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Unveiling the Potential of $Mn_xCo_{3-x}S_4$ Electrocatalyst in Triiodide Reduction for Dye-sensitized Solar Cells

The development of a low-cost and high-efficiency Pt-free counter electrode is an important goal to improve the performance of dye-sensitized solar cells. In this study, we successfully synthesized a $Mn_xCo_{3-x}S_4$-based counter electrode by a facile solvothermal synthesis technique. The electrocatalyst was directly deposited on a fluorine doped titanium oxide (FTO) coated glass substrate. Various characterization techniques such as X-ray diffraction, scanning electron microscopy, energy dispersive X-ray spectroscopy and X-ray photoelectron spectroscopy were employed to analyze the obtained $Mn_xCo_{3-x}S_4$ counter electrode material. The photovoltaic measurements performed on the dye-sensitized solar cells showed a remarkable improvement in energy conversion efficiency with the $Mn_xCo_{3-x}S_4$counter electrode (8.60 %) compared to the conventional Pt (8.11 %). Moreover, the $Mn_xCo_{3-x}S_4$counter electrode exhibited excellent stability, further highlighting its potential as an efficient and durable alternative to Pt in dye-sensitized solar cells. Overall, our results contribute to the further development of Pt-free counter electrode materials for sustainable solar energy applications.

Keywords: $MnCo_2S_4$; ternary sulfide; solvothermal synthesis; Pt-free counter electrodes, dye-sensitized solar cells.

Introduction

The demand for photovoltaic technology continues to increase as the world's population grows and environmental concerns increase. Among the various types of photovoltaic technologies, dye-sensitized solar cells (DSSCs) have emerged as a promising third-generation solution due to their low cost, high efficiency, and ease of fabrication. These characteristics make DSSCs a potential replacement for expensive silicon-based solar cells [1]. However, the commercialization of DSSCs faces challenges such as relatively low efficiency, poor stability, and non-competitive prices. Another hurdle is the use of platinum (Pt) as a counter electrode in DSSCs, which is problematic due to high cost, limited availability, and stability-related issues [2-4]. Consequently, there is an urgent need to develop low-cost and high-efficiency Pt-free counter electrodes to improve the overall affordability of solar cells [5].

Transition metal compounds, especially ternary compounds such as oxides, sulfides, and selenides, have emerged as promising alternatives to Pt due to their excellent electrocatalytic activity, long-term stability, and abundance [6-8]. In this study, we focused on the development of a $MnCo_3S_4$ electrocatalyst as a Pt-free counter electrode for DSSC applications. $MnCo_2S_4$ is a ternary compound derived from Co_3S_4 with one Co atom replaced by Mn. To achieve this, we synthesized a $Mn_xCo_{3-x}S_4$ counter electrode directly on a fluorine-doped titanium oxide (FTO) coated glass substrate using a simple one-step solvothermal method. The resulting $Mn_xCo_{3-x}S_4$/FTO counter electrode was extensively characterized by various spectroscopic and microscopic techniques and then integrated into a DSSC device to evaluate its performance.

Remarkably, the DSSC with the $Mn_xCo_{3-x}S_4$composite counter electrode achieved a higher efficiency (PCE) of 8.60 % compared to the device with a conventional Pt counter electrode (PCE of 8.11 %). These results demonstrate the potential of $Mn_xCo_{3-x}S_4$ counter electrodes as a promising alternative to Pt in DSSCs, offering advantages such as lower cost and higher efficiency. With this research, we contribute to the further development of Pt-free counter electrode materials and pave the way for more affordable and sustainable photovoltaic technologies.

2. Experimental

2.1. Materials

Chemicals and materials were obtained from commercial sources and utilized as received, unless specifically stated otherwise.

