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Full Length Article

Enhanced Hydrogen Evolution Reactions on Nanostructured Cu_2ZnSnS_4 (CZTS) Electrocatalyst

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ABSTRACT

A novel and facile one-step sonochemical method is used to synthesize Cu_2ZnSnS_4 (CZTS) nanoparticles (2.6 ± 0.4 nm) as cathode electrocatalyst for hydrogen evolution reactions. The detailed morphology, crystal and surface structure, and composition of the CZTS nanostructures were characterized by high resolution transmission electron microscopy (HR-TEM), Selected area electron diffraction (SAED), X-ray diffraction, Raman spectroscopy, FTIR analysis, Brunauer–Emmett–Teller (BET) surface area measurements, Electron dispersive analysis, X-ray photoelectron spectroscopy respectively. Electrocatalytic abilities of the nanoparticles toward Hydrogen Evolution Reactions (HER) were verified through cyclic voltammograms (CV) and Linear sweep voltammetry (LSV), electrochemical impedance spectroscopy (EIS), and Tafel polarization measurements. It reveals enhanced activity at lower onset potential 300 mV v/s RHE, achieved at exceptionally high current density -130 mA/cm^2, which is higher than the existing non-nobel metal based cathodes. Further result exhibits Tafel slope of 85 mV/dec, exchange current density of 882 mA/cm^2, excellent stability (> 500 cycles) and lower charge transfer resistance. This sonochemically fabricated CZTSs nanoparticles are leading to significantly reduce cell cost and simplification of preparation process over existing high efficiency Pt and other nobel metal-free cathode electrocatalyst.

1. Introduction

Hydrogen (H_2) has been accounted to be a promising alternative and a renewable energy source, that may replace fossil fuels in future [1]. As their availability does not strictly meet the demand, energy from renewable sources must, however, be stored durably for further use. Moreover, one of the effective and economic approach for H_2 generation is electrochemical water-splitting, which is attracting potential interest because of its simplicity, i.e. it produces H_2 (reduction) and O_2 (oxidation) under the controlled potential [2]. A catalyst is needed for efficient hydrogen evolution reaction (HER) that increases the reaction rate and lowers the generation overpotential. Thus, varieties of catalysts are being explored for improving the H_2 yield. Among all the existing catalytic systems, Pt and Pt group noble metal catalysts show high activity towards HER. However, their large scale production and commercial application is hindered by their scarcity and high cost [3]. Moreover, transition metal chalcogenide, phosphide, carbide and graphene based composites etc. have drawn interest due to their low cost and high current density at lower overpotential. However, the carbon based composite encounter limitations viz. low mass activity, weak catalyst bonding (especially graphene suffering from ineffective 2D packing of sheets) and so on [4]. Thus, electrocatalysts like SnS [4g] and CuS [5] with low onset potential and high current density have been exclusively used to circumvent the limitations. However, it has been noted that the performance decreases when used sulfides individually, which motivated us to fabricate multicomponent system and explore for HER with long term stability [6,7]. Along with this the elements Cu, Zn and Sn are low cost, earth abundant elements and relatively less harmful to the environment. Thus herein, we are considering the benefits of sulfides of Sn, Cu and Zn in electrochemical water splitting and expecting a synergetic effect of these chalcogenides. We have developed a synthetic method for quaternary Cu_2ZnSnS_4 nanoparticles (CZTS NPs) for an efficient electrocatalytic HER. Interestingly, CZTS is an active and stable material used in wide range of applications for high efficient energy conversion based systems [8]. Moreover, the literature survey for water splitting reaction reveals that, CZTS-based systems

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