Single-layer nanosheets with exceptionally high and anisotropic hydroxyl ion conductivity

Pengzhan Sun, Renzhi Ma, Xueyin Bai, Kunlin Wang, Hongwei Zhu, Takayoshi Sasaki

When the dimensionality of layered materials is reduced to the physical limit, an ultimate two-dimensional (2D) anisotropy and/or confinement effect may bring about extraordinary physical and chemical properties. Layered double hydroxides (LDHs), bearing abundant hydroxyl groups covalently bonded within 2D host layers, have been proposed as inorganic anion conductors. However, typical hydroxyl ion conductivities for bulk or lamellar LDHs, generally up to $10^{-3}$ S cm$^{-1}$, are considered not high enough for practical applications. We show that single-layer LDH nanosheets exhibited exceptionally high in-plane conductivities approaching $10^{-1}$ S cm$^{-1}$, which were the highest among anion conductors and comparable to proton conductivities in commercial proton exchange membranes (for example, Nafion). The in-plane conductivities were four to five orders of magnitude higher than the cross-plane or cross-membrane values of restacked LDH nanosheets. This 2D superionic transport characteristic might have great promises in a variety of applications including alkaline fuel cells and water electrolysis.

INTRODUCTION

Two-dimensional (2D) materials are fundamentally and technologically intriguing because of the emergence of novel physical and chemical properties that are distinct from or absent in their bulk counterparts (1–5). This has been most markedly highlighted by the recent burgeoning research on semimetallic graphene (6–8), insulating hexagonal boron nitride (9), semiconducting black phosphorus (10–12), and transition metal dichalcogenides (13, 14), as well as versatile metal oxides such as titania and perovskite-type oxide nanosheets (15–18). The immense interest in 2D materials has been driven not only by the merit of preserving intrinsic properties of bulk layered hosts but also by the prospect of generating additional exotic characteristics arising from the ultimate anisotropy and/or confinement effects. This has led to rapid progress in using these 2D building blocks for a myriad of applications such as nanoelectronics, optoelectronics, flexible devices, catalysis, energy storage, and conversion.

Layered double hydroxides (LDHs) (19–21), with a general formula of $[M^{2+}_{x}M^{3+}_{y}(OH)_{z}]^{x+}[A^{-}\text{sol}]^{y-}\cdot mH_{2}O$ (M represents metal cations, and A represents anions), are an important class of clay-like layered compounds consisting of alternately stacked positively charged host layers and weakly bound charge-balancing interlayer anions. The host layer consists of divalent/trivalent heterogeneous metal cations sandwiched between two hydroxyl slabs. The interlayer hydrated anions locate above/below the trivalent cationic charge centers to balance the positive host charge (22). A hydrogen bond network is thus developed among hydroxyl groups, interlayer anions, and water molecules in the gallery. LDHs are unique in the aspect that a vast majority of layered materials have negatively charged host layers and cations in the interlayer spaces. By appropriately adjusting anionic species, lamellar LDHs can be exfoliated into single-layer nanosheets, which may generate attractive properties arising from the ultimate 2D anisotropy and accessible high surface area, as well as a peculiar positively charged feature (23–30).

Recently, a few papers have reported the excellent proton-conducting properties of 2D-layered materials such as graphene oxide (GO) (31–34) and vermiculite (35). The results indicate that high proton conductivities could be achieved along 2D surfaces or reconstructed interlayer galleries. Bearing abundant hydroxyl groups covalently bonded within 2D host layers, LDHs belong to a relatively rare class of hydroxyl ion conductors. Several research groups have explored the prospect of using LDHs as inorganic solid electrolytes in alkaline fuel cells and water electrolysis (36–41). Current technology on fuel cells and electrolysis mostly involves an acidic environment that requires a dominant use of proton conductors/membranes, electrocatalysts based on precious metals, and anticcorsorelectrodes. Despite the fact that precious metallic catalysts still dominate in achieving good performances in alkaline environment, a shift to alkaline operation environment using hydroxyl ion conductors, where nonprecious metallic catalysts can be used, may raise a feasibility of significantly reducing the cost. Unfortunately, a relatively lower ion mobility of OH$^{-}$ compared to H$^{+}$ limits the hydroxyl ion conductivity. Typical conductivities ($10^{-3}$ to $10^{-2}$ S cm$^{-1}$) for anion exchange membranes (AEMs) are not high enough compared to those for proton exchange membranes (PEMs), for example, Nafion ($10^{-1}$ S cm$^{-1}$). In addition, commercial AEMs based on polymeric quaternary ammonium are usually associated with highly toxic preparation procedures, together with unsatisfactory thermal and chemical stability (42–44). These drawbacks have triggered the need of developing next-generation inorganic hydroxyl ion conductors. LDHs are highly regarded due to their reasonably high ionic conductivity, robust stability in alkaline environment, and resistance to carbonate degradation. However, only ion-conducting properties of bulk or lamellar LDH samples have been studied thus far. Intrinsic ionic conductivity of LDHs, particularly possible anisotropic transport behavior derived from an anisotropic bonding nature, is still unknown. The investigation on exfoliated LDH nanosheets will not only shed light on understanding the fundamental mechanism of hydroxyl ion conduction in LDHs but also have great implications in exploiting 2D building blocks for constructing novel architectures with superionic functions.

