

# Electrochemical deposition of carbon materials incorporated nickel sulfide composite as counter electrode for dye-sensitized solar cells

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**Abstract** The various carbon-based materials incorporated nickel sulfide (NiS) composites have been electrochemically deposited on fluorine-doped tin oxide (FTO) glass substrate. The structure, surface morphology, and elemental composition of the electrodeposited NiS composite materials were characterized by XRD, HR-SEM, and EDS. The electrochemically deposited various NiS composites such as NiS/AB (acetylene black), NiS/VC (Vulcan carbon), and NiS/MWCNT (multi walled carbon nanotubes) have been served as an efficient, low-cost counter electrode (CE) materials for dye-sensitized solar cells (DSSCs). Electrochemical impedance spectroscopy and cyclic voltammetry of NiS/AB CE composite materials exhibits a good conductivity and superior electrocatalytic performance over other various carbon incorporated materials. The positive synergistic effects, which increase the active catalytic sites and improved interfacial charge transfer, may be accountable for the superior

electrocatalytic performance of NiS/AB composite materials. The fabricated DSSC with NiS/AB CE reached a power conversion efficiency of 6.75%, which is equivalent with platinum electrode (7.20%). These results validate that the electrochemically deposited NiS/AB composite film is an auspicious alternative for low-cost and high efficient DSSCs.

**Keywords** Nickel sulfide · Acetylene black · Electrochemistry · Conversion efficiency · Polymer electrolyte · Dye-sensitized solar cell

## Introduction

Nowadays, increasing global demands for energy and global warming concern have urged researchers to focus on clean and renewable energy resources. Solar energy is one of the most abundant energy resources, which can solve energy and environmental related issues [1, 2]. Dye-sensitized solar cell (DSSC) is one of the most favorable renewable energy devices and has received increasing attention among researchers due to its simple fabrication process, low cost, transparency, light weight, better plasticity, environmental friendliness, and capability in large-scale conversion of solar energy to electrical energy [3–5]. Commonly, a DSSC comprises of dye-sensitized TiO<sub>2</sub> photoelectrode, I<sup>-</sup>/I<sub>3</sub><sup>-</sup> redox electrolyte, and platinum (Pt) counter electrode. Under illumination condition, the photoexcited dye molecule introduces an electron into a conduction band (CB) of photoelectrode and the resultant dye molecule is reduced back by iodine/iodide electrolyte and the cycle is accomplished by the incessant flow of electrons from the photoelectrode to the counter electrode (CE) via external circuit [6–8]. The extensive research has been focused on all component of DSSC to advance the power conversion efficiency (PCE) and to lower the production cost. The CE is an indispensable component in DSSCs and

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its role is to gather electrons from the external circuit and catalyze the reduction of  $I_3^-$  ion [9]. The CE with superior electrocatalytic performance over the reduction of  $I_3^-$  to  $I^-$  ions has decreased the device internal series resistance, which resulting in a high fill factor (FF) [10].

Generally, a Pt-deposited fluorine/indium-doped tin oxide (FTO/ITO) glass substrate is most commonly used as the CE in DSSCs [11]. Conversely, noble metal Pt can be easily corroded by  $I^-/I_3^-$  contained electrolytes and the high cost of Pt consumes 40% of the whole device fabrication cost [12, 13]. Moreover, the usage of Pt CE hinders the large-scale production and economical application of DSSCs. This promoted numerous studies to develop an alternative material to Pt CEs to reduce the cost and simultaneously keep the effectiveness of the DSSCs. Pt-free CE material includes carbon-based materials [14, 15], conducting polymers [16, 17], metal oxides [18], sulfides [5, 19, 20], selenides [21, 22], metal carbides [23], and nitrides [24]. Among the inorganic materials, nickel sulfides have been emerged as one of interesting metal sulfides due to its abundance in content, good conductivity, simple fabrication, and high electrocatalytic activity [19]. Many researchers have been studied on NiS-based Pt-free CEs for DSSCs in recent years [25–27]. The varieties of nickel sulfide phases have been formed depending on the synthetic conditions, such as NiS, NiS<sub>2</sub>, Ni<sub>3</sub>S<sub>2</sub>, Ni<sub>3</sub>N<sub>4</sub>, and Ni<sub>9</sub>S<sub>8</sub> [28, 29]. Hydrothermal and electrochemical depositions are the most widely used methods to synthesis of nickel sulfides. Very recently, Maiaugree et al. [30] reported that the carbon coated Ni<sub>3</sub>S<sub>2</sub> as Pt-free CE for DSSCs and the film is fabricated via chemical bath deposition and an arc evaporation process. The fabricated DSSC with carbon/Ni<sub>3</sub>S<sub>2</sub> CE attained a high PCE of 9.64%, which is higher than the Pt CE (8.38%). The enhancement of the PCE using carbon/Ni<sub>3</sub>S<sub>2</sub> was mainly due to the fast electron transfer, high co-electrocatalytic activity, and large surface area of the materials. The addition of carbon as co-catalyst with Ni<sub>3</sub>S<sub>2</sub> is the best way to assist the enhancement of  $I^-/I_3^-$  redox reaction. Xiao et al. [31] have deposited NiS/MWCNT on a titanium (Ti) foil substrate by a two-step process. Firstly, MWCNT was deposited on Ti substrate via electrophoresis method and followed by NiS deposition on MWCNTs surface via pulse potentiostatic method. The fabricated NiS/MWCNT/Ti hybrid film electrodes were served as a Pt-free CE in DSSCs. The DSSC with NiS/MWCNT/Ti CE attained a PCE of 7.90%, while the Pt/Ti CE attained 6.36%. Thus, the enhanced PCE of NiS/MWCNT/Ti hybrid film is mainly due to the synergistic effect of NiS/MWCNTs.

