Efficient One-Step Synthesis of Pt-Free Fe@$NiCo_2S_4$ as a Cost-Effective and High-Performance Counter Electrodes for Dye-Sensitized Solar Cells

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Abstract

Dye-sensitized solar cells (DSSCs) are considered a promising third-generation photovoltaic technology due to their low cost, ease of fabrication, and good performance under low-light conditions. However, the widely distributed application of DSSCs is limited by the use of platinum (Pt) as a counter electrode (CE), owing to its high cost and poor long-term stability in iodide-based electrolytes.

In this study, Fe@$NiCo_2S_4$ was synthesized through a solvothermal method and evaluated as a Pt-free counter electrode in DSSCs. The morphology of the synthesized material was characterized using scanning electron microscopy (SEM) and Energy-dispersive X-ray spectroscopy (EDX)

Among the tested samples, the best-performing device achieved a power conversion efficiency (PCE) of 8.5% and average is 7.4%, significantly outperforming the Pt-based reference cells 7.19% tested under identical conditions. Initial 5-day stability tests indicated no significant drop in efficiency, demonstrating electrochemical and sample stability.

These results suggest that Fe@$NiCo_2S_4$ is a cost-effective and high-performance alternative to Pt, with strong potential for practical application in next-generation DSSC counter electrodes.

1. Introduction

The global push towards sustainable energy solutions has placed dye-sensitized solar cells (DSSCs) as a central topic in photovoltaic research due to their low production cost, facile fabrication, and high-performance under diffuse light conditions. A key component in a DSSC is the counter electrode (CE), which catalyzes the reduction of the redox mediator ($I_3^-/3\,I^-$) which involves a two-electron transfer process, (Equation (1) shows the reduction of triiodide to iodide, while Equation (2) describes the oxidation of iodide back to triiodide). and completes the circuit by transferring electrons back into the cell.

$$I_3^- + 2e^- \longrightarrow 3I^- \quad (1)$$

$$3I^- \longrightarrow I_3^- + 2e^- \quad (2)$$

Traditionally, platinum (Pt) films deposited on fluorine-doped tin oxide (FTO) glass serve this purpose, offering excellent conductivity and catalytic activity. However, the high cost of platinum and its limited natural reserves hinder the large-scale deployment of DSSC technology. Despite its high efficiency, Pt's widespread adoption is hindered by its high cost, limited natural reserves, susceptibility to corrosion in iodide-based electrolytes, and incompatibility with flexible substrates. These limitations motivate the search for low-cost and chemically stable alternatives.

Recent studies have explored inorganic alternatives to platinum for CE in DSSCs. Among them, Fe@$NiCo_2S_4$, a ternary metal sulfide, has shown potential due to its electrocatalytic activity. These materials combine abundant elements with tunable electronic properties and high chemical stability, making them attractive candidates for cost-effective and high-performance DSSCs.

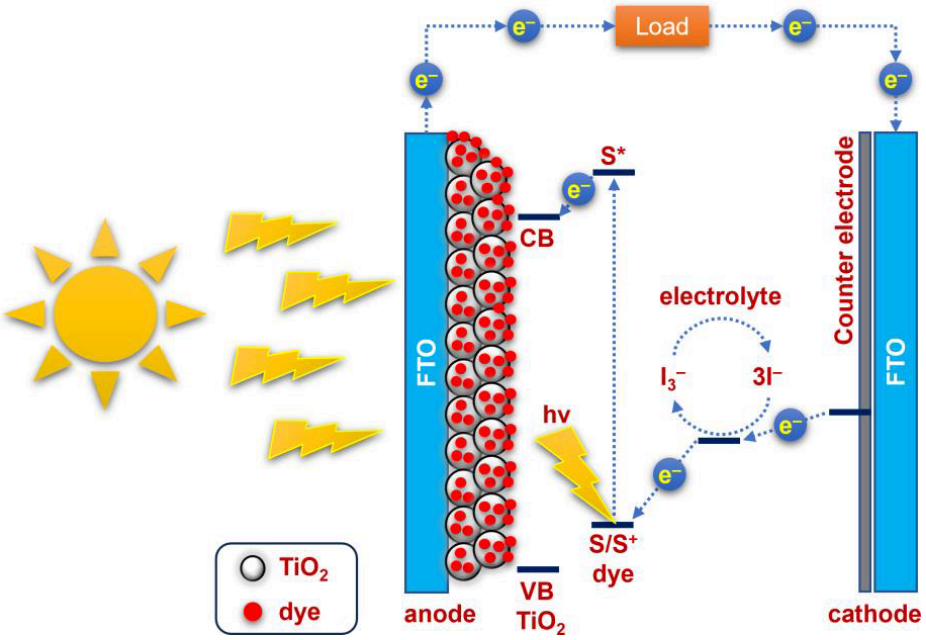


Figure 1. A schematic diagram of the operational principles of DSSC. CB and VB denote the conduction and valence band of the TiO_2, respectively. S/S+ signifies the ground and cationic state dye, and S* represents the excited state of the dye. FTO stands for fluorine-doped SnO_2. (Figure adapted from Efficient One-Step Synthesis of a Pt-Free $Zn_{0.76}Co_{0.24}S$ Counter Electrode for Dye-Sensitized Solar Cells and Its Versatile Application in Photoelectrochromic Devices, MDPI, 2025)

In this project, $Fe@NiCo_2S_4$ was synthesized and characterized as a low-cost and high-performance CE material for DSSCs. This study aims to evaluate whether this material can match or exceed platinum in catalytic performance and device efficiency.

