Cobalt Colloid-derived Efficient and Durable Nanoscale Electrocatalytic Films for High-Activity Water Oxidation

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ABSTRACT: Oxygen evolution reaction is of immense importance and is vitally necessary for devices such as electrolyzers, fuel cells, and other solar and chemical energy conversion devices. The major challenges that remain in this quest are due to the lack of effective catalytic assemblages operating with optimum efficiency and obtainable following much simpler setups and easily accessible methods. Here, we demonstrate that the robust electrocatalytic activity toward water oxidation can be achieved employing straightforwardly obtainable nanoscale electrocatalysts derived from easily made colloidal-cobalt nanoparticles (Co-CNPs) prepared in clean carbonate systems. Thin-film non-noble metal nanoscale electrocatalysts such as simple Co-CNPs/FTO and annealed Co-CNPs/FTO<sub>250</sub> and Co-CNPs/FTO<sub>500</sub> obtained by depositing Co-CNPs on the FTO substrate are shown to initiate water oxidation at much lower overpotentials such as just 240 mV for Co-CNPs/FTO<sub>250</sub> under mildly alkaline conditions while demonstrating an impressive Tafel slope of just 40 mV dec<sup>−1</sup>. Furthermore, the robust catalyst demonstrated a high electrochemical surface area of 91 cm<sup>2</sup> and high turnover frequency and mass activity of 0.26 s<sup>−1</sup> and 18.84 mA mg<sup>−1</sup>, respectively, just at 0.35 V, and superior durability during long-term electrolysis. These outstanding catalytic outcomes using easily prepared Co-CNPs/FTO<sub>250</sub>-type catalytic systems are comparable and even better than other noble and non-noble metal-based nanoscale catalytic assemblages obtained by much difficult methods. Most advantageously, the colloidal route also offers the easiest approach of incorporating carbon contents in the catalytic layer, which can ultimately increase mechanical stability and mass transfer capability of the system.

1. INTRODUCTION

Critical requirements and corresponding intensive searches for a cleaner environment and sustainable energy sources are major issues of concern for scientific and political communities worldwide. Correspondingly, the electrocatalytic processes such as oxygen evolution reaction (OER) are getting famous being central to many clean and eco-friendly energy conversion and storage systems. However, OER is kinetically slothful because of less-favorable kinetics of the four (4e<sup>−</sup>) electron process and the difficulty posed by O–O bond formation, and it ultimately requires high overpotential to overcome the energy barriers. Thus, to realize the industrial applications of these OER-related energy conversion processes, more specifically water-splitting phenomenon, cost-effective and accessible electrocatalytic materials that are obtainable via following much simpler and straightforward synthetic approaches that can drive the reaction at a much lower overpotential and represents remarkable durability are highly desirable.

Currently, the utmost attractive materials for oxygen catalysis are ruthenium-, iridium-, and palladium-based catalytic contenders that are revealed to operate at a much lower overpotential. However, they seriously suffer from high prices and scarceness that limits their large-scale exploitation.

Therefore, there is a continuous quest for replacing those precious metals electrocatalysts with earth-abundant non-noble metals electrocatalytic systems without compromising the catalytic activity. This quest has been tremendously rewarded over the last decade with the discovery of many transition metals specifically Ni-, Co-, and Fe-based MOFs, oxides/hydroxides, selenides, phosphides, and pnictides, showing substantial activity for OER under the employed conditions. A heterogeneous metal oxide-based catalyst such as three-dimensional NiFeO<sub>x</sub> nanosheets grown on iron foam has shown to exhibit substantial activity toward OER under alkaline conditions. However, research studies have proved that many MOFs and chalcogenides behave only as precursors and undergo partial or complete transformation into metal oxide-type catalytic structures during the catalytic
process; thus, metal oxide species formed in situ is completely responsible for the catalytic process.14

Furthermore, nanotexturing of electrocatalytic materials is of significant importance for enhancing electroactive sites for more promising adsorption of various intermediates on the catalytic surface and easier O=O bond formation, leading to the efficient release of molecular oxygen from adjacent nanoparticles constituting the catalytic surface.5,15

Many synthetic approaches have been widely explored for the fabrication of nanoscale-thin films electrocatalysts and nanoparticles immobilized on the conductor surface for water catalysis studied.16 Furthermore, to favor the multiple electron transfer during the water oxidation process, the defect can also be produced in catalytic structures.5 Meantime, many conductive supportive materials such as carbon nanotubes (nanorod and nanosheet array) and graphene sheets have also been exploited as cocatalysts for better activity of electrocatalysts.14

Fe-based catalytic films prepared using the hydrothermal method has been disclosed recently and shown to initiate OER at 383 mV with remarkable durability.1 In another study, transition metals-based catalytic films such as NiFeO4 are deposited on conductive nickel foam via anodic deposition in concentrated carbonate solution and exhibited outstanding performance for OER.16 Likewise, the highly active nickel-iron-copper multishell nanotube array grown on the copper substrate achieves a current density of 100 mA cm−2 at 320 mV.7 All these results provide convincing evidence regarding promising activity of transition metal-based catalysts toward OER.

