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Interfacially Coupled and Synergistic Effect of Ag/Co₃O₄-C Nanocomposites for Enhanced Oxygen Reduction (ORR) and Evolution (OER) Reaction

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ABSTRACT

Overpotentials associated with the oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) remain key challenges hindering the practical deployment of advanced electrochemical energy conversion technologies such as alkaline fuel cells. While Pt/C demonstrates excellent ORR activity, its sluggish OER kinetics and poor durability in alkaline environments significantly limit its applicability. Herein, we report the design of an Ag/Co₃O₄-C nanocomposite, synthesized via a two-step approach involving hydrothermal growth of ultrafine Co₃O₄ nanoparticles having a particle size of 5 nm, followed by uniform deposition of Ag nanoparticles having a particle size of 20–30 nm. TEM/EDS shows Co₃O₄ nanoparticles (~5 nm) uniformly anchored on the carbon matrix with finely dispersed Ag (~28 nm), producing a homogeneous Ag–Co₃O₄ distribution. XPS indicates no substantial charge transfer, with performance arising from ensemble/heterointerface effects. The resulting hybrid exhibits superior ORR activity with an onset potential of 0.10 V vs. Hg/HgO and a half-wave potential of –0.186 V vs. Hg/HgO, while simultaneously delivering enhanced OER activity by reaching 10 mA cm^{–2} at a substantially lower overpotential compared to Ag/C and Co₃O₄-C. In addition, when integrated into Zn–air batteries, the Ag/Co₃O₄-C cathode demonstrates a high discharge capacity of 730 mAh g^{–1}, a peak power density of 67 mW cm^{–2}, and stable cycling for 200 cycles, validating its strong bifunctional electrocatalytic performance. The synergistic coupling of Ag and Co₃O₄ nanoparticles, anchored on a conductive carbon framework, enables efficient interfacial charge transfer and optimizes the adsorption of oxygenated intermediates, thereby accelerating reaction kinetics in alkaline media. Owing to these complementary features, the Ag/Co₃O₄-C catalyst demonstrates excellent bifunctional activity, highlighting its promise for next-generation oxygen electrocatalysis.

1 | Introduction

Rapid industrialization in the last couple of centuries, provided by a fossil fuel-based economy, has taken its toll on the environment.

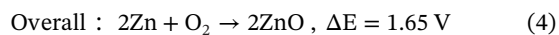
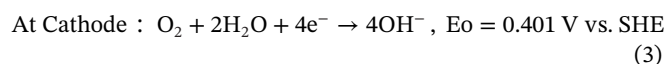
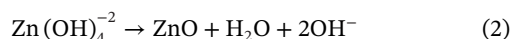
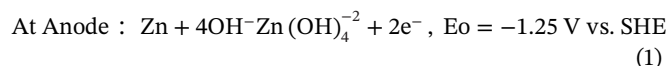
Researchers across the globe are looking for eco-friendly and sustainable sources of energy to meet the ever-rising demand for energy. Metal air battery technology is an attractive answer to this demand because of its theoretically high energy density and

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benign nature toward the environment [1, 2]. However, despite having the highest theoretical value of energy density, Li-air battery has enormous safety issues due to the high reactivity of lithium metal [3, 4]. Contrary to this, Zn-air metal battery has about three and a half times more energy density compared to the state-of-the-art Li-ion battery, along with the low cost, ease of fabrication, eco-friendliness, and use of stable and cheaper zinc compared to lithium metal [5, 6]. The secret behind the high energy density in these systems lies in the fact that, instead of packing oxygen inside the cell, a metal-air battery gets this from the outside air. Oxygen molecules can enter the cell through tiny holes in the cathode made of porous carbon or metallic foam. Water and other molecules already present in the pores of the electrode react with the oxygen on the surface of the electrocatalyst to produce hydroxyl ions [7]. These ions and other preexisting hydroxyls travel through a separator toward the metallic anode. In the case of the Zn-air system, these hydroxyls bond to zinc to form zincate, which then splits into two hydroxyls, a water molecule, and zinc oxide, and as a result, releases two electrons that travel through the external circuit to power the electronic devices.

The issues faced by the alkaline zinc air battery system include failure at i) anode due to dendrite growth or passivation, ii) electrolyte evaporation and carbonation, and iii) sluggish oxygen reduction and evolution reactions because of large overpotentials [8–11]. A great deal of contemporary research is directed toward surmounting these problems. While several solutions for addressing dendrite growth and electrolyte leakage have been proposed by using innovative cell design and membranes, the sluggish oxygen reduction and evolution reaction on the air electrode during discharge and charge cycles are a major issue faced by the zinc-air battery technology. The chemical reactions that take place during discharge in a Zn-air battery are:



During the recharge cycle, aforementioned reactions occur in reverse order with zinc deposition at the anode and oxygen evolution at the cathode.

Pt/C is widely used as the electrocatalyst as electrocatalyst for Zn-air battery systems. Commercial Pt/C is good for oxygen reduction reaction during discharge because of low overpotential for ORR along with positive values for half-wave potential and high value of limiting current density, albeit having a high cost, poor stability in alkaline media, and poor OER activity [12, 13]. Finding an active and stable Platinum Group Metal-free electrocatalyst with activity for both ORR and OER in alkaline media will be a turning point for the realization of Zn-air battery technology. The principal advantage of operating under alkaline conditions is the markedly improved reaction kinetics and substantially lower overpotentials observed for the ORR

[14, 15], potentially allowing the use of inexpensive, platinum free metal catalysts like silver and its alloys [16–19], doped carbons [20, 21], transition metal oxides, including spinel's and perovskites [19, 22, 23], and transition metal macromolecules like metal phthalocyanines [24–26] for the reduction reaction at the cathode. However, apart from transition metal oxides, not many of the aforementioned are active for OER as well. Also, most of the reported transition metal oxides have to be supported onto expensive hetero-atom-doped graphene to get any kind of useful bifunctionality [27–30]. The synthesis of this N-doped graphene starting from graphite powder is costly and labor-intensive, which is a serious drawback [31]. Hence, finding an active and stable bifunctional catalyst with low ORR and OER overpotential will be a major step forward in the realization of an alkaline Zn-air battery.

Silver supported on carbon is reported as a good ORR electrocatalyst with a similar reaction mechanism as Pt/C, marked with a 4e^- pathway and two distinct Tafel slopes [32]. Apart from this, Ag/C is cheaper and more stable in alkaline media compared to commercial Pt/C. However, Ag has poor OER activity. The relatively meager activity of silver can be improved by alloying or supporting on metal oxide support, albeit with a below-par OER activity [33, 34]. On the other hand, Co_3O_4 is an efficient OER/HER electrocatalyst but has poor ORR activity [35, 36]. For Co_3O_4 , the co-existence of Co^{+2} and Co^{+3} oxidation states within the spinel structure is reported spinel framework is reported to be crucial in governing the ORR process [37]. During OER in alkaline media ($\text{pH} = 12\text{--}13$) in the potential window of interest, i.e., $U = 1.2\text{--}1.7 \text{ V vs. RHE}$, $\beta\text{-CoOOH}$ is formed from Co_3O_4 according to the Pourbaix diagrams [38]. The (1014) facet with 1 monolayer of H_2O adsorbed is reported as the one with the lowest surface energy in this range of pH and potential. Also, the same facet is reported as most active for OER because of its lowest value of overpotential and formation of oxygen, limited by the formation of OOH^* . This was related to the higher density of Co^{+3} sites on the (1014) facet compared to the rest. Synergistic Ag/ Co_3O_4 nanoring's anchored on nitrogen-doped carbon nanosheets deliver exceptional ORR activity ($E_{1/2} \approx 0.85 \text{ V vs RHE}$, $84 \text{ mA mg}^{-1}(\text{Ag})$) and durability, offering a cost-effective alternative to state-of-the-art noble metal catalysts [39]. In this study, the electrocatalytic activity was primarily evaluated toward the oxygen reduction reaction (ORR), where the Ag/ Co_3O_4 /NCNS catalyst exhibited remarkable performance with a half-wave potential of $\approx 0.85 \text{ V vs RHE}$, high mass activity ($\approx 84 \text{ mA mg}^{-1}(\text{Ag})$), and excellent long-term durability. In contrast, pure Ag alone is known to display intrinsically poor ORR activity due to weak oxygen adsorption, higher overpotentials, and a tendency toward the less efficient two-electron pathway. Moreover, the limited number of active sites and susceptibility to agglomeration further restricts its standalone catalytic efficiency. The integration of Ag with Co_3O_4 nanoring's and nitrogen-doped carbon nanosheets effectively overcomes these limitations by creating abundant heterointerfaces, enhancing charge transfer, and stabilizing active sites, thereby achieving significantly improved ORR kinetics in alkaline media.

Incorporating nanoparticles of both Ag and Co_3O_4 onto a conductive support is a viable approach to achieve good bifunctionality. Luo et al. reported that the electrocatalytic behavior of a self-optimized Ag- Co_3O_4 catalyst was primarily evaluated for the

oxygen reduction and oxygen evolution reactions (ORR/OER) in Na-Ag/air batteries [40]. The catalyst demonstrated markedly enhanced ORR activity with reduced overpotentials and stable charge plateaus, enabling over 100 cycles with >90% energy efficiency, even at reduced Ag loading. In contrast, the OER process remained comparatively less efficient, contributing only ~50% of the total capacity. This weaker OER activity can be attributed to the inherently sluggish O—O bond formation kinetics, higher energy barriers, and the limited OER capability of silver-based surfaces, despite the synergistic improvements introduced by Co_3O_4 . To the best of our knowledge, bifunctional i.e., ORR and OER in alkaline media on Ag/ Co_3O_4 -C nanocomposite has not been previously reported.

Herein, we report Ag/ Co_3O_4 -C nanocomposite for the first time for both ORR and OER by using a simple two-step synthesis route. A synergistic effect was observed during both ORR and OER on the surface of the Ag/ Co_3O_4 -C nanocomposite. The Ag/ Co_3O_4 -C nanocomposites were reported to have a superior activity compared to Ag/C during ORR and better OER activity compared to Co_3O_4 /C during oxygen evolution. Moreover, a detailed structural analysis was done on the Ag/ Co_3O_4 -C nanocomposite to confirm the synthesis of nanosized Ag and Co_3O_4 on carbon support. The Ag/ Co_3O_4 -C nanocomposite was systematically investigated to elucidate its bifunctional catalytic performance toward ORR and OER in alkaline media.

2 | Experimental Section

2.1 | Chemicals

Silver nitrate (AgNO_3 , >99.8%), cobalt (II) acetate tetrahydrate ($\text{Co}(\text{CH}_3\text{COO})_4 \cdot 4\text{H}_2\text{O}$, > 99.5%) and potassium hydroxide (KOH) from Guangdong chemicals, trisodium citrate dihydrate ($\text{C}_6\text{H}_5\text{Na}_3\text{O}_7 \cdot 2\text{H}_2\text{O}$, 99%), sodium borohydride (NaBH_4 , $\geq 98\%$), Ammonia solution (25%–27%), Zinc acetate dihydrate ($(\text{CH}_3\text{COO})_2\text{Zn} \cdot 2\text{H}_2\text{O}$, >99%) and Zinc strips (Zn, 99.99%) from Tianjin Fuchen, Platinum on carbon (Pt/C, 20%), Nafion ionomer solution (5%), and carbon fiber paper (HCP 120) from Johnson Matthey fuel cells, Ethanol ($\text{C}_2\text{H}_5\text{OH}$, >99.7%) from Tianjin Fuyu chemicals, Vulcan XC-72 from Cabot corporation. Ni foams with a purity of 99.8% (pore per inch: 120, density: $370 \text{ g}\cdot\text{m}^{-2}$, average pore size: $500 \mu\text{m}$, thickness: 1 mm) were purchased from Lizhiyuan Battery Material Co., Ltd. Electrolyte solutions were prepared with deionized water.

