CoSe$_2$/graphene composite: a low-cost, high performance counter electrode for dye sensitized solar cells

C. Tamilselvi$^1$, P. Duraisamy$^{1*}$, N. Subathra$^1$, T. Sumathi$^2$, Sonia R Fredrick$^2$

$^1$PG and Research Department of Physics, Thiruvalluvar Government Arts College, Rasipuram-637401, Tamil Nadu, India
$^2$Department of Physics, Padmavani Arts and Science College for Women, Salem-636011, Tamilnadu, India

Abstract. In this study, Pt-free dye-sensitized solar cells (DSSCs) were fabricated using cobalt selenide (CoSe$_2$)/graphene sheets using facile hydrothermal technique. The Pt free counter electrode (CE) was systematically investigated their physico-chemical properties by using SEM, TEM, XRD, Raman, UV, PL, XPS and BET analysis. Under typical AM 1.5G illumination, the DSSC based on the CoSe$_2$ counter electrode achieves a maximum PCE of 12.2 % (Jsc = 22.3 mA/cm$^2$, Voc= 810 mV, and FF= 0.71), which is 5.8 times higher than that of conventional Pt-based DSSC. The improved electro catalytic activity and photo conversion efficiency of the CoSe$_2$/graphene CE is due to prevent the recombination of electron-hole pair and extended the visible light absorption of composite samples.

1. INTRODUCTION

For the past 30 years, dye-sensitized solar cells (DSSCs) have been considered an acceptable option for producing electricity by converting solar energy due to its low cost, comparatively high photoconversion efficiency (PCE), and eco - friendliness [1, 2]. A photoanode, electrolytes, and CE are arranged in a sandwiches template in a regular DSSC [3]. By sharing electrons with the outside circuit to electrolytes and promoting the reducing agent, CEs play a vital role in the photovoltaic efficiency of DSSCs [4]. Because of its exceptional catalytic properties and electrocatalytic activity, Pt CE has been dubbed "state-of-the-art CE." Regrettably, the noble metal Pt's high cost and rarity prevent its popular use in DSSCs [5]. As a result, low-cost Pt-free CE materials with high electrocatalytic performance are critical. Carbonaceous content [6], polymers [7, 8], and transition metal sulfide and oxides [9-11] are examples of elective CE materials based on earth-abundant and reasonable elements. Due to their high active sites, good combinatorial impact, and geometric structure, transition metal inert ingredients hybrid materials with excellent catalytic activity and stability have been identified as one of the finest substitutes for Pt CE up to now. Nevertheless, the absence of strong contact, adequate active site exposure, and uniform distribution for these hybrid materials of the simple recombine mode has become the primary stumbling block to high efficiency. Transition metal selenides (TMSs) have been proven to be extremely productive because to their exceptional semiconductor characteristics, electro catalytic activity, solar effects, and nonlinear optical features [12-15]. And then, electron diffusion at the CE/electrolyte interface is a big issue due to the material's low conductivity [16]. In this way the combination of CoSe$_2$ with Graphene in the form of CoSe$_2$/graphene composite benefits by incorporating the electrical conductivity of CoSe$_2$ into a single CE material, which is high in graphene and high electrochemical activity [17-21]. As a counter electrode, we present a low temperature hydrothermally induced CoSe$_2$/graphene hybrid composite. As graphene is added to bare CoSe$_2$, its electrocatalytic and photovoltaic performance improves. The
high conductivity, porous structure, and rapid electrolyte species diffusion mechanism of graphene can account for this.