Among other earth-abundant metal-based electrocatalysts, cobalt-based materials being inexpensive and having intrinsic conductivity have received much attention.17 Many cobalt-based materials with inserted carbon, sulfur, and other metals such as CoFeO,18 CoOOH,19 CoO3NiCo2O4,20 CoP,21 Co3O4/NmGO2, CoO3@CN,23 CoC1,24 and CoPe-derived CoO3@FTO16b have been studied so far for water-splitting applications. However, most methods for fabrication of nanostructured efficient catalytic assemblages suffer from lengthy protocols and high costs and are adaptable for screening only at a laboratory level but are not viable for real-life applications.5

Recently, ultrathin nanoplates of Co3O4 were synthesized following the hydrothermal route and were employed for water oxidation catalysis.25 However, again, the maintenance of high pressure and temperature limits their large-scale applications. Hence, the development of the earth-abundant electrocatalytic system employing very economical methods is crucial and need serious considerations for making the overall process industrially feasible.26

Inspired by this statement, here, we have demonstrated a very simple and straightforward method for the synthesis of nanotextured electrocatalytic films derived from easily made cobalt colloidal nanoparticles (Co-CNPs) with assimilated carbon content in the catalytic layer which is thought to enhance structural stability and efficacy of the catalysts. Metal colloidal nanoparticles are easily generated in clean and cost-effective carbonate systems, and so-obtained Co-CNPs are coated on the FTO (fluorine-doped tin oxide) surface to have the anode material to be tested as water oxidation catalysts. Furthermore, the analytical measurements and electrochemical investigations provide us persuasive remarks that easily obtainable Co-CNPs derived electrocatalysts are highly efficient for lowering the overpotential of OER and are very durable without undergoing any loss in catalytic activity for long-term electrolysis applications, and these results are advantageous comparably with other catalytic systems fabricated using complicated methods involving too many chemicals.

2. RESULTS AND DISCUSSION

2.1. Physical and Physicochemical Characterization.

To consent the generation of metal oxides and/or hydroxide-type colloidal nanoparticles, the FRIT spectroscopy is commenced. The FTIR spectrum for Co-CNPs shows the appearance of an intense band in the vicinity of 3300−3600 cm−1, sanctioning the formation of hydroxide of that metal3 (Figure 1a). Furthermore, the UV−visible spectrum for Co-CNPs is also conducted and presented in Figure 1b. It epitomizes the distinct peaks for Co-CNPs at the wavelength of 450 and at 250 nm. The absorption band at 450 nm may represent the octahedral Co2+ of Co(OH)2.27 Thus, initial characterization for Co-CNPs confirms the formation of Co(OH)2-type materials exploiting the clean carbonate system. The average size and homogeneity of colloidal nanoparticles are evaluated using a particle size analyzer. The analysis was carried out at room temperature (RT). The results disclose the average particle size within the range from 10 to 100 nm for Co-CNPs (Figure 1c).

The stability of colloids is investigated via zeta potential analysis as CNPs are expected to be stabilized via electrostatic repulsion between negative anions encapsulating positive metal cations. For the sake of applicability, the nanoparticles must render agglomerations and colloids having zeta potential in between −15 and 15 mV, which is thought to be stable.3 Advantageously, Co(OH)2 CNPs reveal the zeta potential of just 15 mV representing much-enhanced stability of easily obtainable Co-CNPs which is highly desirable for applications specifically in thin-film catalysis, as shown in Figure 1d.
For water oxidation catalysis, the thus-obtained nanoscale Co-colloids are coated on the conductor surface to form thin-film electrocatalysts to be placed in an electrochemical cell as the working electrode. The surface structure and morphology of the catalytic film is then studied via scanning electron microscopy analysis. High-resolution scanning electron microscopy (SEM) images for simple Co-CNPs/FTO and annealed Co-CNPs/FTO$_{250}$ and Co-CNPs/FTO$_{500}$ samples are presented in Figure 2a–f. The SEM image of a simple un-annealed Co-CNPs/FTO sample shows small homogeneous granular-type islands spreading over the exterior of the FTO substrate (Figures 2a and S1). A magnified view shows nanoscale features showing a high surface area of the Co-hydroxide-/oxide-based nanomaterials. However, the film is smooth but not compact, and there are regular empty regions in the CoO$_x$/Co(OH)$_x$ matrix (Figure 2b). The annealing treatment of the Co-CNPs/FTO at 250 °C produced Co-CNPs/FTO$_{250}$-type catalysts that exhibit isolated nanoscale crumb-type structures of nano-electrocatalyst grown outward on the electrode surface in the form of nano-flakes (Figure 2c). The magnified view shows the nanostructures having obvious gaps in between, and they are consistent in size and shape but are arbitrarily distributed throughout the surface instituting a slanted catalytic film (Figures 2d and S2). Co-CNPs become smaller with annealing because of the formation of crystalline structures, and a similar phenomenon was also observed in previous research. This might be due to the nucleation of NPs and phase conversion process under annealing operations.$^{11}$

Further annealing of the thin-film cobalt colloidal sample to 500 °C Co-CNPs/FTO$_{500}$ displays the SEM image of microscale structure banquet in the form of small micro-nano globules on the electrode surface (Figure 2e). There are definite nanostructures entirely covering the globule’s exterior and the presence of nanopattern objects showing the pseudospherical and spherical nanoparticles amassed with each other to form a big sphere-type shape (Figures 2f and S3). The size of each NPs is in the range of 20–30 nm which can be ascribed to the high surface area of NPs constituting the catalytic films. Moreover, the SEM image of the blank FTO electrode did not show any advance morphological features (Figure S3b). This SEM analyses reveal that the thin-film Co-CNPs/FTO, Co-CNPs/FTO$_{250}$ and Co-CNPs/FTO$_{500}$ samples are highly porous, having a large surface area which would facilitate the exposure of more catalytically active sites during catalysis for water oxidation reaction which can make electronic transfer easier which is highly desirable to address the challenges associated with OER.$^{1,3,24}$

Next, the energy-dispersive X-ray spectroscopy (EDS) is undertaken for catalytic bulk composition analysis of Co-CNPs-derived thin-film electrocatalysts. The EDS spectrum illustrated in Figures S4–S6 reveals the presence of cobalt and oxygen as the main elements of catalytic films along with some carbon signatures. The percentage of various metals constituting the catalytic layer is displayed in Table S2. EDS elemental analyses of cobalt-based nano-electrocatalysts demonstrate the successful carbon assimilation in catalytic films from carbonate systems. Carbon incorporation is associated with the robustness and flexibility of the catalytic system and thus enhancing the overall stability and activity of the catalytic samples.$^{24}$

