

## Nickel sulphide-carbon composite hole transporting material for (CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>) planar heterojunction perovskite solar cell

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### Abstract

The present work reports about the low-cost inorganic nickel sulphide-carbon composite synthesized using the simple chemical method and to be used as hybrid hole extraction and as a counter electrode material for perovskite (CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>)-based solar cells (PSCs). The structural analysis confirms the existence of nickel sulphide (NiS) crystalline phase composed of small-sized crystallites. The optimal bandgap values of the prepared perovskite (1.51 eV) and NiS (3.71 eV) materials found to be favorable in achieving the active absorbing and hole extraction properties in PSCs. The surface morphology of the nickel sulphide materials is found to be highly dependent on the NiS-carbon composition. The current density-voltage (J-V) results of the fabricated perovskite solar cells with nickel sulphide-carbon composite hole transporting layer (HTL) suggests that incorporation of commercial carbon paste into the nickel sulphide nanoparticles tends to promote the charge carrier transporting ability and resulted in yielding high power conversion efficiency (PCE) of 5.20%, when compared to that of the bare NiS (1.87%). The results show that this nickel sulphide-carbon composite can serve as an efficient dual role as an HTL to transport holes and as a conductive counter electrode for the planar heterojunction PSCs with the structure FTO/compact-TiO<sub>2</sub>/porous-TiO<sub>2</sub>/perovskite/NiS-carbon. So, nickel sulphide-carbon composite can be considered as an efficient replacement for the other unstable HTMs and high-cost metal counter electrodes used in PSCs.

### Keywords

Nickel sulphide; Nickel sulphide-carbon composite; Hole extraction layer; Doctor blade method.

## Introduction

Perovskite-based solar cells (PSCs) in recent years have attracted much attention because of the outstanding light harvesting nature of the perovskite material and high efficiency achieved so far in photovoltaic technology (PV) [1]. Even though perovskites can be easily synthesized using low-cost solution process methods and are capable of resulting in high-performance devices there are stability issues associated with it. In perovskite solar cells one of the reasons is the instability of the organic hole transporting layer (HTL) or the other adverse effect of the organic HTL. So, it is necessary to develop an inorganic HTL layer which has good energy level compatibility with the perovskite and exhibits good stability [2]. Copper and nickel-based hole transporting materials (HTMs) have been found to exhibit good hole extraction property and have been identified suitable for hole extraction in PSCs. These materials exhibit good optical transparency, prevents electron leakage and has appropriate energy levels which make them suitable to be used as hole transport layers in perovskite solar cells [3]. Also, they have a wide band gap and can act as a p-type transporting layer [4] and as an electron blocking layer suppressing charge recombination and enhancing the hole extraction as the performance of the solid-state PSC devices mainly depends on the charge transport [5]. Among all the inorganic HTMs used in PSCs, nickel-based HTMs have the favorable deep-lying HOMO (valence band edge value) with work function from 5eV – 5.6eV [6]. It has been found that the highly transparent NiS used as a counter electrode in DSSCs helps in achieving a good photovoltaic performance in DSSCs [7]. NiS exhibits good stability and low charge transfer resistance properties, is flexible, has low sheet resistance, and superior corrosion resistance [8, 9]. Hence in the present study, an attempt has been made to develop device quality NiS and NiS-carbon composite layers to be used as hole transport layers in perovskite solar cells. Perovskite solar cells using methylammonium lead iodide as the absorber layer and NiS and NiS-carbon composite as hole transport layer have been fabricated and their characteristics have been studied.

