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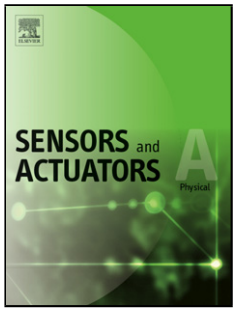

Photosensitive activity of fabricated core-shell composite nanostructured p-CuO@CuS/n-Si diode for photodetection applications

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Photosensitive activity of fabricated core-shell composite nanostructured p-CuO@CuS/n-Si diode for photodetection applications

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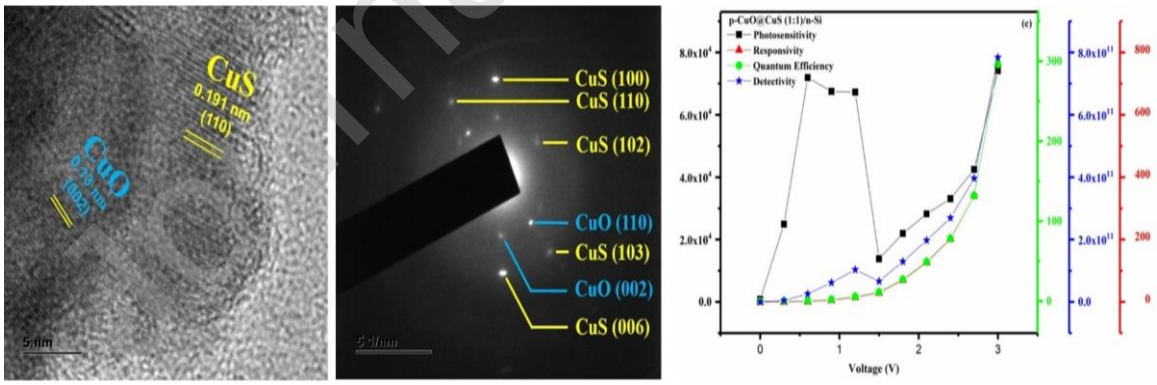
Graphical abstract



Highlights

- *Novel high-performance p-CuO@CuS/n-Si photodetectors have been facilely fabricated for the first time*

- *Structural and vibrational studied confirm the synthesis of fabrication of CuO@CuS nanocomposite system*
- *Core-shell structure like morphology was approved by FESEM & HRTEM analyses*
- *The high photosensitivity (P_s) of ~ 7.76 ×10^4 % and photoresponsivity (R) ~ 798.61mA/W was observed for the fabricated photodetector*
- *The high specific detectivity (D*) of 8.19 ×10^{11} Jones and external quantum efficiency (QE) of ~ 309.66%, was observed for the fabricated photodetector*.

Abstract

Development of photo detectors based on different semiconducting materials with high performance has been in progress in recent past, however, there is a lot of difficulties in developing the more effective photo detectors-based devices with high responsivity, detectivity and quantum efficiency. Hence, we have synthesized pure CuS and CuO@CuS core-shell heterostructure based photo detectors with high performance by simple and cost-effective two-step chemical co-precipitation method. The phase purity of CuS and CuO@CuS composite was observed by XRD analysis and the result were verified with Raman spectroscopy studies. Sphere like morphology of pure CuS and core-shell structure formation of CuO@CuS are observed with scanning and transmission electron microscopes. The presence of expected elements has been confirmed with EDX elemental mapping. Light harvesting photodiodes were fabricated by using n-type silicon substrate through drop cost method. Photo sensitive parameters of fabricated diodes were analyzed by I-V characteristics. The p-CuO@CuS (1:1)/n-Si diode owned a maximum photosensitivity (Ps) ~ 7.76 ×10^4 %, photoresponsivity (R) ~ 798.61mA/W, external quantum efficiency (EQE)~309.66% and specific detectivity (D*) ~ 8.19 ×10^{11} Jones when compared to p-CuS/n-Si diode. The obtained results revealed that the core/shell heterostructure of CuO@CuS is the most appropriate for photo detection.

Keywords: CuS@CuO; Core/shell heterostructure; Photoresponse; Photodetector

1. Introduction

Incorporating novel structure in photo detector is an important task to enhance the opto-electrical performance of the devices. Recently, hybrid nanomaterials and its structural, morphological, and electrical properties are drawn much attention in fabrication of devices such as solar cell, photo detectors, and super capacitors [1]. Many transition metal oxide (TMO) and transition metal chalcogenide (TMC) nanomaterials are well-known semiconducting materials, which are widely used for construction of optoelectronic devices due to its potential light absorbing nature. The generation of charge carriers and the charge carrier transport mechanism of TMO and TMC nanomaterials are most favorable for photo sensitive device fabrication [2]. In previous reports TMO (MoO_3, WO_3, and CuO) and TMC (ZnS, MoS_2, WS_2 and CuS) based photo detectors and are widely studied in terms of effect of morphology, concentration and temperature [3-6].

The heterostructure in optoelectronic application will improve the light abortion rate of the junction and it has strong current carrying nature. The heterojunction with different material with same conducting nature will improve the photo sensing nature of the device. Particular interest, the development of core/shell heterostructure are attractive towards the photo detectors because of their surface to volume ratio, which enable high photo response and charge transport mechanism without any loss of charge carriers [7]. Photo sensitive parameters were effectively influenced by incorporating the core/shell based sensitive layer which reduce the width of the depletion layer, barrier height, and increase the free carrier charge transport [8].

Recently many researchers reported that the fabrication and characterization of photo detectors using the core/shell nanostructures with the composition of organic/inorganic material with different nanostructures [9-11]. Zheng Sun et al. reported that highly sensitive photo detectors based on Ge–CdS core–shell heterojunction nanowires which show better photo response [12]. Improved photo response and carrier transport mechanism of

ZnO/graphene core-shell structure-based photo detector was reported by Shao et al. [13]. In recent past CuO & CuS based core-shell photodetectors has been developed by several scientists like the p-CuO/n-MoS_2 flexible heterojunction photo detector was reported by Zhang et al. with low-dark current ~ 0.039 nA and highest detectivity ~ 3.27×10^8 Jones [14], Wang et al. developed the nanostructured p-CuO/n-ZnO heterojunction photodetector and observed the responsivity ~ 0.040A/W at 1 V and 0.123 A/W at 2V, Xie et al. reported the CuO/SnO_2 UV photodetector and noticed the enhancement [15], Tian et al. fabricated the $In_2Ge_2O_7$ photodetector with CuO coating and observed the high responsivity and quantum efficiency ~ 7.34×10^5 A W^{-1} & 3.5×10^6, respectively [16], Sahatiya et al. reported the MoS_2(n)–CuO(p) flexible diode on cellulose paper with ideality factor 1.89 eV, barrier height 0.243 eV, and responsivity ~ 42 mA/W [17], Shin et al. developed the p-CuO/n-$Cu_{1-x}In_xO$ core/shell UV photodetector and noticed the photoresponsivity ~ 0.045 A/W [18], CuO/ZnO based UV photodetector with improved electrical nature was developed by Noothongkaew et al. [19], UV detector based on ZnO/CuO was fabricated with by Vikas et al. [20], Mohammadi et al. reported the ZnO/NiO(CuO) photodetector with enhanced properties [21], p-CuO/n-ZnO photodetectors has been fabricated by Ji et al. [22]. Xu et al. p- CuS- ZnS/n- ZnO photodetectors with responsivity ~ 12 mA W^{-1} at 300 nm [23], Zhnag et al. developed the n-SrTiO3 (n- STO) and p- CuS- ZnS (p- CZS) photodetectors with highest responsivity ~ 5.4 μA W^{-1} (at 390 nm), detectivity ~ 1.6×10^9 Jones [24], Panigrahi et al. fabricated n-ZnO/p-CuS photodetectors and investigated [25], etc. Along with the above-mentioned materials there are several other materials who has been employed and investigated as UV photodetectors like: $Sr_2Nb_3O_{10}$ with R = 1214 A W^{-1}, EQE = 5.6×10^5 %, D* = 1.4×10^{14} Jones @270 nm and 1 V bias by Li et al. [26], and several other 2D photodetectors (BP, GaSe, MoS2 and SnSe) discussed by Zhang et al. [27], $BaTiO_3/MoS_2$ reported by Ying et al. with R_λ of 120 vs 1.7 A W^{-1} & EQE of 4.78×10^4 vs 4.5×10^2% @365 nm compare to bare MoS_2 [28], and Li et al.

reported the hybrid CuO@In_2O_3 with R = 2.24×10^4 A/W [29]. These studies are showing very high values compare to current results; however, the currently developed photodetector is the first-time report to the literature and further work is in progress to achieve higher photodetection properties by varying the several preparation parameters. As the core/shell combinations of TMO and TMC are expected to enhance the photocurrent and responsivity of the photo detector. Most of the core/shell heterojunction-based photodiodes was reported on p-type or n-type material, still efficiency in Photo response is lagging, to achieve better photo response both material for the heterojunction employed as p-type semiconducting material [30].

