

Review



Cobalt Sulfide (Co₉S₈)-Based Materials with Different Dimensions: Properties, Preparation and Applications in Photo/Electric Catalysis and Energy Storage

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Abstract: Due to their excellent properties and unique structures, transition metal sulfides play an important role in the development of efficient and stable photoelectric catalysts. In recent years, their potential applications have expanded from photoelectric catalysis to energy storage, especially as materials for key components of electrochemical energy storage. As a typical multifunctional metal sulfide catalyst, Co₉S₈ is highly attractive due to its high conductivity, better stability, suitable band structure, enhanced performance and wide applications. A large number of studies have shown that strategically modified Co₉S₈-based materials have greater advantages in various applications compared with pure Co₉S₈. Therefore, this review will evaluate the physicochemical properties and the preparation of different dimensions of Co₉S₈-based materials, and the influence of different structures on the photoelectrochemical energy of materials will be described. In addition, the research progress regarding the evolution of hydrogen photocatalytic, electrocatalytic water splitting and various electrochemical energy storage materials will be emphasized. Finally, the challenges faced by Co₉S₈-based materials and the research directions for their future applications will be discussed.

Keywords: Co₉S₈-based materials; dimensions; energy storage; HER

1. Introduction

The need for large-scale production of renewable energy is driven by the depletion of fossil fuels and serious environmental pollution problems [1–3]. Efficient and environmentally friendly photoelectric catalytic technology has been widely used in energy conversion. However, there are still some problems to be solved, such as the recombination of carriers and the slow kinetics of electrocatalytic reactions, which hinder the further development of photoelectric catalytic technology. Therefore, it is necessary to explore excellent photoelectric catalysts to improve the reaction efficiency.

Metal sulfide (MSx) is considered to be one of the most important materials for the preparation of highly photoelectrochemical active materials, owing to its high stability and excellent redox properties [4–6]. As a typical cobalt-rich sulfide, Co₉S₈ has high conductivity, good stability and a relatively narrow band gap. Meanwhile, Co₉S₈ shows great diversity in size, structure and performance when used by photoelectric catalysts and by various materials for energy storage. In order to obtain more active sites and better performance, Co₉S₈ modification strategies are usually implemented, including morphology control, heterostructure construction, defect engineering, etc. [7–9]. For example, Zhao first developed a hierarchical Co₉S₈@ZnAgInS heterostructure cage to achieve efficient photocatalytic hydrogen production. Li used the doping strategy to prepare an efficient all-pH electrocatalyst Co₉S₈/nitrogen-doped carbo@MoS₂. The Co₉S₈-based materials after modification have a controllable high specific surface area

Citation: Wang, C.; Pang, X.; Wang, G.; Gao, L.; Fu, F. Cobalt Sulfide (CosSs)-Based Materials with Different Dimensions: Properties, Preparation and Applications in Photo/Electric Catalysis and Energy Storage. *Photochem* **2023**, *3*, 15–37. https://doi.org/10.3390/ photochem3010002

Academic Editors: Chuanyi Wang, Wanhong Ma, Myong Yong Choi, Jayaraman Theerthagiri and Seung Jun Lee

Received: 30 November 2022 Revised: 6 January 2023 Accepted: 9 January 2023 Published: 12 January 2023



Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https://creativecommons.org/license s/by/4.0/). and a reasonable pore size distribution, which is conducive to the exposure of the active site, and has made an outstanding contribution to electrocatalytic water splitting and photoelectric catalysis hydrogen evolution. In addition, as a key material for energy storage, Co₉S₈-based materials have been proven to improve the coulomb efficiency and cycle life of batteries, and can also provide rich surface functional groups for Faraday reactions of supercapacitors.

In this review, we first briefly introduce the physicochemical properties of Co₉S₈. Subsequently, the preparation of different dimensions and applications of Co₉S₈-based materials in photoelectric catalysis hydrogen evolution, electrocatalytic water splitting and various means of electrochemical energy storage are discussed (Figure 1). This study will provide prospects for the development of Co₉S₈-based materials as photoelectric catalysts and new-generation energy storage materials in the future.



Figure 1. Properties, preparation and application (photocatalytic hydrogen evolution, electrocatalytic water splitting, batteries and supercapacitors) of Co₉S₈-based materials.

2. Properties

Co₉S₈ nanomaterials have attracted attention from various fields due to their distinct structures and surface areas, thus exhibiting excellent physical and chemical properties. Magnetism, the most fundamental property of Co₉S₈, is profoundly affected by the temperature of the reaction system. For example, Robert F. Heidelberg summarized and described the susceptibility of cobalt–sulfur systems, which mentioned that Co₉S₈ is antiferromagnetic when the Néel temperature is higher than the decomposition temperature [10]. Erika Dutková and colleagues studied the magnetic properties of Co₉S₈ nanoparticles synthesized by mechanical chemistry using a Superconducting Quantum Interference Device (SQUID) magnetometer. The room-temperature magnetic data supports the paramagnetic spin structure of the nanoparticle, and the temperature dependence of the magnetization at low temperatures suggests a transition from paramagnetism to weak ferromagnetism or ferromagnetism [11]. In addition, Zhou and colleagues also studied the magnetic properties of Co₉S₈ hollow microspheres successfully prepared and reached the same conclusion [12]. Therefore, the study of the magnetic properties of Co₉S₈ confirms the potential application of Co₉S₈ in magnetic fields.

A large number of metallic sulfides have outstanding electrical conductivity, such as Co₉S₈ and Ni₃S₂, but magnetic instability and electron interactions make them of insignificant importance [13]. To play metallic sulfides' crucial role, the most common approach is to increase the number of free carriers by introducing different dopants, and an increase in the doping concentration leads to an increase in the conductance [14]. It is worth noting that Co₉S₈ also has rich redox properties, which contributes to the generation of active sites for chemical reactions, especially electrocatalytic hydrogen evolution reaction (HER) and oxygen evolution reaction (OER), which also plays an important role in the further application of Co₃S₈ in the field of photoelectric catalysis [15].

