Bi$_2$WO$_6$ and FeWO$_4$ Nanocatalysts for the Electrochemical Water Oxidation Process

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ABSTRACT: Polyvinylpyrrolidone (PVP)-assisted nanocatalyst preparation was succeeded by employing a controlled solvothermal route to produce efficient electrodes for electrochemical water-splitting applications. Bi$_2$WO$_6$ and FeWO$_4$ nanocatalysts have been confirmed through the strong signature of (113) and (111) crystal planes, respectively. The binding natures of Bi=W–O and Fe=W–O have been thoroughly discussed by employing X-ray photoelectron spectroscopy which confirmed the formation of Bi$_2$WO$_6$ and FeWO$_4$. The freestanding nanoplate array morphology of Bi$_2$WO$_6$ and the fine nanosphere particle morphology of FeWO$_4$ nanocatalysts were revealed by scanning electron microscopy images. With these confirmations, the fabrication of durable, long-term electrodes for electrochemical water splitting has been subjected to efficient oxidation of water, confirmed by obtaining 2.79 and 1.96 mA/g for 0.5 g PVP-assisted Bi$_2$WO$_6$ and FeWO$_4$ nanocatalysts, respectively. The water oxidation mechanism of both nanocatalysts has been revealed with the support of 24 h stability test over continuous water oxidation and faster charge transfer achieved by the smaller Tafel slope values of 75 and 78 mV/dec, respectively. Generally, these nanocatalysts are utilized for photocatalytic applications. The present study revealed the PVP-assisted synthesis to produce electrocatalytically active nanocatalysts and their electrochemical water-splitting mechanism which will offer a pathway for research interests with regard to the production of multifunctional nanocatalysts for both electro- and photocatalytic applications in the near future.

1. INTRODUCTION

For the past few decades, hasty developments of smart electronic, hybrid energy conversion and storage devices have ruled the mankind. Energy conversion and storage have gained interest among researchers, which turned their focus towards producing sustainable clean energy as the replacement of traditional fossil fuels. Among other approaches, electrochemical water splitting is one of the best methods. It is cost-effective, cheap, efficient, and ecofriendly.1–3 Water electrolysis by electrocatalysts through electrochemical water splitting will give promising output for pure and sustainable energy applications.4,5 Precious metals such as platinum (Pt), ruthenium (Ru), iridium (Ir), and so forth have shown almost benchmark results of energy storage applications. However, the limitations of such precious metals are high cost and low availability.6–8 Hence, low-cost, highly stable, and efficient electrodes are still being developed by researchers as alternates for such noble metals. Therefore, tungsten as an earth-abundant and low-cost material is used as an efficient catalyst; moreover, tungsten-based materials are the most important energy materials of inorganic family used for potential applications.9,10 Recently, studies have revealed that Bi$_2$WO$_6$ and FeWO$_4$ are excellent functional materials because of their unique electronic structures. There have been many attempts to study the use of these materials as electrodes for photocatalytic and supercapacitor applications, wherein the tungsten-based nanocomposites are reported as photoanodes and photocatalysts,11,12 symmetric and asymmetric electrodes,13 and so forth. Very few research activities have been initiated to study the electrochemical water-splitting applications of tungstates.14–18 Further, the morphological variations and compactness, more number of active sites, low overpotential, high electrochemical stability, and fast charge transportation mechanism of these electrocatalysts are the significant features for the efficient electrolysis of water.19,20 Hence, nanocatalyst preparation with a diverse morphology assisted by surfactants is a promising approach to tune the material properties, achieved by the research society nowadays. Among other surfactants, polyvinylpyrrolidione (PVP) played a selective role in nanomaterial synthesis. PVP is a nonionic, nontoxic polymer with a large number of polar amide groups within the pyrroldione ring.21,22 These groups in PVP make it a
successful stabilizer, disperser, and growth controller. Hence, PVP has been chosen to control the particle growth and provide a stable chemical environment for the nanocatalyst preparation. Moreover, many research activities have been attempted by using tungstate nanomaterials with carbon-based composites for energy applications.\(^{13-25}\)

In the present study, the preparation of electrochemically active multifunctional carbon-free nanocatalysts using a PVP capping agent that acted as a stabilizer and growth-controlling agent has been reported. The successful synthesis of Bi\(_2\)WO\(_6\) and FeWO\(_4\) nanocatalysts has been confirmed by various fundamental characterization techniques, and an appreciable electrochemical outcome of water oxidation has been reported. The electrochemical water electrolysis mechanism by tungstates has been reported in this study. Within the best of our knowledge, no research activities have reported on carbon-free nanocatalysts such as Bi\(_2\)WO\(_6\) and FeWO\(_4\) synthesized by the PVP-assisted solvothermal optimization growth technique for electrochemical water-splitting applications. The ultimate aim of this work is to produce multifunctional nanocatalysts for both electro- and photocatalytic applications.