In the present investigation, we have electrochemically deposited NiS/AB, NiS/VC, and NiS/MWCNT composite film on FTO glass substrate by using cyclic voltammetry technique. Electrochemical deposition was preferred in this investigation because of its simple procedure, less cost, easy scale up and can control the electrochemically deposited structure by varying the operating conditions. The NiS/AB, NiS/VC,

and NiS/MWCNT composite films were employed as Pt-free CE in DSSCs and examined the effect of the addition of various carbon-based materials as co-catalyst with NiS for an enhancement of PCE of DSSCs. Phthaloylchitosan (PhCh) was served as a polymer electrolyte solution for DSSCs. Though the higher PCE of the DSSCs has been achieved by employing liquid electrolytes ( $I^-/I_3^-$  redox couple) in DSSCs and its short-term stability, electrode corrosion and difficulty in sealing device limit the commercialization of DSSCs. The usage of polymer electrolyte can overcome these problems [7]. Herein, we report the comparison of electrodeposited NiS with various carbon materials as an efficient Pt-free CE for DSSCs.

## Experimental section

### Materials

Nickel(II) chloride hexahydrate (NiCl<sub>2</sub>·6H<sub>2</sub>O), thiourea (CH<sub>2</sub>CSHCH<sub>2</sub>), iodine (I<sub>2</sub>), isopropanol, acetonitrile, and absolute ethanol were purchased from SDFCL, India. Acetylene black (Chevron, USA), MWCNT (Nanolab., Inc., USA), Vulcan XC-72 (Cabot, USA), chitosan (Merck, Germany), phthalic anhydride (Merck, Germany), and Carbowax (Supelco, USA) were purchased from the respective company. N3 dye [cis-diisothiocyanato-bis(2,2'-bipyridyl-4,4'-dicarboxylic acid) ruthenium(II)], fluorine-doped SnO<sub>2</sub> (FTO) (7 Ω/square, TCO22-7) conducting glass, lithium iodide (LiI), and lithium perchlorate (LiClO<sub>4</sub>) were acquired from Sigma Aldrich. Demineralized water was received from Nice chemicals, India.

### Electrochemical deposition of NiS/carbon composite films

The electrochemical deposition of NiS/AB, NiS/VC, and NiS/MWCNT on FTO glass substrate was carried out in a single compartment cell with three-electrode assembly using a CHI608E electrochemical work station. The electrode setup comprises of a cleaned FTO-coated glass substrate as a working electrode (WE), a Pt-wire as a CE, and a saturated aqueous silver/silver chloride (Ag/AgCl) as a reference electrode (RE). The solution for electrochemical deposition was prepared by dispersing 5 mg of carbon material (AB/VC/MWCNT) in 50 mL of de-ionized water and sonicated for 30 min. Then, NiCl<sub>2</sub>·6H<sub>2</sub>O (0.05 M) and thiourea (1.0 M) were added into the carbon-dispersed solution. The potential range of cyclic voltammetry electrochemical deposition of NiS/carbon composites was performed from −0.9 to 0.7 V at a scan rate of 0.05 Vs<sup>−1</sup> for 25 cycles. The as-prepared NiS/AB, NiS/VC, and NiS/MWCNT electrodes were rinsed in demineralized water and dried at room temperature for 2 h. For comparison,

the bare NiS film was also electrochemically deposited under same condition.

### Preparation of polymer electrolyte

The phthaloylchitosan (PhCh)-based polymer electrolyte was used as an electrolyte for the fabrication of DSSCs in this investigation. Polymer electrolyte composition was discussed in our earlier reports [32, 33].

