CoS₂ Nanoparticles Supported on rGO, g-C₃N₄, BCN, MoS₂, and WS₂ Two-Dimensional Nanosheets with Excellent Electrocatalytic Performance for Overall Water Splitting: Electrochemical Studies and DFT Calculations

Priyakshree Borthakur, Purna K. Boruah, Manash R. Das, Mohamed M. Ibrahim, Tariq Altalhi, Hamdy S. El-Sheshtawy, Sabine Szunerits, Rabah Boukherroub, and Mohammed A. Amin*  

Cite This: dx.doi.org/10.1021/acsaem.0c02509

ABSTRACT: Efficient electrochemical splitting of water with exceptional durability can be a solution for growing global demand for energy. Herein, we systematically investigated the influence of the supporting two-dimensional (2D) substrate (rGO, g-C₃N₄, BCN, MoS₂, and WS₂) on the electrocatalytic performance of CoS₂ nanoparticles (NPs) for overall water splitting. CoS₂ NPs decorated onto rGO, g-C₃N₄, BCN, MoS₂, and WS₂ sheets were synthesized by adopting a facile hydrothermal technique using cobalt salt and sulfur source as precursors. Compared to unsupported CoS₂, the synthesized nanohybrids supported on 2D materials, namely, CoS₂/rGO, CoS₂/g-C₃N₄, CoS₂/BCN, CoS₂/MoS₂, and CoS₂/WS₂, exhibited significantly higher water oxidation and reduction and overall water splitting efficiencies in 1.0 M KOH aqueous solution, with CoS₂/MoS₂ and CoS₂/WS₂ catalysts being the most effective ones. In the case of the hydrogen evolution reaction (HER), CoS₂/WS₂ performed as the best catalyst and was able to provide a current density of 10 mA cm⁻² at an overpotential of 130 mV, whereas it only required 298 mV to generate the same current density for the oxygen evolution reaction (OER). The bifunctional nanohybrid CoS₂/WS₂ catalyst achieved a current density of 10 mA cm⁻² over 96 h for the alkaline overall water splitting at a cell voltage of 1.6 V. Density functional theory (DFT) calculations were also performed to further describe and determine the HER catalytic performance of the studied catalysts. Comparing the absolute values of the studied catalysts’ Gibbs free energy of adsorbed hydrogen intermediate, H*, (ΔGₗH*), revealed that both CoS₂/MoS₂ and CoS₂/WS₂ hybrid catalysts exhibited the best surface stability and the highest HER catalytic performance.

KEYWORDS: CoS₂, 2D nanosheets, DFT calculations, HER, OER, water splitting

1. INTRODUCTION

In recent decades, the problems related to the energy storage and releasing of sulfur and carbon oxides during the burning of traditional fossil fuels in automobiles, various industries, etc., have led to a serious problem for the environment as well as to mankind. Therefore, replacement of traditional fossil fuels by renewable and environmentally friendly energy sources has become the top priority in recent years. Hydrogen (H₂) is universally recognized as an ideal energy source because of its environmentally friendly chemical composition, extremely high energy density, high calorific values, and lack of greenhouse gases produced during its burning. Among the numerous approaches for H₂ production, splitting of sustainable energy sources like H₂O to hydrogen and oxygen by an electrocatalysis process has attracted widespread attention and remarkable achievement for its cost-effectiveness, clean and environmentally friendly forthcoming ecology, and economy. Till now, many transition-metal-based electrocatalysts have been developed toward the water splitting process because of their high efficiency in energy conversion. Among the different electrocatalysts, cobalt sulfide (CoS, CoS₂, Co₅S₈, Co₇S₉) nanoparticles (NPs) exhibit remarkable advantages due to earth abundance of cobalt, potential redox-dependent electrochemical properties, high conductivity, and efficient activity. However, because of the restacking tendency of the metal sulfide NPs by van der Waals forces, their practical performance as a...
catalyst is significantly hindered. Decoration of metal sulfide nanoparticles on different two-dimensional (2D) support materials, including reduced graphene oxide (rGO), graphitic carbon nitride (g-C₃N₄), boron carbon nitride (BCN), molybdenum disulfide (MoS₂), tungsten disulfide (WS₂), etc., can inhibit their agglomeration, increase the catalytic active sites, and improve their cycling stability.1,11

CoS₂ exhibits low energy for chemisorption of hydrogen atoms on its surface12 and is intrinsically metallic and conductive,13 which makes it an efficient electrocatalyst material in HER. The synthesis of CoS₂ nanoparticles on various 2D nanosheets is expected to afford nanostructured materials with better physical and chemical stabilities, increased exposed active sites, and superior electrocatalytic activity in comparison to bare CoS₂ nanoparticles due to the synergistic effect. The presence of the 2D nanosheets could facilitate both electrical conductivity as well as ionic transportation during the HER process.14

Among the different support materials, graphene, the 2D conjugated sheets consisting of sp²-hybridized carbon atoms with honeycomb structure, possesses high specific surface area and high electron mobility (230 000 cm² V⁻¹ s⁻¹) at room temperature. It has been considered as a promising guest material for the development of electrocatalysts.15 Yang et al. reported the fabrication of porous CoS₂/rGO cathode material, which exhibited enhanced HER activity with a low overpotential value (only 180 mV at 10 mA cm⁻² vs. reversible hydrogen electrode), a low Tafel slope (75 mV dec⁻¹), and high stability in acidic condition (up to 18 h).16 Guo and his group utilized Pt-decorated mesoporous WS₂ and rGO nanosheets in the hydrogen evolution process with an excellent performance, featuring a small Tafel slope of 47 mV dec⁻¹, long time durability, and an overpotential of 95 mV in 0.5 M H₂SO₄.17 Other graphene-based electrocatalysts exhibiting HER capacity with excellent activity have been described in several reports.17,18 Similarly, 2D polymeric semiconductor-based support material, g-C₃N₄, also has been used for the fabrication of electrocatalysts because of its high abundance and high thermal and chemical stability.18 However, its low electrical conductivity limits its application in HER. Incorporation of NPs on g-C₃N₄ surface improved its catalytic efficacy toward HER.19,20 Another graphene-like 2D semiconductor material, borocarbonitride (BCN), also possesses excellent catalytic properties due to its excellent thermal stability, high hardness, and unique mechanical properties.21 Pramoda and his group synthesized MoS₂–borocarbonitride nanocomposites through covalent cross-linking between BCN and MoS₂ sheets, which exhibited electrochemical HER efficacy with a current density of 10 mA cm⁻² at an overpotential of −35 mV and an onset potential of −30 mV (vs. RHE).22 Two-dimensional transitional metal sulfides (MoS₂ and WS₂) are widely explored as electrocatalysts for HER because of their exceptional properties, such as atomically thin nature, tunable crystallographic arrangement, chemical stability, and high electron density with controlled conducting properties.23 However, because of weak van der Waals interactions, 2D transitional metal sulfides tend to aggregate and subsequently lose their catalytic activity. Therefore, the synthesis of nanocomposite materials with the aim to greatly enhance their electrocatalytic properties by decoration of transition metal sulfide nanoparticles needs to be explored. An et al. developed NiS₂–MoS₂ interlaced nanoflakes exhibiting excellent HER catalytic activity with a low onset potential (76 mV) and a Tafel slope of 70 mV dec⁻¹ in 1 M KOH aqueous solution.24 Ni₃S₄ nanorod implanted oxygen-incorporated MoS₂ (O-MoS₂) nanosheets were examined as a free-binder electrode for HER. The nanocomposite achieved high electrocatalytic properties toward hydrogen production with an onset overpotential of −150 mV and a low Tafel slope of −81 mV dec⁻¹.25 Heterostructured Co₃S₄@MoS₂-based nanocomposite was utilized as a highly active and stable bifunctional catalyst for both HER and oxygen evolution reaction (OER) in an alkaline medium with low overpotential values of 280 mV for OER and 136 mV for HER at a current density of 10 mA cm⁻².26 Yang et al. reported that metal–organic framework-derived hollow Co₃S₄@MoS₂ microcubes can achieve enhanced efficiency for the HER in acidic medium with a low overpotential of 239 mV at 10 mA cm⁻² and a Tafel slope of 103 mV dec⁻¹ in 0.5 M H₂SO₄.27 Similarly, WS₂ nanosheets decorated with different transition metal sulfide nanoparticles were reported as excellent HER catalysts.28,29