## Experimental Procedure

### (i) Synthesis of NiS and NiS-carbon composites

Equimolar ratios of nickel nitrate hexahydrate ( $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ) and thiourea ( $\text{CH}_4\text{N}_2\text{S}$ ) were taken as precursor solutions. 0.2 M (1.827 g) of  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and 0.2 M (0.7612 g) of  $\text{CH}_4\text{N}_2\text{S}$  was dissolved in 50 mL of double distilled water and the mixture was sonicated for 1 hour. The obtained deep green solution turned into black color after some time on adding dropwise 0.1 M of NaOH solution. The obtained black precipitate was again sonicated for 1

hour and was washed with double distilled water and twice with ethanol so as to remove sodium ions. Then the filtered precipitate was dried at 80 °C for 24 hours and was annealed at 300 °C for 30 min which resulted in the formation of NiS. Beyond 300 °C, nickel oxide phase starts to evolve.[10] [11]. For the preparation of NiS-carbon composites, the prepared NiS was taken and weighed (90 %, 80 %, and 70 wt %) and was mixed with 10 %, 20 % and 30 wt % of commercial carbon paste respectively and was mixed well in an agate mortar. Further, the well-mixed NiS-carbon composite pastes were annealed at 300 °C for 30 min. The final black NiS-carbon composite flakes obtained were used as a hole transporting layer in the PSCs. 3M of methylammonium was dissolved in 1 ml dimethylformamide and 1M of lead iodide was added into the methylammonium solution and the solution was stirred overnight at 80°C and this resulted in the formation of methylammonium lead iodide based perovskite solution.

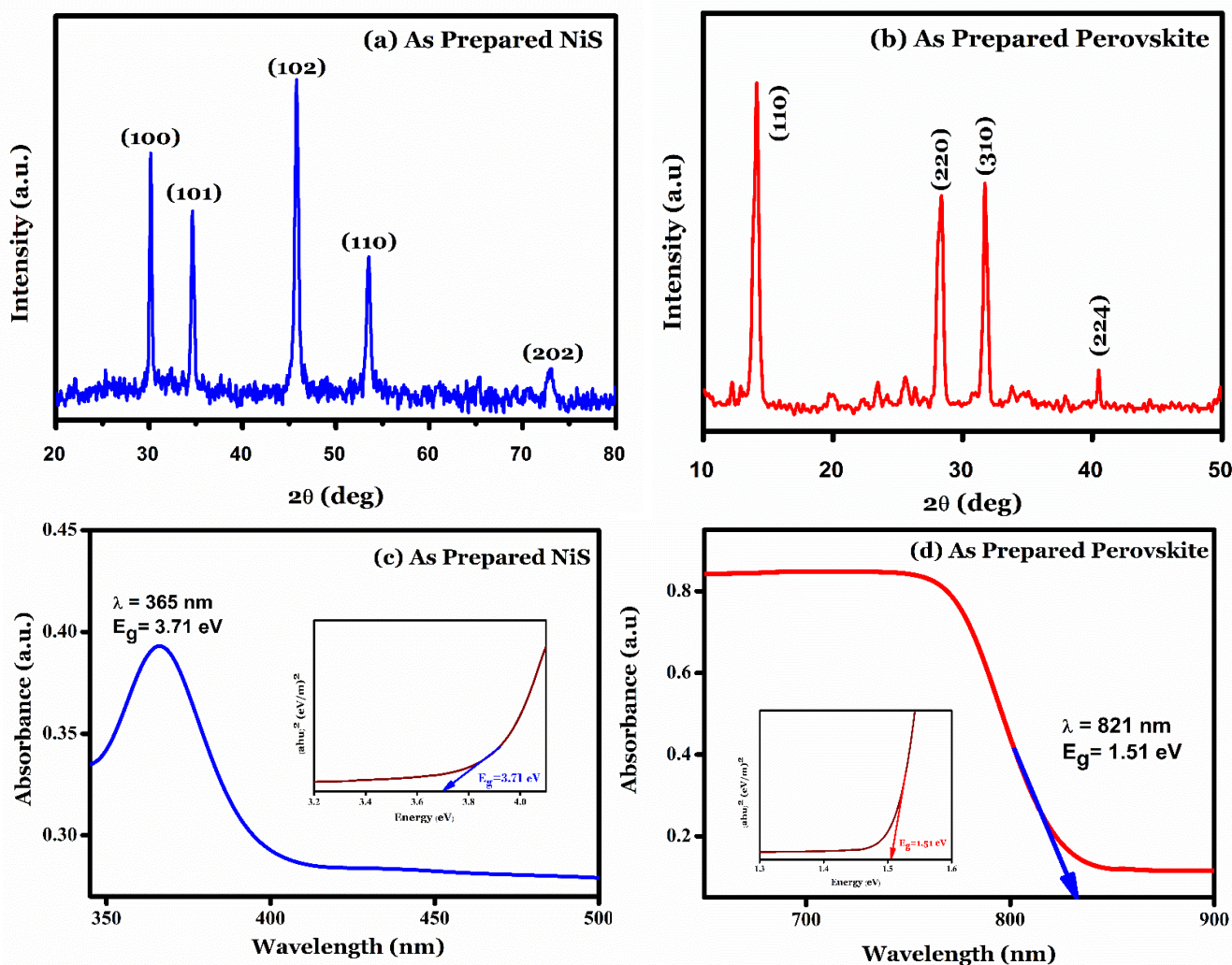
## **(ii) Fabrication of perovskite solar cell**