2.2 | Catalyst Synthesis

Cobalt oxide (Co_3O_4) nanoparticles were synthesized by a hydrothermal technique described by Dong et al. [41]. Briefly, 20 mM of $\text{Co}(\text{CH}_3\text{COO})_4 \cdot 4\text{H}_2\text{O}$ and 33 mg of Vulcan XC-72 were both mixed with 25 mL of ethanol separately. The mixture of carbon was put for sonication for 15 mins. Both mixtures were added and further stirred for 10 min. To this, 2.5 mL of ammonia solution was added, and the mixture was vigorously stirred for 10 min. The slurry was then transferred to a 100 mL Teflon-lined autoclave and put on for 3 h at 150°C . The resulting solid was repeatedly washed and purified by centrifugation using ethanol as the solvent. Later, the Co_3O_4 on carbon was collected by

freeze drying, as shown in Figure S7. Silver was then deposited onto these particles by the citrate protect method [42]. For the preparation of 5 wt.% Ag on Co_3O_4 , 18.5 mL of 10 mM AgNO_3 and 18.5 mL of 50 mM sodium citrate solution were mixed, and to this, 25 mL of 7.4 mM NaBH_4 was added dropwise under vigorous stirring to obtain a brownish-yellow Ag colloid. 380 mg of Co_3O_4 /C was added to this mixture, and stirring was continued for 12 hrs. Finally, Ag/ Co_3O_4 -C were collected by centrifugation and washed several times with deionized water. The Ag/ Co_3O_4 -C nanocomposite powder was later dried for 12 h at 80°C under vacuum, as depicted in Figure 1.

2.3 | Structural and Morphological Characterization

X-ray diffraction (XRD) and high-resolution transmission electron microscopy (HRTEM) analyses were employed to verify the crystalline structure and morphology of the synthesized materials. The surface morphology and elemental composition were further characterized using transmission electron microscopy (TEM, FEI Tecnai F30, operated at 200 kV) coupled with energy-dispersive X-ray spectroscopy (EDS). X-ray photoelectron spectroscopy (XPS) measurements were carried out on an ULTRA ESCALAB 250 system equipped with an Al $K\alpha$ radiation source ($h\nu = 1486.6 \text{ eV}$) under an ultrahigh vacuum of approximately 10^{-9} mbar. High-resolution spectra of O1s, Co2p, and Ag3d were recorded without the need for charge compensation. The binding energy scale E_b was calibrated with respect to the Fermi level E_c of a gold reference plate.

2.4 | Electrochemical Characterization

All electrochemical evaluations were conducted using a conventional three-electrode configuration. A Hg/HgO electrode (0.1 M KOH, 0.098 V vs. SHE) served as the reference electrode, while a platinum wire functioned as the counter electrode. The working electrode was prepared by drop-casting catalyst ink onto a rotating glassy carbon electrode (GCE, 5 mm diameter). Electrochemical measurements were performed on a CHI660C workstation to assess the catalytic performance of the synthesized materials. Cyclic voltammetry (CV) analyses were carried out in both N_2 and O_2 -saturated 0.1 M KOH electrolytes, whereas rotating disk electrode (RDE) polarization curves were recorded in O_2 -saturated 0.1 M KOH at room temperature. The potential window ranged from 0 to -0.8 V vs. Hg/HgO, with a scan rate of $10 \text{ mV}\cdot\text{s}^{-1}$ and rotation speeds of 400, 900, 1600, 2500, and 3200 rpm. Prior to each measurement, N_2 and O_2 gas was purged through the electrolyte for at least 15 min to ensure complete saturation. The catalyst ink for CV and linear sweep voltammetry (LSV) was prepared by dispersing 4 mg of catalyst in 1 mL of ethanol containing 10 μL of 5 wt.% Nafion solution, followed by 30 min of ultrasonication to achieve a homogeneous suspension. Subsequently, 5 μL of the resulting ink was drop-cast onto the GCE surface and air-dried, yielding a catalyst loading of approximately $0.1 \text{ mg}\cdot\text{cm}^{-2}$. All recorded potentials were corrected for iR drop to ensure accurate electrochemical interpretation.

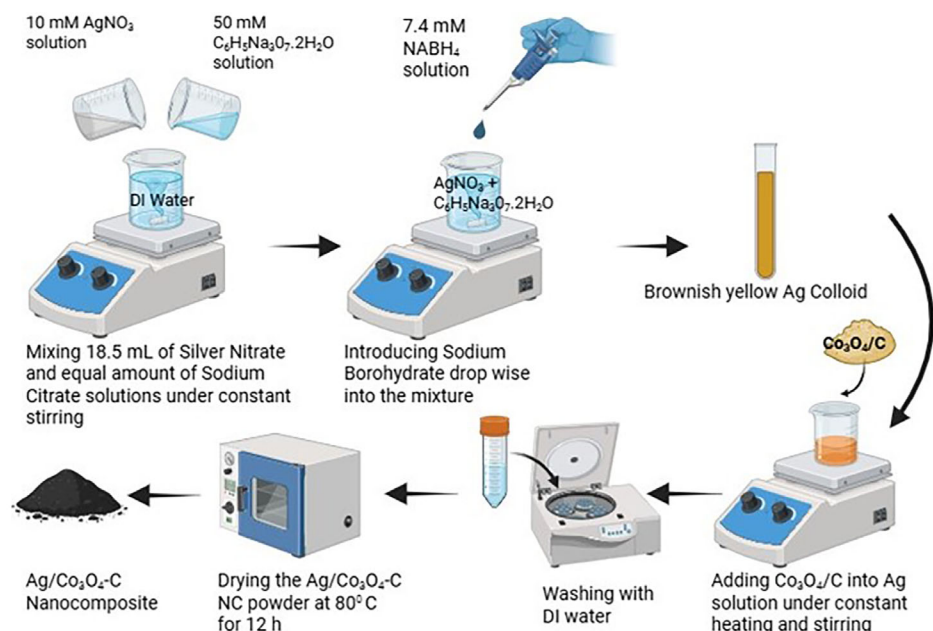


FIGURE 1 | Schematic illustration of the synthesis of Ag/Co₃O₄-C nanocomposite.

TABLE 1 | Summary of lattice parameters of Co₃O₄ and Ag Nanoparticles.

	Co ₃ O ₄	Ag
Lattice parameter, a (Å)	8.0850	4.0857
c (Å)	8.0850	4.0857
c/a (Å)	1	1
FWHM	0.4286	0.4345
Dislocation density (nm ⁻²)	0.04	0.0012
Crystallite size (nm)	5	28

For the fabrication of primary and secondary Zn–air batteries, the catalyst ink was prepared by dispersing 4 mg of catalyst powder (Ag/Co₃O₄-C or Pt/C) along with 2 mg of Vulcan XC-72 carbon in a mixture containing 1 mL of ethanol and 40 µL of 5 wt.% Nafion solution. The resulting suspension was ultrasonicated for 30 min to ensure uniform dispersion. Subsequently, the prepared ink was drop-cast onto a hydrophobic carbon paper substrate, achieving an approximate catalyst loading of 1.6 mg. cm⁻². The coated carbon paper was then dried at 70°C for 30 min and assembled with a zinc foil anode using 6 M KOH electrolyte to construct the Zn–air battery.

3 | Results and Discussions

3.1 | Physical Characterization

Figure 2 and Table 1 provide a comprehensive structural analysis of the spinel cobalt oxide Co₃O₄ and Ag Nanoparticles. The X-ray diffraction pattern of the Ag/Co₃O₄-C nanocomposite confirms the presence of both pure Ag and Co₃O₄, as shown in Figure 2. The peaks at 31.3°, 36.8°, 44.8°, 59.3° and 65.2° correspond to spinel cobalt oxide according to JCPDS card # 43–1003. On the other hand, the peaks at 38.1°, 44.2°, 64.4° and 77.4° agree with the metallic Ag as per JCPDS card # 04–0783.

It is important to note that the lattice parameters listed in Table 1 correspond to the standard bulk values taken from the JCPDS reference cards for Co₃O₄ (43–1003) and Ag (04–0783). These bulk parameters were used solely to index and confirm the crystalline phases present in the nanocomposite.

Because the nanoparticles exhibit significant peak broadening and partial overlap of Ag (111)/(200) and Co₃O₄ (220)/(311) reflections, reliable Rietveld refinement of lattice parameters for nanosized Ag (~28 nm) and Co₃O₄ (~5 nm) was not possible.

Therefore, only crystallite size, FWHM, and defect-related metrics were extracted from Scherrer analysis, whereas the listed lattice parameters should be interpreted as reference values rather than refined nanoparticle lattice constants.

In supplementary data, Figure S1a,b show the XRD patterns for the Co₃O₄/C and Ag/C. The crystallite size for Co₃O₄ and Ag NPs was estimated from the Scherrer Equation (5) to be approximately 5 and 28 nm, respectively, which is also in agreement with the TEM data, as shown in Figure 3.

$$D = k\lambda/\beta\cos\theta \quad (5)$$

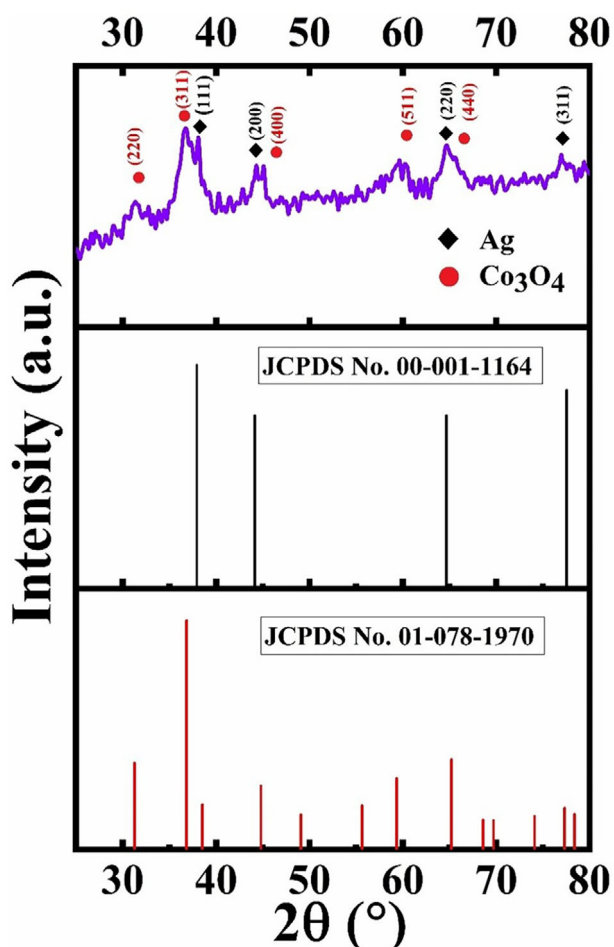


FIGURE 2 | Represents the XRD pattern of Ag- Co_3O_4 composite showing characteristic peaks of spinel Co_3O_4 and metallic Ag. The coexistence of both phases provides abundant active sites, enhanced conductivity, and defect-assisted pathways that collectively accelerate ORR/OER kinetics.

