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Two-Dimensional Mn-Co LDH/Graphene Composite towards High-Performance Water Splitting

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Abstract: The oxygen evolution reaction (OER) is a complex multi-step four-electron process showing sluggish kinetics. Layered double hydroxides (LDH) were reported as promising catalysts for the OER, but their low electrical conductivity restricts their widespread applications. To overcome this problem, a composite material containing Mn-Co LDH ultrathin nanosheet and highly conductive graphene was synthesized for the first time. Benefited from the high electrocatalytic activity and the superior charge transfer ability induced by these components, the new material shows superior OER activity. Used as the OER catalyst, a high current density of 461 mA cm⁻² at 2.0 V vs. RHE (reversible hydrogen electrode) was measured besides shows a low overpotential of 0.33 V at 10 mA cm⁻². Moreover, the new composite also shows a superior bifunctional water splitting performance as catalyst for the OER and HER (hydrogen evolution reaction) catalysts. Our results indicate that the presented material is a promising candidate for water splitting which is cheap and efficient.

Keywords: ultrathin structure; oxygen evolution reaction; graphene; two-dimensional; layered double hydroxide

1. Introduction

Growing energy consumption and global environmental concerns have attracted lots of interests in seeking clean and sustainable energy sources. In that field, electrocatalytic water splitting has been applied as an effective pathway to realize the conversion of electric energy and the production of hydrogen [1–15]. As a half reaction of the electrocatalytic water splitting, oxygen evolution reaction (OER) is a multi-step four-electron process and shows sluggish kinetics, thus an active catalyst is needed to lower the overpotential of the process [16–18]. Nowadays, noble metals and their oxides based on Ir and Ru are the state-of-art OER catalysts. However, their limited reserve and high price restrict their practical applications [19]. Thus, developing electrocatalysts with high catalytic activity and low price is significantly demanded.

Nowadays, the non-noble metal materials based on 3d transition metals, have been widely investigated and became the most potential alternatives for the noble metal catalysts attributed to

its good availability, low price, environmental friendliness and relatively high activity. Several kinds of catalysts such as transition metal oxides [20–27], hydroxides [3,10,28–31], phosphates [32,33] and sulfides [34–36] have been explored. In addition, the layered double hydroxides (LDH), which are composed of positively charged metal hydroxide layers with intercalated anions, have been regarded as potential catalysts for OER. Compared with unary metal hydroxides, the involvement of two or more transition metals is proved to be beneficial for improving the catalytic activity. The Ni-Fe LDH [10,37], Ni-Co LDH [38], and Ni-V LDH [39] have been investigated and shown better catalytic activity than $\text{Ni}(\text{OH})_2$ owing to the novel LDH structure. Furthermore, the ultrathin two-dimensional (2D) structure of LDH also allows it with fast diffusion of ions, which is believed to be important for increasing the OER efficiency [40]. However, the poor electrical conductivity of LDH restricts the proton-coupled electron transfer process and thus limits its practical applications in electrocatalysis.

In order to solve the problem, anchoring the LDH on a conductive substrate, such as carbonaceous materials or metal foams, to boost fast electron transport is considered to be highly effective. As an ideal 2D conductive material, graphene with its atomic thickness, chemical stability, large surface area, and good conductivity has been regarded as an excellent substrate for LDH [41,42]. In this respect, the combination of LDH with highly conductive graphene is expected to realize higher charge-transfer ability and achieve a superior water oxidation performance. Meanwhile, the strategy of integrating of nanosheets on graphene was also reported to tailor the distance between individual nanosheets, prevent the aggregation of the nanosheets and introduce extra interfaces at the interlayer areas to facilitate the electrolyte infiltration into the electrode [43]. These advantages could improve OER performance.

In spite of the electrical conductivity, the active sites of the electrode materials are another significant factor in OER performance. With the development of 2D ultrathin materials, their advantageous feature such as large specific surface area is beneficial for OER performance. For example, the Fe-Co oxide, Ni-Fe LDH, and Ni-Co LDH ultrathin nanosheets were synthesized and exhibited enhanced OER performances [44–46]. Attributed to the exposure of more active sites on the surface, the ultrathin structure could effectively promote the catalytic reaction. In addition, the low thickness should also reduce the charge transport pathway, thus improving OER performance.