X-ray diffraction (XRD) measurements are investigated to determine the active phase of the catalytic films derived from Co-CNPs. Figure 3 illustrates the 2θ scan XRD patterns for simple Co-CNPs/FTO and annealed Co-CNPs/FTO$_{250}$ and Co-CNPs/FTO$_{500}$ samples. The XRD pattern for the Co-CNPs/FTO sample obtained by depositing Co-CNPs on FTO substrate (Figures 2a and S1). A magnified view shows nanoscale features showing a high surface area of the Co-hydroxide-/oxide-based nanomaterials. However, the film is smooth but not compact, and there are regular empty regions in the CoO$_x$/Co(OH)$_x$ matrix (Figure 2b). The annealing treatment of the Co-CNPs/FTO at 250 °C produced Co-CNPs/FTO$_{250}$-type catalysts that exhibit isolated nanoscale crumb-type structures of nano-electrocatalyst grown outward on the electrode surface in the form of nano-flakes (Figure 2c). The magnified view shows the nanostructures having obvious gaps in between, and they are consistent in size and shape but are arbitrarily distributed throughout the surface instituting a slanted catalytic film (Figures 2d and S2). Co-CNPs become smaller with annealing because of the formation of crystalline structures, and a similar phenomenon was also observed in previous research. This might be due to the nucleation of NPs and phase conversion process under annealing operations.$^{11}$

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Further annealing of the thin-film cobalt colloidal sample to 500 °C Co-CNPs/FTO$_{500}$ displays the SEM image of
shows that the major diffraction peaks appeared at 31.1, 33.2, 37.9, and 47.9°, which confirms that as-deposited film is primarily composed of the Co(OH)₂ type structure which is a dominant phase in the un-annealed catalyst film, whereas annealing the as-deposited film Co-CNPs/FTO at 250 °C produces a compact black catalytic layer on FTO, indicating the formation of Co₃O₄-type phase, as observed previously. The diffraction peaks observed at 31.2, 36.8, 55, and 59.3° are ascribed to the Co₃O₄ type structure.

However, there are few signals directing to the presence of the Co(OH)₂ phase as well. The single peak confirming the presence of elemental cobalt is also observed in Co-CNPs/FTO and Co-CNPs/FTO₂₅₀ (Figure 3). By further increasing the annealing temperature up to 500 °C, the CoO₂ type state was observed for the Co-CNPs/FTO₅₀₀ sample as the dominating catalytic phase (Figure 3) and is in good agreement with the work reported previously. Moreover, the appearance of intensive bands confirms that all the electrocatalysts constitute the crystalline surface features.

In order to explore more about surface phases of catalytic films, Raman spectroscopy is undertaken. Raman spectra for simple Co-CNPs/FTO and annealed Co-CNPs/FTO₂₅₀ and Co-CNPs/FTO₅₀₀ samples are illustrated in Figure S7. The Raman spectra for Co-CNPs/FTO specify the presence of various transition modes at 190, 490, 680, and 1055 cm⁻¹ attributed to Co(OH)₂ as the dominating phase (Figure S7a), whereas RAMAN spectrum for Co-CNPs/FTO₂₅₀ shows the peaks at 190, 430, 510, 608, and 675 cm⁻¹ which are assignable to the Co₃O₄-type structure, while a single peak at 1055 cm⁻¹ is due to presence of Co(OH)₂ in the catalytic film (Figure S7b). The RAMAN spectrum for Co-CNPs/FTO₅₀₀ illustrates some distinct transition modes, confirming the presence of various phases of cobalt oxides/hydroxides in the catalytic film (Figure S7c). Convincingly, all the data presented above discussed analytical measurements that provide convincing evidence that Co-CNPs-derived electrocatalytic films owned mixed surface structures and nanoscale, porous morphological attributes. However, the main phase constituting the unannealed catalyst is the metal hydroxide type, and annealed electrocatalytic films contain metal oxides with mixed oxidation states as the foremost catalytic phases.

Next, to exactly scrutinize the surface elemental composition and to determine possible oxidation states of cobalt in the catalytic layer, X-ray photoelectron spectroscopy (XPS) analysis are conducted for active catalyst Co-CNPs/FTO₂₅₀ and is shown in Figure 4. The elemental detection on the XPS survey for Co-CNPs/FTO₂₅₀ signifies the presence of cobalt, oxygen, and carbon in the catalyst layer (Figure 4a). High-resolution XPS spectrum for Co 2p spectrum showing two peaks at binding energies (BEs) of 780 and 796 eV corresponds to Co 2p₁/₂ and Co 2p₃/₂ respectively. Therefore, Co 2p is primarily composed of Co²⁺ and Co³⁺ bound to oxygen. Weak XPS signals at 63 and 101 eV emerged because of the presence of Co 3s and Co 3p (Figure 4b). Moreover, oxygen BEs from 529 to 532 eV indexed to metal-bound oxygen in the catalyst. The appearance of another weak peak at about 531 eV suggests the presence of OH⁻ species (Figure 4c). Carbon incorporation is evidenced by the subsequent signals for C 1s at 283–287 eV (285.0, 285.5, 287.3, 289.1, and 292 for C≡C, C–O, C=O, O=C=O respectively) in the deconvoluted C 1s core XPS spectrum which shows oxygenated carbon contributions as −C–O and/or C(O)O− in the catalyst. C≡C at 285.0 eV represents the distinct oxygen-free carbon. The intense peak at 284.1 could probably be attributed to the C–Co bond in Co-CNPs/FTO₂₅₀ (Figure 4d). The XPS analysis clearly indicates that the catalysts consist of cobalt oxide and hydroxide carbonate systems. Furthermore, the synergistic bonding of Co–C is also observed via XPS which is thought to improve facile electronic transfer and catalytic performance of the system during OER. Conclusively, the characterization techniques demonstrate the successful fabrication of highly porous, nanocolloid-derived catalytic film, as revealed by SEM analysis and having mixed structural features.

