CoSe$_2$@N-Doped Graphene Nanocomposite High-Efficiency Counter Electrode For Dye-Sensitized Solar Cells

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Research Article

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Abstract

Photovoltaics is defined as a group of solar cells that convert solar energy into electricity. Among these cells, dye-sensitized solar cells (DSSCs) have received considerable attention due to their low cost and high efficiency for energy conversion. In present study, CoSe$_2$@N-doped graphene nanocomposite has been prepared in an inert atmosphere and used as a DSSC counter electrode. The fabricated nanocomposite was characterised using analytical techniques including FTIR, TGA, XRD, Raman, XPS, and BET. The assembled DSSC obtains a photoelectric conversion efficiency (PCE) of 7.65%, which is higher than the PCE (7.19%) of the Pt electrode assembly cell under the same conditions. The promising performance of the fabricated counter electrodes may be due to the excellent surface area of the nanocomposites, the doping of heteroatoms which provide the active sites to boost the catalytic activities towards I$_3^-$ reduction.

Introduction

The sun has long been the most important renewable energy source on earth and the researchers are trying to utilize this vital source of energy for the benefit of humans. Even though, the world’s biggest oil exporter, Saudi Arabia, has also pledged to cut its carbon emissions to net zero by 2060 and the plans and objective of Vision 2030, Saudi Arabia has focused on producing 50 percent of its electricity from renewable sources by 2030 to meet the growing demand for energy, and to provide favourable climatic conditions and suitable economic feasibility. Solar radiation can be converted directly into electricity by solar cells (photovoltaic cells) (Ahamad et al., 2021; Aldalbahi et al., 2021; Wang et al., 2021). Among these solar cells, dye-sensitized solar cells (DSSC) have attracted widespread attention due to their low cost, easy preparation, and high solar energy conversion efficiency (Hagfeldt et al., 2010; O’Regan and Grätzel, 1991). Generally, a typical DSSCs composed of a dye-adsorbed TiO$_2$ anode, a redox shuttle (I$_3^−$/I$^-$), and a counter electrode (CE). The function of CE is to collect the electron from the external circuit and catalyse the reduction of I$_3^-$ into I$^-$(Jin et al., 2017; Leu et al., 2017; Meng et al., 2018). Pt is widely used as a counter electrode (CE) to fabricate DSSC due to its high conductivity and excellent catalytic activity towards I$_3^-$ reduction, however, the limited resources and high price of Pt limits its industrial application (Hou et al., 2018; Yu et al., 2016). Therefore, current studies are focused on finding alternatives to Pt. Some non-Pt materials such as porous carbon have been used as counter electrode to fabricate the DSSC due to their large surface area, high conductivity, and low cost (Tapa et al., 2021; Yue et al., 2018). Moreover, several transition metal based compounds specially, transition metal selenides, such as CoSe$_2$, NbSe$_2$, NiSe$_2$, and ZnSe$_2$ have excellent catalytic activity towards I$_3^-$ reduction (Gao et al., 2018; Singh et al., 2017; Wang et al., 2016). Among these, cobalt selenide (CoSe$_2$) has attracted much attention because of its high catalytic activity, low cost and excellent long-term stability (Huang et al., 2018; Wang, X. et al., 2019; Yang et al., 2020). However, the electron conductivity of CoSe$_2$ is not meet to the required standard due to its semiconducting behaviour and poor conductivity (Chiu et al., 2016; Li et al., 2021; Ou et al., 2020). On the other hand, the carbon based materials such as graphite carbon, carbon
nanotubes, graphene and graphene oxide not only show the excellent electrical conductivity but also the high surface area to enhance the catalytic activity. Recently, it was noticed that the doping of the heteroatoms such as N and S into carbon provide the additional active sites, which enhance the charge transfer behaviour as well as enhance the catalytic activity of the nanocomposites (Ding et al., 2022; Su et al., 2022; Wei et al., 2022). Therefore, the nanocomposite based counter electrode materials have attracted wide attention because they combine the advantages of each component and help improve the catalytic activity and the stability of the electrode (Silambarasan et al., 2021; Wang et al., 2022; Zhao et al., 2021). Being inspired by the above investigations, here we have design low-cost, effective and environmentally friendly counter electrode for DSSC using CoSe₂@N-doped graphene nanocomposite. The electrode materials were characterized using FTIR, XRD, Raman, BET, XPS, SEM and TEM. The electrochemical performance of CoSe₂@N-doped graphene was analysed by electrochemical impedance spectroscopy (EIS), cyclic voltammetry (CV), and Tafel polarization curve, and the effects of N-doped graphene (NGN) loading with CoSe₂ were discussed in details. The DSSC fabricated using the CoSe₂/NGN-15 electrode exhibits excellent PCE value of 7.65% higher than that of other fabricated electrode even higher than that of the Pt electrode (7.19%) under the same experiment condition. This may be due to the synergetic effect between the CoSe₂ nanoparticles and graphene moreover the doping of the nitrogen into the graphene matrix also improve the DSSC performance and have good corrosion resistance to a corrosive redox electrolyte as CE materials. We hope that, the present work offers to fabricate Pt free counter electrode for DSSC and provides an opportunity to develop a highly efficient and low cost DSSC as the plans and objectives of Vision 2030.