Upon this view, the composite containing active ultrathin LDH and highly conductive graphene is assumed to be an ideal candidate to enhance OER performance. In this work, Mn-Co LDH/graphene composite (denoted as MnCo-G) with ultrathin structure was created for the first time. As expected, the composite achieves a high current density of 461 mA cm^{-2} at 2.0 V vs. RHE and shows a low overpotential of 0.33 V at 10 mA cm^{-2} . Moreover, the composite shows superior bifunctional water splitting performance as both OER and HER catalysts, thus exhibiting it as a highly active material for OER.

2. Results and Discussion

The ultrathin Mn-Co LDH nanosheets (denoted as MnCo) were obtained through a convenient room-temperature coprecipitation method. In order to investigate the resulting product, X-ray diffraction (XRD) was done as shown in Figure 1A. The diffraction peaks in the XRD pattern at 12° and 23° can be assigned to (003) and (006) facets of the LDH phase. The inset figure shows the crystal structure of the Mn-Co LDH with a typical layered arrangement. Figure 1B represents a transmission electron microscopy (TEM) image showing nanosheet with a size of ca. 100 nm and a clearly transparent contrast to the substrate can be identified, suggesting the ultrathin nature. Figure 1C,D are the high-resolution TEM (HRTEM) images for a nanosheet that an interplanar spacing of 0.17 nm in the lattice fringes, corresponding to the (012) facets. The selected area electron diffraction (SAED) pattern (inset of Figure 1D) shows a six-fold point pattern, further indicating the phase of Mn-Co LDH.

Figure 1. (A) X-ray diffraction (XRD) pattern of the Mn-Co layered double hydroxide (LDH) nanosheets; (B) Transmission electron microscopy (TEM) image of the Mn-Co LDH nanosheets; (C) High-resolution TEM (HRTEM) image of the Mn-Co LDH nanosheets; (D) corresponding selected area electron diffraction (SAED) of the Mn-Co LDH nanosheets.

For the purpose of improving the charge transfer ability of the material, the Mn-Co LDH was combined with the highly conductive graphene. Figure 2A shows the XRD pattern of the obtained composite. Two reflection peaks of the product at 12° and 23° can be designated as the layered reflection peaks of Mn-Co LDH. It is worthy to note that the peak at 26° can be assigned to the (002) peak of graphene. In order to confirm the presence of graphene, a Raman spectrum of the product was taken and shown in Figure 2B. Owing to the presence of D band and G band (located at 1347 and 1576 cm^{-1}) [47], the graphene component is further confirmed in the composite. The morphology and composition of the sample were further evaluated by the TEM. As shown in Figure 2C, the Mn-Co LDH nanosheets are evenly distributed on the graphene flakes, thus revealing the composite structure of the product. A successful hybridization benefits the electrostatic interaction between the LDH nanosheets and graphene sheets which arise from the residual oxygen-containing functional groups [48]. All these results show that an ultrathin Mn-Co LDH/graphene composite was obtained.

Figure 2. (A) XRD pattern of MnCo-G; (B) Raman spectrum; (C) TEM image of MnCo-G.

For purpose of evaluating the surface structure and chemical valence in the composite, the X-ray photoelectron spectroscopy (XPS) spectra of the product were collected. Figure 3A is the survey

spectrum, in which typical characteristic peaks of Mn, Co, and O elements can be recognized. Especially, the spectrum of Mn 2p shows peaks similar to those of MnOOH and Mn₂O₃, indicating the presence of Mn³⁺ in the product [49]. In Figure 3C, two peak components can be fitted under the Co 2p_{3/2} and Co 2p_{1/2}, indicating the existence of the Co²⁺ and Co³⁺ in the material [50]. Furthermore, Figure 3D shows the O 1s spectrum which represents the metal-oxygen bonds. The peak located at 531.5 eV is assigned to the OH[−] groups [51]. It is worthy to note that Co³⁺ could be oxidized to Co⁴⁺ which is considered as the active sites for OER. In addition, the Mn³⁺ could also tune the electronic structure of the LDH thus obtained an improved OER performance. The presence of Co³⁺ and Mn³⁺ is considered to be beneficial to OER process.

Figure 3. (A) X-ray photoelectron spectroscopy (XPS) survey spectrum, (B) high-resolution XPS spectrum of Mn 2p, (C) Co 2p and (D) O 1s for the MnCo-G sample.