Most of the industrial applications of the energy conversion devices are conducted in alkaline solutions.30 However, plentiful publications revealed that the majority of HER electrocatalysts that perform well in acidic media experience a significant loss of their catalytic activity in alkaline media.30,31 For instance, based on electrochemical measurements, the HER’s kinetics (in terms of the exchange current density, jₒ) in alkaline solutions are 2–3 orders of magnitude lower than those recorded in acidic ones.31,32 Even on Pt, the HER’s most promising electrocatalyst, the HER displayed slower kinetics in alkaline electrolytes compared to acidic ones.33 Therefore, high overpotential, and hence increased energy consumption, is needed to improve the HER’s indolent kinetics in an alkaline medium. This decreased HER rate in alkaline solutions has delayed advances in techniques for the generation of high-purity hydrogen, such as water splitting.30,34

To date, some of the CoS₂-based electrocatalysts and many others have been used as electrocatalysts for the HER in alkaline electrolytes and traditional alkaline water electrolyzers.30,34 Although most of these materials are nonprecious, they are not effective enough to produce large quantities of hydrogen at low overpotentials to subrogate Pt-based electrocatalysts in power conversion devices. This has made it a major challenge to develop highly efficacious, cheap, and stable electrocatalysts to generate hydrogen from alkaline solutions.30,34 In addition, the research aiming at developing highly stable and efficient HER electrocatalysts in alkaline media is meaningful and auspicious for commercial viability.

This work aims to investigate the catalytic impact of various 2D supports like rGO, g-C₃N₄, BCN, MoS₂, and WS₂ nanosheets on the durability and electrocatalytic performance of CoS₂ nanoparticles for both HER and OER in alkaline solution. It is also the objective of the present work to study the catalytic influence of such 2D supports on the durability and bifunctional electrocatalytic activity of CoS₂ NPs for overall water splitting in alkaline medium. The CoS₂/2D nanocomposite materials were synthesized by a simple hydrothermal method. Results of the present work demonstrated that the CoS₂/WS₂ hybrid nanocomposite stands as the best performing electrocatalyst for the HER, OER, and overall water-splitting in alkaline medium. Its catalytic activity exceeded that of the CoS₂ nanotube array/carbon cloth (CoS₂ NAT/CC) electrocatalyst, one of the most effective CoS₂-based electrocatalysts reported in the literature for the HER in alkaline solutions.3 This catalyst, namely, the CoS₂ NAT/CC electrocatalyst with a loading density of 1.2 mg cm⁻², required an overpotential of 193 mV to deliver a current density of 10 mA cm⁻² in 1.0 M KOH. In this
work, a much lower overpotential (130 mV) was sufficient for our best catalyst CoS$_2$/WS$_2$ (loading density 0.28 mg cm$^{-2}$) to generate the same current in the same electrolyte. In addition, because of its high HER and OER catalytic activities, the bifunctional CoS$_2$/WS$_2$ nanohybrid catalyst achieved a current density of 10 mA cm$^{-2}$ with intense evolution of the gas on both electrodes over 96 h for the alkaline overall water splitting at a cell voltage of 1.6 V. This made the CoS$_2$/WS$_2$/CoS$_2$/WS$_2$/alkaline water electrolyzer’s performance comparable to other efficient nonprecious bifunctional electrocatalysts in 1 M KOH.

2. EXPERIMENTAL SECTION

2.1. Synthesis of Different Two-Dimensional (2D) Sheets.

The detailed synthesis of different 2D sheets is described in Section S1.

2.2. Synthesis and Characterization of Cobalt Sulfide NPs Decorated on Different 2D Sheets.

To prepare cobalt sulfide (CoS$_2$) nanoparticles decorated onto different two-dimensional (2D) sheets viz. boron carbon nitride (BCN), graphic carbon nitride (g-C$_3$N$_4$), molybdenum disulfide (MoS$_2$) and tungsten disulfide (WS$_2$), we added 0.1 mmol of Co(NO$_3$)$_2$·6H$_2$O to a suspension of the 2D sheets (1 mg/mL) and kept under magnetic stirring for 1 h for complete homogeneous distribution. After that, 0.2 mmol of Na$_2$S$_2$O$_3$·5H$_2$O was added and the resulting mixture was stirred for another 1 h at 25 °C. The mixture was then transferred into a Teflon-lined autoclave and heated at 180 °C for 10 h. The product was separated by simple filtration and washed with DI water and ethanol. The obtained product was dried at 60 °C for 4 h.

The details of the synthesis and characterization of CoS nanoparticles and CoS/GO nanocomposite are discussed in our previous paper.

The detailed characterization of cobalt sulfide NPs decorated on different 2D sheets are discussed in Section S2. The optimum concentration of the Co and S precursors and the doping amount of Co and S in the different nanocomposites are summarized in Table S1.

2.3. Electrocatalytic Activity Measurements.

2.3.1. Electrochemical Setup.

A conventional double-jacketed three-electrode electrochemical cell was used to conduct electrochemical characterizations. In this cell, the auxiliary and the reference electrodes were respectively a graphite rod (Sigma-Aldrich, 99.999%) and mercury/mercury oxide, Hg/HgO, NaOH (0.1 M). A glassy carbon (GC, 3 mm) loaded with catalysts powder served as the working electrode (WE). The preparation of the WE for electrochemical measurements is described in Section S3. Various electrochemical techniques were applied to assess the synthesized electrocatalysts' performance and stability toward the HER, OER, and overall water splitting. Such electrochemical techniques are fully described in Section S4.

The catalysts’ electrochemically active surface area (ECSA) was calculated using cyclic voltammetry (CV) measurements conducted at various potential scan rates (ν: 20–120 mV s$^{-1}$) covering the range of potential (0.37–0.47 V vs. RHE), which only allows the capacitive current to flow. The difference in current density between anodic and cathodic scans (ΔJ = J$_{\text{cathodic}}$ − J$_{\text{anodic}}$) was measured at 0.42 V vs. RHE and plotted against the slope of the ΔJ vs ν plot for the determination of the catalyst ECSA.

The HER and OER Faradaic efficiencies of the investigated electrocatalysts were estimated by quantifying by gas chromatography the amounts of H$_2$ or O$_2$ released during 1 h of a controlled galvanostatic electrolysis and dividing that by the expected volume of H$_2$ or O$_2$ theoretically calculated during that electrolysis, as reported in Section S4.3.

3. RESULTS AND DISCUSSION

The CoS$_2$ NPs decorated on different 2D nanosheets were synthesized adopting a facile hydrothermal technique using cobalt salt and thiourea as precursors. The synthesized nanocomposites were separated by simple filtration and dried at 60 °C to obtain the final products.

3.1. Characterization of the Nanocomposites.

Before carrying out the characterization of the nanocomposites, we analyzed the XRD patterns of different support materials and pure CoS$_2$ nanoparticles. Figure S1 displays the XRD patterns of CoS$_2$, GO, g-C$_3$N$_4$, BCN, MoS$_2$, and WS$_2$ nanosheets. The XRD pattern of CoS$_2$ shows the characteristics peaks at 2θ values of 35.53°, 46.87°, and 54.76° corresponding to the (210), (220), and (311) diffraction planes, respectively. For the support g-C$_3$N$_4$, diffraction patterns are observed at 2θ values of 13.04° and 27.38° due to the (100) and (002) planes, respectively. In the case of GO, the XRD pattern comprises a diffraction peak at a 2θ value of 10.98° assigned to the (001) crystalline plane. The XRD pattern of BCN shows the characteristic XRD peaks located at 2θ of 25.58° and 43.92° attributed respectively to the (002) and (100) planes. The powder XRD diffractogram of MoS$_2$ sheets consists of the major diffraction peaks at 2θ values of 14.52°, 32.68°, 39.70°, and 49.94° ascribed respectively to the (002), (100), (103), and (105) planes, revealing the formation of hexagonal MoS$_2$ sheets. The XRD pattern of WS$_2$ comprises diffraction peaks located at 2θ values of 14.41°, 28.32°, 34.60°, and 49.89° assigned to the (002), (004), (101), and (105) planes of WS$_2$, respectively.

