Electronically coupled layered double hydroxide/MXene quantum dot metallic hybrids for high-performance flexible zinc–air batteries

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Funding information
Ministry of Education, Grant/Award Number: NRF-2019R1A6A1A10073079; National Research Foundation of Korea, Grant/Award Numbers: 2020M2D8A2070866, 2020R1A3B2079803

Abstract
Precise control of the local electronic structure and properties of electrocatalysts is important for enhancing the multifunctionality and durability of electrocatalysts and for correlating the structure/chemistry with the catalytic properties. Herein, we report electronically coupled metallic hybrids of NiFe layered double hydroxide nanosheet/Ti3C2 MXene quantum dots deposited on a nitrogen-doped graphene surface (LDH/MQD/NG) for high-performance flexible Zn–air batteries (ZABs). As verified from the Mott–Schottky and Nyquist plots, as well as spectroscopic, electrochemical, and computational analyses, the electronic and chemical coupling of LDH/MQD/NG modulates the local electronic and surface structure of the active LDH to provide metallic conductivity and abundant active sites, leading to significantly improved bifunctional activity and electrocatalytic kinetics. The rechargeable ZABs with LDH/MQD/NG hybrids are superior to the previous LDH-based ZABs, demonstrating a high power density (113.8 mW cm−2) and excellent cycle stability (150 h at 5 mA cm−2). Moreover, the corresponding quasi solid-state ZABs are completely flexible and practical, affording a high power density of 57.6 mW cm−2 even in the bent state, and in real-life operation of tandem cells for powering various electronic devices.

KEYWORDS
2D quantum dots, flexible battery, metallic hybrids, oxygen electrochemistry, Zn–air battery

1 | INTRODUCTION

Rechargeable zinc–air batteries (ZABs) are considered as promising electrochemical energy storage devices owing to their safety, low cost, and high theoretical energy density.1–3 Nevertheless, their industrial applications are severely hindered by the sluggish electrocatalytic kinetics of the oxygen evolution reaction (OER) and oxygen reduction reaction (ORR) during the charge/discharge process.4–7 Ir/Ru- and Pt-based materials are recognized

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as efficient electrocatalysts for the OER and ORR, respectively, but their high cost and poor stability greatly limit their implementation.\textsuperscript{8–10} Moreover, these noble metal-based electrocatalysts suffer from inferior bifunctionality and sluggish kinetics for reverse reactions involved in the charge/discharge cycles of rechargeable ZABs.\textsuperscript{11} Therefore, extensive efforts have been made to develop low-cost and highly efficient bifunctional oxygen electrocatalysts for rechargeable ZABs.\textsuperscript{12–15} However, achieving high performance and flexibility of rechargeable ZABs is quite challenging, despite great potential of ZABs in flexible and wearable electronics.

Two-dimensional (2D) nanomaterials are considered as promising electrocatalysts for energy conversion and storage applications owing to their abundant exposed active sites, large surface area, and unique surface chemistry. 2D Ni- and/or Fe-containing layered double hydroxides (NiFe-LDH) exhibit remarkable catalytic activity for the OER\textsuperscript{16–21} but are limited by their low ORR performance, which restricts the rechargeability of ZABs. Integrating heteroatom-doped carbon-based materials is an effective strategy to endow NiFe-LDH-based electrocatalysts with bifunctional activities.\textsuperscript{22–26} Despite the progress, the intrinsically low conductivity and inefficient activity utilization of semiconducting NiFe-LDH hamper electron transfer and restrict optimization of the catalytic activity and kinetics.\textsuperscript{27,28} Modulating the electronic structure and intrinsic conductivity of NiFe-LDH is highly desirable for resolving this problem and improving the rechargeability of ZABs. Owing to their hydrophilic surface and metallic conductivity, 2D MXenes can modify the properties of LDH-based materials.\textsuperscript{29–32} Moreover, the transformation of 2D MXene into 0D MXene quantum dots (MQDs) provides new functionality and modulates the electronic properties owing to the quantum confinement effect and surface-terminated functional groups in the latter.\textsuperscript{33,34} Therefore, the chemical coupling of NiFe-LDH with MQDs has been proposed an approach for modulating the electronic structure and improving the electrocatalytic properties of NiFe-LDH.

Herein, we report electronically coupled metallic hybrids of NiFe-LDH nanosheet/Ti$_3$C$_2$ MXene quantum dots deposited on the surface of nitrogen-doped graphene (LDH/MQD/NG). The composite provides bifunctional ORR/OER and high electrocatalytic activities and durabilities as high-performance flexible ZAB cathodes. The chemical and electronic coupling of LDH/MQD/NG can modulate the local electronic structure and electrical conductivity of the active LDH to significantly improve the bifunctional activity and electrocatalytic kinetics. Consequently, the rechargeable ZAB employing the LDH/MQD/NG hybrids delivers a high power density (113.8 mW cm$^{-2}$) and excellent cycle stability (150 h at 5 mA cm$^{-2}$), exceeding those of previous LDH-based ZABs. More importantly, these ZABs are highly flexible and durable, as confirmed by the high power density (57.6 mW cm$^{-2}$) in the bent state and in the real-life operation of tandem cells to power electronic devices (i.e., timer and mini electric fan).