3. Different Dimensions of Co₉S₈-Based Materials

Pokropivny and Skorokhod proposed a classification scheme for nanostructured materials (NSMs) in 2007, namely zero-dimensional (0D), one-dimensional (1D), two-dimensional (2D) and three-dimensional (3D) [16]. It is noteworthy that the physical, chemical and electronic properties of nanomaterials with different dimensions could be quite different from one another, which is attributed to the fact that the intensity of electron motion increases with the increase of dimension [17]. So far, many technologies have been developed for controllable preparation of 0D–3D Co₉S₈ nanomaterials, and 0D nanoparticles, 1D nanotubes, nanorods, nanowires and needles, 2D nanosheets, nanoplates, nanolayers and nanowalls, 3D hollow spheres and flower-like structures have been obtained. Therefore, based on the above classification, this section discusses the structure and preparation method of Co₉S₈ nanomaterials from 0D–3D.

3.1. Zero-Dimensional (0D) Structure

In recent years, the great potential of 0D-nanostructured materials in photoelectric catalysis, solar cells and lithium ion batteries has promoted the synthesis of 0D-structured Co₉S₈-based materials. Feng prepared carbon-coated Co₉S₈ nanoparticles (Co₉S₈@C) from a mixture of cobalt nitrate and trithiocyanuric acid by direct heat treatment in N_2 atmosphere at 700 °C. It is noteworthy that trithiocyanuric acid is both a sulfur and a carbon source in this reaction system [18]. Wang also produced well-coated Co₉S₈@C nanomaterials using the vulcanization method (Figure 2a) [19]. Furthermore, unlike the above, Liu prepared Co₉S₈@C ultrafine nanomaterials using sucrose as the carbon source and using solid state reaction and mechanical ball milling (Figure 2b). It is certain that ball milling is not only a process of particle size reduction, but also promotes more effective binding between carbon and Co₉S₈ [20]. Lu synthesized carbon-decorated and graphene-fixed amorphous Co₉S₈ hollow nanoparticles using a "thermal injection" method [21]. A large number of experimental studies have shown that wrapping unique structurally modified nanoparticles in a doped mesoporous network with more active sites is an effective way to obtain ideal materials with high activity. Zhang, Luo, Du and Wang have reported that metal-organic framework (MOFs)-derived Co₉S₈ nanoparticles embedded in nitrogen and sulfur co-doped carbon composites show excellent performance [22-25]. Using inorganic salt as a template, Yu prepared a series of Co₉S₈ nanoparticles embedded with N and S co-doped carbon through three steps of grinding, carbonation and acid leaching (Figure 2c). It is suggested that the ratio of precursor, annealing temperature and the type of salt can adjust the porosity, heteroatomic content and crystal structure of the product [26-28]. Different synthesis methods have different advantages. Zhang used carbon dots (CDs) to prepare Co₉S₈ nanoparticles in N and S co-doped carbon materials. CDs distributed uniformly in the matrix of Co₉S₈ nanoparticles and played a key role in improving specific surface area and electrical conductivity (Figure 2d) [29]. Wang grew monodispersed Co₉S₈ nanoparticles with a particle size of about 8 nm due to the restriction of organic ligand oleamine on the surface of Reduced Graphene Oxide (RGO) by a simple thermal injection method [30]. Li prepared hollow carbon nanotubes with single cobalt atoms integrated with Co₉S₈ nanoparticles. The structure of the material was verified by X-ray absorption spectroscopy and aberration-corrected scanning transmission electron microscopy [31]. Zhang reported a mild ion exchange method for the preparation of carbon nanofibers modified with Co₉S₈ nanoparticles. Specifically, Co₉S₈ nanoparticles were converted from cobalt oxide precursor nanoparticles in a microwave hydrothermal process and then modified on the carbon nanofiber skeleton. The composition of nanofibers can be adjusted by changing the content of cobalt acetate in the precursor. In terms of materials, Co₉S₈ nanoparticles with favorable dispersion act as redox centers for energy storage, while porous carbon nanofibers provide fast electron transfer pathways [32].



Figure 2. (a) SEM images of Co₉S₈/C-T precursor. Reprinted with permission from Reference [19]. Copyright (2018) Elsevier Ltd. All rights reserved. (b) TEM images of Co₉S₈/C Nanocomposite. Reprinted with permission from Reference [20]. Copyright (2018) Springer Ltd. All rights reserved. (c) The synthetic strategy of the alkali metal doped Co₉S₈ NPs embedded, N, S co-doped carbons. Reprinted with permission from Reference [26]. Copyright (2020) Elsevier Ltd. All rights reserved. (d) The synthesis process of Co₉S₈/NS-C. Reprinted with permission from Reference [29]. Copyright (2017) Royal Society of Chemistry.

3.2. One-Dimensional (1D) Structure

Recently reported 1D Co₉S₈-based nanomaterials can be divided into nanowires, nanotubes and nanorods according to their morphology. The application of nanowire in an energy storage system is beneficial to the strong contact area between electrode and electrolyte. In addition, the high electrochemical activity is due to the abundance of active sites, rapid electron transport and gas release. Yang grew Co₉S₈ nanowires on carbon fiber paper by using a hydrothermal method (Figure 3a). Notably, Co₉S₈ nanowires were encapsulated in a fluffiness shell consisting of a continuous N, S co-doped carbon coating decorated with abundant vertically growing N, co-doped carbon nanotube materials. The

material not only provides excellent voids for rapid mass transfer, but also provides a large specific surface area for loading of active sites [33]. Dong constructed a one-dimensional cobalt sulfide and vanadium sulfide heterojunction nanowire bi-functional electrocatalyst grown on carbon cloth (Figure 3b). The 1D linear Co₉S₈-V₃S₄ heterojunction has strong electron coupling, which is favorable for hydrogen evolution reaction [34]. Similar to nanowire, nanotubes and nanorods have attracted the attention of researchers because of their extreme specific surface area. Liu obtained a core-shell nanotube array with rich oxygen vacancy Co₉S₈@NiCo-LDH (Figure 3c). In situ growth and electrodeposition of flexible carbon cloth carrier were used [35]. Similarly, Zhu successfully fabricated Co₉S₈@Ni(OH)₂ core-shell nanotube arrays with very large specific surface area by electrodeposition (Figure 3d) [36]. Zhang and Li assembled one-dimensional Co₉S₈ nanotubes and two-dimensional nanosheets to prepare materials with excellent synergistic properties (Figure 3e) [37,38]. Wu synthesized a novel hybrid material of Molybdenum sulfide laminate modified by Co₉S₈ nanotubes through continuous solvent heat treatment. X-ray diffraction, field emission scanning electron microscopy, transmission electron microscopy and other techniques were used to characterize the material, which not only proved that the decoration was amorphous MoS_x, but also showed that there was a strong interface interaction between the two phases [39]. Du successfully synthesized a series of Co₉S₈ nanorod arrays with dual-function electrocatalysts doped with Mo on nickel foam for the first time by using a hydrothermal sulfidation process (Figure 3f) [40]. In addition, Du reported an in situ deposition method for adjusting the Ni(OH)₂ loading capacity on a Co₉S₈ surface by adjusting the number of deposition cycles (Figure 3g,h). As a perfect carrier, one-dimensional Co₉S₈ nanorods enhanced the uniform dispersion of amorphous Ni(OH)₂ nanoparticles. The electrolytic deposition of amorphous Ni(OH)2 nanoparticles coated on the surface of Co₉S₈ nanorods greatly improved the interface effect and provided a more effective active center for the water splitting reaction [41].