These reports indicate that the core-shell system based on CuO & CuS both possess highly improved photodetection properties which makes it more useful in nanoelectronics devices with fascinating functions. Also, among several materials CuO & CuS are a versatile p-type semiconducting material with extensive properties such as earth abundance, mechanical stability, narrow band gab, cost effective, are increasing attention in the fabrication of photo detector [31, 32]. Till date the CuS with CuO as core/shell heterojunction is not documented. So, in this report, synthesis of pure CuS and CuS@CuO core/shell nanocomposite was done by the two-step co-precipitation method. The photo response properties of fabricated photodiodes such as p-CuS/n-Si and p-CuO@CuS-n/Si are explored in detail.

2. Materials and method

2.1. Materials

Copper (II) chloride dihydrate (98.5%, $CuCl_2.2H_2O$), Thiourea (99%, CH_4N_2S), Ammonia Solution (assay 25%, NH_3OH) were procured from Merck Life Sciences. All the chemicals used in this work are used as purchased.

2.2. Preparation of CuS nanoparticle

The synthesis of CuS was carried out through co-precipitation method. $CuCl_2.2H_2O$ (5 mmol) was dissolved in 80 ml of distilled water and CH_4N_2S (10 mmole) was added. The solution was subjected to vigorous stirring about 30 minutes at room temperature. The solution was adjusted to pH 10 using NaOH solution at 60 ºC. The above solution was stirred for 2 h and formed precipitate was centrifuged (3000 rpm for 10 minutes) and collected. Obtained precipitate was washed about three times using distilled water and ethanol. The precipitate was dried at 50 ºC in hot air oven and stored for further characterization.

2.3. Fabrication of CuO nanoparticles

Pure CuO nanoparticles were co-precipitationally achieved. In this method, 0.2 mole of $CuCl_2.2H_2O$ dissolved in 100 mL distilled water and stirred for 30 minutes to get homogenous green solution. The pH of above solution was adjusted to pH 9 using NH_4OH solution. The color of the solution turned in to black, when the solution attained pH 9. The collection of the precipitate was done after centrifuging at 3000 rpm for 5 minutes and washing with ethanol and distilled water.

2.4. Preparation of CuO@CuS nanocomposite

The core-shell CuO@CuS (1:0.5) prepared through by two-step chemical co-precipitation method. Previously prepared 0.440 g of CuO was completely dispersed in 80 ml of distilled water and stirred for 10 min after that 2.5mmole of $CuCl_2$ $2H_2O$was added as a copper source and stirred about 20 minutes for homogeneous dispersion. Thiourea (5 mmole) is added as a sulfur source after a continuous stirring about 30 minutes the solution changed from greenish to navy blue color. pH of the Solution was adjusted to 9 at 60 ºC and stirred for 2 hours. Formed precipitate was centrifuged at 3000 rpm and washed several times with distilled water and ethanol. The procedure was repeated for CuO@CuS (1:1) as mentioned above except Cu (5 mmole) and sulfur source (10 mmole).

2.5. Photodiode fabrication

The photodiodes are constructed by using one side polished n-Si substrate (1×1). Before starts the coating process the substrate was well cleaned to remove dust particle, oil and grease, organic/inorganic impurities, and native oxide layer over the surface of Si substrate. Substrates are immersed in 2 mL of iso-propanol and ultrasonicate for 5 minutes to remove the dust particle, then it transferred to another beaker which contains acetone in order to remove the oil and grease on the substrate. Next step in the cleaning process, substrate was cleaned using piranha solution (H_2SO_4-H_2O_2) (2:1) to eliminate inorganic/organic residues on Si substrate. Finally, substrates were immersed in (HF: H_2O) solution (1:10 ratio) for 10 minutes after that washed with DI water to eradicate the native SiO_2 layer [33]. As synthesized (50 mg) nanoparticle were dispersed in solution of cyclohexane (1 mL) and oleylamine (20 µL) to form ink type coating solution. Prepared pure CuS, CuO@CuS(1:0.5) and CuO@CuS(1:1) ink was coated on the n-Si substrate by drop cost method. The n-Si substrate was dried in room temperature about 1 hour further annealed at 220 °C for one hour under N_2 atmosphere after coating a desired layer. An adhesive silver paste was applied on both sides to make the better contact and dried at ambient temperature about 5 hours. Schematic diagram of diode fabrication was presented in Figure 1.

2.6. Material characterization methods

Structural analysis of synthesized CuS and CuO@CuS were performed by Philips PAN alytical Xpert pro powder X-ray diffractometer equipped with CuK_α radiation source of 1.54 Å. Raman spectra of the synthesized samples were recorded by Jobin Yvon HR 800 spectrometer with 532 nm laser sources. Morphology and elemental combination were analyzed using S-3400N Hitachi field emission scanning electron microscope (FESEM). The morphology of CuO@CuS (1:1) core/shell structure was recorded by JEOL-JEM transmission electron microscopy (TEM) (model: 2100-Japan) at the accelerating voltage of 200 kV with SEAD pattern. The current-voltage characteristics were performed by Keithley source analyzer (6517-B) and the dark and

photocurrent were measured with transferrable solar simulator (PEC-L01). The optimized white light with intensity of 100 mW/cm^2 was used for the diode parameter measurement.

3. Results and discussion

3.1 Structural & optical analyses

The XRD pattern obtained for pure CuO, CuO@ CuS (1:0.5) and CuO@CuS (1:1) are compared in Figure 2. Obtained XRD pattern of CuS nanoparticle (Figure 2 (a)) was well matched with standard hexagonal CuS structure (JCPDS card No: 00-001-1281) space group P63/mmc and cell parameters (a = 3.8020 b = 16.4300). CuO@CuS (1:0.5) and CuO@CuS (1:1) formation were agreed to usual hexagonal CuS and monoclinic CuO systems (JCPDS card no 00-041-0254; space group C2/c and a = 4.6850, b = 3.4230, and c = 5.1320 cell parameters). The broad and sharp reflection patterns were observed for CuS and CuO, respectively, which indicates the major size difference between core and shell particles [1, 34]. No impurities from the other phases incorporated in the specimen are observed.

The optical absorption spectra of CuS, core-shell CuO@ CuS (1:0.5) and CuO@CuS (1:1) specimens were recorded as displayed in Fig. S1 (see supporting data). The band gap values were determined through Kubelka-Munk theory and the plots are presented in Fig. S2(see supporting data). The E_g values for CuS, CuO@ CuS (1:0.5) & CuO@CuS (1:1) were noted ~ 2.07, 1.91 and 1.88 eV, respectively.

3.2. Raman analysis

The Raman spectrum of the CuS, core-shell CuO@ CuS (1:0.5) and CuO@CuS (1:1) nanoparticle were compared in Figure 3 (a-c). An intense peak observed around ~ 474 cm^{-1} and a tiny peak ~ 266 cm^{-1} in Figure 3(a) are assigned to characteristic vibrational modes present in covellite CuS and the strong peak at ~ 476 cm^{-1} confirm the formation of covalite CuS formation which represents S-S stretching vibration mode of S_2 ions at 4e sites [35]. This result is well matched with Adhikar et al. and Kundu et al. and aligned in periodic array atom was revealed

[36-38]. A tiny shoulder peak observed in the spectra at ~266 cm^{-1} is arising from the A_{1g} vibration bond of Cu-S [39]. Figure 3(b) shows the Raman spectra of core shell CuO@CuS (1:0.5) nanocomposite exhibits both the characteristic Raman vibrational modes of CuO and CuS respectively. These results are good agreement with XRD results. In this spectrum two shorten peaks at 295, 333 cm^{-1} are corresponding to A_g mode and B_g mode of CuO formation respectively [40]. Similarly, high intensity Raman characteristic peaks are observed for CuO@CuS(1:1) nanoparticle corresponding to CuS (Figure 3(c)), which explores that the high concentration of CuS particle over the surface of CuO of the core/shell formation. Characteristic peak at 473 cm^{-1} for both CuO@CuS (1:0.5) and CuO@CuS (1:1) samples, which is clearly red shifted when compared to bare CuS sample. The reason for the shifted peak may be raised at the junction of core-shell structure, because low ionic radii oxygen atoms replaced some of the high ionic radii sulphur site of CuS.