The crystalline structure of the synthesized nanocomposites was also assessed using XRD analysis. Figure 1 depicts the XRD pattern of CoS$_2$/g-C$_3$N$_4$, where major diffraction peaks at the 2θ values of 32.52°, 36.50°, 40.04°, 46.58°, and 55.20° corresponding respectively to the (002), (210), (211), (220), and (311) diffraction planes with d-spacing values of 2.75, 2.45, 2.25, 1.94, and 1.66 Å could be observed. The results revealed the formation of CoS$_2$ nanoparticles on g-C$_3$N$_4$ sheets corresponding to the JCPDS card No. 00-003-0772. In the XRD pattern of CoS$_2$/BCN nanocomposite, the presence of the (210) and (211) crystalline planes respectively at 2θ values of 32.38°, 36.32°, 40.04°, 46.48°, and 54.98° with d-spacing values of 2.76, 2.47, 2.25, 1.95, and 1.66 Å, respectively (JCPDS card No. 00-003-0772) is a good indication of CoS$_2$/WS$_2$ nanocomposite, the characteristic crystalline planes at 2θ values...
of 32.36°, 36.58°, 46.54°, and 55.08° with d-spacing values 2.76, 2.45, 1.94, and 1.66 Å assigned respectively to the (200), (210), (220), and (311) planes are clearly visible. Additionally, the presence of the (006) diffraction plane at a 2θ value of 28.06° signifies the presence of WS2 sheets in CoS2/WS2 nanocomposite.

The specific surface area, pore volume, and pore radius values of the synthesized nanocomposites are summarized in Table 1. It can be observed that the specific surface area of the nanocomposites is higher than that of the bare 2D nanosheets. The nanocomposites are therefore expected to display higher catalytic activity in comparison to 2D nanosheet counterparts. The values of specific surface area of the nanocomposites were determined to be for CoS2/rGO (26.161 m²/g), CoS2/g-C3N4 (20.976 m²/g), CoS2/BCN (64.235 m²/g), CoS2/MoS2 (33.885 m²/g), and CoS2/WS2 (85.032 m²/g). The CoS2/WS2 exhibited the highest specific surface area and is likely to achieve superior electrocatalytic activity compared to other nanocomposites.

The morphology and particle size of the nanocomposites were investigated by transmission electron microscopy (TEM) and high-resolution TEM analysis. The TEM images of CoS2/g-C3N4 (Figure 2a, b) revealed that the CoS2 NPs are distributed as clusters composed of both spherical and rod-shaped NPs on g-C3N4 sheets with an average particle size of 34.52 nm, as calculated from particle size analysis (Figure 2f) using ImageJ software.

The TEM images in Figure 2c–d indicated the crystallinity of the NPs with clear lattice fringes with an interplanar spacing of 0.22 nm corresponding to the (211) plane of CoS2. The crystalline nature of the sample was further corroborated by the (200), (220), and (311) crystalline planes in the selected area electron diffraction (SAED) pattern (Figure 2e). These findings confirmed the formation of crystalline CoS2 NPs on g-C3N4 sheets.

The TEM images of CoS2/BCN (Figure 2g, h) showed the formation of spherical-shaped CoS2 NPs with an average particle size of 4.38 nm distributed on WS2 sheets. The HRTEM image in Figure 3h revealed clear lattice fringes with an interplanar spacing of 0.16 nm corresponding to the (311) plane of CoS2. The crystalline nature of the sample was further confirmed by the SAED pattern with (200), (220), and (311) crystalline planes (Figure 3h, inset). Thus, the presence of different 2D nanosheets affects the distribution of CoS2 nanoparticles, and expected to influence significantly the electrocatalytic activity of the nanocomposites. The CoS2/WS2 nanocomposite, with the smallest average particle size, performed as the most efficient electrocatalyst toward HER and OER among the other nanocomposites, as will be discussed later.

The chemical bonding information and elemental composition of the synthesized nanocomposites were examined by X-ray photoelectron spectroscopy (XPS). The survey XPS spectrum of CoS2/g-C3N4 comprises S, C, N, O, and Co elements at binding energies of 168.1, 284.7, 398.8, 531.4, and 78(256,586),(702,712) eV, respectively (Figure 4a). The relative atomic percentages of S, C, N, O, and Co, deduced from the XPS survey scan, are 8.27, 8.8, 28.97, 44.11, 5.58, and 4.2 atom %, respectively. The high-resolution Co2p XPS spectrum is deconvoluted into two strong peaks located at 781.3 and 797.2 eV assigned to spin–orbit splitting of Co2p3/2 and Co2p1/2 respectively (Figure 4b). The other peaks at 786.2 and 802.7 eV correspond to the satellite peaks of Co2p, which indicates the presence of cobalt(IV). The deconvoluted high resolution C1s spectrum displays peaks at 284.6 and 289.8 eV attributed to the C−C and an electron-rich C−O environment (Figure 4c). The N1s spectrum is curve-fitted with two peaks at 398.4 and 401.3 eV due to N=C−N and −NH groups, respectively (Figure 4d).

The XPS survey spectrum of CoS2/BCN consists of S, B, C, N, O, and Co (Figure 5a). The relative atomic percentages of S, B, C, N, O, and Co, deduced from the survey scan, are 8.27, 8.8, 28.97, 44.11, 5.58, and 4.2 atom %, respectively. The high-resolution spectrum of the Co2p exhibits two strong peaks located at 781.3 and 797.2 eV, corresponding to Co2p3/2 and Co2p1/2, respectively (Figure 5b). The other peaks at 786.4 and 802.6 eV are attributed to the satellite peaks of Co2p, signifying the existence of Co in +4 state. The high-resolution spectrum of the B1s is fitted with a single peak at 190.2 eV attributed to B−N bond in BCN (Figure 5c). The high-resolution spectrum of the C1s (Figure 5d) can be curve-fitted with several components corresponding to C−C, C−N, C−O, and O−C=O species located at binding energy values of 284.1, 285.1, 286.1, and 288.3 eV, respectively. The N1s spectrum can be deconvoluted with one symmetrical peak at 400.1 eV due to the B−N bond in BCN (Figure 5e).

The peaks located at 232.8, 779.8, and 162.7 eV in the survey spectrum of CoS2/MoS2 indicate the existence of Mo, Co, and S (Figure 6a). The relative atomic percentages of Mo, S, and Co in CoS2/MoS2, determined from the XPS survey scan, are 20.5, 65.0, and 14.5 atom %, respectively. The high-resolution spectrum of the Co2p exhibits two strong peaks located at 781.3 and 797.5 eV corresponding to Co2p3/2 and Co2p1/2, respectively (Figure 6b). The peaks at 786.2 and 802.7 eV are attributed to the satellite peaks of Co2p, suggesting the existence of cobalt in +4 state. The high-resolution spectrum of the Mo4d is fitted with four different peaks; the main peaks located at 228.8 and 232.6 eV are assigned to Mo4d5/2 and Mo4d3/2, indicating Mo(IV) chemical state (Figure 6c). The peak at 236 eV is due to Mo(VI) 3d of MoO3 formed upon air oxidation. The peak located at 226.4 eV indicates the presence of S in MoS2.
The existence of Co, S, and W atoms in CoS$_2$/WS$_2$ was confirmed from the survey XPS spectrum, consisting of peaks at 36.72, 163.9, 532.1, and 779.4 eV due to W, S, O, and Co, with relative atomic percentages of 32.74, 55.01, 2.42, and 9.83 atom %, respectively (Figure 7a). The high-resolution spectrum of the Co$_2p$ exhibits two strong peaks at 781.1 and 797.0 eV belonging to Co$_{2p3/2}$ and Co$_{2p1/2}$, respectively (Figure 7b). The other peaks at 786.1 and 802.7 eV can be attributed to the satellite peaks of Co$_{2p}$, which signifies the existence of cobalt in $+$4 state. The high-resolution spectrum of the W 4f can be fitted with four components at 33.7, 35.8, 36.7, and 38.9 eV. The peaks at 33.7, 35.8, and 38.9 eV are ascribed to the spin–orbit splitting of W$_{4f7/2}$, W$_{4f5/2}$, and W$_{3p5/2}$, respectively. The peak at 36.7 eV originates from W–O bond, referring to low surface oxidation (Figure 7c). The high-resolution spectrum of the S$_2p$ could be fitted with two peaks at 162.2 and 163.4 eV assigned to S$_{2p3/2}$ and S$_{2p1/2}$ of the divalent sulfide ion ($S^{2-}$), respectively (Figure 7d).