Figure 3. (a) The synthetic process for CFP supported Co₃S₈@N,S-codoped carbon nanowires with surfaces. Reprinted with permission from Reference [33]. Copyright (2018) Royal Society of Chemistry. (b) Schematic diagram of the synthesis of 1D Co₃S₈-V₃S₄/CC nanowires. Reprinted with permission from Reference [34]. Copyright (2021) Springer Ltd. All rights reserved. (c) Schematic diagram of the detailed synthesis process of Co₃S₈@OV-NiCo-LDH core-shell nanotube arrays. Reprinted with permission from Reference [35]. Copyright (2022) Elsevier Ltd. All rights reserved. (d) Schematic fabrication process of Co₃S₈@Ni(OH)₂ core–shell NT arrays on CFs. Reprinted with permission from Reference [36]. Copyright (2017) Royal Society of Chemistry. (e) Illustration of the fabrication process of hierarchical Co₃S₈/ZnIn₂S₄ tubular photocatalyst. Reprinted with permission from Reference [37]. Copyright (2019) Elsevier Ltd. All rights reserved. (g–h) SEM of Co₃S₈/NF. Reprinted with permission from Reference [41]. Copyright (2019) Elsevier Ltd. All rights reserved.

3.3. Two-Dimensional (2D) Structure

This section demonstrates the preparation of various 2D nanoplates and nanosheets made from Co₉S₈-based nanomaterials. Due to its elevated surface volume ratio, nanometer thickness and fascinating electrocatalytic activity, Co₉S₈ is considered as an ideal material for electrocatalysts. By changing the filling coefficient, Yang and colleagues synthesized cobalt sulfide precursors with different morphs by hydrothermal method and obtained ultra-thin Co₉S₈ nanosheets under the condition that the filling rate of hot autoclaves reached 60% (Figure 4a) [42]. Li successfully designed and synthesized du-

al-function electrocatalyst Co₉S₈/C nanosheets by reducing Co₃O₄/CNS precursor with sodium sulfide (Figure 4b) [43]. One of the benefits of using 2D materials is that such composites can easily interact and combine with other materials of different dimensions. For example, Zhang designed a novel two-dimensional hexagonal WS2-sided Co3S8 heterostructure nanosheet structure on the surface of a carbon nanofiber skeleton [44]. Xing reported and characterized, in detail, layered Co₃O₄@ Co₉S₈ nanowalls assembled from numerous nanosheets [45]. The material with a large number of defects can induce positive effects on the atoms in the ultrathin two-dimensional structure to improving its intrinsic activity, which is beneficial to improve the excellent properties of the material. Wang and colleagues first synthesized porous 2D Co₉S₈ nanosheets rich in defects and applied them to the cathode of Li-O₂ batteries (Figure 4c). It is worth mentioning that the two-dimensional structure and in-plane holes of the catalyst not only facilitate mass transfer, but also provide active sites for sulfur-rich substances [46]. In addition, using cobalt dibutyl dithiocarbamate as raw material, Zhang and colleagues prepared defective Co₉S₈-based ultrathin nanosheets by direct pyrolysis in organic amine solvent [47]. Doping is a particularly popular method to improve material properties. Both Wang and Li successfully synthesized two-dimensional Co₉S₈ nanosheets uniformly distributed on the surface of two-dimensional N-doped graphene [48,49]. Li reported a sandwich structure in which Co₉S₈ is confined between the graphene scaffold folding layer and the N-carbon layer (Figure 4d). Due to the synergistic effect of graphene and carbon layers, the structural stability of the material is highly improved. Hao focused on Co₉S₈ nanosheet arrays grown on carbon cloth under optimal nickel incorporation conditions. The addition of Ni can optimize the electronic structure of Co₉S₈ and improve the conductivity and charge transfer efficiency. In addition, the nanosheet structure endows a two-dimensional charge transfer pathway, exposing more active sites [50]. Tang and Fu both obtained N and S co-doped Co₉S₈ nanoplates [51,52]. Tang prepared nitrogen-sulfur double-doped graphene and quasihexagonal Co₉S₈ nanoplates by a simple ion assembly method (Figure 4e). Fu used Co₉S₈ nanosheets and ethyl orthosilicate to directly form two-dimensional carbon precursors and disperse them into thiourea solution, and then removed them through pyrolysis and template to obtain N and S co-doped Co₉S₈/NSC porous carbon plates.



Figure 4. (a) Schematic illustration of the controllable synthesis of Co₉S₈ catalysts. Reprinted with permission from Reference [42]. Copyright (2018) Elsevier Ltd. All rights reserved. (b) Schematic illustration of synthesis of Co₉S₈/C. Reprinted with permission from Reference [43]. Copyright (2019) Royal Society of Chemistry. (c) Schematic illustration for the synthesis of the holey Co₉S₈ nanosheets Reprinted with permission from Reference [46]. Copyright (2020) Elsevier Ltd. All rights reserved. (d) Schematic illustration of synthesis of N–C@Co₉S₈@G sandwich structure. Reprinted with permission from Reference [49]. Copyright (2020) Elsevier Ltd. All rights reserved. (e) Schematic demonstration of the preparation process for Co₉S₈/NSG_{g-C3N4}. Reprinted with permission from Reference [51]. Copyright (2017) American Chemical Society.