3.3. FESEM analysis

The surface morphology of the synthesized pure CuS (Figure 4), CuO@CuS (1:0.5) (Figure 5) and CuO@CuS (1:1) (Figure 6) was investigated by FE-SEM. In Figure 4 (a-c), CuS particles were appeared as sphere like morphology and particles agglomeration may be due to physisorption of individual particles. It is clearly found that the size of particles is ~20 nanometre. EDX and elemental imaging of synthesised CuS were presented in Figure 4 (d-g), which evident the presence of Cu and S elements. Figure 5 (a-c) clearly indicates the formation CuO@CuS (1:0.5) particles. CuS nanospheres were spreaded over the CuO crossed sheets as core/shell structure. Lesser amount of CuS was used to construct CuO@CuS core/shell; core particles which are easily recognisable in the micrographs. EDX and elemental imaging of synthesised CuO@CuS(1:0.5) core/shell were presented in Figure 5 (d-h), which revealed the percentage of Cu and S presence as 1:0.5 ratio and elemental mapping supports the above core/shell above results. FESEM micrographs of CuO@CuS (1:1) were presented in Figure

6(a-c). CuS nanospheres were fully occupying the surface of the CuO nano crossed sheets. EDX and elemental imaging of synthesised CuO@CuS (1:1) core/shell systems are presented in Figure 6 (d-h), which shows the percentage presence of Cu and S elements in (1:1) ratio. Remarkably, the plate like shapes was found because of CuO particles and CuS were randomly dispersed over plates as illustrated in Figure 5 and 6. The reason could be the incorporation of different concentration of CuS to CuO gives a plate like shapes of metal oxide and metal sulphide spheres, respectively.

3.4 HRTEM analysis

TEM analysis was done for as synthesised CuO@CuS (1:1) Core@shell particles to understand the core/shell formation in detail and captured pictures were shown in Figure 7(a-f). The micrographs Figure 7 (a-c) clearly indicate that ~100 nm CuO sheets were surrounded by CuS particles, this approved the core/shell system formation. Figure 7 (d-e) shows the HRTEM pictures of core@shell CuO@CuS. The crystal space distance was measured at 0.13 nm agreement with the CuO of (002) [41] and the adjacent inter-planar spacing (0.191 nm) were measured in agreement with the CuS plane of (110) [42]. Interplanar spacing results confirms that the core is CuO and shell is CuS particles. The SAED pattern of CuO@CuS (1:1) Core@shell is shown in Figure 7 (f) and confirms that the CuO@CuS nanoparticle appeared crystalline in nature.

3.5. I-V characterization of p-CuS/n-Si and p-CuO@CuS/n-Si diode

I-V curve of fabricated p-CuO@CuS/n-Si diodes with different level of CuS were shown in figure 8. The dark and photocurrent were measured in between the voltage range -3 and +3 V. The performance of the p-CuO@CuS/n-Si diode was examined by with and without light using portable solar simulator. From the Figure 8, the photocurrent seems to very high under light condition which shows the better rectifying behaviour of the fabricated diodes. The current

transport mechanism of p-CuO@CuS/n-Si diode was explained by the Thermionic Emission (TE) theory [43]:

$$I = I_0 \left[\exp\left(\frac{q(V-IR_s)}{nK_BT}\right) - 1\right] \quad (1)$$

where n is Ideality factor, K_B is Boltzmann constant, T is temperature in kelvin, R_s is series resistance, I_o is reverse saturation current and V is applied voltage. The reverse saturation current (I_o) calculated from the following equation [44].

$$I_o = AA^*T^2 \exp\left(-\frac{q\phi_B}{K_BT}\right) \quad (2)$$

here A is area of contact and A^* is the Richardson constant, ϕ_B is zero bias barrier height. The dark current and photo current were found to be varied from 1.21 $\times 10^{-5}$ to 0.15$\times 10^{-6}$ A and 1.09 $\times$ 10^{-4} to 0.14$\times 10^{-3}$ A with CuS level. The high photo current of the diode is reflecting the surface modification of CuS sphere over the CuO nano-rod which reduce the trapping of charge carriers by surface absorption of oxygen. The same trend observed in ZnO-TiO_2 core/shell-based photo detector reported by Shao et. Al. [45]. The reverse saturation current (I_o) was improved from 10^{-5} to 10^{-3} due to the flow of minority charge carriers. The ideality factor (n) was calculated from the slop and intercepts of semi logarithmic plot (Figure 9) using the following equation [46].

$$n = \frac{q}{k_BT}\frac{dV}{d(\ln J)} \quad (3)$$

The experimental values of n reduced from 11.49 to 2.94 with CuS level. For ideal diode, the n value should be unity (n=1). Here, the n value of p-CuO@CuS/n-Si diode is greater than one which suggest the non-ideal behaviour of the fabricated diodes. The non-ideal behaviour of the diodes is mostly due to in homogeneity in the surface state, native oxide layer, diffusion current [47, 48]. The decrease in ideality factor will enable the interface state to reduce the recombination of charge carriers in the junction [49]. The lower value of n under light condition for p-CuO@CuS (1:1)/n-Si evident that the decrease in recombination rate of electron hole pair

at the junction, the similar result is reported by Mohan raj et al. [50]. The barrier height (Φ_B) for the fabricated device can be calculated by the following equation [51].

$$\Phi_B = \frac{K_B T}{q} \ln\left(\frac{AA^* T^2}{I_0}\right) \quad (4)$$

where A^* is Richardson constant. The estimated value of barrier height was summarized in Table 1 which is varied between 0.631 to 0.802 eV. Under light condition, the obtained barrier height values are smaller than under dark condition exhibiting the more charge carrier which penetrates the higher barrier height to achieve conductivity [52]. The photosensitivity (P_S), responsivity (R), quantum efficiency (QE), specific directivity (D^*) are the vital parameters to investigate the photodiode/detector performance of the p-CuO@CuS/n-Si device. The photosensitivity (P_S) of the diode can be calculated from the following equation [53].

$$P_s\ (\%) = \frac{I_{Ph} - I_D}{I_D} \times 100 \quad (5)$$

here I_{ph} and I_d are related to current under photo & dark environments. The photosensitivity of diode improved linearly with applied potential as shown in Figure 10. The CuO@CuS(1:1)/n-Si diode reached a highest photosensitivity of 7.76×10^4 % at 3 V. The responsivity (R) was obtained from [54]:

$$R = \frac{I_{Ph}}{P \times S} \quad (6)$$

The estimated values of P_s, R, QE and D* for different systems are listed in Table 1. From Table 1, the responsivity was enhanced from 12. 82 to 798.61 mA/W while increasing CuS level. The maximum responsivity (R = 798.61 mA/W) is achieved for p-CuO@CuS(1:1)/n-Si diode which is 65 times higher than that of p-CuS/n-Si. Hence, the addition of Cu ions can effectively increase Ps of the p-CuS/n-Si diode. Resulting implies that the p-CuO@CuS (1:1)-n/Si is more adoptable for optoelectronic application. The R values of the currently developed p-CuO@CuS(1:1)/n-Si diode is higher than previously reported values for CuO or CuS core-shell based photodetectors like Wang et al. reported the nanostructured p-CuO/n-ZnO photodetector with responsivity ~ 0.040A/W at 1 V and 0.123 A/W at 2V [55],

Sahatiya et al. reported the MoS_2(n)–CuO(p) flexible diode with responsivity ~ 42 mA/W [17], Shin et al. developed the p-CuO/n-$Cu_{1-x}In_xO$ core/shell UV photodetector with responsivity ~ 0.045 A/W [18], Xu et al. p- CuS- ZnS/n- ZnO photodetectors with responsivity ~ 12 mA W^{-1} at 300 nm [23], Zhnag et al. developed the n- SrTiO3 (n- STO) and p- CuS- ZnS (p- CZS) photodetectors with highest responsivity ~ 5.4 μA W^{-1} (at 390 nm), detectivity ~ 1.6×10^9 Jones [24], etc. These reports signify the current developed photodetectors is a good one as p-n junction.

The quantum efficiency is an additional factor used to analyse the performance of the device. The QE can be defined as the fraction of incident photons which contribute to the external photocurrent [56-58].

$$EQE = \frac{Rhc}{q\lambda} \qquad (7)$$

here h is plank constant, c is light speed, R is responsivity, q is electron charge and λ is used light wavelength. The variations of QE with forward voltage and CuS levels are shown in Figure 10. The p-CuO@CuS (1:1)-n/Si diode recorded a maximum QE of 309.66% for 4 V. The increased lifetime of the photocarrier, superior creation of electron-hole and lower recombination are the reason for obtained maximum QE. The maximum outcome of quantum efficiency ensures the photo conducing nature of the present device. The specific detectivity is a key factor which is mostly influenced by dark current and it can be calculated from the following equation [59-62].

$$D^* = \frac{R\,S^{1/2}}{(2qI_D)^{1/2}} \qquad (8)$$

The optimum signal detecting nature of detector is interrupted by noise produced in photodiode which is due to the thermal motion of charge carriers and electron hole pair recombination [63, 64]. The detectivity is relatively low for the p-CuS/n-Si diode due to the large dark current and generation of weak photocurrent. The higher value of detectivity (D*= 8.19×10^{11} Jones) was noticed for p-CuO@CuS(1:1)/n-Si based diode which indicates that the lesser noise level of the device. The detectivity of the currently developed photodetector is better as well as comparable to earlier reported ones

based on CuO and CuS core-shell photodetectors such as Zhang et al. reported p-CuO/n-MoS_2 with detectivity ~ 3.27×10^8 Jones [14], and Zhang et al. developed the n- SrTiO3 (n- STO) and p- CuS- ZnS (p- CZS) photodetectors with detectivity ~ 1.6×10^9 Jones [24]. Possible band diagram of p-CuO@CuS/n-Si diode is presented in the Figure 11. For more and better comparison, we have listed a number of reported photodetectors related values for developed photodetectors based on different type of materials in Table 2 [12, 65-67].