The Raman spectra of CoS$_2$/rGO, CoS$_2$/g-C$_3$N$_4$, and CoS$_2$/BCN nanocomposites are displayed in Figure S2a. The Raman spectrum of CoS$_2$/rGO shows the graphene characteristic peaks located at $\sim$1355 cm$^{-1}$ (D band) and $\sim$1609 cm$^{-1}$ (G band) corresponding to the vibration of sp$^3$ defects and disorder of hexagonal graphitic layers, respectively. The peak at 446 cm$^{-1}$ is attributed to T$_g$ vibration mode of CoS$_2$. In the Raman spectrum of CoS$_2$/g-C$_3$N$_4$, the peak at 395 cm$^{-1}$ is attributed to $T_g$ vibration mode of CoS$_2$. The peaks located at 532 and 707 cm$^{-1}$ are the characteristic peaks associated with the breathing modes of the s-triazine ring, whereas the peaks at 1377 and 1695 cm$^{-1}$ are assigned to the disorder in the graphite structure and stretching vibrations of C≡N and C–N heterocycles. The Raman spectrum of CoS$_2$/BCN displays the characteristic peak...
of Co–S vibration of CoS₂ at 397 cm⁻¹. The peaks centered at 1352 cm⁻¹ (D band) and 1615 cm⁻¹ (G band) are ascribed to the breathing mode of A₁g symmetry in aromatic rings and the first-order scattering from the doubly degenerate E₂g phonon mode as well as stretchings of all C–C, B–C, C–N, and B–N bonds in both rings and chains. The Raman spectrum of CoS₂/MoS₂ (Figure S2b) displays the common band at 385 cm⁻¹ corresponding to the characteristic peak of Co–S vibration of CoS₂ and the peak at 409 cm⁻¹ due to the out-of-plane vibration of MoS₂. In the case of CoS₂/WS₂, the peaks at 355 and 423 cm⁻¹ correspond to the E₂g (in-plane optical mode) and A₁g modes (out-of-plane vibrations of sulfur atoms) in WS₂, respectively. The Co–S vibrational peak is observed at 386 cm⁻¹, which confirms the formation of CoS₂/WS₂ nanocomposite.

### 3.2. Electrochemical Studies

#### 3.2.1. Electrochemically Measured HER Activity

Figure 8a depicts the linear cathodic polarization curves measured for the investigated catalysts as well as pure CoS₂ NPs, bare GCE, and commercial Pt/C catalyst. Table 2 lists the various electrochemical parameters describing the kinetics of the HER over the surfaces of the tested catalysts. These parameters were derived from the corresponding Tafel plots, Figure 8b. All currents are referred to the electrochemical active surface area (EASA), calculated from CV measurements (see later). The HER catalysts’ activity was first assessed from their onset potential (E₉怢) values, the potential at which the HER commences and beyond which the cathodic current increases steeply. This potential is considered as one of the most important kinetic parameters characterizing electrocatalytic activity, as any change in its position in the j–E plots results in marked variation in the numerical value of the exchange current density (jₒ). Literature data showed that the anodic shift in E₉怢 enhances the kinetics of the HER thus, improving electrocatalytic activity, as it leads to effective hydrogen production at low overpotentials with higher exchange current density values, jₒ. Table 2 shows that the commercial Pt/C catalyst exhibited the lowest E₉怢 value (E₉怢 = −10 mV vs. RHE) followed by a steep
cathodic current, revealing its outstanding HER catalytic activity. On the contrary, as expected, bare rGO displayed inferior catalytic activity due to its sufficiently larger $E_{\text{HER}}$ value ($-710 \text{ mV vs. RHE}$) and very low reduction currents. The five studied supporting materials alone (rGO, g-C$_3$N$_4$, BCN, MoS$_2$, and WS$_2$), including CoS$_2$ itself, possessed HER catalytic activity much higher than that of the bare GCE, but still humble versus that of the Pt/C catalyst. It is obvious that CoS$_2$ NPs alone (curve 6) exhibits HER catalytic activity that is located between those of MoS$_2$ (curve 5) and WS$_2$ (curve 7). This is expected, as CoS$_2$ NPs’ BET value (11.901 m$^2$/g) is between those of MoS$_2$ (2.818 m$^2$/g) and WS$_2$ (48.418 m$^2$/g). The catalytic activity of the synthesized nanostructured hybrid materials, namely, CoS$_2$/rGO, CoS$_2$/g-C$_3$N$_4$, CoS$_2$/BCN, CoS$_2$/MoS$_2$, and CoS$_2$/WS$_2$ catalysts, stand far beyond that of their respective supporting materials and CoS$_2$ alone, with CoS$_2$/WS$_2$ and CoS$_2$/MoS$_2$ catalysts approaching Pt/C catalyst’s activity. These results revealed the role of the supporting materials in catalyzing the HER activity (the hybrid effect) and imply that CoS$_2$/WS$_2$ and CoS$_2$/MoS$_2$ catalysts achieving Pt/C catalyst’s activity. This trend was obvious from their $E_{\text{HER}}$ values presented in Table 2. The $E_{\text{HER}}$ value of CoS$_2$/WS$_2$ catalyst was found to be $-30 \text{ mV vs. RHE}$, which approached that of the Pt/C ($-10 \text{ mV vs. RHE}$) and $77 \text{ mV vs. RHE}$ less negative (i.e., more anodic, active) than that obtained for the CoS$_2$/MoS$_2$ catalyst ($-107 \text{ mV vs. RHE}$). The $E_{\text{HER}}$ value of the later is anodic versus those recorded for CoS$_2$/BCN, CoS$_2$/g-C$_3$N$_4$, and CoS$_2$/rGO catalysts by 108, 123, and 148 mV vs. RHE, respectively. In addition, the CoS$_2$/MoS$_2$ catalyst’s $E_{\text{HER}}$ value is 168 mV, which is far from that of the most active supporting material, namely, WS$_2$ ($-275 \text{ mV vs. RHE}$).

The overpotential required to afford a current density of 10 mA cm$^{-2}$ ($\eta_{10}$), Table 2, is another important electrochemical kinetic parameter used to compare and evaluate catalysts’ activities and performance. CoS$_2$/WS$_2$ catalyst showed the lowest $\eta_{10}$ value (130 mV), which matched with that of the Pt/C catalyst (124 mV), among the other tested catalysts (208, 292, 322, and 337 mV for CoS$_2$/MoS$_2$, CoS$_2$/BCN, CoS$_2$/g-C$_3$N$_4$, and CoS$_2$/rGO, respectively). These findings demonstrated that CoS$_2$/WS$_2$ and CoS$_2$/MoS$_2$ catalysts achieved the most promising catalytic activities in this study.

The low $E_{\text{HER}}$ value of CoS$_2$/WS$_2$ catalyst is translated into a high $j_0$ value (0.50 mA cm$^{-2}$), estimated from Tafel extrapolation method. This value approached that of the Pt/C catalyst (0.75 mA cm$^{-2}$) and is about 4, 31, 39, and 42 times higher than those measured for CoS$_2$/MoS$_2$ (0.14 mA cm$^{-2}$), CoS$_2$/BCN (0.016 mA cm$^{-2}$), CoS$_2$/g-C$_3$N$_4$ (0.013 mA cm$^{-2}$), and CoS$_2$/rGO (0.012 mA cm$^{-2}$).