3.4. Three-Dimensional (3D) Structure

It is well known that the properties of nanomaterials depend on their morphology and size. Therefore, compared with 2D materials, 3D materials have a very wide application potential due to their controllable structure, large specific surface area, strong absorption capacity, superior electron and ion transport performance and additional advantages. Rajith Illathvalappil synthesized Co₉S₈-Ni₃S₂ layered nanoflower arrays which were self-supporting on nickel foam with the required porosity and structural characteristics using a one-pan hydrothermal method without using any adhesives (Figure 5a). The active modulation achieved in this experiment is attributed to the existence of the open pore morphology of Co₉S₈-Ni₃S₂ nanoflowers formed on the nickel foam, which is conducive to the adsorption of reactants and the transformation of gaseous products [53]. Xia successfully prepared a Co₉S₈-based photocatalyst for efficient hydrogen evolution (Figure 5b). They combined CdS quantum dots with hollow dodecahedron Co₉S₈ to form a Co₉S₈/CdS heterostructure using a low-energy atmospheric single-pot strategy [54]. Similarly, Qiu designed a hollow cobalt sulfide cube embedded with cadmium sulfide quantum dots as a template using the one-pot hydrothermal method (Figure 5c). Hollow CdS/Co₉S₈ utilizes multi-light reflection in the cube structure to achieve enhanced photocatalytic activity [55]. Zhao synthesized CoNi₂S₄/Co₉S₈ nanostructures with high porosity, suitable pore size distribution and novel structure using simple chemical bath deposition [56]. By using a simple triethanolamine-assisted self-template strategy, Wang and colleagues prepared a unique three-dimensional honeycomb cobalt sulfide network composed of cross-linked nanosheets (Figure 5d). It was found for the first time that the introduction of triethanolamine in the reaction can effectively increase the proportion of high-priced Co³⁺ in the final product [57]. Li reported the atomic layer deposition of cobalt sulfide. In this process, high quality Co₉S₈ films with layer-by-layer growth behavior were produced using H₂S as reactant. Co₉S₈ films can also be conformally deposited into deep and narrow grooves with an aspect ratio of 10:1, which indicates that this process has a high application prospect for Co₉S₈ conformal coating on 3D nanostructures with elevated aspect ratio [58].



Figure 5. (a) Schematic illustration of the synthesis of Co₃S₈ -Ni₃S₂ /NF through the hydrothermal route and the use of this system as the bi-functional electrode in water electrolysis. Reprinted with permission from Reference [53]. Copyright (2020) Wiley-VCH. (b) Preparative Process for CdS, Co₃S₈, and Co₃S₈/CdS. Reprinted with permission from Reference [54]. Copyright (2021) American Chemical Society. (c) The preparative process for CdS/Co₃S₈ and corresponding TEM images; scale bar (200 nm). Reprinted with permission from Reference [55]. Copyright (2017) Wiley-VCH. (d) Schematic illustration of the formation of the Co₃S₇-TNSs. Reprinted with permission from Reference [57]. Copyright (2021) Springer Ltd. All rights reserved.

4. Applications

As mentioned above, Co₉S₈-based nanomaterials are technically valuable functional materials for various applications. For photocatalytic technology, the keys to its excellent light capture and charge transfer are its higher specific surface area, more abundant active sites, shorter charge carrier migration distance and electronic structure. In addition to being the matrix material, Co₉S₈-based nanomaterials also promote the transformation of reaction kinetics and finally improve the electrode output. In the following sections, we will selectively review some typical examples involving Co₉S₈-based nanomaterials.

4.1. Photoelectric Catalysis

4.1.1. Photocatalytic Hydrogen Evolution Reaction (HER)

H₂, as a high energy density zero-pollution emission energy carrier, is considered as a promising alternative to fossil fuels. In general, Pt-based materials have been shown to be the most effective HER catalysts. However, their high cost and low reserves make them difficult to realize for large-scale industrial applications. Therefore, the development of greatly active and stable earth-rich catalysts to reduce or eliminate the dependence on noble metal-based catalysts for HER remains a great challenge. Co₉S₈-based catalysts have been used as H₂-generating catalysts for non-noble metals and great progress has been made. To further improve the catalytic performance of Co₉S₈-based catalysts, several modification strategies such as defect engineering, doping and heterojunction engineering have been developed. For example, Zhang fabricated Co₉S₈-based ultrathin sheets with a thickness of 4 to 6 nm that are rich in edge defects, cavity defects and dislocation defects. Moreover, the catalytic activity of hydrogen evolution was optimized by tuning the coordination solvent and pyrolysis parameters to control the defects of Co₉S₈-based nanosheets. As shown in Figure 6a,b, the apparent defects on the surface of Co₉S₈-based nanosheets were confirmed by HRTEM images. They also assessed the thickness of Co₉S₈-based nanosheets as ~4 nm by AFM analysis (Figure 6c) [47]. In addition to the defects mentioned above, appropriate heteroatomic doping can adjust the electronic structure, which is an effective way to improve the performance of the electrocatalyst for hydrogen evolution. N, S, P heteroatom-doped composites have attracted much attention due to their high HER activity [58–60]. Among them, the study found that phosphorous-doped metal sulfide is particularly interesting, because P atoms have a similar atomic radius and electronegativity to S atoms, which makes it easy for P atoms to be doped into sulfide by replacing S atoms to bond with metal atoms and cause lattice distortion [61,62]. Such small changes to the parent lattice structure may provide new active sites, optimize the adsorption energy of hydrogen, or regulate the electronic band structure, which may be beneficial to improve its electrocatalytic performance [63]. Gao's team systematically studied the effect of the amount of P doping on the electrocatalytic properties of CoS₂. Through theoretical and experimental studies, Jin and colleagues established ternary pyrite cobalt phosphorus sulfide (CoPS) as a HER electrocatalyst with high performance [64]. Although the above two have made great contributions to exploring the application of P-doped CoS₂ and CoPS to HER, there are few studies on the catalysis of P-doped Co1-xS, Co9S8 and other cobalt sulfide compounds. Qu reported a general synthesis method for various P-doped cobalt sulfide compounds, including CoS₂/Co_{1-x}S, Co_{1-x}S and Co₉S₈ phase [65] (Figure 6h,i). It is found that hydrothermal temperature has a crucial influence on the phase of final products. Therefore, different phase products are synthesized by controlling the hydrothermal temperature. Because P atoms and S atoms have a similar atomic radius and electronegativity, P atoms are easily doped into sulfide by replacing the S atoms and bonding with metal atoms, which leads to lattice distortion. Through experimental study and theoretical calculation, it is shown that the introduction of P can effectively improve the conductivity of cobalt sulfide and optimize the hydrogen adsorption energy. This study provides guidance for the design of P-doped Co₉S₈ and other cobalt sulfide compounds as HER electrocatalysts. In order to improve HER efficiency, the construction of heterogeneous catalysts is also a popular strategy at present. Wu successfully prepared MoS₂/Co₉S₈ heterostructure and showed excellent catalytic performance and good stability [66]. As shown in Figure 6f,g, MoS2 is evenly distributed on the surface of Co₉S₈, which is conducive to MoS₂ exposing more boundary active sites. In addition, the heterostructure formed between MoS2 and Co₂S₈ is more favorable for electron transfer. The LSV curve and Tafel slope results show that, as shown in Figure 6h, *i*, the heterogeneous structure of MoS₂/Co₉S₈ greatly improves HER catalytic performance. In summary, to obtain high performance Co₉S₈-based HER electrocatalysts, the following points should be paid more attention. The intrinsic activity of