4. Conclusion

In summary the CuS and core/shell CuO/CuS heterostructure were synthesized through chemical co-precipitation method. The XRD patterns were conforms the phase purity of samples which confirmed by the Raman analysis. SEM image confirms Sphere and Core/shell heterostructure of Pure CuS and CuO@CuS. The photodiodes are fabricated using satellite samples and diode behaviour are studied under dark and light condition. The highest photosensitivity (P_s) of 7.76×10^4 %, photoresponsivity (R) of 798.61mA/W, maximum detectivity of D*= 8.19×10^{11} Jones and EQE of 309.66 % were obtained for p-CuO@CuS (1:1)/n-Si diode. We observed the p-CuO@CuS (1:1)/n-Si diode will be highly suitable for photodetectors and can also be used in UV region.

The authors declares that:

- **The manuscript has not been previously published,**
- **is not currently submitted for review to any other journal,**
- **and will not be submitted elsewhere before a decision is made by this journal**

Conflict of interest

Authors declares that there is no conflict of interest in current article

Declaration of conflict of interest

Authors have no conflict to declare in current work

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Biography

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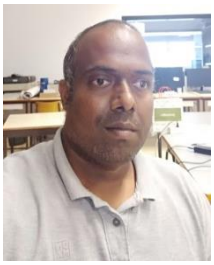

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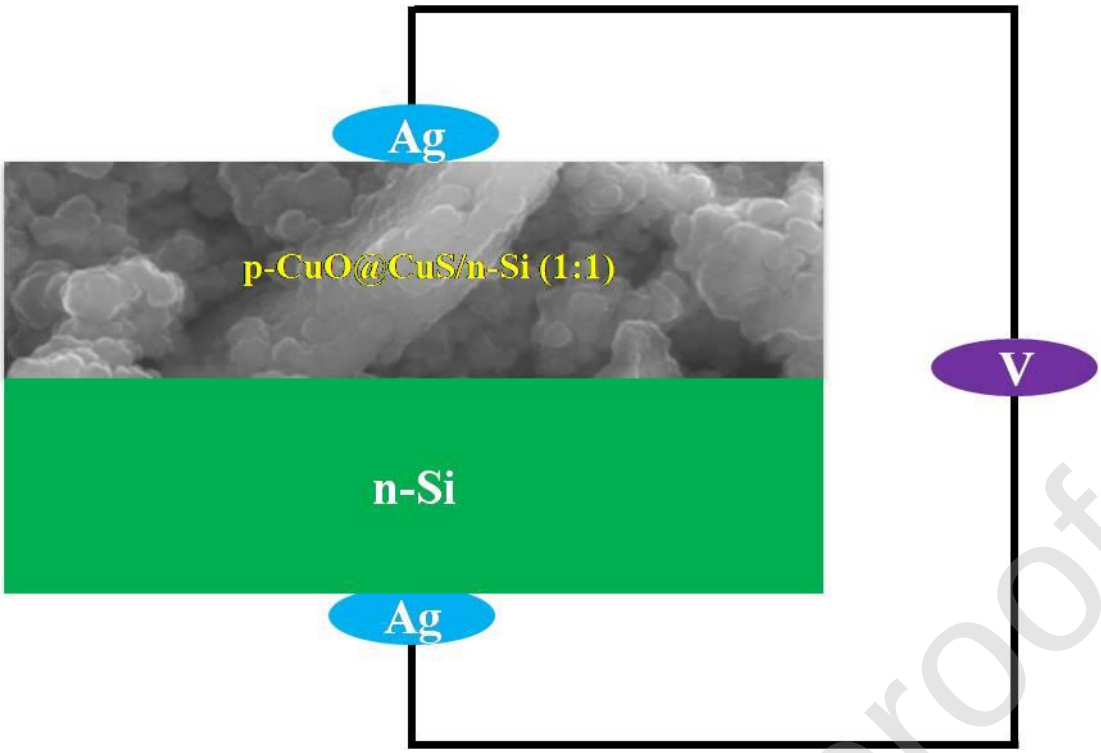

Figure 1 : Schematic diagram of p-CuO@CuS(1:1)/n-Sidiode.

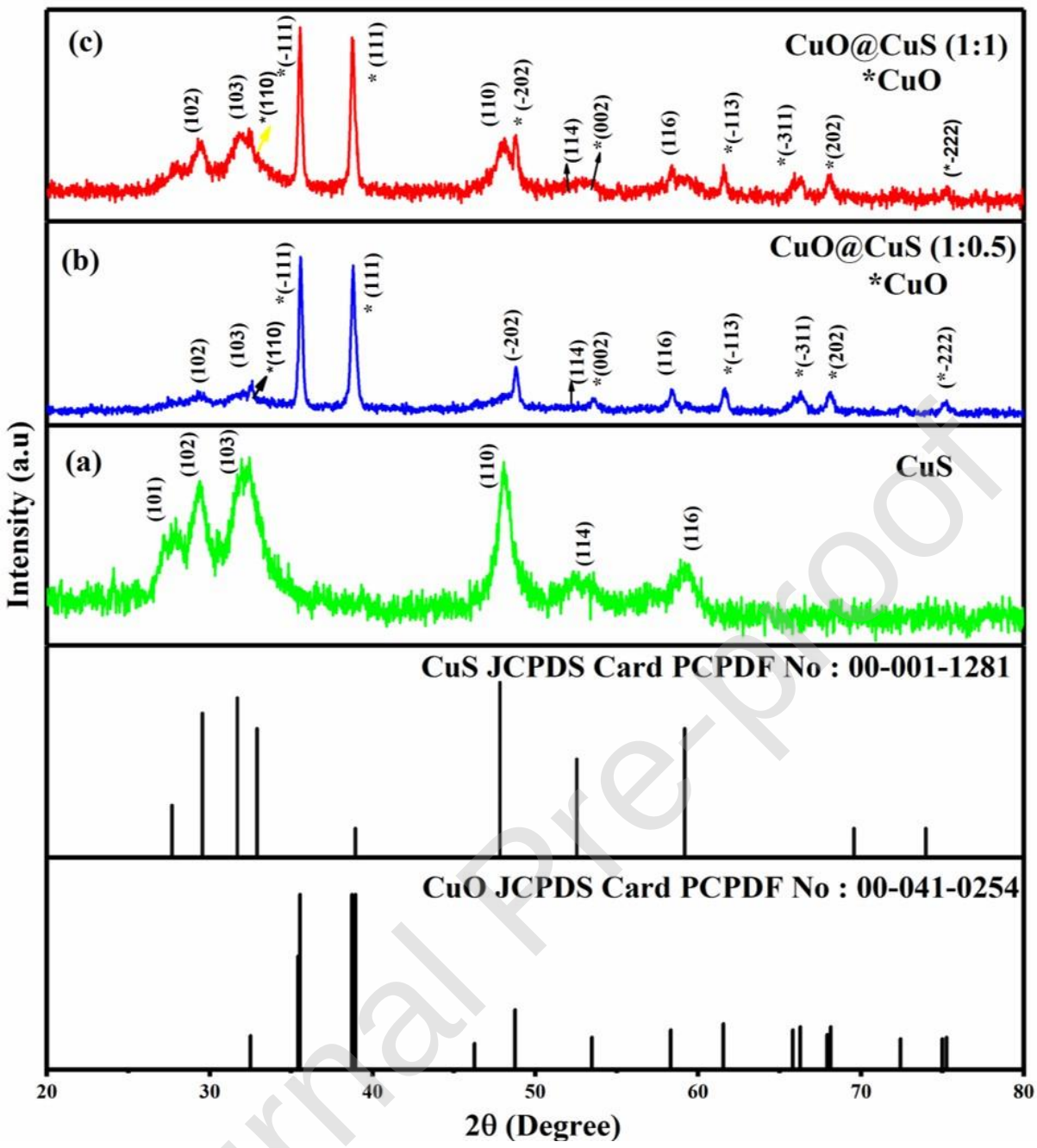

Figure 2 : Comparative XRD graph of for (a) CuS,(b)CuO@CuS (1:0.5),(c) CuO@CuS(1:1)

