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Research Article

Novel $ZnCo_2O_4/WO_3$ nanocomposite as the counter electrode for dye-sensitized solar cells (DSSCs): study of electrocatalytic activity and charge transfer properties

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Highlights

- New counter electrode based on $ZnCo_2O_4/WO_3$ nanocomposite.
- Enhanced electrocatalytic activity of nanocomposite counter electrode.
- DSSC with 7.76% efficiency, over than 40% improvement compared with ZCO.

Abstract

Nowadays, Pt coated FTO is used conventionally as the counter electrode in dye-sensitized solar cell (DSSC). In addition to the high price of the Pt electrode, it reduces the stability of the DSSC. In this study, we introduce and study a new counter electrode based on the $ZnCo_2O_4/WO_3$ composite that is used in DSSC. We show that the efficiency of the DSSC can be enhanced even more then the Pt-based one by employing the $ZnCo_2O_4/WO_3$ as counter electrode. By examining the structural, morphological, optical, and electrochemical properties of the synthesized electrodes, we investigate the counter electrodes synthesized under different conditions. The XRD patterns and FESEM images confirm that the composite phase of the $ZnCo_2O_4/WO_3$ layers is formed. Additionally, electrochemical studies by CV, Tafel, EIS, and Mott-Schottky methods indicate the electrocatalytic activity of the $ZnCo_2O_4/WO_3$ sample have significantly increased compared to $ZnCo_2O_4$ and WO_3 electrodes. Furthermore, the characterization of DSSCs with TiO_2 photoanode and different counter electrodes show that the efficiency of the solar cells based on $ZnCo_2O_4/WO_3$ has a promising efficiency of 7.76%, which has increased by 7% compared to the Pt one.

Introduction

Since the introduction of dye-sensitized solar cells (DSSCs) in 1991 by O'Regan and Gratzel [1], they have emerged as a potential alternative for thin-film solar cells. DSSCs have always been affordable due to their low manufacturing cost and non-toxicity, and have also attracted the consideration of environmentalists [2,3]. A typical DSSC consists of photoanode, counter electrode, electrolyte, and adsorptive dye molecules. In the last two decades, extensive research has been carried out on different parts of the DSSC. Investigating the possible structures for the photoanode and using different materials has been studied frequently [4,5]. Widespread studies have been done to replace conventional electrolytes such as I^-/I_3^- and Co^{3+}/Co^{2+} [6,7]. Also, many researchers have sought to find metal coordination complex or organic dye molecules instead of the conventional N719 [8,9]. However, in most cases, non-toxic and inexpensive TiO_2 as photoanode and N719, which has appropriate molecular level aligning with TiO_2, have been the best option. Likewise, due to the proper compatibility of the redox levels of the I^-/I_3^- electrolyte with N719, their joint use is not far from expectation.

In recent years, replacing Pt as the counter electrode and getting rid of this expensive material has attracted the attention of studies [[10], [11], [12], [13], [14]]. The use of materials such as carbon black, graphene-based and carbon-based nanoparticles, PEDOT and even some conductive polymers such as PANI has raised hopes for replacing Pt. Narudin et al. [15], by using carbon black-graphite counter electrode enhance the efficiency of DSSC up to 5.74%. Kasi Reddy et al. [16], demonstrate the high electrocatalytic activity of bilayer PEDOT:PSS/SWCNH counter electrodes for achieving 5.1% power to current efficiency. Employing PANI counter electrodes, Karakuş et al. [17], succeeded to attain 6.3% efficiency for standard liquid electrolyte based DSSCs.

Using composite materials and taking advantage of the simultaneous properties of each component can be inspiring. Composite structures can be effective as they have demonstrated before [18]. Gao et al. [19], achieved 8.72% efficiency by synthesizing In_4SnS_8@MoS_2@CNTs composite through hydrothermal method and using it as counter electrode. By replacing the standard Pt counter electrode with PANI/WSe_2 composite one, Sheela et al. [20], attained an 8.22% power to current efficiency, which was higher than that of the pure PANI and WSe_2 or even Pt counter electrodes. Yang et al. [13], elevated the electrocatalytic activity of CZTS counter electrodes by covering Co_9S_8 on CZTS thin film prepared by the spin-coating method. This composite counter electrode demonstrated an improved efficiency of 6.41% in comparison with 3.92% efficiency of bare CZTS counter electrode. Nitrogen-decorated CeO_2/reduced graphene oxide nanocomposite (CeO_2/N-rGO) used as counter electrode in DSSC structure and the electrocatalytic activity for triiodide/iodide reduction been investigated by Wei et al., [21]. The DSSC fabricated based on CeO_2/N-rGO demonstrated an advanced efficiency of 3.20%.