2.2. Synthesis of $Mn_xCo_{3-x}S_4$ counter electrode

A composite material, $Mn_xCo_{3-x}S_4$, was synthesized by the solvothermal method. In this method, the precursors $Mn(NO_3)_2$, $Co(NO_3)_2$, and thiourea were dissolved in ethanol in an ultrasonic bath. The resulting solution, together with the FTO glass, was then transferred to a 50-mL stainless steel autoclave lined with Teflon and kept at a temperature of 180 °C for 14 hours. The stoichiometric ratio of manganese and cobalt nitrates to thiourea was 1:2:10, respectively. Subsequently, the electrocatalyst-coated FTO substrates were washed with water and ethanol and dried at 70 °C for 12 hours in a vacuum oven.

2.3. Fabrication of dye-sensitized solar cells

Preparation of the working electrode (WE) included the following steps: First, the FTO glass slides (2.2 mm thick, surface resistivity 7 Ω/sq, Sigma-Aldrich) were cleaned with ethanol and ultrasound and then air dried. A compact TiO_2 layer was formed by soaking the FTO in a 50 mM titanium (IV) isopropoxide solution in 2M HCl at 70ºC for 30 minutes and sintering at 500ºC for 30 minutes. A transparent TiO_2 paste (particle size: 18-20 nm, DN -EP03, Dyenamo) was doctor bladed the compact TiO_2 layer. After the transparent TiO_2 layer was air dried for 30 minutes, the electrodes were sintered in an oven at different temperatures: 125ºC for 5 minutes, 325ºC for 10 minutes, 425ºC for 15 minutes, and 500ºC for 30 minutes. Once the electrodes were cooled to 70ºC, a light-scattering TiO_2 layer (particle size: 150-250 nm, Greatcell Solar WER2-O, Sigma-Aldrich) was doctor bladed over the transparent TiO_2 film and air dried for 1 hour before sintering as described above. After cooling, the electrodes were immersed in a dye solution containing 0.25 mM of ruthenium-based standard dye N719 (Sigma-Aldrich) and 0.75 mM chenodeoxycholic acid (CDCA, Sigma-Aldrich) in an acetonitrile: tert-butanol mixture (1:1) for 24 hours. After loading the dye, the electrodes were rinsed with ethanol to remove unbound dye molecules from the surface of the TiO_2 film and then dried.

The counter electrode (CE) was prepared using a Pt-based approach. A commercial Pt paste (containing terpineol and hexachloroplatinic acid, Sigma-Aldrich) was doctor bladed onto a clean and dry FTO glass substrate and then sintered at 500ºC for 30 minutes.

To construct the dye-sensitized solar cell, an MPN-based iodine/iodide redox electrolyte (DN-OD03 S104, Dyenamo) was applied to the dye-loaded TiO_2 photoanode and the CE (either Pt or $Mn_xCo_{3-x}S_4$) was placed on top. The two electrodes were separated with double-sided adhesive tape.

2.4. Characterization

The electrocatalyst was subjected to various characterization techniques to evaluate its properties. X-ray diffraction (XRD) patterns were obtained using a Rigaku SmartLab system. The structure and morphology were analyzed using a Zeiss Crossbeam 540 scanning electron microscope (SEM). Energy dispersive X-ray spectroscopy (EDS) and NEXSA Thermoscientific X-ray photoelectron spectroscopy (XPS) were used to determine material composition.

The photovoltaic analysis of the solar cells was performed using Dyenamo Toolbox (DN -AE01). Electrochemical analysis, on the other hand, was performed in the dark using the IM6 electrochemical station from Zahner Elektrik. The measurements were performed with a bias voltage of -0.72 V, an amplitude of 10 mV and a frequency range of 0.1 — 100000 Hz. The obtained data were further processed and fitted using the EIS Spectrum Analyzer.