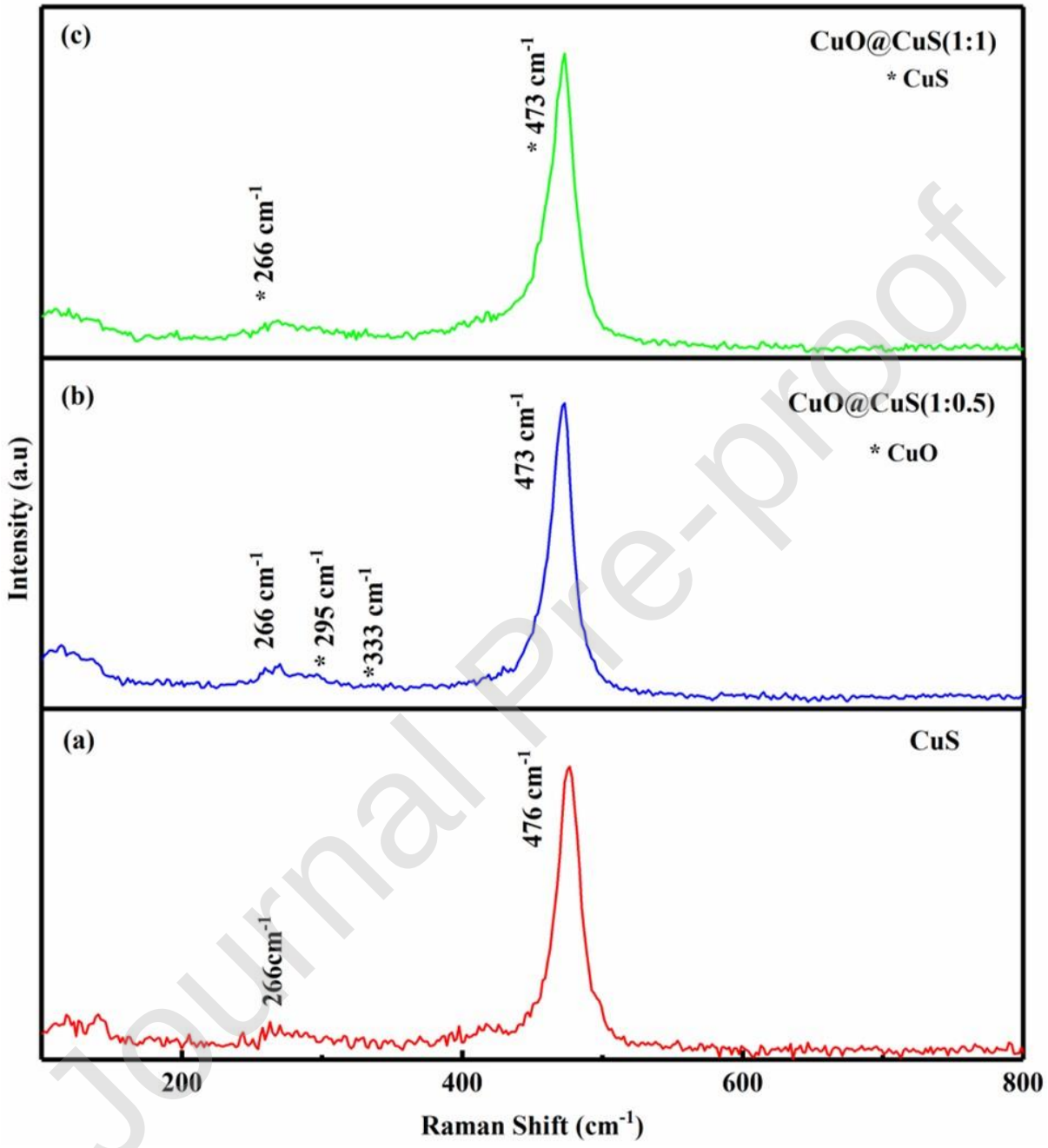

Figure 3: Comparative graph of Raman for (a) CuS, (b) CuO@CuS (1:0.5), (c) CuO@CuS(1:1)

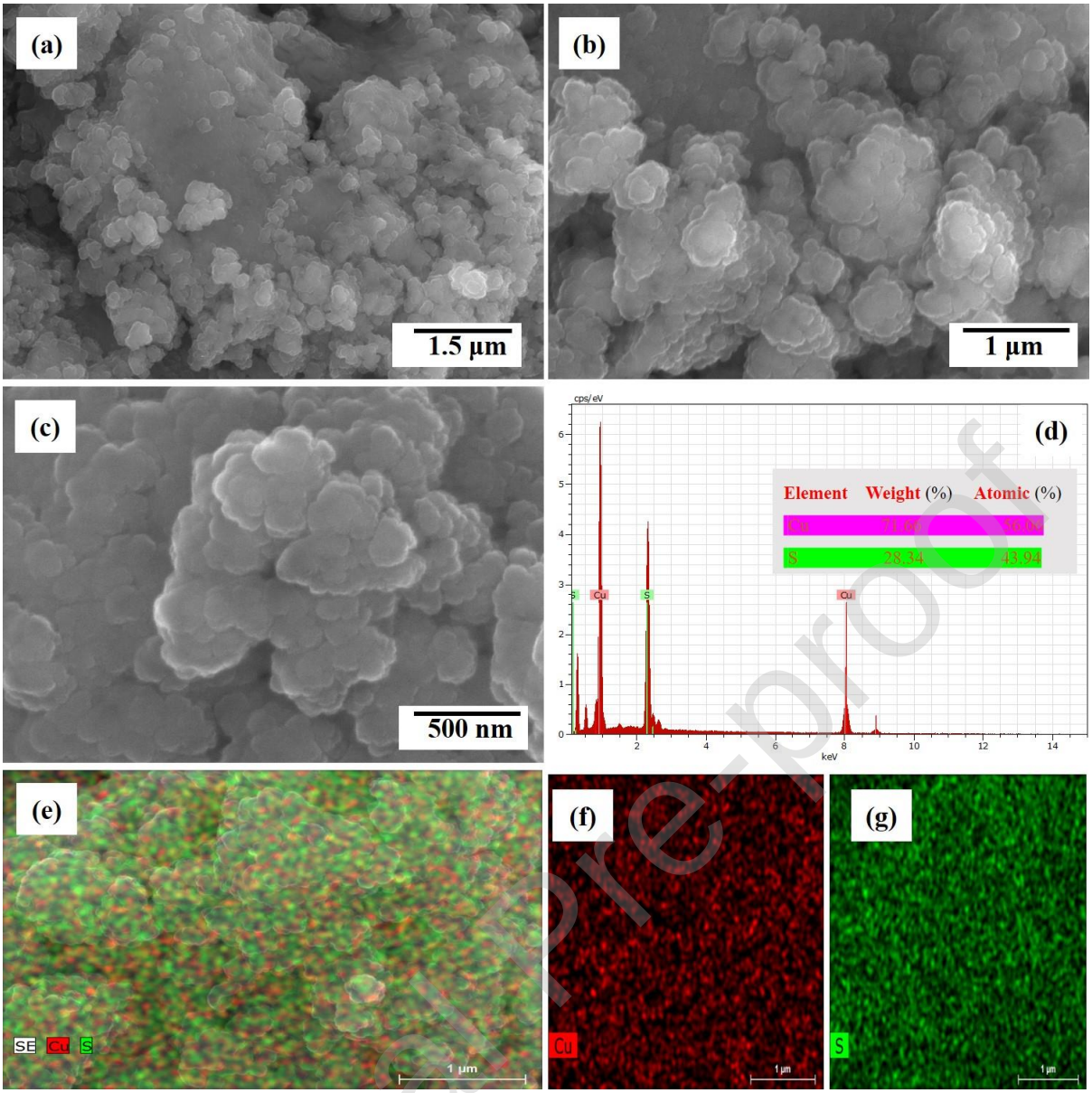

Figure 4: FESEM images of CuS (a-c),EDX spectra (d) and Elemental mapping (e-g).