**Experimental**

**2.1 Materials**

Cobalt nitrate hexahydrate (Co(NO₃)₂·6H₂O, Graphene, selenium powder, N719 dye, are from Sigma-Aldrich. Ethylene glycol, Ethanol, Potassium iodide (KI), and Iodine (I₂) were obtained from Merck, Germany. TiO₂ paste (TPP3, 20 nm; TPP200, 200 nm) and FTO glass (sheet resistance 15 Ω) were purchased from Dalian Seven Color Technology Co., Ltd.

**2.2 Preparation of CoSe₂@NGN**

The counter electrode materials were prepared as following; 20 mg of the NGN was dispersed into 50 mL ethanol and sonicated for 30 min., Then 0.40 mmol of Co(NO₃)₂·6H₂O and then 26 mmol (CH₃COO)Na were added to this mixture and stirred continuously. After that 0.80 mmol of SeO₂ was added to this solution and stirred again for 3 h, under N₂ gas, and then 4.92 mmol NaBH₄ dissolved in 20 mL ethanol was dropped to the above mixture and stirred overnight. The obtained precipitate was filtered, washed dried and then annealed at 400 °C for 4 h in N₂ atmosphere to remove amorphous selenium. Resulting product CoSe₂@NGN-20, was washed and saved for further uses. Other compositions were prepared
using similar procedure after changing the amount of NGN as 5, 10 and 15 as CoSe$_2$@NGN-5, CoSe$_2$@NGN-10 and CoSe$_2$@NGN-15 respectively.

## 2.3 Cell fabrication and measurement

The detailed of counter electrode (CE) and DSSC fabrication processes, material characterization, and electrochemical measurement could be found in the Supporting Information.

### Results And Discussion

The CoSe$_2$@NGN nanocomposite was prepared using reduction and post calcination method as shown in figure-1.