Perovskite solar cells have been constructed using the synthesized perovskite and the synthesized NiS and NiS-carbon composites. The structures of the fabricated solar cells are of the form FTO/compact-TiO<sub>2</sub>/porous-TiO<sub>2</sub>/perovskite/NiS/Cr/Pt-coated FTO counter electrode and FTO/compact-TiO<sub>2</sub>/porous-TiO<sub>2</sub>/perovskite/NiS-carbon composite. The compact-TiO<sub>2</sub> layer was coated using spray method. The porous-TiO<sub>2</sub> and the active perovskite layers were coated using spin coating method at 3000 rpm for 20s and 1500 rpm for 30s respectively. NiS and NiS-carbon HTM layers were coated using doctor blade method. The J-V characteristics of the fabricated devices were measured under (Newport, solar simulator) simulated AM 1.5G solar irradiation at 100 mW/cm<sup>2</sup> using Keithley 2400 source meter.

## **Results and Discussion**

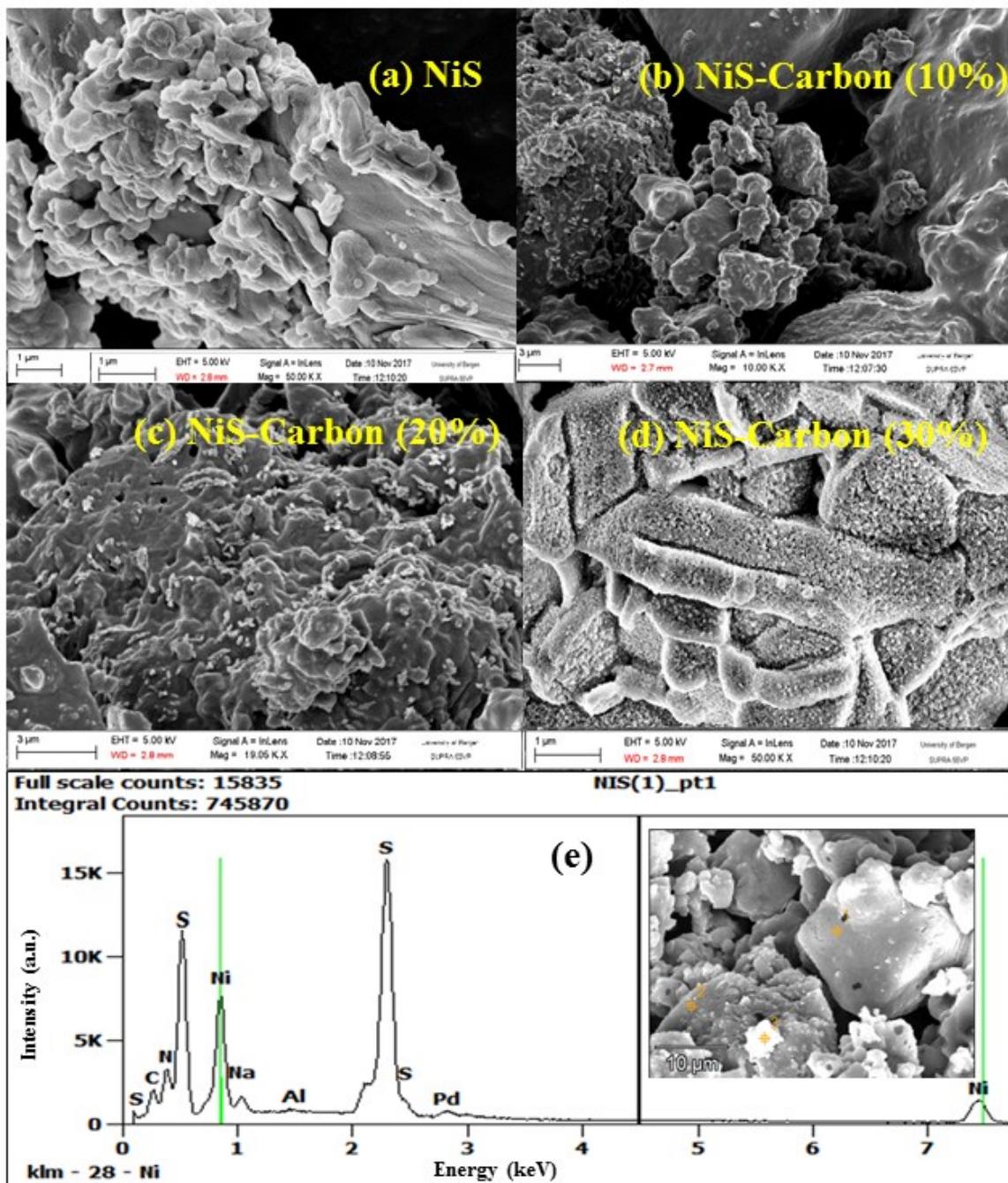
The crystalline structure and the phase purity of the NiS were analyzed using X-ray diffraction (XRD) method. Fig. 1 (a) is the X-ray diffraction pattern of NiS and it exhibits all the major reflection peaks of pure NiS and the peaks correspond to (100), (101), (102), (110) and (201) planes and are in agreement with the standard JCPDS Card No. 12-0041 [10]. The apparent broadening of peaks confirms that the prepared material is of crystalline nature and is composed of small size crystallites. Fig. 1 (c) represents the optical absorbance spectra of NiS and the bandgap energy has been found to be of 3.71 eV from the Tauc's plot (Fig. 1c inset) and the band gap value is in agreement with the previously reported work [12]. The diffraction pattern of the synthesized methylammonium lead iodide perovskite is shown in figure 1 b and the peaks (110), (220) (310) and (224) correspond to the tetragonal phase of perovskite. The band gap energy has been determined using the absorbance spectra shown in figure 1d and by

plotting the Tauc's plot (inset) and is found to be 1.51eV which matches well with the reported work [13].