The absence of CoO , $\text{CoO}(\text{OH})$, and $\text{Co}(\text{OH})_2$ in XRD data confirms the successful transformation of cobalt precursor into Co_3O_4 , which does not need any further heat treatment. This is because of the correct volumetric ratio of precursor slurry to total volume available, i.e., ~50%. A higher ratio of slurry to available volume leads to the formation of secondary oxides and hydroxides of cobalt during hydrothermal treatment [43].

X-ray diffraction (XRD) analysis confirmed the formation of crystalline Ag nanoparticles and spinel-type Co_3O_4 with well-defined cubic symmetry. The Ag phase, indexed to the face-centered cubic (fcc) structure (space group Fm-3m), exhibited a refined lattice parameter of $a = c = 4.0857 \text{ \AA}$ with a c/a ratio of unity, consistent with the intrinsic isotropic nature of the cubic lattice. The narrow full-width at half maximum (FWHM = 0.4345) reflects the high crystallinity and uniformity of the Ag nanoparticles, which play a critical role in providing efficient active sites for the oxygen reduction reaction (ORR). The dislocation density of Ag was calculated by using the relation.

$$\rho = \frac{1}{D^2} \quad (6)$$

where ρ represents dislocation density, and D is the crystallite size.

The dislocation density of Ag using the relation explained in Equation (6) was found to be $1.2 \times 10^{-3} \text{ nm}^{-2}$, suggesting a relatively low density of crystallographic defects that favor enhanced electron mobility and catalytic durability.

Similarly, Co_3O_4 crystallized in the cubic spinel structure (space group Fd-3m) with a lattice constant of $a = c = 8.0850 \text{ \AA}$ and a c/a ratio of unity, confirming the absence of tetragonal distortion. The sharp diffraction peaks (FWHM = 0.4286) indicate excellent crystallinity, which is essential for facilitating charge transport and ensuring structural stability during redox cycling. The dislocation density of Co_3O_4 was determined to be $4.0 \times 10^{-2} \text{ nm}^{-2}$, significantly higher than that of Ag, which implies the presence of abundant defect sites. Such defect states are advantageous for catalytic processes, as they provide additional adsorption sites for oxygenated intermediates and promote faster charge transfer during the OER.

The TEM micrographs in Figure 3a,b clearly demonstrate the homogeneous distribution of Ag and Co_3O_4 nanoparticles over the Vulcan carbon matrix. The Co_3O_4 nanoparticles, with an average diameter of 5 nm, are firmly anchored onto the carbon support, forming a stable hybrid nanostructure with an average diameter of 50 nm. Such intimate nanoparticle support interactions are widely recognized to improve the electrochemical stability and electronic conductivity of carbon-supported oxides, as reported in recent studies [44]. The subsequent Ag deposition occurs in a finely dispersed manner across the Co_3O_4 /carbon interface (Figure 3b), which is crucial for maximizing the number of electrochemically accessible active sites and enhancing catalytic turnover. Uniform dispersion of Ag has previously been correlated with superior oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) activity due to synergistic metal oxide support interactions.

HRTEM analysis further reveals the structural features at the atomic scale. Figure 3c shows a relatively larger Ag nanoparticle with ellipsoidal morphology, surrounded by several ultrasmall spherical Co_3O_4 nanoparticles. Such a spatial configuration suggests the formation of nanoscale heterojunctions, which can significantly facilitate interfacial charge transfer, as also highlighted in hybrid noble metal-oxide systems reported in the recent literature [46]. The inverse fast Fourier transform (IFFT) analysis of the Ag nanoparticle confirms that the observed lattice spacing of 0.234 nm corresponds to the (111) crystallographic plane of face-centered cubic Ag (inset Figure 3c). This plane is well-documented as the most catalytically active facet for Ag in ORR, due to its optimal adsorption energy for oxygenated intermediates [47].

In addition, the HRTEM image in Figure 3d displays distinct lattice fringes with interplanar spacings of 0.285 and 0.244 nm, assignable to the (220) and (311) planes of Co_3O_4 , respectively. The coexistence of these crystalline domains at close proximity provides direct evidence of strong interfacial coupling between Ag and Co_3O_4 nanoparticles on the conductive carbon framework. Such structural coupling has been shown to improve electronic conductivity, reduce charge-transfer resistance, and

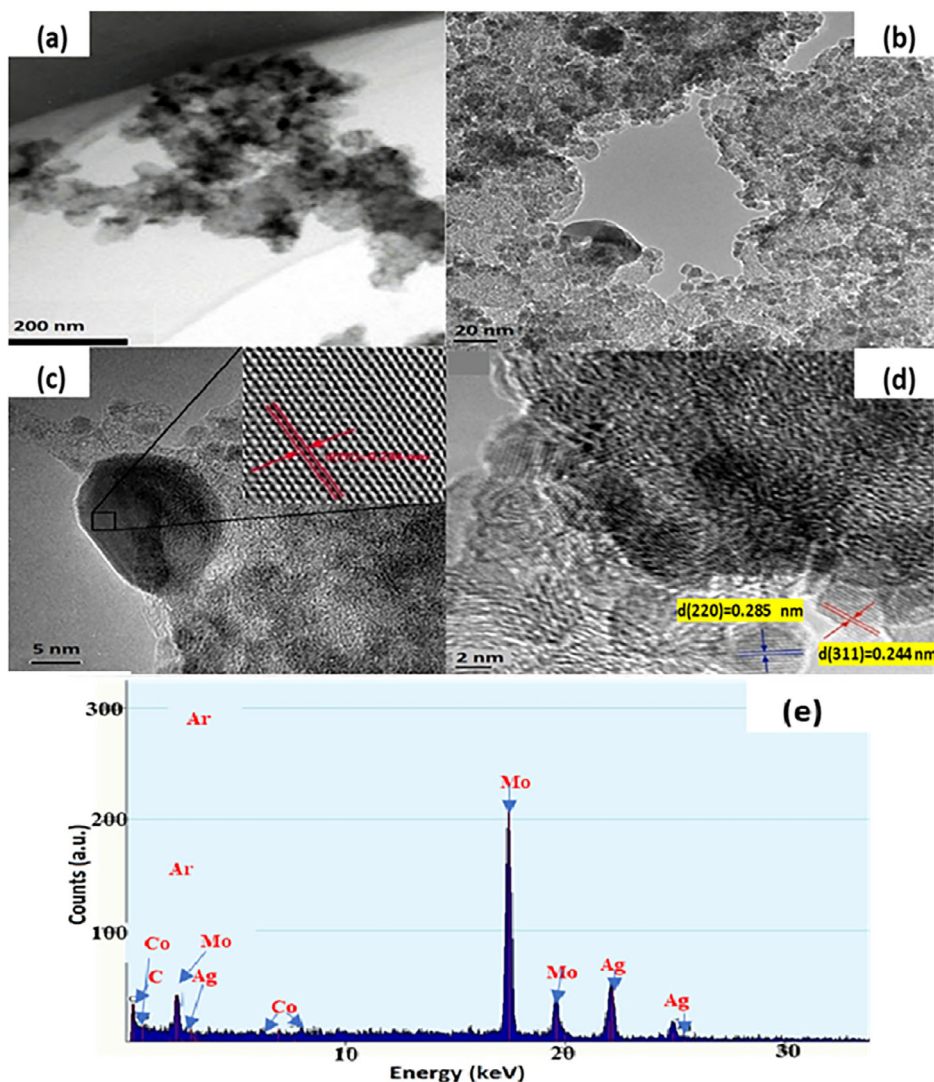


FIGURE 3 | (a–d) TEM images and (e) EDS mapping of Ag- Co_3O_4 composite. EDS elemental mapping further validates the homogeneous distribution of Co, O, and Ag, ensuring efficient electron transport and abundant active sites.

promote bifunctional electrocatalytic activity [48]. Furthermore, the hierarchical distribution of small Co_3O_4 nanoparticles around Ag generates abundant metal-oxide contact sites, which may serve as preferential centers for enhanced oxygen adsorption and accelerated electron-ion transport during electrochemical reactions. Although some variation in Ag nanoparticle size is visible in Figure 3, this arises from the intrinsic polydispersity of citrate-reduced Ag nanoparticles rather than from secondary agglomeration during composite formation. The individually resolved lattice fringes in the HRTEM images and the uniform elemental distribution in the EDS maps support the conclusion that the Ag domains remain well dispersed across the carbon matrix. The crystallite size derived from XRD (≈ 28 nm) further confirms the presence of isolated Ag nanoparticles rather than fused aggregates.

The TEM and HRTEM analyses confirm the successful fabrication of a ternary Ag/ Co_3O_4 -C nanohybrid with uniform nanoparticle dispersion, strong anchoring onto the carbon support, and well-defined lattice ordering. These structural attributes are expected to endow the catalyst with enhanced stability and

catalytic activity through maximized electrochemically active surface area, accelerated charge transfer across heterointerfaces, and synergistic effects between Ag, Co_3O_4 , and carbon. Such nanoscale structural engineering strategies are increasingly recognized as key to designing next-generation, cost-effective, and high-performance electrocatalysts for sustainable energy conversion technologies [49].

The elemental composition of the synthesized Ag/ Co_3O_4 -C nanohybrid was further confirmed by Energy-Dispersive X-ray Spectroscopy (EDX), as shown in Figure 3e. The strong signals of C arise from the conductive carbon matrix, while the well-resolved peaks of Co and O confirm the presence of crystalline Co_3O_4 . The characteristic peaks of Ag at ~ 3 keV and higher energy regions provide direct evidence of metallic silver deposition. Such clear identification of multiple constituent elements corroborates the TEM/HRTEM findings and supports the uniform distribution of nanoparticles observed earlier.

In addition, minor peaks corresponding to Mo and Au are observed, which can be ascribed to the molybdenum TEM

grid and gold coating occasionally used to minimize charging effects during sample preparation. These extraneous signals are commonly encountered in EDX analyses and do not interfere with the interpretation of the main elemental composition [50]. The quantitative analysis derived from the EDX spectrum reveals the relative abundance of Ag and Co within the hybrid structure, further confirming the targeted stoichiometry. Importantly, the simultaneous detection of Ag and Co in close association with the carbon backbone indicates the formation of a ternary nanohybrid system, which is essential for synergistic electrocatalytic activity. Previous studies have emphasized that the coexistence of noble metals (e.g., Ag, Pd, Ni) with transition metal oxides (e.g., Co_3O_4) anchored on conductive supports promotes interfacial charge transfer and optimizes adsorption energies of oxygenated intermediates, thereby boosting oxygen reduction and evolution [51]. Furthermore, the absence of extraneous elemental peaks (other than grid/coating signals) highlights the high purity of the synthesized hybrid nanostructure, a feature that directly correlates with improved catalytic performance and long-term electrochemical durability [52].

The EDX results not only confirm the successful synthesis of $\text{Ag}/\text{Co}_3\text{O}_4$ nanoparticles uniformly dispersed on the carbon support but also reinforce the structural insights obtained from TEM and HRTEM analyses. The combination of phase purity, appropriate stoichiometry, and homogeneous distribution of active elements is expected to underpin the excellent electrocatalytic activity of the hybrid material for energy conversion applications. Also, the UV-vis absorbance spectrum of the silver colloid shows an absorbance peak at nearly 390 nm, further endorsing the formation of Ag nanoparticles (Figure S3) [53]. Figure 3d is an HRTEM of Co_3O_4 nanoparticles decorated on the carbon support. The lattice fringes mentioned in the HRTEM correspond to the (311) and (220) planes with a d-spacing of 0.285 and 0.244 nm, respectively. The size of Co_3O_4 nanoparticles is dependent on the solvent used for hydrothermal synthesis [54]. Using only ethanol as a solvent for cobalt salt, very fine Co_3O_4 nanoparticles supported on Vulcan carbon were obtained. The smaller particle size provides a larger surface area, which renders a higher density mixed valence of $\text{Co}^{+2}/\text{Co}^{+3}$ on the surface, which plays a vital role for catalytic activity in spinel Co_3O_4 NPs [55].