2. EXPERIMENTAL

2.1. Synthesis of pristine CoSe₂ and CoSe₂/graphene nanocomposites
A one-step hydrothermal process was used to make the CoSe₂/graphene nanocomposites. In a nutshell, 0.48 g Se powder (99.99 percent, Sigma Aldrich) was dissolved in 40 mL NaOH aqueous suspension (6 g, > 99.5 percent, Aladding). After that, significant concentrations of synthesised GO (0.25, 0.5, and 1 g) were introduced to the NaOH aqueous, and the liquid was incubated for 30 minutes before being labelled as solution A. The combination was then marked as solution B after 0.95 g Co(NO₃)₂•6H₂O (99.99 percent, Sigma Aldrich) was diluted in 20 mL of 0.25M EDTA-2Na (> 99.999 percent, Aladding). To make a homogenous solution, the two solutions were combined in a 100 mL Teflon walled autoclave and agitated for 0.5 hour. The autoclave was completely sealed and heated to 180°C for 12 hours. The precipitate was centrifuged and rinsed with ethanol at least five times before being processed in a vacuum oven at 80 °C for 12 hours. CoSe₂/G-0.25, CoSe₂/G-0.5, and CoSe₂/G-1 have been the names of the final products that included 0.25, 0.5, and 1 g GO, respectfully.

3. RESULTS AND DISCUSSION

3.1. Powder X-ray diffraction (XRD) analysis

![Figure 1. XRD pattern of the samples](image)

Figure 1 shows a sharp peak at 24.1°, which belongs to the (002) plane of graphene after the hydrothermal exfoliation phase. The pristine CoSe₂ exhibits a orthorhombic structure of CoSe₂ (JCPDS card no. 53-0449) [22]. There is no contaminant peak, indicating that the synthesized samples were of very high purity. As compared to pure CoSe₂, the diffraction of the composite sample becomes higher. This may be attributed to the composite samples have high crystalline nature. The crystalline nature of the composite samples were further confirmed their average grain size, which is
measured Scherrer's formula [23]. The average crystalline size of was found to be 12.5±0.5, 16.5±0.5, 22.45±0.5, and 31.45±0.5 nm for graphene, CoSe$_2$/G-0.25, CoSe$_2$/G-0.5, and CoSe$_2$/G-1, respectively.

3.2. Morphological analysis
SEM representations of bare graphene, CoSe$_2$, and CoSe$_2$/G-1 samples are seen in Figure 2 (a-c). The photographs clearly display the 2D structure of graphene nanosheets as well as a spherical CoSe$_2$ nanoparticle randomly scattered on the 2D graphene nanosheets in the composite samples. Furthermore, the visible wrinkles and folds exposed the versatility of graphene nanosheets in the TEM picture of pristine graphene (Fig. 2(d)). CoSe$_2$ nanoparticles with a small size distribution in the range of 10 - 30 nm uniformly decorated the 2D graphene sheet surface (Fig. 2(f)), as seen in the TEM illustration in Fig. 2(e). The interatomic distances of the lattice fringes are 0.282 nm and 0.243 nm, respectively, in the HRTEM picture of the CoSe$_2$/G-1 sample (Fig. 2 (g)), which can be indexed to the (111) plane orthorhombic configuration of CoSe$_2$ and (002) plane of graphene. The proper amount of Co and Se elements in the CoSe$_2$/G-1 composite samples was verified by EDX elemental mapping in Fig. 2 (h) and (i).

Figure 2. SEM images of (a) graphene; (b) CoSe$_2$; (c) CoSe$_2$/G-1; TEM images of (d) graphene; (e) CoSe$_2$; (f) CoSe$_2$/G-1; HRTEM image of (g) CoSe$_2$/G-1; (f) EDAX spectra of CoSe$_2$/G-1

3.3. Raman spectra analysis
The Raman spectra of pure CoSe$_2$ and graphene composite samples are seen in Figure 3. The two Raman modes of pure graphene are localized at 13561 cm$^{-1}$ and 1591 cm$^{-1}$, respectively, which refer to the D and G bands of graphene. The graphene sample's D and G bands are caused by sp3-hybridized carbon [23]. In pristine CoSe$_2$, there are two peaks at 480 and 640 cm$^{-1}$, which may be due to the orthorhombic crystalline of CoSe$_2$ [24, 25]. CoSe$_2$ and graphene are visible in the composite samples, indicating that CoSe$_2$ has been directly integrated into the 2D graphene network. CoSe$_2$/G-1 had a somewhat higher ID/IG value (0.93) than bare graphene (0.83), indicating that carbonaceous materials had more defects or edges introduced.
3.4. UV-Vis DRS analysis

