

Article

Solid-State Ball-Milling of Co_3O_4 Nano/Microspheres and Carbon Black Endorsed LaMnO_3 Perovskite Catalyst for Bifunctional Oxygen Electrocatalysis

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Abstract: Developing a highly stable and non-precious, low-cost, bifunctional electrocatalyst is essential for energy storage and energy conversion devices due to the increasing demand from the consumers. Therefore, the fabrication of a bifunctional electrocatalyst is an emerging focus for the promotion and dissemination of energy storage/conversion devices. Spinel and perovskite transition metal oxides have been widely explored as efficient bifunctional electrocatalysts to replace the noble metals in fuel cell and metal-air batteries. In this work, we developed a bifunctional catalyst for oxygen reduction and oxygen evolution reaction (ORR/OER) study using the mechanochemical route coupling of cobalt oxide nano/microspheres and carbon black particles incorporated lanthanum manganite perovskite ($\text{LaMnO}_3\text{@C-Co}_3\text{O}_4$) composite. It was synthesized through a simple and less-time consuming solid-state ball-milling method. The synthesized $\text{LaMnO}_3\text{@C-Co}_3\text{O}_4$ composite was characterized by scanning electron microscopy, energy dispersive X-ray spectroscopy, transmission electron microscopy, Brunauer-Emmett-Teller (BET) analysis, X-ray diffraction spectroscopy, and micro-Raman spectroscopy techniques. The electrocatalysis results showed excellent electrochemical activity towards ORR/OER kinetics using $\text{LaMnO}_3\text{@C-Co}_3\text{O}_4$ catalyst, as compared with Pt/C, bare $\text{LaMnO}_3\text{@C}$, and $\text{LaMnO}_3\text{@C-RuO}_2$ catalysts. The observed results suggested that the newly developed $\text{LaMnO}_3\text{@C-Co}_3\text{O}_4$ electrocatalyst can be used as a potential candidate for air-cathodes in fuel cell and metal-air batteries.

Keywords: perovskite oxide materials; solid-state method; oxygen reduction reaction; oxygen evolution reaction; surface coating



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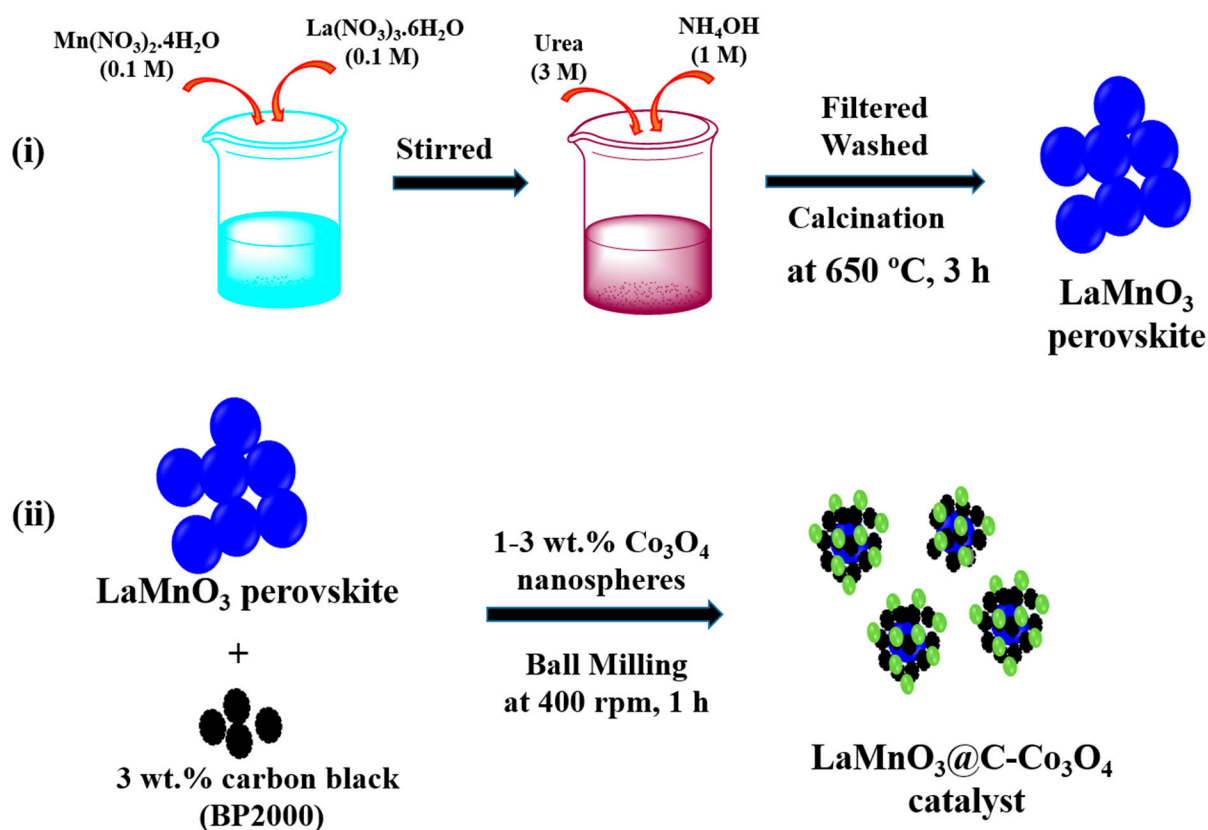
1. Introduction

There remains serious demand in the modern search for sustainable and renewable clean energy to make reliable and highly economical energy storage and conversion device. Moreover, the clean energy storage devices, including fuel cells, metal-air batteries, and hydrogen storage by electrolytic water splitting have to offer pleasant alternatives to the outdated fossil-fuel systems, which inspire to conduct more extensive studies on energy storage devices [1,2]. Particularly, metal-air batteries are considerably more popular systems in renewable energy due to their high theoretical energy density, a huge amount of oxygen supply, and more secure operation [3]. Nevertheless, the metal-air batteries are still restricted by extremely high overpotential, low efficiency, poor cycle stability, and

slow kinetics of oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) [4]. To overcome these problems, sufficient bifunctional electrocatalysts are required to speed up the electrochemical reactions with long-term durability, reusable, and low cost. To date, the Pt-supported composites are well-known electrocatalyst for ORR, while IrO₂ and RuO₂-based composites are targeted as an OER electrocatalyst. Indeed, those catalysts are still suffering in its bifunctional activity (ORR and OER) and more costly for large-scale applications [5,6]. Therefore, it should be necessary for designing a low cost and highly efficient bifunctional electrocatalyst in the renewable clean energy system.