The FTIR spectra of the nanocomposites illustrate in figure 2(a) and the peaks at 1567 cm$^{-1}$ and 1647 cm$^{-1}$ assigned to the C=C and C=N bonds. Other peaks at 1334, 1402, and 1054 cm$^{-1}$ peak are assigned to the C-O, C–N, and C–O–C stretching, respectively (Ahamad et al., 2020a; Ahamad et al., 2019). While the peaks in the region of 3170-3382 cm$^{-1}$ are corresponding to N–H, -NH$_2$, and O–H bonds, respectively and the FTIR peak at 587 cm$^{-1}$ support the bond Co-Se. The thermal stability of the nanocomposites was determine using TGA analysis and the results were illustrated in the figure 2(b). The TGA outcomes revealed that as the amount of the NGN was increased from 5–20% the thermal stability of the nanocomposites was decreased and the reduced weight was found to be 49.02%, 41.64%, 38.43% and 34.88% corresponding to CoSe$_2$@NGN-5, CoSe$_2$@NGN-10, CoSe$_2$@NGN-15 and CoSe$_2$@NGN-20 respectively at 800 °C (Ahamad and Alshehri, 2013; Naushad et al., 2015). The purity and the crystalline nature of the nanocomposites were also determine using XRD, as shown in figure 2(c), The diffraction peaks at 2θ = 30.78, 34.52, 35.96, 40.38, 47.72, 50.23, 53.48, 56.95 and 63.29 can be assigned to the (101), (111), (120), (210), (211), (002), (031), (131) and (122) planes are assigned to the orthorhombic CoSe$_2$ (PDF-53–0449). The doping of the nitrogen atoms into to the graphene and growing the CoSe$_2$ nanoparticles into the NGN matrix was further determine using Raman spectra. As shown in figure 2(d), two main Raman peaks were observed at 1354 cm$^{-1}$ and 1592 cm$^{-1}$ known as D and G bands, respectively. The G band assigned to the sp$^2$ hybridized C=C bonds, whereas the D band assigned to the sp$^3$ hybridized C-C bond (Ahamad et al., 2020c; Ahamad et al., 2020d; Alhokbany et al., 2020). The intensity of these two peaks increased with increasing the contents of NGN in to the nanocomposites. Other peaks at 163.46, 469.23 and 670.21 cm$^{-1}$ assigned to the CoSe$_2$ nanoparticles. The defect density of carbon is proportional to the value of $I_D/I_G$ and found to be 1.24 in the case of CoSe$_2$@NGN-15.

The results indicated that the doping of N atoms and the existence of sp$^3$ C-C and C-N bonds enhanced the disordered of graphene lattice. Which lead the electron transfer and catalytic efficiency for I$_3^-$ reduction in DSSC. The microstructure and the morphology of the fabricated electrode materials were determine using SEM and TEM techniques. As shown in figure 3(a), the SEM image of the CoSe$_2$@NGN-15 nanocomposite show the porous structure and grown the nanoparticles in the NGN matrix. The
enlarged pattern of the SEM image is shown in figure 3(b) and the results revealed that revealed that the spherical shaped CoSe$_2$ nanoparticles with the diameter range of 20-50 nm are well dispersed into the NGN matrix. These results support that the fabricated electrode material contains hetrostructure which being conducive to the exposure the active sites at the surface of the catalyst to reduce the I$_3^−$. To deep understand the microstructural of CoSe$_2$@NGN-15, TEM analysis was used. As shown in figure 3(c), CoSe$_2$ nanoparticles with an average size of $\sim$38.9 nm are uniformly embedded in the NGN matrix.

The HRTEM image as shown in figure 3(d), displayed inter-planar spacing of 0.29 nm, and 0.19 nm in the high-resolution TEM (HRETM) images are indexed to the (101), and (211) oriented facets of CoSe$_2$ nanoparticles. The inserted figure od selected area electron diffraction show the polycrystalline nature of the CoSe$_2$ nanoparticles. To porosity of the nanocomposites were further characterized using the nitrogen adsorption-desorption isotherm and the curves were illustrated in figure 4(a).

It was noticed that all the nanocomposites show type-IV hysteresis loops and demonstrating the mesoporous structure (Alshehri et al., 2017; Alshehri et al., 2016; Vinu et al., 2018). In the case of the CoSe$_2$@NGN-15, the hysteresis loops were observed from 0.40 to 0.99 and the specific surface area was found to be 421.0 m$^2$/g, while for CoSe$_2$@NGN-5, CoSe$_2$@NGN-10, CoSe$_2$@NGN-20 the surface area was found to be 440.2, 436.4 and 414.12 m$^2$/g respectively. These results demonstrate that the surface area of the nanocomposites were increased with increasing the contents of NGN into the electrode materials.

Figure 4(b) show the pore size diameter was observed about in the range of 20-67 nm in the case of all the nanocomposites. The large surface area and nanoscale pore size of the CoSe$_2$@NGN based electrode materials not only support the additional catalytic sites but also enhance the electron transfer during the I$_3^−$ reduction. The elemental composition and the valance state of the elements present in the nanocomposite as monitored by XPS analysis, as shown in figure 5(a), the XPS spectra of CoSe$_2$@NGN-15 show the presence of C, N, Co, Se and O into the nanocomposite. As shown in figure 5(b), the C 1s peak was deconvoluted into four peaks and centered at at 284.68, 285.71, 286.90 and 287.78 eV and assigned to the C-C, C-N, C=N, and O=C-O function groups presence into the NGN matrix.