2.2. Electrochemical Investigations. Primarily, the electrocatalytic activity of Co-CNPs derived simple Co-CNPs/FTO and annealed Co-CNPs/FTO₂₅₀ and Co-CNPs/FTO₅₀₀ electrocatalysts for water oxidation reaction is investigated via cyclic voltammetry (CV) approach in 0.1 M aq. KOH electrolyte solution (pH ≈ 13) and presented in Figure 5. The CV profile for Co-CNPs/FTO shows the appearance of oxidative current at about 1.1 V (vs RHE) followed by a pronounced oxidative pre facultant at 1.2 V (vs RHE). Oxidative peak rises in amplitude, and after undergoing a decline, it is then followed by a catalytic peak at the onset potential of about 1.54 V (vs RHE). This onset potential is much better than previously reported CoO₂-based electrocatalyst which is shown to initiate OER at 1.71 V (vs RHE). The catalytic peak increases sharply and achieves the current density of about >18 mA cm⁻² at a potential of 1.77 V (vs RHE). The OER onset overpotential was η = 310 mV and a current density of 10 mA cm⁻² was achieved just under the potential of Eₓₓ,=10mA cm⁻² = 1.69 V (vs RHE) [η = 460 mV]. The CV curve for the sample annealed at 250 °C, Co-CNPs/FTO₅₀₀ indicate the appearance of the oxidative peak at about 1.35 V (vs RHE). The oxidative peak after rising up undergoes a slight downfall and is then followed by a catalytic peak at about 1.47 V (vs RHE). The onset potential of water oxidation reaction initiated just above 1.46 V (vs RHE) (because of the appearance of the broad metal redox reaction peak just prior to
the water oxidation catalytic wave, it is often difficult to clearly find a precise onset potential region. Therefore, we calculated the exact onset potential for OER from backward sweep, as described previously.\textsuperscript{35a} A current density of >40 mA cm\textsuperscript{-2} is achieved just under the potential of 1.76 V (vs RHE). The OER onset overpotential was $\eta = 240$ mV and a current density of 10 mA cm\textsuperscript{-2} was achieved just under the potential of $E_{i=10mA .cm^{-2}} = 1.61$ V (vs RHE) [$\eta = 380$ mV] (Figure 5).

The electrochemical activity of the Co-CNPs sample annealed at 500 °C Co-CNPs/FTO\textsubscript{500} presented the oxidative prefaces at about 1.36 V (vs RHE). This oxidative peak undergoes a minor waning and is trailed by a sharp catalytic wave at above 1.52 V (vs RHE) with an overpotential of about $\eta = 290$ mV (Figure 5). A current density of \texttimes31 mA cm\textsuperscript{-2} was achieved under 1.82 V (vs RHE) and a current density of 10 mA cm\textsuperscript{-2} was attained just under the potential of $E_{i=10mA .cm^{-2}} = 1.68$ V (vs RHE) [$\eta = 450$ mV] (Figure S8a). Conclusively, all the cobalt-based electrocatalytic materials derived from easily made Co-CNPs presented substantial catalytic activity for OER. Very low onset overpotential observed for the straightforwardly prepared cobalt-based nano-electrocatalyst can be attributed to the fine unique nanoscale structure and the presence of carbon content in them which might have facilitated the intrinsic electron transfer. It has been previously discovered that highly efficient and durable Co–C–C-based water oxidation can be generated with 30% carbon content in the catalyst layer.\textsuperscript{33} The cobalt-based system shown here with significant carbon content (13–28%) embedded in them, as revealed by EDS analysis and XPS data presented here, is relatively much easy to prepare using a very inexpensive setup and much simpler and applied methods.

Based on CV data for comparatively lowest onset overpotential and high current density, it is considered that Co-CNPs/FTO\textsubscript{250} is the best-performing OER electrocatalyst discussed here. The high-performance of Co-CNPs/FTO\textsubscript{250} might be due to the formation of a compact catalytic layer strongly adherent to FTO that also reveals least intrinsic resistivity as observed by electrochemical impedance spectroscopy (EIS) (discussed in later section). Co-CNPs/FTO\textsubscript{250} also exhibits nanoscale-enzyme-type structures grown outward on the electrode surface in the form of nanoflakes. This structure also facilitates charge transfer at the catalyst/FTO interface and catalyst–electrolyte boundary. Further, Co-CNPs/FTO\textsubscript{250} has the predominantly Co\textsubscript{3}O\textsubscript{4}-type phase, as suggested by XRD, and is ascribed to the better performance for water oxidation.\textsuperscript{34}

Furthermore, high stability is of tremendous importance for a good electrocatalyst for ensuring its economic applications.\textsuperscript{1} Therefore, to further examine the stability of the above catalyst under harsh oxidative conditions accelerated electrochemical testing is performed. The first and 500th concurrent CV cycles shown to produce similar catalytic signature during continuous electrolysis without any drop in catalytic activity on Co-CNPs/FTO\textsubscript{250} where the 500th cyclic curve almost exactly overlaps the initial one (Figure S8b). This presents excellent stability of the system under the employed electrochemical conditions.

The durability of the catalyst is further assessed by incremental multistep-controlled potential electrolysis (CPE) and controlled current electrochemical experiments. Figure S9 represents a multistep chronopotentiometry curve for Co-CNPs/FTO\textsubscript{250} with the current densities from 4 to 32 mA cm\textsuperscript{-2}. At the initial step of 4 mA cm\textsuperscript{-2}, the operating potential instantaneously gets stabilized just at 1.55 V (vs RHE), and almost remains stable for the next 400 s. The consequent analysis under the identical conditions by increasing linearly current density values presents a similar phenomenon and ascribed to remarkable conductivity, efficient mass transfer ability, and mechanical stability of the system under considerations. In addition to this, the multistep chronoamperometric test, as presented in Figure S10, also proved high consistency in the catalytic activity of Co-CNPs/FTO\textsubscript{250} for OER during various applied potentials from 1.1 to 1.8 V (vs RHE) and keeping the catalyst at each potential for about 300 s. These results further affirm good durability and robustness of the catalyst in the electrochemical environment.

