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CZTS/MoS_2-rGO Heterostructures: An efficient and highly stable electrocatalyst for enhanced hydrogen generation reactions

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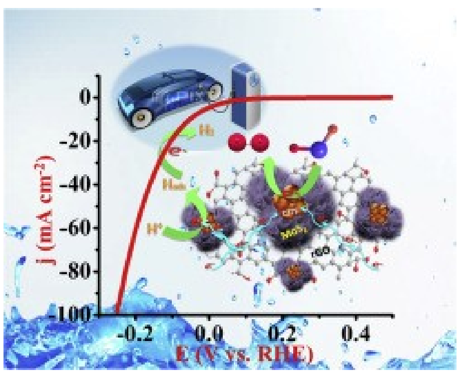
Highlights

- An economical fabrication of sonochemical CZTS/MoS_2-rGO electrocatalyst
- Electrocatalytically converting H_2O into H_2 with high energy efficiency is proposed.
- CZTS/MoS_2-rGO electrocatalyst is shown to be superior for HER compared to CZTS
- This article explore the non precious metal highly stable electrocatalytic system for HER

Abstract

The design and intensification of inexpensive highly efficient electrocatalysts for hydrogen production underpins numerous promising clean-energy technologies. In this work we have demonstrated facile sonochemical approach for novel heterostructured electrocatalyst consisting of MoS_2-rGO coupled with Cu_2ZnSnS_4 (CZTS) NPs (CZTS/MoS_2-rGO) for enhanced hydrogen generation reactions (HER). The CZTS/MoS_2-rGO heterostructured electrocatalyst exhibits the highest HER activity, i.e. potential of 50 mV vs. RHE at 10 mA cm^{-2}, Tafel slope of 68 mV dec^{-1} and it reveals the Volmer-Heyrovsky mechanism for HER. The electrochemical impedence spectroscopy (EIS) showed smaller semicircle (R_{ct}=4.5 Ω) with excellent stability upto the ~6 h confirmed from chronoamperometric (i-t) measurements. Such a high HER activity is superior than most of CZTS based electrocatalysts reported so far, and attributed to the presence of MoS_2-rGO with augmented charge severance by rGO and a higher number of catalytically active edges from MoS_2 further improves the electrocatalytic performance of CZTS and which demonstrating synergestic effect leading to the enhanced electrical conductivity. This work demonstrates promising performance of MoS_2 and rGO on HER activity of CZTS based catalysts.