$ZnCo_2O_4$ as an intrinsic p-type material benefits from high conductivity, structural stability, and high electrocatalytic activity [22]. It shows superior electrical conductivity and electrochemical activity than ZnO and Co_3O_4 [23,24]. Meanwhile, it has low manufacturing price due to inexpensive and earth-abundant components, which guarantees the reduced cost-effective production [25]. By environmental friendliness, high electrochemical activity and conductivity, $ZnCo_2O_4$ can be a proper candidate as counter electrode in DSSCs. Also, WO_3 with unique optical and electrochemical properties is another candidate for appropriate reduction of electrolyte species [26]. It also includes good physico-chemical and electrical properties, which can help to improve the electrocatalytic activity of the counter electrode along with the $ZnCo_2O_4$ [27].

$ZnCo_2O_4$ and WO_3 nanostructures have previously been used in DSSC structure as the counter electrode. Hou et al. [28] synthesized flower-like $ZnCo_2O_4$ and graphene oxide nanostructures using solvothermal and common Hummers technique, respectively, and fabricated $ZnCo_2O_4$/RGO nanohybrids as counter electrode using hydrothermal method. Their DSSC based on this hybrid counter electrode has shown an efficiency of 7.22%. Wang et al. [29] have also achieved 6.73% efficiency for DSSC using $ZnCo_2O_4$/RGO composite as the counter electrode. Abdullaev et al. [30] have succeeded in producing core-shell ZnO@$ZnCo_2O_4$ nanostructures that yielded 8.39% efficiency for a DSSC based on this counter electrode. By synthesizing $ZnCo_2O_4$@$NiMoO_4$ composite on carbon paper (CP) by two-step hydrothermal method, Zhang et al. [31] have succeeded in achieving 9.30% efficiency for DSSC with this counter electrode. ZnO@WO_3 core-shell nanoparticles were prepared by Mahajan et al. [32] by sol-gel method, which yielded 5.73% efficiency for DSSC based on this counter electrode. Sulfurization treatment of mesoporous WO_3/carbon film coated on fluorine-doped tin oxide (FTO) glass yielded WO_3@WS_2@carbon CE by Shen et al. [33]. Photovoltaic performance measurements have showed that the DSSC with the WO_3@WS_2@carbon core-shell counter electrode attained a power conversion efficiency of 7.71%. Tungsten trioxide was sprayed onto ITO conductive glass and filled with activated charcoal powder (ACP) for use as counter electrode in DSSC by Cui et al. [34]. The power conversion efficiency of WO_3@ACP-based DSSC was 5.04%, which has been 3.15 times better than the 1.61% of WO_3 DSSC.

In this research, by preparing a composite layer of $ZnCo_2O_4$ (ZCO) and WO_3 materials and using it as the counter electrode in DSSC, we investigate its properties. WO_3 structures can play an effective role in electron transport due to their proper conductivity. Simultaneously, ZCO nanoparticles can improve the performance of the counter electrode in combination with WO_3 due to their proper electrocatalytic activity and charge transfer properties.

Section snippets

Synthesis of nanoparticles

A simple and rapid combustion method is used for the synthesis of ZCO nanoparticles. Primary, 1 g $Zn(NO_3)_2{\cdot}6H_2O$ and 2 g $Co(NO_3)_2{\cdot}6H_2O$ were dissolved in 8 g double distilled water, and while stirring vigorously, its temperature raised to 85 °C. Then, 6.5 g $C_6H_8O_7$ was added to the solution and the stirring continued for 15 min. The solution was transferred to an oven to heat at 300 °C for 20 min. After drying, the resulting powder was crushed in a mortar and then annealed for 5 h at a temperature …

Results and discussion

Fig. 1 depicts the diffraction patterns for ZCO, WO_3 and ZCO/WO_3 samples. The peaks appearing for the ZCO sample at diffraction angles of 18.98, 31.33, 36.93, 38.52, 44.88, 55.64, 59.35 and 65.18°, respectively, represent the crystal planes (111), (220), (311), (222), (400), (422), (511) and (440) from the cubic phase of zinc cobalt oxide with Fd3m spatial symmetry. These peaks have a good coincidence with the standard card number 23-1390. According to the pattern, there are no additional…

Conclusion

In this research, we fabricated $ZnCo_2O_4$ (ZCO), WO_3 and ZCO/WO_3 layers using combustion, sol-gel and solid-state reaction methods and employed them as counter electrodes in DSSC structure. Examining the structural, morphological, and optical properties of the ZCO/WO_3 sample shows that this layer is a composite of ZCO and WO_3. Also, the investigation on the electrochemical properties shows that the electrocatalytic activity of the counter electrodes is improved by the formation of the composite.…

Declarations

No funding was received to assist with the preparation of this manuscript.

The authors have no relevant financial or non-financial interests to disclose.…

CRediT authorship contribution statement

Raed H. Althomali: Methodology, Writing – original draft, Formal analysis. **Ebraheem Abdu Musad Saleh:** Formal analysis, Investigation, review & editing. **Ramesh S. Bhat:** Project administration, Conceptualization, review & editing. **Shavan Askar:** Formal analysis, Investigation, review & editing. **I.B. Sapaev:** Formal analysis, Investigation, review & editing. **Mazin A.A. Najm:** Formal analysis, Investigation, review & editing. **Benien M. Ridha:** Visualization, Data curation, review & editing. **Ali H.**…

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.…

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