Hierarchical 3D Architectured Ag Nanowires Shelled with NiMn-Layered Double Hydroxide as an Efficient Bifunctional Oxygen Electrocatalyst

Soressa Abera Chala,[a,c] Meng-Che Tsai,*[b,c] Wei-Nien Su,*[b,c] Ting-Shan Chan,[e] Jyh-Fy Lee,[e] Hongjie Dai,[d] and Bing-Joe Hwang*[a,b,c,e]

[a]*NanoElectrochemistry Laboratory, Department of Chemical Engineering, National Taiwan University of Science and Technology, Taipei 106, Taiwan.*

[b]*NanoElectrochemistry Laboratory, Graduate Institute of Applied Science and Technology, National Taiwan University of Science and Technology, Taipei 106, Taiwan*

[c]*Sustainable Energy Development Center, National Taiwan University of Science and Technology, Taipei 106, Taiwan*

[d]*Department of Chemistry, Stanford University, Stanford, California 94305, United States*

[e] *National Synchrotron Radiation Research Center, Hsin-Chu, 30076, Taiwan*

[*]*Corresponding Authors: E-mail: bjh@mail.ntust.edu.tw (BJ Hwang);wsu@mail.ntust.edu.tw (WN Su); and snowild0326@gmail.com (MC Tsai)*

ABSTRACT: Promising approach to develop a highly active, low-cost, and durable electrocatalysts for bifunctional oxygen reduction/evolution reaction (ORR/OER) is a grand challenge in water splitting and metal-air batteries. Herein, we report a hierarchical 3D NiMn-layered double hydroxide (NiMn-LDHs) shells grown on conductive silver nanowires (Ag NWs) cores as efficient, low cost and durable bifunctional electrocatalysts for metal-air batteries. The hierarchical 3D architectured Ag NW@NiMn-LDHs catalysts exhibit superb OER/ORR activities in alkaline condition. X-ray absorption spectroscopy (XAS), X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM), and other characterization techniques were employed to investigate and offer a comprehensive insight toward the superb OER/ORR activities of the hybrid materials. The outstanding bifunctional activities of Ag NW@NiMn-LDHs are essentially attributed to increasing both site activity and site populations. The synergistic contributions from the hierarchical 3D open-pores structure of the LDHs shells, improved electrical conductivity and small thickness of the LDHs shells are associated with more accessible site populations. Moreover, the charge transfer between Ag cores and metals of LDHs shells, and the formation of defective and distorted sites strongly enhance the site activity. Thus, Ag NW@NiMn-LDH hybrids exhibit 0.75 V overvoltage difference between ORR and OER with excellent durability for 30 h, demonstrating the distinguished bifunctional electrocatalyst reported to date. Interestingly, the home-made rechargeable Zn-air battery using the hybrid catalyst as the air electrode exhibits the charge-discharge voltage gap of ~0.77 V at 10 mA cm^{-2} and shows excellent cycling stability. Thus, the concept of the hierarchical 3D architecture of Ag NW@NiMn-LDHs considerably advances the practice of LDHs towards metal-air batteries and oxygen electrocatalyst.

KEYWORDS: Oxygen electrocatalyst, vacancy defects, hierarchical core-shell nanostructure, silver nanowires, layered double hydroxides

Introduction

The oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) are the key electrode reactions in rechargeable metal-air batteries.[1] However, the sluggish kinetics of ORR/OER leads to high overpotential, low efficiency, and considerable energy loss of the devices.[2] The preeminent catalyst known to date for ORR is Pt-based material, while IrO_2 and RuO_2 are the OER benchmark catalysts, but their resource is not sustainable.[3] Consequently, the utilization of highly efficient electrocatalysts is rapidly needed to reduce

the energy loss that is essential in energy conversion technologies. Recently, Ni-based layered double hydroxides (LDHs) appeared as an efficient OER catalysts due to their ease of scalability and abundant source, however they are ORR inactive. One fruitful strategy to improve the bifunctional activity of LDHs is integrating LDHs with ORR active and conductive substrates. Herein, we successfully developed a hierarchical 3D architecture NiMn-LDHs nanosheets shells grown on conductive Ag NWs cores, denoted as Ag NW@NiMn-LDHs. The hybrid material exhibited superior OER/ORR activity.

Experimental sections

Ag NW@NiMn-LDHs was prepared via hydrothermal methods as shown in Fig. 1.

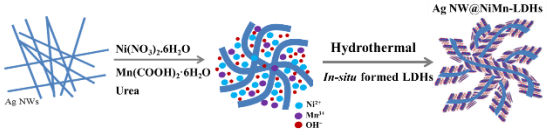

Fig. 1. Schematic fabrication process of hierarchical 3D architectured Ag NW@NiMn-LDH hybrids.

Results and discussions

The electrocatalytic properties (Fig. 2) show that the hierarchical 3D architectured Ag NW@NiMn-LDH hybrids exhibit a much higher OER/ORR activity with the lower onset potential than the pristine NiMn-LDHs (OER active) and commercial Pt/C (ORR benchmark). The significantly enriched bifunctional performance of Ag NW@NiMn-LDHs(1:2) is attributed to its optimal structural characteristics for electrocatalysis including less dense packing of NiMn-LDHs nanosheets, highly exposed coordinatively unsaturated metal active sites (as shown in Fig. 3), improved electrical conductivity and a combination of hierarchical 3D open-pore nanostructure of the LDHs shells.

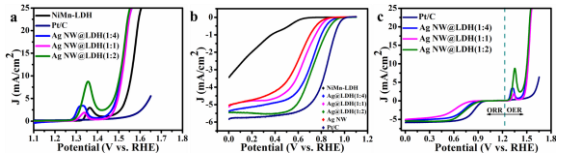

Fig. 2. (a) OER (b) ORR (c) OER/ORR LSV curves the hierarchical Ag NW@NiMn-LDH hybrids and commercial Pt/C.

Thus, the electronic effect between Ag NWs core and metals in LDHs shell has been tuned the site activity and synergistically promoted the ORR/OER activity.

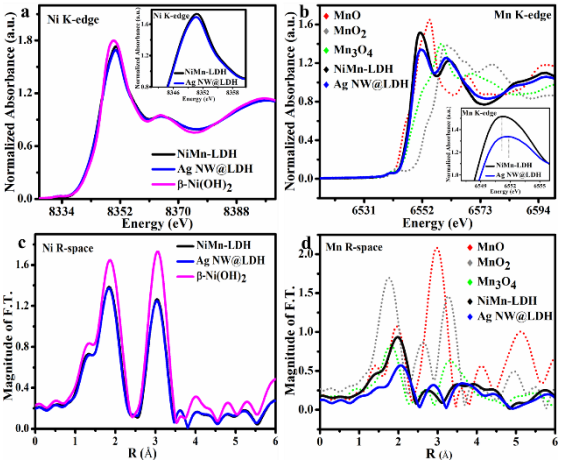

Fig. 3. (a) Ni K-edge (b) Mn K-edge XANES spectra, (c) FT-EXAFS spectra of Ni K-edge, (d) FT-EXAFS spectra of Mn K-edge for NiMn-LDHs, Ag NW@NiMn-LDHs and commercial samples.

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