## RESULTS AND DISCUSSION

As illustrated in Figure 1(A), the LDH/MQD/NG hybrids were synthesized by urea-assisted co-precipitation of Ni$^{2+}$ and Fe$^{2+}$ in the presence of MQDs and NG. First, MQDs were prepared by the top-down conversion of MXene, as previously reported.\textsuperscript{34} The UV-visible spectrum of the MQDs shows an clear absorption peak at 262 nm, with a tail extending to the visible range (Figure S1a). The pale-yellow color of the MQDs is shown in the inset of Figure S1a. As shown in the transmission electron microscopy (TEM) image, the as-converted MQDs exhibited an almost spherical shape with an average diameter of 5 nm (Figure S1b). The high-resolution TEM (HR-TEM) image shows a lattice spacing of 2.66 Å (inset in Figure S1b), corresponding to the (0010) facet of hexagonal crystalline MXene.\textsuperscript{21}

The structure and morphology of the LDH/MQD/NG hybrids were investigated using field-emission scanning electron microscopy (FE-SEM), TEM, and atomic force microscopy (AFM). The LDH/MQD/NG hybrids consisted of flower-shaped LDH/MQDs assembled by the nanosheets, which were anchored onto the NG surface, demonstrating a three-dimensional (3D) hierarchical porous structure (Figure 1(B)). The 3D porous LDH/MQD/NG hybrids have a large specific surface area (141.2 m$^2$ g$^{-1}$), with a pore volume of 0.82 m$^3$ g$^{-1}$, as evaluated from the nitrogen adsorption–desorption isotherm (Figure S2). This 3D open-porous structure favors mass/ion transport and facile access to the active sites. The microscopic structures of the LDH/MQD/NG hybrids were further investigated using TEM and AFM. As shown in Figure 1(C), the flower-shaped LDH/MQD hybrids are intimately coupled with NG, which is consistent with the FE-SEM results. The thickness of the corresponding LDH nanosheets was approximately 8 nm (Figure 1(D)), whereas MQDs with a size of 5 nm were decorated onto the LDH surface, indicating no change in the size of the MQDs during synthesis (Figure 1(E)). The HR-TEM images show well-resolved lattice spacings of 2.66 Å (Figure 1(E1)) and 1.96 Å (Figure 1(E2)), corresponding to the (0010) and (018) crystalline planes of the MXene and LDH phases, respectively. Moreover, the uniform distribution of Ni, Fe, Ti, and O species on the NG surface was visualized by elemental mapping analyses (Figure 1(F)). For comparison, NiFe-LDH/NG...
(LDH/NG) hybrids with a structure similar to that of
LDH/MQD/NG were synthesized by following the same
process in the absence of MQDs (Figure S3).

The crystalline, chemical, and electronic structures of
the LDH/MQD/NG hybrids, together with LDH/NG as a
reference, were analyzed using X-ray diffraction (XRD),
Raman spectroscopy, and X-ray photoelectron spectroscopy (XPS). The XRD peaks of LDH/NG at 11.5°, 23.2°, 34.4°, and 38.9° (Figure 1(G)) were indexed to the (003), (006), (012), and (015) facets of the LDH characteristic phase, respectively, while the peak at 26.6° was assigned to the (002) plane of NG. In the case of the LDH/MQD/NG hybrids, the two additional peaks at 18.4° and 33.6°, corresponding to the (006) and (0010) planes of the MXene phase, confirm the presence of crystalline MQDs. The Raman spectra of the LDH/NG and LDH/MQD/NG hybrids (Figure 1(H)) both exhibit two main peaks of the D and G bands of NG at approximately 1342 and 1580 cm⁻¹, and three relatively weaker peaks in the range of 400–600 cm⁻¹ due to the M=O–M and M=OH (M = Ni and Fe) vibrations. The M=OH vibration of the LDH/MQD/NG hybrids is slightly weaker than that of LDH/NG, with a red-shift of 12 cm⁻¹, which indicates electronic coupling of the MQDs and LDH nanosheets. This coupling is supported by the XPS results (Figure 1(I)). The Ni 2p XPS spectra of pristine LDH/NG show signals of two distinct Ni species, corresponding to Ni²⁺ (2p₃/₂ peak at 855.5 eV and 2p₁/₂ peak at 873.3 eV) and Ni³⁺ (2p₃/₂ peak at 857.5 eV and 2p₁/₂ peak at 875.5 eV). The Fe 2p spectra were fitted to the Fe 2p₃/₂ and Fe 2p₁/₂
states, with signals centered at 712.7 and 725.9 eV, respectively, suggesting that the Fe$^{3+}$ is the main Fe species.\textsuperscript{41} Compared to LDH and LDH/NG, the relative fraction of Ni$^{3+}$ to Ni$^{2+}$ was much higher in the LDH/MQD/NG hybrids (Table S1). Furthermore, new Fe 2p peaks emerged at 714.9 and 728.2 eV in the XPS profile of the LDH/MQD/NG hybrids, corresponding to Fe$^{4+}$.\textsuperscript{42,43} These results indicate modulation of the electronic structure of the Ni and Fe cations in the LDH/MQD/NG hybrids, arising from the chemical interactions between the MQDs and LDH. Moreover, NG can modify the local electronic structure of the Ni cations (Figure S4 and Table S1), plausibly owing to the chemical interactions between LDH and NG (C–N–Ni–O).\textsuperscript{16} The C 1s XPS spectra of the LDH/NG and LDH/MQD/NG hybrids were deconvoluted into four peaks (Figure S5a): C= (284.6 eV), C=N (285.6 eV), C=N (286.4 eV), and C=O (287.2 eV).\textsuperscript{44–47} Additionally, the N 1s XPS spectra of the LDH/MQD/NG hybrids were fitted to pyridinic N (398.3 eV) and pyrrolic N (399.8 eV) in the NG structure, favoring the electrocatalytic ORR activity (Figure S5b).\textsuperscript{45,48,49}