each active site was improved by optimizing the hydrogen adsorption energy of the electrocatalyst. Moreover, improving the conductivity of electrocatalysts is equally important for accelerating the charge transfer. Furthermore, attention should be paid to improving the macroscopic structure, hydrophilic and hydrophobic characteristics, and enhancing the mass diffusion between the H₂ catalyst and the electrolyte.

Photocatalysis as a green and efficient H₂-generation pathway has also received extensive attention [67–69]. Co₉S₈ is an interesting visible light active photocatalyst with a special electronic structure, tunable optical properties and wide corresponding range of light. Despite the encouraging progress, the catalytic efficiency of pure Co₉S₈ photocatalysts is still not ideal. Therefore, coupling Co₉S₈ to a semiconductor with an appropriate bandgap to form a heterostructure is a successful technique to efficiently collect electrons and induce charge transfer at the interface. Taraka Prabhu Yendrapati constructed an efficient and stable Co₉S₈@CdIn₂S₄ heterostructure for the photocatalytic generation of H₂ in visible light [70]. On the basis of retaining the polyhedral form of Co₉S₈, CdIn₂S₄ is uniformly decorated on the Co₉S₈ cage, as shown in Figure 6j,l. Two photoactive sulfide semiconductors are reasonably incorporated, and this hollow heterostructure can effectively achieve the separation and transfer of photoinduced charge, providing a broad surface area and abundant exposure sites for the photocatalytic redox reaction, so that it has stronger light-trapping ability and significant HER catalytic activity.



Figure 6. (a) HRTEM images of DR-Co₉S₈-II with pore defects and dislocation. (b) Schematic drawing of defective structures in DR-Co₉S₈-II nanosheets. (c) AFM images of DR-Co₉S₈-II. Reprinted with permission from Reference [47]. Copyright (2018) Royal Society of Chemistry. (d) LSV curves of bare carbon cloth, P-Co₉S₈, P-Co_{1-x}S, P-CoS₂/Co_{1-x}S and Pt sheet. (e) Nyquist plots of P-Co₉S₈, P-Co_{1-x}S and P-CoS₂/Co_{1-x}S. Reprinted with permission from Reference [65]. Copyright (2021) Elsevier Ltd. All rights reserved. (f) SEM images of MoS₂@Co₉S₈/CC. (g) HRTEM. The electrochemical measurements of all synthesized catalysts in 1 M KOH. (h) HER polarization curves. (i) Tafel plots. Reprinted with permission from Reference [66]. Copyright (2019) Springer Ltd. All

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4.1.2. Electrocatalytic Water Splitting

With the exhaustion of non-renewable resources such as fossil fuels and the increasingly serious environmental pollution, people are focusing on renewable clean energy. Electrochemical water decomposition is an efficient method to produce H₂ and O₂. Electrocatalytic water separation in the reaction process consists of two half reactions: HER at the cathode and OER at the anode. There are problems of high overpotential and slow kinetics in the reaction process. As a result, many scholars try to develop noble metal-free OER/HER dual-function catalysts to improve gas production rate and reduce energy consumption, among which, Co₉S₈-based materials have made great progress (Table 1). For example, Dong successfully prepared 1D Co₉S₈-V₃S₄/CC heterojunction dual-function electrocatalysis for water splitting and obtained good HER and OER performance, as shown in Figure 7a,b [34]. In this study, the researchers not only tested the performance of the catalyst, but also explained its catalytic mechanism. As shown in Figure 7c, XPS results confirmed the formation of the Co₉S₈-V₃S₄ heterojunction. It is noteworthy that the Co peak of Co₉S₈-V₃S₄/CC shifted to a positive position compared with Co₉S₈/CC and the V peak of Co₉S₈-V₃S₄/CC shifts negatively with respect to V₃S₄/CC. These results indicate that there is a strong electron interaction at the interface, where V₃S₄ acts as an electron attractor to obtain electrons from Co₉S₈, resulting in the higher Co^{3+} and lower valence V²⁺ states in Co₉S₈-V₃S₄/CC. In conclusion, the electron transfer from Co₉S₈ to V₃S₄ occurs at the interface due to the strong electron coupling effect of the $Co_9S_8-V_3S_4$ heterojunction, where the electron attraction of V_3S_4 (V²⁺) optimizes the adsorption of H* active substance and is favorable for HER. The electron loss of Co₉S₈ (Co³⁺) responds to the enhancement of OER activity. In addition to being a dual-function electrocatalyst, Co₃S₈-based materials are also widely used as three-function electrocatalysts. Based on the concept of sustainable energy development, Liang designed a three-function electrocatalytic material containing Co₉S₈/Co in situ encapsulated in N-doped carbon nanotubes (Figure 7d), achieving efficient electrocatalytic reactions of oxygen reduction, oxygen evolution and hydrogen evolution [71]. The microstructure analysis shows that Co₉S₈ and Co nanoparticles are in situ integrated into N-doped graphite carbon tube (Figure 7e). In this study, they highlight the importance of the rich Co-N and Co-N-C coupling centers generated by in situ engineering of the conversion of metal sulfides to carbon-nitrogen frameworks for the multifunctional catalytic conversion of sustainable energy. As shown in Figure 7f,g, XPS confirmed the existence of abundant Co-N and Co-N-C coupled active sites at the interface. In addition, Li also reported Co₉S₈ as a multifunctional electrocatalytic material [31]. The theoretical calculation and experimental results showed that the synergistic effect between Co₉S₈ nanoparticles and single cobalt atom will reduce the reaction barrier, as shown in Figure 7h,i, thus promoting the generation of ORR, OER and HER. According to the above studies, it can be concluded that bifunctional or even trifunctional catalysts with excellent HER and OER performance reflect the diversity of their catalytic functions and may show great potential in other types of applications [41].