2. Materials and Methods

All chemical reagents and materials are from commercial sources and have been used without further modification unless otherwise noted. Fluorine-doped SnO_2 (FTO) coated glass (7 Ω/sq, 2.2 mm, Sigma Aldrich); light scattering titania paste (Greatcell Solar WER2-O TiO_2 Paste, Sigma-Aldrich); transparent

TiO_2 electrode paste (DN-EP03, Dyenamo); Electrolyte preparation. The composition of a typical LE is as follows: 0.03 M I_2, 0.05 M LiI, 0.10 M Guanidinium Thiocyanate (GuSCN), 0.6 M 1-butyl-3-methylimidazolium iodide (BMII), 0.5 M 4-tert-butylpyridine (tBP) in Acetonitrile (ACN): 3-methoxypropionitrile (MPN) (1:1).

2.1. Synthesis and preparation of Fe@$NiCo_2S_4$ counter electrodes

In this work, a one step solvothermal method is chosen for preparing Fe@$NiCo_2S_4$ nanoflowers. In this procedure, at room temperature 0.2 mmol of $Ni(NO_3)_2 \cdot 6H_2O$, 0.2 mmol of $Fe(NO_3)_2 \cdot 9H_2O$ and 0.4 mmol of $Co(NO_3)_2 \cdot 6H_2O$ were dissolved in 10 mL of deionized water a 30 min to achieve a homogenous solution. Later, 0.8 mmol of thiourea ($SC(NH_2)_2$ was dissolved in 10 mL of ethanol and added in a dropwise manner to the above mixture. After 3 hours of stirring, the final solution was transferred into a 25 mL Teflon-lined stainless autoclave with a vertically positioned fluorine-doped SnO_2 (FTO) glass sealed on 1.5×2cm² and heated at 170 °C for 15 hours. After the indicated time the FTO glasses with Fe@$NiCo_2S_4$ were allowed to cool naturally before rinsing them with deionized water (DI) water, ethanol and drying overnight at 60^{o}C.

2.2. Fabrication of Dye-Sensitized Solar Cells

To prepare for the working electrode, FTO glass slides were initially cleaned with ethanol using sonication for 30 minutes and then dried. A compact TiO_2 layer was subsequently grown on the cleaned FTO by immersing it in a 50 mM titanium (IV) isopropoxide solution in 2 M HCl (such as Figure 2) at 70 °C for 30 min, followed by sintering at 500 °C for another 30 min.



Figure 2. Picture demonstrates mixing the solutions of-Titanium (IV) isopropoxide and HCl transparent solution to form a white suspension.

Next, a transparent TiO_2 paste was applied onto the compact layer using a doctor blade technique,The transparent TiO_2 layer was applied using the doctor blade technique with a blade gap of approximately 1mm leaving a 1 mm margin from the edge of the conductive side of the FTO glass. Two uniform layers were deposited to achieve optimal thickness and surface coverage. Similarly, the scattering TiO_2 layer was applied on top with the same gap and allowed to dry naturally before sintering (such a Figure 3a). Air dried for 30 min, and then subjected to stepwise sintering: 125 °C for 5 min, 325 °C for 10 min, 425 °C for 15 min, and finally 500 °C for 30 min, also view of prepared FTO glasses. After cooling to 70 °C, a scattering TiO_2 layer was applied using the same doctor blading method (Figure 3b). The film was air dried for 1 hour, and the sintering process was repeated.(shown in Figure 4). Once the electrodes cooled to 70 °C, they were immersed in a solution containing 0.25 mM Di-tetrabutylammonium-



Figure 3. Using the doctor blade technique with TiO_2 paste to FTO glasses: (a) transparent TiO_2 paste (b) The central circle should be cut out as in the photo to take the active zone.