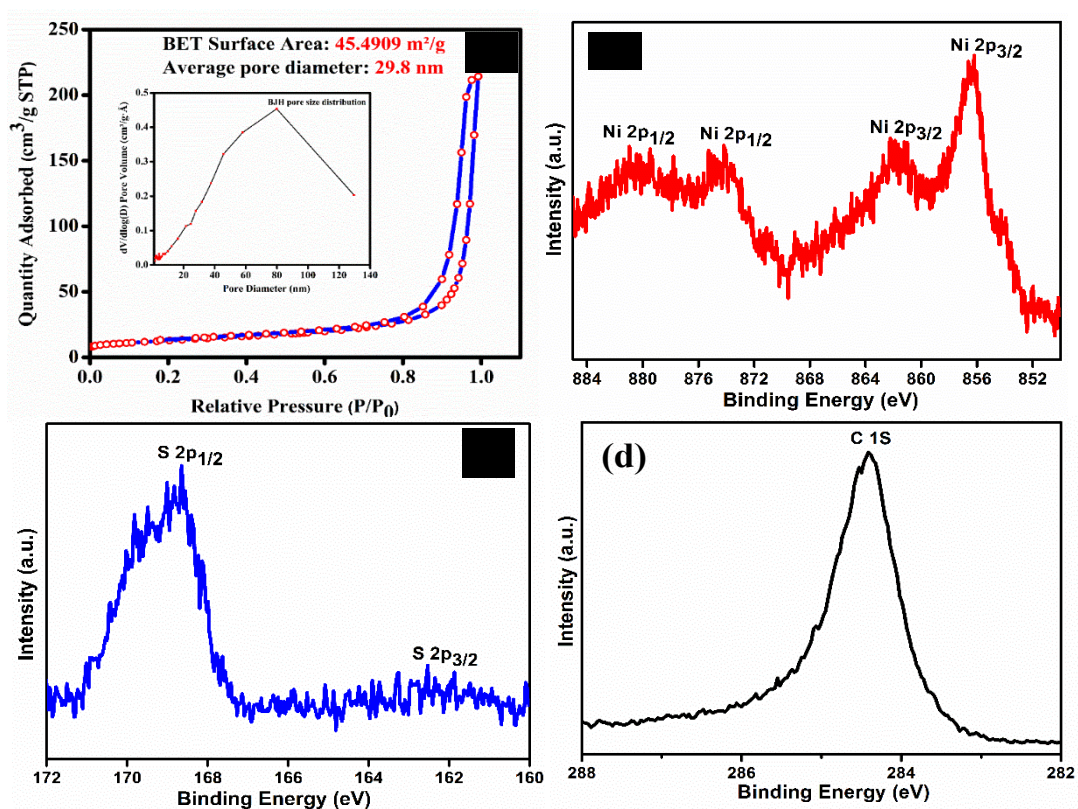
**Fig. 1 (a & b) XRD patterns and (c & d) UV-Visible spectra with Tauc's plot (inset) for the as-prepared NiS and perovskite.**

The surface morphology of the prepared NiS and all the NiS-carbon composites have been studied using SEM. The scanning electron microscope images are shown in figure 2, the image of NiS reveals that the material is made of agglomerated particles and similar results have been reported Nisari et. al., [12]. The surface morphology of the NiS-carbon composite shows that the surface is of porous nature. It is also observed that increase in carbon in NiS increases the porous nature of the surface and resulted in a reduction of agglomeration. The chemical constituents present in the synthesized NiS has been studied using EDS analysis and it has been found that both Ni and S are present.



**Fig. 2 (a-d) SEM images of the prepared NiS and with different NiS-carbon composites (e) shows the elemental composition of the prepared NiS (inset shows the region EDS spectrum was measured)**