3. Results and Discussion

3.1. Characterization of $Mn_xCo_{3-x}S_4$ electrocatalyst

Figure 1 shows the XRD patterns of $Mn_xCo_{3-x}S_4$. In addition to the prominent peaks originating from the FTO substrate, specific diffraction peaks can be observed at 32.09°, 36.73°, 48.36°, and 55.83° corresponding to the (311), (400), (511), and (440) crystal planes of Co_3S_4, respectively (PDF42-1448) [9]. It is noteworthy that the XRD diffraction peaks of $Mn_xCo_{3-x}S_4$ are very similar to those of Co_3S_4, indicating the substitution of a single Co atom by Mn and the similarity of crystal structure between the two[10]. Therefore, we can conclude that the doping process led to the formation of $MnCo_2S_4$.

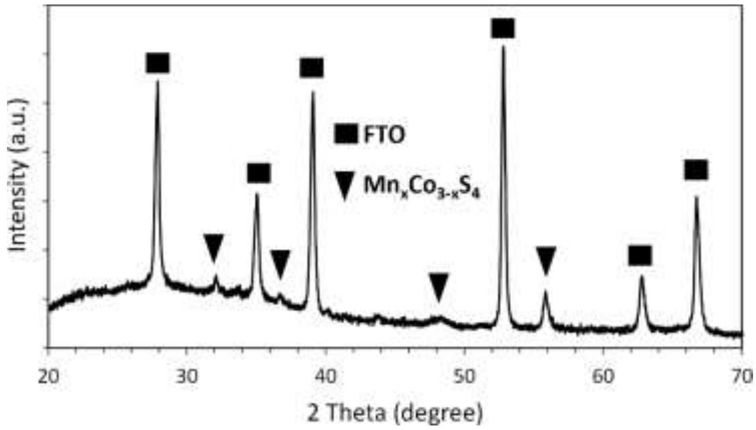

Figure 1: X-ray diffraction pattern of a thin film of $Mn_xCo_{3-x}S_4$on an FTO substrate.

The elemental composition and valence states were analyzed by X-ray photoelectron spectroscopy, and the corresponding spectra are shown in Figure 2. The full XPS spectrum of the $Mn_xCo_{3-x}S_4$ composites shows distinct peaks attributable to Mn, Co, and S, confirming the presence of these elements and their corresponding valence states in the sample. It is worth noting that the elements C, N and O are normally present in air.

The Co 2p spectrum shows two spin-orbit doublet peaks. The dominant peaks at 781.8 and 797.0 eV correspond to the 2p3/2 and 2p1/2 spin-orbit states of Co^{2+}, respectively, while the weaker peaks at 777.6 and 792.8 eV are associated with Co^{3+}[10]. The presence of Co^{3+} peaks in the spectrum indicates possible oxidation of the surface when exposed to air. As can be seen in Figure 2, the Mn 2p orbitals show spin splitting leading to two singlet pairs: Mn 2p3/2 (642.8 eV) and Mn 2p1/2 (654.6 eV), which can be attributed to the Mn^{2+} binding energy[11]. In the S 2p XPS spectra, a satellite peak at 168.7 eV and three peaks representing different sulfur species are observed. The peaks at 162.3 and 163.5 eV correspond to S 2p3/2 and S 2p1/2, respectively. In addition, the peak at 164.6 eV indicates metal-bonded sulfur (S-M) [12].