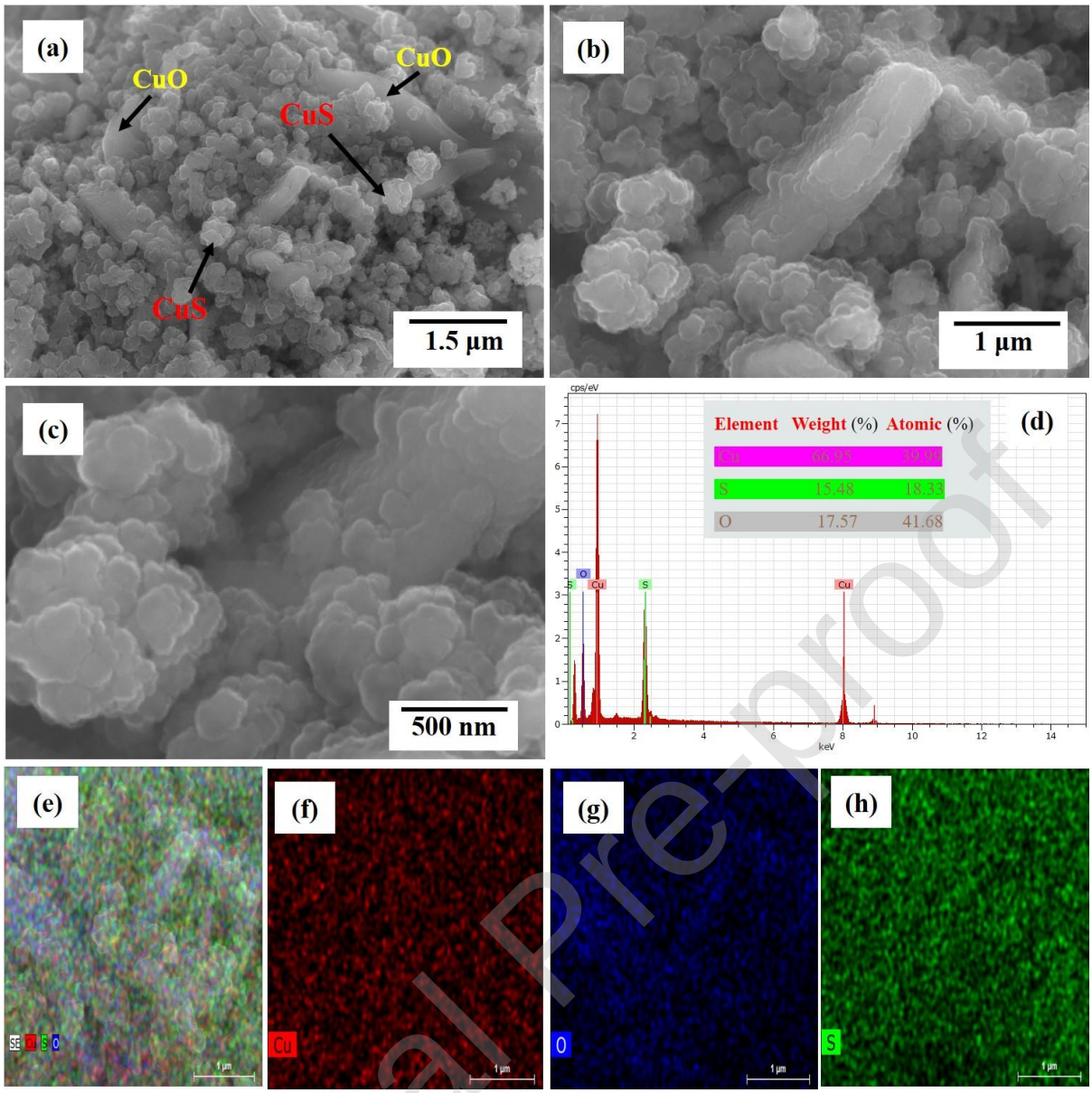

Figure 5. FESEM images of CuO/CuS(1:0.5) (a-c),EDX spectra (d) and Elemental mapping (e-h).

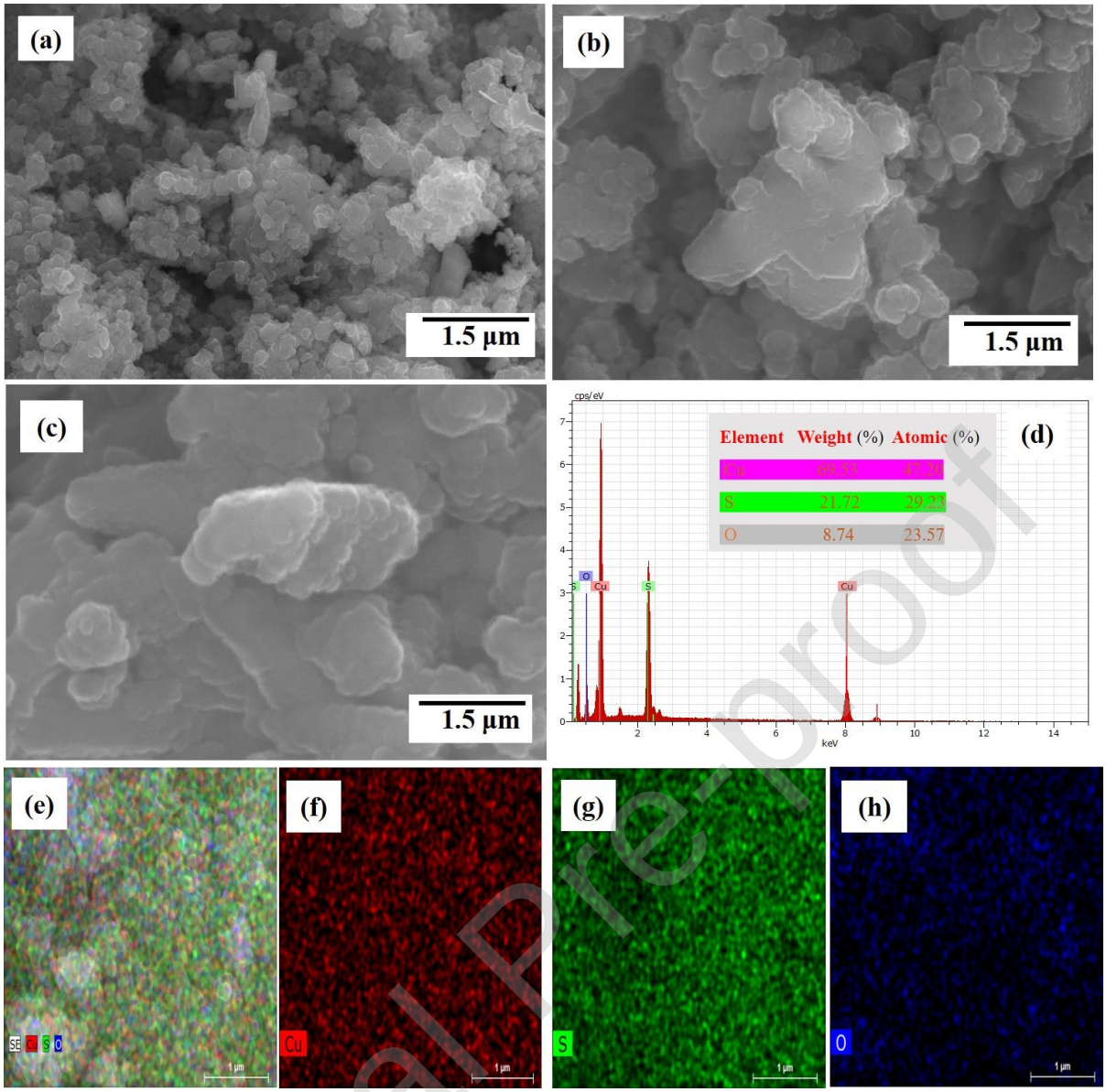

Figure 6: FESEM images of CuO/CuS(1:1) (a-c),EDX spectra (d) and Elemental mapping (e-h).

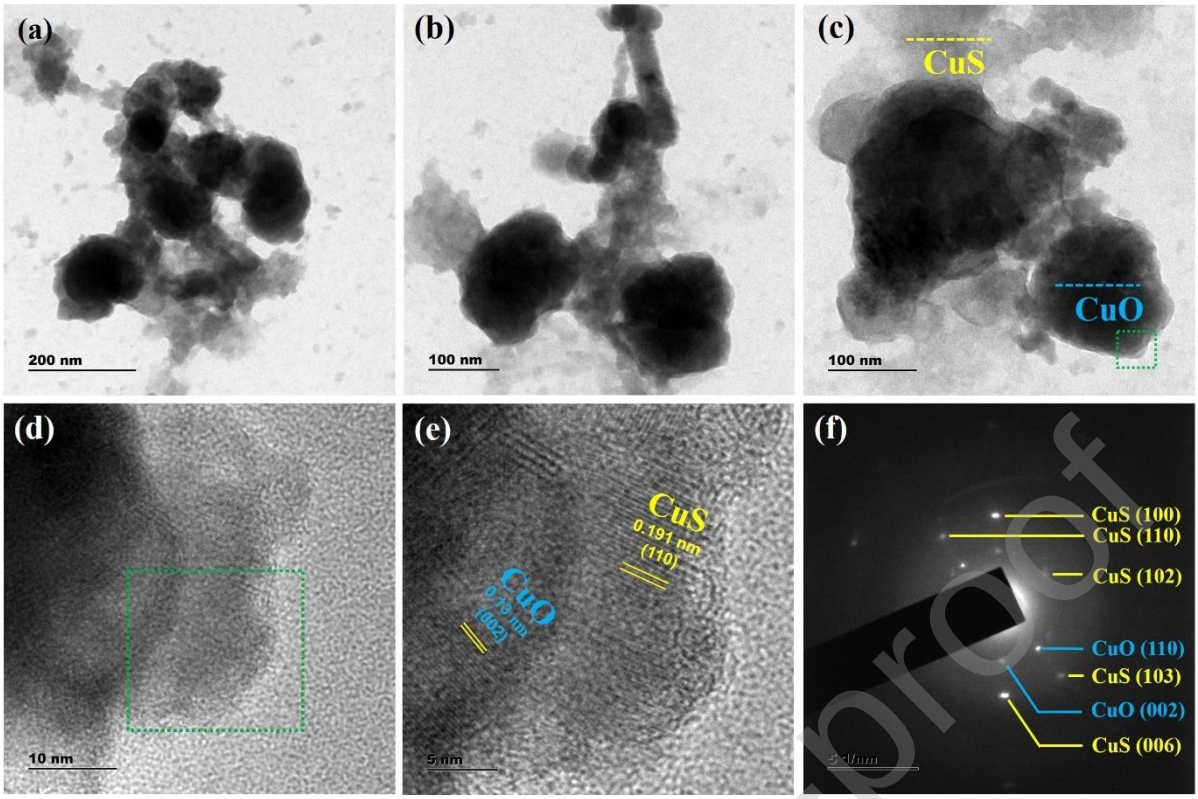

Figure 7: HRTEM images of CuO/CuS(1:1) (a-c) lattice image (d-e) and SAED pattern (f).