XPS survey scan confirms the presence of Ag, Co, O, and C in the sample without contamination from impurities (Figure 4a). Figure 4d shows the high-resolution spectrum of Co 2p, where $2p_{1/2}$ and $2p_{3/2}$ can be readily identified. The Co $2p_{1/2}$ (795.92 eV) and Co $2p_{3/2}$ (780.12 eV) show a characteristic peak difference of ~ 16 eV [56]. Moreover, the flatness and weakness of the satellite peaks in XPS spectra are in agreement with the formation of pure spinel phase in which the divalent and trivalent cations of cobalt occupy tetrahedral and octahedral sites, respectively [57].

The surface chemical states and interfacial electronic structure of the $\text{Ag}/\text{Co}_3\text{O}_4$ -C catalyst were elucidated by X-ray photoelectron spectroscopy (XPS) to unravel its superior bifunctional electrocatalytic behavior in rechargeable Zn-air batteries. The survey spectrum (Figure 4a) confirms the coexistence of Ag, Co, O, and C, verifying the successful integration of metallic Ag into the Co_3O_4 -carbon matrix. In the Ag 3d region (Figure 4b), two well-defined peaks at 368.06 and 374.03 eV, corresponding to

Ag $3d_{5/2}$ and Ag $3d_{3/2}$, respectively, are characteristic of metallic Ag^0 , indicating that Ag nanoparticles retain their zero-valent state without oxidation. The Co 2p spectrum of pristine Co_3O_4 -C (Figure 4c) exhibits main peaks at 780.23 and 795.71 eV for Co $2p_{3/2}$ and Co $2p_{1/2}$, accompanied by intense satellite peaks, confirming the coexistence of Co^{2+} and Co^{3+} species intrinsic to the spinel Co_3O_4 structure. After Ag incorporation, Co $2p_{3/2}$ and $2p_{1/2}$ peaks exhibit very small shifts (≤ 0.1 eV). These minor variations reflect subtle changes in surface coordination at the Ag- Co_3O_4 interface rather than a measurable or chemically significant electron transfer between the two phases. The overall XPS profiles therefore, indicate interfacial interaction without substantial charge redistribution [58, 59]. The modulated electronic environment enhances the intrinsic conductivity and accelerates the oxygen reduction and evolution reactions (ORR and OER), ultimately contributing to the superior round-trip efficiency and durability of the $\text{Ag}/\text{Co}_3\text{O}_4$ -C based Zn-air battery [60].

3.2 | Electrochemical Characterization

Detailed cyclic voltammetry was done on the surface of all the samples prepared in both N_2 and O_2 -saturated 0.1 M KOH (Figure 5). Prior to the recording of data, successive readings were taken till a stable profile was obtained. Figure 5a presents the CV curves for the Ag/C catalyst. In the N_2 saturated 0.1 M KOH, a single reduction peak is observed. This cathodic peak is related to the transformation of silver oxide to metallic silver. The anodic peak is ascribed to the oxidation of silver in 0.1 M KOH at potentials higher than 0.23 V vs. Hg/HgO [61]. On the other hand, a second reduction peak is observed for CV in an O_2 -saturated electrolyte. This second reduction peak is ascribed to the reduction of molecular oxygen on the surface of Ag/C to OH^- . Similarly, only cobalt redox couples are observed in the CV of $\text{Co}_3\text{O}_4/\text{C}$ in N_2 -saturated electrolyte as shown in Figure 5b. The first redox couple corresponds to $\text{Co}^{+2}/\text{Co}^{+3}$ transition, while the other, at higher potentials, is ascribed to $\text{Co}^{+3}/\text{Co}^{+4}$ transition [62, 63]. A reduction peak owing to ORR is observed at -0.25 V vs. Hg/HgO in the case of in O_2 -saturated 0.1 M KOH. For the case of $\text{Ag}/\text{Co}_3\text{O}_4$ -C, there is an overlap among anodic faradaic peaks (Figure 5c). A distinct large reduction peak owing to ORR is observed for $\text{Ag}/\text{Co}_3\text{O}_4$ -C at -0.145 V vs. Hg/HgO . Finally, a comparison of CVs in O_2 -saturated 0.1 M KOH is provided in Figure 5d. The reduction peak of silver oxide to metallic silver shifts to a more negative potential, which shows the stronger chemisorption of oxygenated species onto the surface of $\text{Ag}/\text{Co}_3\text{O}_4$ -C compared to Ag/C . Also, a positive shift in the reduction peak for the molecular oxygen confirms the better ORR activity of the $\text{Ag}/\text{Co}_3\text{O}_4$ -C nanocomposite.

Figure 6 reveals the LSV and corresponding data for the electrocatalysts in 0.1 M KOH. It is evident from the ORR plots that a distinct improvement in oxygen reduction activity is observed in terms of onset ' E_o ', half wave ' $E_{1/2}$ ', and limiting current ' j_L ' density for $\text{Ag}/\text{Co}_3\text{O}_4$ -C compared to both Co_3O_4 -C and Ag/C . $\text{Ag}/\text{Co}_3\text{O}_4$ -C has an onset potential of 0.1 V, half-wave potential of -0.186 V vs. Hg/HgO , respectively, compared to 0.2 and 2.03 V vs. Hg/HgO , for Pt/C . The $\text{Ag}/\text{Co}_3\text{O}_4$ -C demonstrated a higher activity toward oxygen reduction compared to Pt/C at potentials higher than 0.36 V vs. Hg/HgO . Apart from a substantial improvement in ORR activity in the case of $\text{Ag}/\text{Co}_3\text{O}_4$ -C compared to Co_3O_4 -

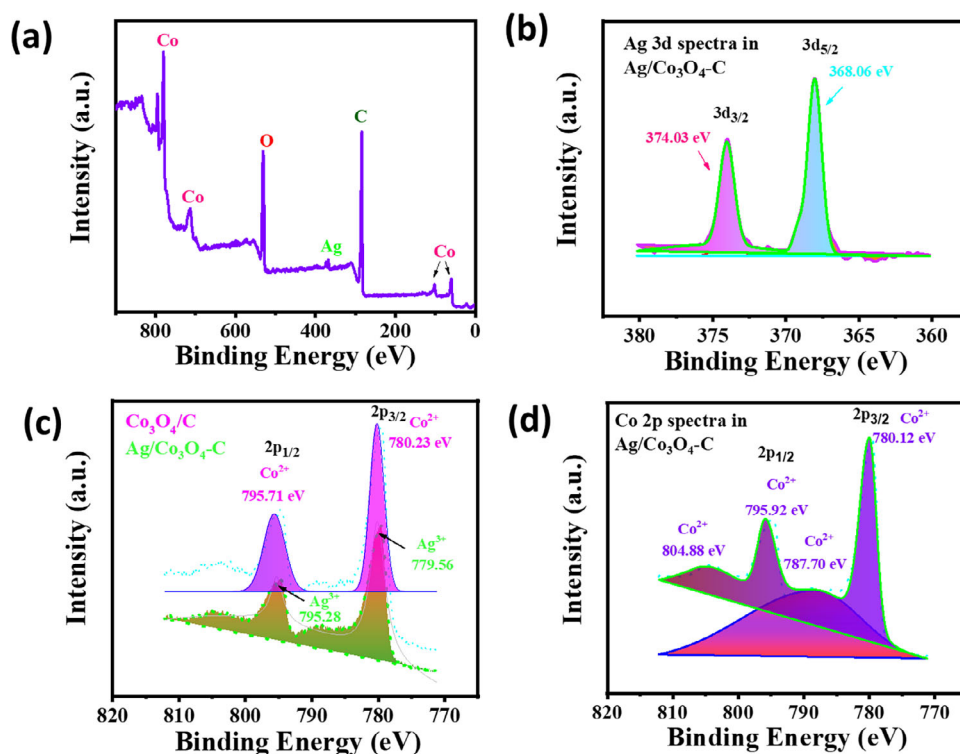


FIGURE 4 | Displays XPS spectra of Ag- Co_3O_4 composite. The Co 2p region reveals the coexistence of Co^{2+} and Co^{3+} oxidation states, characteristic of the spinel structure, while the Ag 3d signals confirm the presence of metallic Ag. The O 1s spectrum indicates both lattice oxygen and surface oxygen vacancies, highlighting defect states that facilitate oxygen adsorption and enhance charge transfer. These electronic features collectively underscore the strong metal–oxide interaction and the crucial role of defects in promoting efficient ORR/OER activity.

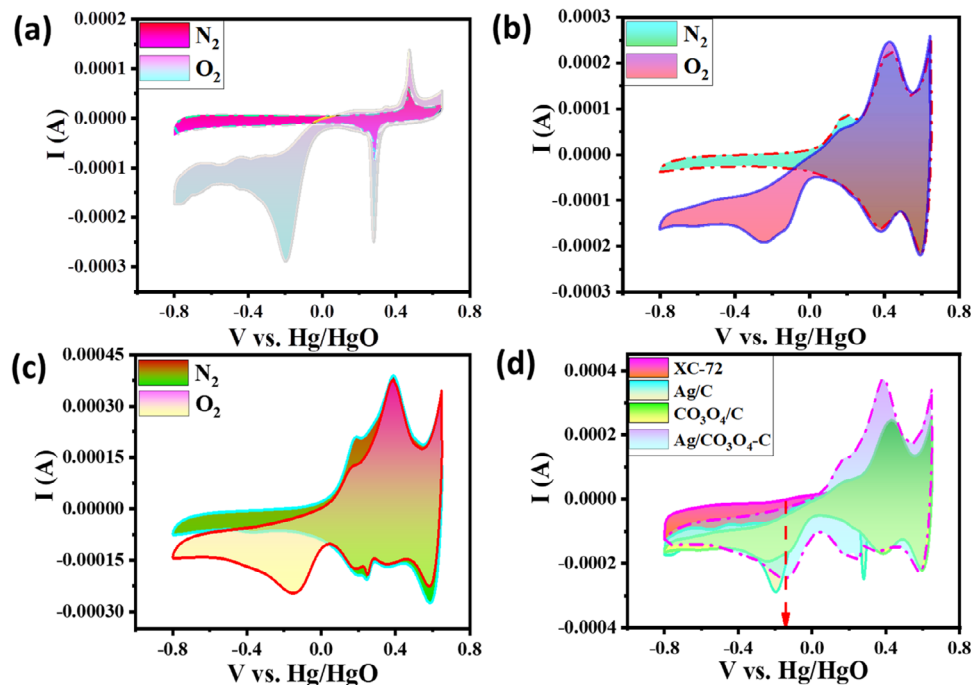


FIGURE 5 | Depicts Cyclic voltammetry (CV) curves of different electrocatalysts. (a) XC-72 displays negligible electrochemical activity, serving as the baseline carbon support, (b) Ag/C exhibits improved current response, reflecting the intrinsic catalytic contribution of silver, (c) $\text{Co}_3\text{O}_4\text{-C}$ shows characteristic redox transitions, demonstrating the active role of cobalt oxide in electron transfer, and (d) Ag/ $\text{Co}_3\text{O}_4\text{-C}$ delivers the highest current density and lowest overpotential, evidencing the synergistic interplay of Ag and Co_3O_4 for superior electrocatalytic kinetics.