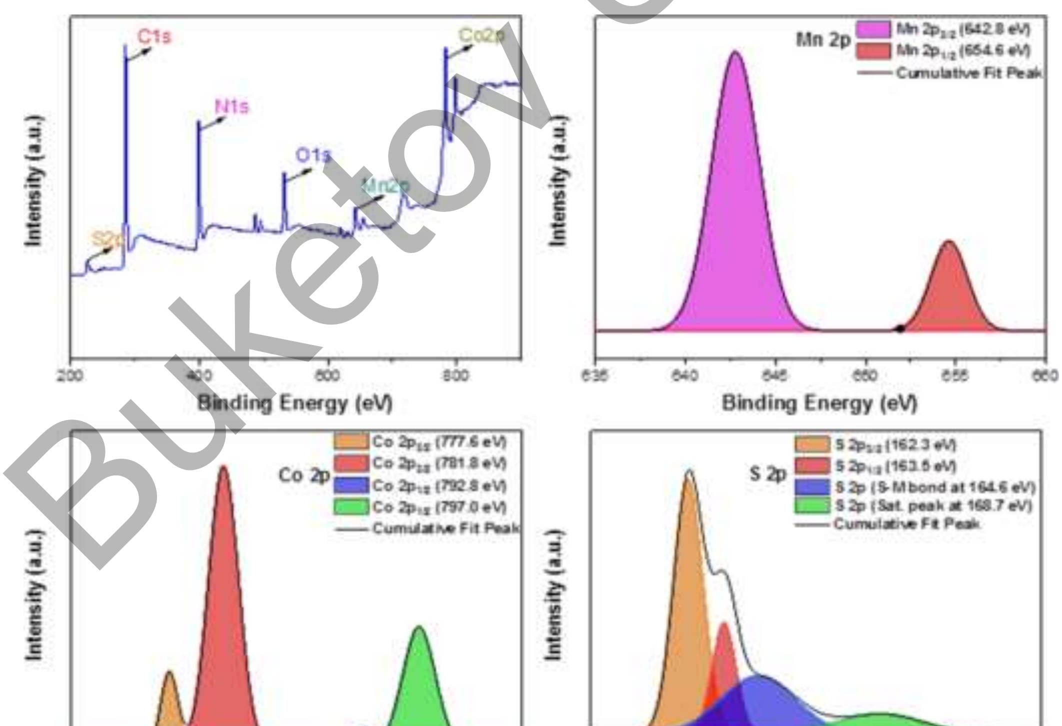

Figure 2. XPS spectra of the $Mn_xCo_{3-x}S_4$ electrocatalyst.

Uniformly grown $Mn_xCo_{3-x}S_4$ nanoflakes were prepared on the surface of FTO glass by a solvothermal reaction. The resulting electrocatalyst had nanoflakes with an average diameter of about 260 nm and a plate thickness of 36.5 nm, as shown in the upper part of Figure 3. The lower part of Figure 3 shows the spectrum of energy dispersive X-ray spectroscopy of the synthesized $Mn_xCo_{3-x}S_4$ composite, which confirms the presence of elements Mn, Co and S in the prepared material.