The HER catalytic performance of the studied catalysts was also evaluated by another essential electrochemical parameter, namely, the Tafel slope. The HER of a catalyst is pure kinetically controlled if the measured Tafel parameters follow a Tafel behavior, described by the Tafel equation:

$$\eta = \alpha + \beta \log j_0$$

(1)

Where $\eta$ and $j_0$ denote the applied overpotential and the exchange current density, respectively. The symbol $\beta$ represents the Tafel slope, and $\alpha$ is the intercept related to symmetry. A comparison of the Tafel slope values recorded here (Table 2) with the standard ones given below in eq 2–4, which represent

![Figure 4](https://dx.doi.org/10.1021/acsaem.0c02509)
the HER route on a specific catalyst in alkaline electrolytes,\[51\] will help us understanding the main mechanism by which the HER proceeds under these conditions.

\[ \begin{align*}
H_2O + e^- & \rightarrow H_{ads} + HO^- \text{(Volmer step)} \\
 b & = \frac{2.34RT}{aF} \cong 120 \text{ mV/dec} \end{align*} \tag{2} \]

The Volmer step is followed by either a combination of adsorbed species to form molecular H\(_2\):

\[ \begin{align*}
H_{ads} + H_{ads} & \rightarrow H_{ads} \text{(Tafel step)} \\
b & = \frac{2.34RT}{(1 + \alpha)F} \cong 30 \text{ mV/dec} \end{align*} \tag{3} \]

or the desorption Heyrovsky step:

\[ \begin{align*}
H_2O + e^- + H_{ads} & \rightarrow H_2 + HO^- \text{(Heyrovsky)} \\
b & = \frac{2.34RT}{2F} \cong 40 \text{ mV/dec} \end{align*} \tag{4} \]

According to Table 2, the values of \(b\) recorded for the five tested supporting materials were found to decrease from 164 mV dec\(^{-1}\)
for rGO to 156, 150, 123, and 121 dec$^{-1}$ for g-C$_3$N$_4$, BCN, MoS$_2$, and WS$_2$, respectively. This obvious decrease in $\beta$ signifies accelerated kinetics of the HER, because lower Tafel slopes generally refer to profusion in the availability of the catalytic active sites.$^{52}$ The Tafel lines of the five hybrid catalysts, namely CoS$_2$/rGO, CoS$_2$/g-C$_3$N$_4$, CoS$_2$/BCN, CoS$_2$/WS$_2$, and CoS$_2$/MoS$_2$ are all parallel to each other, and also seem parallel to the Pt/C catalyst’s Tafel line, with $\beta$ values covering the narrow range of 116–121 mV dec$^{-1}$, comparable to the value measured for the Pt/C catalyst, 119 mV dec$^{-1}$. This $\beta$ value obtained for the Pt/C catalyst agrees well with that reported in the literature,$^{53}$ representing a good evidence of the reliability of the electrochemical measurements employed here. This result proposes a HER mechanism on the surfaces of the five studied hybrid catalysts matching with that occurring on the Pt/C catalyst in alkaline solutions. This mechanism involves the Volmer step as the rate-limiting step for the HER.$^{53}$

The above findings highlight the efficient catalytic performance of both CoS$_2$/MoS$_2$ and CoS$_2$/WS$_2$ catalysts toward the HER in 1.0 M KOH solution, which is comparable with the most active HER electrocatalysts reported in the literature under the same operating conditions (Table S2).

3.2.2. Electrocatalytic Activity Studies for the OER. The electrocatalytic performance of the investigated catalysts for the OER was also studied, and the results of the polarization measurements are depicted in Figure 9. Here again, the two catalysts CoS$_2$/WS$_2$ and CoS$_2$/MoS$_2$ possessed the highest OER catalytic activity among the investigated catalysts. CoS$_2$/rGO, CoS$_2$/g-C$_3$N$_4$, and CoS$_2$/BCN catalysts displayed an anodic potential of $\eta_{10} = 434, 417$, and 376 mV, respectively. In contrast, CoS$_2$/MoS$_2$ and CoS$_2$/WS$_2$ catalysts delivered the same anodic current density at much lower $\eta_{10}$ values of 332 and 298 mV, respectively. The CoS$_2$/WS$_2$ catalyst’s $\eta_{10}$ value (298 mV) is very close to that achieved by RuO$_2$ catalyst ($\eta_{10} = 290$ mV), the state-of-the-art electrocatalyst for the OER.$^{54}$ Similar trend was observed concerning the onset potential value for the OER, $E_{OER}$.

Tafel slope values were also calculated to further understand the OER activity. The CoS$_2$/WS$_2$ and CoS$_2$/MoS$_2$ catalysts displayed Tafel slopes of 110 and 125 mV dec$^{-1}$, respectively, smaller than those recorded for CoS$_2$/rGO (155 mV dec$^{-1}$), CoS$_2$/g-C$_3$N$_4$ (138 mV dec$^{-1}$), and CoS$_2$/BCN (130 mV dec$^{-1}$) catalysts. The Tafel slope value recorded for the CoS$_2$/WS$_2$ catalyst (110 mV dec$^{-1}$) approached that obtained for the RuO$_2$ catalyst (100 mV dec$^{-1}$). These results suggest fast OER kinetics on CoS$_2$/WS$_2$ and CoS$_2$/MoS$_2$ surfaces. Literature data revealed that the alkaline OER mechanism over metal sulﬁdes can be represented by eqs 5–8.$^{55}$

$$\text{M}_{\text{cat}}\text{OH}^- \rightarrow \text{M}_{\text{cat}}\text{OH} + e^- \quad (5)$$
$$\text{M}_{\text{cat}}\text{OH} + \text{OH}^- \rightarrow \text{M}_{\text{cat}}\text{O}^- + \text{H}_2\text{O} \quad (6)$$
$$\text{M}_{\text{cat}}\text{O}^- \rightarrow \text{M}_{\text{cat}}\text{O} + e^- \quad (7)$$
$$\text{M}_{\text{cat}}\text{O} + \text{M}_{\text{cat}}\text{O} \rightarrow \text{M}_{\text{cat}} + \text{M}_{\text{cat}} + \text{O}_2 \quad (8)$$

The adsorption of OH$^-$ anions on the catalyst surface plays a pivotal role in accelerating the kinetics of the OER.$^{55}$ Sulfur atoms in the CoS$_2$/WS$_2$ and CoS$_2$/MoS$_2$ catalysts expedite the
adsorption and desorption of the OH\(^-\) anions.\(^{53}\) This in turn enhances the rate of the OER, thus corroborating low Tafel slopes.\(^{57}\) The low Tafel slope values recorded for CoS\(_2/\)WS\(_2\) and CoS\(_2/\)MoS\(_2\) catalysts further support the fast OER kinetics as compared with the other tested catalysts, which recorded higher Tafel slope values. This is also confirmed from the OER mass activities of studied catalysts. Mass activity is given by the ratio \(j/c\), where \(j\) is the current density generated at a specific potential and \(c\) is the catalyst loading amount on the GC electrode, which is 0.28 mg cm\(^{-2}\) in our experiment. CoS\(_2/\)WS\(_2\), CoS\(_2/\)MoS\(_2\), CoS\(_2/\)BCN, CoS\(_2/g\)-C\(_3\)N\(_4\), and CoS\(_2/r\)GO catalysts generated an anodic current density of 0.14, 0.068, 0.048, 0.024, and 0.018 A cm\(^{-2}\) at 1.7 V vs. RHE, respectively. Based on this, OER mass activities of 500, 243, 171, 86, and 66 A g\(^{-1}\) were estimated for CoS\(_2/\)WS\(_2\), CoS\(_2/\)MoS\(_2\), CoS\(_2/\)BCN, CoS\(_2/g\)-C\(_3\)N\(_4\), and CoS\(_2/r\)GO catalysts, respectively. The CoS\(_2/\)WS\(_2\) catalyst’s mass activity (500 A g\(^{-1}\) @ 1.7 V vs. RHE) matches well with that of the state-of-the-art RuO\(_2\) catalyst (571 A g\(^{-1}\), with 0.16 A cm\(^{-2}\) generated @ 1.7 V vs. RHE), thus confirming its promising OER activity. In addition, the significantly higher mass activity of such catalysts compared to those of the supporting materials (11.1, 17.1, 19.6, 21.4, and 35 A g\(^{-1}\) for rGO, g-C\(_3\)N\(_4\), BCN, MoS\(_2\), and WS\(_2\), respectively) highlights the catalytic impact of the hybrid effect. These results place CoS\(_2/\)WS\(_2\) hybrid catalyst among the most effective nonprecious OER electrocatalysts reported in the literature (see details in Table S3).