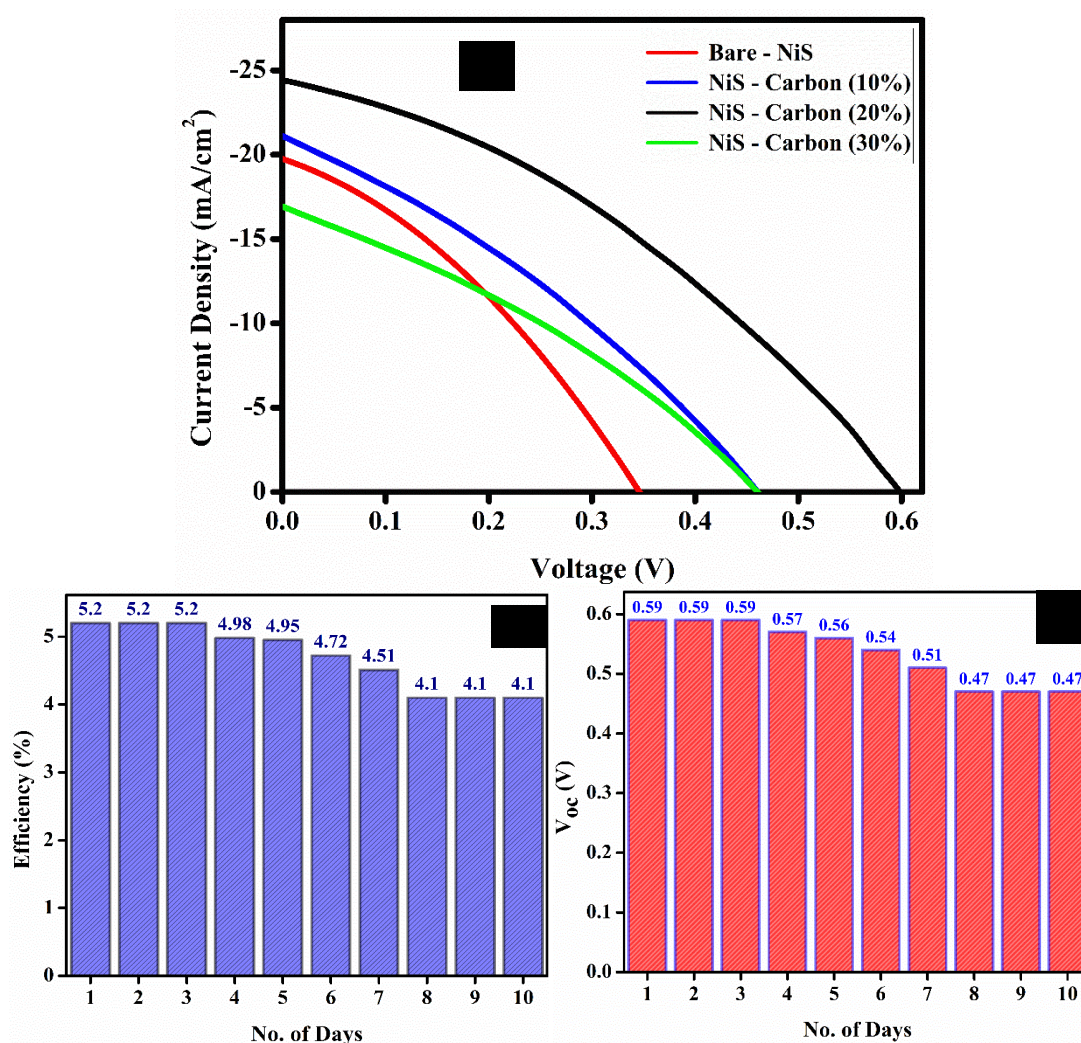
Further, Brunauer–Emmett–Teller (BET)  $N_2$  adsorption-desorption isotherms are shown in Fig. 3a for the NiS having 20% carbon composition. The isotherms exhibit type IV, according to IUPAC classification. The adsorption and desorption branch at the relative pressure between 0.5-1 indicates the mesoporous nature of the prepared material [14]. Surface area was found to be  $45.5 \text{ m}^2/\text{g}$ . From BJH analysis the average pore size is calculated to be 79 nm (fig. 3(a) inset). This confirms that the NiS having 20% carbon composition seems to be highly porous in nature and correlates with the surface morphology.



**Fig. 3** (a) shows the BET adsorption-desorption analysis (the inset shows BJH pore size distribution), Fig. 3 (b, c, and d) shows the XPS analysis of Ni 2p, S 2p, and C 1s states.