The coupling effect of MQDs on the electronic conductivity of the LDH nanosheets was studied using a two-point probe method and electrochemical impedance spectroscopy (EIS). To rule out the effect of NG, LDH/MQDs were also characterized. The two-point probe cell is schematically illustrated in Figure 2(A), and the corresponding $I$–$V$ plots are shown in Figure 2(B). No current response was detected for pristine LDH, confirming the insulating nature of LDH in the applied potential range. However, the metallic features of the LDH/MQD hybrids were confirmed, demonstrating a linear increase in the current response with respect to the applied potentials. Moreover, EIS measurements further confirmed the improved electrical conductivity of the LDH/MQD hybrids (Figure S6). Despite the metallic behavior of the pristine MQDs (Figure S7), the physical mixture of LDH and MQDs (LDH + MQDs) was nearly

![Figure 2](image_url)
nonconductive (Figure 2(B)). To obtain more electronic information, Mott–Schottky plots were collected to investigate the flat band potential \( (E_{FB}) \) and carrier density, which were derived from the intercept and slope, respectively. The \( E_{FB} \) value (Figure S8) of the pristine MQDs was estimated to be \(-0.48 \) V versus the reversible hydrogen electrode (VRHE). As shown in Figure 2(C), a negative shift in the \( E_{FB} \) value was observed for the LDH/MQD hybrids \((-0.46 \) VRHE) compared to that of the pristine LDH \((-0.03 \) VRHE) and LDH + MQDs \((-0.35 \) VRHE). Moreover, the slope of the Mott–Schottky plot for the LDH/MQD hybrids was smaller than that of the pristine LDH and LDH + MQDs, demonstrating a higher carrier density of the former. These results indicate that the metallic characteristics and improved electronic conductivity of the LDH/MQD hybrids are associated with the electronic and chemical coupling effects of the MQDs.

To gain atomistic insight into this coupling effect between the LDH and MQDs, first-principles calculations based on the density function theory (DFT) approach were performed to determine the geometric structure models of pristine LDH and LDH/MQD (Ni:Fe = 3:1) (Figure S9). The density of states (DOS) and projected density of states (PDOS) of the pristine LDH confirm that the M-d (M = Ni and Fe) and O-p orbitals are split by the ligand field into several discontinuous energy states above the Fermi energy level, with an energy band gap of \(-0.8 \) eV, which indicates the semiconducting nature and limited electronic transport. In contrast, the pristine MQD exhibits typical metallic features (Figure S10), consistent with the electrical characterization results (vide supra). The interfacial distance in the LDH/MQD hybrid was calculated to be approximately 1.84 Å (Figure S9b), indicating coupling interaction between the LDH and MQD. Mulliken charge analysis revealed electron transfer (0.73 e per unit cell) from LDH to MQD (Figure 2(H)), resulting in a higher positive charge on the Ni and Fe species compared to those in the pristine LDH, which is in good agreement with the XPS results (vide supra). Furthermore, coupling with MQD can trigger the Fermi energy level of the LDH to deepen into the O-p band. Compared to pristine LDH, the DOS and PDOS of the LDH/MQD hybrids were enhanced at the Fermi energy level (Figure 2(F,G)), revealing the improved electronic conductivity and metallic behavior owing to the modulated electronic structure.

The electrocatalytic OER and ORR activities of the LDH/MQD/NG hybrids were investigated using a three-electrode cell in O2-saturated 0.10 M KOH solution. The bare NG, LDH/NG, pure MQDs, mixture of LDH/NG + MQDs, commercial Pt/C, and IrO2 + Pt/C catalysts were compared under the same conditions. The pristine NG had no measurable anodic current, suggesting that the high OER activity was solely due to the LDH/MQD catalyst (Figure S11). As shown in Figure 3(A), the LDH/MQD/NG hybrids displayed higher OER activity than pristine LDH/NG. A lower potential of 1.50 VRHE for the LDH/MQD/NG hybrids compared to that of LDH/NG (1.52 VRHE) was required to deliver the same current density of 10 mA cm\(^{-2}\). Faster OER kinetics of the LDH/MQD/NG hybrid electrode was confirmed, demonstrated by the smaller Tafel slope of 57 mV dec\(^{-1}\) compared to 60 mV dec\(^{-1}\) for LDH/NG (Figure 3(B)). Considering that the OER activity of the pristine MQDs was not measurable (Figure 3(A)), the electrocatalytic OER activity and kinetics of the LDH/MQD/NG hybrids were improved by modulating the electronic structure LDH/NG via coupling with the MQDs. Similar results could be also observed in a comparison to LDH/MQDs and pristine LDH catalysts (Figure S12). The modulated electronic structure of the LDH/MQD/NG hybrids was further confirmed using cyclic voltammetry (CV) (Figure S13). The Ni\(^{2+}/\)Ni\(^{3+}\) redox wave of the LDH/MQD/NG hybrids was anodically shifted with respect to that of LDH/NG, indicating that Ni\(^{2+}\) oxidation becomes difficult, as supported by the increased fraction of Ni\(^{3+}\) species in previous studies (Figure 1(I) and Table S1). Moreover, faster charge transfer was indicated by the smaller charge transfer resistance of the LDH/MQD/NG hybrids compared to that of LDH/NG (Figure S14). In addition to the OER activity, long-term stability was achieved for the LDH/MQD/NG hybrids, as indicated by the slight decay (7.7%) of the current density after 10 h of continuous testing and almost negligible degradation in the polarization curves after 5000 CV cycles (Figure 3(C)). Upon repeated OER cycling, the flower-shaped LDH/MQD hybrids remain uniformly and intimately attached to the NG surface, while the morphology was well preserved (Figure S15).