Graphical abstract



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Introduction

Hydrogen (H_2) is believed to be the most promising clean energy source with the potential to replace fossil fuels as it is carbon-free, sustainable and renewable [1]. However, the major challenge for the worldwide scientists is its large scale and economic production. Large number of attempts have been made to develop technologies dealing with electrolysis of water for generation of hydrogen, nevertheless, it is energy intensive approach [2]. On the other hand, the hydrogen evolution reaction (HER) is a basic reaction involving splitting of water, and is considered as a one of the most promising method for the production of H_2 massively and more efficiently [3]. Although, several HER catalysts have been reported earlier their practical application are severely hampered due to the high cost and low reserves [4]. It is impending to develop inexpensive and earth-abundant electrocatalysts to replace the noble metals. Various transition metal sulfides including Mo, Cu, Co, Fe, Ni with their derivatives [5] and metal-free catalysts like graphitic-carbon nitride coupled with nitrogen-doped graphene have been widely reported for HER [6]. However, these non-precious metal catalysts suffer from instability and low catalytic activity in acidic conditions [7]. Recently, it is realized that Cu_2ZnSnS_4 (CZTS) could be a potentially low cost, non-toxic and earth-abundant multifunctional material to be used as an electrocatalyst in water splitting processes i.e. for both H_2 and O_2 evolution which has been demonstrated in our previous report [8]. However, understanding the electrochemical behavior of CZTS on the HER activity is still in its infancy and yet to be explored [9]. Furthermore, molybdenum disulfide (MoS_2) is among the top most priority electrocatalyst due to its low cost, earth abundance and excellent electrocatalytic activity for HER and has been considered as a promising alternative candidate to replace Pt as electrocatalysts [10]. Experimental and theoretical results have demonstrated that HER activity of MoS_2 is proportional to the number of active sites and unsaturated sulfur atoms [7b]. However, insufficient number of active sites inhibits the transport of electrons to MoS_2 electrodes thereby limiting its catalytic activity and widespread applications. Therefore, use of MoS_2 in conjunction with other potential candidates is a key to improve the catalytic activity of MoS_2-based electrocatalysts [11]. Carbon based materials such as graphene oxide were always explored to enhance the activity of electrocatalyst for HER due to their best conductivity, high chemical stability, large surface area and unique structures [11]. It is understood that the mixture of MoS_2 and rGO increases the number of active sites and the electrical contact between MoS_2-rGO and forms a promising pathway to further improve the electrocatalytic performance. With this motivation, MoS_2-rGO coupled with CZTS is explored for its enhanced elcectrocatlytic performance towards HER. Wu et al. fabricated Mn-MoS_2/rGO electrocatalyst for HER evolution and demonstrated higher catalytic activity, small overpotential (~110 mV), small charge transfer resistance (1.5 Ω), Tafel slope (76 mV dec^{-1}) and fine stability in acidic medium due to the synergetic effect between MoS_2 and rGO [12]. Li et al. reported the composite of Cu and MoS_2 on the reduced graphene oxide (rGO) (Cu-MoS_2/rGO) showing high catalytic activity towards HER. It was found that the contribution of rGO enhanced the electrical conductivity of the catalyst and the MoS_2 with a higher number of exposed edges exhibited higher HER activity. Electrocatalytic activity demonstrated that the catalyst exhibited excellent HER activity with large cathode currents and a Tafel slope as small as 90 mV dec^{-1} [13]. Bo Ma et al. developed MoS_2 NFs/rGO electrocatalyst towards HER performance exhibiting the inferior overpotential −0.19 V with Tafel slope of ~95 mV dec^{-1}. The growth of MoS_2/rGO electrode gives a promising and inexpensive way to make other multifunctional electrodes [14]. The literature survey suggests that MoS_2-rGO shows high electrocatalytic activity owing to its outstanding properties. Furthermore, in our preceding work we have demonstrated that CZTS electrocatalyst shows excellent HER activity and thus additional efforts need to be made to further improve the HER activity. With this motivation, herein, we report a novel flexible HER heterostructured catalyst that is constructed by the one-step sonochemical method. In this work, CZTS is coupled with MoS_2-rGO to form CZTS/MoS_2-rGO heterostructured catalyst which shows an onset potential of 50 mV at 10 $mAcm^{-2}$, a small Tafel slope of 68 mV dec^{-1}, smaller charge transfer resistance (R_{ct}=4.5 Ω) and excellent stability exhibiting the best performance among all non-precious metal HER electrocatalysts. This study provides a new avenue for the development of non-precious metal based electrocatalysts with enhanced HER performance and a good substitute to the state-of-the-art precious metal electrocatalysts.

Section snippets

Chemicals and materials

Copper chloride ($CuCl_2.2H_2O$ 98%), zinc chloride ($ZnCl_2.2H_2O$ 96%), tin chloride ($SnCl_2.2H_2O$ 98%), ammonium molybdate ($(NH_4)_6Mo_7O_{24}$), thiourea (CN_2H_4S) thioacetamide (TAA), 2-methoxyethanol, monoethanolamine (MEA) cetyltrimethylammonium bromide (CTAB) and absolute ethanol of AR grade from s.d. fine chemicals ltd. India were used for sonochemical synthesis of CZTS nanoparticles. All the chemicals were procured and were used without any further purification.…