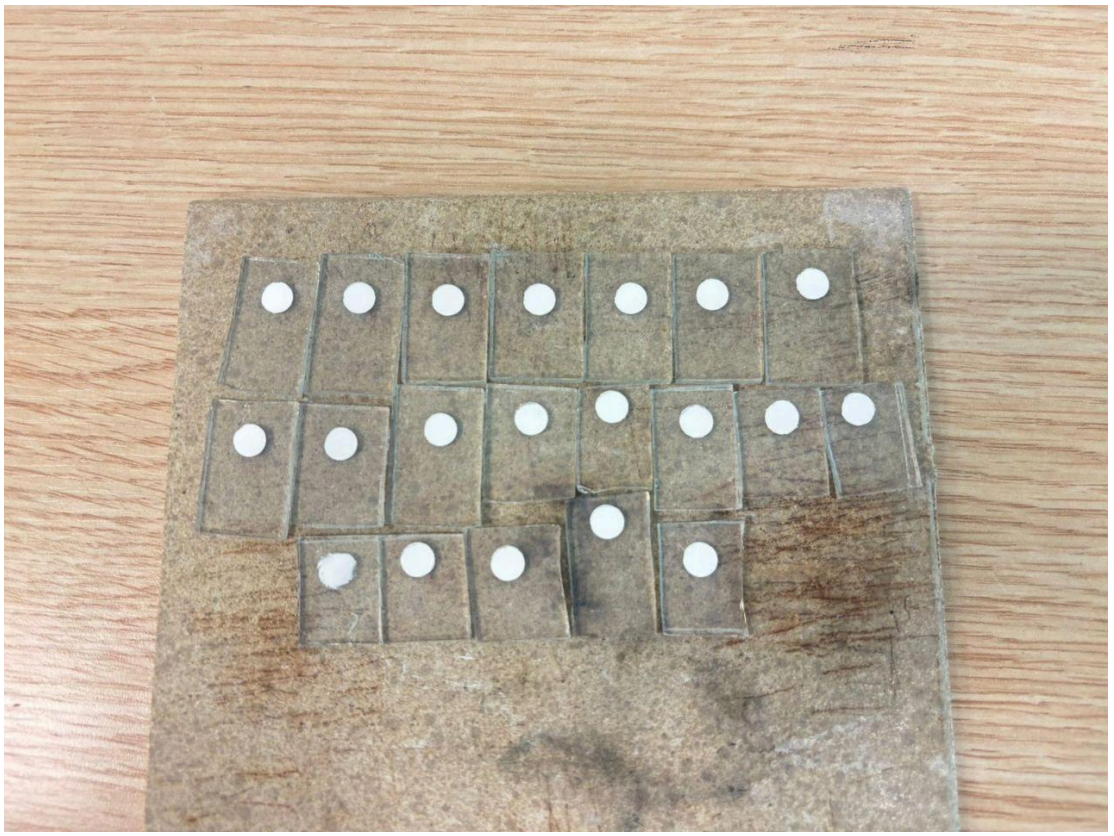


Figure 4. FTO glasses after the oven.

cis-bis isothiocyanato bis (2,2′-bipyridyl-4,4′-dicarboxylato) ruthenium(II) (N719) and 0.75 mM chenodeoxycholic acid (CDCA) dissolved in an acetonitrile:*tert*-butanol (1:1) mixture for 24 hours. Subsequently, the dye-loaded electrodes were gently rinsed with ethanol and dried at 70 °C for 15 minutes. Results of washed FTO glasses (in Figure 5).

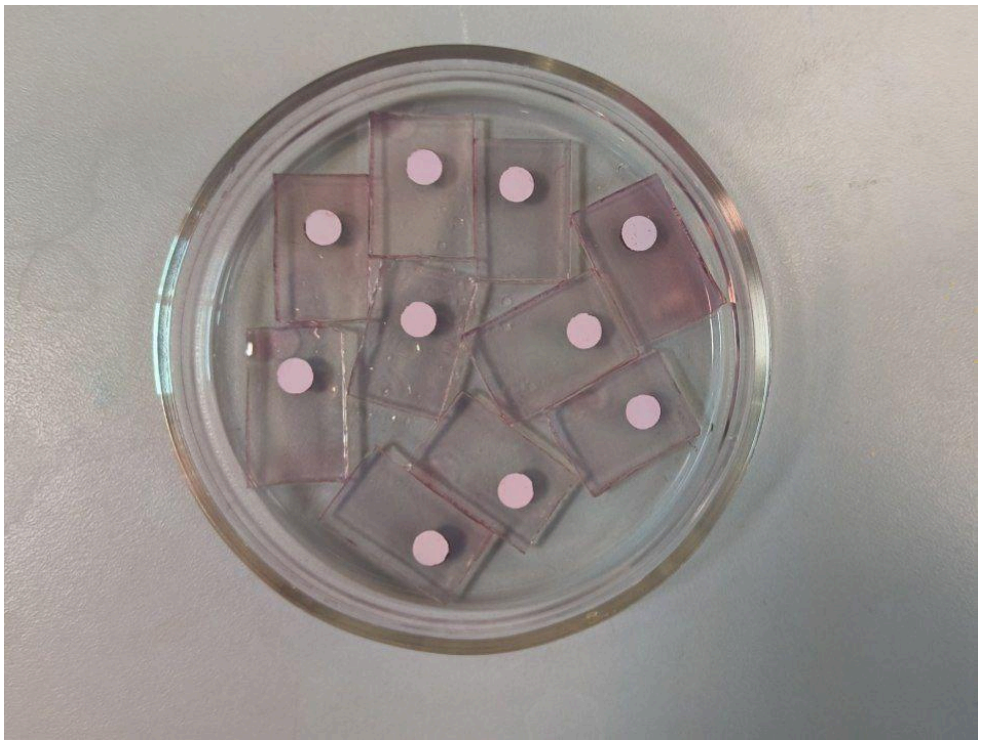


Figure 5. FTO glasses with N719.