To evaluate the bifunctional activity of the LDH/MQD/NG hybrids, the ORR activity was also characterized by CV analysis in N\(_2\)/O\(_2\)-saturated 0.1 M KOH solution. No clear redox peak was observed in the N\(_2\)-saturated solution, while the oxygen reduction peak was evident in the O\(_2\)-saturated solution. No clear redox peak was observed in the N\(_2\)-saturated solution, while the oxygen reduction peak was evident in the O\(_2\)-saturated solution. The corresponding Koutecky–Levich (K–L) plots were analyzed to explore the ORR kinetics (Figure S16). All the K–L plots of the LDH/MQD/NG hybrids were linear in the potential range of 0.40–0.55 V, indicating the first-order reaction.
The average electron transfer number ($n$) of the LDH/MQD/NG hybrids was estimated to be 3.94, which is close to that of Pt/C (3.95) and IrO$_2$ + Pt/C (3.88 V), and larger than that of LDH/NG (3.62), suggesting a predominant four-electron reduction pathway. The superior ORR kinetics of the LDH/MQD/NG hybrids was confirmed by the smaller Tafel slope of 81 mV dec$^{-1}$ (Figure 3(F)). Analogous to the case in the OER process, the ORR activity and kinetics of the LDH/MQD/NG hybrids were improved by modulating the electronic structure and increasing the electrical conductivity. In addition to the enhanced activity, the ORR stability is an important parameter for practical applications. As shown in Figure 3(G), the LDH/MQD/NG hybrids exhibited 98.8% current retention after 10 h of operation, exceeding 84.3% for the commercial Pt/C catalyst. This ORR stability was also verified by accelerated potential cycling tests, where the half-wave potential of the LDH/MQD/NG hybrids shifted slightly toward a negative value (by 7.6 mV). Finally, the potential difference ($\Delta E$) between the OER potential at 10 mA cm$^{-2}$ and the ORR half-wave potential was measured to evaluate the bifunctional activity. As shown in Figure 3(H), $\Delta E$...
FIGURE 4 (A) Charge/discharge polarization curves and power density plots of rechargeable ZABs with LDH/MQDs/NG hybrids, LDH/NG hybrids, LDH/NG + MQDs, bare NG, commercial Pt/C, and IrO$_2$ + Pt/C air cathodes. (B) Specific capacities and (C) energy densities of rechargeable ZABs with LDH/MQDs/NG hybrids, LDH/NG hybrids, LDH/NG + MQDs, bare NG, commercial Pt/C, and IrO$_2$ + Pt/C air cathodes at a discharge current density of 5 mA cm$^{-2}$. (D) Open-circuit plots of rechargeable ZABs with LDH/MQDs/NG hybrids, LDH/NG hybrids, LDH/NG + MQDs, bare NG, commercial Pt/C, and IrO$_2$ + Pt/C air cathodes. The inset shows the digital photograph of LED panel lit by two-in-series of LDH/MQDs/NG hybrids-based ZABs. (E) Galvanostatic charge/discharge cycling stability curves at 5 mA cm$^{-2}$ for rechargeable ZABs with LDH/MQDs/NG hybrids, LDH/NG hybrids, LDH/NG + MQDs, bare NG, commercial Pt/C, and IrO$_2$ + Pt/C air cathodes. (F) Charge/discharge polarization curves and power density plots, and (G) rate performance of the flexible quasi-solid state ZABs with LDH/MQDs/NG hybrids air cathode. (H) Galvanostatic charge/discharge cycling stability curves at 1 mA cm$^{-2}$ under different bending states for flexible quasi-solid state ZAB with LDH/MQDs/NG hybrids air cathode. (I) Open-circuit plots of different ZAB packs connected in series for the flexible quasi-solid state ZABs with LDH/MQDs/NG hybrids air cathodes. The inset shows the digital photographs of different electronics powered by LDH/MQDs/NG hybrid-based flexible quasi-solid state ZABs.
for the LDH/MQD/NG hybrids was 0.81 V, which is much lower than that of LDH/NG (0.92 V), Pt/C (1.01 V), and IrO2 + Pt/C (0.91 V) and other bifunctional electrocatalysts (Table S2), confirming the outstanding bifunctionality for rechargeable ZABs.