Figure 4 a) shows the UV-Vis absorption spectra of the synthesized materials (a). The absorption of bare CoSe$_2$ was detected at 430 nm, and graphene migrated it to the higher wavelength edge in composite samples. The fact that minimizing the band gap energy of the composite samples shortens the band gap energy. The band gap energy (E$_g$) of the samples was calculated by Tauc relation [26]. The estimated band gap energies are 1.85, 1.75, 1.61 and 1.51 eV for CoSe$_2$, CoSe$_2$/G-0.25, CoSe$_2$/G-0.5, and CoSe$_2$/G-1, respectively (Fig. 4 (b)). For improving the PCE of the DSSC, a substantial reduction in the band gap and prolonged abortion potential in the visible light area of the composite sample would be beneficial.
3.5. Photoluminescence spectra analysis

Figure 5. Photoluminescence spectra of the electrode samples

Figure 5 PL spectra of samples of wavelengths ranging from 400 to 700 nm. At 1.91 eV, the band in the red area is easily identifiable. This agrees quite well with the absorption value calculated from the UV results previously described. This emission band occurs due to the band-to-band transition for indirect CoSe₂ transition. The emission rate seemed to decrease even further as the graphene loaded material increased. The composite sample's lower pressure is due to the absence of electron-hole pair injection, which allows the DSSC's PCE to develop.

3.6. N₂ adsorption and desorption analysis

Figure 6. (a) N₂ adsorption and desorption and (b) pore size curve

The N₂ adsorption-desorption and pore size distribution of graphene, CoSe₂, and CoSe₂/G-1 samples as shown in Figures 6 (a) and (b), respectively. The isotherm specifically shows the samples'
mesoporous origin due to the type IV isotherm and H3 magnetization loop [27, 28]. Based on the BET and BJH curves, the estimated surface area and pore diameter of CoSe₂/G-1 sample is 95.6 m²/g and 38.6 nm. These values are quite higher than the other samples such as graphene (67.3 m²/g and 21.4 nm.) and CoSe₂ (48.6 m²/g and 16.5 nm.). The high surface area and unusual porous design of the composite sample assisted the close contact between CoSe₂ and graphene and liquid electrolyte, as well as the diffusion of I₃⁻ [29].

3.7. XPS analysis

Figure 7. XPS spectra of CoSe₂/G-1 sample (a) survey; (b) C 1s; (c) Co 2p; (d) Se 3d.

Figure 7 (a) shows the wide range spectra of CoSe₂/G-1 sample. The survey spectra display the presence of major elements such as C, Co and Se. In the high resolution spectrum of C 1s, the peaks at 284.4 eV, 285.8 eV, and 288.5 eV were corresponding to C-C, C-O and C=O configurations, respectively (Fig. 7 (b)). In Co 2p high resolution spectra, the the Co2p3/2 and Co2p1/2 related peaks were found with the corresponding BE of 781.5 eV and 793.1 eV, respectively (Fig. 7 (c)). In high-resolution Se 3d spectra (Fig. 7 (d)), two peaks at 54.5 eV and 59.1 eV were ascribed to Se 3d₅/₂ and Se 3d₃/₂ [30, 31].

3.8. Photovoltaic characteristics

Figure 8 (a) depicts the DSSC unit construction schematically. The functional surface area of the solar cell is 4 x 4 mm². The J-V curves of distinct solar cells have been monitored on a CHI660E electrochemical work desk under projected solar light from a xenon arc lamp with a brightness controlled to 100mWcm⁻². Figure 8 (b) shows the photovoltaic output of the fabricated DSSC with Pt, CoSe₂, and various CoSe₂/G composite CE. The J-V parameters are summarized in Table 1. CoSe₂/G-1 CE delivered a maximum PCE of 12.2%, Figure 8c) depicts the IPCE. The CoSe₂/G-1 DSSC curve is greater than that of Pt and other CE products between 400 and 750 nm, with an 88 % at 530 nm, according to the spectral. The CoSe₂/G-1 DSSC’s higher IPCE value can be attributed to the DSSC’s
higher Jsc value, which is in line with J-V curve efficiency. Stability is one of the most important factors to remember when using practical software implementations. As a result, the PCE was tested for 60 days under the same experimental conditions with a 10-day standard cycle to show long-term durability. Figure 8 (d) depicts the stability graph. The results indicate that at the end of the 60-day tracking period, there was just a marginal increase in PCE %. As a result, the fabricate CE is a reliable material that can replace Pt as the effective CE of a DSSC.