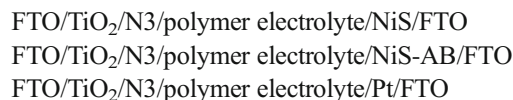
### Characterization techniques

The X-ray diffraction (XRD) patterns were logged via Rigaku X-ray diffractometer (Mini Flex II) with Cu K $\alpha$  radiation ( $\lambda = 0.54$  nm) in the  $2\theta$  range  $10$ – $80^\circ$  at a scan rate of  $5^\circ/\text{min}$ . The shape and morphology of the sample were examined by using FEI Quanta FEG 200-high resolution scanning electron microscope (HR-SEM) at an accelerating voltage of 20 kV. The elemental compositions of electrochemically deposited samples were analyzed using an energy dispersive X-ray spectroscopy (EDS) equipped with HR-SEM. The electrocatalytic activity of the materials was assessed by cyclic voltammetry (CV) in electrochemical work station (CHI608E). The CV was carried out in a three-electrode assembly in acetonitrile solution containing 0.1 M LiClO $_4$ , 10 mM LiI, and 1.0 mM I $_2$  in work station in the potential ranging from  $-1.3$  to  $+1.2$  V at a scan rate of  $150$  mVs $^{-1}$ . The polymer electrolyte solution was purged with N $_2$  gas for 30 min prior to CV measurements.

### Assembly of DSSCs

The TiO $_2$  photoelectrode was prepared on the FTO substrates in two layers. Firstly, the TiO $_2$  compact layer was arranged by the addition of TiO $_2$  (0.5 g, P90) powder with 2 mL of HNO $_3$  (0.1 M) and grinding well for 30 min. Then, the obtained paste was spin coated on FTO glass substrate at 2650 rpm for 60 s and then sintered at  $450^\circ\text{C}$  for 30 min. The obtained TiO $_2$  compact layer on FTO improves adhesion and also inhibits the back electron flow from FTO into electrolyte solution [3]. Secondly, the TiO $_2$  paste for the second porous layer was fabricated by grinding of 0.5 g of TiO $_2$  (P25) with 2 mL of 0.1 M HNO $_3$ , 0.1 g carbowax, and 2 drops of Triton-X 100. Then, the obtained TiO $_2$  (P25) paste was coated above the compact layer via doctor blade technique and followed by sintering at  $450^\circ\text{C}$  for 30 min. The prepared TiO $_2$  photoanode was dye sensitized by immersing in  $3 \times 10^{-4}$  M ethanol solution of N3 dye for 24 h, and then, the dye-sensitized TiO $_2$  electrodes were rinsed with absolute ethanol and dried in the air before assembling with different CEs. A sandwich-type configuration of DSSCs was gathered by clamping both the dye-sensitized TiO $_2$  photoanode and CE. Prior to the assembly, the polymer electrolyte was evenly spread on the surface of dye-sensitized TiO $_2$

photoanode. In addition, Pt CE was prepared by spin coating of plastisol solution on FTO plate and sintered at  $500^\circ\text{C}$  for 30 min and this was used as a reference cell for comparison studies. The effective cell area was  $0.2$  cm $^2$  and photovoltaic measurements were completed in the open air atmosphere. The cell configuration of the fabricated DSSC is as follows:

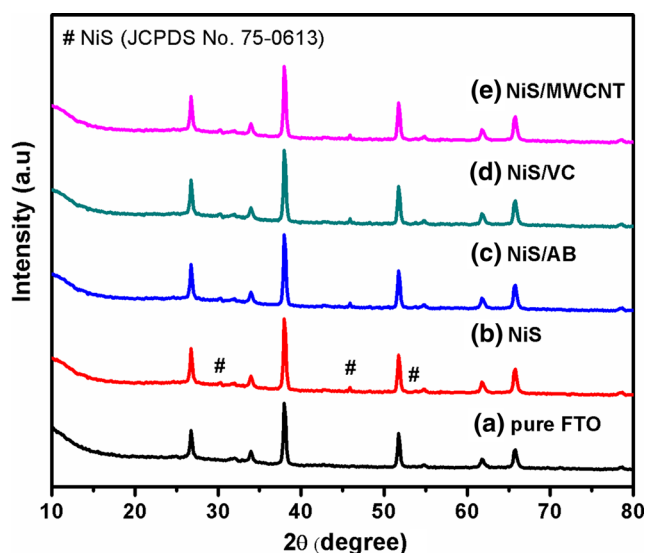


The photocurrent density-voltage ( $J$ - $V$ ) characteristics of the DSSCs were measured under an illumination of 1 sun ( $100$  mW/cm $^2$ ) using a PEC-L01 (PECCELL Inc., Japan) solar simulator. The photovoltaic parameters (i.e., fill factor (FF) and overall PCE ( $\eta$ )) of the fabricated DSSCs are calculated and it was described in our earlier reports [34, 35].