In the present work, we show that superior in-plane hydroxyl ion conductivities approaching $10^{-1}$ S cm$^{-1}$ could be achieved with LDH single-layer nanosheets, which were one to three orders of magnitude higher than the corresponding bulk precursors. A clear 2D anisotropy was attested by the poor cross-plane conductivities of restacked nanosheets, which were four to five orders of magnitude lower than the
in-plane values. In contrast, the conductivities of lamellar LDH platelets along the plate plane direction lay in the same order of magnitude as those of cold-pressed pellets containing randomly orientated platelets. These results clearly revealed an exceptionally high and anisotropic hydroxyl ion conduction of single-layer LDH nanosheets as a consequence of exposing the whole 2D surfaces. The exotic 2D-conducting properties might promise a great potential in a large array of energy- or environment-related applications.

RESULTS

Synthesis and characterization of LDH platelets and nanosheets, experimental setup, and determination of the conducting ionic species of LDH nanosheets

Well-crystallized, micrometer-sized, hexagon-shaped lamellar LDH platelets with various bimetallic host layer compositions [for example, Mg$^{2+}$-Al$^{3+}$, Co$^{2+}$-Al$^{3+}$, Co$^{2+}$-Co$^{3+}$, and Ni$^{2+}$-(Co$^{2+}$)-Co$^{3+}$] were synthesized according to the previously developed soft-chemical procedures (24–27). After exchanging the interlayer galleries for suitable anions, typically NO$_3^{-}$, LDH platelets were exfoliated in formamide for single-layer nanosheets. Detailed protocols and characterizations were provided in Materials and Methods and in figs. S1 to S3. The ion-conducting property of single-layer nanosheets was studied in comparison with the ion-conducting properties of parental LDH platelets and restacked nanosheets (Fig. 1A). As schematically illustrated in Fig. 1B, hydroxyl ions are supposed to be transported along adsorbed water molecules and hydroxide host layers through rapid hydrogen bond formation and cleavage, that is, a plausible Grotthuss mechanism (45). The ion conductivity was determined from AC impedance spectroscopic measurements on the LDH specimens at different temperatures and relative humidities (RHs) (31–33, 46). In particular, in-plane or 2D ion conductivity could be evaluated by depositing LDH nanosheets on comb-like microelectrodes (Fig. 1C and fig. S4).

The conducting ionic species of LDH nanosheets were determined by measuring the electromotive forces in a water vapor concentration cell by sending a humidified and dry O$_2$ gas stream on each side of a membrane (see the Supplementary Materials) (36). Electromotive forces were measured as open-circuit potentials or electrical voltages developed by charge separation across the membrane. The sign of electromotive forces determines the conducting ionic species, that is, a positive sign for cation conductors and vice versa. The electromotive forces of LDH (Mg-Al, Co-Al) nanosheet membranes were compared with commercial PEM (Nafion 117, DuPont) and AEM (AHA, ASTOM Co.), as well as GO membrane. As shown in Fig. 2, the same sign was observed for AEM (AHA) and LDH (Mg-Al, Co-Al) nanosheet membranes. GO membrane, which is already confirmed as a proton conductor (31), showed the same sign as PEM (Nafion). These results indicated that LDH nanosheets were conductors of negatively charged species. In addition, a huge sheet resistance ($10^7$ to $10^8$ ohms/square) was measured on LDH nanosheet membranes by a resistance meter (MCP-HT450, Mitsubishi Chemical Analytech). This was consistent with a recent study by Zhao et al. (47) on the electronic transport properties of 2D LDHs, demonstrating a hole conduction with a low carrier mobility. Therefore, a possible electronic conduction might be convincingly excluded, and LDH nanosheets were anion conductors.