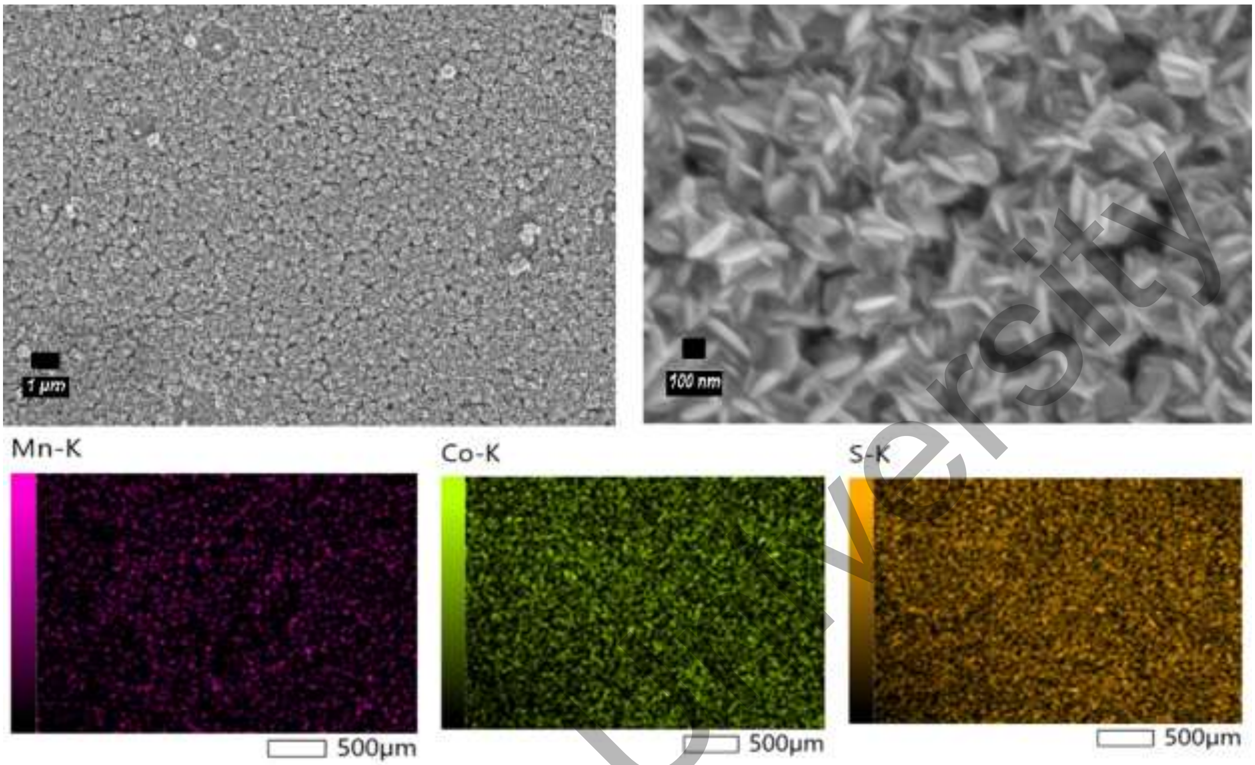

Figure 3. Top: FE-SEM images of the $Mn_xCo_{3-x}S_4$ coated FTO electrode showing magnifications of 5000 (left) and 40000 (right). Bottom: EDS mapping of the electrocatalyst.

3.2. Photovoltaic and electrochemical performance of $Mn_xCo_{3-x}S_4$ electrocatalyst

To investigate the photovoltaic and electrochemical performances of an electrocatalyst, dye-sensitized solar cells were constructed using $Mn_xCo_{3-x}S_4$ and Pt as counter electrodes. The photovoltaic measurements were performed under the standard solar conditions AM 1.5 and an illuminance of 1000 W/cm^2. The obtained results are summarized in Table. Figure 4a shows the current-voltage (J-V) curve of the solar cells, while Figure 4b presents the Nyquist diagrams. It is worth noting that the $Mn_xCo_{3-x}S_4$ composite cell has an excellent performance with a power conversion efficiency (PCE) of 8.60 %, slightly exceeding the Pt cell efficiency of 8.11 %. The main factor contributing to the increase in PCE efficiency is the short circuit current (J_{SC}), which was 16.60 mA/cm^2 for the $Mn_xCo_{3-x}S_4$ cell and 15.87 mA/cm^2 for the Pt control device. This higher J_{SC} indicates better electrocatalytic activity of the $Mn_xCo_{3-x}S_4$ electrocatalyst compared to Pt. The electrochemical impedance spectroscopy measurements confirm this result (Fig. 4b). The Nyquist diagrams of the solar cells consist of two semicircles: The smaller arc represents the charge transfer resistance at the interface between the counter electrode and the electrolyte (R_{CT}), while the larger arc corresponds to the charge transfer resistance at the interface between the semiconductor and the electrolyte (R_{TiO_2}). The intersection of the graph with the x-axis indicates the series resistance of the device (R_S). It is worth noting that the $Mn_xCo_{3-x}S_4$ cell has a lower series resistance (19.2 Ω) compared to Pt (22.6 Ω), indicating better contact between $Mn_xCo_{3-x}S_4$ and FTO. In addition, the R_{CT} of the $Mn_xCo_{3-x}S_4$cell was also lower than that of the Pt solar cell, indicating improved electrocatalytic activity of the novel Pt-free counter electrode and improved electron flow at the counter electrode-electrolyte interface. This electron flow, referred to as the exchange current (J_o), is indirectly proportional to the charge transfer resistance R_{CT} and can be expressed as

$$J_o = \frac{RT}{nFR_{CT}},$$

where R is the universal gas constant, T is the absolute temperature, n is the number of electrons involved in the triiodide reduction process, and F is Faraday's constant. The superior electrocatalytic activity of $Mn_xCo_{3-x}S_4$ provides an explanation for the improved J_{SC} in the DSSCs compared to Pt.