The rare-earth-based metal oxides have vastly considered as an efficient electrocatalyst without the usage of any noble metals. Massive efforts have been undertaken focusing on the development of low-cost, efficient, and reusable bifunctional electrocatalysts [7]. Specifically, the ABO₃ perovskite-type oxides (A = rare earth or alkaline earth metal; B = transition metal) have been broadly utilized as a bifunctional oxygen electrocatalyst due to its remarkable specific characteristics such as low cost, abundant resources, and eco-friendly [8–10]. Moreover, the perovskite family includes various materials, and the physical and chemical assets of perovskite oxides is closely correlated to their A- or B-site components. Thus, A- or B-site elements of perovskite oxides are moderately or completely replaced to form new composite materials with required remarkable properties [11,12]. Mn-based perovskite oxides (LaMnO₃) have been mostly considered as a superior catalyst for ORR activity, due to their low cost and high earth abundance [13,14]. However, it suffers a poor OER catalytic activity due to its chemical instability, lack oxygen vacancies, and high charging overpotential [3,15,16]. To further improve the electrochemical performances of the LaMnO₃, doping or hybridization strategy is necessary to increase the oxygen vacancy concentration and also to adjust the valence of Mn⁴⁺/Mn³⁺ ratio [17–19]. In addition, the transition metals, and their metal oxides (e.g., Fe₃O₄, Mn₃O₄, Co₃O₄, etc.) are considered as a low-cost metal oxide and more essential in the research family for developing efficient bifunctional electrocatalyst [20–22]. Typically, cobalt-based metal oxides have been mostly used as a versatile electrocatalyst for OER due to their large catalytic performance [23]. Additionally, the Co-supported carbonaceous materials, such as porous carbon, reduced graphene oxide, and carbon nanotubes have revealed boost the electrocatalytic activity as well as enhanced the facilitated mass transport, electrical conductivity, improved dispersion, and exposure of catalytic sites [11,21,23–25]. Furthermore, in recent years, hybridization of perovskite materials with other materials (e.g., MoS₂) has also been enhanced the water oxidation properties in both an acidic and alkaline environment. Indeed, a study indicates that the mechanochemical coupling via ball-milling process creates intimately connected heterointerfaces between the perovskite and MoS₂ that can synergistically boost the OER activity [26,27]. By all these studies, we predict that the incorporation of Co₃O₄ nano/microspheres with carbon black supported LaMnO₃ perovskite catalyst can be a potential material to improve the conductivity, stability, and electrocatalytic activity in an alkaline media.

In this study, for the first time, we introduce a highly efficient and long durable LaMnO₃@C-Co₃O₄ composite as a bifunctional electrocatalyst for ORR and OER in an alkaline media. Firstly, the LaMnO₃ was prepared by a simple co-precipitation method. Finally, LaMnO₃@C-Co₃O₄ composite was synthesized by a solid-state ball-milling process, which clearly detailed in Scheme 1. The prepared composite sample was characterized by scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDX), transmission electron microscopy (TEM), X-ray diffraction spectroscopy (XPS), and micro-Raman spectroscopy techniques. The electrocatalytic activity of LaMnO₃@C-Co₃O₄ composite was verified by CV and LSV in an alkaline media.



Scheme 1. Schematic for the synthesis details of $\text{LaMnO}_3@\text{C}-\text{Co}_3\text{O}_4$ composite catalyst.

2. Results and Discussion

2.1. Characterization

The surface morphologies of Co_3O_4 , $\text{LaMnO}_3@\text{C}$ and $\text{LaMnO}_3@\text{C}-\text{Co}_3\text{O}_4$ were investigated by SEM and TEM analyses, the results were shown in Figure 1. The as-prepared Co_3O_4 (Figure 1A inset) shows nano/microsphere morphology that was obtained from the glucose-based carbon sphere template method. The particle size of Co_3O_4 spheres also confirmed by particle size analyzer (the data can be seen in supporting information Figure S1), which is about 312 nm (d_{10}) to 2.3 μm (d_{50}). Figure 1A also shows the SEM image of the LaMnO_3 sample, revealed a homogeneous distribution of nano/microspheres-like particles. However, the SEM image of $\text{LaMnO}_3@\text{C}-\text{Co}_3\text{O}_4$ composite (Figure 1B) showed a uniform distribution or coating of carbon and Co_3O_4 particles on perovskite nanostructure, which is further confirmed by TEM (Figure 1C,D). The TEM images of $\text{LaMnO}_3@\text{C}-\text{Co}_3\text{O}_4$ have clearly displayed the surface coating of carbon black and Co_3O_4 nanosphere over the LaMnO_3 surface. These coating materials were well interconnected themselves and physically attached to the perovskite particles. The results clearly revealed that these interconnected particles can create the large number of mesopores in catalyst design that can facilitates more electrolyte ions and oxygen molecule storing and transportation during the reaction.

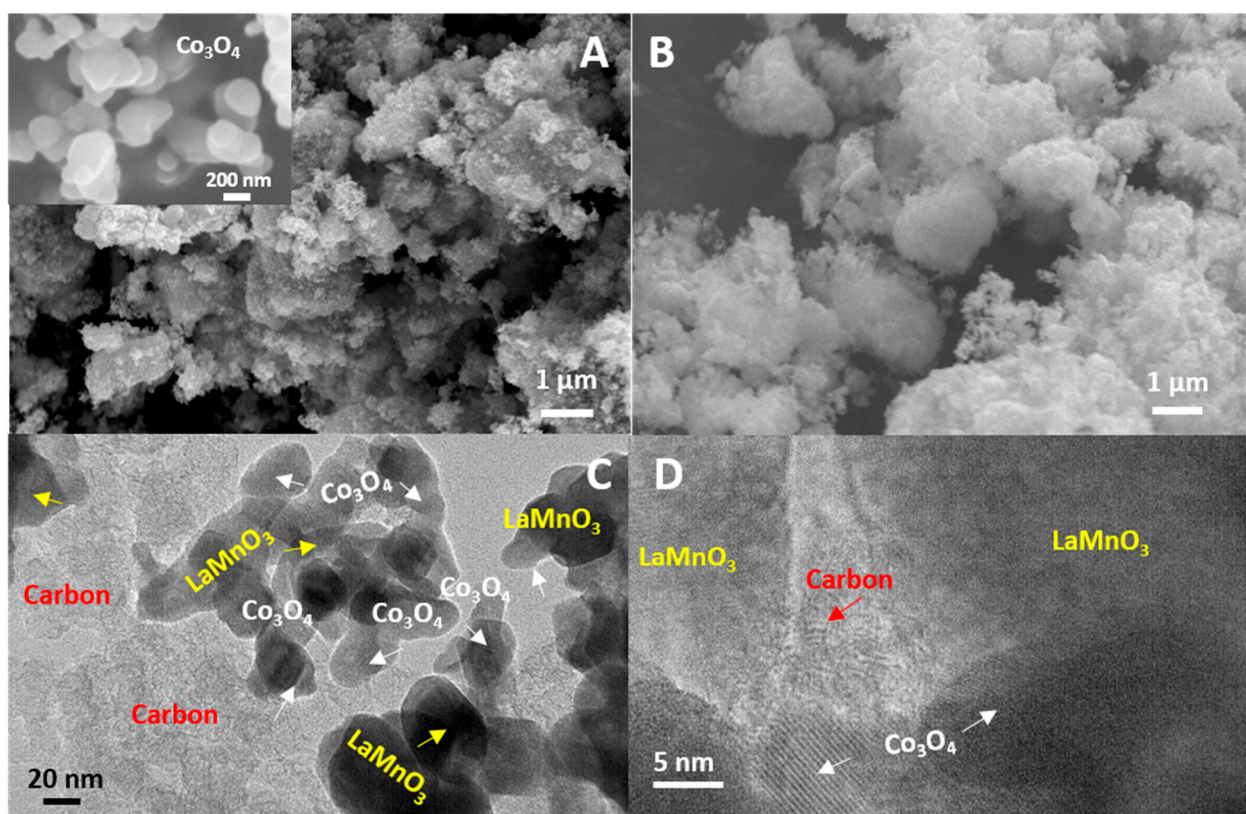


Figure 1. SEM image of LaMnO_3 (A) and $\text{LaMnO}_3@\text{C-Co}_3\text{O}_4$ composite (B); Inset (A) shows the SEM image of Co_3O_4 nano/microspheres; (C,D) TEM images of $\text{LaMnO}_3@\text{C-Co}_3\text{O}_4$ composite catalyst.