2. RESULTS AND DISCUSSION

Multifunctional nanocatalysts such as Bi\(_2\)WO\(_6\) and FeWO\(_4\) synthesized via a solvothermal route assisted by the PVP capping agent have been extensively investigated by X-ray diffraction (XRD), as shown in Figure 1a–f. The structural properties and crystalline nature of the prepared nanocatalysts are thoroughly discussed through the highly resolved diffraction peaks centered at \(2\theta\) values at 28.3, 32.8, 47.2, 55.8, 58.6, 69.1, 76.1, and 78.5\(^\circ\) relevant to the crystalline planes of (113), (200), (220), (313), (040), (333), and (046), respectively, for Bi\(_2\)WO\(_6\). On the other hand, for FeWO\(_4\), the \(2\theta\) values observed at 15.5, 18.8, 23.8, 24.4, 30.4, 36.3, 38.0, 41.2, 44.2, 48.7, 51.6, 52.6, 53.7, 61.6, 65.2, 70.9, and 73.0\(^\circ\) are relevant to the crystalline planes of (010), (100), (011), (110), (111), (021), (200), (121), (112), (022), (120), (122), (221), (113), (023), (321), and (312), respectively.

The JCPDS data numbers #73-2020 and #74-1130 concurrently matched with the orthorhombic Bi\(_2\)WO\(_6\) and monoclinic FeWO\(_4\) respectively. The strong signature of the diffraction peaks revealed the good crystalline nature of the nanocatalysts. As compared to Bi\(_2\)WO\(_6\), FeWO\(_4\) nanocatalysts exhibited a slight amorphous nature. No other significant peaks were predicted except for the characteristic peaks of the prepared nanocatalysts, which provided good correlation with the single-phase bimetal oxide nanocatalysts reported by previous studies.\(^{26,27}\) The role of PVP as a capping agent could not be appreciably noticed in the diffraction peak shift or any other changes in the diffraction peaks of the samples. However, the variation in the crystallite sizes with the addition of different concentrations of the PVP capping agent was revealed by the Debye–Scherrer formula, \(D = 0.9\lambda/\beta\cos\theta\), where \(\lambda\), \(\beta\), and \(\theta\) are attributed to the wavelength of X-ray, full width at half-maximum intensity, and Bragg’s angle, respectively. The calculated crystallite sizes of the samples are 33.32, 23.80, 27.77, 27.92, 23.91, and 23.94 nm for bare Bi\(_2\)WO\(_6\) 0.5 g PVP-assisted Bi\(_2\)WO\(_6\), 1 g PVP-assisted Bi\(_2\)WO\(_6\), bare FeWO\(_4\), 0.5 g PVP-assisted FeWO\(_4\), and 1 g PVP-assisted FeWO\(_4\), respectively. It can be visibly seen that the smallest crystallite size is obtained for the optimum concentration of 0.5 g of the PVP capping agent for both the nanocatalysis, which may be due to the controlled nucleation of particle growth provided by the optimum PVP level in synthesis. Hence, the XRD spectra confirmed the formation of Bi\(_2\)WO\(_6\) and FeWO\(_4\) nanocatalysts.

Scanning electron microscopy (SEM) images of the synthesized nanocatalysts are displayed in Figures 2 and 3 in different scale ranges. Generally, using polymers in nanomaterial synthesis is a traditional way of controlling the growth kinetics, which can change the reaction environment and can support the solubility rate of the precursor materials.\(^{28}\) The present study reported the synthesis of PVP-assisted Bi\(_2\)WO\(_6\) and FeWO\(_4\) nanocatalysts by means of the surface morphology and modifications with respect to the concentration of the capping agent (PVP). The formation mechanism of the Bi\(_2\)WO\(_6\) and FeWO\(_4\) nanocatalysts with respect to the PVP concentration has been revealed. Figure 2a,d displays the aggregated clumsy nanocluster-like flake morphology of bare Bi\(_2\)WO\(_6\). In the case of the Bi\(_2\)WO\(_6\) nanoplate array synthesis, the actual surface morphology of bare Bi\(_2\)WO\(_6\) was clumsy with aggregated nanocluster-like flakes, as shown in Figure 2a,d in 2 \(\mu\)m and 200 nm scale ranges. The addition of 0.5 g PVP stabilized the reaction environment and supported the completion of nanoflakes as nanofilms with organized freestanding ability. Further, it reduced the aggregation of nanofilms by forming a capping layer around the nuclei which controls the particle growth. Moreover, it performed a crucial role as a dispersant at the optimum concentration, which resulted in dispersed, ordered, and freestanding nanoplate arrays as shown in Figure 2b,e. Moreover, increasing the concentration of PVP from 0.5 to 1 g provided aggregation and distortion in a well-aligned nanoplate morphology. Further, the particle size also seems to be decreased with larger agglomeration as shown in Figure 2c,f, which may be due to the excess amount of PVP that failed to cover the entire surface of the nuclei, promoting the nucleation rate, which resulted in the distorted nanofilms with higher agglomeration.\(^{29}\) This implies that a well-defined plate-like morphology with good dispersion was obtained at an optimum concentration of the capping agent. Similarly, PVP-assisted FeWO\(_4\)
nanosphere synthesis evidenced the optimum concentration of 0.5 g of PVP abundantly reducing the self-aggregation of nanoparticles and providing less agglomeration.