It is worth noting that the composite structure hybridized by catalytically active Mn-Co LDH nanosheet and highly conductive graphene may significantly boost the OER process. In particular, the electroactive Mn-Co LDH nanosheet with ultrathin feature supplies a high surface area, thus increasing the number of active sites number and decreasing the transfer distance of the ions. Furthermore, graphene provides an increased electrical conductivity with a superior charge transfer efficiency. The ultrathin property of the composite could also efficiently reinforce the contact between the catalyst and the substrate [51]. Hence, the composite of Mn-Co LDH/graphene might be an effective catalyst for the water splitting.

For purpose of the investigation for OER performance of the MnCo-G in alkaline solution, the composite was uniformly coated onto a commercial glassy carbon electrode (GCE) for recording linear sweep voltammetry (LSV) curve in a standard three-electrode configuration. In addition, the MnCo LDH ultrathin nanosheets without graphene and the benchmarking RuO₂ catalyst were also tested as references. Figure 4A and Figure S1 shows the LVS curves of these samples. The Mn-Co LDH/graphene composite exhibits a small overpotential of 0.33 V to achieve an OER current density of 10 mA cm^{−2}, that value is much lower than the Mn-Co LDH nanosheet without graphene composition. Furthermore, the current density reaches 461 mA cm^{−2} at 2.0 V for the composite, which is not only higher than the Mn-Co LDH nanosheet but also higher than the benchmarking RuO₂. Apart from the low overpotential and high current density, a Tafel slope is used to evaluate the performance of the OER process. By plotting the overpotential versus log current as shown in Figure 4B. The Tafel

slope of MnCo-G is 48 mV decade⁻¹, that is lower than the MnCo LDH nanosheet (63 mV decade⁻¹), and even comparable to the noble metal catalyst, RuO₂ (42 mV decade⁻¹), indicating its facile reaction kinetics for OER catalysis. To prove the durability of MnCo-G, continuous CV cycling was conducted. As shown in Figure 4C, a negligible degradation of the activity is observed even after 1000 CV cycles, demonstrating the good stability for the MnCo-G composite.

Figure 4. (A) Linear sweep voltammetry (LSV) curves of the catalysts; (B) Corresponding Tafel slopes; (C) LSV curves after 1000 CV cycles for the MnCo-G electrode; (D) comparison of current achieved at the potential of 2.0 V vs. reversible hydrogen electrode (RHE) and overpotential for 10 mA cm⁻². All tests were conducted in 1.0 M KOH.

In order to highlight OER performance of the composite, the reported materials based on transition metal oxide and hydroxide were listed in Table 1. As shown, the MnCo-G owns a smaller overpotential and lower Tafel slope than most of the reported materials and is even comparable to the reported NiFe-LDH, thus confirming its superior OER performance [33,36,38,52–56].

Table 1. Comparison of oxygen evolution reaction (OER) performance with various transition metal oxide and hydroxide.

Materials	Electrolyte	Overpotential for 10 mA cm ⁻² /V	Tafel Slope/mV decade ⁻¹	Ref.
MnCo-G	KOH	0.33	48	This work
RuO ₂	1 M KOH	0.3	42	This work
Ni ₅ Mn-LDH-MWCNT	1 M KOH	0.35 (iR-corrected)	83	[52]
Co ₅ Mn-LDH-MWCNT	1 M KOH	0.3 (iR-corrected)	74	[52]
CoNi-LDH/Fe-PP-M	1 M KOH	0.32	53	[53]
CuCo ₂ O ₄ /N-rGO	1 M KOH	0.36	64	[54]
Co ₃ S ₄ @MoS ₂	1 M KOH	0.33	59	[36]
CoMoO ₄	1 M KOH	0.31	56	[55]
CoP	1 M KOH	0.36	66	[33]
CoFe LDH	0.1 M KOH	0.36	49	[56]
NiFe LDH	1 M KOH	0.33	41	[38]

Inspired by the superior OER catalytic activity, the catalytic performance for complete water splitting process was investigated by loading MnCo-G and MnCo onto a nickel foam (NF) substrate.

As depicted in Figure 5A,B, the MnCo-G/NF shows a higher current density and lower onset overpotential for both the OER and HER processes. Moreover, a two-electrode system with MnCo-G/NF used as anode and cathode was tested in 1 M KOH electrolyte. In Figure 5C, the MnCo-G sample shows a lower applied voltage at 60 mA cm^{-2} compared to the MnCo sample. The current density was very steady and maintained for at least 22 h (Figure S2). These data undoubtedly show the excellent water splitting performance of the obtained MnCo-G sample.