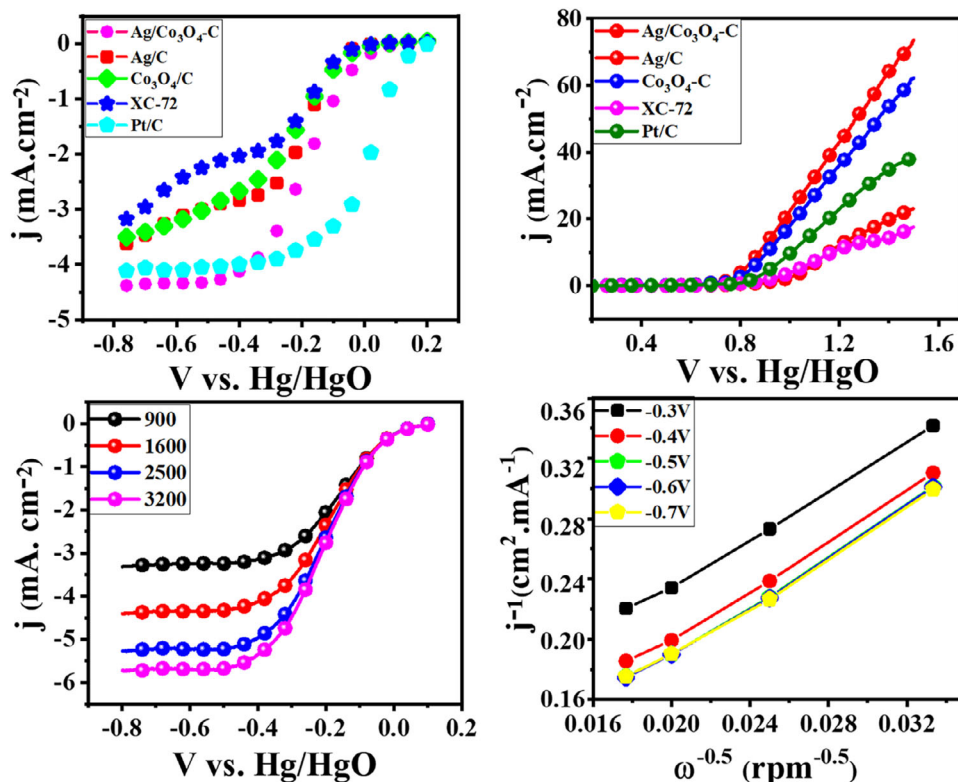


FIGURE 6 | Shows Linear sweep voltammetry (LSV) curves of XC-72, Ag/C, Co₃O₄-C, and Ag/Co₃O₄-C electrodes compared with Pt/C for ORR and OER. (a) XC-72 exhibits negligible ORR and OER activity, confirming its role only as a conductive baseline, (b) Ag/C shows improved onset potential and current density, indicating the catalytic contribution of metallic Ag toward oxygen electrocatalysis, (c) Co₃O₄-2C presents enhanced bifunctional activity with distinct potential shifts, reflecting the redox activity of cobalt oxide centers in both ORR and OER, and (d) Ag/Co₃O₄-C achieves the lowest overpotential and highest current response, demonstrating the synergistic effect of Ag and Co₃O₄ that optimizes electron transfer and affords superior bifunctional catalytic performance, rivaling Pt/C.

C and Ag/C, a discernible superior OER catalytic activity was also observed for the Ag/Co₃O₄-C nanocomposite (Figure 6b). The improved bifunctional performance of Ag/Co₃O₄-C arises from synergistic interactions at the Ag-Co₃O₄ heterointerfaces rather than from direct charge transfer, as confirmed by XPS. Ag nanoparticles provide highly active Ag (111) sites for rapid 4e⁻ ORR pathways, while the defect-rich ~5 nm Co₃O₄ particles offer abundant Co²⁺/Co³⁺ redox centers essential for OER. Their close spatial proximity enables cooperative adsorption and activation of oxygen intermediates (O₂, OH*, OOH*), effectively lowering reaction barriers. In addition, Ag significantly enhances the conductivity of the composite, reducing charge-transfer resistance during OER. The combined effects of optimized oxygen adsorption, abundant defect sites, and improved electron transport account for the superior ORR/OER activity observed for the Ag/Co₃O₄-C catalyst. The Ag/Co₃O₄-C nanocomposite reaches the OER current density of 10 mA.cm⁻² 'j₁₀' at a lower overpotential compared to Co₃O₄-C, Ag/C, and Pt/C, which is an important figure of merit for devices involving ORR and OER [64]. The ΔE measured at ORR current of 3 mA.cm⁻² and OER current of 10 mA.cm⁻² was found to be 1.12 V for Ag/Co₃O₄-C, which is only 70 mV higher than the ΔE measured for Pt/C, i.e., 1.05 V.

To further investigate the ORR pathway on the surface of Ag/Co₃O₄-C electrocatalyst, Koutecky Levich analysis was performed on the system by performing LSV at different rotations

and estimating the number of electron transfer from the slope of KL plots at different potentials (Figure 6c,d). The curves are described by the famous Koutecky Levich equation [65]. The selectivity of the 4e⁻ or 2e⁻ pathway is estimated via the Koutecky Levich equation.

$$1/j = 1/j_k + 1/j_L \quad (7)$$

where j_k is the kinetic current density, and j_L is the diffusion limiting current density.

Also

$$j_k = nFkC_o \quad (8)$$

And

$$j_L = 0.2nFC_oD_o^{2/3}\nu^{-1/6}\omega^{1/2} \quad (9)$$

In this context, ω denotes the angular rotation rate (rpm), n represents the number of electrons transferred, F is the Faraday constant (96,485 C.mol⁻¹), C_o refers to the bulk concentration of dissolved O₂ (1.15 × 10⁻³ mol.L⁻¹), D_o is the diffusion coefficient of O₂ in the electrolyte (1.9 × 10⁻⁵ cm².s⁻¹), ν corresponds to the kinematic viscosity of the electrolyte (1.1 × 10⁻² cm².s⁻¹), and k signifies the electron transfer rate constant. The calculated electron transfer number (n) for the Ag/Co₃O₄-C electrocatalyst

was found to lie in the range of 3.4–3.7 within the potential window of -0.2 to -0.6 V vs. Hg/HgO (Figure 6d; Figure S4), indicating a predominant four-electron reduction pathway for molecular oxygen. The Koutecky–Levich (K–L) analysis performed on commercial Pt/C further confirmed the occurrence of a $4e^-$ oxygen reduction process (Figure S5). The linear and nearly parallel K–L plots obtained for Ag/Co₃O₄-C reveal first-order reaction kinetics with respect to the concentration of dissolved O₂ [66, 67]. The near-four value of n suggests that peroxide formation during the oxygen reduction reaction (ORR) on Ag/Co₃O₄-C is minimal. This low peroxide yield is advantageous, as excessive peroxide generation typically diminishes the overall catalytic efficiency and stability of the ORR process.

On the other hand, n values of 2.4 and 2.9 for the Ag/C and Co₃O₄/C, respectively, confirm the formation of a larger fraction of peroxide during ORR on these catalysts. The Koutecky Levich plots and the corresponding data confirm the synergistic effect achieved from the ensemble of Ag and Co₃O₄ nanoparticles deposited onto Vulcan XC-72. The ORR parameters, such as onset potential ' E_o ', half-wave potential ' $E_{1/2}$ ', limiting current ' j_L ' density, and electron transfer number for individual Ag or Co₃O₄ deposited onto XC-72 have meager value, but by bringing the Ag and Co₃O₄ NPs in close proximity on conductive carbon support, we found a pronounced improvement in these parameters. It is important to emphasize that the observed synergy is not due to a simple macroscopic mixture of Ag/C and Co₃O₄/C, but to their nanoscale co-location and cooperative action on the same carbon framework. The Ag/Co₃O₄-C nanocomposite displays higher ORR/OER activity and a more favorable ORR electron-transfer number than either Ag/C or Co₃O₄/C alone, indicating that a mere physical combination of the two components is insufficient to explain the performance. TEM confirms that Ag and Co₃O₄ nanoparticles are intimately co-decorated on Vulcan carbon, creating short transport paths and a shared reaction microenvironment. XPS, in turn, shows only minor binding-energy shifts, consistent with slight interfacial electronic modulation but no substantial net charge transfer between Ag and Co₃O₄. Taken together, these results suggest that the synergistic effect mainly arises from cooperative ensemble behavior at Ag–Co₃O₄ heterointerfaces, where Ag enhances conductivity and facilitates the initial ORR steps, while Co₃O₄ offers defect-rich Co²⁺/Co³⁺ redox sites for OER and intermediate transformation—rather than from strong charge transfer or a strain-dominated mechanism.

The Tafel plots of Ag/Co₃O₄-C and commercial Pt/C electrocatalyst were made after making the mass transport correction. Ag/Co₃O₄-C was observed to have a similar plot shape to Pt/C, marked by two distinct slope regimes. The Tafel slope of $-2.3RT/F$ (approximately -60 mV.dec⁻¹) observed in the low overpotential region is consistent with the Temkin adsorption isotherm, indicative of intermediate oxide coverage resulting from ORR intermediates. At higher overpotentials, the Tafel slope increases to $-2 \times 2.3RT/F$ (approximately -120 mV.dec⁻¹), where adsorption behavior aligns with the Langmuir isotherm, reflecting the diminished oxide coverage at these potentials [68, 69]. The close resemblance of the Tafel profiles to those of Pt/C suggests that the ORR on Ag/Co₃O₄-C proceeds via a comparable reaction pathway. This correlation further implies that the initial

electron transfer step serves as the rate-determining step in the Ag/Co₃O₄-C catalytic system, analogous to the mechanism observed for Pt/C [46, 70].

Beyond the geometric ensemble effects described earlier, an additional contributor to the enhanced activity is the complementary functional role of each component within the composite. Ag provides electronically accessible surface sites with a low barrier for O₂ dissociation and rapid electron delivery during ORR, while Co₃O₄ offers a dynamic Co²⁺/Co³⁺ redox couple known to facilitate oxygen intermediate formation during OER. When positioned in close proximity on a conductive carbon scaffold, these two functions operate in a coordinated manner: Ag accelerates the initial electron-transfer steps, whereas Co₃O₄ mediates the subsequent chemical transformations of oxygenated species. This division of catalytic labor enables the composite to bypass the limitations of each material when used alone.

Furthermore, the nanoscale architecture of the composite promotes short diffusion pathways for reactants and intermediates, ensuring that the Ag and Co₃O₄ domains interact within the same local reaction environment. This spatial coupling allows oxygen species generated or adsorbed on Ag to be transferred rapidly to Co₃O₄ sites and vice versa without requiring direct electronic charge transfer between the two phases. Such proximity-based cooperation is well documented in heterogeneous bifunctional catalysts and is consistent with the XPS observation of minimal electronic perturbation.

Taken together, the enhanced ORR/OER behavior arises from the coordinated action of Ag-assisted electron injection, Co₃O₄-mediated oxygen intermediate handling, and short-range diffusion and shared reaction environments created by the composite architecture. These coupled yet independent processes provide a plausible and experimentally supported explanation for the observed synergy in the absence of strong Ag–Co charge transfer.