## Results and discussion

### XRD studies

The XRD patterns of pure FTO glass substrate, the electrochemically deposited NiS, NiS/AB, NiS/VC, and NiS/MWCNT, are shown in Fig. 1. The diffraction peaks of NiS and carbon NiS composite films can be observed at  $2\theta = 30.2^\circ$ ,  $46.1^\circ$ , and  $53.6^\circ$ , which can be indexed to the (100), (102), and (110) diffraction planes of NiS (JCPDS No. 75-0613). These diffraction peaks are in good agreement with earlier report by Xiao et al. [11]. All other strong diffraction peaks correspond to the pure FTO glass substrate. The XRD patterns of NiS in NiS/AB, NiS/VC, and NiS/MWCNT



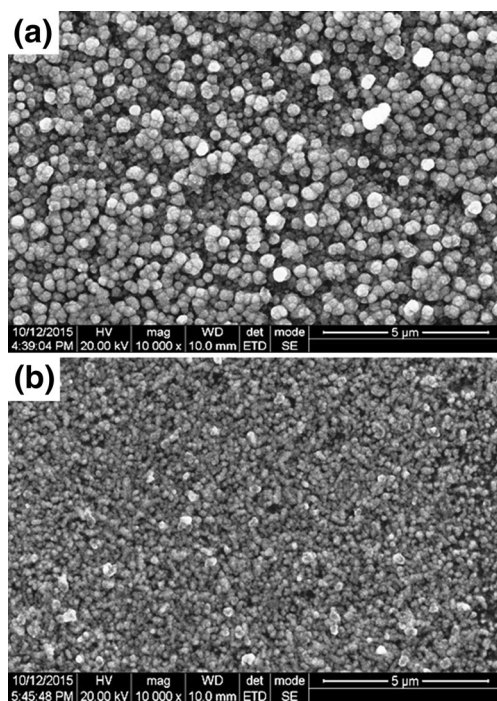
**Fig. 1** XRD patterns of (a) pure FTO glass substrate, electrodeposited, (b) NiS, (c) NiS/AB, (d) NiS/VC, and (e) NiS/MWCNT films



(Fig. 1c–e) are unaltered with the incorporation of different carbon materials suggesting that the low content of carbon with dense covering of NiS on its surface and with no specific diffraction peaks of carbon in the NiS/C samples was observed. However, it can be noted that the little changes in the peak intensity of NiS/FTO were noticed which may be due to the incorporation of carbon atoms at the interstitial positions or substitutional sites producing considerable contraction and expansion of the lattice constants.

### Morphology and elemental studies

The shape and surface morphology of the electrochemically deposited NiS and NiS/AB were observed by HR-SEM. The characteristic HR-SEM images of NiS and NiS/AB films are presented in Fig. 2a, b. The SEM images appear to be tight and random distribution of NiS over the surface of FTO glass substrate. The pure NiS (Fig. 2a) exhibited a spherical shape with some aggregated particles comprising of a large number of irregular smaller particles having a size of ~200 nm. The morphology of NiS/AB (Fig. 2b) clearly shows that the addition of AB into NiS does not change its morphology. It can be seen that NiS/AB appeared in spherical shape and the average particle size of the electrodeposited NiS/AB varied between 50 and 200 nm. It can be evidenced from the SEM analysis that NiS/AB shows smaller particle size with less agglomeration of particles on incorporating carbon content into pure NiS. The surface morphology of the electrochemically deposited NiS and NiS/AB layer was observed as good adhesion on



**Fig. 2** Typical HR-SEM images of electrochemically deposited **a** NiS and **b** NiS/AB films

the FTO glass substrate. Adhesion plays a significant role in the electrochemical deposition of thin films. The good adhesion of the electrocatalytic material on FTO glass substrate is a key factor for defining the long-term stability and efficiency of the DSSCs, when these films are used as CEs.

The elemental analysis of electrochemically deposited NiS and NiS/AB was examined by EDS and the obtained results are presented in Fig. 3a, b. The formation of NiS on the surface of FTO glass substrate was confirmed from EDS results (Fig. 3a). It clearly showed that NiS consisted of Ni and S atoms and NiS/AB composed of Ni, S, and C atoms only (Fig. 3b). In addition, the observed other peaks of Sn, O, Si, and F are ascribed to the FTO substrate [2], and no other impurity peaks are found. The atomic ratios of species noticed by EDS are displayed in Fig. 3 inset. We can conclude from the XRD and EDS results that NiS and NiS/AB are well deposited on the surface of FTO glass substrate.