For the preparation of the Pt counter electrode, PT-1 Platinum paste was doctor bladed onto clean and dry FTO glass (in Figure 6) and then sintered at 500 °C for 30 min. To assemble the DSSC devices, transparent tape was used to

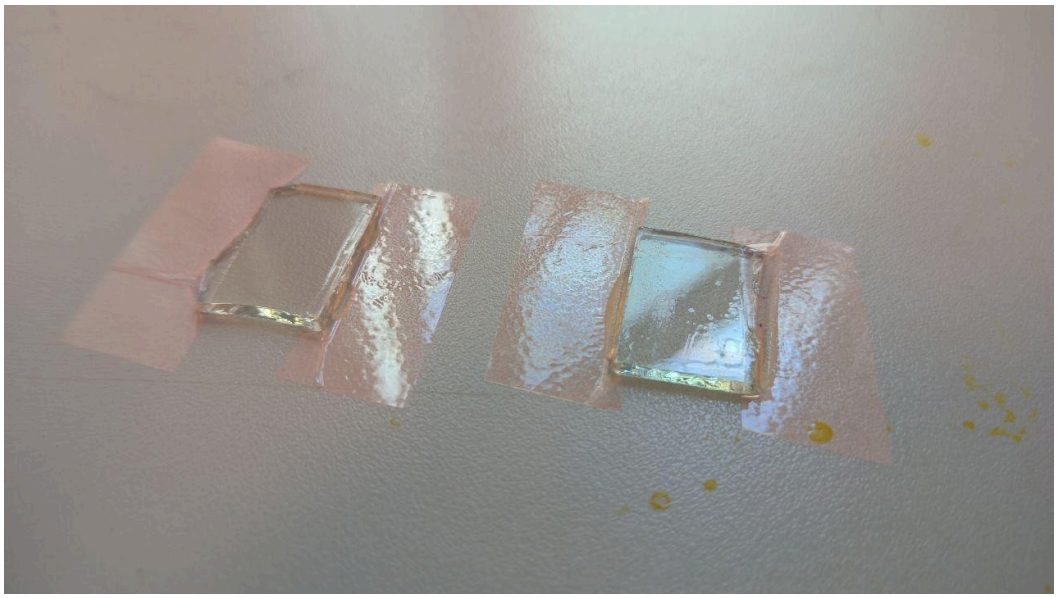


Figure 6. fixed with adhesive tape and applied with Pt paste with doctor blade technique.

define an active area of 1 cm² on the conductive side of the photoanode. The exposed TiO_2 layer was aligned with the counter electrode (CE), also placed with its conductive side facing inward. The two electrodes were sealed using Surlyn film to ensure proper hermeticity, and the $I_3^-/3\ I^-$ electrolyte was injected into the internal space (shown in Figure 7). Liquid electrolyte was introduced into the sealed cell via capillary action, by placing a drop near the open edge of the Surlyn spacer. The electrolyte gradually filled the cell cavity between the photoanode and the counter electrode without applying vacuum or pressure.

Three identical devices of each Pt and Fe@$NiCo_2S_4$ were fabricated following this procedure (as an Figure 8)**.** Each assembled device was placed into the fridge at 3°C and tested every 24 hours over a 5 day period to monitor power conversion efficiency (PCE) stability. Care was taken to ensure full sealing To ensure hermetic sealing, adhesive tape was applied tightly around the edges of the electrodes during assembly. The active area was visually inspected to confirm full contact between the TiO_2 and CE surfaces, and no air gaps or electrolyte leakage were observed. Resistance measurements were also taken before testing to verify consistent electrical contact across all three fabricated samples and reproducibility of contact between layers.