Figure 3a–f demonstrates the surface morphology of FeWO$_4$ nanocatalysts in the scale ranges of 2 and 1 μm. The SEM images clearly revealed the nanosphere surface morphology of the nanocatalysts with some agglomeration. The overall agglomeration of the nanocatalysts is due to the interaction between the magnetic nanoparticles and the calcination treatment effect. Figure 3a,d represents the highly agglomerated nanosphere formation. Figure 3b,e shows the drastic reduction in agglomeration of the nanocatalysts synthesized with the use of 0.5 g of the PVP capping agent with the precursor solution. In this case, PVP acts as an effective stabilizer and a dispersive agent of nanomaterial synthesis. Further, a higher concentration of PVP led to aggregation of particles, which may be because of the same effect of a rapid nucleation rate (Figure 3c,f). The particle sizes show resemblance in all the samples, but the agglomeration completely depends on the concentration of the capping agent. The SEM images of the FW2 and FW3 nanocatalysts show almost similar morphology, but the aggregation of the FW3 nanocatalysts is higher than that of FW2. This may be due to the rapid nucleation rate of synthesis. Therefore, more metal ions interact with PVP and the growth kinetics are reasonably controlled, which produce finer nanoparticles, resulting in more aggregation of particles. Further, the mechanism of PVP is supporting the nanoparticle synthesis which was highly emphasized the growth kinetics and the concentration of PVP is also an important role in deciding the dispersive nature of nanostructures. Hence, it is evidenced that the capping agent played a crucial role in deciding the particle shape, size, and distribution in nanomaterial synthesis.

As shown in Figures 2 and 3, the final morphology of a material is obtained after the calcination process at 400 °C for 2 h. Further, the purpose of PVP used in the reaction is to form fine nanostructures with a controlled morphology. Calcination was done after the completion of the whole synthesis procedure. Therefore, the calcination temperature did not have any effect on PVP during synthesis, rather it had an
influence during the calcination process. PVP was used as a stabilizer in our work, and its influence was investigated on the morphological properties of the synthesized nanostructures by SEM, which showed that PVP stabilized the metallic ions with its amide group. During the drying process (at 80 °C), the long-chain polymers of PVP were decomposed to short-chain polymers. During the calcination process (at 400 °C), the PVP content and other impurities were completely removed from the material.32 Hence, the calcination temperature made an influence and effect on PVP during the calcination process.

The Raman spectra of the prepared nanocatalysts have been displayed in Figure 4A,B. Figure 4A(a−c) represents the well-determined characteristic peaks of Bi2WO6 centered at 296, 412, 473, 714, and 794 cm$^{-1}$. It shows the predominant peak at 794 cm$^{-1}$, which is attributed to the symmetric stretching mode of the vibrations of WO$_6$ octahedra because of the apical oxygen atom perpendicular to the layer.33 The small intense peak observed at 714 cm$^{-1}$ is attributed to the asymmetric stretching mode of WO$_6$ octahedra, mainly because of the equatorial oxygen atoms vibrating inside the layer. The second strong peak at 296 cm$^{-1}$ is attributed to the bending mode of the bismuth–oxygen polyhedral.34 Other small intense peaks around 412 and 473 cm$^{-1}$ are the characteristic vibration modes of the orthorhombic Bi$_2$WO$_6$ nanoplate arrays. Figure 4B(a−c) represents the characteristic peaks of the FeWO$_4$ nanocatalysts centered at 272, 357, 479, 607, 730, 823, and 856 cm$^{-1}$ respectively. The peaks at 823 and 856 cm$^{-1}$ correspond to the Ag symmetric mode of terminal WO$_2$.35 The peak around 730 cm$^{-1}$ corresponds to the asymmetric stretching mode of vibration. The peaks at 272, 357, and 479 cm$^{-1}$ correspond to the vibration modes of tungsten anions.36 Hence, the confirmation of monoclinic FeWO$_4$ nanospheres is further evidenced by Raman spectra.

The photoluminescence (PL) spectra of the prepared nanocatalysts are displayed in Figure 5a−f. The peaks are obtained for the given excitation wavelength of 320 nm. Three defined peaks were observed for both the samples at 492, 505, and 522 nm. The obtained PL spectra of these emissions revealed the good charge transfer and oxygen vacancies present in the samples. The strong predominant peak centered at 492 nm could be attributed to the intrinsic luminescent behavior of the Bi$_2$WO$_6$ and FeWO$_4$ nanocatalysts.37 The other peaks at 505 and 522 nm purely depend on the higher oxygen vacancies present in the samples, which revealed that the more number of oxygen vacancies encountered by the nanocatalysts provided very good electrocatalytic response over higher electronic conductivity.19,38