### Cyclic voltammetry studies

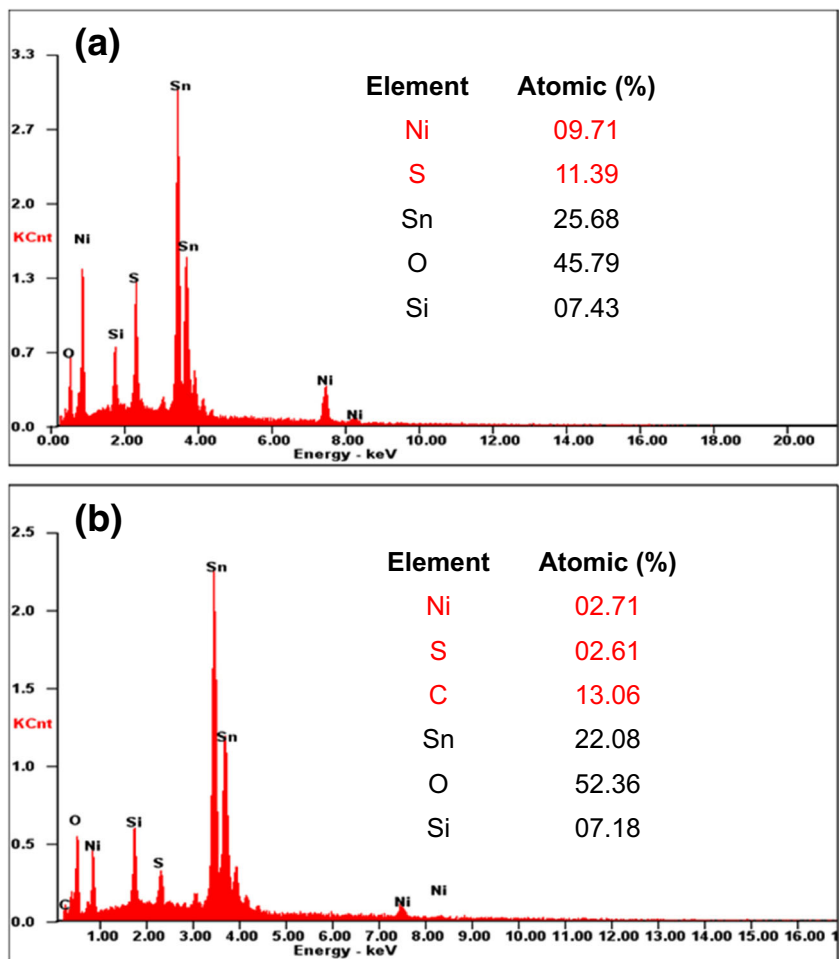
The electrocatalytic activity of the synthesized CE materials towards the reduction of  $I_3^-$  to  $I^-$  ions was assessed using CV studies. The cyclic voltammograms of the bare NiS, NiS-AB, NiS/VC, NiS/MWCNT, and Pt electrodes for  $I^-/I_3^-$  redox couple are shown in Fig. 4. Typically, there are two pairs of oxidation and reduction peaks (Ox-1/Red-1, Ox-2/Red-2, as labeled in Fig. 4) that were witnessed for all the electrodes. It can be seen that the obtained redox peaks of NiS, NiS/AB, NiS/VC, and NiS/MWCNT are similar to Pt, suggesting a similar electrocatalytic behavior for the  $I_3^-$  reduction. The pair of redox peaks observed at left side at low potential (Ox-1/Red-1) could be attributed to the redox reaction shown in Eq. (1), and the pair of redox peaks observed at right side at high potential (Ox-2/Red-2) are ascribed to the redox reaction shown in Eq. (2), respectively.



The characteristic peaks of Ox-1 and Red-1 are at great observation in our measurements because the CE is accountable for the catalyzing reduction of  $I_3^-$  to  $I^-$  ions in DSSCs [5]. The peak current density and peak-to-peak separation ( $E_{pp}$ ) are two significant parameters to assess the electrocatalytic performance of various CEs [19].

The higher peak current density and lower  $E_{pp}$  values are beneficial for the CE to achieve high catalytic performance. The observed  $E_{pp}$  values for NiS, NiS/AB, NiS/VC, NiS/MWCNT, and Pt CEs were recorded in Table 1. It can be seen that NiS/AB CE exhibited higher peak current density and smaller  $E_{pp}$  (0.78 V) than the NiS, NiS/VC, and NiS/MWCNT and almost similar to Pt CE indicating that NiS/

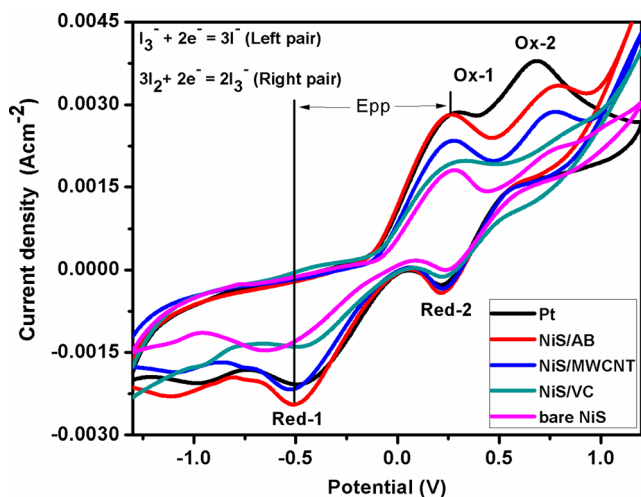
**Fig. 3** EDS spectra of electrochemically deposited **a** NiS and **b** NiS/AB films



AB CE can show better electrocatalytic activity for  $I_3^-$  reduction than other CEs. This may be due to a positive synergetic effect offered when NiS and AB are combined together, and this increases the active catalytic sites and improves interfacial

charge-transfer rate. Zuo et al. [19] synthesized NiS/RGO via solvothermal route and Li et al. [5] for NiS<sub>2</sub>/RGO composite synthesized via hydrothermal route.