2.2.1. Short-term Catalytic Stability. The stability of the catalyst under test is a decisive factor for practical implications.\textsuperscript{34} During the harsh oxidative environment, the proposed catalytic material may undergo deterioration and degradation in catalytic activity over time which may hinder their large-scale applications.\textsuperscript{35} The preliminary electrochemical data suggesting the excellent performance of all three Co-based catalytic materials let us perform a short-time stability test of the catalysts under the oxidative conditions. The short-term stability tests of all the catalytic materials are performed by holding the catalyst at the constant potential for the time interval of 2 h, and the value of current density achieved at $t = 0$ and $t = 2 \text{ h}$ was observed. If the $J@$ t = 0 and $t = 2 \text{ h}$ are the same, then it is a clear indication that the catalyst is stable under the employed conditions for at least 2 h. If $J@$ t = 0 > $t = 2 \text{ h}$, then it represents catalyst deactivation or degradation over time. However, if the $J@$ t = 0 < $t = 2 \text{ h}$, then it shows that the catalyst under study is an electroactive species.\textsuperscript{36} From Figure S11 and Table S4, it can be observed that all the Co-based catalysts are electrochemically stable under the vigorous oxidative conditions without any notable degradation for at least 2 h during CPE experiments under the conditions mentioned in Table S4.

In another experiment, the stability of employed catalysts was also evaluated using a chronopotentiometry approach.
applying a constant current density of 2 and 10 mA cm$^{-2}$ for the time interval of 2 h, while the operating potential is measured as a function of time. A representative controlled current electrolysis (CCE) at a fixed current of 2 and 10 mA cm$^{-2}$ for all the nano-electrocatalysts is presented in Figure S12. From the potential versus time curve, it is observed that catalysts showed no significant change in the value of measured potential after 2 h of the constant polarization test; therefore, the activity loss was negligible which confirms that all the catalysts are durable for OER catalysts for 2 h of continuous electrolysis under employed electrochemical conditions. The stability measurement protocol employed in this manuscript is useful for the rapid screening of catalyst durability. However, it is notable that the catalyst representing high stability during 2 h of continuous electrolysis may not show the same stability over a longer period of time. In the same way, the catalyst showing little degradation during 2 h of electrolysis may become active when evaluated for an extended period because in electrocatalytic films, some active sites are not readily available for electrolysis which may become available after a few hours of continuous electrolysis or may not get explored at all. For an in-depth study of the promising catalyst, kinetics and long-term stability measurements are also needed to be investigated.

2.2.2. Electrochemical Kinetics. Above-discussed initial data based on CVs, short-term CCE, and CPE provide captivating arguments that all the catalytic samples derived from easily made cobalt-based colloidal nanoparticles are electrochemically active and stable under electrochemical conditions for OER. Here, the sluggish OER at lower energy input is significantly driven because of the high intrinsic activity of the catalysts which can facilitate the four-electron transfer process between the catalyst and adsorbed water species, and this might be due to carbon assimilation in the catalytic layer from the carbonate system which further increases the mechanical stability and flexibility of the catalytic film. Therefore, to further comparatively explore the catalytic efficacy of all the candidates under similar electrochemical conditions, some widely exploited kinetic parameters including Tafel slopes, electrochemically active surface area (ECSA) analysis, electrochemical accessibility, mass activity (MA), exchange current density, and turnover frequency (TOF) analyses are conducted in 0.1 M aq. KOH solution. In this quest, the Tafel slopes are calculated from the linear polarization curve considering the linear region of CV scan close to the onset potential where small overpotential and current density is considered as the feasible region for these kinetic investigations at lower scan rate such as 5 mV s$^{-1}$. Corresponding Tafel plots comprising $\eta$ versus the log of $J$ are illustrated in Figure 6a–c.

Co-CNPs/FTO, Co-CNPs/FTO$_{250}$ and Co-CNPs/FTO$_{500}$ present the Tafel slopes of 129, 78, and 86 mV dec$^{-1}$ respectively. The relatively smaller Tafel slope of 78 mV dec$^{-1}$ for Co-CNPs/FTO$_{250}$ even with much high solution resistance represents the faster kinetics of the electrode system coated with an annealed Co-CNPs sample. However, the Tafel slopes derived from polarization curves might contain contributions of electron transport resistance, thus illustrating somewhat higher values.$^3$ The effect of solution resistance can be minimalized by taking 100% IR compensation, which is not possible for the catalytic materials demonstrating solution resistance values greater than 6 $\Omega$ and charge transfer resistance.$^3$ Therefore, to completely minimize the effect of uncompensated resistance, we also calculated the Tafel slope of our best performing catalyst such as Co-CNPs/FTO$_{250}$ via EIS measurements.$^{37}$

Nyquist plots are collected at various applied potentials 120 mV above the onset overpotential with a difference of 5 mV in between. Here, $1/R_{CT}$ demonstrates the exact intrinsic exchange current density of the catalyst and kinetics of the overall electrode process under a wider potential window. The corresponding Nyquist plots and plots of applied potential versus the inverse of $R_{CT}$ on a logarithmic scale are shown in Figure 7. The slope of the linear portion of overpotential versus the log of inverse $R_{CT}$ gives the Tafel slope of 40 mV dec$^{-1}$ for Co-CNPs/FTO$_{250}$. Here, the Tafel slope of 40 mV dec$^{-1}$ indicates the 3rd step (M–OOH bond formation) as the rate-determining step.$^{38}$ The smaller value of the Tafel slope is highly desirable as it represents the resistance-free intrinsic nature of the catalyst under the employed electrochemical conditions. Furthermore, to get more insight into the intrinsic kinetics of CNPs derived catalytic systems in terms of charge transfer resistance at so-called electrolyte–electrode/catalyst interphase impedance spectroscopy is investigated. Nyquist plots are measured at an overpotential of 0.35 V. Choice of 0.35 V is based on the assumption that 10% efficient solar water splitting devices should operate to produce 10 with the maximum overpotential of 0.35 V for the water oxidation reaction.$^{3}$