Fourier transform infrared (FTIR) spectroscopy has been carried out for the samples in the wavenumber range 500−4000 cm$^{-1}$. Figure 6a−c displays the FTIR spectra of the Bi$_2$WO$_6$ nanocatalysts array catalysts. The band observed at 555 cm$^{-1}$ corresponds to the Fe–O stretching vibration, and the band at 763 cm$^{-1}$ corresponds to the W–O lattice vibration.41 The other bands observed for all nanocatalysts around 1635, 2352, 2927, and 3452 cm$^{-1}$ correspond to the O–H bending, CO$_2$ vibration, C–H symmetric stretching, and O–H stretching vibration modes, respectively. Further, the appreciable variation observed in the FTIR spectra, especially in the 500–1000 cm$^{-1}$ range, for BW3 compared to bare may be due to the particle size effect.42 This demonstrated that the lower wavenumber shift observed in

Figure 4. (A) Raman spectra of (a) bare Bi$_2$WO$_6$, (b) 0.5 g PVP-assisted Bi$_2$WO$_6$, and (c) 1 g PVP-assisted Bi$_2$WO$_6$. (B) Raman spectra of (a) bare FeWO$_4$, (b) 0.5 g PVP-assisted FeWO$_4$, and (c) 1 g PVP-assisted FeWO$_4$.

Figure 5. PL spectra of (a) bare Bi$_2$WO$_6$, (b) 0.5 g PVP-assisted Bi$_2$WO$_6$, (c) 1 g PVP-assisted Bi$_2$WO$_6$, (d) bare FeWO$_4$, (e) 0.5 g PVP-assisted FeWO$_4$, and (f) 1 g PVP-assisted FeWO$_4$. 
addition to the variation in the FTIR profile in the range 500–1000 cm\(^{-1}\) may be due to the aggregation of particles and variation in their sizes.\(^{43}\) Further, more concentration of PVP affected the crystal structure by the distortion in the lattice during the nucleation process itself which resulted in the suppression of signals in the BW3 and FW3 samples in the FTIR spectra.\(^{44}\)

The UV−DRS spectra have been displayed in Figure 7A(a−f). The absorption edge of the samples was clearly obtained from the graph. It shows the clear absorption edge around 450 nm for the Bi\(_2\)WO\(_6\) nanoplate arrays and 700 nm for FeWO\(_4\) nanospheres. These results absolutely coincided with that of the literature.\(^{45,46}\) Further, the band gaps of the prepared nanocatalysts have been estimated by the Tauc graph (Figure 7B) using the formula: \(\alpha h\nu = A(\nu - E_g)^n\), where \(\alpha\), \(h\nu\), \(A\), and \(E_g\) denote the absorption coefficient, incident photon energy, constant, and band gap energy, respectively. As per the Tauc plot, the band gap values of the prepared nanocatalysts are predicted as 2.8 eV for the Bi\(_2\)WO\(_6\) nanoplate arrays and 2.1 eV for the FeWO\(_4\) nanospheres, respectively. There is no appreciable change observed in the band gap structure of the nanocatalysts with respect to the capping agent concentration. Hence, it is explored that the influence of the capping agents could be verified in the application studies.

The X-ray photoelectron spectroscopy (XPS) spectra of Bi\(_2\)WO\(_6\) and FeWO\(_4\) nanocatalysts have been depicted in Figures 8 and 9, respectively. An XPS study was carried out to investigate the chemical composition and valence state of the prepared nanocatalysts. It is a valid experiment to confirm the phase purity of the samples. In the present study, the composition analysis was carried out only for the best-performed optimized nanocatalysts prepared by 0.5 g of PVP-supported solvothermal synthesis. Figures 8 and 9 represent that the peaks obtained at certain binding energies are the characteristic peaks of the corresponding nanocatalysts. Figure 8a illustrates the survey spectrum of the Bi\(_2\)WO\(_6\) nanoplate arrays that consist of Bi, W, and O elements and some carbon trace. The presence of carbon may be due to the usage of a carbon tape during the XPS analysis. Figure 8b represents the W\(^{6+}\) crystal structure of the Bi\(_2\)WO\(_6\) nanocatalyst by two strong peaks at 35.6 and 38.1 eV, attributed to the 4f\(_{7/2}\) and 4f\(_{5/2}\) states, respectively. Figure 8c represents the presence of an oxygen element by the sharp strong peak at 530.2 eV. Further, the inhomogeneous nature of the O 1s spectrum observed for the Bi\(_2\)WO\(_6\) nanocatalyst may be due to the presence of oxygen in the nanocatalyst existing in the form of a hydroxyl oxygen state on the surface.\(^{47}\) Hence, the chemical environment and chemical states of the impurity-free Bi\(_2\)WO\(_6\) nanocatalyst has been confirmed by the XPS analysis.