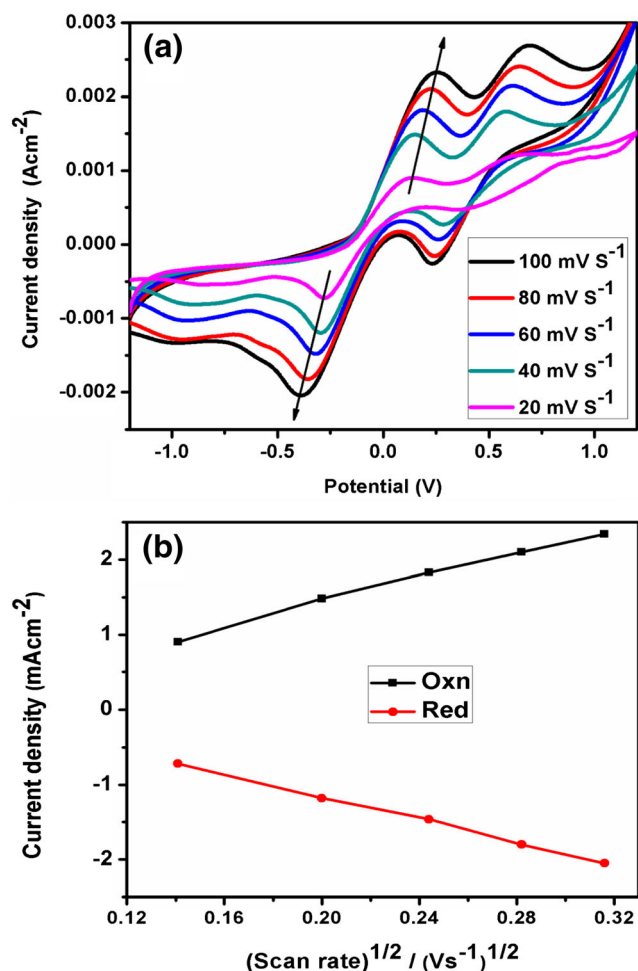
Figure 5a shows the cyclic voltammograms of NiS/AB CE for  $\Gamma^-/I_3^-$  redox system at various scan rates. It can be seen that the cathodic and anodic peaks gradually and regularly shifted to the negative and positive direction with increasing scan rates indicating the inner sites of the sulfide electrodes becomes more reactive in a high scan rate [25]. Figure 5b displays the linear relationship between the peak current density versus square root of the scan rates and it reveals the diffusion limitation of the redox reactions, which affect the transport of  $\Gamma^-$  on the CE surface [36].



**Fig. 4** Cyclic voltammograms for bare NiS, NiS/VC, NiS/MWCNT, NiS/AB, and Pt CEs at a scan rate of 150 mVs<sup>-1</sup> in 10 mM LiI, 1 mM I<sub>2</sub>, and 0.1 M LiClO<sub>4</sub> as supporting electrolyte in acetonitrile

**Table 1** Electrochemical parameters for different CEs

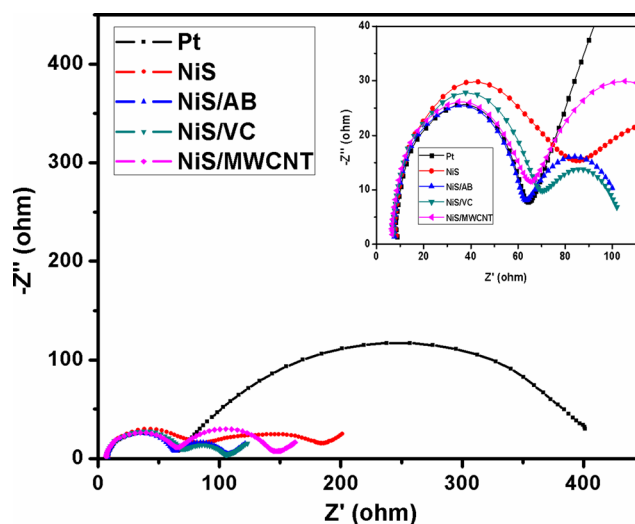
CEs	$E_{pp}$ (V)	$R_s$ ( $\Omega$ )	$R_{ct}$ ( $\Omega$ )	$R_b$ ( $\Omega$ )
NiS	0.92	8.50	86.29	94.8
NiS/AB	0.78	7.67	63.42	71.1
NiS/VC	0.82	7.17	72.42	79.6
NiS/MWCNT	0.80	6.59	71.40	78.0
Pt	0.77	8.71	61.58	70.3