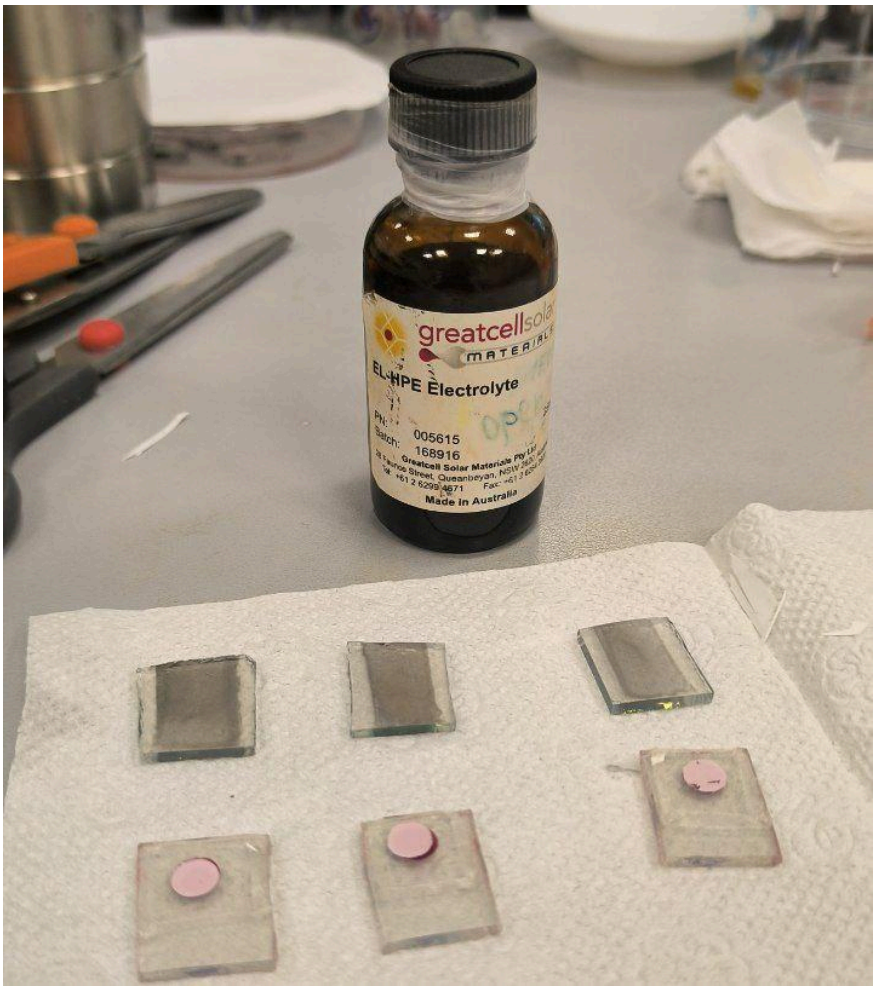


Figure 7. Using the commercial Electrolyte placed with its conductive side facing inward.

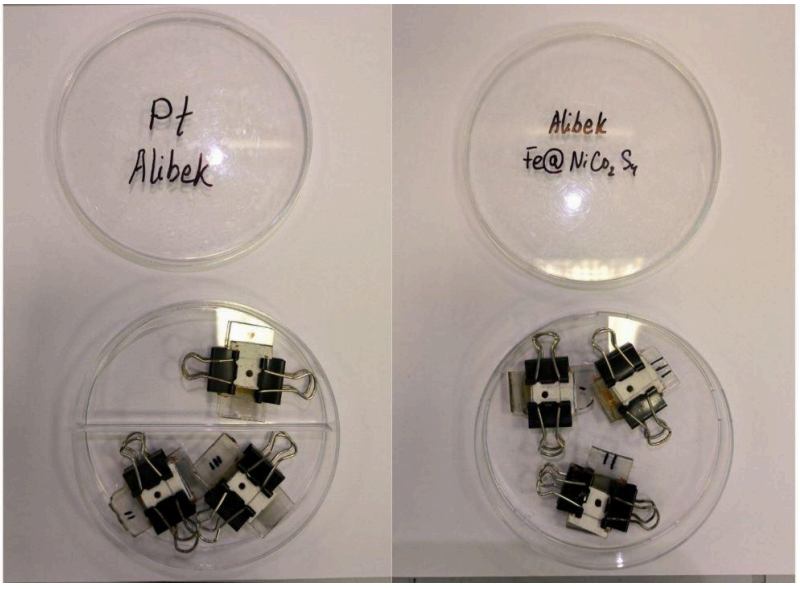


Figure 8. The results of Pt and Fe@$NiCo_2S_4$ CE

3. Results and Discussion

$Fe@NiCo_2S_4$ was synthesized using a one-step solvothermal method as (shown in Figure 9). The precursors of the elements Fe, Ni, Co, and S were taken in suitable molar ratios and exactly dissolved by stirring. Heating the prepared solution at 170°C for 15 hours together with a glass FTO substrate in a Teflon-lined autoclave reactor resulted in the formation of a $Fe@NiCo_2S_4$ coated FTO glasses.

To obtain a comprehensive understanding of the morphological and structure characteristics of the $Fe@NiCo_2S_4$ sample on the FTO , the material was analyzed using scanning electron microscopy (SEM) (in Figure 10a and 10b). The observed morphology provides a high surface area, which is beneficial for catalytic activity at the electrode, electrolyte interface. This structural arrangement likely contributes to the enhanced short-circuit current density (Jsc) observed in the photovoltaic measurements.