Figure 9a represents the survey spectrum of FeWO\(_4\) nanospheres. It consists of the presence of elements such as Fe, W, and O in the FeWO\(_4\) nanocatalyst. This spectrum also consists of some carbon traces which may be due to the carbon present in the instrument itself. Figure 9b represents the presence of the Fe element confirmed by two peaks at 710.8 and 724.7 eV that could be attributed to the 2p\(_{3/2}\) and 2p\(_{1/2}\) states of Fe in the FeWO\(_4\) nanocatalyst. Figure 9c represents the W\(^{4+}\) state of the W element confirmed by two peaks obtained at 35.4 and 37.6 eV attributed to the 4f\(_{7/2}\) and 4f\(_{5/2}\) states, respectively.\(^{48}\) Figure 9d represents the presence of oxygen species at 530.3 eV and also the small hump-like peak.
observed at 532–533 eV which could be attributed to the presence of hydroxyl radicals on the surface of the nano-
catalyst.\(^6\) Hence, the XPS spectra confirm the formation of good-quality FeWO\(_4\) nanocatalyst.
Figure 10 demonstrates the specific surface area analysis of the best-performed 0.5 g PVP-assisted Bi$_2$WO$_6$ and 0.5 g PVP-assisted FeWO$_4$ nanocatalysts. From the studies, obviously, a higher surface area is exhibited by the Bi$_2$WO$_6$ nanocatalysts than FeWO$_4$. The relevant Barrett–Joyner–Halenda (BJH) analysis revealed the pore size, pore volume, and surface area, as depicted in Table 1. From Table 1, it is clear that 0.5 g of PVP-assisted Bi$_2$WO$_6$ possessed a surface area of 31.92 m$^2$/g, which is 4 times greater than that of FeWO$_4$ nanocatalysts, which may be due to the distribution of well-aligned, nanosized plates with less agglomeration which will facilitate faster ionic transfer and more number of active sites during the electrochemical oxygen evolution reaction (OER). According to the pore size and volume of the nanocatalysts, it is exploited that both the nanostructures exhibited a microporous nature that also favors the electrochemical OER activity of the electrode.

Table 1. Specific Surface Area and Pore Volume of γ-Bi$_2$O$_3$ Nanoflowers

| sample name and code | BJH (m$^2$/g) | pore volume (cc/g) | pore size (Å) |
|----------------------|--------------|--------------------|---------------|
| Bi$_2$WO$_6$ (BW2)   | 31.09        | 0.100              | 74.75         |
| FeWO$_4$ (FW2)       | 7.95         | 0.076              | 74.58         |

Figure 11A,B represents the linear sweep voltammogram (LSV) graph of the nanocatalysts prepared in 1 M KOH electrolyte solution at a scan rate of 10 mV/s. The potential window has been fixed from −0.2 to 0.6 V in which Hg/HgO has been used as the reference electrode. The potential has been converted into a reversible hydrogen electrode (RHE). In general, the water electrolysis process needs 1.23 V versus the RHE potential to start OER. In our case, Figure 11A,B shows the good OER response of the fabricated working electrodes of the prepared nanocatalysts. The LSV graph represents that the drastic change in the current density values observed for different candidates is purely dependent on the morphology of the nanocatalysts. In general, the electrocatalysts require more number of active sites to be available in the electrode/electrolyte region, lower overpotential, and good electrochemical stability. All these features make the electrocatalysts to perform efficient water electrolysis. Further, the influence of morphology-dependent electrochemical activity tuned by the PVP capping agent and the electrochemical mechanism of Bi and Fe tungstates based on their morphologies has been explored in our work as follows. The current densities observed from the LSV graph in Figure 11A(a–c) are 0.18, 2.79, and 1.06 mA/g for bare Bi$_2$WO$_6$, 0.5 g PVP-assisted Bi$_2$WO$_6$, and 1 g PVP-assisted Bi$_2$WO$_6$ nanocatalysts, respectively. The highest current density achieved for the 0.5 g PVP-assisted synthesis of Bi$_2$WO$_6$ nanocatalyst may be due to the well-defined nanoplate array morphology of the electrode which facilitated more number of active sites for enhancing the electrochemical reaction. The optimized concentration of the capping agent provided a suitable environment for well-dispersed, completely full filled growth kinetics of nanoplate arrays which results in the overall defined morphology of the nanocatalyst. Further, the bare Bi$_2$WO$_6$ nanocatalysts possessed very low current densities, denoting very low efficiency toward electrolyzing the water. These clumsy nanostructures may be aggregated more during the electrochemical reaction in the electrode/electrolyte region which reduces the number of active sites on the surface of the working electrode. The same may happen for the 1 g PVP-assisted Bi$_2$WO$_6$ nanocatalysts because of the agglomerated nanoplate array morphology. Further, the lower overpotential of 210 mV was successfully achieved for our optimized nanocatalysts. This is the lowest overpotential achieved for the Bi$_2$WO$_6$ nanocatalyst in the field of electrochemical water oxidation within our knowledge. However, the current density indicating the OER response of our optimized nanocatalyst is lower than the values reported in other literatures$^{9,10}$ for different electrocatalysts. Furthermore, the moderate current density value with a lower overpotential for Bi$_2$WO$_6$ nanocatalysts in the electrochemical water-splitting reaction is quite a novel result. Figure 11B(a–c) represents the electrochemical water-splitting behavior of FeWO$_4$ nanocatalysts synthesized in different chemical environments with and without the PVP capping agent. The current density observed for the nanocatalysts are 0.71, 1.96, and 1.27 mA/g for bare FeWO$_4$, 0.5 g PVP-assisted FeWO$_4$, and 1 g PVP-assisted FeWO$_4$ respectively. In case of FeWO$_4$ nanosphere electrocatalysts, there is not much difference in the morphology observed, but the dispersive nature and agglomeration of the nanocatalysts played a crucial role in the water electrolysis process during the electrochemical reaction. The optimized FeWO$_4$ nanocatalysts synthesized with 0.5 g of PVP possessed good current density with an overpotential of 320 mV among other FeWO$_4$ samples, which may be due to the lesser agglomeration of particles that provided more active sites that enhanced the conductivity of the working electrode, which resulted in the good OER activity of the optimized electrode. Further, the variation in current densities in the range of 1.0–1.1 V in the LSV profiles of PVP-assisted FeWO$_4$ and bare FeWO$_4$ may be due to the initiation of some hydrogen evolution reaction of the bare and optimum PVP-assisted electrodes during the electrochemical water oxidation process. It may be due to the favorable band gap and suitable morphology of the FeWO$_4$ (FW1 and FW2) electrodes. The focus of our study is to investigate the extensive OER activity of the fabricated electrode. Therefore, the initiation of the HER activity was not concerned. Hence, optimized nanocatalysts synthesized using the capping agent supported the enhanced electrochemical response toward...
efficient oxidation of water because of their compact, well-defined, and dispersed morphologies.