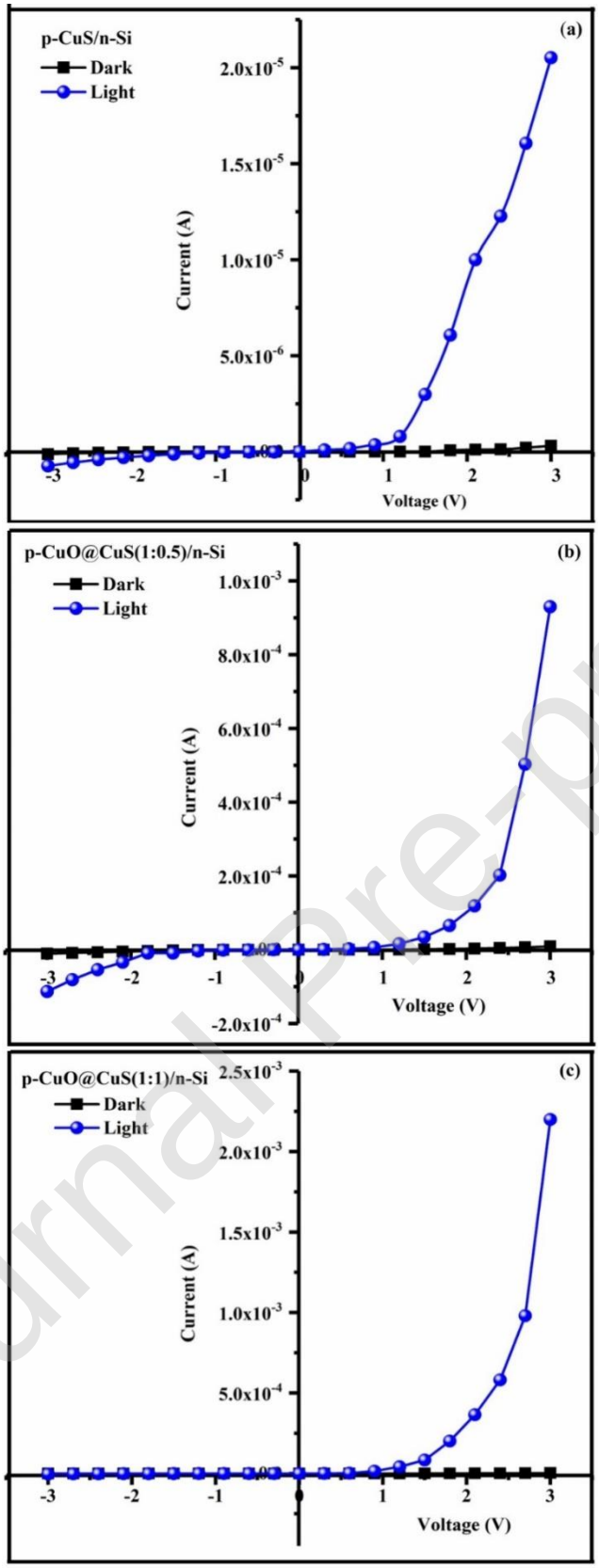

Figure 8 : I–V characteristics of (a) p-CuS/n-Si,(b) p-CuO@CuS/n-Si (1:0.5), (c) p-CuO@CuS/n-Si (1:1).

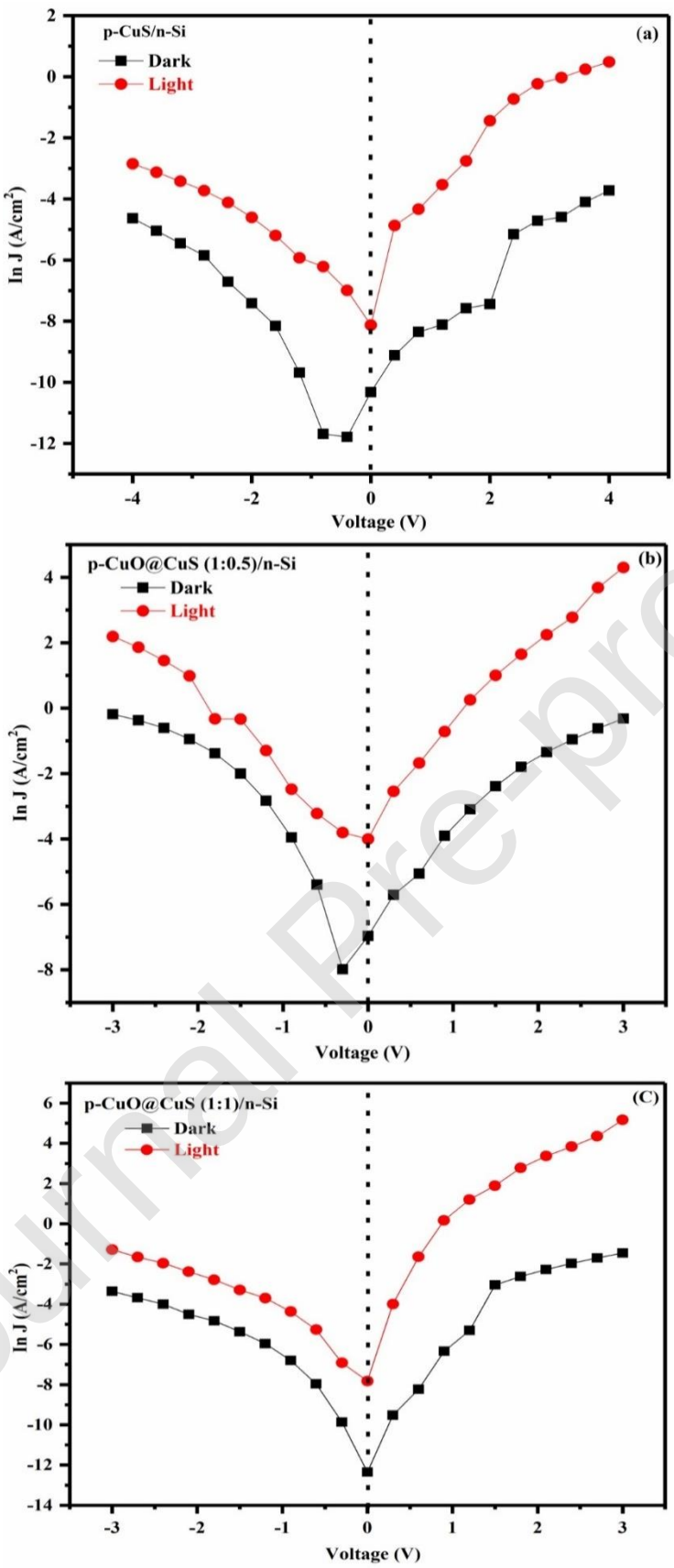

Figure 9: Semi-logarithmic plot of ln (J) vsV of (a) p-CuS/n-Si,(b) p-CuO@CuS/n-Si (1:0.5),(c) p-CuO@CuS/n-Si (1:1)