The electrochemical active surface area (EASA) is another important parameter used to compare activity of electrocatalysts.\(^{58}\) However, the inaccurate evaluation of the specific capacitance of the composites made measuring EASA for binary and ternary catalysts very complicated.\(^{59}\) This was the reason why the electrochemical double-layer capacitance (\(C_{dl}\)) of the electrocatalysts, which has a direct relationship with EASA, is used as an alternative way to compare their catalytic activities.\(^{60}\) Herein, the values of \(C_{dl}\) were estimated from cyclic voltammetry (CV) measurements executed at various potential scan rates. CV measurements were conducted over the voltage range of 1.41–1.45 V to determine the capacitive currents associated only to double-layer charging, as shown in Figure S5a–k. Half the difference in current density between anodic and cathodic sweeps, \((\Delta J = J_{anodic} - J_{cathodic})/2\), at 1.435 V is plotted versus the potential scan rate, Figure S5. The slope of such plots is equal to \(C_{dl}\).\(^{61}\)

The values of \(C_{dl}\) were calculated as 31, 41.5, 46.2, 52, and 61 mF cm\(^{-2}\) for CoS\(_2/r\)GO, CoS\(_2/g\)-C\(_3\)N\(_4\), CoS\(_2/\)BCN, CoS\(_2/\)MoS\(_2\), and CoS\(_2/\)WS\(_2\) catalysts, respectively. These values are always higher than the \(C_{dl}\) values recorded for CoS\(_2\) alone (26.5 mF cm\(^{-2}\)) and the corresponding supporting materials (4.6, 14, 18, 23, and 28 mF cm\(^{-2}\) for rGO, g-C\(_3\)N\(_4\), BCN, MoS\(_2\), and WS\(_2\), respectively).

The obtained results confirm the catalytic impact of the hybrid effect. A higher \(C_{dl}\) value of catalysts is an indication of increased density of accessible catalytically active surface sites for adsorption and desorption processes. This in turn facilitates efficient charge transfer, as evidenced from EIS measurements (Section S5), resulting in high catalytic performance.

The EASA from \(C_{dl}\) can be estimated following eq 9.\(^{62}\)

\[
EASA = C_{dl}/C_s
\] (9)

where \(C_s\) is the specific capacitance for an electrode with 1.0 cm\(^2\) of a flat standard surface area, usually between 20 and 60 \(\mu\)F cm\(^{-2}\).\(^{62}\) Applying the average value of 40 \(\mu\)F cm\(^{-2}\) for the flat...
electrode, EASA values of 775, 1037.5, 1155, 1300, and 1525 cm$^2$ were determined for CoS$_2$/rGO, CoS$_2$/g-C$_3$N$_4$, CoS$_2$/BCN, CoS$_2$/MoS$_2$, and CoS$_2$/WS$_2$, respectively. Such EASA values are larger than those of the corresponding supporting materials, namely, rGO (115 cm$^2$), g-C$_3$N$_4$ (350 cm$^2$), BCN (450 cm$^2$), MoS$_2$ (575 cm$^2$), and WS$_2$ (700 cm$^2$).

### 3.2.3. Turnover Frequency (TOF) Calculations.

Cyclic voltammetry measurements, Figure S6, were used to calculate the turnover frequency (TOF) for the synthesized catalysts. Measurements were conducted in 1.0 M KOH solution at a scan rate of 5 mV s$^{-1}$ at room temperature. (1) bare GCE, (2) rGO, (3) g-C$_3$N$_4$, (4) BCN, (5) MoS$_2$, (6) CoS$_2$/rGO, (7) WS$_2$, (8) CoS$_2$/MoS$_2$, (9) CoS$_2$/g-C$_3$N$_4$, (10) CoS$_2$/BCN, (11) CoS$_2$/MoS$_2$, (12) CoS$_2$/WS$_2$, and (13) Pt/C commercial catalyst.

### Table 2. Mean Value (Standard Deviation) of the Electrochemical HER Kinetic Parameters of the Synthesized Catalysts

<table>
<thead>
<tr>
<th>tested cathode</th>
<th>onset potential $E_{HER}$ (mV vs. RHE)</th>
<th>Tafel slope $-\beta_\text{c}$ (mV dec$^{-1}$)</th>
<th>exchange current density $j_0$ (mA cm$^{-2}$)</th>
<th>overpotential at $j = 10$ mA cm$^{-2}$ ($\eta_{10}$/mV vs RHE)</th>
</tr>
</thead>
<tbody>
<tr>
<td>bare GCE</td>
<td>138 (1.4)</td>
<td>5 (0.06) $\times$ 10$^{-5}$</td>
<td>739 (7.8)</td>
<td></td>
</tr>
<tr>
<td>rGO</td>
<td>710 (6.8)</td>
<td>164 (1.76)</td>
<td>654 (7.3)</td>
<td></td>
</tr>
<tr>
<td>g-C$_3$N$_4$</td>
<td>316 (3.5)</td>
<td>156 (1.64)</td>
<td>590 (6.2)</td>
<td></td>
</tr>
<tr>
<td>BCN</td>
<td>295 (3.2)</td>
<td>150 (1.6)</td>
<td>526 (5.6)</td>
<td></td>
</tr>
<tr>
<td>MoS$_2$</td>
<td>290 (3.3)</td>
<td>123 (1.3)</td>
<td>407 (4.4)</td>
<td></td>
</tr>
<tr>
<td>CoS$_2$</td>
<td>280 (3.3)</td>
<td>121 (1.3)</td>
<td>386 (4.0)</td>
<td></td>
</tr>
<tr>
<td>WS$_2$</td>
<td>275 (3.1)</td>
<td>121 (1.28)</td>
<td>377 (4.1)</td>
<td></td>
</tr>
<tr>
<td>CoS$_2$/rGO</td>
<td>255 (2.4)</td>
<td>121 (1.3)</td>
<td>337 (3.6)</td>
<td></td>
</tr>
<tr>
<td>CoS$_2$/g-C$_3$N$_4$</td>
<td>230 (2.2)</td>
<td>120 (1.32)</td>
<td>322 (3.4)</td>
<td></td>
</tr>
<tr>
<td>CoS$_2$/BCN</td>
<td>215 (2.3)</td>
<td>121 (1.35)</td>
<td>292 (3.3)</td>
<td></td>
</tr>
<tr>
<td>CoS$_2$/MoS$_2$</td>
<td>107 (1.6)</td>
<td>120 (1.25)</td>
<td>208 (2.4)</td>
<td></td>
</tr>
<tr>
<td>CoS$_2$/WS$_2$</td>
<td>30 (0.9)</td>
<td>116 (1.1)</td>
<td>130 (1.6)</td>
<td></td>
</tr>
<tr>
<td>Pt/C</td>
<td>10 (0.2)</td>
<td>119 (0.8)</td>
<td>124 (1.3)</td>
<td></td>
</tr>
</tbody>
</table>

*Measurements were conducted at room temperature in deaerated KOH solution (1.0 M).*
the number of active sites \( n \) for the five tested hybrid materials using eq 10.63

\[
n = \frac{Q}{2F}
\]  

(10)

where the number 2 is the stoichiometric number of electrons ingested by the HER reaction of the electrode, and \( F \) is the Faraday constant (96485 C/mol). The catalyst’s net voltammetry charge (\( Q \)) was calculated via subtracting charges resulting from the bare glassy carbon electrode. The formula presented in eq 11 was employed to calculate the per-site turnover frequencies (TOFs, s\(^{-1}\)), where \( I \) (measured in A cm\(^{-2}\)) is the value of current at a specific overpotential.

\[
\text{TOF} = \frac{I}{2F n}
\]  

(11)

Combining eqs 10 and 11 yields eq 12:

\[
\text{TOF} = \frac{I}{Q}
\]  

(12)