Table

Photovoltaic parameters comparison between DSSCs with $Mn_xCo_{3-x}S_4$ composites and Pt counter electrodes.

DSSCs	PCE (%)	V_{OC}(V)	J_{SC} (mA/cm^2)	FF	R_S (Ω)	R_{CT} (Ω)	R_{TiO_2} (Ω)
$Mn_xCo_{3-x}S_4$	8.60	0.73	16.60	0.71	19.2	12.9	47.9
Pt	8.11	0.73	15.87	0.70	22.6	13.1	54.6

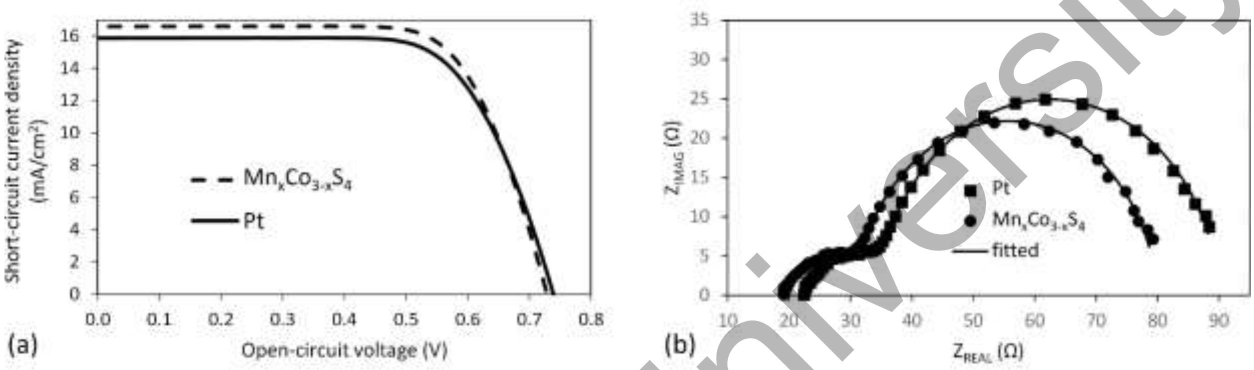

Figure 4. (a) Current-voltage curves and (b) Nyquist plots depicting the performance of dye-sensitized solar cells.

4. Conclusions

In this study, Pt-free counter electrodes based on $Mn_xCo_{3-x}S_4$ were successfully synthesized by a one-pot solvothermal method. The electrocatalytic activity of $Mn_xCo_{3-x}S_4$ proved to be excellent and exceeded that of Pt, as further measurements showed. In particular, the dye-sensitized solar cell with $Mn_xCo_{3-x}S_4$ composites as the counter electrode achieved an efficiency of 8.60 %, slightly outperforming the DSSC with Pt counter electrode (PCE: 8.11 %). These results highlight the potential of $Mn_xCo_{3-x}S_4$ composites as a promising alternative to Pt for DSSC counter electrodes due to their improved electrocatalytic performance and cost efficiency. Moreover, this research introduces a novel idea and strategy for fabricating efficient base metal counter electrode materials for DSSCs. The convenient solvothermal method used in this study provides a practical and scalable approach to fabricate $Mn_xCo_{3-x}S_4$ composites. This technique can potentially be extended to other metal sulfide materials, allowing the development of a broader range of base metal counter electrodes. The successful implementation of $Mn_xCo_{3-x}S_4$ composites as Pt-free counter electrodes not only solves the problem of scarcity and high cost of Pt, but also provides a sustainable and environmentally friendly solution for DSSC technology. Future studies can address the optimization of the composition and morphology of $Mn_xCo_{3-x}S_4$ composites to further improve their performance in DSSCs and ultimately advance the field of renewable energy.