3.3 | Electrochemical Performance

Based on the good ORR and superior OER activity of Ag/Co₃O₄-C electrocatalyst, we investigated the electrochemical performance of the catalyst in both primary and secondary Zn-air batteries. The tests were done in homemade cells working under ambient atmosphere. The primary battery showed an open circuit voltage (OCV) of 1.52 and 1.48 V for Pt/C and Ag/Co₃O₄-C, respectively. (Figure 7a) The OCV values are in good agreement with the published data on Pt/C [71, 72]. The peak power density was found to be 67 mW.cm⁻² for Ag/Co₃O₄-C compared to 87 mW.cm⁻² for the case of Pt/C. The peak power density is acceptable, keeping in mind the fact that the cells are working under ambient air and not pure O₂. Higher peak power densities have been reported for primary Zn-air cells, albeit using complex cell designs and employing pure O₂ rather than natural atmosphere [73]. Moreover, the primary cells were tested for long-time discharge trend, and they were observed to have stable discharge voltage of 1.2 and 1.1 V for Pt/C and Ag/Co₃O₄-C, respectively, at a discharge current density of 20 mA.cm⁻². (Figure S6) A minimal potential drop was observed during this long-term galvanostatic discharge

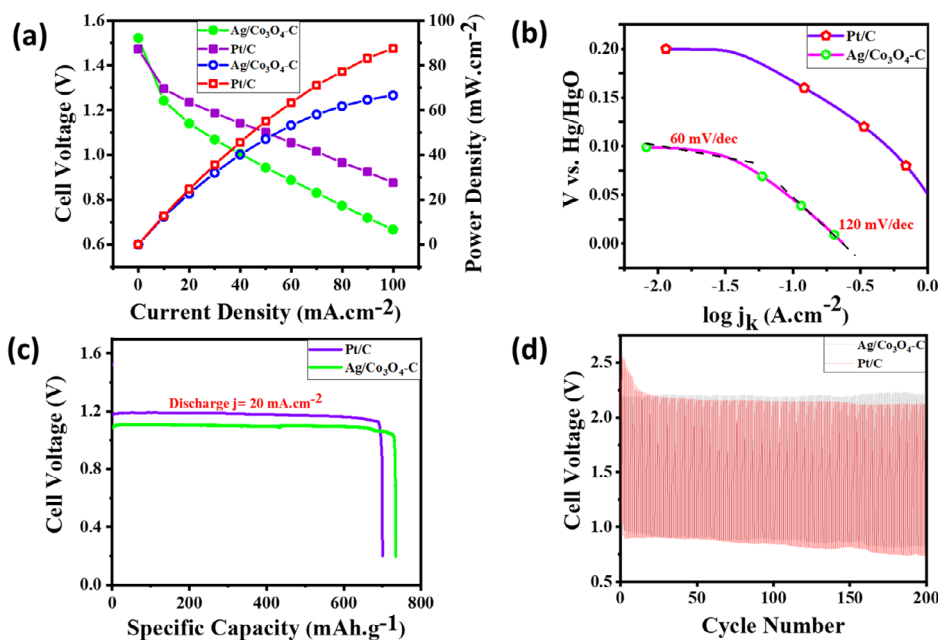


FIGURE 7 | Electrochemical performance of rechargeable Zn-air batteries using Ag/Co₃O₄-C and Pt/C cathodes: (a) polarization and corresponding power density curves of Zn-air batteries, (b) the Tafel slope comparison of Ag/Co₃O₄-C and Pt/C catalysts, Pt/C exhibits a low Tafel slope, confirming its benchmark kinetics for oxygen electrocatalysis, and Ag/Co₃O₄-C shows a comparable and only slightly higher Tafel slope, demonstrating efficient charge-transfer kinetics and highlighting its potential as a cost-effective alternative to Pt/C for bifunctional oxygen reactions (c) specific capacity plots of Zn-air batteries at 20 mA cm⁻², and (d) long-term cycling stability of Zn-air batteries under repeated charge-discharge cycles.

test. The primary Zn-air cell was observed to have a high discharge capacity of 730 mAh.g⁻¹. (Figure 7c) Finally, the charge discharge performance of the Ag/Co₃O₄-C nanocomposite was evaluated as well in a secondary Zn-air cell (Figure 7d).

The charge-discharge profile was obtained by cycling in a 30-min period with 15 min of charge and 15 min of discharge. The Ag/Co₃O₄-C derived cell was observed to have a stable charge discharge profile throughout the 200 cycles. Pt/C was found to fluctuate in the first few cycles, and later the profile became stable. The initial aberrance can be ascribed to the surface reorganization under cycling because of the use of Vulcan XC-72 in ink formulation. The round-trip efficiency was found to be 41% during the first 50 cycles for Ag/Co₃O₄-C nanocomposites, whereas it was 40% for the commercial Pt/C. After 100 cycles, this value was observed to be 40% for Ag/Co₃O₄-C and 38% for Pt/C, showing a stable charge-discharge performance over the first 100 cycles. Finally, during the next 100 cycles, the charge discharge gap was observed to increase for both Ag/Co₃O₄-C and Pt/C. For Ag/Co₃O₄-C, the charge discharge voltage gap increases from 1.29 to 1.39 V, revealing a 100 mV increase for Ag/Co₃O₄-C. A similar increase in C–D potential gap was observed for the case of Pt/C.

Although direct post-cycling structural characterization (e.g., TEM or XPS) was not carried out in this study, the electrochemical data provide strong indirect evidence of catalyst stability. The Ag/Co₃O₄-C cathode exhibits only a modest increase (~100 mV) in charge–discharge voltage gap after 200 cycles, and the round-trip efficiency remains essentially unchanged during the first 100 cycles. Such stable cycling behavior consists of minimal degradation of the Ag and Co₃O₄ domains and the preservation

of their interfacial catalytic environment. Similar stability trends have been reported for Ag- and Co₃O₄-based catalysts, where structural robustness is reflected in sustained electrochemical activity. Nonetheless, we acknowledge that post-OER microscopic and spectroscopic analysis would further strengthen this conclusion, and we plan to pursue such studies in future work to provide direct evidence of the catalyst's long-term structural integrity.

Additionally, we note that conventional i–t stability testing and methanol tolerance measurements were not conducted in this study, as these protocols are primarily relevant for fuel-cell cathodes and methanol-containing systems rather than for rechargeable Zn-air batteries. In alkaline Zn-air configurations, methanol crossover is not encountered, and the most informative stability indicators are cycling durability and discharge retention, both of which are already presented in this work. The long-term cycling behavior therefore, serves as the appropriate durability assessment for the intended device architecture. Although further electrochemical stress tests could provide additional insights, they fall outside the scope of the present Zn-air-focused investigation. The possibility of Ag dissolution or partial transformation of Co₃O₄ into CoOOH during cycling was also considered. Although direct post-operando characterization was not carried out, the stable ORR/OER performance and modest 200-cycle voltage-gap increase indicate that substantial phase degradation is unlikely. Pronounced Ag leaching or complete CoOOH formation typically leads to rapid loss of activity, which was not observed here. Future work will include post-cycling TEM and XPS studies to directly assess any structural or chemical evolution. Table 2 shows the comparison of bifunctional electrocatalysts and their composites for ORR/OER in alkaline media.

TABLE 2 | Comparison of Bifunctional Electrocatalysts and Their Composites for ORR/OER in Alkaline Media.

#	Catalyst (Ref)	ΔE (V)	Electrolyte	ORR	Development route	Prototype Zn-air battery?	Reference
1	Ag/Co ₃ O ₄ -C (This work) -	1.12	0.1 M KOH	3.4–3.7	Hydrothermal Co ₃ O ₄ on carbon; citrate reduction of Ag (Facile, Scalable)	Yes (rechargeable Zn-air)	This Work
2	Ag/Co ₃ O ₄	Not reported	1 M KOH	~3.9	Combustion synthesis	No (fundamental study)	[74]
3	Ag@CoCO ₃ (Gui et al., 2021)	~0.9–1.1 (range reported)	0.1 M KOH	~3.6–3.9	Silver decorated cobalt carbonate via wet-chem methods	Yes	[75]
4	Co-N ₄ /NC	~0.79 (E _{1/2} ORR basis)	0.1 M KOH	~3.9–4.0	Ultrasonic plasma / pyrolysis to create Co-N ₄ single-site catalysts	Yes	[76]
5	MnO _x /CNT-400	0.92 (E _{1/2} ORR basis)	0.1 M KOH	3.6	Redox on CNT	No	[77]
6	Y and Fe co-doped LaNiO ₃ perovskite	1.15	1.0 M KOH	3.53	A-site Y and B-site Fe co-doped La _{0.85} Y _{0.15} Bi _{0.7} Fe _{0.3} O ₃	Yes	[78]
7	PtNi/Mn ₂ O ₃ -NiO spinel, anatase	1.03	0.1 M KOH	3.99	Chemical Precursors calcined at High Temperatures	No	[79]
8	Pt/Mn ₂ O ₃ -TiO ₂ , spinel, anatase	1.22	0.1 M KOH	4	Chemical Precursors calcined at High Temperatures	No	[79]
9	Mesoporous Ni/NiO Nanosheets	1.07	0.1 M KOH	3.8	Hydrothermal	Yes	[80]
10	MOF/ Pervoskite composite	~0.9–1.2	0.1 M KOH	—	Complex (Sol-Gel & Calcination)	Yes	[81]
11	NiCoO ₂	0.92	0.1 M KOH	3.86	Solution Combustion	No	[82]
12	Pt/C	1.07	0.1 M KOH	~4	ORR Benchmark	—	[83]
13	Ir/C	~1	0.1 M KOH	2-2.5	OER Benchmark	—	[84, 85]

Note: ΔE measured at ORR current of 3 mA.cm⁻² and OER current of 10 mA.cm⁻²

4 | Conclusions

Improved electrocatalytic activity toward both ORR and OER in alkaline media is reported by supporting Ag NPs onto Co₃O₄ decorated carbon support. Ag/Co₃O₄-C electrocatalyst was observed to be the most active in terms of highest activity at lower overpotential among Ag/C, Co₃O₄-C, and Ag/Co₃O₄-C. Though the ORR activity of Ag/Co₃O₄-C was lower than the commercial Pt/C, the OER activity in alkaline solution was observed to be much higher than Pt/C. XPS analysis indicates that while slight interfacial electronic modulation occurs upon Ag deposition, no substantial or chemically meaningful charge transfer takes place. This confirms that enhanced catalytic behavior arises primarily from nanoscale heterointerface effects rather than from net electron transfer between Ag and Co₃O₄. Primary Zn-air battery made from Ag/Co₃O₄-C cathode showed a high discharge capacity of 730 mA.g⁻¹ with stable discharge voltage of 1.1 V at a discharge current of 20 mA.cm⁻². The secondary Zn-air battery showed better round-trip efficiency compared to the commercial

Pt/C owing to the superior OER activity of Ag/Co₃O₄-C compared to the commercial Pt/C.

Author Contributions

A.Q., M.S., F.C., and M.Z.K. conceptualized the study. A.Q., M.S., A.S., J.H.K., K.K., I.S., and M.T.M. were characterized and analyzed. A.Q., M.S., A.S., J.H.K., K.K., I.S., and M.T.M. did the writing and characterizations. A.Q. and F.C. carried out the measurement. A.Q. and F.C. conducted the electrochemical experiment. A.Q., M.S., A.S., J.H.K., K.K., I.S., and M.T.M. commented on the manuscript. All the authors discussed the results and contributed to the manuscript preparation.