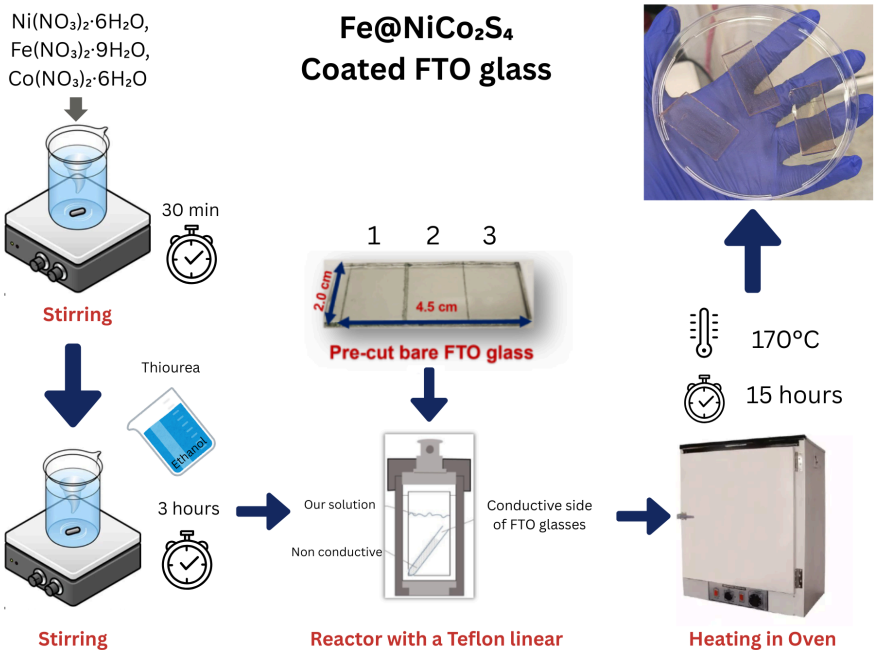
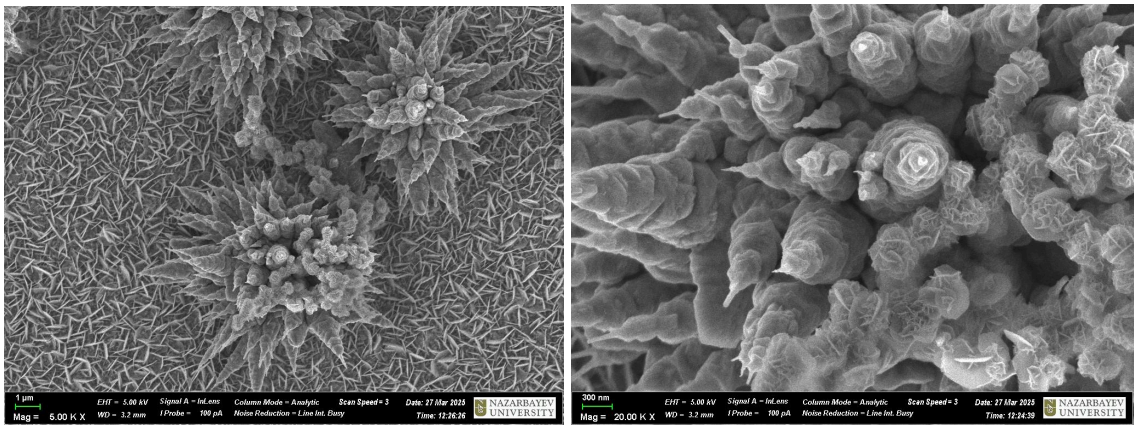


Figure 9. Visual illustration of the one-step synthesis of a $Fe@NiCo_2S_4$ counter electrode on an FTO substrate.

Elemental analysis by energy dispersive X-ray spectroscopy confirms the homogeneous distribution of the elements Fe, Ni, Co, and S in the sample (Figure 11), confirming the formation of $Fe@NiCo_2S_4$ without impurities.Overall, the $Fe@NiCo_2S_4$-based devices demonstrated strong initial efficiency and maintained relatively stable output over the 5-day testing period, suggesting good short-term durability under ambient conditions. These results confirm the material's potential for practical DSSC integration. After cooling, the substrates were rinsed thoroughly with deionized water and ethanol to remove unreacted precursors, then dried at 70 °C overnight. Subsequent SEM analysis (Figure 10) revealed a uniform nanoflower morphology with individual clusters measuring 300 nm in diameter. EDX mapping demonstrated a homogeneous distribution of Fe, Ni, Co, and S across the FTO surface.



(a) (b)

Figure 10. Scanning electron microscope images of the $Fe@NiCo_2S_4$: (a) top view and (b) prosperity perspective.

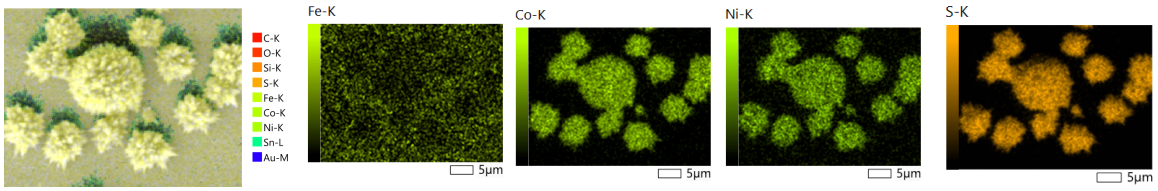


Figure 11. EDX elemental mapping images of $Fe@NiCo_2S_4$.