The elemental compositions of $\text{LaMnO}_3@\text{C-Co}_3\text{O}_4$ composite were also presented in Energy-dispersive X-ray spectroscopy (EDX) spectra, as shown in Figure 2. EDX spectral data indicated that some strong peaks appeared for the corresponding elements, such as C, La, Mn, Co, and O, presented in the composite samples. The quantification data (Figure 2A inset table) reveals the presence of an appropriate amount of the transition elements, which confirms the compound of LaMnO_3 and Co_3O_4 structure. In addition, the elemental mapping was also conducted for further confirmation of the corresponding $\text{LaMnO}_3@\text{C-Co}_3\text{O}_4$ composite formation. Figure 2B shows the overall elemental mapping and corresponding individual arrangement of C, La, Mn, Co, and O elements. As seen in C elemental mapping, most of the bright spot is not visible on the sample area that means the carbon black species are fully covered by Co_3O_4 nano/microspheres, which can also be played important role as a bridge between to connect the LaMnO_3 perovskite and Co_3O_4 spinel particles. These results further confirm that the successful formation of a $\text{LaMnO}_3@\text{C-Co}_3\text{O}_4$ composite which is intimately connected by the mechanochemical coupling via the solid-state ball-milling process.

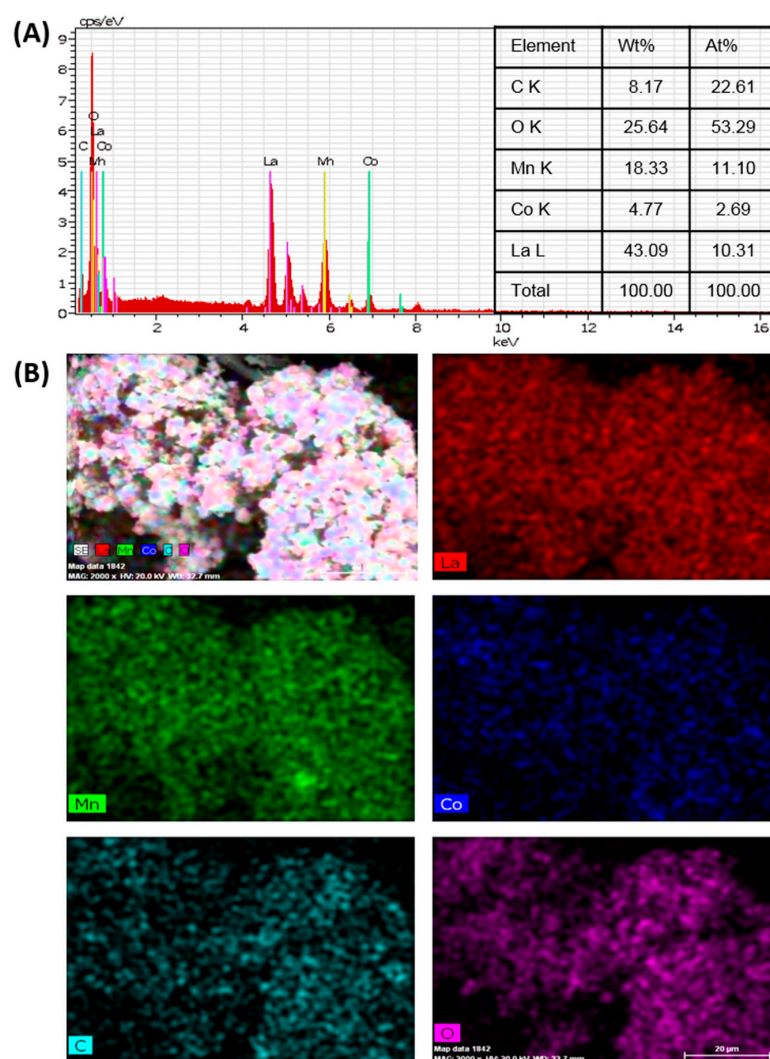


Figure 2. (A) EDX spectra for qualitative and quantitative analysis for the La, Mn, Co, C and O elements present in the LaMnO₃@C-Co₃O₄ composite; (B) EDX elemental mapping of LaMnO₃@C-Co₃O₄ composite.

The surface properties of LaMnO₃@C-Co₃O₄ composite further examined by XPS analysis, all elements, such as C, O, Mn, Co, and La, have clearly existed in the composite sample which is confirmed from the full scan survey spectra (Supplementary Figure S2). All the deconvoluted peaks were fitted by Gaussian-Lorentzian (G-L) method, the G-L ratio was fixed as 30%. In general, there are three different background, namely linear, Shirley (or iterative Shirley) and Tougaard, were used to fit the core level spectrum in XPS analysis [28]. The simple linear background suffers from large peak area changes depending on the position of the chosen end points and is the least accurate. The Tougaard background is the most accurate but suffers from complications in practical use, particularly if there are numerous peak overlaps. The Shirley background falls somewhere in between for accuracy, this background drives up in proportion to the total number of photoelectrons below its binding energy position. Although, its ease of use has resulted in its widespread adoption. In this work, the Shirley background was used to get the acceptable peak fitting parameters. As seen in high-resolution O 1s spectra (Figure 3A), the binding energies at 529.6 eV and 531–533 eV indicates the presence of lattice oxygen and surface adsorbed oxygen functionalities (O₂^{2−}/O[−] and OH[−]) in the composite sample, which is corresponding to the M–O and M–OH species [16]. The peak around 533.8 eV can be ascribed to the adsorbed water molecules on the surface. According to the literature, the presence of

lattice hydroxide (OH^-) ions on the LaMnO_3 catalyst surfaces can be a positive effect on bifunctional ORR/OER activities [3,16,29,30]. Figure 3B also shows the high-resolution spectra of Mn 2p exhibits a doublet such as $2p_{3/2}$ and $2p_{1/2}$ at 642.1 and 653.9 eV with the binding energy separation of 11.8 eV. The Mn $2p_{3/2}$ peak also consists of two other deconvolution peaks at 641.8 and 643.2 eV, which are ascribed to Mn^{3+} and Mn^{4+} oxidation states. It has been proven that the coexistence of mixed oxidation states (Mn^{3+} and Mn^{4+}) of Mn can increase the conductivity and ORR activity of LaMnO_3 perovskite [14,19]. The high ratio of Mn^{3+} indicates more oxygen vacancies were presented in our $\text{LaMnO}_3/\text{C-Co}_3\text{O}_4$ composite, which would be helpful for the enhancement of electrocatalytic activities [16]. In addition, the high-resolution spectra of La 3d (Figure 3C) shows two spin-orbit components such as $3d_{5/2}$ and $3d_{3/2}$, these spins are further split into multiple peak splitting at the binding energies of 834.6/838.2 eV and 851.3/854.9 eV, respectively. The La $3d_{5/2}$ versus La $3d_{3/2}$ spin-orbit splitting is observed to 16.8 eV and the relative intensity ratio for La $3d_{5/2}$ and La $3d_{3/2}$ is ca. 1.48, these values are in close relation with literature results [31]. The La $3d_{5/2}$ doublet splitting shows the separation (ΔE) value around 3.6 eV, indicates the presence of lanthanum hydroxides [31–33]. Hence, the clear separation of these spin-orbit splitting indicates the La 3d is about +3 oxidation states. Although, a very low signal observed from Co 2p high-resolution spectrum, it may be due to the occurrence of less amount of Co_3O_4 coating components on the LaMnO_3 surface (Figure 3D). The spectra displays a doublet ($2p_{3/2}$ and $2p_{1/2}$) at 779.6 and 795.1 eV which, separated by 15.5 eV, confirms the presence of cobalt species on the as-synthesized materials. The XPS fit parameters of these elements are clearly summarized in Table S2. As a result, all these above data clearly evidenced that the successful formation of LaMnO_3 perovskite with a surface coating of carbon and Co_3O_4 nano/microspheres.