To explore the potential of LDH/MQD/NG hybrids as bifunctional catalysts, aqueous rechargeable ZABs were fabricated. As shown in Figure 4(A), the LDH/MQD/NG hybrids exhibited the narrowest charge/discharge voltage gap among the five samples, suggesting the highest round-trip efficiency and excellent rechargeability. The ZAB with the LDH/MQD/NG cathode delivered a high power density of 113.8 mW cm−2, which is comparable to that of the ZABs with the commercial Pt/C catalyst (117.4 mW cm−2) and is much greater than that of the other electrocatalysts (Table S3). In addition, the ZABs with LDH/MQD/NG hybrids showed a voltage plateau of 1.18 V at 5 mA cm−2, with a high specific capacity of 598 mAh gZn−1 (Figure 4(B)), which is superior to that of the Pt/C catalyst (549 mAh gZn−1) and much higher than those of the LDH/NG (565 mAh gZn−1), LDH/NG + MQDs (559 mAh gZn−1), IrO2 + Pt/C catalyst (510 mAh gZn−1), and bare NG (489 mAh gZn−1). Accordingly, the energy density of the LDH/MQD/NG-based ZAB was as high as 706 Wh kgZn−1 (Figure 4(C)), surpassing 694 Wh kgZn−1 for the commercial Pt/C catalyst. Notably, the LDH/MQD/NG-based ZAB afforded a stable open-circuit voltage of 1.42 V (Figure 4(D)). Furthermore, two LDH/MQD/NG-based ZABs connected in series could illuminate 46 light-emitting diodes (LEDs) with two colors, demonstrating the tandem ZABs connected serially could drive a timer and an arrangement of two and three could drive a multifunction alarm clock, respectively. The functional operation of the tandem ZABs connected serially in five series (Figure S19). The open-circuit voltage was controlled by serially connecting different numbers of tandem ZAB packs, where the assembly was stable for practical applications (Figure 4(I)). The tandem ZABs connected serially in an arrangement of two and three could drive a timer and a multifunction alarm clock, respectively. The functional operation of the tandem ZABs connected in five series was further confirmed by powering a mini electric fan (inset in Figure 4(I) and Supporting Movie S1).

For potential applications in flexible electronics, flexible quasi-solid-state ZABs were assembled using an alkaline poly(vinylalcohol) gel electrolyte sandwiched between a LDH/MQD/NG hybrid cathode and a zinc foil anode (see Supporting Information for details). Figure 4(F) presents the discharge/charge polarization curves of the LDH/MQD/NG-based ZABs, where the voltage gap between the discharge and charge for the flexible cell is similar to that of the Pt/C-based battery. A maximum power density of 57.6 mW cm−2 was achieved for the LDH/MQD/NG-based flexible ZABs. Additionally, a small potential drop and stable potentials were observed at various discharge current densities from 1 to 5 mA cm−2, indicating the excellent rate performance of the flexible ZABs with the LDH/MQD/NG hybrid cathode (Figure 4(G)). More importantly, the LDH/MQD/NG-based flexible ZABs exhibited relatively stable charging (1.79 V) and discharging (1.12 V) potentials at 1 mA cm−2, affording a duration of 24 h, indicating outstanding cycling stability (Figure S18). To further assess the flexibility, the LDH/MQD/NG-based flexible ZABs were folded at bending angles of 45°, 90°, 135°, and 180°, and the corresponding discharge/charge curves were collected, as shown in Figure 4(H). At different bending angles, the discharge and charge potentials of the flexible ZABs remained unchanged, with negligible fluctuation in the voltage gap, demonstrating the decent mechanical flexibility and stable operation. In addition, two flexible ZABs were connected in series to light up 46 LEDs in both the flat and bent states, where the change in brightness was negligible, even at different bending angles (Figure S19). The open-circuit voltage was controlled by serially connecting different numbers of tandem ZAB packs, where the assembly was stable for practical applications (Figure 4(I)). The tandem ZABs connected serially in an arrangement of two and three could drive a timer and a multifunction alarm clock, respectively. The functional operation of the tandem ZABs connected in five series was further confirmed by powering a mini electric fan (inset in Figure 4(I) and Supporting Movie S1).

3 | CONCLUSION

In summary, we demonstrated 3D hierarchically porous LDH/MQD/NG hybrids, in which the catalytically active LDH nanosheets were synergistically coupled with metallic MQD in an electronic and chemical manner. The electronic structure of the LDH/MQD/NG hybrids was locally modified, as confirmed by the change in the valence states of Ni and Fe, M—OH vibration, flat band potential, carrier density, metallic conductivity, and Fermi energy level through experimental and computational analyses.
The modulated electronic structure of the LDH/MQD/NG was associated with a significant improvement in the ORR/OER activity and kinetics, as verified by the onset and half-wave potentials, Tafel slope, charge transfer resistance, electron transfer number, and ORR/OER potential difference. Therefore, the resulting ZABs employing the LDH/MQD/NG hybrids afforded a high round-trip efficiency of 61.5%, power density of 113.8 mW cm\(^{-2}\), and excellent cycle stability of 150 h at 5 mA cm\(^{-2}\), which are much better than those of previous LDH-based ZABs. The superiority of the corresponding flexible ZABs was confirmed by the high power density of 57.6 mW cm\(^{-2}\), even in the bent state, and functional operation of tandem cells to power various electronic devices such as timers and mini electric fans. This coupling approach favors the rational design of structurally well-defined and highly efficient bifunctional electrocatalysts for high-performance flexible ZABs and provides a fundamental basis for the correlation between the local electronic structure of LDHs and their catalytic activity.