The comparative Nyquist plots measured under similar conditions for Co-CNPs derived un-annealed and annealed electrocatalytic systems, as illustrated in Figure S13. The diameter of the semicircle is directly associated with the kinetics of the electrode system. Ultimately, the smaller diameter for Co-CNPs/FTO$_{250}$ ($R_{CT} = 10 \Omega$) signifies the active role of the catalyst in lowering the resistance of the electrochemical process. $R_{CT}$ values of other Co-CNPs-based catalytic systems are presented in Table S5. The MA of Co-CNPs-derived electrodes discussed in this study, at the fixed potential of 0.35 V, is also investigated. The relatively high value of MA is demonstrated by Co-CNPs/FTO$_{250}$ (18.84 mA mg$^{-1}$ @0.35 V), among other candidates, which is consistent with CV data and showing the substantial activity of the catalyst (Figure 8a, Table S5). The exchange current density is
calculated from charge transfer resistance. Co-CNPs/FTO\textsubscript{250} (0.64 mA cm\textsuperscript{−2}) shows a relatively high value of \(j^0\) because of the lowest observable charge transfer resistance (Figure 8a, Table S5).

To evaluate the ECSA of catalysts, we measured double-layer capacitance at the so-called solid–liquid interphase by CV experiments. Figures S14−S16 represents the cyclic voltammograms collected at specific potential regions where no signatures for faradaic currents are observed, and all the current is supposed to originate because of double-layer charging. Co-CNPs/FTO\textsubscript{250} presented a much higher electro-active area of 91 cm\textsuperscript{2} relative to other electrocatalytic systems (Figure S15, Table S5). This signifies the presence of more electro-active sites on the aforementioned catalytic system facilitating the OER catalysis. Double-layer capacitance measurements and ECSA of other catalytic systems are illustrated in Figures S14 and S16. High ECSA of catalysts might originate because of the presence of the nanostructure and more electro-active sites and the insertion of carbon content in the catalytic film.

To further reflect the intrinsic catalytic activities of the thus-prepared catalytic systems, TOF measurements associated with generating oxygen molecule per second are employed. Prior to TOF calculations, surface electroactive Co\textsuperscript{2+} sites are quantified by integrating the area under the reduction peak of CV curve measures for all the catalytic systems at 20 mV s\textsuperscript{−1}, as presented in Figure S17. TOF values for all the catalytic systems are comparatively determined at various applied potentials and are represented in Figure 8b and Table S6. Co-CNPs/FTO\textsubscript{250} presents a high TOF of \((0.26\text{ s}^{-1}@0.35\text{ V})\) and is attributed to the fast-electrochemical process taking place at the electrode surface relative to other catalytic candidates discussed here (Table S5).

Furthermore, the TOF value for the Co-colloids system fabricated following the modest colloidal strategy and calculated at just 0.35 V is higher than other previously reported cobalt-based catalytic systems including Co-Pi (TOF@410 mV = 0.002 s\textsuperscript{−1}),\textsuperscript{39} Co\textsubscript{3}S\textsubscript{4} (TOF@500 mV = 0.00132 s\textsuperscript{−1}),\textsuperscript{40} and Co−Bi (TOF@400 mV = 0.0015 s\textsuperscript{−1})\textsuperscript{41} which shows a promising feature of the catalyst obtainable using a much simpler approach.

A comparison with the previously published Co-based catalysts is provided in Table 1. A direct comparability of catalytic activity is problematic because of variations in catalyst loading, film thickness, electrode materials, and overall
electrochemical conditions. Nevertheless, the published data are compiled and compared with our catalyst prepared using a very simple and straightforward method. Best-performing catalysts are evaluated on the basis of previously discussed electrochemical parameters and are compared with previously reported catalysts. Table 1 shows that Co-CNPs/FTO$_{350}$ exhibits the lowest onset potential for OER and a comparatively low Tafel slope of just 40 mV dec$^{-1}$ under mildly alkaline electrochemical conditions.

### 2.2.3. Figure of Merit for Comparative Analysis of the OER Catalyst

McCrorry et al. described a method to benchmark the OER catalyst. For example, they carried out a short-term stability test for thin-film catalysts by holding the catalyst at a stable current density of 10 mA cm$^{-2}$ for a time interval of 2 h and overpotential as a function of time was studied. Here, as a descriptive exercise, the catalytic stability is evaluated at 10 mA cm$^{-2}$ for at least 2 h, and overpotential is studied as a function of time. In Figure 9, the overpotential at 10 mA cm$^{-2}$ $\eta(t=0)$ is plotted against the overpotential at $t=2$ h for all the cobalt-based catalysts discussed in this study. It is concluded from a detailed discussion in the literature that any material whose overpotential value to achieve a stable current density of 10 mA cm$^{-2}$ lies after 500 mV in the x-axis or y-axis is not very attractive for applications in water oxidation catalysis, and its performance can be marked as only satisfactory for water-splitting catalysis unless otherwise its activity is improved. A catalyst lying in the range of 400–500 mV from both axes is good for water oxidation catalysis. Any material that lies in 300–400 mV in any axis is excellent for large-scale applications, and the catalyst that lies below this range such as from 200 to 300 mV can be regarded as an ideal catalytic material. Results reveal that all the catalytic materials studied in this manuscript are capable of producing a stable current density of 10 mA cm$^{-2}$ at an overpotential range of 400–450 mV. Therefore, all Co-based materials can be regarded as good catalysts and are showing substantial catalytic performance for OER. From the comparative analysis, it can be concluded that all the electrocatalyst materials obtained using a very simple and cost-effective colloidal method are highly applied. Their remarkable stability and activity can be due to the high surface area, carbon assimilation, and facilitate electronic transfer in the film, as revealed by EIS, ESCA, EDS spectroscopy, and XPS analysis.