3.1. Photovoltaic Performance of Fe@$NiCo_2S_4$

The current–voltage (J-V) characteristics of the fabricated DSSC with Fe@$NiCo_2S_4$ and standard Pt CE were measured in order to evaluate and compare their photovoltaic performance (In Figure 12). The electrochemical parameters were received from the results of electrochemical impedance spectroscopy and are shown in Table 1 and Figure 10. Analysis of the cyclic voltammetry data indicates a higher rate of triiodide reduction on the Fe@$NiCo_2S_4$ CE compared to the Pt CE. This accelerated reduction facilitates the formation of iodide species and accelerates the dye regeneration process.

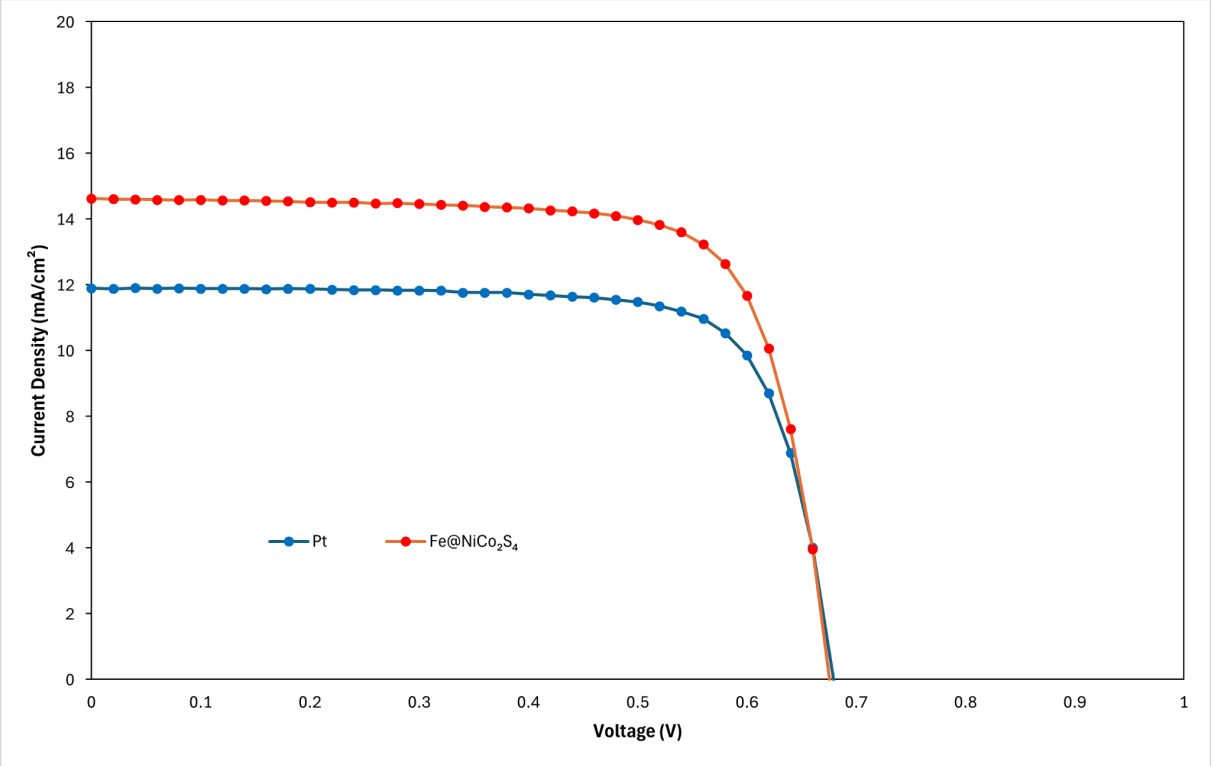


Figure 12. Current density-voltage curves

Basically, work assessed the stability of DSSC devices fabricated with both Fe@$NiCo_2S_4$ and Pt counter electrodes at room temperature.

Table 1. Photovoltaic parameters and electrochemical impedance spectroscopy results of Pt- and $Fe@NiCo_2S_4$ -based CEs

CE	PCE (%)	Voc (V)	Jsc (mA^2/cm^2)	FF (%)
$Fe@NiCo_2S_4$	7,41	0,69	14,63	74
Pt	6,15	0,68	11,9	76,5

Photovoltaic parameters were periodically monitored for up to 120 hours or 5 days (Figure 13).