Figure 11C(a−c) illustrates the EIS spectra of the Bi$_2$WO$_6$ nanocatalysts, which consist of three regions such as the solution resistance ($R_s$) region, charge-transfer resistance ($R_{ct}$-semicircle) region, and Warburg’s conductive (spike) region. The EIS graph clearly demonstrates the exact semicircle region for the three electrodes, but the variations in the semicircle and spike regions denote the different conductivities possessed by different electrocatalysts which suggested that the drastic changes observed in LSV depend on the morphology and conductivity of the prepared nanocatalysts. The charge-transfer resistances of the bare, 0.5 g PVP-, and 1 g PVP-assisted Bi$_2$WO$_6$ nanocatalysts are 0.030, 0.014, and 0.016 $\Omega$, respectively. Hence, it proved that the optimized nanocatalyst is governed by very low charge-transfer resistance which undoubtedly increases the charge transfer. Moreover, the ions gained a higher mobility, thereby enhancing the electrochemical OER activity of the optimized electrode. Figure 11D(a−c) represents the EIS spectra of FeWO$_4$ nanocatalysts. The charge-transfer resistances of the bare, 0.5 g PVP-, and 1 g PVP-assisted FeWO$_4$ nanocatalysts are 0.030, 0.014, and 0.016 $\Omega$, respectively. In this case, the optimized electrode possessed lower $R_{ct}$ values which improved the charge-transfer mechanism of the candidate that strongly supported the efficient OER activity. Hence, the EIS spectra provided a strong relevance to the LSV spectra by means of promoting the mobility of charge carriers, assisted by the optimum concentration of the capping agent-supported nanocatalysts, for an efficient electrochemical water oxidation process.

Figure 12A,B represents the Tafel slope of the prepared nanocatalysts. Tafel slope is an efficient way to evaluate the electrodes and its catalytic activity toward proficient oxidation of water. It displayed the graph between the potential and log($j$). Figure 12A,B represents clearly that the electrocatalytic activity of the optimized electrodes prepared by 0.5 g of PVP-supported synthesis played a noteworthy role in the electrochemical water oxidation process. Based on Tafel plot, the slope values obtained are 119, 75, 98, 151, 78, and 107 mV/dec for bare Bi$_2$WO$_6$, 0.5 g PVP-assisted Bi$_2$WO$_6$, 1 g PVP-assisted Bi$_2$WO$_6$, bare FeWO$_4$, 0.5 g PVP-assisted FeWO$_4$, and 1 g PVP-assisted FeWO$_4$, respectively. The smallest Tafel slope value denoted the fast charge-transfer kinetics and outstanding electronic conductivity of the optimized nanocatalyst. It may be due to the well-dispersed, less agglomerated, defined morphology of the nanocatalyst providing more active sites for the successful electrochemical reaction to enhance the OER activity of the electrode.