### 2.2.4. Extended Electrocatalytic Stability

Co-CNP-derived nano-electrocatalyst films were also investigated for long-term water oxidation applications. To test the robustness of Co-CNPs/FTO, Co-CNPs/FTO$_{350}$, and Co-CNPs/FTO$_{500}$ CPE experiments for water oxidation were conducted in 0.1 M aq. KOH solution ($\mathrm{pH} \approx 13$). Figure 10 illustrates that the simple catalyst Co-CNPs/FTO produces a remarkably stable current density of $>3$ mA cm$^{-2}$ at a fixed potential of 1.6 V (vs RHE) [$\eta = 370$ mV] which is persisted through the course of electrolysis without any degradation. For the catalyst, Co-CNPs/FTO$_{350}$ a current density of 11.8 mA cm$^{-2}$ was achieved just at an operating potential of 1.65 V (vs RHE) [$\eta = 420$ mV]. During analysis, only a very slight degradation was observed, and because of this, the current density decreased and achieved a value of 10.6 mA cm$^{-2}$ which can be due to drastic solution perturbation and oxygen bubbling during continuous electrolysis. Thus, the catalyst showed excellent durability in alkaline conditions. The catalyst remained stable up to 20 h of continuous electrolysis with only <10% degradation. The chronoamperometry experiment conducted for Co-CNPs/FTO$_{500}$ also presented admirable results, and the catalyst achieves a current density of 6 mA cm$^{-2}$ at the mere operating potential of 1.65 V (vs RHE) [$\eta = 420$ mV]. Although the value of current density is smaller, it was observed that the current density remained stable for continuous 20 h of electrolysis without any observable degradation (Figure 10). Long-term stability testing of all the electrocatalyst suggests that all materials discussed here are highly durable, robust, and did not show prominent deprivation in performance; thus, all

### Table 1. Comparison of Co-CNP-Derived Nano-Electrocatalysts with Other Co-Based Systems for OER *

| catalyst/system | electrolyte | $\eta$@ onset (mV) | $\eta$ (mV) at 10 (mA cm$^{-2}$) | Tafel slope (mV dec$^{-1}$) | refs |
|----------------|-------------|-------------------|-------------------------------|--------------------------|-----|
| Co-CNPs/FTO$_{350}$ | 0.1 M aq. KOH | 240 | 380 | 40 | TW |
| Co$_3$O$_4$/SWCNTs | 0.1 M KOH | 530 | 104 | 42 | |
| CoPc$_{350}$/FTO | 0.1 M NaOH | 310 | 560 | 60 | 16b |
| Fe–Co$_3$O$_4$@Fe–Co–Bi/GC | 0.1 M K–Bi | 420 | 121 | 43 | |
| Co–N/GF | 1.0 M KOH | 313 | 84 | 44 | |
| NiCo@NC (N-doped carbon nanofiber) | 0.1 M KOH | 539 | 98 | 45 | |

*TW = this work; GF = graphite foam; Co$_3$O$_4$/SWCNTs = Co$_3$O$_4$ nanocrystals on a single-walled carbon nanotube; Fe–Co$_3$O$_4$@Fe–Co–Bi/GC = Fe–Co–Bi layer on a Fe doped Co$_3$O$_4$ nanoarray.

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**Figure 9.** Plot of catalytic stability. The x-axis is the overpotential required to achieve the current density of 10 mA cm$^{-2}$ per geometrical area of the electrode at $t = 0$ and the y-axis is the overpotential needed to achieve the current density of 10 mA cm$^{-2}$ per geometrical area of the electrode at $t = 2$ h during CCE. The diagonal line is the expected response of the catalyst that does not alter during 2 h. The catalyst below the diagonal line is regarded as electroactive, that on the line is regarded as stable, and that above the line has shown some degradation.
the materials are economically viable for long-term water oxidation catalysis (Table S7).

2.3. Post-Catalytic Stabilities Studies. The post-catalytic analysis of the electrode after OER testing is performed after 20 h of continuous electrolysis via XPS, as presented in Figure S18. Results reveal no significant elemental changes in the chemical structure of Co–CNPS/FTO_{250}. Thus, the catalyst is shown to sustain its integrity even after continuous hours of electrolysis that is highly desirable from a practical and economical perspective. Notably from post catalytic analysis, this does not affect the chemical structure of the catalyst. In addition, no flaking of the material was observed from the catalyst surface during long-term electrolysis.

3. SUMMARY AND OUTLOOK

The high redox potential of transition metal oxide/hydroxide-based nanoscale electrocatalytic assemblies makes them extremely reliable for water oxidation catalysis. The nanostructured feature generation in electrocatalysts is an advancement that ultimately facilitates the abstraction of four electrons from water and the ultimate conversion of water into molecular oxygen. However, complex synthetic strategies, sophisticated experimental setups, and usage of too many chemicals make the reaction less viable. Therefore, time-effective, inexpensive, and applied methods for nano-electrocatalyst fabrication are required to be developed for large-scale exploitation of water splitting catalysis with optimum efficiency. In this regard, we have shown here easily prepared Co-CNPs-derived nanoscale electrocatalysts to accelerate OER at the lower energy input. The catalyst is thoroughly analyzed via various analytical tools that reveal nanopattern morphological attributes and mixed structured features for catalytic films. Furthermore, detailed electrochemical characterizations provide a fascinating remark that all the catalytic candidates are electroactive, durable, and show well-balanced kinetic for OER under alkaline conditions, and Co-CNPs/FTO_{250} presented much superior activity, initiating OER just at 1.47 V (vs RHE). Promising electro-catalytic performance during long-term electrolysis experiments, low Tafel slope, high MA, TOF, and ECSA may be ascribed to the unique surface structure, porous texture, and insertion of carbon content in these materials. It is believed that the colloidal approach for producing the highly efficient electrocatalysts for water oxidation is very striking for large-scale applications. This study provides a very profound widespread electrode/electrocatalyst for efficient electrochemical water splitting toward clean H₂ production from plentiful water. From these results, we further forecast the use of various colloidal single metal and binary metal hydroxide/oxide materials with assimilated carbon, boron, and sulfur content in them for superior water-splitting catalysis for the production of clean hydrogen fuels.