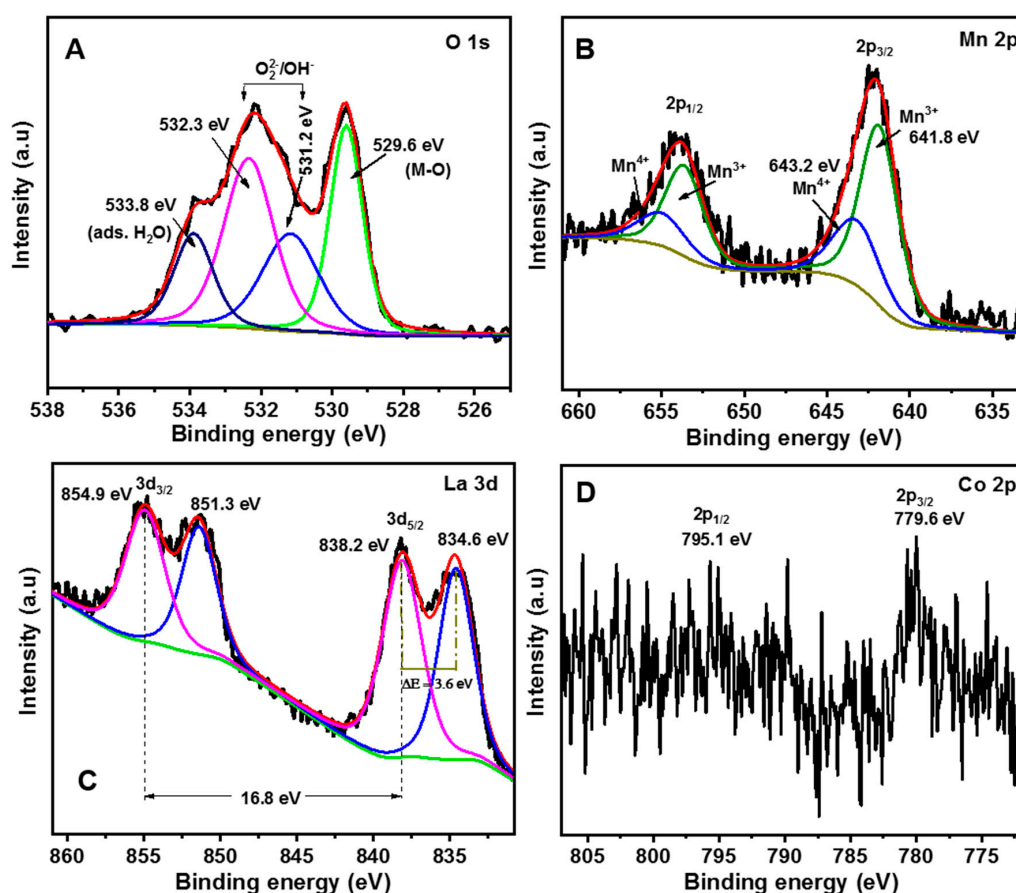


Figure 3. XPS curve of high-resolution spectra of O 1s (A), Mn 2p (B), La 3d (C), and Co 2p, (D) in $\text{LaMnO}_3/\text{C-Co}_3\text{O}_4$ composite.

The crystalline nature of the as-prepared composite catalyst was confirmed by X-ray Diffraction Spectroscopy (XRD). Figure 4 shows the XRD pattern of LaMnO₃@C-Co₃O₄ composite (A), Co₃O₄ (B), and LaMnO₃ (C) and it is worthy to note that from the XRD pattern of LaMnO₃, the obtained all characteristic peaks were perfectly matched with the perovskite structure of LaMnO₃ (Joint Committee on Powder Diffraction Standards Number (JCPDS No.) of 75-0440), indicating the successful formation of the pure cubic crystal structure of LaMnO₃ with a space group of Pm-3m. Figure 4B also displays the XRD pattern of the as-synthesized Co₃O₄ hollow nano/microspheres, which clearly matched with the standard pattern of JCPDS No. 65-3103. A lower angle shift (from 32.87° to 32.44°) was observed in the corresponding characteristics peaks and the peak intensity was also reduced after surface modification of LaMnO₃ by carbon black and Co₃O₄, which is due to the incorporation of carbon and Co₃O₄ hollow nano/microspheres over LaMnO₃ particle surface via the ball-milling process. Furthermore, micro-Raman spectra clearly revealed the presence of carbon and Co₃O₄ species on the LaMnO₃ perovskite sample. Figure 4D curve (a) displays the vibrational modes at 493 and 591 cm⁻¹ can be ascribed to the A_g (bending vibration) and B_{2g} (stretching vibration) symmetry of LaMnO₃ [34], respectively. Also, the spectra do not show any carbon (disorder) peaks, indicating the pure crystallinity of LaMnO₃ perovskite crystal structure. However, curve (b) shows the D- and G-band at 1334 and 1598 cm⁻¹ with an intensity (I_D/I_G) ratio of 0.99. The I_D/I_G ratio indicates that the LaMnO₃ surface contains only a small amount of graphitized carbon species and large amounts defect carbons [11,35,36]. This is due to the attachment of metal oxide species and the carbon interface. The residual amount of carbon was also measured to ca. 4.13 wt.% by the elemental analyzer (see Supplementary Table S1). The spectra also show A_{1g} symmetry [24] of Co₃O₄ spinel structure at 669 cm⁻¹ including with A_g and B_{2g} symmetry of LaMnO₃, reveals the Co₃O₄ particles are well interacted with carbon spheres and subsequently coated on the LaMnO₃ surface. Hence, these above results confirmed that the successful formation of LaMnO₃@C-Co₃O₄ composite bi-functional catalyst by a dry coating solid-state ball-milling process.

In addition, the surface area and pore size distribution of the materials were characterized by N₂ adsorption-desorption isotherm analysis. From the results, the BET surface area of LaMnO₃ (Figure 4E) and LaMnO₃@C-Co₃O₄ composite (Figure 4F) was obtained to ca. 16.5 and 30.85 m² g⁻¹. The pore size distribution curve (inset of Figure 4E,F) indicates the pore volume and pore size of LaMnO₃ and LaMnO₃@C-Co₃O₄ sample is ca. 0.23 cm³ g⁻¹/43.04 nm and 0.41 cm³ g⁻¹/65.02 nm, respectively. The obtained isotherm curves are also shown type-II adsorption isotherm behavior, indicating LaMnO₃@C-Co₃O₄ composite may contain both meso- and microporous-structures for oxygen and electrolyte ion storing/transport. Hence, the results suggest that the multiple nanostructures with a high specific surface area is an essential character to increase the catalytic activity of the catalyst [37,38].