### 4 | METHODS

#### 4.1 | Synthesis of NG

Typically, a commercial graphene oxide (GO) solution (2%, 5 ml) was thoroughly mixed with urea (500 mg) in water (15 ml) by stirring for 30 min and freeze-dried for 3 days. The as-dried sample was then placed in a covered crucible at the center of a tube furnace. Subsequently, the temperature of the furnace was raised to 600°C at a heating rate of 3°C min\(^{-1}\) and maintained for 1 h under Ar flow. Afterward, the temperature was rapidly increased to 900°C at a heating rate of 5°C min\(^{-1}\) and the sample was annealed for 3 h.

#### 4.2 | Synthesis of MQDs

Typically, Ti\(_3\)C\(_2\) MXene was first prepared by etching MAX powder (1.0 g) in a concentrated HF solution (10 ml) under continuous magnetic stirring for 18 h at 50°C and then collected by several centrifugation-rinsing cycles with deionized water. Thereafter, Ti\(_3\)C\(_2\) MXene (300 mg) was dispersed in dimethyl sulfoxide (5 ml) and stirred for 18 h at room temperature. The as-obtained slurry of few-layered MXene was collected and washed with deionized water several times, followed by sonication for 2 h with argon bubbling for delamination. Finally, the Ti\(_3\)C\(_2\) MQDs were prepared by hydrothermal treatment of the as-delaminated Ti\(_3\)C\(_2\) MXene in the presence of ammonia (pH = 9) at 180 °C for 30 min.

### 4.3 | Synthesis of LDH/MQDs/NG hybrids

The LDH/MQD/NG hybrids were prepared using the urea-assisted co-precipitation method. Typically, NG (20 mg) was first dispersed in N-methylpyrrolidone (10.0 ml) by ultrasonic treatment for 1 h. Thereafter, Ni(NO\(_3\))\(_2\)-6H\(_2\)O (43.6 mg), FeSO\(_4\)-7H\(_2\)O (13.9 mg), and urea (60.0 mg) were dissolved in the MQD dispersion (30 ml, 0.16 mg ml\(^{-1}\)). The as-obtained solution was mixed with the NG dispersion under magnetic stirring for 10.0 min. The mixed solution was transferred to a Teflon-lined stainless steel autoclave (40 ml) and heated at 100°C for 6 h. After filtering and washing with deionized water several times, the resulting precipitate was freeze-dried for 24 h, yielding the final LDH/MQD/NG hybrids. For comparison, LDH/NG hybrids were also prepared under the same conditions, without using the MQDs.

### ACKNOWLEDGMENTS

This work was supported by the National Research Foundation of Korea (NRF) grant funded by the Korea government (MSIT) (NRF-2020R1A3B2079803 and 2020M2D8A2070866) and the Ministry of Education (No. NRF-2019R1A6A1A10073079).

### CONFLICT OF INTEREST

The authors declare no conflict of interest.

### AUTHOR CONTRIBUTIONS

Xiaotong Han and Nannan Li contributed equally to this work. Xiaotong Han performed the electrochemical experiments, analyzed the data, and wrote the manuscript. Min Gyu Jung synthesized the samples. Nannan Li performed the DFT calculations. Jin Yong Lee supervised the DFT calculations. Qingyun Dou and Peixun Xiong analyzed the electrochemical results. Yingbo Kang and Qing Liu performed the SEM, TEM, XPS, and XRD characterizations. Ho Seok Park supervised the project. All authors contributed to discussion of the results and manuscript preparation.

### DATA AVAILABILITY STATEMENT

All data needed to evaluate the conclusions in the paper are present in the paper and/or the Supporting Information. Additional data related to this paper may be requested from the authors.

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### REFERENCES

1. Tang C, Wang HF, Zhang Q. Multiscale principles to boost reactivity in gas-involving energy electrocatalysis. Acc Chem Res. 2018;51:881-889.
2. Fu J, Cano ZP, Park MG, Yu A, Fowler M, Chen Z. Electrically rechargeable zinc-air batteries: progress, challenges, and perspectives. Adv Mater. 2017;29:1604685.

3. Li Y, Lu J. Metal–air batteries: will they be the future electrochemical energy storage device of choice? ACS Energy Lett. 2017;2:1370-1377.

4. Zhang M, Dai Q, Zheng H, Chen M, Dai L. Novel MOF-derived co@N-C bifunctional catalysts for highly efficient Zn-air batteries and water splitting. Adv Mater. 2018;30:1705431.

5. Cao R, Lee JS, Liu M, Cho J. Recent progress in non-precious catalysts for metal-air batteries. Adv Energy Mater. 2012;2:816-829.

6. Septianli NLW, Kaneti YV, Fathoni KB, et al. Self-Assembly of Two-Dimensional Bimetallic Nickel–Cobalt Phosphate Nanoplates into One-Dimensional Porous Chainlike Architecture for Efficient Oxygen Evolution Reaction. Chem Mater. 2020;32: 7005-7018.

7. Kaneti YV, Guo Y, Septianli NLW, et al. Self-templated fabrication of hierarchical hollow manganese-cobalt phosphide yolk-shell spheres for enhanced oxygen evolution reaction. Chem Eng J. 2021;405:126580.