Elemental composition of the sample was analyzed by XPS analysis and has been shown in Fig 3 (b, c, and d). The XPS analysis showed (Fig. 3b) the binding energy peaks of 856.0, 860.6, 873.7 eV and 879.9 eV corresponding to Ni  $2P_{3/2}$  and Ni  $2P_{1/2}$  [15]. In Fig. 3c, the binding energy peaks at 162.4 and 167.7 eV are assigned to the binding energy of S  $2P_{3/2}$  and  $2P_{1/2}$  [16]. The C 1s spectrum in NiS-Carbon shows a peak at 284.6 eV (Fig. 3d), which can be ascribed to  $sp^2$  bonded carbon (C-C) [17].

Fig. 4 (a) illustrates the J-V characteristics of the perovskite solar cell devices with NiS and with different NiS-carbon composites used as hole extraction layer. The photovoltaic parameters of the prepared perovskite devices are given in Table 1. From the J-V characteristics, it is observed that the solar cell with NiS layer as HTL exhibits a PCE of 1.87%. From this result, it could be observed that the agglomerated morphology of the NiS is responsible for the lower performance and this is because the agglomerated porous structured nanoparticles possibly lead to the electrical shorting and pave way for fast charge recombination which may affect the photovoltaics performance [13]. The perovskite solar cells fabricated using NiS with 10%, 20% and 30% carbon composition as HTL exhibited a power conversion efficiency of 3.13%, 5.20%, and 2.40% respectively.



**Fig. 4 (a) shows the J-V characteristic curve for PSCs, Fig. 4 (b and c) shows the stability of PSCs device performance for the 20% NiS-carbon composite HTMs in terms of (b) efficiency, (c) open circuit voltage ( $V_{OC}$ ) for a period of 10 days completely at ambient condition.**

It is observed that the device with NiS having 20% carbon composition used as HTL showed a  $V_{OC}$  of 0.59 V,  $J_{SC}$  of 24.42 mA/cm<sup>2</sup> and an FF of 36% with a PCE of 5.20%. The better performance of the device with increased  $V_{OC}$  and  $J_{SC}$  may be due to the porous nature of the material which shows the complete pore filling effect between the active perovskite layer and the hole extraction layer. When further increasing the carbon composition to 30% in NiS it eventually decreases the performance of the device and achieved a PCE of 2.40%. The presence of more porous nature in 30% carbon composition NiS decreases the performance of the device which may be attributed to the discontinuity in transporting charge carriers between the active and the HTL layers [18]. From this, it is understood that the performance of the fabricated PSC device using NiS and NiS-carbon composite materials as HTL layers depends on the porous nature of the prepared materials [19]. Fig. 4b and 4c show the efficiency

and the open circuit voltage ( $V_{oc}$ ) stability of the best fabricated PSCs device for a period of 10 days at ambient condition. From the stability test, it is inferred that deterioration in efficiency and  $V_{oc}$  to 22 % and 20 % respectively were observed.

**Table 1 The photovoltaic parameters for the prepared perovskite devices using NiS and NiS-carbon composites.**

Device with HTL layer	$J_{sc}$ (mA/cm <sup>2</sup> )	$V_{oc}$ (V)	Fill Factor	Efficiency (%)
NiS	19.65	0.34	0.28	1.87
NiS-Carbon (10%)	21.28	0.46	0.32	3.13
NiS-Carbon (20%)	24.42	0.59	0.36	5.20
NiS-Carbon (30%)	16.89	0.46	0.31	2.40

## Conclusion

In summary, NiS and NiS-carbon composites have been synthesized using simple solution technique and have been employed as an HTL and as a counter electrode for perovskite-based solar cells. The optimal bandgap of the prepared NiS material has been found to be favorable in achieving the hole extraction property. The surface morphology of the nickel sulphide materials is found to be highly dependent on the NiS-carbon composition. The perovskite solar cell fabricated using NiS with 20% carbon composition as HTL exhibited a power conversion efficiency of 5.20%.

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## Notes

The authors declare no competing financial interest.

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