Table 1. Electrocatalytic Activity of Co₉S₈-Based materials.

Material	Electrolytes	OER (mV)	Tafel Slope (mV dec ⁻¹)	HER (mV)	Tafel Slope (mV dec ⁻¹)	Ref.
Co ₉ S ₈ -V ₃ S ₄ /CC	1.0 M KOH	232@10 mA cm ⁻²	59	85@10 mA cm ⁻²	51	[34]
CdS@Co9S8/Ni3S2	1.0 M KOH	285@20 mA cm ⁻²	96.8	69.6@-10 mA cm ⁻²	121	[72]
Co ₉ S ₈ @MoS ₂	1.0 M KOH	342@10 mA cm ⁻²	94	147@10 mA cm ⁻²	117	[73]
MoO2@MoS2@Co9S8	1.0 M KOH	310@10 mA cm ⁻²	70	160@10 mA cm ⁻²	96	[74]
C09S8@Ni(OH)2	1.0 M KOH	140@60 mA cm ⁻²	70	119@10 mA cm ⁻²	80	[41]
Mo-Co ₉ S ₈ /NF	1.0 M KOH	210@50 mA cm ⁻²	-	139@10 mA cm ⁻²	-	[40]

Co ₉ S ₈ -Ni ₃ S ₂ HNTs/Ni	1.0 M KOH	281@50 mA cm ⁻²	53.3	85@10 mA cm ⁻²	83.1	[37]
Co ₉ S ₈ -Ni ₃ S ₂ /NF	1.0 M KOH	102@25 mA cm ⁻²	105.3	227@25 mA cm ⁻²	171.2	[53]
Co ₉ S ₈ /CNFs	1.0 M KOH	230@10 mA cm ⁻²	72	165@10 mA cm ⁻²	83	[75]
Co/Co ₉ S ₈ -MoS ₂	1.0 M KOH	325@10 mA cm ⁻²	69	128@10 mA cm ⁻²	65	[76]
Co ₉ S ₈ -NSC@Mo ₂ C	1.0 M KOH	293@10 mA cm ⁻²	59.7	89@10 mA cm ⁻²	86.7	[23]
Co ₉ S ₈ @NiCo LDH/NF	1.0 M KOH	278@30 mA cm ⁻²	83	168@10 mA cm ⁻²	103	[77]
Co ₉ S ₈ /Cu ₂ S/CF	1.0 M KOH	195@10 mA cm ⁻²	78.8	165@10 mA cm ⁻²	80.2	[78]
CFP@Co ₉ S8@C	1.0 M KOH	290@10 mA cm ⁻²	74	175@10 mA cm ⁻²	97	[33]
C09S8/C03O4	1.0 M KOH	250@10 mA cm ⁻²	73.54	-	-	[79]
Co/Co ₉ S ₈ @SNGS	1.0 M KOH	290@10 mA cm ⁻²	80.2	350@20 mA cm ⁻²	96.1	[80]
Co ₉ S ₈ @MoS ₂ /N	1.0 M KOH	223@10 mA cm ⁻²	56.3	126@-10 mA cm ⁻²	74.1	[81]



Figure 7. (a) Polarization curves of bare CC, V₃S₄/CC, Co₉S₈/CC, Co₉S₈-V₃S₄/CC and Pt-C/CC catalysts with a scan rate of 2 mV s⁻¹ in 1.0 mol L⁻¹ KOH for HER. (b) Polarization curves of bare CC, V₃S₄/CC, Co₉S₈/CC, Co₉S₈-V₃S₄/CC and RuO₂/CC catalysts with a scan rate of 2 mV s⁻¹ in 1.0 mol L⁻¹ KOH for OER. (c) XPS survey spectrum of S 2p of Co₉S₈-V₃S₄/CC. Reprinted with permission from Reference [34]. Copyright (2019) Elsevier Ltd. All rights reserved. (d) Proposed synthetic protocol for Co₉S₈/Co-NCNT nanotube. (e) HRTEM images of Co₉S₈/Co-NCNT-0.05. (f-g) High resolution XPS spectra of Co₉S₈/Co-NCNT-0.05. Reprinted with permission from Reference [71]. Copyright (2020) Wiley-VCH. (h) Free energy diagrams for the thermodynamic limiting potentials of OER steps. (i) Free energy diagrams of Co₉S₈, CoN₄, and CoSA + Co₉S₈/HCNT. Reprinted with permission from Reference [31]. Copyright (2021) Springer Ltd. All rights reserved.

4.2. Electrochemical Energy Storage

Electrochemical energy storage devices such as supercapacitors, Li/Na ion batteries, Li-S batteries and Zn-air batteries play an important role in modern society. In order to follow the needs of social development, it is very desirable to obtain a better, new generation of batteries. Therefore, as a key component of energy storage devices, the performance of electrode materials is particularly important. Co₉S₈-based materials have the natural advantage of building better electrode materials. By carefully adjusting the chemical composition and microstructure of transition metal sulfides, significant electrical conductivity can be obtained, thus solving many existing problems and bringing significant development to supercapacitors and batteries.

4.2.1. Batteries

Lithium-Ion Batteries

Rechargeable lithium-ion batteries (LIBs) have been widely used in many modern electronic products, such as electric vehicles and portable electronic devices, due to their high energy density, environmental friendliness and long-term cycle stability. However, the theoretical capacity of graphite used as an anode material limits the development of LIBs. Transition metal Co₉S₈, which has become a high-performance LIBs electrode material, has been widely studied because of its large theoretical capacity and high safety. For example, as shown in Figure 8a, Chen prepared N and S co-doped carbon skeleton cobalt sulfide nanoparticles (Co₃S₈/NSC) by a one-step method [82]. As an anode for lithium-ion batteries, the composite material has good reversible capacity, high velocity performance and long-term cycling stability (Figure 8b,c). Although Co₉S₈-based nanomaterials have made great progress as electrode materials, their further development is still greatly hindered by their volume expansion and electrical conductivity. Therefore, many scholars adjust the structure of materials or compound Co₉S₈ with other materials to get better electrode materials [49,83,84]. He demonstrated an expandable electrostatic spinning method for preparing Co₉S₈/Ni₃S₂@S-CNFs materials as independent anode materials [85]. In particular, this study forms an independent 3D nanofiber network that allows lithium ions to easily access the active nanoparticles, thereby enhancing the activity and stability of the material.