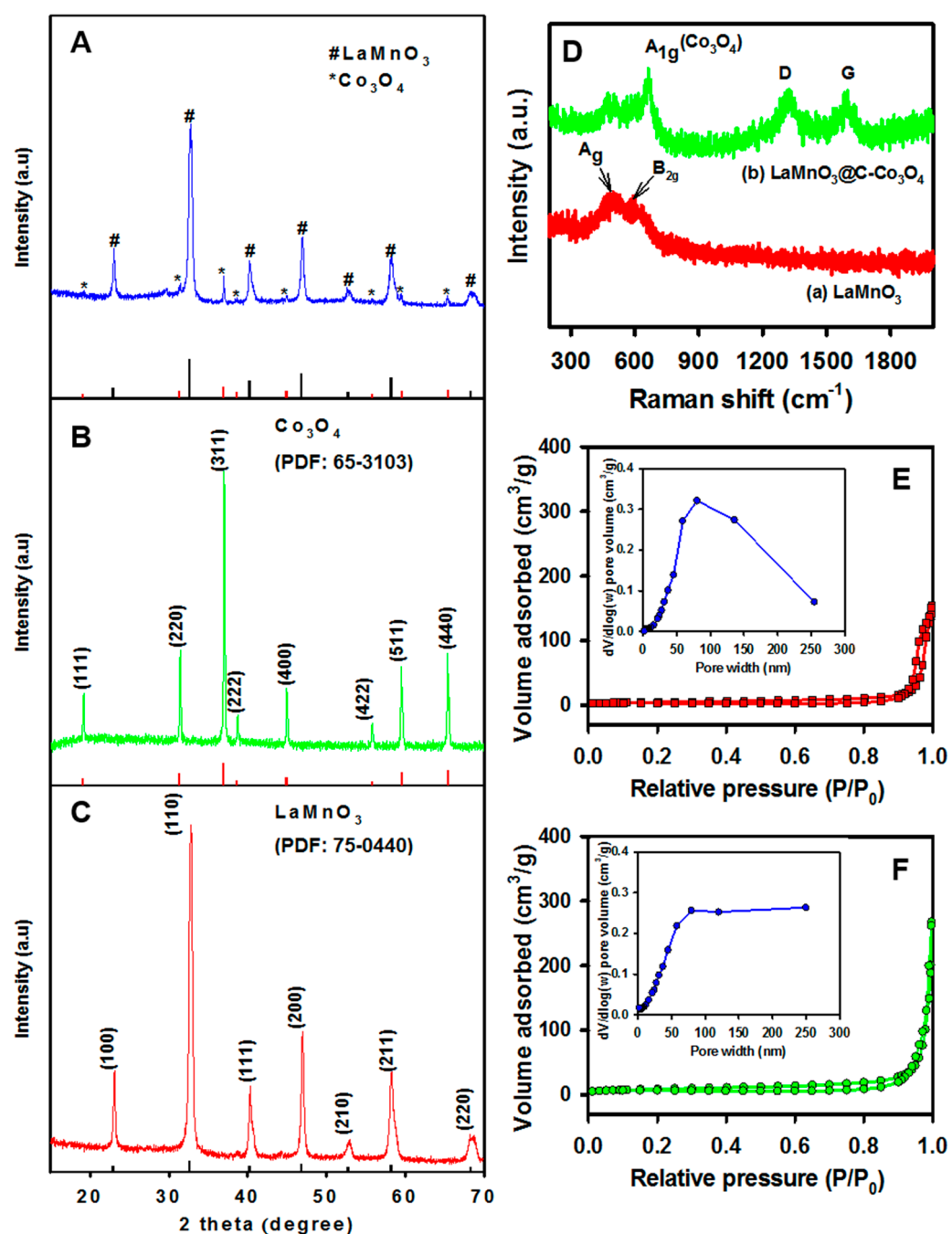


Figure 4. XRD pattern, (A) $\text{LaMnO}_3\text{@C-Co}_3\text{O}_4$ composite, (B) Co_3O_4 , and (C) LaMnO_3 , (D) Raman spectra of LaMnO_3 (a) and $\text{LaMnO}_3\text{@C-Co}_3\text{O}_4$ composite (b). BET adsorption-desorption isotherm curves of LaMnO_3 (E), and $\text{LaMnO}_3\text{@C-Co}_3\text{O}_4$ composite catalyst (F).

2.2. Electrocatalytic Activity of the Catalyst

The bifunctional electrocatalytic activity of the as-prepared catalysts was assessed by CV and LSV in O_2 -saturated electrolyte, as shown in Figure 5. The CV curve $\text{LaMnO}_3\text{@C-Co}_3\text{O}_4$ towards ORR activity in N_2 and O_2 -saturated 0.1 M KOH electrolyte was recorded, and the obtained results were displayed in Figure 5A. No obvious oxidation-reduction peak was observed using $\text{LaMnO}_3\text{@C-Co}_3\text{O}_4$ catalyst electrode (a) in N_2 saturated 0.1 M KOH. Conversely, the $\text{LaMnO}_3\text{@C-Co}_3\text{O}_4$ electrode (b) showed a higher reduction peak at the peak potential of -0.35 V while using O_2 -saturated 0.1 M KOH electrolyte, indicating a good electrocatalyst for ORR activity in an alkaline media. In addition, CV was further performed using $\text{LaMnO}_3\text{@C-RuO}_2$ (c), $\text{LaMnO}_3\text{@C}$ (d) and LaMnO_3 (e) electrodes in

O₂-saturated 0.1 M KOH, all the catalysts showed ORR activity in the peak potential range of -0.5 to -0.35 V. When compared with LaMnO₃@C-RuO₂, LaMnO₃@C, and LaMnO₃ electrodes, the LaMnO₃@C-Co₃O₄ composite electrode showed highest reduction peak potential and lower onset potential, demonstrates a higher electrocatalytic activity toward ORR due to the successful modification of carbon black and Co₃O₄ nano/microspheres on the LaMnO₃ surface.