**Fig. 5** a Cyclic voltammograms for NiS/AB electrode at different scan rates. b Relationship between redox peak current vs. square root of the scan rates

### Electrochemical impedance spectroscopy studies

The electrochemical impedance spectroscopy (EIS) measurements were further performed to evaluate the electrocatalytic activity of the electrochemically deposited NiS, NiS/AB, NiS/VC, NiS/MWCNT, and Pt CEs. The EIS is a powerful technique to investigate internal resistance, charge-transfer process, and correlation between the electrocatalytic activities of the CEs [37]. Figure 6 shows the Nyquist plot of EIS for different CEs. The enlarged view of lower part of the spectra is displayed in the inset of Fig. 6. Generally, the high-frequency intercept on the real axis ( $Z'$ -axis) agrees to the series resistance ( $R_s$ ), and the high-frequency region of semicircle (left side) is attributed to the charge-transfer resistance ( $R_{ct}$ ) at the CE/electrolyte interface [5, 36]. The  $R_s$  and  $R_{ct}$  are mainly composed of the bulk resistance ( $R_b$ ) of the CE materials. The Nyquist plots were fitted by the Z-view software to obtain the EIS parameters and the corresponding resistances ( $R_s$  and  $R_{ct}$ ) are listed in Table 1. It can be noted that all CEs have closely same  $R_s$  value, and therefore, the effect on photovoltaic performance by the  $R_s$  can be omitted [38]. However, the



**Fig. 6** Nyquist plots of EIS for bare NiS, NiS/AB, NiS/VC, NiS/MWCNT, and Pt CEs. Inset shows the zoomed view of lower part of the Nyquist spectra

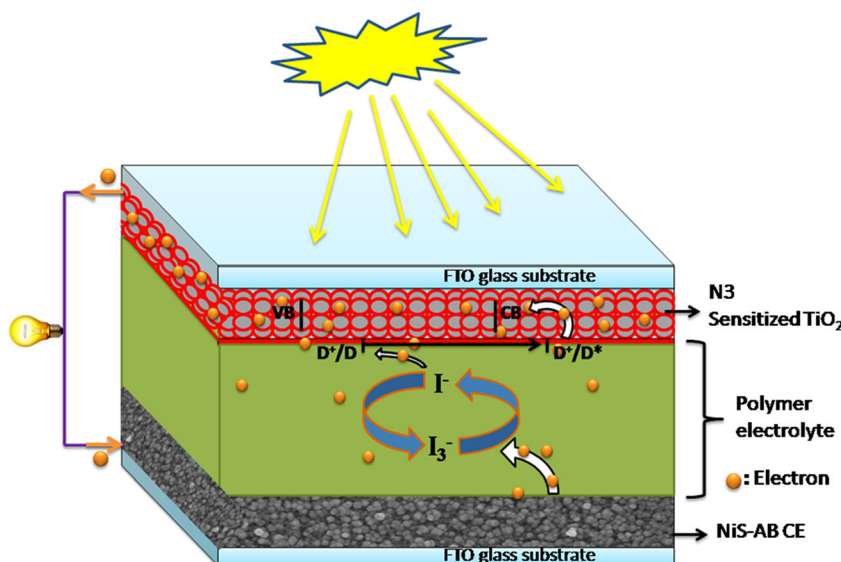
$R_{ct}$  values are different for different electrodes. The  $R_{ct}$  value is actually related to the electrocatalytic activity for the reduction of  $I_3^-$  to  $I^-$  ions. A lower  $R_{ct}$  value means higher electrocatalytic activity and higher charge-transfer rate between the CE and electrolyte [25].

In Nyquist plot, the high-frequency region of the first semicircle represents the electron transfer from the counter electrode to  $I_3^-$  ions in the electrolyte, that is, the charge-transfer resistances at the CE/electrolyte interface. The second (large) semicircle represents the charge recombination between the injected electrons in  $TiO_2$  and  $I_3^-$  ions in the electrolyte, that is, the charge-transfer resistances at the  $TiO_2$ /dye/electrolyte interface. In our study, the characteristics of the first semicircle are the focus of our analysis because the CE material with low  $R_{ct}$  value at the CE/electrolyte interface provides high electrocatalytic activity for the reduction of  $I_3^-$  to  $I^-$  ions in DSSCs. In the present study, the electrodeposited NiS/AB electrode showed the lowest  $R_{ct}$  value (63.42  $\Omega$ ) than pure NiS, NiS/VC, and NiS/MWCNT electrodes and close to Pt CE (61.58  $\Omega$ ). Hence, the NiS/AB would be expected to show higher electrocatalytic activity for  $I_3^-$  reduction than NiS and other carbon incorporated NiS materials. The observed EIS results are in well accordance with the results obtained from CV measurements.