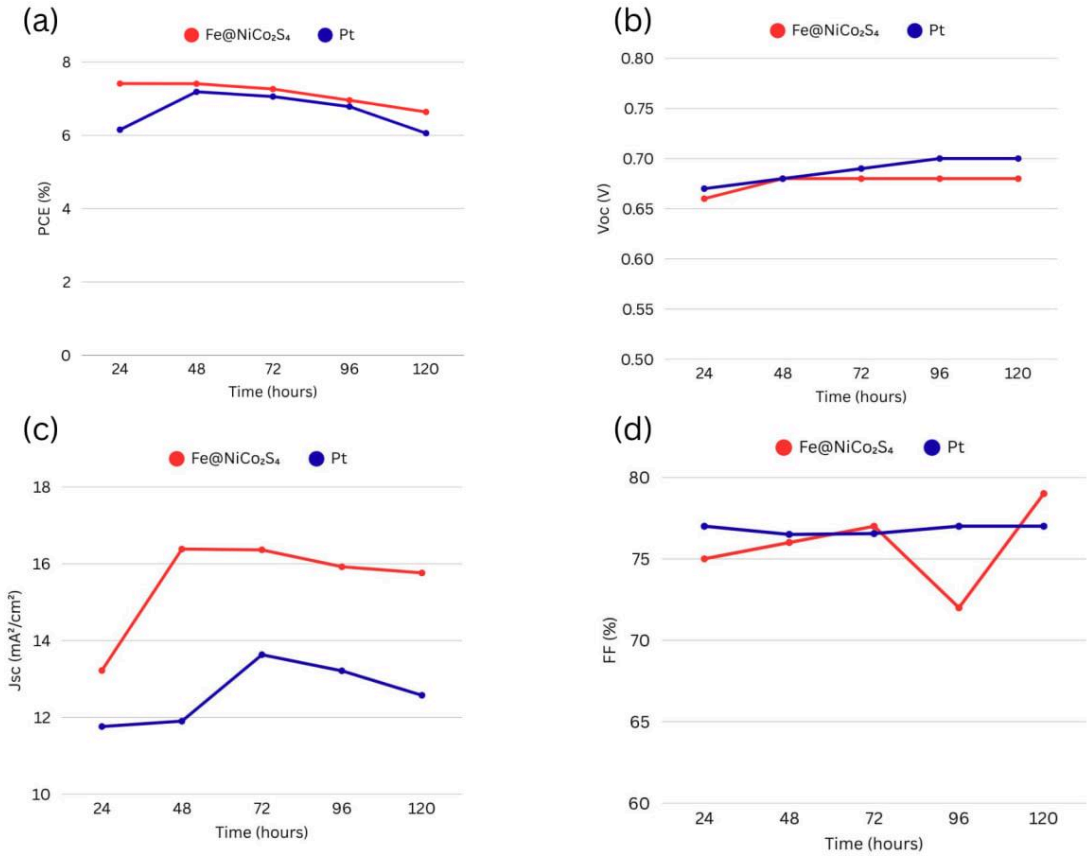


Figure 13. Photovoltaic stability of the different CEs used in DSSCs. (a) It is shown how the efficiency (PCE) has changed over time. (b) This is a graph of the voltage in an open circuit (Voc). (c) Current density graph (d) The fill factor (FF) fluctuated.

The observed Jsc, Voc, FF and PCE values recorded by average value of data. The PCE of $Fe@NiCo_2S_4$ reached a maximum of 7.41% at 24 and 48 hours and

stayed above 6.5% even after 5 days. After 24 h, the PCE was 7.41%; after 72 h, it slightly decreased to 6.9%; and after 120 h it remained at 6.955%, while the standard Pt-based device showed a final efficiency of 6.78%, demonstrating the superior stability of the Fe@$NiCo_2S_4$-based DSSC. Also, the Jsc values were higher for Fe@$NiCo_2S_4$, showing better electron flow. Voc values were close, but Pt was slightly higher at the end. The fill factor (FF) changed more for Fe@$NiCo_2S_4$ but recovered after 96 hours. These results indicate that Fe@$NiCo_2S_4$ not only enhances the initial efficiency but also support relatively good stability, making it a strong candidate for replacing Pt CE in cost-effective and durable DSSCs.

4. Conclusion

In summary, Fe@$NiCo_2S_4$ was successfully synthesized using a one-step solvothermal method and tested as a Pt-free counter electrode in DSSCs. The best-performing Fe@$NiCo_2S_4$-based DSSC achieved a PCE of 8.5%, with an average PCE of 7.4% (± 0.5%). By comparison, the Pt-based reference averaged 7.19% (± 0.3%).

The improved performance was mainly due to the higher short-circuit current density (Jsc) and low charge-transfer resistance of the Fe@$NiCo_2S_4$ electrode. In addition, the fabricated DSSCs showed stable operation over 5 days, maintaining PCE values above 6.5%, indicating good stability in ambient conditions. These results suggest that Fe@$NiCo_2S_4$ is a promising, low-cost, and high-performance alternative to platinum for use in DSSCs, offering both strong initial performance and short-term stability. Further optimization and long-term testing may unlock even greater potential for viability for real-world applications.

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