The N1s spectra of the nanocomposites was split into three peaks and show the binding energy at into 398.24, 400.36, and 401.43 eV, corresponding to pyridinic, pyrrolic/pyridonic, and graphitic nitrogen functional groups respectively as shown in figure 5(c) (Ahamad et al., 2020b; Khalaf et al., 2020). The XPS peak of Co 2p was deconvoluted into four characteristic peaks as shown in figure 5(d), two of them are the main peaks and the binding energy centered at 778.71 and 793.89 eV corresponding to the Co 2p$_{3/2}$ and Co 2p$_{1/2}$, respectively, and other two peaks were observed at binding energy 780.23 and 796.91 eV are assigned to the satellite peaks of Co 2p$_{3/2}$ and Co 2p$_{1/2}$ respectively. Figure 5(e), shows the XPS spectrum of Se 3d and the main peak was split into two peaks and centered at 54.74 and 55.83 eV and assigned to Se 3d$_{3/2}$ and Se 3d$_{5/2}$ respectively (Liu et al., 2016). The XPS results shows that the O atoms also present into the matrix and the O 1 s spectrum was deconvoluted into binding energies of 530.44, and 531.88 eV and assigned to the presence of C-O and Se-O bonds respectively.
Photovoltaic Performance

The DSSC was fabricated as sandwich structure using the the N719 dye-loaded TiO$_2$ as a photo-anode, an iodine solution ($I_3^−/I^-)$ as an electrolyte, and CoSe$_2$@NGN (or Pt) as a counter electrode. The current density voltage curve (J–V) of the fabricated DSSCs using CoSe$_2$@NGN-5, CoSe$_2$@NGN-10, CoSe$_2$@NGN-15, and CoSe$_2$@NGN-20 and Pt under 100 mW/cm$^2$ AM 1.5 G are illustrated in figure 6(a). The values of photovoltaic factors including short circuit current density ($J_{sc}$), open circuit voltage ($V_{oc}$), filling factor (FF) and maximum power ($P_{max}$) are summarized in table-1. It was observed that DSSC fabricated using CoSe$_2$@NGN-15, show excellent photovoltaic performance than other electrode materials prepared in this study. The short-circuit photocurrent ($J_{sc}$) of DSSC fabricated using CoSe$_2$@NGN-15 CE was found to be 15.40 mA/cm$^2$, higher than that of CoSe$_2$@NGN-5 (13.58 mA/cm$^2$), CoSe$_2$@NGN-10 (14.21 mA/cm$^2$), and CoSe$_2$@NGN-20 (15.10 mA/cm$^2$), even outperforming that of Pt CEs (14.56 mA/cm$^2$). The higher value of the $J_{sc}$ is help to boost the reduction of $I_3^-$ and dye regeneration (Niu et al., 2018; Wang, Q. et al., 2019). The open-circuit voltage ($V_{oc}$), fill factor (FF) and the PCE was found to be 0.74 V, 66.45% and 7.65% respectively for CoSe$_2$@NGN-15, while these values were obtained about to 0.74, 66.10%, 7.19% with Pt counter electrode. The excellent performance of CoSe$_2$@NGN-15 can be attributed due to the synergetic effect between CoSe$_2$ nanoparticles and NGN matrix, because the NGN matrix has excellent conductivity and the uniformly dispersed CoSe$_2$ nanoparticles provide excellent catalytic activity for $I_3^-$ reduction.