A CA test for the optimized nanocatalysts was carried out for 24 h to evaluate the durability of the electrode materials. Figure 12C shows the stability test for 24 h on 0.5 g PVP-supported Bi$_2$WO$_6$ nanocatalysts which long-lasted their performance throughout the experiment under an electrochemical reaction, exhibiting a current density value of 1.58 mA/g from the start to the end of the experimental process. There was no decay observed in the current density value throughout the experiment, which evidenced the longtime durability of the electrode material. Figure 12D represents the stability test over 24 h on optimized 0.5 g PVP-supported FeWO$_4$ nanocatalysts with a current density of 1.39 mA/g. There is a strange performance exhibited by the candidate...
observed in the CA test, which showed a gradual decrease in performance from 1 to 5 h with the current density value of 0.64 mA/g, but there was a drastic increment in the current density value with the higher performance of the candidate.
observed after 6 h of time duration, which may be caused by the longtime immersion of the FeWO₄ nanocatalysts in KOH alkaline electrolyte that might have led to the formation of hydroxyl species of Fe and induced the electrical conductivity of the electrode during the electrochemical reaction, resulting in the appreciable improvement in the electrochemical performance of FeWO₄ nanocatalysts. It has been elaborately discussed with the help of XPS spectra performed after the stability test, as shown in Figure 13.

Figure 13a–c represents the XPS spectra of the 0.5 g PVP-assisted Bi₂WO₆ electrode after 24 h of the stability test that clearly evidenced that there is no significant difference between the XPS peak before (in Figure 8) and after the stability test except for the positive shift of the Bi 4f state identified for the Bi₂WO₆ electrode after 24 h of stability. It concurrently demonstrated that there were no structural disorders observed for the BW2 electrode, and the positive shift also indicated that there was a partial transfer of electrons that succeeded between the Bi₂O₃ and WO₃ phases in the orthorhombic Bi₂WO₆ nanocatalysts during continuous electrochemical OER. Further, the influential positive shift in binding energy observed for Bi 4f from Figure 13a implicitly suggests that the valence state of Bi may be positively larger than tungsten. Such kind of electron transfer may occur because of the long-term durability test under continuous water oxidation. Figure 13d–f evidenced the XPS spectra of the 0.5 g PVP-assisted FeWO₄ electrode after 24 h of stability test. In this case also, a positive shift is observed for the Fe 2p state, which indicates the partial electron transfer between the Fe₂O₃ phase and WO₃ phase of the monoclinic FeWO₄ nanocatalysts. Further, the peculiar nature of the W 4f state peak observed around the binding energy of the characteristic W 4f state may be due to the change in oxidation states during the incessant electrochemical process; the clear signature of the Fe(OH)₂ phase is evidenced by the satellite peak around 727 eV, and the hydroxyl species of Fe may also be confirmed by the peak around 538 eV. Moreover, the observed evidence may be caused by the increasing thickness of the hydrated Fe layer on the surface of the FeWO₄ electrode after 5 h of stability test. Hence, this hydroxide layer increased the conductivity, thereby enhancing the overall OER activity of the FeWO₄ electrode. In addition, the decreased intensity of the Fe 2p state may be due to the less diffusive nature on the surface of the electrode after the longtime stability test. The surface rigidity of the electrode has been further elucidated by the SEM images in Figure 14.

Figure 14(a,c),(b,d) represents the surface morphology of the Bi₂WO₆ and FeWO₄ electrodes after the stability test at different scale ranges such as 2 μm and 200 nm, respectively. Figure 14a,c clearly illustrates the aggregated nature of the nanoplates after the durability test that might be due to the aggregated electrolysis process of the best-performed Bi₂WO₆ nanoplate electrode. Figure 14b,d clearly evidenced the aggregation of nanospheres with some clear cracks, which undoubtedly is the reason for the rigidity of the electrode surface because of the intensive OER succeeded during the CA test.

Figure 15a represents the CV curve of the best-performed 0.5 g PVP-assisted Bi₂WO₆ electrode at different scan rates such as 10, 30, 50, 80, and 100 mV/s, respectively, in between the potential window of −0.4 to 0.6 V. The corresponding capacitive density versus Ag/AgCl has been displayed. The result represents the linear relationship between the current density and the corresponding scan rates. As a result, the specific capacitance of the electrode has been calculated as 327 F/g for 10 mV/s scan rate and also the electrochemically active surface area (ECSA) has been calculated from the graph as 0.013 m²/g. Hence, we have achieved a very good ECSA for our best-performed electrode which provided a greater description about the presence of more catalytically active sites to achieve an enhanced electrocatalytic ability of the electrode toward the electrochemical oxidation of water. The oxygen percentage evolved from the CA test has been detected by using the Ocean Optics Foxy-R and FOXY-CAL (SO#644877) sensor through NeoFox software. The oxygen detection test for 1 h under CA test has been displayed in Figure 15b. This evidenced the evolution of oxygen during the electrochemical water oxidation by the fabricated BW2 electrode and also the average value of oxygen evolved was 24.2% throughout the 1 h exploration of the OER activity.

Hence, the entire electrochemical investigations confirmed the good, longtime durability of the optimized nanocatalysts prepared in our work and will undoubtedly explore the utility of multifunctional nanocatalysts for multiple energy-related applications and will appreciate the attempts for fabricating such kinds of multifunctional catalysts in future.