Sodium-Ion Batteries

In recent years, with the increasing demand for low-cost, long-life, high-energy density storage systems, sodium ion batteries (SIBs) have been considered as a promising alternative to LIBs due to the abundant supply and low cost of sodium [86-88]. At present, Co₉S₈-based materials has good conductivity as SIBs electrode material and can be a cathode material with great potential for commercialization. Li and his colleagues demonstrated that the rich grain boundaries and three-layer exposed interfaces of the prepared Co₉S₈-carbon material are the main capacitors for the storage performance of high sodium ions through experiments and simulation analysis [89]. Wang and colleagues prepared Co₉S₈@S-CF materials by in situ pore-forming, sulfurization, sulfur doping, and carbonization [90]. As shown in Figure 8d, sulfur-doped foam carbon has abundant voids. These interstitial spaces can construct three-dimensional ion/electron paths to accelerate the transport of sodium ions/electrons to Co₉S₈ nanoclusters. In addition, the reversible capacity retention rate is up to 80% after 1000 cycles, and the Coulomb efficiency is over 95%, which is very close to the theoretical capacity of hybrid material, as shown in Figure 8e. The results show that the material has a unique foam-like structure and is superior to Co₉S₈ nanosheets in terms of reversible capacity, capacity retention and cyclic stability. According to the above research, it can be found that Co₉S₈-based materials pave a new way for the development of advanced electrodes for SIBs, and can, therefore, be extended to the development of various metal sulfide based electrodes for SIBs.

Lithium–Sulfur Batteries

Lithium-sulfur batteries have been widely explored because of their rich sulfur resources and high energy density, which overcomes the limitations of existing energy storage devices [91-93]. However, there are still many limitations that restrict the large-scale commercial development of lithium-sulfur batteries, such as large volume changes, irreversible loss of soluble lithium polysulfide in electrolytes and reduced number of electrochemical active reaction sites. To address the above technical obstacles, Co₉S₈-based nanomaterials can be combined with the electrode matrix to maximize the use of sulfur and inhibit the dissolution of polysulfides due to their excellent physical and chemical properties. Chen proposed that injecting Co₉S₈ into N-doped graphene to improve the electronic conductivity of the base. It is worth noting that the highly polar Co₉S₈ is considered to be an excellent chemical adsorbent and catalyst. It not only effectively immobilized the soluble lithium polysulfide through chemical binding, but also significantly catalyzed the electrochemical conversion of the soluble lithium polysulfide, and finally, inhibited its shuttle effect [94]. In addition, Li prepared Co₉S₈-doped graphene as the main material for a lithium–sulfur battery [95]. As shown in Figure 8f, the electron spin resonance spectrum verified the presence of sulfur vacancies in the sample. The use of UV-Vis adsorption spectrum indicates that the sulfur vacancy generated in the material effectively improves the adsorption capacity of polysulfide anions. In addition, density functional theory has calculated the adsorption energy of the material for polysulfide (Figure 8g,h). Finally, electrochemical experiments showed that the sulfur vacancy promoted the electrode kinetics of polysulfide catalytic conversion. The results showed that it is an effective way to develop high performance lithium-sulfur batteries by using sulfur vacancy to enhance sulfur conversion kinetics. Although the Co₉S₈-based materials play a role in promoting the performance of Li-S batteries, the shuttle effect, large amount of variation of sulfur and the formation of polysulfide have not been completely solved, and the real reality of Li-S batteries still needs a lot of exploration.



Figure 8. (a) Schematic drawing of the formation process to obtain the hybrid composite Co₉S₈/NSC. (b) the cycling performance at 0.1 A g 1 of Co₉S₈/NSC. (c) rate capability. Reprinted with permission from Reference [82]. Copyright (2019) Royal Society of Chemistry. (d) Schematic illustration for in situ formation of Co₉S₈ nanoclusters confifined in sulfur-doped carbon foam (denoted as Co₉S₈@S-CF). (e) Cycling performance of the Co₉S₈@S-CF and Co₉S₈ nanosheets and S-CF electrodes at 0.25 C (1 C = 400 mA g⁻¹). Reprinted with permission from Reference [90]. Copyright (2019) American Chemical Society. (f) Electron spin resonance spectra of Co₉S₈/N-doped graphene and Co₉S₈-x/N-doped graphene. (g) Assignment of absorption bands in UV-Vis spectrum of Li₂S₆ DOL/DME solution. (h) UV-Vis spectra of the Li₂S₆ solution and after static adsorption of the different host materials. Reprinted with permission from Reference [95]. Copyright (2013) Royal Society of Chemistry.

Zn-Air Batteries

Dual-function electrocatalytic materials are an important part of many renewable energy devices. For example, in the water splitting mentioned above, HER and OER are the two main reactions. In metal–air batteries, the ORR and OER activity at the side of the air electrode is a key parameter that determines the performance of the battery, and the voltage difference between the two reactions determines the efficiency and energy consumption of the device. Although a simple mixture of a single catalytically active catalyst can also achieve the effect of dual-function catalyst, the corresponding energy density and power density will decrease owing to the increase of mass load. Therefore, it is reasonable to study the corresponding dual-function catalysts, especially for demanding batteries. Co₉S₈-based materials are an excellent choice for metal-air batteries, especially for zinc-air batteries, due to their excellent bi-functional properties in ORR and OER [96,97]. Zheng synthesized a series of N- and S-doped carbon NSC/Co₉S₈ materials. Considering that the structure of the electrode material is an important factor in the optimization of the electrocatalyst, they introduced homogeneous mesopores or macropores in the carbon structure [98]. Excellent electrocatalytic activity of the oxygen reduction reaction was obtained, which was mainly due to the improvement of wettability and the interaction with O₂. Although Co₉S₈ is a promising non-noble metal bi-functional electrocatalyst, the electrocatalytic performance of cobalt-based nanocatalysts is still unsatisfactory due to the poor electrical conductivity and easy aggregation during continuous operation. In order to solve the above problems, Cao synthesized the honeycomb structure porous carbon (Co₉S₈/NSC) in situ composite by a simple method inspired by honeycomb in nature [99]. Co₉S₈ nanoparticles embedded in the carbon matrix of a 3D interconnection network gave it high electrical conductivity, which not only promoted the electron transfer and charge transfer at the interface, but also promoted the exposure and rapid transfer of active sites of ORR/OER-related species, and the obtained composite material exhibited high cyclic stability.