5. Author contributions

Diana Suleimenova was responsible for the conception and design of the analysis and for performing the synthesis, characterization, and electrochemical and photovoltaic measurements. She was also involved in writing the first draft of the manuscript. Yerbolat Tashenov played a key role in the analysis of the data. Bakhytzhan Baptayev contributed to the conception and design of the analysis, performed an overall analysis of the data, and provided the necessary funding. Mannix P. Balanay contributed to the conception and design of the analysis and provided critical revisions to the overall manuscript.

6. Conflicts of interest

There are no conflicts to declare.

7. Acknowledgements

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References

1 O'Regan, B. & Grätzel, M. (1991). A low-cost, high-efficiency solar cell based on dye-sensitized colloidal TiO2 films. *Nature, 353*(6346), 737-740.

2 Olsen, E., Hagen, G. & Eric Lindquist, S. (2000). Dissolution of platinum in methoxy propionitrile containing LiI/I2. *Sol. Energy Mater. Sol. Cells, 63*(3), 267-273.

3 Shu, Z. X. & Bruckenstein, S. (1991). Iodine adsorption studies at platinum. J. Electroanal. *Chem. Interfacial Electrochem, 317*(1-2), 263-277.

4 Kay, A. & Grätzel, M. (1996). Low cost photovoltaic modules based on dye sensitized nanocrystalline titanium dioxide and carbon powder. *Sol. Energy Mater. Sol. Cells, 44*(1), 99-117.

5 Ahmed, U., Alizadeh, M., Rahim, N.A., Shahabuddin, S., Ahmed, M.S. & Pandey, A.K. (2018). A comprehensive review on counter electrodes for dye sensitized solar cells: A special focus on Pt-TCO free counter electrodes. *Sol. Energy, 174,* 1097-1125.

6 Liu, K., Wei, A., Liu, J., Liu, Z., Xiao, Z. & Zhao, Y. (2018). NiCo2S4 nanosheet thin film counter electrodes prepared by a two-step approach for dye-sensitized solar cells. *Mater. Lett. 217,* 185-188.

7 Theerthagiri, J., Senthil, R.A., Buraidah, M.H., Madhavan, J., Arof, A.K. & Ashokkumar, M. (2016). One-step electrochemical deposition of Ni1−xMoxS ternary sulfides as an efficient counter electrode for dye-sensitized solar cells. *J. Mater. Chem. A, 4*(41), 16119-16127.

8 Hou, W., Xiao, Y. & Han, G. (2017). An interconnected ternary MIn2S4 (M=Fe, Co, Ni) thiospinel nanosheet array: A type of efficient platinum-free counter electrode for dye-sensitized solar cells. *Angew. Chem., 129*(31), 9274-9278.

9 Li, Y., Wang, N., Xu, J., Liu, Z. & Yu, H. (2019). Significant effect of advanced catalysts Co3S4 modified CuWO4·2H2O under visible light condition photocatalytic hydrogen production. *J. Nanopart. Res., 21*(4), 80.

10 Dai, Z., Feng, X., Li, Q., Su, P., Shen, X., Zheng, Y., Jiao, Q., Zhao, Y., Li, H. & Feng, C. (2021). Construction of porous core-shell MnCo2S4 microrugby balls for efficient oxygen evolution reaction. *J. Alloys Compd., 872.*

11 Raghavendra, K.V.G., Gopi, C.V. V. M., Vinodh, R., Rao, S.S., Obaidat, I.M. & Kim, H.-J. (2020). Facile synthesis of nanoparticles anchored on honeycomb-like MnCo2S4 nanostructures as a binder-free electroactive material for supercapacitors. *J. Energy Storage, 27.*

12 Wang, H., Zhang, K., Song, Y., Qiu, J., Wu, J. & Yan, L. (2019). MnCo2S4 nanoparticles anchored to N- and S-codoped 3D graphene as a prominent electrode for asymmetric supercapacitors. *Carbon, 146,* 420-429.