Eventually, it is possible to convert the current densities derived from the LSV polarization curve, revisit Figure 8a, into TOF values using eq 12. For instance, at an overpotential of \(-200\) mV vs. RHE, CoS\(_2\)/rGO, CoS\(_2\)/g-C\(_3\)N\(_4\), CoS\(_2\)/BCN, CoS\(_2\)/MoS\(_2\), and CoS\(_2\)/WS\(_2\) generated current densities of \(5.4 \times 10^{-4}\), \(6.7 \times 10^{-4}\), \(2.3 \times 10^{-3}\), \(1.2 \times 10^{-2}\), and \(2.85 \times 10^{-2}\) A cm\(^{-2}\), respectively. Q values of 0.0099, 0.01, 0.013, 0.015, and 0.018 C were recorded for CoS\(_2\)/rGO, CoS\(_2\)/g-C\(_3\)N\(_4\), CoS\(_2\)/BCN, CoS\(_2\)/MoS\(_2\), and CoS\(_2\)/WS\(_2\) catalysts, respectively. Introducing the values of \( I \) and \( Q \) in eq 12 yielded TOF values of 0.055, 0.067, 0.177, 0.8, and 1.58 s\(^{-1}\) for CoS\(_2\)/rGO, CoS\(_2\)/g-C\(_3\)N\(_4\), CoS\(_2\)/BCN, CoS\(_2\)/MoS\(_2\), and CoS\(_2\)/WS\(_2\) catalysts, respectively. The high TOF value of the CoS\(_2\)/WS\(_2\) catalyst (1.58 s\(^{-1}\)) adds another evidence for its outstanding catalytic activity. This is also clear from its highest number of active sites (\( n \), mol) calculated from eq 10, where \( n \) values of \(5.1 \times 10^{-8}\), \(5.2 \times 10^{-7}\), \(6.85 \times 10^{-8}\), \(7.85 \times 10^{-7}\), and \(9.27 \times 10^{-7}\) mol were estimated for CoS\(_2\)/rGO, CoS\(_2\)/g-C\(_3\)N\(_4\), CoS\(_2\)/BCN, CoS\(_2\)/MoS\(_2\), and CoS\(_2\)/WS\(_2\) catalysts, respectively.

3.2.4. Faradaic Efficiency Calculations for the HER and OER. The investigated catalysts’ Faradaic efficiency (\( \% \)) for the HER and OER is also estimated to further assess and compare their electrocatalytic performance. The amount of the gas evolved (expressed in \( \mu \)mol) per hour during a controlled galvanostatic electrolysis (CGE), symbolized here as \( V_{\text{m}} \), is first measured by gas chromatography (GC), as described in Section S4.3, see eq 13:

\[
V_{\text{m}} = \text{mol gas(GC)}
\]  

(13)

The value of \( V_{\text{m}} \) is the expected quantity of the liberated gas theoretically calculated based on the charge passed (presuming 100% Faradaic efficiency) during that CGE, is then calculated using eq 14.64

\[
V_{\text{c}} = \frac{Q_{\text{CGE}}}{n F}
\]  

(14)

where \( F \) is the Faraday constant (\( F = 96485 \) C) and \( Q_{\text{CGE}} \) is the charge passed through the WE during the CGE process. The factor \( n \) represents the number of electrons transferred during the HER \((2H^{+} + 2e^{-} = H_{2}, n = 2)\) and OER \((4OH^{-} = 2H_{2}O + 4e^{-} + O_{2}, n = 4)\). The value of \( \varepsilon \) is calculated by dividing \( V_{\text{m}} \) by \( V_{\text{c}} \), the expected quantity of the liberated gas theoretically calculated based on the charge passed (presuming 100% Faradaic efficiency) during that CGE. Finally, the tested electrocatalyst’s Faradaic efficiency (\( \% \)) is calculated via multiplying the quotient of the ratio \((V_{\text{m}}/V_{\text{c}})\) by 100, eq 15.64

Faradaic efficiency (%)

\[
= \left[ \frac{\text{mol gas}(\text{GC})}{100}\right] / Q_{\text{CGE}}
\]  

(15)

The obtained data, namely the calculated and measured amounts of \( H_{2} \) and \( O_{2} \), evolved for the studied electrocatalysts during 1 h of CGE are collected in Figures S7 and S8 and Tables S4 and S5.

The CoS\(_2\)/WS\(_2\) is once again the best performing catalyst for both HER and OER among, since it recorded the largest quantity of \( H_{2} \) (28.5 \( \mu \)mol h\(^{-1}\)) and \( O_{2} \) (9.9 \( \mu \)mol h\(^{-1}\)), measured by GC, among the other studied electrocatalysts. This catalyst achieved the HER and OER with \( \varepsilon \) values of 99.3 and 99.0%, respectively, which are very close to those measured for their corresponding state-of-the-art electrocatalysts, namely, Pt/C (99.7%) and RuO\(_2\) (99.5%).

3.3. DFT Elucidation of the HER Activity. DFT calculations were also performed to support experimental findings. The optimized structures of the adsorbed hydrogen on the surface of the pristine and 2D nanostructures were constructed, Figueras S9–S17. As proposed by Nørskov and coworkers, HER catalytic activity can be evaluated from the Gibbs free energy of \( H^{\star} (\Delta \text{G}^{\star}_{H^{\star}}) \), where \( \star \) stands for the free surface adsorption site on which a hydrogen atom (\( H^{\star} \)) is adsorbed. Since various adsorption sites may display different HER catalytic performance, all the possible surface adsorption sites are considered and the corresponding \( \Delta \text{G}^{\star}_{H^{\star}} \) values are depicted in Figure 10.

![Figure 10. Gibbs free energy of \( H^{\star} (\Delta \text{G}^{\star}_{H^{\star}}) \) on the best adsorption sites of studied catalysts.](https://dx.doi.org/10.1021/acsaem.0c02509)

ACS Appl. Energy Mater. XXXX, XXX, XXX–XXX


ACS Appl. Energy Mater. XXXX, XXX, XXX–XXX
\[ \Delta E_{\text{ZPE}} = \text{ZPE}(H^*) - 0.5\text{ZPE}(H_2) \]  

\[ \Delta S_H = S^0(H^*) - 0.5S^0(H_2) \sim -0.5S^0(H_2) \]  

(S(H_2) refers to the entropy of gaseous H_2 at STP, and S(H*) represents the adsorbed state vibrational entropy. Because S(H*) is small, it can be neglected in eq 16 so that \( \Delta S_H = -0.5S^0(H_2) \). Because the additional terms (ABC and TBC)' total contribution is 0.24 eV, the ideal thermo neutral reaction adsorption energy value is estimated to be in the vicinity of around -0.24 eV.\(^{65}\)

According to the DFT calculations, the pristine catalysts, namely, the supporting materials rGO, g-C_3N_4, CoS_2, WS_2 and MoS_2, recorded \(|\Delta G_H|\) values of 2.43, 2.35, 2.31, 1.84, and 1.42 eV, respectively. These values, which are close to those reported in the literature,\(^{66,67}\) reveal that pristine catalysts exhibit relatively low HER catalytic activity due to the slow kinetics of the HER. Upon immobilizing CoS_2 on rGO, g-C_3N_4, WS_2, or MoS_2 nanosheets, the values of \(|\Delta G_H|\) significantly decreased to 1.07, 0.59, 0.41, and 0.21 eV, respectively, Figure 10. Taking into account that \( \Delta G \) values close to zero favor fast HER kinetics, CoS_2/MoS_2 hybrid catalyst can be considered as the best one among the studied catalysts. However, experimental data show that the HER catalytic performance of CoS_2/WS_2 catalyst was the highest among. The higher EASA (1525 cm\(^2\)) and specific surface area values (85.032 m\(^2\)/g) recorded for the CoS_2/WS_2 catalyst, as compared with those of CoS_2/MoS_2 (1300 cm\(^2\), 33.885 m\(^2\)/g), may be the main reasons behind the superior catalytic activity of the former, despite its \( \Delta G \) value (0.66 eV) being much higher than that of CoS_2/MoS_2 (0.035 eV).

![Figure 11. Long-term stability tests recorded for the best catalyst (CoS_2/WS_2) in 1.0 M KOH solution at room temperature for the (a) HER and (b) OER. LSV measurements were conducted at a scan rate of 50 mV s\(^{-1}\). Insets are chronoamperometry measurements (j vs t) performed on the catalyst at a constant applied potential of (a) -1.0 V vs. RHE and (b) 2.0 V vs. RHE.](https://dx.doi.org/10.1021/acsaem.0c02509)
3.4. Best Catalyst’s Stability and Durability Tests.

