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Additional Information

Porous NiFe-LDH grown on graphene oxide towards highly efficient OER electrocatalysis

Jiyan Xie¹, Chen Li¹, Jinan Niu^{1,*}, Shenghui Zhang¹, Xuemei Ou¹, Peizhong Feng², Hermenegildo Garcia^{3,*}

¹School of Materials Science and Physics, China University of Mining and Technology, Xuzhou 221116, China

²Advanced Analysis and Computation Center, China University of Mining and Technology, Xuzhou 221116, China

³Instituto de Tecnologia Quimica CSIC-UPV, Universitat Politecnica de Valencia, Valencia 46022, Spain

*Corresponding author

jinan.niu@cumt.edu.cn (Jinan Niu)

School of Materials Science and Physics, China University of Mining and Technology, Xuzhou 221116, China

hgarcia@qim.upv.es (Hermenegildo Garcia)

Instituto de Tecnologia Quimica CSIC-UPV, Universitat Politecnica de Valencia, Valencia 46022, Spain

Abstract

Porous few-layer NiFe-layered double hydroxide (PLDH)/graphene oxide (GO) composite electrocatalysts (PLDH/GO) were successfully synthesized through a formamide-assisted coprecipitation method. The ratio of PLDH to GO was optimized, and the structure, morphology and electrochemical properties of samples were systematically investigated. The results show that PLDH with obvious porous and few-layer features uniformly grows on GO, and part of PLDH layer is perpendicular to GO layer and part parallel to GO layer. PLDH/0.1GO sample exhibits the best oxygen evolution reaction performance with the overpotential of 236 mV at 10 mA cm⁻², and the Tafel slope of 52 mV dec⁻¹, which is far superior to commercial IrO₂ and pure LDH in the same test condition.

Keywords: porous LDH; OER; graphene oxide; microstructure; nanocomposites

1. Introduction

Energy shortage and environmental pollution call for the emergence of new technologies towards clean energy generation [1]. Oxygen evolution reaction (OER) is a key process in water splitting for hydrogen generation [2,3]. However, this process involves a complex four electron transfer reaction requiring a high overpotential to achieve a meaningful reaction rate, which is considered to be the main bottleneck of developing good OER electrocatalysts [4,5]. IrO₂ and RuO₂ have been proved to be two most efficient OER catalysts in alkaline system, whose application, however, are greatly limited by low resource reserves and high price [6,7]. So, the development of non-noble metal electrocatalysts with high OER activity has become an urgent need in water splitting [8].

Among non-noble metal catalysts, layered double hydroxide (LDH) has attracted much attention due to their unique two-dimensional layered structure and high catalytic activity [9,10], NiFe-LDH composed of earth abundant elements is one of the most promising OER catalysts. However, the poor conductivity and lack of active sites limits the further applications of bulk NiFe-LDH as an OER electrocatalyst [11]. So far, many efforts have been devoted to improve OER performance of bulk NiFe-LDH (BLDH), e.g. doping additional element, constructing nanostructures, creating oxygen vacancy, or combining with conductive bases (carbon materials, etc.) [12-14]. Compared with BLDH, porous LDH and few-layer LDH can expose more active sites naturally resulting in higher electrocatalytic performance. Additionally, graphene-based materials are often used as additives or carriers in electrochemistry due to their large surface area and excellent conductivity [15].

Here, a facile one-step coprecipitation approach was employed to settle NiFe-based porous LDH (PLDH) with few layers on graphene oxide (GO) as OER catalyst, and the ratio of PLDH to GO in PLDH-GO composites (PLDH/GO) was optimized. The obtained sample shows significantly improved

OER performance compared with commercial IrO_2 and pure LDH.

2. Experimental

PLDH/GO composites were synthesized *via* a formamide-assisted coprecipitation strategy with GO as nucleation substrate of PLDH and conductive additive. The details of synthesis, characterization and electrochemical test can be found in the Supporting Information.

3. Results and discussion

X-ray diffraction (XRD) patterns of PLDH/GO with different GO contents are shown in Fig.1. For reference, XRD result of BLDH is also provided (Fig.S1), the strong and sharp diffraction peaks at $2\theta = 11.3^\circ, 22.7^\circ, 34.4^\circ, 59.1^\circ$, could be well indexed to (003), (006), (012) and (110) planes of NiFe-LDH (PDF#40-0215), respectively [16]. For pure PLDH, although the intensity of (003) and (006) peaks are very weak, (012) and (110) peaks can be still seen obviously, confirming successful synthesis of NiFe-LDH with few layers [17]. After adding GO, XRD patterns of samples are similar to that of pure PLDH and no GO signal is observed, as well in BLDH-GO composites (BLDH/GO) (Fig.S1), accounting for the low content of GO in the samples. The similar phenomenon also appears in Fourier transform infrared (FTIR) spectra results (Fig.S2), indicating that only a small amount of GO can greatly improve OER performance of LDH in our strategy, through analysis combined with the following OER results.