8. Yang H, Han X, Douka AI, et al. Advanced Oxygen Electrocatalysis in Energy Conversion and Storage. Adv Funct Mater. 2020;31:2007602.

9. Zhang J, Zhao Z, Xia Z, Dai L. A metal-free bifunctional electrocatalyst for oxygen reduction and oxygen evolution reactions. Nat Nanotechnol. 2015;10:444-452.

10. Wang H, Yin S, Xu Y, et al. Direct fabrication of tri-metallic PtPdCu tripods with branched exteriors for the oxygen reduction reaction. J Mater Chem A. 2018;6:8662-8668.

11. Wang HF, Tang C, Zhang Q. A review of precious-metal-free bifunctional oxygen electrocatalysts: rational design and applications in Zn–air batteries. Adv Funct Mater. 2018;28:1803329.

12. Jiang Y, Deng Y, Liang R, et al. D-orbital steered active sites through ligand editing on heterometal imidazole frameworks for rechargeable zinc-air battery. Nat Commun. 2020;11:5858.

13. Douka AI, Xu Y, Yang H, et al. A zeolitic-imidazole frameworks-derived interconnected macroporous carbon matrix for efficient oxygen electrocatalysis in rechargeable zinc–air batteries. Adv Mater. 2020;32:2002170.

14. Wang B, Tang C, Wang HF, Li BQ, Cui X, Zhang Q. Anion-regulated hydroxy sulfide monoliths as OER/ORR/HER electrocatalysts and their applications in self-powered electrochemical water splitting. Small Methods. 2018;2:1800055.

15. Yin J, Li Y, Lv F, et al. NiO/CoN porous nanowires as efficient bifunctional catalysts for Zn–air batteries. ACS Nano. 2017;11: 2275-2283.

16. Tang C, Wang HS, Wang HF, et al. Spatially confined hybridization of nanometer-sized NiFe hydroxides into nitrogen-doped graphene frameworks leading to superior oxygen evolution reactivity. Adv Mater. 2015;27:4516-4522.

17. Li P, Duan X, Kuang Y, et al. Tuning electronic structure of NiFe layered double hydroxides with vanadium doping toward high efficient electrocatalytic water oxidation. Adv Energy Mater. 2018;8:1703341.

18. Gong M, Li Y, Wang H, et al. An advanced Ni–Fe layered double hydroxide electrocatalyst for water oxidation. J Am Chem Soc. 2013;135:8452-8455.

19. Song F, Hu X. Exfoliation of layered double hydroxides for enhanced oxygen evolution catalysis. Nat Commun. 2014;5:4477.

20. Salmanion M, Najafpour MM. Dendrimer-Ni based material: toward an efficient Ni–Fe layered double hydroxide for oxygen evolution reaction. Inorg Chem. 2021;60:6073-6085.

21. Zhang J, Yu L, Chen Y, Lu XF, Gao S, Lou XW. Designed formation of double-shelled Ni–Fe layered-double-hydroxide nanocages for efficient oxygen evolution reaction. Adv Mater. 2020;32:1906432.

22. Wang Q, Shang L, Shi R, et al. NiFe layered double hydroxide nanoparticles on co,N-Codoped carbon nanoframes as efficient bifunctional catalysts for rechargeable zinc-air batteries. Adv Energy Mater. 2017;7:1700467.

23. Wang W, Liu Y, Li J, Luo J, Fu L, Chen S. NiFe LDH nanodots anchored on 3D macro/mesoporous carbon as a high-performance ORR/OER bifunctional electrocatalyst. J Mater Chem A. 2018;6:14299-14306.

24. Yu H, Hou J, Namin RB, et al. Pre-cryocrushing of natural carbon precursors to prepare nitrogen, sulfur co-doped porous microcellular carbon as an efficient ORR catalyst. Carbon. 2021;173:800-808.

25. Yan J, Huang Y, Zhang Y, et al. Facile synthesis of bimetallic fluoride heterojunctions on defect-enriched porous carbon nanofibers for efficient ORR catalysts. Nano Lett. 2021;21:2618-2624.

26. Zhang S, Xia W, Yang Q, et al. Core-shell motif construction: highly graphitic nitrogen-doped porous carbon electrocatalysts using MOF-derived carbon@COF heterostructures as sacrificial templates. Chem Eng J. 2020;396:125154.

27. Lv L, Yang Z, Chen K, Wang C, Xiong Y. 2D layered double hydroxides for oxygen evolution reaction: from fundamental design to application. Adv Energy Mater. 2019;9:1803358.

28. Han X, Yu C, Yang J, et al. Mass and charge transfer coenhanced oxygen evolution behaviors in CoFe-layered double hydroxide assembled on graphene. Adv Mater Interfaces. 2016; 3:1500782.

29. Naguib M, Mochalin VN, Barsoum MW, Gogotsi Y. 25th anniversary article: MXenes: a new family of two-dimensional materials. Adv Mater. 2014;26:992-1005.

30. Ling Z, Ren CE, Zhao MQ, et al. Flexible and conductive MXene films and nanocomposites with high capacitance. Proc Natl Acad Sci. 2014;111:16676-16681.

31. Ghidivi M, Lukatskaya MR, Zhao MQ, Gogotsi Y, Barsoum MW. Conductive two-dimensional titanium carbide ‘clay’ with high volumetric capacitance. Nature. 2014;516: 78-81.