Preparation of MoS_2 nanoparticles

MoS_2 were synthesized by facial…

Result and discussion

The CZTS/MoS_2-rGO electrocatalyst was synthesized by a simple sonochemical method and as as shown schematically in Scheme 1**.**

Fig. 1(a) shows the superimposed X-ray diffraction (XRD) patterns of pure rGO, MoS_2, CZTS, MoS_2-rGO, and CZTS/MoS_2-rGO heterostructural electrocatalyst. XRD pattern of rGO shows a broad peak near 24.9° which can be attributed to the (002) plane of rGO [15]. XRD pattern of pure CZTS shows (112), (200), (220), (312) and (332) lattice planes which can be indexed to the…

Conclusion

In conclusion, we have synthesized the CZTS/MoS_2-rGO heterostructure electrocatalyst by a single step sonochemical approach. The CZTS/MoS_2-rGO demonstrates an outstanding HER performance with an onset potential as low as 50 mV vs. RHE at 10 mA cm^{-2} along with Tafel slope of 68 mV dec^{-1} and an exchange current density of 962 mA cm^{-2}. The CZTS has shown the synergistic effect when combined with MoS_2-rGO making the heterostructure electrocatalyst an excellent H_2 evolution electrocatalytic system…

Author credit statement

R. V. D. designed and conducted all experiments, and V·S·S supervised and contributed to some of the synthesis and functionalization of graphene oxide experiments. R.V. D. conducted the experiments and wrote the first draft of the manuscript. A.V. G. help in data analysis, interpretation of data and corrected the manuscript. B. R. S. proposed and supervised the whole project and assisted in the writing process and data analysis.…

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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> *Citation Excerpt :*
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> …Typically, the impedance indicates the combined effect of electrode surface (RE) and charge-transfer resistance (Rct) in the electrolyte. The presence of a semicircular region is the indication of charge-transfer resistance which is directly related to the diameter of the semicircular higher frequency section [34–38]. Herein, it can be clearly observed that the semicircular region is more clearly visible in pristine-CZTS compared to CZTS/PANI composite and hence, the redox phenomena became more possible in the case of CZTS/PANI composite material.…

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CuO/g-C<inf>3</inf>N<inf>4</inf>/rGO multifunctional photocathode with simultaneous enhancement of electron transfer and substrate mass transfer facilitates microbial electrosynthesis of acetate

2022, International Journal of Hydrogen Energy

> *Citation Excerpt :*
>
> …The Tafel slopes of rGO and CuO/g-C3N4 under dark condition were 0.33 V dec−1 and 0.72 V dec−1, respectively. The results implied that the introduction of rGO into the catalyst can improve HER performance, and the highest HER performance can be achieved when combined with the photocatalyst [40–42]. Acetate, as

the final product in all the MES groups, gradually accumulated over a 14-day reaction period (Fig. 4a)....

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Enhanced hydrogen evolution by rGO decorated copper nickel tin sulphide (CNTS-rGO) in acidic medium by water splitting

2022, International Journal of Hydrogen Energy

Citation Excerpt :

...Thus, it is found that the catalytic stability and hydrogen production is excellent where Ni plays a vital role in Ni–Mo–S [18]. As a result, numerous researchers experimented with MoS2 grown on reduced graphene oxide (rGO) started to gain attention among researchers [19]. MoS2 nanowires, mesoporous double gyroid MoS2 bicontinuous layer [20], defect rich MoS2 nanosheets and edge orientated MoS2 were few of these....

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Reduction of metal nanoparticle decorated flexible graphene oxide by laser at various temperatures and under selected atmospheres

2022, Carbon Trends

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...Subsequently, the ID/IG ratio of (GO + MNP) drastically drops at room temperature according to Fig. 1, Eq. (2). The catalytic activity of Au has always been inferior to those of other noble metals [64,65]. The performance of (GO + Au-NPs) is substantiated by studying the role of functionalized GO in governing the geometrical structure and thermal stability of supported Au nanoparticles under reaction conditions [34]....

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