Stability over the long-term is an important criterion for excellent electrocatalysts. Two major electrochemical techniques were applied to evaluate the best catalyst stability for both hydrogen and oxygen evolution reactions. These include continuous (repetitive) cyclic polarization (CP) up to 10,000 cycles and 72 h of controlled potential electrolysis (chronoamperometry) measurements. Figure 11 depicts the results obtained from such measurements. According to CP measurements, Figure 11a, b, the polarization curve of the catalyst remains nearly similar to marginal current losses after the 10,000th cycle. This indicates that there is no pronounced decay in the catalytic activity observed before and after such number of cycles. Results derived from electrolysis at a static overpotential, Figure 11a, b, supported CP measurements; a nearly constant current results throughout the run. It follows from such long-term stability tests that the maximum cathodic current density achieved by CoS2/WS2 during the HER was about 375 mA cm−2 @ −1.0 V (RHE), whereas OER on CoS2/WS2 catalyst delivered a maximum anodic current density of about 850 mA cm−2 @ 2.5 V (RHE).

Further inspection of Figure 11 reveals that the LSV curve after the 10,000th cycle is quite noisy compared to the initial one. This phenomenon is observed at high overpotentials in the LSV curve, appears as current oscillations (spikes) in the corresponding chronoamperometry measurements (as shown in the insets of Figure 11), and is produced as a result of gas bubbles accumulation and release.68 Bubble accumulation is expected to isolate the active site from the electroactive species in the electrolyte, thus impeding charge transfer and resulting in a diminished current (catalyst deactivation). The current is then enhanced because of gas release (catalyst reactivation).68 The process of bubble accumulation and release repeats itself within very short periods of time, leading to the appearance of current noise.

These findings reveal that the CoS2/WS2 catalyst possesses prominent stability for both hydrogen and oxygen evolution reactions in alkaline solutions. Thus, in order to move one step closer to a true overall water-splitting device in 1 M KOH, a two-electrode electrolyzer system in which the CoS2/WS2 hybrid catalyst was used as both anode and cathode (CoS2/WS2/CoS2/WS2) was designed. A cell voltage of 1.6 V was found to be sufficient for the electrolyzer to deliver a current density of 10 mA cm−2 with intense evolution of the gas on both electrodes. This made the CoS2/WS2/CoS2/WS2 alkaline water electrolyzer’s performance comparable to other efficient nonprecious bifunctional electrocatalysts in 1 M KOH (Table S6). The electrolyzer’s long-term durability was also assessed in 1 M KOH for 96 h (Figure S18). The potential was initially 1.6 V to obtain a current density of 10 mA cm−2, with trivial decay (total loss of about 7%) occurring in the static potential value after 96 h of continuous electrolysis testing. Such results imply that CoS2/WS2 has considerable capacity as a cheap, highly efficacious catalyst electrode for the electrochemical water splitting application.

4. CONCLUSION

Various 2D nanosheets (rGO, g-C3N4, BCN, MoS2, and WS2) were synthesized as supporting materials for CoS2 NPs. These nanomaterials were synthesized using a facile hydrothermal technique and characterized by different analytical methods like XRD, TEM, and XPS analyses. TEM analysis revealed that CoS2 NPs are well distributed on WS2 nanosheets and had the smallest average particle size and largest surface area in comparison to other nanocomposites. The catalytic activity of the obtained hybrid materials toward hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) were studied in 1.0 M KOH solution using various electrochemical techniques. Experimental findings placed CoS2/WS2 hybrid catalyst as the most efficient and robust bifunctional electrolyzer among. It afforded a current density of 10 mA cm−2 for the HER at an overpotential of 130 mV. The same current density was delivered for the OER at 298 mV. This current outcome at such low overpotential values, in addition to its high TOF value (1.58 s−1), high stability, and durability (evidenced after 10,000 cycles of repetitive cathodic cyclic polarization and 72 h of chronoamperometry measurements at high overpotential), placed CoS2/WS2 hybrid catalyst among the most effective bifunctional electrocatalysts. Moreover, this active bifunctional nanohybrid electrocatalyst delivered 10 mA cm−2 current density with 96 h of long-term stability for the alkaline overall water splitting at a cell voltage of 1.6 V.

■ ASSOCIATED CONTENT

* Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsaem.0c02509.

Materials and methods; synthesis; characterization techniques; XRD patterns; Raman spectra; electrochemical techniques; EIS studies; plot of complex-plane impedance; image of the equivalent circuit used to fit the experimental impedance data for the catalysts; plot of CV measurements of different catalysts; plots of Faradaic efficiency measurements; method of DFT calculations; images of optimized structure of H atom adsorption on the surface of different catalysts; plot of two-electrode cell durability of CoS2/WS2/CoS2/WS2 alkaline water electrolyzer (chronoamperometric measurements); table of the optimum concentrations of the Co and S precursors and the doping amount of Co and S in the different nanocomposites; comparisons of HER catalytic performance of the synthesized catalysts with reported electrocatalysts; comparison of OER catalytic performance of the synthesized catalysts with reported electrocatalysts; comparative studies of the mean value of Vf/2 and VO2 obtained after controlled galvanostatic electrolysis (CGE) and Faradaic efficiency values η (%) for the studied catalysts; comparison of two-electrode water splitting cell voltage of CoS2/WS2 electrocatalyst with other efficient bifunctional electrocatalysts (PDF).

■ AUTHOR INFORMATION

Corresponding Authors

Manash R. Das – Advanced Materials Group, Materials Sciences and Technology Division, CSIR-North East Institute of Science and Technology, Jorhat 785002, Assam, India; Academy of Scientific and Innovative Research (AcSIR), Ghaziabad 201002, India; orcid.org/0000-0002-6317-7933; Email: mnsrdas@yahoo.com, mrdas@heist.res.in

Rabah Boukherroub – Université de Lille, CNRS, Centrale Lille, Université Polytechnique Hauts-de-France, UMR 8520 - IEMN, Lille F-59000, France; orcid.org/0000-0002-9795-9888; Email: rabah.boukherroub@univ-lille.fr

Mohammed A. Amin – Department of Chemistry, College of Science, Taif University, Taif 21944, Saudi Arabia;

https://doi.org/10.1021/acsaem.0c02509
ACS Appl. Energy Mater. XXXX, XXX, XXX–XXX
Department of Chemistry, Faculty of Science, Ain Shams University, Abbassia 11566, Cairo, Egypt; Email: mohamed@tu.edu.sa

Authors
Priyakshree Borthakur — Advanced Materials Group, Materials Sciences and Technology Division, CSIR-North East Institute of Science and Technology, Jorhat 785006, Assam, India; Academy of Scientific and Innovative Research (AcSIR), Ghatiabud 201002, India
Purna K. Boruah — Advanced Materials Group, Materials Sciences and Technology Division, CSIR-North East Institute of Science and Technology, Jorhat 785006, Assam, India; Academy of Scientific and Innovative Research (AcSIR), Ghatiabud 201002, India
Mohamed M. Ibrahim — Department of Chemistry, College of Science, Taif University, Taif 21944, Saudi Arabia; Chemistry Department, Faculty of Science, Kafrelsheikh University, Kaf El Sheikh 33516, Egypt
Tariq Altalhi — Department of Chemistry, College of Science, Taif University, Taif 21944, Saudi Arabia
Hamdy S. El-Sheshtawy — Chemistry Department, Faculty of Science, Kafrelsheikh University, Kaf El Sheikh 33516, Egypt; orcid.org/0000-0002-3430-4374
Sabine Zsuznerti — Université de Lille, CNRS, Centrale Lille, Université Polytechnique Hauts-de-France, UMR 8520 - IEMN, Lille F-59000, France; orcid.org/0000-0002-1567-4943

Complete contact information is available at: https://pubs.acs.org/10.1021/acsaem.0c02509

Notes
The authors declare no competing financial interest.

ACKNOWLEDGMENTS
The authors are thankful to the Director, CSIR-NEIST, Jorhat, for his support and interest in carrying out the work. P.B. and P.K.B. thank DST, New Delhi, and CSIR, New Delhi, for financial support. The authors are also thankful to the Taif University Researchers Supporting Project (TURSP-2020/03), Taif University, Taif, Saudi Arabia.

REFERENCES