Table 1: PCE values and relevant parameters of the different CEs

| Counter Electrode | $J_{sc}$ (mA cm$^{-2}$) | $V_{oc}$ (V) | FF (%) | PCE (%) |
|-------------------|-------------------------|--------------|--------|---------|
| CoSe$_2$@NGN-5    | 13.58                   | 0.731        | 66.73  | 6.62    |
| CoSe$_2$@NGN-10   | 14.21                   | 0.755        | 67.77  | 7.27    |
| CoSe$_2$@NGN-15   | 15.40                   | 0.745        | 66.66  | 7.65    |
| CoSe$_2$@NGN-20   | 15.10                   | 0.757        | 64.32  | 7.35    |
| Pt                | 14.56                   | 0.746        | 66.10  | 7.19    |

Moreover, the CoSe$_2$@NGN-15 nanocomposite has proper distribution as well as as greater the specific surface area of the counter electrode, and the higher the catalytic activity, and the better the photovoltaic performance of DSSC. On the other hand, the nanocomposites CoSe$_2$@NGN-5 and CoSe$_2$@NGN-10 show the DSSC performance lower than that of Pt. Based on the above results the proposed photovoltaic mechanism of the CoSe$_2$@NGN-5 CE is illustrated in Figure 7.

Electrochemical Performance Of Ce Materials
The relationship between the photoelectric conversion efficiency of the fabricated DSSC with the counter electrode was further carried out using CV, EIS and Tafel plots. As shown in figure 8(a), the cyclic voltammetry cure of the DSSC fabricated using CoSe\textsubscript{2}@NGN-5, CoSe\textsubscript{2}@NGN-10, CoSe\textsubscript{2}@NGN-15, and CoSe\textsubscript{2}@NGN-20 and Pt show the peaks due to the redox reaction of I\textsubscript{3}\textsuperscript{-} as: \( I\textsubscript{3}^- + 2e^- \rightarrow 3I^- \) (i) and \( 3I_2 + 2e^- \rightarrow 2I_3^- \) (ii). It was noticed that the current density (J) and the potential (\( \Delta E_{pp} \)) difference between the two peaks are important factors for comparing the catalytic activity of different CE materials. It was observed that the CE based on CoSe\textsubscript{2}@NGN-15 nanocomposite show higher current density and lower peaks difference than these of Pt, indicating that CoSe\textsubscript{2}@NGN-15 has superior catalytic ability than Pt for I\textsubscript{3}\textsuperscript{-} reduction (Kavan et al., 2011; Swami et al., 2015). The stability experiment was carried out using CV cycles as shown in figure 8(b), and the outcomes revealed that after 50 cycles on 50 mV/sec scan rate, the current density, peak positions and \( E_{pp} \) value is substantially unchanged, indicating CoSe\textsubscript{2}@NGN-15 having excellent electrochemical stability.

The electrocatalytic activity of the CoSe\textsubscript{2}@NGN-5, CoSe\textsubscript{2}@NGN-10, CoSe\textsubscript{2}@NGN-15, and CoSe\textsubscript{2}@NGN-20 and Pt electrode were further determine using the Tafel polarization curves as illustrated in figure 8(c). All the Tafel polarization plots were divided into three zones, first the polarization zone occurs due to the electrochemical reaction and noticed at low over potential (\(|V| < 120\text{ mV}\)), in the second zone is sharp slope is and it is Tafel zone, in which, the current density (\( J_o \)) is changed and noticed at moderate over-potentials (120 mV < \(|V| < 400\text{ mV}\)), third is the limiting diffusion zone, which depend on the transport of ions and occurs at high over-potential (\(|V| > 400\text{ mV}\)), and used to determine the limiting diffusion current density (\( J_{lim} \)). The value of of \( J_o \) and \( J_{lim} \) related to the catalytic activity of the counter electrode. As shown in figure 8(c), it has been noticed that CoSe\textsubscript{2}@NGN-15 has a higher value of \( J_o \) as compared to Pt based CE, resulting shown higher catalytic activity towards I\textsubscript{3}\textsuperscript{-} reduction, and the higher \( J_{lim} \) value of CoSe\textsubscript{2}@NGN-15, indicate that CoSe\textsubscript{2}@NGN-15 based CE has a faster ion diffusion rate than standard Pt CE (Roy-Mayhew et al., 2010). The electrochemical impedance spectroscopy (EIS) measurements of the DSSC fabricated using CoSe\textsubscript{2}@NGN-5, CoSe\textsubscript{2}@NGN-10, CoSe\textsubscript{2}@NGN-15, and CoSe\textsubscript{2}@NGN-20 and Pt based CE is illustrated in figure 8(d). The EIS results used to determine various resistances, charge-transfer between the interface of electrode/electrolyte and the catalytic efficiency of the counter electrode.