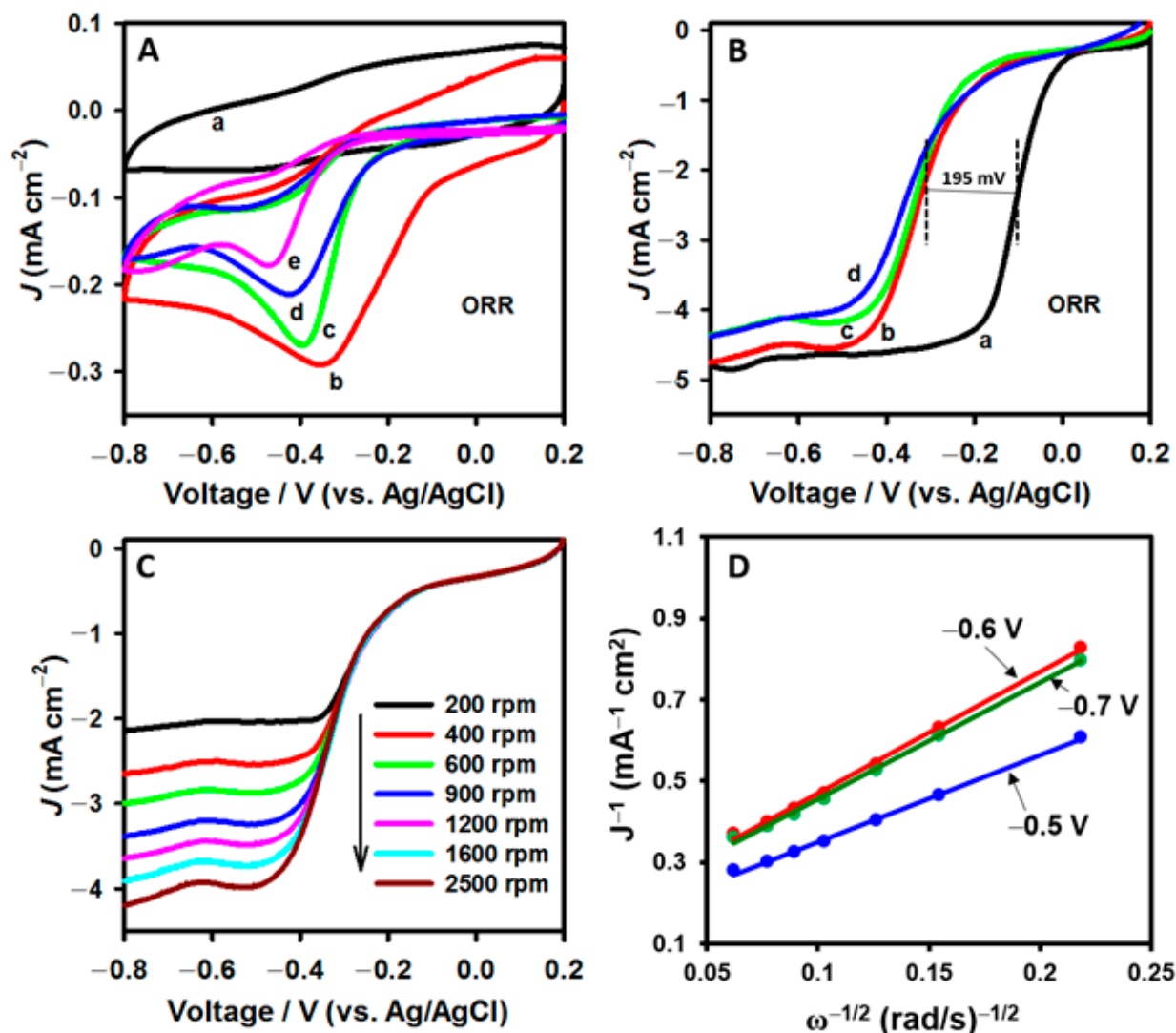


Figure 5. (A) CV curves of ORR activity at LaMnO₃@C-Co₃O₄ catalyst electrode (a) in N₂-saturated and LaMnO₃@C-Co₃O₄ (b), LaMnO₃@C-RuO₂ (c), LaMnO₃@C (d) and LaMnO₃ (e) in O₂-saturated 0.1 M KOH electrolyte at a scan rate of 50 mV Scheme 1. (B) LSV polarization curves for ORR activity at Pt/C (a), LaMnO₃@C-Co₃O₄ (b), LaMnO₃@C-RuO₂ (c), LaMnO₃@C (d) in O₂-saturated 0.1 M KOH electrolyte at a scan rate of 20 mV s⁻¹ with rotation speed of 1600 rpm. (C) RDE measurements of LaMnO₃@C-Co₃O₄ catalyst electrode at different rotation speeds of 200–2500 rpm. (D) Koutecky-Levich relation between j^{-1} and $\omega^{-1/2}$ at LaMnO₃@C-Co₃O₄ electrode at different potentials.

To further verify the catalytic activity on our composite sample, LSV was performed using LaMnO₃@C, LaMnO₃@C-Co₃O₄ composite electrode with other precious material modified electrodes. Figure 5B shows the ORR activity of 20% Pt/C (a), LaMnO₃@C-Co₃O₄ (b), LaMnO₃@C-RuO₂ (c), and LaMnO₃@C (d) electrodes in O₂-saturated 0.1 M KOH. It can be noticed that a clear difference was observed in the ORR onset potential for these electrodes, such as 20% Pt/C (-0.02 V), LaMnO₃@C-Co₃O₄ (-0.17 V), LaMnO₃@C-RuO₂ (-0.21 V), and LaMnO₃@C (-0.20 V). Moreover, the limiting current density of the

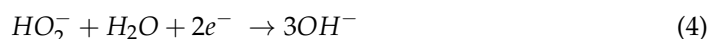
LaMnO₃@C-Co₃O₄ (ca. 4.17 mA cm⁻²) electrode is almost similar to commercial Pt/C (ca. 4.32 mA cm⁻²) electrode and it was higher than the LaMnO₃@C-RuO₂ (3.84 mA cm⁻²) and LaMnO₃@C (3.54 mA cm⁻²) electrodes. As noted, the half-wave potential difference ($\Delta E_{1/2} = E_{1/2, \text{catalyst}} - E_{1/2, \text{Pt/C}}$) between commercial Pt/C and LaMnO₃@C-Co₃O₄ composite catalyst exhibited to 195 mV, reveals the excellent ORR catalytic performance for our composite catalyst. The results confirmed that even the precious metal oxide coating at the LaMnO₃ surface can just increase the limiting current density rather than to improve the ORR onset potential. It means that the LaMnO₃ perovskite has significant ORR property than the RuO₂ based catalyst. On the other hand, the ORR property is highly enhanced when LaMnO₃ was coated with carbon and Co₃O₄ nanostructures. Because Co₃O₄ and carbon materials are well-known common catalyst for oxygen cathode in fuel cells and metal-air batteries, their contribution to surface modification of the oxygen cathode has extremely improved ORR activity, near to commercial Pt/C catalyst.

The RDE measurements were carried out to understand the ORR kinetics of LaMnO₃@C-Co₃O₄ catalyst that performed by LSV in O₂-saturated 0.1 M KOH electrolyte, the data is shown in Figure 5C. The limiting current density of LaMnO₃@C-Co₃O₄ electrode exhibits linear increment with increasing the rotation speed of 200–2500 rpm. The ORR kinetics to calculate the number of electron transfer of the catalyst is determined by using the Koutecky-Levich relation while plotting the inverse of limiting current density (data obtained from the different potentials of each rotation curve) and rotation speed in radian per seconds. The linear plot reveals the first-order kinetics ORR is observed at the LaMnO₃@C-Co₃O₄ catalyst electrode. The relation of Koutecky-Levich equations are as follows [15]:

$$\frac{1}{J} = \frac{1}{J_k} + \frac{1}{B\omega^2} \quad (1)$$

$$B = 0.62nFA\nu^{-1/6} \cdot C_o \cdot (D_o)^{2/3} \quad (2)$$

From the slope of the linear relation between j^{-1} and $\omega^{-1/2}$, the average value of electron number of the LaMnO₃@C-Co₃O₄ catalyst is found to be 3.32, which is an almost a higher value than LaMnO₃@C-RuO₂ (2.43), LaMnO₃@C (1.98) catalysts. The obtained electron number value of LaMnO₃@C-Co₃O₄ catalyst is an approximately close relation with Pt/C catalyst, indicates the ORR kinetics at this catalyst surface not follows 4e⁻ transfer directly, instead of following the multi-step electron transfer mechanism [9].