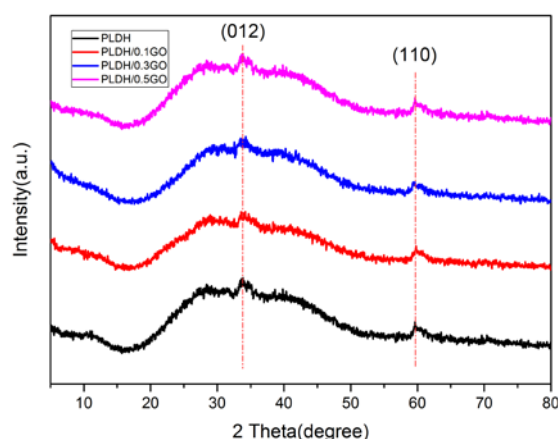


Fig.1 XRD patterns of PLDH/GO samples with various GO contents

The morphologies of GO and typical PLDH/0.1GO were characterized by transmission electron morphology (TEM) technology (Fig.2a and b). GO displays the large thin smooth layers in micron scale with several folds (Fig.2a), and can be thus easily distinguished in PLDH/GO composites. In PLDH/0.1GO, LDHs are uniformly distributed on GO surface, and the edges of LDHs like blades with the length of 100~200 nm are nearly perpendicular to GO layers (Fig.2b). High resolution TEM (HRTEM) reveals some twists existing at the edges (Fig.2c). The edges are about 1.5 nm thick and correspond to 2 layers of LDH sheets [17], further indicating the few-layer nature of PLDHs on GO. The lattice fringes in two different regions (red circle) near the fold, parallel to the GO layer, have the same spacing of 0.25 nm indexed to (012) plane, and almost the same evolution direction to these in vertical edge (yellow lines), suggesting that part of LDH layer grows parallel to GO layer, and part (i.e. edge) nearly perpendicular to GO layer.

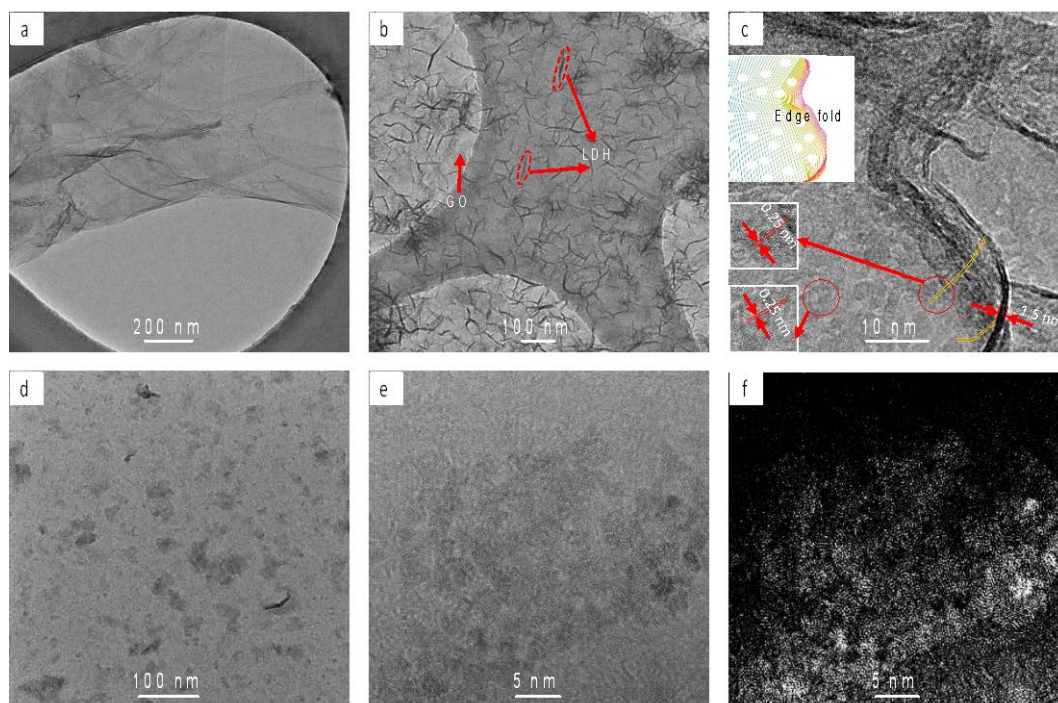


Fig. 2. TEM images of (a) GO, (b) PLDH/0.1GO, (c) HRTEM image of PLDH/0.1GO with a schematic diagram of a vertical edge with folds, (d and e) TEM images of pure PLDH with different

magnifications, (f) inverse color image of (e).