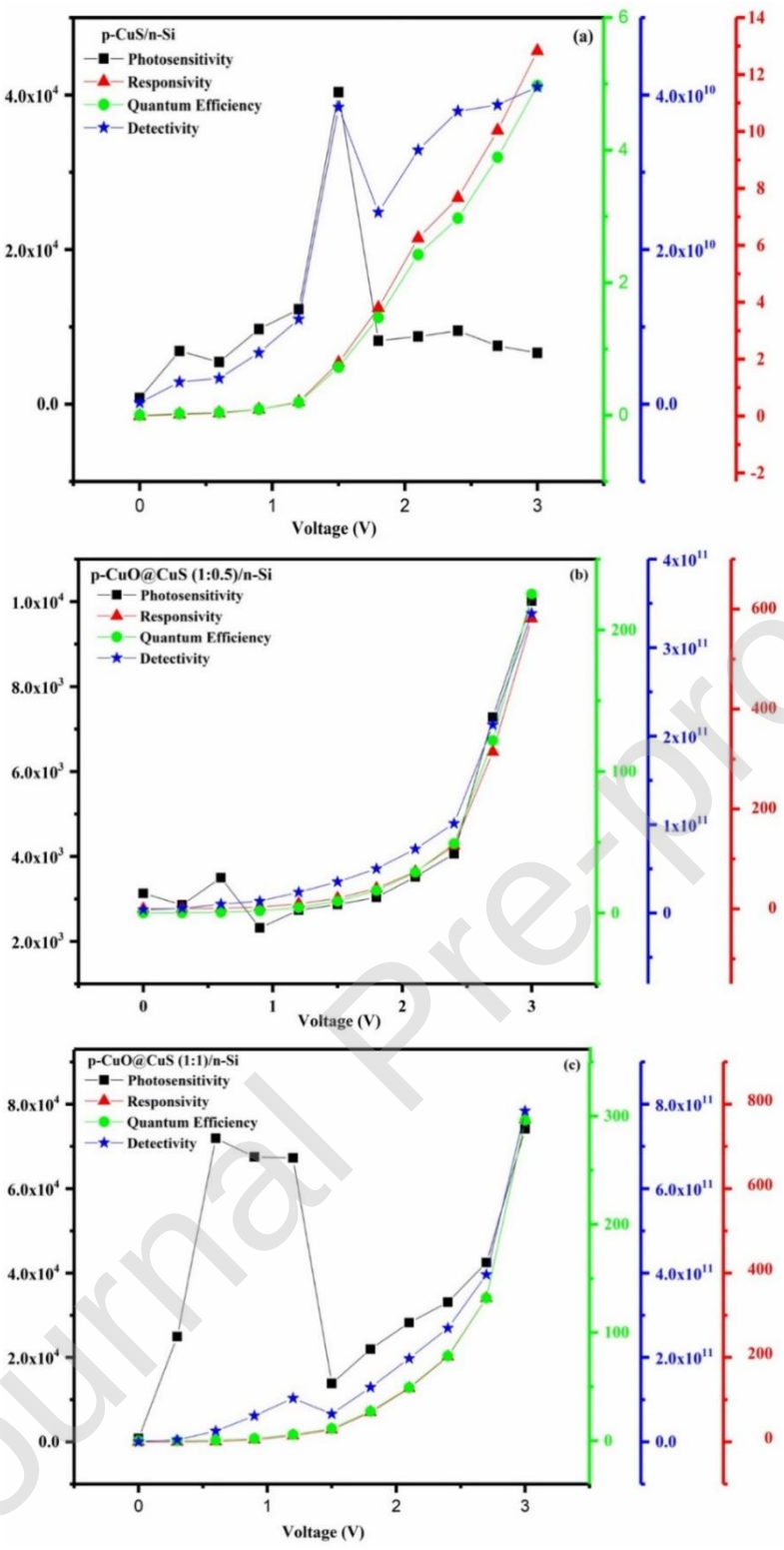

Figure10:Comparative plotof Ideality factor (n), Barrier height (Φ_B), Photosensitivity (P_S), Photoresponsivity (R), Quantum efficiency (QE)%, Specific detectivity (D*) vs Voltage graph of (a) p-CuS/n-Si,(b) p-CuO@CuS/n-Si (1:0.5),(c) p-CuO@CuS/n-Si (1:1)

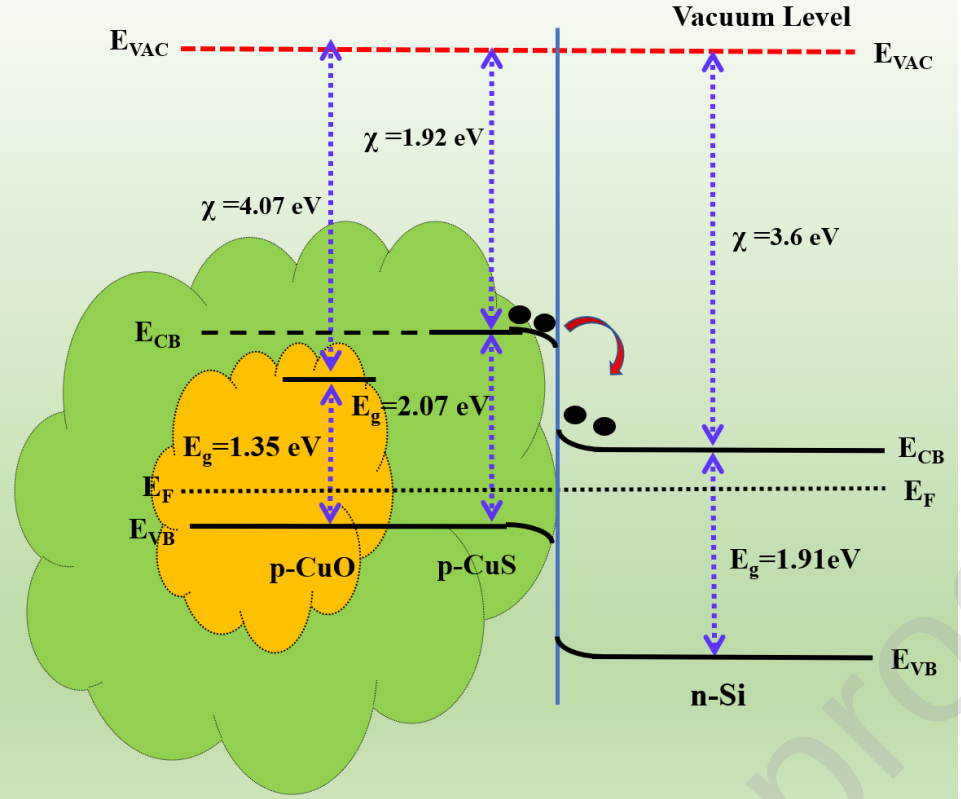

Figure 11: Band diagram of p-CuO@CuS/n-Si diode

Table 1: Photodiode parameter of (a) p-CuS/n-Si,(b) p-CuO@CuS/n-Si (1:0.5),(c) p-CuO@CuS/n-Si (1:1) based diode such as Idealityfactor (n), Barrier height (Φ_B), Photosensitivity (P_S), Photoresponsivity (R),External Quantum efficiency (EQE)%, Specific detectivity (D*).

Diode Composition	Ideality factor n		Barrier height Φ_B (eV)		I_o (A)		Photo Sensitivity P_S (%)	Photo Responsivity R (mA/W)	Quantum Efficiency EQE (%)	Specific Detectivity D^* (Jones)
	Dark	Light	Dark	Light	Dark	Light				
CuO	9.57	11.49	0.749	0.692	1.21×10^{-5}	1.09×10^{-4}	6.63×10^{3}	12.82	4.97	4.1×10^{10}
CuO/CuS (1:0.5)	8.84	7.18	0.664	0.631	3.48×10^{-4}	1.12×10^{-3}	1.00×10^{4}	581.23	225.37	3.39×10^{11}
CuO/CuS (1:1)	4.10	2.94	0.802	0.744	0.15×10^{-4}	0.14×10^{-3}	7.76×10^{4}	798.61	309.66	8.19×10^{11}

Table 2:Comparison of the performance of various photodetectors with current one CuO@CuS.

Photodetectors	Photosensitivity P_s (%)	Photoresponsivity R	External quantum efficiency EQE (%)	Detectivity (Jones)	Target Wavelength	Reference
Ge/CdS	18000	--	--	2.5×10^{10}	white light (1.9 mW cm^{-2})	10
p-CuO/n-MoS_2	--	---	--	3.27×10^{8} Jones	532 nm Laser Illumination	12
MoS_2(n)–CuO(p)	--	42 mA/W	--	--	554 and 780 nm	15
p-CuS-ZnS/n-ZnO		12 mA/W			300 nm	21
p-CuS-ZnS (p-CZS)	--	5.4 μA W^{-1}	--	1.6×10^{9} Jones	390 nm	22
p-CuO/n-ZnO	--	0.040 to 0.123 A/W	--	--	365 nm	48
MoS_2/Graphene	--	12.3 mA/W	--	1.8×10^{10}	532 nm Laser Ilumination	58
ZnSe/ZnO	--	6.7 mA/W	--	4.1×10^{13}	365 nm	59
InS	58.58	0.598 mA/W		10.46×10^{7}	Visible light (100 mW/cm^2)	60
p-CuO@CuS/n-Si (1:1)	7.76×10^{4}	798.61mA/W	309.66	8.19×10^{11}	Visible light (100 mW/cm^2)	Current work