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Бояғышқа сезімтал күн батареялары үшін триодидтерді тотықсыздану кезінде $Mn_xCo_{3-x}S_4$ электрокатализаторының әлеуетін ашу

Қымбат емес және жоғары тиімді, құрамында платинасы жоқ қарсыэлектродты жасау бояғышқа сезімтал күн батареяларының өнімділігін жақсартудың маңызды міндеті болып табылады. Бұл зерттеуде біз қарапайым солвотермиялық синтез әдісін қолдана отырып, MnxCo3-xS4 қарсы электродты сәтті синтездедік. Электрокатализатор тікелей фтор легирленген титан оксидімен (FTO) қапталған шыны төсенішке қолданылды. Алынған $Mn_xCo_{3-x}S_4$ қарсыэлектрод материалын талдау үшін рентгендік дифракциялық спектроскопия, сканерлеуші электрондық микроскопия, энергиялық дисперсиялық рентгендік спектроскопия және рентгендік фотоэлектрондық спектроскопия сияқты әртүрлі сипаттама әдістері пайдаланылды. Бояғышқа сезімтал күн батареяларында жүргізілген фотоэлектрлік өлшеулер әдеттегі Pt (8,11 %) салыстырғанда $Mn_xCo_{3-x}S_4$ есептегіш электродпен (8,60 %) қуатты түрлендіру тиімділігінің айтарлықтай жақсарғанын көрсетті. Сонымен қатар, $Mn_xCo_{3-x}S_4$ қарсыэлектроды тамаша тұрақтылықты көрсетті, бұл оның әлеуетін одан әрі бояғышқа сезімтал күн батареяларында Pt-ге тиімді және берік балама ретінде әлеуетін одан әрі көрсетеді. Тұтастай алғанда, біздің нәтижелеріміз күн энергиясын тұрақты пайдалану үшін Pt-сіз контрэлектродтық материалдарды одан әрі дамытуға ықпал етеді.

Кілт сөздер: $MnCo_2S_4$, үштік сульфид, солвотермиялық синтез, Pt жоқ қарсы электродтар, бояғышқа сезімтал күн батареялары.

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Раскрытие потенциала электрокатализатора $Mn_xCo_{3-x}S_4$ в восстановлении трийодидов для солнечных элементов, сенсибилизированных красителем

Разработка недорогого и высокоэффективного противоэлектрода, не содержащего платины, является важной задачей для улучшения характеристик солнечных элементов, сенсибилизированных красителем. В этом исследовании мы успешно синтезировали противоэлектрод на основе $Mn_xCo_{3-x}S_4$ с помощью простого метода сольвотермического синтеза. Электрокатализатор наносили непосредственно на стеклянную подложку с покрытием из легированного фтором оксида титана (FTO). Для анализа полученного материала противоэлектрода $Mn_xCo_{3-x}S_4$ использовались различные методы характеризации, такие как рентгеновская дифракционная спектроскопия, сканирующая электронная микроскопия, энергодисперсионная рентгеновская спектроскопия и рентгеновская фотоэлектронная спектроскопия. Фотогальванические измерения, выполненные на солнечных элементах, сенсибилизированных красителем, показали заметное улучшение эффективности преобразования энергии с противоэлектродом $Mn_xCo_{3-x}S_4$ (8,60 %) по сравнению с обычным Pt (8,11 %). Кроме того, противоэлектрод $Mn_xCo_{3-x}S_4$ продемонстрировал превосходную стабильность, что еще больше подчеркивает его потенциал в качестве эффективной и долговечной альтернативы Pt в солнечных элементах, сенсибилизированных красителем. В целом, наши результаты способствуют дальнейшему развитию материалов противоэлектродов, не содержащих Pt, для устойчивого использования солнечной энергии.

Ключевые слова: $MnCo_2S_4$, тройной сульфид, сольвотермальный синтез, бесплатиновые противоэлектроды, солнечный элемент, сенсибилизированный краситель.