4.2.2. Supercapacitors

Supercapacitors have become a research hotspot because of their advantages, such as high power density, high coulomb efficiency and long cycle span [100,101]. In the field of energy storage, supercapacitors play an important role in complementing or even replacing conventional batteries. However, capacitors still have disadvantages beyond battery devices, such as low energy density and self-discharge. Therefore, in order to improve the electrochemical performance of supercapacitors, many scholars have conducted a lot of research and gained some new understandings. For example, only specific functional groups such as pyridine- or pyrrole-type nitrogen are favorable for Faraday reactions, the transfer of electrons and ions on the surface is critical to the rate capacity, and the morphology is also related to electrochemical properties [102–104]. In addition, it is also crucial to find excellent electrode materials for capacitors. Co₉S₈-based materials can improve the conductivity by introducing a pseudocapacitance reaction, expanding specific surface area and constructing porous structure [105,106].

Based on the above, Co₉S₈-based materials provide a good opportunity to construct capacitor electrodes with excellent performance. In order to further improve the conductivity of Co₉S₈-based materials in supercapacitor electrodes, Emad S. Goda successfully designed a novel structure encapsulated by nitrogen-doped graphene (Al-doped Co₉S₈@NG) as the positive electrode of the capacitor [107]. As shown in Figure 9a,b, the composite developed has a maximum capacity value of about 736 C/g at a current density of 1 A/g and has an ultra-long cycle stability after 10,000 cycles. These results indicate that carbon substrate, as a fast charge transfer agent, can balance the change of electrode volume and enhance the conductivity of nanoparticles, thus obtaining electrodes with good electrochemical characteristics. However, in addition to electrical conductivity, the structural instability of Co₉S₈-based materials often reduces their electrocatalytic activity during the long-term cycle, and reasonable improvement of their structural stability is still a challenge for energy conversion and storage applications. Wang used density functional theory to predict the stability of Co₉S₈, as shown in Figure 9c-f [108]. The calculation results show that compared with pure Co₉S₈, Fe that is doped in an octahedral position can improve its stability. In order to verify the theoretical results, Co₉S₈ hollow spheres with different Co/Fe molar ratios were prepared by one-step hydrothermal experiment and showed excellent electrocatalytic performance. As shown in Figure 9g-i, the Tafel slope is 63.9 mV dec⁻¹ and its overpotential is 268 mV at the current density of 10 mA cm⁻². To be sure, these impressive findings open the door to the use of Co₉S₈-based materials as electrodes for high-efficiency energy storage capacitors.



Figure 9. (a) GCD patterns performed at various applied current densities from 1 to 40 A/g for core-shell Al-Co₉S₈@NG600. (b) Cyclic life analysis for Al-Co₉S₈, Al- Co₉S₈@NG600 electrodes at an applied current density value of 20 A/g. Reprinted with permission from Reference [107]. Copyright (2022) Elsevier Ltd. All rights reserved. (c) The primitive unit cell of Co₉S₈, Green is octahedral metal, Blue is tetrahedral metal, and Yellow is sulfurs. (d) The phonon dispersions of Co₈FeS₈. (e) Calculated band structures. (f) charge density difference. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article). (g) The LSV curves for different catalysts in 1.0 M KOH at 5 mV s⁻¹. (h) Tafel slopes. (i) Corresponding overpotential at 10 mA cm⁻² and Tafel slopes of different catalysts, respectively. Reprinted with permission from Reference [108]. Copyright (2022) Elsevier Ltd. All rights reserved.

5. Conclusions and Outlooks

This paper reviews the theoretical and experimental results of non-noble metal Co₉S₈-based materials in photoelectric catalysis and electrochemical energy storage. These results provide valuable reference for further elucidating the reaction mechanism of catalyst or electrode materials. In addition, the physicochemical properties and synthesis strategies of Co₉S₈-based materials with different dimensions are discussed in detail. It should be noted that there are still some key issues that need to be resolved and explored, even though the excellent properties of Co₉S₈-based materials facilitate their application in many fields.

- (i) The research regarding their reaction mechanism was not thorough, which restricts the further development of Co₉S₈-based materials as excellent catalyst and electrode materials.
- (ii) As an ideal catalyst, excellent results in different pH must be shown to make the water splitting process more efficient. However, experimental studies have shown that the proton concentration is bound to change during the HER process, which leads to different degrees of influence on Co₉S₈-based materials working in acidic or alkaline media.
- (iii) Some renewable energy installations typically require excellent bi-functional catalytic performance, such as the Zn-air batteries mentioned above. However, the role of bi-functional catalytic activity in different electrolytes is not the same, which hinders its practical application.
- (iv) We review the applications of Co₉S₈-based materials as photocatalysts and energy storage materials in recent years, but not limited to this, we can also explore its applications in biosensors, organic catalytic synthesis and other new fields, which are of great value for facilitating multi-field applications.

In summary, Co₉S₈-based materials have shown great advantages as catalysts and electrode materials, but their applications in other fields remain a challenge. Therefore, this paper mainly aims to introduce the research progress of properties, preparation strategies and applications of Co₉S₈-based materials in different dimensions. It provides reference for better design of Co₉S₈-based materials for wider applications to alleviate these challenges. We believe that the extraordinary physical and chemical properties of Co₉S₈-based materials will enable exciting advances in high performance energy storage devices and energy applications in the future.

Author Contributions:-Conceptualization and writing, C.W. and X.P.; investigation and supervision, G.W. and L.G.; validation, F.F. All authors have read and agreed to the published version of the manuscript.

Funding: This work was supported by the National Training Program of Innovation and Entrepreneurship for Undergraduates (202110719055).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Conflicts of Interest: The authors declare no conflict of interest.

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