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Conflicts of Interest

The authors declare no conflicts of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

References

1. S. Mitra, S. Ray, and D. K. Maiti, "Green Nanotechnology for Harnessing Energy," *Green Nanotechnology Applications for Ecosystem Sustainability* (Springer, 2025): 307–331.
2. D. Gupta and Z. Guo, "Aqueous Rechargeable Zn–Air Batteries for Sustainable Energy Storage," *Carbon Neutralization* 4 (2025): 70023.
3. X. Bi, Y. Jiang, R. Chen, et al., "Rechargeable Zinc–Air Versus Lithium–Air Battery: From Fundamental Promises Toward Technological Potentials," *Advanced Energy Materials* 14 (2024): 2302388.
4. T. Wang, T. Yang, D. Luo, M. Fowler, A. Yu, and Z. Chen, "High-Energy-Density Solid-State Metal–Air Batteries: Progress, Challenges, and Perspectives," *Small* 20 (2024): 2309306.
5. C. Zhao, Y. Xin, F. Zhang, B. He, Y. Yang, and H. Tian, "Electrodeposition Chemistry Toward High-Safety and High-Energy-Density Rechargeable Multivalent Ion Batteries," *Advanced Functional Materials* 35 (2025): 2501894.
6. L. Tang, H. Peng, J. Kang, et al., "Zn-Based Batteries for Sustainable Energy Storage: Strategies and Mechanisms," *Chemical Society Reviews* 53 (2024): 4877–4925.
7. M. A. Alemu, M. Z. Getie, and A. K. Worku, "Advancement of Electrically Rechargeable Multivalent Metal-air Batteries for Future Mobility," *Ionics* 29 (2023): 3421–3435.
8. H. Zhao, L. Wang, and M. Dargusch, "Mechanisms of Anode Interfacial Phenomena and Multi-Perspective Optimization in Aqueous Alkaline Zinc–Air Batteries," *Advanced Functional Materials* 35 (2025): 2510263.
9. H. Wang, L. Kang, K. Wang, et al., "Failure Mechanisms and Strategies Toward Flexible Zinc–Air Batteries," *Advanced Functional Materials* 34 (2024): 2407347.
10. S. Li, Z. Liu, X. Wei, H. Wu, H. Mei, and J. Liu, "Advanced Strategies for Suppressing the Self-Corrosion of the Anode in Al–Air Batteries," *Metals* 15 (2025): 760.
11. K. Bogomolov and Y. Ein-Eli, "Alkaline Ni–Zn Rechargeable Batteries for Sustainable Energy Storage: Battery Components, Deterioration Mechanisms, and Impact of Additives," *Chemsuschem* 17 (2024): 202300940.
12. T. Gu, et al., "High-Entropy Electrocatalytic Materials in Zn–Air Batteries: From Fundamentals to Applications," *Advanced Materials* 38 (2025): 12274.
13. A. K. Pradhan, S. Halder, and C. Chakraborty, "Less is More": Carbon Nanostructure-Tailored Low Platinum Containing Electrocatalysts for Improved Zinc–Air Battery Efficiency," *Journal of Energy Storage* 98 (2024): 113008.
14. Q. Ding, Q. Zhang, M. Chen, B. Li, D. Cai, and W. Wu, "Bifunctional Oxygen Evolution Reaction and Oxygen Reduction Reaction Catalysts Prepared by High Gravity-hydrothermal Method for Rechargeable Zinc Air Batteries," *Journal of Power Sources* 653 (2025): 237764.
15. F. Liu, et al., "Metal-Organic Framework Materials as Bifunctional Electrocatalyst for Rechargeable Zn–Air Batteries," *Batteries & Supercaps* 7 (2024): 202400402.
16. G. Montserrat-Siso and B. Wickman, "Tuning the Activity of Silver Alloys for the Oxygen Reduction Reaction in Alkaline Media," *ACS Applied Energy Materials* 6 (2023): 6428–6442.
17. S. Mondal, S. S. Deshpande, S. K. De, et al., "Dynamic Strain-Engineered Au–Ag Alloy Nano-Seed Network for Enhanced Electrochemical Oxygen Reduction and High-Performance Alkaline Membrane H₂ Air Fuel Cells," *Small* 21 (2025): 2500555.
18. J. Milikić, et al., "Facile Synthesis of Low-cost Copper-silver and Cobalt-silver Alloy Nanoparticles on Reduced Graphene Oxide as Efficient Electrocatalysts for Oxygen Reduction Reaction in Alkaline media," *Nanomaterials* 12 (2022): 2657.
19. A. Han and G. Liu, "Recent Advances in Metal-based Electrocatalysts: From Fundamentals and Structural Regulations to Applications in Anion-exchange Membrane Fuel Cells," *Materials Chemistry Frontiers* 8 (2024): 903–929.
20. Y. Irmawati, B. Prakoso, F. Balqis, et al., "Advances and Perspective of Noble-Metal-Free Nitrogen-Doped Carbon for pH-Universal Oxygen Reduction Reaction Catalysts," *Energy & Fuels* 37 (2023): 4858–4877.
21. M. A. Alemu, A. A. Assegie, M. Ilbas, R. Al Afif, and M. Z. Getie, "Biomass-Derived Metal-Free Nanostructured Carbon Electrocatalysts for High-Performance Rechargeable Zinc–Air Batteries," *Advanced Energy and Sustainability Research* 6 (2025): 2400414.
22. S. Ingavale, M. Gopalakrishnan, C. M. Enoch, et al., "Strategic Design and Insights Into Lanthanum and Strontium Perovskite Oxides for Oxygen Reduction and Oxygen Evolution Reactions," *Small* 20 (2024): 2308443.
23. K. Lakshmanan, P. Govindasamy, P. Govindasami, S. Marappan, and L. Jintae, "Facile Synthesis of Perovskite-type CeCuO₃ Nanoparticles as a Robust Bifunctional Electrocatalyst for Highly Stable Overall Water-splitting," *Journal of Alloys and Compounds* 1014 (2025): 178635.
24. Y.-C. Feng, X. Wang, and D. Wang, "Metal Porphyrins and Metal Phthalocyanines as Designable Molecular Model Electrocatalysts," *Materials Chemistry Frontiers* 8 (2024): 228–247.
25. S. Gaddimath, S. Aralekallu, K. Prabhu CP, et al., "Developments in Cobalt-based Soft Materials as Electrocatalysts for Oxygen Evolution Reaction," *International Journal of Hydrogen Energy* 110 (2024): 181–207.
26. J. Liu, J. Yang, Y. Dou, X. Liu, S. Chen, and D. Wang, "Deactivation Mechanism and Mitigation Strategies of Single-Atom Site Electrocatalysts," *Advanced Materials* 37 (2025): 2420383.
27. A. De, M. S. Kim, A. Adhikari, R. Patel, and S. Kundu, "Sol-gel-Derived Nanostructured Electrocatalysts for Oxygen Evolution Reaction: A Review," *Journal of Materials Chemistry A* 12 (2024): 19720–19756.
28. S. Wang, M. Zhang, X. Mu, S. Liu, D. Wang, and Z. Dai, "Atomically Dispersed Multi-Site Catalysts: Bifunctional Oxygen Electrocatalysts Boost Flexible Zinc–Air Battery Performance," *Energy & Environmental Science* 17 (2024): 4847–4870.
29. G. Dhakal, S. Sahoo, K. P. Sharma, and G.-L. Zhao, "A Review on the Recent Advancements of Ni-Based Sulfides and Mixed Sulfides for Supercapacitors and Electrocatalysis (Oxygen Evolution Reaction)," *Molecules (Basel, Switzerland)* 30 (2025): 2877.
30. P. Saha, M. Z. Islam, S. S. Shah, et al., "Harnessing the Power of Marine Biomass-Derived Carbon for Electrochemical Energy Storage," *Battery Energy* 4 (2025): 20240055.
31. U. Cortes, "A Review on Pulsed Laser-Based Synthesis of Carbon and Graphene Quantum Dots in Liquids: From Fundamentals, Chemistry to Bio Applications and Beyond," *The Journal of Physical Chemistry C* 129 (2025): 10378–10414.
32. A. Yatheendran, A. M. Narayanan, J. S. Babu, R. Rajan, and N. Sandhyarani, "Synergistic Effect of Ag-Doped Mn₃O₄ and AgCl Composite as a Regenerable and High-Performance Catalyst for the Oxygen Reduction Reaction," *Journal of Materials Chemistry A* 12 (2024): 24318–24327.
33. I. E. P. Pech and A. G. García, "Core-Shell Catalysts for Oxygen Reduction Reaction in Acidic Medium," in *Nano-Electrocatalyst for Oxygen Reduction Reaction* (CRC Press, 2024): 215–246.
34. J. Qiu, et al., "Activating the Microsized Cubic Co₃O₄ With Doping Y₂O₃ Phase Inlaid on the Plasma-Treated Soft Carbon Fiber for a