Pure PLDH displays the uniformly distributed nanoparticles with the lateral size of several to tens of nanometers (Fig.2d). Enlargement of a randomly selected particle reveals porous characteristics of LDH prepared by the formamide-assisted coprecipitation method [17] (Fig.2e), which can be further confirmed by the black and white contrast in the reverse color image (Fig.2f). Actually, LDHs in PLDH/0.1GO also exhibit the similar porosity (part parallel to GO layer, Fig.2c). Compared to pure PLDH, LDH in PLDH/0.1GO has the larger size indicating that the addition of GO can cause heterogeneous nucleation and growth of LDH, and eventually lead to the morphology of LDH partially parallel and partially perpendicular to GO layer.

OER activity of as-prepared PLDH/GO catalysts were investigated by linear sweep voltammetry (LSV) polarization curves (Fig. 3). Pure PLDH exhibits an overpotential of 310 mV at the current density of $10 \text{ mA}\cdot\text{cm}^{-2}$ (Fig.3a). After settling PLDH on GO layers, OER performance of obtained PLDH/GO hybrids was obviously improved. PLDH/0.1GO with 0.1% GO shows the best OER activity with an overpotential of 236 mV at $10 \text{ mA}\cdot\text{cm}^{-2}$. Increasing GO content can cover some active sites of LDH, and/or aggregate by themselves leading to reduced utilization in hybrids. Therefore, PLDH/0.3GO and PLDH/0.5GO show slightly increased overpotential, 265 and 286 mV, respectively. All PLDH/GO hybrids have the better OER performance than commercial IrO_2 . For comparison, BLDH/GO hybrids were also prepared. It shows that OER performance of all BLDH/GO hybrids is higher than that of pure BLDH, but significantly lower than PLDH/GO and even pure PLDH (Fig.S3).

OER kinetics of samples is investigated by the Tafel slope. Generally, a smaller Tafel slope represents a more favorable reaction process. PLDH/0.1GO shows the smallest Tafel slope of 52 mV dec^{-1} (Fig.3c) confirming excellent OER performance, compared with pure PLDH and IrO_2 . In the

electrochemical active surface area (ECSA) measurement, PLDH/0.1GO exhibits the larger value of 0.0102mF cm^{-2} than other composites (Fig.3d), suggesting more active sites exposed [18].

Electrochemical impedance spectroscopy (EIS) was further measured to study the electron transfer kinetics during OER process. PLDH/0.1GO exhibits the smallest semicircular radius in the Nyquist plots, corresponding to high charge transfer rate (Fig.3e) [6]. Several reasons can account for the excellent OER kinetics of PLDH/GO composites: first, the in-site growth of PLDH on GO surface produces a close contact between LDH layers and conductive GO, facilitating quick electro transfer cross the interface; second, PLDHs are uniformly distributed on GO surface to greatly reduce the stacking of PLDH sheets and expose more active sites; third, the novel morphology of hybrids with LDH layer partially parallel and partially perpendicular to GO layer can help more LDH to react with electrolyte; the last, the porous and few-layer structure of PLDH generates numerous edge sites bringing PLDH/GO the essential improvements of OER activity that is distinct from simple hybrid between GO and common LDH.