Figure 8. (a) DSSC schematic; (b) J-V plot; (c) IPCE spectra; (d) stability test

Figure 9 a) shows the CV curves of Pt, CoSe₂, and various CoSe₂/G composite CE. All of the CEs' CV curves are identical, indicating that the prepared CEs have equal electrocatalytic function. Despite this, the CoSe₂/G-1 CE has a improved catalytic activity and lower over potential to minimize I₃⁻ to I⁻. According to the findings, the CoSe₂/G-1 CE has marginally greater J₀ and Jlim than the Pt CE, suggesting improved catalytic activity and electron diffusion potential (Fig. 9b) [32, 33].
Table 1. Photovoltaic parameters

| Parameters | Pt   | CoSe₂ | CoSe₂/G-0.25 | CoSe₂/G-0.5 | CoSe₂/G-1 |
|------------|------|--------|--------------|-------------|-----------|
| Jsc (mA/cm²) | 8.8  | 10.5   | 14.2         | 16.3        | 22.3      |
| Voc (mV)    | 610  | 651    | 681          | 710         | 810       |
| Fill Factor | 48   | 50     | 61           | 63          | 71        |
| Efficiency η (%) | 2.4  | 3.4    | 6.2          | 7.1         | 12.2      |

Table 2. EIS parameters

| Samples       | Rs/Ωcm² | Rct/Ωcm² | r/ns |
|---------------|---------|----------|------|
| CoSe₂         | 9.5     | 30.5     | 154  |
| CoSe₂/G-0.25  | 8.8     | 32.2     | 99   |
| CoSe₂/G-0.5   | 7.5     | 36.3     | 59   |
| CoSe₂/G-1     | 5.1     | 40.1     | 37   |

The charge transfer and mutation processes of the DSSC were further investigated by EIS. Figure 9 (c) shows the Nyquist plot of all the CE samples of equivalent circuit (inset). The identical circuit consists
of two charge transfer resistances (RCT), series resistances (RS), and a constant phase component (CPE). The parameters that were calculated are mentioned in Table 2. CoSe₂/G-1 CE has a higher RCT value than other CEs, according to the results. This finding may be attributed to CoSe₂/G-1 CE's strong electrocatalytic activity for I₃⁻ reduction, as shown by CV and Tafel findings. Figure 9 (d) shows a schematic image of the DSSC's PV reaction mechanism. In comparison to bare Pt and CoSe₂, the overall PV and electrochemical results show that CoSe₂/graphene is more effective. It's possible that this is due to the sun's high absorption strength, which reduces the band gap energy and prevents electron-hole pair coupling. In addition, graphene has the ability to have conductivity, resulting in a high electron transfer rate. When graphene and CoSe₂ are combined, a porous surface with a wide surface area is formed, which is beneficial for electrolyte penetration. As a result, graphene improved the photovoltaic and electrocatalytic properties of bare CoSe₂.

4. CONCLUSION

Finally, CoSe₂/graphene Pt free CE was effectively prepared using a simple hydrothermal method. Using the doctor blade method, a wedge type DSSC was constructed on an FTO substrate. Under typical AM 1.5G irradiation, the DSSC based on the CoSe₂ counter electrode achieves a maximum PCE of 12.2 percent (Jsc = 22.3 mA cm⁻², Voc = 0.81V, and FF = 71 percent), which is 5.8 times better than that of commercial Pt-based DSSC. The CoSe₂/graphene composite CE had stronger catalytic activities for the deletion of triiodide to iodide and better mass transfer resistance at the CE/electrolyte intersection than the other active ingredients, as per CV, EIS and Tafel polarisation measurements. Additionally, the constructed CoSe₂/G-1 electrode exhibited good catalytic efficiency and stability.

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