4. EXPERIMENTAL SECTION

4.1. Materials and Methods. All the chemicals and reagents were of analytical grade and obtained from Aldrich and used as received without following any purification step otherwise mentioned. Prior to use, ethanol, methanol, and acetone were double-distilled. All the solutions involving water were made in ultrapure water (Milli-Q 18.2 MΩ cm, 2–4 ppb total organic contents). All the solutions were freshly prepared before use. All the analyses are carried out at RT.

4.2. Preparation of Co-CNPs. Cohydroxide carbonate colloidal nanoparticles are synthesized at RT and atmospheric pressure, following the colloidal synthetic route in 0.1 M HCO_{3}⁻ solution. Colloids are obtained while mixing 1 mL of clear solution of 0.1 M Co²⁺ ions with 60 μL of 0.1 M carbonate solution (pH = 8.2) under slow stirring. Ultimate formation of the turbid solution is indicative of colloidal generation. Prior to use, colloids are frequently filtered using microfilter syringes to have homogeneously sized colloidal nanoparticles. (Further details for the preparations of colloidal NPs are described in the Supporting Information, Table S1).

4.3. Fabrication of the Working Electrode. Thin-film anode material for water catalysis is generated by placing Co(OH)₂/HCO_{3}⁻ colloidal NPs on the FTO surface using the simple drop-casting approach. In this quest, just a 20 μL drop of as-prepared Co-CNPs is placed on the conducting side of the FTO surface using micropipettes and air-dried. The thus-obtained electrode coated with a catalytic layer is directly employed as the anode for water oxidation catalysis. Furthermore, to foresee the structural and electrocatalytic modification in the anode material, the electrode/electrocatalyst is annealed for 1 h at 250 and 500 °C. The FTO slide coated with the thin-film electrocatalyst (unannealed and annealed) obtainable as mentioned above is put inside the grove of the home-made stainless-steel rod and fixed with Teflon tape before placing into the electrochemical cell as the working electrode.

4.4. Analytical Measurement. Fourier-transform infrared spectroscopy and UV–visible spectroscopy are undertaken to confirm the formation of metal hydroxide colloidal NPs on the Agilent Cary 630 FTIR spectrometer within the frequency range from 650 to 4000 cm⁻¹ and Agilent Cary 60 UV–visible spectrophotometer, respectively. Particle size and zeta potential analyses are conducted on an Anton Paar’s PSA analyzer. The morphology and surface structure of thin-film catalysts are viewed via SEM using the Nova Nano SEM microscope (NOVA FEI SEM-450 equipped with EDX detector). Surface and bulk compositional analysis are carried out via EDS and XPS techniques using a NOVA FEI SEM-450.
overpotential is calculated using eq S3. Tafel slopes are nullifying uncompensated resistance up to 50% using eq S2. All the electrochemical data, IR corrections are made manually. Concentration of OH⁻ increases from 0.25 to 5 M. For overpotential is calculated using eq S3. Tafel slopes are nullifying uncompensated resistance up to 50% using eq S2. All the electrochemical data, IR corrections are made manually. Concentration of OH⁻ increases from 0.25 to 5 M.

4.5. Electrochemical Investigations. All the electrochemical measurements such as CV, CCE, CPE, and electrochemical EIS are commenced employing a standard three-electrode configuration Pyrex glass cell covered with a Teflon cap on a computer-controlled potentiostat (PG-Stat10). The electrochemical cell and all glassware are well cleaned, following a previously described method. FTO coated with the Co-CNP-derived electrocatalyst is directly employed as the working electrode having an exposed area (1 cm²), a spiral-shaped platinum wire (thickness = 0.5 mm) as the counter electrode, and saturated silver/silver chloride electrode (SSCE = Ag/AgCl) and saturated calomel electrode (SCE) as the reference electrode. Before being placed into the electrochemical cell, platinum wire is cleaned by immersing in a 20% solution of nitric acid and rinsed many times with distilled water. All the potentials cited in this work are referenced to the reversible hydrogen electrode scale, according to Nernst eq S1. Considering the best catalytic performance of colloidal nanoparticle-derived catalysts under alkaline conditions, all the electrochemical data are collected in 0.1 M aq. KOH electrolyte solution having pH ≈ 13. Low concentration of KOH was intentionally used because of the fact that cobalt can be dissolved and leached out from the conductor surface during the catalytic process, as the concentration of OH⁻ increases from 0.25 to 5 M. For all the electrochemical data, IR corrections are made manually nullifying uncompensated resistance up to 50% using eq S2. Overpotential is calculated using eq S3. Tafel slopes are collected from the polarization curves measured at a low scan rate of 5 mV s⁻¹ (eq S4) and electrochemical impedance spectroscopy (details are given in the Supporting Information). Impedance spectroscopy is undertaken to evaluate solution resistance and charge transfer resistance at the electrode—electrolyte interphase within the frequency range from 0.1 Hz to 100 KHz. The ECSA is calculated by measuring double-layer capacitance (Cdl) of all Co-CNPs derived electrocatalysts in 0.1 M aq. KOH solution. Briefly, multiple CV scans at varying scan rates in the non-faradaic region were recorded. The plot of scan rate versus charging current is constructed. The slope of the above is equivalent to Cdl. ECSA is calculated by taking Cdl as a function of specific capacitance of the system (0.035 cm²) (further details are given in the Supporting Information). Widely used kinetic parameters such as MA and exchange current density (J°) are theoretically calculated using eqs S7 and S8. Electrochemical accessibility of Co-CNP-derived electrocatalysts is evaluated by integrating the area under the reduction peak of the polarization curve, assuming that the oxygen atom is chemisorbed on cobalt atoms. TOF is calculated following eq S9 at various applied potential values.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.9b03576.

Method for calculations of electrochemical parameters evaluating activity of the catalyst, deposition and brief catalytic comparison, and schematic illustrations of the preparation process along with SEM, EDS, Raman, ECSA, more electrocatalytic data, and post-catalysis experimental data. The material is complementary to the main work (PDF).

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Notes

The authors declare no competing financial interest.

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