3. CONCLUSIONS

The solvothermal route-assisted PVP capping agent was successfully optimized for producing novel multifunctional electrodes for electrochemical water-splitting applications. Bi₂WO₆ and FeWO₄ nanocatalysts has been prepared and confirmed through several characterization techniques such as XRD, Raman, PL, UV−DRS, and FTIR studies. Well-defined and less-agglomerated nanoplate array and nanosphere morphologies of the Bi₂WO₆ and FeWO₄ nanocatalysts were confirmed by the SEM images. The preparation of durable, long-term, and good-quality electrodes was succeeded by achieving 2.79 and 1.96 mA/g for the optimized 0.5 g PVP-assisted Bi₂WO₆ and FeWO₄ nanocatalysts, respectively. The durability of 24 h with 100% retention in the performance of optimized nanocatalysts was revealed by faster charge-transfer kinetics obtained from the relatively lower Tafel slope values of 75 and 78 mV/dec, respectively, for OER activity. The
produced Bi₂WO₆ and FeWO₄ nanocatalysts. To begin with, the used. The solvothermal route was optimized with PVP to tungstate dihydrate (Na₂WO₄·5H₂O) was then transferred into a 250 mL stainless steel Te solution. The above solution was further stirred for 24 h and ethylene glycol (C₂H₆O₂), nitric acid (HNO₃), deionized water, absolute ethanol (C₂H₅OH), and methanol (CH₃OH) were dissolved in 80 mL of deionized water. The above solutions were mixed together under constant stirring. After 2 h of hydrolyzation in water. Then, 2 M Na₂WO₄·5H₂O was dissolved in 80 mL of deionized water which consists of HNO₃ (1 mol/L) to prevent Bi³⁺ hydrolyzation in water. Then, 2 M Na₂WO₄·2H₂O was dissolved in 80 mL of deionized water. The above solutions were mixed together under constant stirring. After 2 h of continuous stirring, 5 mL of C₂H₅OH was added into the solution. The prepared active nanocatalysts were the same as that of the previous literature reports.9,15–1557

4. EXPERIMENTAL SECTION

Bismuth nitrate pentahydrate [Bi(NO₃)₃·5H₂O], sodium tungstate dihydrate (Na₂WO₄·2H₂O), polyvinylpyrrolidone (C₆H₉NO)·2H₂O, iron sulfate heptahydrate (FeSO₄·7H₂O), ethylene glycol (C₂H₄O₂), nitric acid (HNO₃), deionized water, absolute ethanol (C₂H₅OH), and methanol (CH₃OH) were used. The solvothermal route was optimized with PVP to produce Bi₂WO₆ and FeWO₄ nanocatalysts. To begin with the Bi₂WO₆ nanocatalysts without PVP synthesis, 0.1 M Bi(NO₃)₃·5H₂O was dissolved in 80 mL of deionized water which consists of HNO₃ (1 mol/L) to prevent Bi³⁺ hydrolyzation in water. Then, 2 M Na₂WO₄·2H₂O was dissolved in 80 mL of deionized water. The above solutions were mixed together under constant stirring. After 2 h of continuous stirring, 5 mL of C₂H₅OH was added into the solution. The above solution was further stirred for 24 h and was then transferred into a 250 mL stainless steel Teflon-lined autoclave at 180 °C for 16 h. Similarly, the above solution was prepared with 0.5 and 1 g of PVP, and the other procedure was the same as that of bare sample preparation. After naturally cooling down to room temperature, the precipitations were filtered by a Whatman filter sheet and calcined at 400 °C for 2 h and were named BW-1, BW-2, and BW-3, respectively. In a similar way, FeWO₄ nanocatalysts were prepared by a controlled solvothermal route and named FW-1, FW-2, and FW-3. The characterization techniques explored for the entire nanocatalysts were the same as that of the previous literature reports.

Binder-free electrode preparation needed cautious steps to follow. The prepared active nanocatalysts were first measured, and 3 mg of active material was dispersed in 1 mL of ethanol under 20 min of ultrasonication. A glassy carbon electrode (GCE) was ultrasonicated for 5 min for cleaning purpose. Then, 10 μL of the dispersed active material was drop-casted on a cleaned GCE that was left for 24 h at room temperature. Approximately, 30 μg of the material was loaded on the GCE that was then utilized as a working electrode to study the efficient electrochemical water splitting in a conventional three-electrode cell setup through the SP-150 Biologic workstation. The electrolyte solution used was 1 M KOH. Platinum wire and Hg/HgO electrode were used as the counter and reference electrodes, respectively.

5. RESULTS AND DISCUSSION

The fabricated electrodes will provide a facile path to the young researchers for the production of multifunctional nanocatalysts for multiple potential applications.

Figure 15. (a) Cyclic voltammogram of the 0.5 g PVP-assisted Bi₂WO₆ electrode in ferric ferrocyanide electrolyte and (b) oxygen sensing evolved from the CA test in a two-electrode system.

The characterization techniques explored for the entire nanocatalysts were the same as that of the previous literature reports.9,15–1557

4. EXPERIMENTAL SECTION

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