### DSSC studies

The graphic representation of the electron transfer mechanism of DSSCs with NiS/AB CE is presented in Fig. 7. Under illumination condition, the photoexcited N3 dye molecule introduces an electron into a CB of  $TiO_2$  photoelectrode and the resultant dye molecule is reduced back by iodine/iodide electrolyte and the cycle is accomplished by the incessant flow of electrons from the  $TiO_2$  photoelectrode to the NiS/AB CE via external circuit.

**Fig. 7** The schematic illustration of the electron transfer mechanism taking place in the fabricated DSSCs

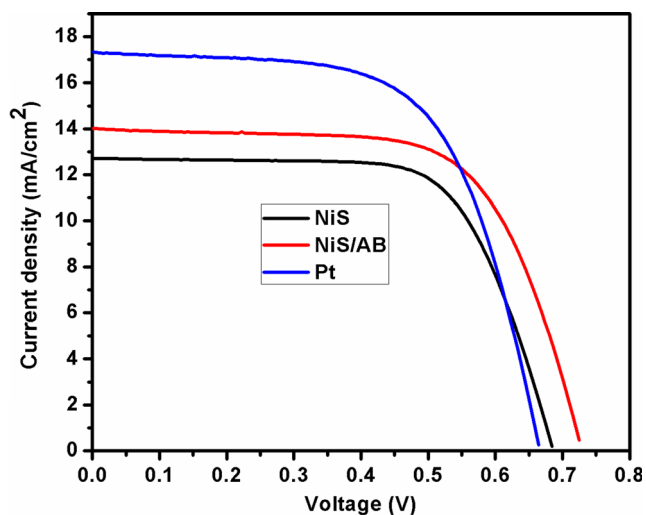


The photovoltaic performances of fabricated DSSCs were analyzed by assessing the photocurrent density-voltage ( $J$ - $V$ ) curves. The  $J$ - $V$  curves obtained for the DSSCs with NiS, NiS/AB, and Pt CEs are presented in Fig. 8, and the corresponding photovoltaic parameters such as  $V_{oc}$ ,  $J_{sc}$ , FF, and  $\eta$  are summarized in Table 2. The photovoltaic parameters of fabricated DSSC with NiS/AB CE exhibited power conversion efficiency (PCE) of 6.75% with  $V_{oc}$  of 0.72 V,  $J_{sc}$  of 14.01 mA/cm<sup>2</sup>, and FF of 0.67. The observed photovoltaic performance using NiS/AB CE was comparable to the Pt CE, which gives a PCE of 7.20% with  $V_{oc}$  of 0.66 V,  $J_{sc}$  of 17.32 mA/cm<sup>2</sup>, and FF of 0.63. The improved PCE of NiS/AB CE is mainly due to an improved FF and  $V_{oc}$ , which could arise from the more active catalytic sites and improved interfacial charge transfer by the combination of NiS and AB. This result suggests that the

electrodeposited NiS/AB on FTO is a favorable substitute electrocatalyst to the Pt-free CE in DSSCs.

**Conclusions**

In summary, the various carbon materials (AB, VC, MWCNT) incorporated NiS composites were fabricated on FTO glass substrate by a simple electrochemical deposition using cyclic voltammetry studies. The electrochemically deposited sulfide materials were characterized by XRD, HR-SEM, and EDS studies. Subsequently, the electrochemically deposited NiS, NiS/AB, NiS/VC, and NiS/MWCNT films were applied as a Pt-free low-cost CE for DSSCs. The CV and EIS measurements revealed that the NiS/AB CE exhibited an excellent electrocatalytic activity and have good conductivity for the reduction of I<sub>3</sub><sup>-</sup> to I<sup>-</sup> ions than the bare NiS, NiS/VC, and NiS/MWCNT. The NiS/AB composite offered positive synergistic effects, which increases the active catalytic sites and improves the interfacial charge-transfer rate. The PCE of DSSC fabricated with NiS/AB CE achieved a 6.75%, which is equivalent with Pt CE (7.20%). The observed results indicated that electrochemically deposited NiS/AB composite film can be a favorable substitute to Pt electrode for low-cost and high efficient DSSCs.



**Fig. 8** Photocurrent-voltage curve of DSSCs fabricated with NiS, NiS/AB, and Pt CEs

**Table 2** The photovoltaic parameters of DSSCs fabricated with different CEs

Counter electrode	$V_{oc}$ (V)	$J_{sc}$ (mA/cm <sup>2</sup> )	Fill factor	Efficiency, $\eta$ (%)
NiS	0.68 ± 0.02	12.71 ± 0.04	0.69 ± 0.03	5.96 ± 0.01
NiS/AB	0.72 ± 0.02	14.01 ± 0.02	0.67 ± 0.02	6.75 ± 0.01
Pt	0.66 ± 0.02	17.32 ± 0.03	0.63 ± 0.03	7.20 ± 0.01



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