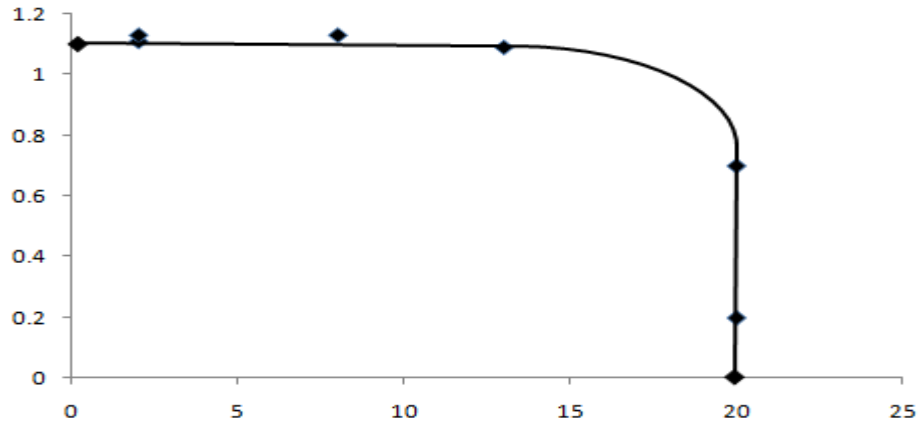

Figure. 4: The graph of Cu-Cu_2O photoelectrochemical solar cell before surface adjustment

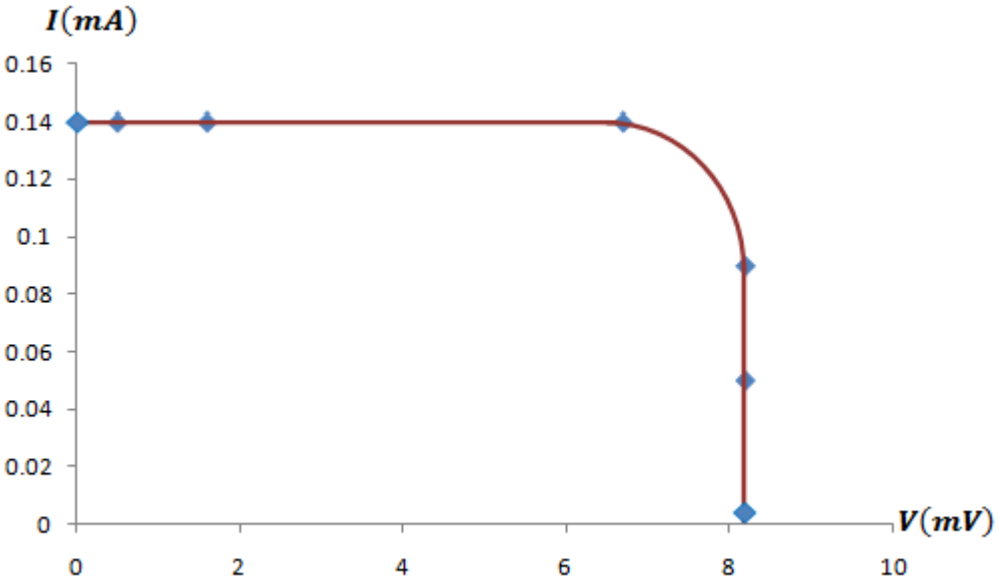

Figure. 5: The graph of Cu- $MoS_2/g-C_3N_4/Cu_2O$ photoelectrochemical solar cell after surface modification

Table 3: Assessment of Findings with other Works in Literature

Authors (Year)	Structures	Method	Efficiency	findings	References
	Cu_2O		1%		[48]
J. Herion, *et al.*,(1979)	Cu/Cu_2O	partial thermal oxidation	0.4%	V_{oc}	
R. P. Wijesundera *(2010)*	Ti/CuO/Cu_2O/Au	Electro-deposition	0.02%	*FF, Isc, Voc*	[49]
Katayama et al (2004)	Cu_2O/ZnO/ITO	Electro-deposition	0.117%	*FF, Isc, Voc*	[50]
Septina et al (2011)	Cu_2O/AZO	Electro-deposition	0.60%	*FF, Isc, Voc*	[51]
Seyed, A.J (2013)	Cu_2O	Electro-deposition	0.082%	*FF, Isc, Voc*	[52]
Y.-K. Hsu, et al *(2015)*	Cu_2O	Electro-deposition	0.42	*FF, Isc, Voc*	[53]
Abdu Y, *(2017)*	Cu_2O	Thermal oxidation	0.08	*FF, Isc, Voc*	[54]
Vijayaraghavan, et al *(2018)*	CdTe	SPD technique	0.062	*FF, Isc, Voc*	[55]

Roza, et al *(2014)*	ZnO	Hydrothermal	0.050	*FF, Isc, Voc*	[56]
Abdurrahman, M *,(2019)*	Cu_2O	Thermal oxidation	0.046	*FF, Isc, Voc*	[57]
Sutripto, et al *(2019)*	CdO	chemical method	0.21	*FF, Isc, Voc*	[58]
Tadatsugu Minami, *et al(2016)*	Zn_2GeO_4	Thin film deposition	0.12	*FF, Isc, Voc*	[59]
Tadatsugu Minami, *et al(2016)*	Zn_2SiO_4	Thin film deposition	0.03	*FF, Isc, Voc*	[59]
Tadatsugu Minami, *et al(2016)*	$ZnSnO_3$	Thin film deposition	0.01	*FF, Isc, Voc*	[59]
This work		Thermal oxidation	0.33	*FF, Isc, Voc*	
Abdurrahman, M *,(2022)*	Cu_2O	Thermal oxidation	4.80	*FF, Isc, Voc*	[4]

III. Conclusion

A ternary hybrid composed of MoS_2, $g-C_3N_4$ and Cu_2O thin film was synthesized for photoelectrochemical solar cell applications. The $MoS_2/g-C_3N_4$ binary hybrid was prepared by partial thermal oxidation processing of MoS_2 and $g-C_3N_4$ in a sealed high temperature furnace. The epitaxial growth of MoS_2 and that of $g-C_3N_4$ on the surfaces of Cu_2O thin film were taken place during the partial thermal oxidation process. Full structure and PEC analysis specify that the improved PEC activity could be attributed to the synergy between the two 2D materials. In addition, 2D materials exhibit a passivation effect that not only improves photo-excitation voltage and current by tumbling the reunification rate of charge carriers, but also increases surface photoelectrochemical to enhance the photocurrent by rushing the separation of the surface charge and utilization. The subsequent efficacious electric filed stoutness in the space charge coating drastically increases the separation efficiency of photogenerated electron-hole pairs and ultimately enhancing their PEC performances. The synthesized $MoS_2/g-C_3N_4/Cu_2O$ showed a higher efficiency of 0.33% than that of the Cu_2O 0.036% sample.

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