Figure 5. (A) OER and (B) HER polarization curves of MnCo-G and MnCo catalysts loaded onto nickel foam substrate; (C) full water splitting characteristics in a two-electrode configuration for the two samples; (D) schematic image for the full water splitting process.

In order to investigate the factors that influence the catalytic activity, the MnCo-G and MnCo LDH samples were loaded onto GCE to evaluate the electrochemical double-layer capacitance (C_{dl}) in Figure 6A,B. The higher C_{dl} value represents the larger electrochemically active surface area (ECSA) of the sample [57–59]. In Figure 6A and Figure S3, a current density from 1 to 9 mV s^{-1} was measured in a non-Faradic region, which can be plotted as a function of the sweep rate to evaluate the C_{dl} . As can be seen, the MnCo-G electrode exhibits a higher C_{dl} of 0.23 mF cm^{-2} than the MnCo electrode with 0.18 mF cm^{-2} , thus revealing an increased active area of the MnCo-G sample. This is attributed to the introduction of graphene which prevents the aggregation of the ultrathin nanosheets and increases the overall conductivity of the product, thus leading to an increased specific surface area. Furthermore, a larger C_{dl} means more ion accessible surface area and surface active sites for electrolyte permeation, which would enhance the electrocatalytic process. Furthermore, catalytic kinetics of MnCo and MnCo-G were estimated with electrochemical impedance spectroscopy (EIS, Figure 6C) to clarify the role of graphene. Compared to MnCo, the MnCo-G catalyst shows a smaller semicircle in the EIS which demonstrates a faster charge transfer. The impedance results obtained by fitting the equivalent circuit (Figure 6E) are tabulated in Figure 6D. The C_{dl} is the double-layer capacitance and R_s is the solution resistance. The R_p and R_3 are corresponding to the kinetics of the charge transfer process. The polarization resistance R_p is an indicator of the catalytic performance of the OER [52]. As can be seen, the MnCo-G composite shows lower R_p and R_3 thus indicating a higher charge transfer capability. This is due to the introduction of graphene which provides a high electrical conductivity thus accelerating the charge transport during the OER process. All the above data

confirm the advantageous composite structure of electroactive Mn-Co LDH and electrically conductive graphene in the water oxidation application.

Figure 6. (A) CVs of the Mn-Co LDH/graphene loaded onto GCE and measured at scan rates from 1 to 9 $mV s^{-1}$; (B) C_{dl} plots for the MnCo-G and MnCo sample; (C) Nyquist plots of Mn-Co LDH/graphene electrode and Mn-Co LDH; (D) summary of the fitted values of C_{dl} , R_s , R_3 , and R_p ; (E) the equivalent circuit for modeling impedance data. All the tests were conducted in 1M KOH.

The structural advantage based on ultrathin Mn-Co LDH nanosheets integrated on graphene sheets is summarized as follows. Firstly, graphene can serve as a highly conductive substrate for ultrathin Mn-Co LDH nanosheets, thus leading to an improved electrical conductivity boosting the charge transfer process. Meanwhile, the Mn-Co LDH integrated on graphene can potentially tailor the distance between individual nanosheets, prevent the aggregation of the nanosheets, and introduce extra interfaces at the interlayer areas to facilitate the electrolyte infiltration into the catalyst during the water splitting processes. Furthermore, owing to the high exposure of the catalytically active surface metal atoms, the ultrathin structure could also effectively promote the catalytic reaction. Altogether, the Mn-Co LDH/graphene composite is an effective catalyst for water oxidation.

3. Experimental Section

3.1. Syntheses of the Mn-Co LDH/Graphene Ultrathin Composition Structure

All the chemicals were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). Typically, 0.135 g $Co(NO_3)_2 \cdot 6H_2O$, 0.005 g $Mn(NO_3)_2 \cdot 4H_2O$, 0.07 g $NaNO_3$ and 0.09 g NH_4F were dissolved in 100 mL H_2O under N_2 protection at room temperature. Then 12.5 μL H_2O_2 (30 wt %) was dropped into the solution with vigorous stirring for 30 min. The addition of 35 mL NaOH solution (0.08 M) was used to adjust the pH of the solution to 10. The obtained suspension was aged overnight. Then it was isolated by centrifugation, washed with H_2O and anhydrous ethanol, and dried in ambient conditions. The obtained LDH material was dispersed into the N_2 saturated solution contained 1 M NaCl and 3.3 mM HCl, after vigorous stirring, the suspension was washed with water and ethanol

(saturated with N₂). 10 mg of graphene (Ningbo Institute of Industrial Technology, Ningbo, China) raw solution was added to 20 mL of N,N-Dimethylformamide (DMF) with ultrasonication for 12 h. After that, the dispersion was centrifuged with a low speed of 1000 rpm to get the exfoliated graphene. Then, 10 mg of LDH was dispersed into the deionized water and 2 mL of graphene suspension was added into the dispersion agent. After the ultrasonication and the following magnetic stirring, the suspension was collected, washed with water and dried in the vacuum oven. The content of graphene in the composite is about 9 wt %.