The EIS Nyquist plots, show three semicircles, the \( R_s \) is represent to resistance between the FTO and CE materials, the \( R_{ct-1} \) is representing to the charge transfer resistance between the electrolyte and CEs and the \( R_{ct-2} \) represents the electron transfer resistance between the TiO\textsubscript{2}/electrolyte and the dye. It was noticed that in all the Nyquist plots the value of \( R_{ct-2} \) is unchanged and almost similar, these results may have been due to the use of similar type photoanode materials. While the value of \( R_s \) and \( R_{ct-1} \) was changed. The results reveal that CoSe\textsubscript{2}@NGN-15 show almost similar value of \( R_s \) to the Pt and support that these is a good connection between the FTO glass and the electrode materials. While the \( R_{ct-1} \) value of CoSe\textsubscript{2}@NGN-15 was found to be lower, than that of other electrodes even lower than that of Pt based CE. On the other hand, it was noticed that the the CoSe\textsubscript{2}@NGN-15 nanocomposite show lower value of
Nernst diffusion impedance ($Z_w$) than the Pt base CE for diffusion of $I^-/I_3^-$ redox couple within the electrolyte (Kavan et al., 2011; Swami et al., 2015). This may be due to the existence of active site to contact with the electrolyte without any hindrances and resulting show excellent photoelectric conversion efficiency in the fabricated DSSC.

**Conclusion**

Sustainability has been the focus of researcher vision; therefore, we have fabricated novel counter electrode materials for DSSC using CoSe$_2$ nanoparticles embedded into NGN. The fabricated nanocomposites CoSe$_2$@NGN were characterized using several analytical techniques. The experimental results show that the CoSe$_2$@NGN electrode has excellent catalytic activity. Among them, the DSSC assembled by CoSe$_2$@NGN-15 obtains 7.65% PCE, which is higher than that of the DSSC assembled with Pt electrode (7.19%). The influence of different film thickness on the photovoltaic performance of DSSC was studied and discussed in depth. The excellent performance of CoSe$_2$@NGN-15 is attributed due to the synergetic effect of CoSe$_2$ nanoparticles and N-doped graphene matrix, because the N-doped graphene exhibit excellent conductivity and uniformly dispersed CoSe$_2$ which boost the catalytic activity of the nanocomposites. The preparation of this new type of non-Pt material provides a new method for DSSCs counter electrode research and promotes its industrialization process to utilised the sustainable solar energy for the benefit of humans.

**Declarations**

6. **Acknowledgement**

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Figures

Figure 1

The synthesis routes for N-doped graphene and CoSe$_2$@NGN nanocomposite
Figure 2

(a) FTIR spectra and (b) TGA curves (c) XRD spectra of CoSe$_2$@NGNs and (d) Raman spectra of CoSe$_2$@NGNs-15

Figure 3

(a) SEM image of CoSe$_2$@NGNs-15 (b) TEM image of CoSe$_2$@NGNs-15 (c) HRTEM image of CoSe$_2$@NGNs-15; and (d) HRTEM image and SAED of CoSe$_2$@NGNs-15
Figure 4

(a): \( N_2 \) adsorption and desorption isotherm (b) Pore size distribution of the nanocomposites

Figure 5

(a) A wide XPS spectra for the CoSe\(_2@\)NGNs-15 nanocomposites (b) C1s, (c) N1s (d) Co2p (e) Se3d and (f) O1s

Figure 6

(a) \( J\)-\( V \) curve and (b) IPCE curve of DSSC with CoSe\(_2@\)NGN and Pt as the counter electrode

Figure 7
(a) Schematic diagram of dye-sensitized solar cell (DSSC) assembly

Figure 8

(a) Cyclic voltammetry (CV) curves (b) Stability test at scan rate of 50 mv/sec (c) Tafel polarization curves (d) Nyquist EIS plots of DSSC cells with different CEs.

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