ABSTRACT

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Title: BIFUNCTIONAL CATALYSIS OF SOME METAL CHALCOGENIDES IN HYDROGEN AND OXYGEN EVOLUTION REACTIONS

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In the vanguard of the 21stcentury, the quest for renewable and eco-friendly energy sources stands as a paramount scientific and technological endeavor. The escalating energy deficit and ecological ramifications stemming from the heightened reliance on and depletion of conventional fossil fuels have catalyzed the advancement of innovative energy transmutation technologies, including electrocatalysis and photocatalysis, alongside energy retention mechanisms such as supercapacitors and batteries.

Hydrogen, hailed as the fuel of tomorrow, boasts a superior gravimetric energy quotient of 120 MJ kg^{-1} eclipsing that of gasoline at 44 MJ kg^{-1}in addition to unmatched energy transformation proficiency, ecological harmony, and the virtue of emitting solely water as a byproduct, thus ensuring zero carbon dioxide release. Furthermore, the application spectrum of hydrogenextends to the production of ammonia via the Haber process, methanol creation, the hydrocracking of crude oil, hydrochloric acid manufacturing, and the hydrogenation of oils and fats. Given the absence of naturally occurring hydrogen on our planet, its current production predominantly transpires through the steam reformingof hydrocarbons under elevated temperatures and pressures. This process not only consumes our finite fossil fuel reserves but also contributes to carbon dioxide emissions. Additionally, the hydrogen procured through this method is often tainted with oxides of carbon, nitrogen, and sulfur, which detrimentally affect the surface of the catalysts and diminish its lifespan. Hydrogen, as the exemplary sustainable energy vector,that is distinguished by environmental congeniality, high energy density, and efficient conversion capabilities. It is anticipated to facilitate the seamless integration of diverse energy networks, and thereby fulfilling the fundamental energy requisites of the future.

The pursuit of pristine and inexhaustible energy reserves is a cornerstone of modern scientific innovation. Electrochemical water splitting, energized by sustainable power sources like solar, wind, and hydroelectricity, stands as a beacon of hope for the generation of high-fidelity hydrogen (H_2). This technique, colloquially termed as "water splitting", has garnered significant attention over the previous decade as a captivating solution to transmute renewable electric currents into a reservoir of chemical energy. This energy is encapsulated in the form of hydrogen and oxygen, harvested at the anode and cathode of the apparatus, respectively. There has been a burgeoning advancement in this sector of energy capture technology.

Harnessing solar energy through nanoparticulate photocatalysts for the photocatalytic division of water is at the forefront of sustainable, low-carbon hydrogen (H_2) production. This process, a non-spontaneous chemical reaction, necessitates the transfer of four electrons from a minimum of two water molecules to facilitate the oxidation of water into oxygen (O_2). The theoretical threshold energy to spark this

reaction stands at 1.23 eV. Yet, the evolution of O_2 from water is marred by slow kinetics and substantial kinetic overpotentials, necessitating the use of sacrificial agents to donate electrons for efficient photocatalytic H_2 generation. Notably, the oxygen evolution reaction (OER) suffers from overpotential losses up to 30%, leading to considerable energy dissipation. Moreover, the absence of efficient techniques to segregate the resultant O_2 and H_2 gases poses a significant hurdle for the practical deployment of photocatalytic water splitting. These impediments have shifted the focus towards novel alternatives to the OER, which promise to bolster the burgeoning global hydrogen economy.

The process of overall water splitting reaction can be characterized by two different half-cell reactions at two different electrodes: at cathode, the hydrogen evolution reaction (HER) and at anode, the oxygen evolution reaction (OER). The thermodynamic potential for this process is $\sim$1.23 V that is equivalent to the minimum energy requirement of the process, $\Delta G=237.1$ kJ/mol under standard conditions.The anodic OER is notably more complex than the HER, involving four synchronized proton-electron transfer steps and the generation of various oxygenated intermediates, such as HO*, O*, and HOO*. This complexity accounts for approximately 80% of the total energy consumption in the water electrolyzer. Furthermore, despite significant progress and innovations in crafting high-efficiency OER electrocatalysts, the journey towards optimal performance continues. In this study cost-effective non noble metal-based catalysts, nanoparticles of some transitional metal chalcogenides like CuSe, CuS, NiS, NiSe, etc. are synthesized by similar hydrothermal methods, characterized and their electro catalytic performances are compared and analyzed by varying the chalcogens,e.g.,oxygen, sulphur, and selenium. The synthesized metal nanoparticles have been characterized by microscopic (FE-SEM, HR-TEM), X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), Energy dispersive X-ray spectroscopy (EDX), cyclic voltammetry and chronoamperometry techniques. The study provides a comparison on the effects of various transition metals regarding the catalytic activity of the corresponding chalcogenides and composites.In addition, it may help to get the better catalyst for synthesis of green energy source, hydrogen and understanding the mechanism of the reactions.

To surmount the prevailing challenges, a triad of strategies is commonly employed to enhance the electrochemical efficacy of catalysts. Initially, the fundamental reactivity of the active sites of the catalysts can be markedly augmented through diverse electronic structure optimization techniques, encompassing strategies like doping with cations or anions, defect engineering, manipulation of crystal phases and facets, as well as the alteration of surface strain. Subsequently, the accessibility of these active sites can be significantly expanded through innovative designs in catalyst morphology. Lastly, the proficiency of charge transfer can be elevated by the strategic deposition of catalysts onto structured conductive supports. In this scenario, the vanguard of advanced materials is poised to revolutionize the electrocatalyst design landscape, paving the way for effective and durable water splitting methodologies.

Recommended and forwarded

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