3.2. Materials Characterizations

The XRD measurements were taken on a Philips X'Pert Pro Super diffractometer (Amsterdam, The Netherlands) with Cu K α radiation ($\lambda = 0.154178$ nm). The HRTEM and corresponding SAED were taken at a JEOL-2010 (JEOL, Tokyo, Japan) operated at 200 kV. The Raman spectrum was tested at a LABRAM-HR (Horiba-Jobin Yvon, Edison, NJ, USA) Confocal laser Raman spectrometer. The X-ray photoelectron spectrometry (XPS) was performed on an ESCALAB 250Xi Instrument (ThermoFisher Scientific, Waltham, MA, USA).

3.3. Electrochemical Tests

The electrochemical tests were conducted in the three-electrode configuration using CHI660B potentiostat (Shanghai Chenhua Instrumental Co. Ltd., Shanghai, China). An Ag/AgCl electrode was taken as the reference electrode. 4 mg of catalyst and 25 μ L Nafion solution (Sigma Aldrich, St. Louis, MO, USA) were dissolved in a water/isopropanol solution (1 mL, 3:1 *v/v*). Then, the solution was further sonicated for 30 min. After that, 5 μ L of the catalyst ink suspension was coated onto a commercial glassy carbon electrode (GCE, 3 mm diameter, 0.07 cm²) with a mass loading of 0.285 mg cm⁻² and dried at room temperature. Then, the OER test was conducted in N₂-saturated 1 M KOH and 0.1 M KOH solution. LSV curve with a scan rate of 5 mV s⁻¹ was carried out in 1 M and 0.1 M KOH. CV was done in the voltage range of 0 to 1.0 V vs. Ag/AgCl at 5 mV s⁻¹ to test cycling stability. The EIS was done in the frequency range from 100 kHz to 1 Hz at an amplitude voltage of 5 mV. For overall water splitting, the catalysts were loaded onto the nickel foam substrate (2 mg cm⁻²) and tested in the 1 M KOH solution, with a Pt plate and carbon rod as the counter electrode for OER and HER test, respectively. The corresponding characterizations and properties of graphene and nickel foam are shown in Figures S4–S7 and Table S1.

4. Conclusions

Mn-Co LDH/graphene composite was synthesized for the first time in order to solve the problem of the low electrical conductivity of Mn-Co LDH. Due to the enhanced charge transfer ability, the Mn-Co LDH/graphene composite shows an excellent OER performance. As the OER catalyst, the composite achieves a high current density of 461 mA cm⁻² at 2.0 V and require a low overpotential of 0.33 V to reach an OER current density of 10 mA cm⁻². These data are not only better than the conventional electrode materials based on the transition metal oxides and hydroxides but also comparable to the state-of-the-art RuO₂. By the way, the composite also shows superior full water splitting performance when used as a bifunctional catalyst. In the end, this work reveals the promising catalytic properties of Mn-Co LDH/graphene composite material and expands the scope of non-noble metal catalysts with an excellent performance for the water oxidation reaction.

Supplementary Materials: The following are available online at <http://www.mdpi.com/2073-4344/8/9/350/s1>. Figure S1: LSV curves in 0.1 M KOH solution, Figure S2: I–t curve for the overall water splitting process, Figure S3: CVs of the Mn-Co LDH electrode measured in 1 M KOH at scan rates from 1 to 9 mV s⁻¹, Figure S4: XRD patterns of nickel foam (A) and graphene (B), Figure S5: The LSV curves of NF for the OER (A), HER (B) and overall water splitting (C), Figure S6: The LSV curve of graphene for the OER process, Figure S7: CVs of the graphene electrode measured in 1 M KOH at scan rates from 1 to 9 mV s⁻¹, (B) Current density as a function of scan rate for the graphene. (C) Nyquist plots of graphene electrode in 0.6 V, Table S1: The ICP results in graphene, nickel foam and electrolyte after stability test.

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