To evaluate the long-term stability of the electrode, chronoamperometry was employed at fixed ORR peak potential for commercial Pt/C (a) and LaMnO₃@C-Co₃O₄ (b) catalyst. The current vs. time of chronoamperometry curves was observed at 1600 rpm rotation speed for 5000 s in O₂-saturated 0.1 M KOH electrolyte, as shown in Figure 6. In comparison, LaMnO₃@C-Co₃O₄ catalyst exhibits the best relative current response with retention of 91.99% for 5000 s relative to commercial Pt/C (59.19%). The results indicated that the as-prepared composite catalyst is highly stable than the Pt/C catalyst. SEM images were taken to observe the morphology of the composite materials before and after the chronoamperometry test and the data provided in supporting information Figure S3. The SEM images demonstrated that the surface of the catalyst was not found any significant degradation and damages. Because the surface coating materials can be well mixed with LaMnO₃, the parent catalyst leads to a closed packed architecture as well as uniform dispersion in catalyst ink for electrode fabrication. On the one hand, a film at the electrode surface has strongly adhered to with the help of Nafion binder. On the other hand, transition metal oxide catalysts are highly stable in the alkaline electrolyte medium. Moreover, in this catalyst structure, LaMnO₃ perovskite and Co₃O₄ spinel oxides are strongly connected by carbon black particles; therefore, the ORR activity and stability of the electrode reveals

superior performance. Based on our analyses results, the $\text{LaMnO}_3\text{@C-Co}_3\text{O}_4$ composite catalyst is a highly promising material to fabricate the electrode for fuel cells and metal-air battery applications.

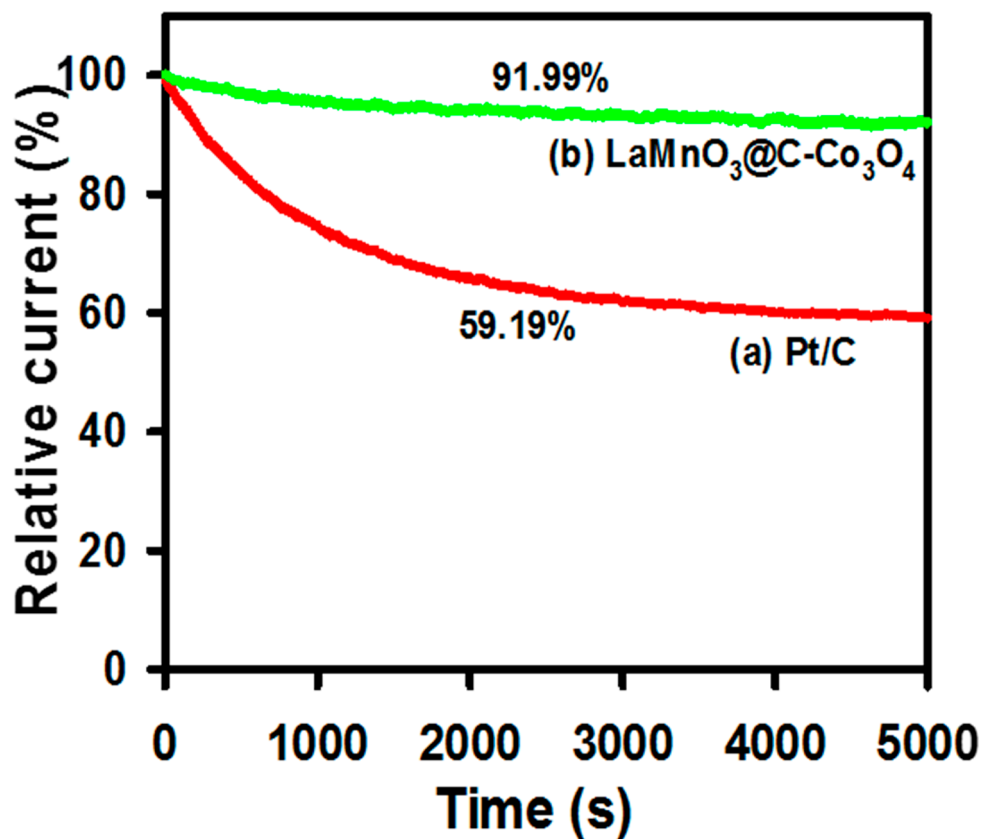


Figure 6. Chronoamperometry curves for stability of Pt/C (a) and $\text{LaMnO}_3\text{@C-Co}_3\text{O}_4$ composite electrode, (b) in O_2 -saturated 0.1 M KOH electrolyte at a fixed peak potential with rotation speed of 1600 rpm.

In this study, we have also confirmed the bifunctional (ORR/OER) activity of the as-prepared $\text{LaMnO}_3\text{@C-Co}_3\text{O}_4$ catalyst by LSV in O_2 -saturated 0.1 M KOH electrolyte at 1600 rpm rotation speed. As seen in Figure 7, the carbon black coated LaMnO_3 perovskite (a) catalyst shows significant ORR and OER activity. However, its bifunctionality is extremely increased to higher-order kinetics while coating with RuO_2 (b) and Co_3O_4 (c) materials. As compared to noble RuO_2 , the non-noble Co_3O_4 material coated LaMnO_3 perovskite exhibits very high bifunctional activity by increasing the current density and lowering the onset potential for both oxidation and reduction of oxygen molecules. More interestingly, the enhancement in bifunctional behavior is due to the attractive electrode design that consists of different crystal structure catalysts with carbon materials. LaMnO_3 perovskite is the best ORR catalyst among the other perovskites and Co_3O_4 has been explored as the superior catalyst for both ORR and OER activity in an alkaline environment, among which the incorporation carbon black can markedly increase the conductivity of these metal oxides. Therefore, the $\text{LaMnO}_3\text{@C-Co}_3\text{O}_4$ composite catalyst is highly stable and active in both the reduction and oxidation behavior of oxygen catalysis.

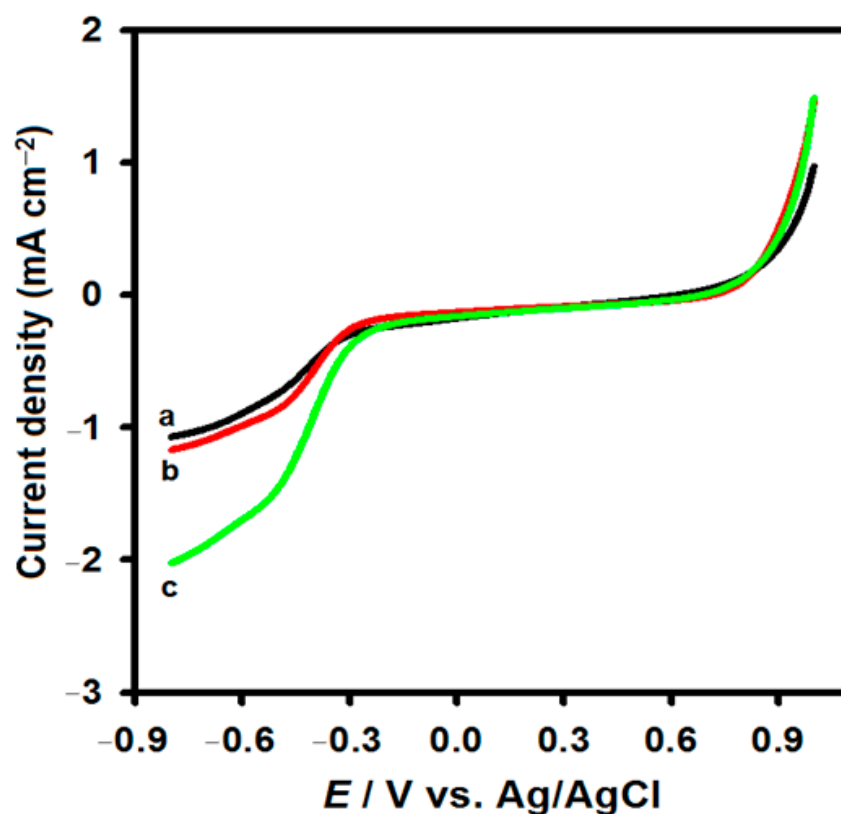


Figure 7. LSV polarization curves for ORR/OER activity at LaMnO_3/C (a), $\text{LaMnO}_3/\text{C-RuO}_2$ (b), and $\text{LaMnO}_3/\text{C-Co}_3\text{O}_4$ (c) in O_2 -saturated 0.1 M KOH electrolyte at a scan rate of 20 mV s^{-1} with rotation speed of 1600 rpm.