32. Yu M, Zhou S, Wang Z, Zhao J, Qiu J. Boosting electrocatalytic oxygen evolution by synergistically coupling layered double hydroxide with MXene. Nano Energy. 2018;44:181-190.

33. Xue Q, Zhang H, Zhu M, et al. Photoluminescent Ti3C2MXene quantum dots for multicolor cellular imaging. Adv Mater. 2017; 29:1604847.

34. Nguyen DN, Gund GS, Jung MG, et al. Core–shell structured MXene@carbon nanodots as bifunctional catalysts for solar-assisted water splitting. ACS Nano. 2020;14:17615-17625.

35. Alhabeb M, Maleski K, Anasori B, et al. Guidelines for synthesis and processing of two-dimensional titanium carbide (Ti3C2TxMXene). Chem Mater. 2017;29:7633-7644.

36. Han X, Yu C, Zhou S, et al. Ultrasensitive iron-triggered nanosized Fe-CoOOH integrated with graphene for highly efficient oxygen evolution. Adv Energy Mater. 2017;7:1602148.
37. Huang H, Yu C, Han X, et al. Ni, co hydroxide triggers electrocatalytic production of high-purity benzoic acid over 400 mA cm\(^{-2}\). *Energy Environ Sci*. 2020;13:4990-4999.

38. Guo W, Yu C, Li S, et al. A universal converse voltage process for triggering transition metal hybrids in situ phase restriction toward ultrahigh-rate supercapacitors. *Adv Mater*. 2019;31:1901241.

39. Zhao D, Jiang K, Pi Y, Huang X. Superior electrochemical oxygen evolution enabled by three-dimensional layered double hydroxide nanosheet superstructures. *ChemCatChem*. 2017;9:84-88.

40. Liang H, Meng F, Cabán-Acevedo M, et al. Hydrothermal continuous flow synthesis and exfoliation of NiCo layered double hydroxide nanosheets for enhanced oxygen evolution catalysis. *Nano Lett*. 2015;15:1421-1427.

41. Han X, Niu Y, Yu C, et al. Ultrafast construction of interfacial sites by wet chemical etching to enhance electrocatalytic oxygen evolution. *Nano Energy*. 2020;69:104367.

42. Zhu J, Guo S, Chu Z, Jin W. CO2-tolerant oxygen-permeable perovskite-type membranes with high permeability. *J Mater Chem A*. 2015;3:22564-22573.

43. Rajagopalan R, Chen B, Zhang Z, et al. Improved reversibility of Fe\(^{3+}/Fe^{4+}\) redox couple in sodium super ion conductor type Na\(_3\)Fe\(_2\)(PO\(_4\))\(_3\) for sodium-ion batteries. *Adv Mater*. 2017;29:1605694.

44. Yu C, Han X, Liu Z, et al. An effective graphene confined strategy to construct active edge sites-enriched nanosheets with enhanced oxygen evolution. *Carbon*. 2018;126:437-442.

45. Li R, Wei Z, Gou X. Nitrogen and phosphorus dual-doped graphene/carbon nanosheets as bifunctional electrocatalysts for oxygen reduction and evolution. *ACS Catal*. 2015;5:4133-4142.

46. Liu Z, Li S, Yang J, et al. Ultrafast construction of oxygen-containing scaffold over graphite for trapping Ni\(^{2+}\) into single atom catalysts. *ACS Nano*. 2020;14:11662-11669.

47. Chang J, Yu C, Song X, et al. A C-S-C linkage-triggered ultrahigh nitrogen-doped carbon and identification of active site in triiodide reduction. *Angew Chem Int Ed*. 2020;60:3587.

48. Li J, Li X, Zhao P, et al. Searching for magnetism in pyrrolic N-doped graphene synthesized via hydrothermal reaction. *Carbon*. 2015;84:460-468.

49. Lai L, Potts JR, Zhan D, et al. Exploration of the active center structure of nitrogen-doped graphene-based catalysts for oxygen reduction reaction. *Energy Environ Sci*. 2012;5:7936.

50. Görlin M, Chernev P, Ferreira de Araújo J, et al. Oxygen evolution reaction dynamics, faradaic charge efficiency, and the active metal redox states of Ni–Fe oxide water splitting electrocatalysts. *J Am Chem Soc*. 2016;138:5603-5614.

51. Friebel D, Louie MW, Bajdich M, et al. Identification of highly active Fe sites in (Ni,Fe)OOH for electrocatalytic water splitting. *J Am Chem Soc*. 2015;137:1305-1313.

52. Trotochaud L, Young SL, Ranney JK, Boettcher SW. Nickel–iron oxyhydroxide oxygen-evolution electrocatalysts: the role of intentional and incidental iron incorporation. *J Am Chem Soc*. 2014;136:6744-6753.

**SUPPORTING INFORMATION**

Additional supporting information may be found online in the Supporting Information section at the end of this article.

**How to cite this article:** Han X, Li N, Xiong P, et al. Electronically coupled layered double hydroxide/MXene quantum dot metallic hybrids for high-performance flexible zinc–air batteries. *InfoMat*. 2021;1–11. [https://doi.org/10.1002/inf2.12226](https://doi.org/10.1002/inf2.12226)