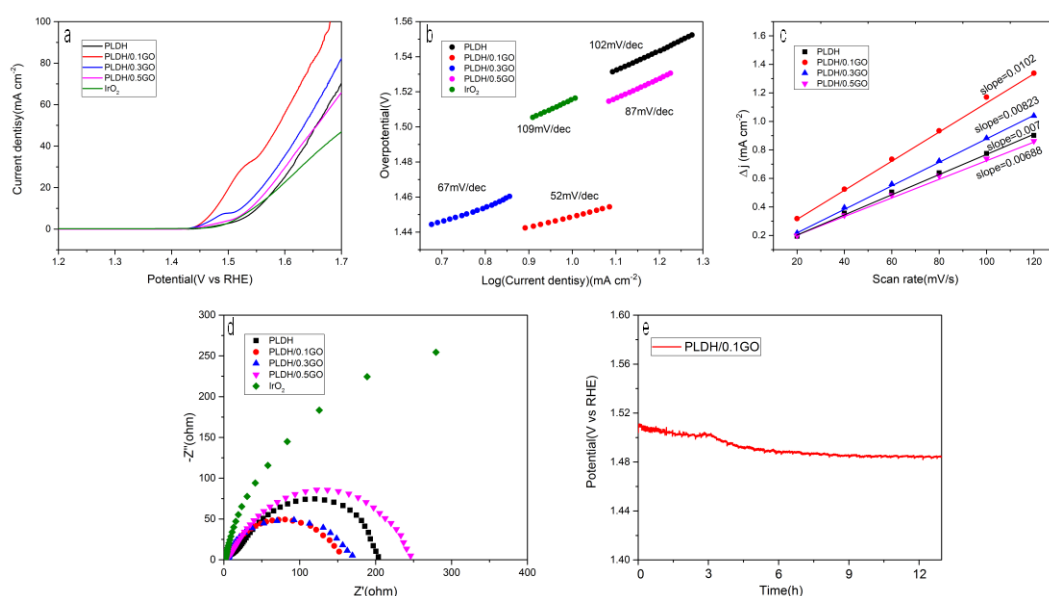


Fig. 3. (a) LSV curves, (b) Tafel plots, (c) Charge current density difference (Δj) plotted against scan

rate, (d) EIS spectra for PLDH/GO with various GO contents, and (f) Current-time curve for

PLDH/0.1GO.

Moreover, overpotential versus time tests were performed at 10mA cm^{-2} to test the electrocatalytic stability of PLDH/0.1GO. The result displays the OER activity of PLDH/0.1GO could be maintained for a test period of 13 h, indicating good stability of PLDH/0.1GO composite in water splitting application.

3. Conclusions

In this work, PLDH/GO composites were successfully synthesized as the high efficient OER catalyst. LDHs in composites exhibit obvious porous and few-layer features, and part of LDHs grow perpendicular to GO layer and part grow parallel to GO layer. PLDH/0.1GO with 0.1% GO has the best OER performance with the overpotential of 236 mV at 10 mA cm^{-2} , and the Tafel slope of 52 mV dec^{-1} . The work provides a new avenue for the development of non-noble metal based electrocatalysts towards the clean energy production.

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References

- [1] J. Niu, J. Albero, P. Atienzar, H. Garcia, *Adv. Funct. Mater.* 30(15) (2020) 1908984.
- [2] P.G. Bruce, S.A. Freunberger, L.J. Hardwick, J.M. Tarascon, *Nat. Mater.* 11 (2011) 19–29.
- [3] J. Huang, Y. Zhang, Y. Ding, *ACS Cat.* 7 (2017) 1841-1845.
- [4] M.T. Koper, *J. Electroanal. Chem.* 660 (2011) 254–260.
- [5] M. W. Kanan, D. G. Nocera, *Science* 321 (2008) 1072–1075.

- [6] G. Shi, C. Yu, Z. Fan, J. Li, M. Yuan, ACS Appl. Mater. Interfaces 11(3) (2018) 2662-2669.
- [7] J. Shen, P. Zhang, R. Xie, L. Chen, M. Li, J. Li, B. Ji, Z. Hu, J. Li, L. Song, Y. Wu, X. Zhao, ACS Appl. Mater. Interfaces 11(14) (2019) 13545-13556.
- [8] Y. K. Zhang, C. Q. Wu, H. L. Jiang, Y. X. Lin, H. J. Liu, Q. He, S. G. Chen, T. Duan, L. Song, Adv. Mater. 30 (2018) 1707522.
- [9] Q. Wang, D. O. Hare, Chem. Rev. 112 (2012) 4124-4155.
- [10] P. F. Liu, S. Yang, B. Zhang, H. G. Yang, ACS Appl. Mater. Interfaces 8 (2016) 34474-34481.
- [11] R. Liu, Y. Y. Wang, D. D. Liu, Y. Q. Zou, S. Y. Wang, Adv. Mater. 29 (2017) 1701546.
- [12] G. D. Shi, L. Yu, X. Ba, X. Z. Zhang, J. Q. Zhou, Y. Yu, Dalton Trans. 46 (2017) 10569-10577.
- [13] R. Ruoff, Graphene: calling all chemists, Nat. Nanotechnol. 3 (2008) 10.
- [14] M. Gong, Y. Li, H. Wang, Y. Liang, J. Z. Wu, J. Zhou, J. Wang, T. Regier, F. Wei, H. Dai, J. Am. Chem. Soc. 135 (2013) 8452.
- [15] Y. R. Xue, Z. C. Zuo, Y. J. Li, H. B. Liu, Y. L. Li, Small 13 (2017) 1700936.
- [16] X.Q. Han, N. Suo, C. Chen, Z.H. Lin, Z.Y. Dou, X.Q. He, L.L. Cui, Int. J. Hydrogen Energy 44 (2019) 29876-29888.
- [17] X. Zhang, Y. Zhao, Y. Zhao, R. Shi, G.I.N. Waterhouse, T. Zhang, Adv. Energy Mater. 9(24) (2019) 1900881.
- [18] C. Liang, P. Zou, A. Nairan, Y. Zhang, J. Liu, K. Liu, S. Hu, F. Kang, H. Fan, C. Yang, Energy Environ. Sci. 13 (2020) 86-95.