3. Experimental Section

3.1. Materials and Techniques

Lanthanum nitrate hexahydrates ($\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$), manganese nitrate tetrahydrates ($\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$), cobalt acetate tetrahydrates ($\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$), potassium hydroxide (KOH), Ruthenium dioxide (RuO_2), 20 wt.% Pt/C, glucose, and 5 wt.% Nafion solution were purchased from Alfa Aesar, Taipei, Taiwan and Sigma-Aldrich chemicals, Taipei, Taiwan and used as-is. Carbon black-BP2000 (BET surface area = $1475 \text{ m}^2 \text{ g}^{-1}$) was also received from CABOT Corporation, Boston, MA, USA. Deionized water with a resistivity of ≥ 18 mega ohm was used in the whole part of the work for washing and solution preparation during materials synthesis and electrochemical studies.

SEM (Hitachi-S2600, Tokyo, Japan), TEM (JEOL JEM-2100, Tokyo, Japan), and XRD (BRUKER D2 PHASER, Karlsruhe, Germany, $\text{Cu K}\alpha$, $\lambda = 0.15406 \text{ nm}$, 30 kV, 10 mA) were used to study morphology and crystal structure analysis. Micro-Raman spectroscopy was also performed for structural analysis of the materials using a micro-Raman microscope (In Via confocal micro Renishaw, Gloucestershire, UK) with 633/514 nm laser sources. Surface area measurements were performed by N_2 adsorption-desorption isotherm of BET analysis using Micromeritics, Gemini VII ASAP 2000, Rostock, Germany. XPS analysis was also carried out using VG Scientific ESCALAB 250, Waltham, MA, USA (XR5 Monochromated X-ray Gun, with a maximum energy of 15 kV, 200 W, aluminum target with a beam size of 650–120 μm); the applied pass energy was 100 eV for survey scan and 20 eV for narrow scan. Carbon tape is used for electrical contact and sample loading and no flood gun was used. The peak fitting was carried out using the XPSPEAK software with the adventitious C 1s signal at 284.6 eV as a reference. Dynamic light scattering particle size distribution analysis (DLS) was performed by a laser diffraction particle size analyzer (Beckman Coulter LS 13 320, Indianapolis, IN, USA). The amount carbon content was estimated by the elemental analyzer (2400 CHN/O Analyzer, Perkin Elmer, Waltham,

MA, USA). Electrochemical experiments were performed using CHI 405 (CH Instruments, Austin, TX, USA) electrochemical workstation with three-electrode system; glassy carbon electrode as a working electrode, Ag/AgCl (sat. KCl) as a reference electrode, and Pt wire as a counter electrode.

3.2. Synthesis of LaMnO_3 Perovskite Catalyst

LaMnO_3 perovskite material was synthesized by the co-precipitation method at room temperature. In brief, 0.1 M $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and 0.1 M $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ aqueous solution were separately prepared in 50 mL deionized water and mixed them together with magnetic stirring at room temperature. Then, 3 M of aqueous urea solution (50 mL) was also added to the above mixture and the solution pH was adjusted to 10 with 1 M NH_4OH . The reaction mixture was constantly stirred for 12 h at room temperature, finally, the product was collected by vacuum filtration followed by washing with deionized water and ethanol. The precipitate was dried in an oven at 80 °C for 12 h and calcined at 650 °C in the air atmosphere for 3 h. The final product is denoted as LaMnO_3 perovskite catalyst.

3.3. Preparation and Fabrication of $\text{LaMnO}_3\text{@C-Co}_3\text{O}_4$ Composite Electrode

Prior to surface modification of LaMnO_3 perovskite, a solid-state ball-milling process was carried out in a dry environment with carbon black and Co_3O_4 hollow nanosphere particles. Here, Co_3O_4 hollow nano/microspheres were synthesized through the carbon spheres template method. Initially, carbon nanospheres were obtained from glucose precursors via the hydrothermal route, as previously reported [39]. Later, 0.5 g carbon spheres were dispersed in 50 mL cobalt acetate (0.3 M) solution with the aid of ultrasonication for 20 min. The resulting suspension was further aged for 12 h at 30 °C in a water bath, then filtered with a vacuum pump and washed with DI water three times, and then dried at 80 °C in an oven for 12 h. The resultant composite powder was heated to 400 °C in the air for 2 h. The Co_3O_4 hollow nano/microspheres were collected as black powders. Finally, approximately, 1–3 wt.% Co_3O_4 and 3 wt.% carbon black powders were mixed with 200 mg of LaMnO_3 sample and dry ball-milled for 1 h at 400 rpm rotation speed. The as-synthesized $\text{LaMnO}_3\text{@C-Co}_3\text{O}_4$ composite catalyst was used for further characterization and fabrication of the electrode to evaluate the oxygen electrocatalysis.

To fabricate the electrode, 10 mg of $\text{LaMnO}_3\text{@C-Co}_3\text{O}_4$ catalyst powder was dispersed in isopropyl alcohol and deionized water (3:1 v/v) with 50 μL of 5 wt.% Nafion (Sigma Aldrich, Taiwan) and ultrasonication (Model-DC300H, Taiwan; 300 W; 40 kHz) for 30 min at 25 °C. Then, the homogeneously dispersed catalyst ink was drop cast (around 8 and 24 μL) onto alumina polished glassy carbon electrode (GCE) and rotating disc electrode (RDE) surface and dried at 25 °C. All these $\text{LaMnO}_3\text{@C-Co}_3\text{O}_4$ catalyst modified electrodes were used for the electrochemical measurements in a 0.1 M KOH containing electrolyte system.

4. Conclusions

A new strategy has been proposed in this work to design a catalyst for oxygen electrocatalysis. The solid-state ball-milling method was utilized to construct our $\text{LaMnO}_3\text{@C-Co}_3\text{O}_4$ composite catalyst, which revealed an excellent ORR and OER activity in an alkaline environment. Numerous physical methods were applied to characterize the $\text{LaMnO}_3\text{@C-Co}_3\text{O}_4$ composite materials, resulting in a highly porous and nano/microstructure morphology that can enable more oxygen molecules adsorption and electrolyte ion storage, exhibiting outstanding oxygen reduction and oxidation reaction kinetics. The half-wave potential of $\text{LaMnO}_3\text{@C-Co}_3\text{O}_4$ catalyst exhibited around 195 mV relative to Pt/C catalyst and demonstrated excellent bifunctionality behavior, as compared to RuO_2 coated $\text{LaMnO}_3\text{@C}$ catalyst. Thus, the overall performances indicated that our proposed catalyst is a very stable and low-cost cathode material as well as the best alternative for commercial noble metal catalysts in fuel cells and metal-air (Li-, Na-, or K-air) battery applications.

Supplementary Materials: The following are available online at <https://www.mdpi.com/2073-4344/11/1/76>. Figure S1: Particle size distribution curve of Co₃O₄ sample. Table S1: Elemental carbon content analysis in composite sample. Figure S2: XPS survey spectrum of LaMnO₃@C-Co₃O₄ composite sample. Table S2: Summary of XPS fit parameters. Figure S3: SEM images of LaMnO₃@C-Co₃O₄ composite electrode before (A) and after (B) chronoamperometry test.

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