- Robust Electrocatalytic Alkalized-Seawater Splitting,” *Advanced Functional Materials* 35 (2025): 2508158.
35. R. Liu, G. Chen, Y. Guo, et al., “Designing Persimmon-liked FeOOH-(CrCo)Ox on the Plasma-treated Cobalt Foam for a Highly Efficient Oxygen Evolution in an Alkaline-seawater Electrolyte,” *Chemical Engineering Journal* 500 (2024): 157098.
 36. H. Zeng, Y. Guo, T. Li, et al., “Plasma Engineering Defect for Constructing High-Density Ru Single Atoms and RuCo Alloy Nanoparticles Synergistic Catalytic System to Achieve Efficient Hydrogen Evolution,” *Chemical Engineering Journal* 524 (2025): 169094.
 37. N. Bhuvanendran, M. G. Choi, D. Kim, and S. Y. Lee, “Improved Trifunctional Electrocatalytic Performance of Integrated Co₃O₄ Spinel Oxide Morphologies With Abundant Oxygen Vacancies for Oxygen Reduction and Water-splitting Reactions,” *Journal of Alloys and Compounds* 935 (2023): 168079.
 38. R. Ding, B. Y. Xia, and B. You, “Cobalt-Based Noble-Metal-Free Electrocatalysts for Acidic Oxygen Evolution Reaction Toward Practical Proton Exchange Membrane Water Electrolysis,” *Chemcatchem* 17 (2025): 202401653.
 39. F. Nasim, H. Malik, G. Xu, H. Dong, and M. A. Nadeem, “Exploring the Heterointerface of Silver Nanoparticles and Cobalt Oxide Nanorings Toward the Oxygen Reduction Reaction,” *Journal of Materials Chemistry A* 13 (2025): 23981–23997.
 40. Y. Luo, X. Zhan, F. Cui, et al., “Ultra-Stable and Efficient All-Solid-State Sodium-air Hybrid Batteries With Catalyst via Ag-Co₃O₄ Electrochemical Interface Reconstruction,” *Chemical Engineering Journal* 522 (2025): 168142.
 41. D. Yuming, et al., “A facile route to controlled synthesis of Co₃O₄ nanoparticles and their environmental catalytic properties,” *Nanotechnology* 18 (2007): 435602.
 42. J. Zeng, et al., “Preparation of Carbon-Supported Core–Shell Au–Pt Nanoparticles for Methanol Oxidation Reaction: The Promotional Effect of the Au Core,” *The Journal of Physical Chemistry B*, 110 (2006): 24606–24611.
 43. S. Neha, L. Vergeynst, and P. Biller, “Evaluating Hydrothermal Liquefaction Hydrochar From Sewage Sludge as a Phosphorus Resource Through Struvite Production,” *Journal of Environmental Chemical Engineering* 12 (2024): 113014.
 44. Z. U. Khan, J. Jiang, and M. Atif, “Nanostructured Bimetallic Oxide/Graphene Nanocomposites for Next-Generation High-Performance Energy Storage,” *International Journal of Environmental Research* 19 (2025): 223.
 45. M. Zhang, J. Wang, and Y. Gong, “Atomically Dispersed Silver Atoms Incorporated in Spinel Cobalt Oxide (Co₃O₄) for Boosting Oxygen Evolution Reaction,” *Journal of Colloid and Interface Science* 659 (2024): 203–212.
 46. Y. Wang, L. Miao, R. Shi, M. Lu, and P. Wang, “Unraveling the Synergistic Effect of Hollow Sea Urchin-Like Ag–Co₃O₄ Heterostructures in Electrochemical Dehydrogenation Reactions: Interface-Enhanced Electron Transfer and Desorption Process,” *ACS Catalysis* 15 (2025): 7966–7978.
 47. M. A. Alam, S. I. Sadia, M. K. H. Shishir, et al., “Crystallinity Integration and Crystal Growth Behavior Study of Preferred Oriented (111) Cubic Silver Nanocrystal,” *Inorganic Chemistry Communications* 173 (2025): 113834.
 48. S. Yang, J. Gu, B. Dai, and L. Zhang, “A Critical Review of the Synthesis and Applications of Spinel-Derived Catalysts to Bio-Oil Upgrading,” *Chemsuschem* 18 (2025): 202401115.
 49. X. Cui, M. Wu, X. Liu, et al., “Engineering Organic Polymers as Emerging Sustainable Materials for Powerful Electrocatalysts,” *Chemical Society Reviews* 53 (2024): 1447–1494.
 50. G. A. De Oliveira, D. E. Sanchez, A. J. Sredenschek, et al., “Insight Into Mo₂C Nanoplates Growth by Means of Scanning Electrochemical Cell Microscopy for High-Resolution Electrocatalytic Hydrogen Evolution Activity Mapping,” *Small Science* 5 (2025): 2500220.
 51. S. Riaz, M. Ahmad, G. Tasam, et al., “Bimetallic Nickel-Cobalt Selenides Nanoparticles Supported on Flexible Carbon Nanotubes Fibers as Efficient Bifunctional OER and ORR Electrocatalysts,” *Diamond and Related Materials* 158 (2025): 112642.
 52. A. Kumar, et al., “Tailored Yb@ SrMoO₄/MoS₂ Hybrid Nanostructures: Application in High-Performance Asymmetric Supercapacitors,” *Topics in Catalysis* (2025): 1–15.
 53. R. S. Bhat, A. M. Al-Dbass, A. I. A. Khayyat, and S. Al-Daihan, “Utilizing Biomolecule-rich Citrus Fruit Waste as a Medium for the Eco-friendly Preparation of Silver Nanoparticles With Antimicrobial Properties,” *Inorganics* 12 (2024): 180.
 54. D. Yuming, et al., “A Facile Route to Controlled Synthesis of Co₃O₄ Nanoparticles and Their Environmental Catalytic Properties,” *Nanotechnology* 18 (2007): 435602.
 55. P. Saha, S. Shaheen Shah, M. Ali, M. Nasiruzzaman Shaikh, M. A. Aziz, and A. J. Saleh Ahammad, “Cobalt Oxide-Based Electrocatalysts With Bifunctionality for High-Performing Rechargeable Zinc-Air Batteries,” *The Chemical Record* 24 (2024): 202300216.
 56. M. Huo, Y. Liang, W. Liu, et al., “Synergistically Promoting Oxygen Electrocatalysis Through the Precise Integration of Atomically-Dispersed Fe Sites and Co Nanoparticles,” *Advanced Energy Materials*(2024): 2405155.
 57. J. Li, “Oxygen Vacancies in Spinel,” *Composite Materials - Science and Engineering* (IntechOpen, 2025).
 58. T. K. N. Nguyen, F. Grasset, S. Ishii, H. Fudouzi, and T. Uchikoshi, “Tunable Slow Photon Effect and Local Surface Plasmon in Ag-immobilized TiO₂ Inverse Opal Films for Enhancing Pollutant Photodegradation,” *Materials Advances* 5 (2024): 8615–8628.
 59. X. Liu, T. Yasuoka, G. T. Dang, L. Liu, and T. Kawaharamura, “The Effects of Oxygen Flow Ratio on the Properties of Ag X O Thin Films Grown by Radio Frequency Magnetron Sputtering,” *RSC Advances* 14 (2024): 23215–23224.
 60. S. Wolf, M. Roschger, B. Genorio, et al., “Ag-MnxOy on Graphene Oxide Derivatives as Oxygen Reduction Reaction Catalyst in Alkaline Direct Ethanol Fuel Cells,” *Catalysts* 12 (2022): 780.
 61. K. Kawashima, R. A. Márquez, Y. J. Son, et al., “Accurate Potentials of Hg/HgO Electrodes: Practical Parameters for Reporting Alkaline Water Electrolysis Overpotentials,” *Acs Catalysis* 13 (2023): 1893–1898.
 62. X.-L. Li, J. Bao, Z. Shadike, et al., “Stabilizing Transition Metal Vacancy Induced Oxygen Redox by Co²⁺/Co³⁺ Redox and Sodium-Site Doping for Layered Cathode Materials,” *Angewandte Chemie International Edition* 60 (2021): 22026–22034.
 63. S. Roy, P. Dahiya, T. K. Mandal, and S. Roy, “The Role of Reducibility Vis-à-vis Oxygen Vacancies of Doped Co₃O₄/CeO₂ in the Oxygen Evolution Reaction,” *Dalton Transactions* 53 (2024): 5484–5494.
 64. A. A. Feidenhans’l, Y. N. Regmi, C. Wei, D. Xia, J. Kibsgaard, and L. A. King, “Precious Metal Free Hydrogen Evolution Catalyst Design and Application,” *Chemical Reviews* 124 (2024): 5617–5667.
 65. C.-C. Chang, J.-C. Kao, Y.-C. Lo, et al., “Specific Cu₂O Surfaces for Electrocatalytic Oxygen Reduction Reaction,” *Journal of Materials Chemistry A* 13 (2025): 13186–13194.
 66. A. Ashok and A. Kumar, “Ag/Co₃O₄ as an Effective Catalyst for Glycerol Electro-oxidation in Alkaline Medium,” *International Journal of Hydrogen Energy* 46 (2021): 4788–4797.
 67. H. Guo, T. Guo, M. Zhao, Y. Zhang, W. Shangguan, and Y. Liao, “Improving Benzene Catalytic Oxidation on Ag/Co₃O₄ by Regulating the Chemical States of Co and Ag,” *Journal of Environmental Sciences* 143 (2024): 201–212.

68. A. M. Elseman and S. M. Abdelbasir, "Nanosilver-Based Electrocatalytic Materials," *Electrocatalytic Materials for Renewable Energy* (John Wiley & Sons, 2024): 71–110.
69. B. A. Brandes, Y. Krishnan, F. L. Buchauer, H. A. Hansen, and J. Hjelm, "Unifying the ORR and OER With Surface Oxygen and Extracting Their Intrinsic Activities on Platinum," *Nature Communications* 15 (2024): 7336.
70. A. Hrnjic, A. R. Kamsek, L. Bijelic, et al., "Metal-Support Interaction Between Titanium Oxynitride and Pt Nanoparticles Enables Efficient Low-Pt-Loaded High-Performance Electrodes at Relevant Oxygen Reduction Reaction Current Densities," *ACS Catalysis* 14 (2024): 2473–2486.
71. G. Nazir, A. Rehman, J.-H. Lee, et al., "A Review of Rechargeable Zinc-Air Batteries: Recent Progress and Future Perspectives," *Nano-Micro Letters* 16 (2024): 138.
72. N. C. Buggy, *Investigations of Interfaces for Electrochemical Devices Using Tunable Block Copolymer Electrolytes* (Colorado School of Mines 2021).
73. Q. Lu, X. Zou, and Y. Bu, "Introduction to Zinc-air Batteries," *Zinc-Air Batteries: Introduction, Design Principles and Emerging Technologies*, (John Wiley & Sons, 2022): 1–34.
74. A. Ashok, A. Kumar, M. A. Matin, and F. Tarlochan, "Synthesis of Highly Efficient Bifunctional Ag/Co₃O₄ Catalyst for Oxygen Reduction and Oxygen Evolution Reactions in Alkaline Medium," *ACS Omega* 3 (2018): 7745–7756.
75. L. Gui, Y. Xu, Q. Tang, et al., "Silver Decorated Cobalt Carbonate to Enable High Bifunctional Activity for Oxygen Electrocatalysis and Rechargeable Zn-air Batteries," *Journal of Colloid and Interface Science* 603 (2021): 252–258.
76. K. Chen, et al., "Ultrasonic Plasma Engineering Toward Facile Synthesis of Single-Atom M-N₄/N-Doped Carbon (M = Fe, Co) as Superior Oxygen Electrocatalyst in Rechargeable," *Zinc-Air Batteries Nano-Micro Letters* 13 (2021): 60.
77. M. He, X. Jin, F. Chen, et al., "Synergistic Effect of Mn³⁺ and Oxygen Vacancy on the Bifunctional Oxygen Electrocatalytic Performance of MnOX/CNTs Composites," *Journal of Alloys and Compounds* 933 (2023): 167728.
78. Z. Lu., et al., "Y and Fe co-doped LaNiO₃ perovskite as a novel bifunctional electrocatalyst for rechargeable zinc-air batteries," *International Journal of Hydrogen Energy* 48 (2023): 8082–8092.
79. D. Mladenovic, D. M. F. Santos, G. Bozkurt, et al., "Tailoring Metal-Oxide-Supported PtNi as Bifunctional Catalysts of Superior Activity and Stability for Unitised Regenerative Fuel Cell Applications," *Electrochemistry Communications* 124 (2021): 106963.
80. P. Liu, J. Ran, B. Xia, S. Xi, D. Gao, and J. Wang, "Bifunctional Oxygen Electrocatalyst of Mesoporous Ni/NiO Nanosheets for Flexible Rechargeable Zn-Air Batteries," *Nano-Micro Letters* 12 (2020): 68.
81. Y. Arafat, M. R. Azhar, Y. Zhong, X. Xu, M. O. Tadé, and Z. Shao, "A Porous Nano-Micro-Composite as a High-Performance Bi-Functional Air Electrode With Remarkable Stability for Rechargeable Zinc-Air Batteries," *Nano-Micro Letters* 12 (2020): 130.
82. A. Ashok, A. Kumar, J. Ponraj, S. A. Mansour, and F. Tarlochan, "Highly Active and Stable bi-Functional NiCo₂O₄ Catalyst for Oxygen Reduction and Oxygen Evolution Reactions in Alkaline Medium," *International Journal of Hydrogen Energy* 44 (2019): 16603–16614.
83. A. Qaseem, F. Chen, C. Qiu, et al., "Reduced Graphene Oxide Decorated with Manganese Cobalt Oxide as Multifunctional Material for Mechanically Rechargeable and Hybrid Zinc-Air Batteries," *Particle & Particle Systems Characterization* 34 (2017): 1700097.
84. C. Adjah-Tetteh, K. S. Smith, Z. He, Y. Wang, N. Xu, and X.-D. Zhou, "Exploring Redox Behavior of Mixed Manganese-Cobalt Spinel Oxides Through in Situ Analysis," *Journal of the American Ceramic Society* 108 (2025): 70103.
85. D. Ji, S. Peng, D. Safanama, et al., "Design of 3-Dimensional Hierarchical Architectures of Carbon and Highly Active Transition Metals (Fe, Co, Ni) as Bifunctional Oxygen Catalysts for Hybrid Lithium-Air Batteries," *Chemistry of Materials* 29 (2017): 1665–1675.

Supporting Information

Additional supporting information can be found online in the Supporting Information section.

Supporting File: advs73605-sup-0001-SupMat.docx.