**Ionic conduction of LDH nanosheets**

Single-layer Mg-Al LDH nanosheets with a lateral size of several micrometers and a thickness of ~0.8 nm (Fig. 3A) were deposited discretely on comb microelectrodes (Fig. 3, B and C). The resistance of bare comb electrodes was extremely high (on the order of 10$^8$ ohms; fig. S5), indicating that the coupling effect between adjacent comb teeth and the parasitic impedance contribution from bare electrodes was negligible. Typically, two types of nanosheets existed (Fig. 3B): (i) the bridging ones, connecting two opposite comb teeth, and (ii) the interior ones,

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**Fig. 1. LDH and its hydroxyl ion conduction.** Schematic diagrams for (A) the structure of LDH platelet, its exfoliation into single-layer nanosheets, and ion-conducting scenarios; (B) the plausible Grotthuss mechanism responsible for hydroxyl ion conduction; and (C) the measurement of in-plane ion conductivities of LDH nanosheets on comb electrodes.
locating on a single comb tooth or in a gap between two opposite teeth. Only bridging nanosheets were considered as contributing to the measurement and counted throughout the comb electrode for analyzing in-plane conductivities (see the Supplementary Materials). Figure 3D shows representative Nyquist plots at 80% RH, revealing that the ionic conductivity increased with temperature. Temperature and RH dependencies of in-plane ionic conductivity were plotted in Fig. 3E. It can be seen that the conductivities were generally on the order of $10^{-2}$ S cm$^{-1}$ and approaching $10^{-1}$ S cm$^{-1}$ at 80% RH and 60°C. Also shown in Fig. 3E, calculated activation energies ($E$) for in-plane ion conduction decreased with the increment of RH (from 50 to 80%), indicating that the presence of water promoted anion conduction.

In bulk aqueous solutions, protons and hydroxyl ions could propagate through the hydrogen bond networks among water molecules following the Grotthuss mechanism (45) with an extremely high ion mobility. By contrast, other hydrated ions mostly propagated via physical migration with a low ion mobility, which was generally about one order of magnitude smaller than that for protons and hydroxyl ions (48–50). Thus the wide-extended hydrogen bond network provided by adsorbed water molecules and covalently bonded hydroxide host layer in LDH nanosheets might facilitate the ultrafast conduction of hydroxyl ions through rapid hydrogen bond breaking/reformation. Therefore, the possible conduction of physically migrated interlayer hydrated anions should be much slower than that of hydroxyl ions and thus could be neglected.

By depositing LDH nanosheets into multilayers (tens to hundreds of layers) on comb electrodes (fig. S6), in-plane hydroxyl ion conductivities of the multilayer assemblies were evaluated (figs. S7 to S9). Both Mg-Al and Co-Al LDH nanosheets showed increased conductivities with raised temperature and RH (fig. S7). At 80% RH and 60°C, the measured values reached an order of $10^{-2}$ S cm$^{-1}$ (fig. S7), indicating that the high in-plane hydroxyl ion conductivity might be retained as a general characteristic of 2D LDH materials. Notably, reducing the nanosheet lateral dimension from micrometers to several hundred nanometers led to the increase of in-plane ion conductivities (fig. S8). Considering that the only difference between these two kinds of nanosheets lay in the lateral dimension, because of the almost identical synthesis procedures used, this observation was presumably attributed to the production of more intersections for the propagating ions to change their paths, which reduced the interference from the enriched intersheet charge-balancing anions around the trivalent host cations and further accelerated ion movement, similar to the cases of ion transport through lamellar membranes composed of overlapped and stacked GO nanosheets (51). Nevertheless, it is noteworthy that the in-plane conductivities of multilayer assemblies were apparently lower than those of single-layer nanosheets, indicating that the in-plane transport may be compromised to some extent by increased steric confinement from narrowed...
interlayer gallery spacing as well as electrostatic repulsion from sandwiched and doubled interlayer anions.

With one representative sample of multilayer Mg-Al LDH nanosheets deposited on comb electrodes, the temperature dependences of in-plane ionic conductivity were measured during a large time interval of over half a year (fig. S9). The results show that the variations in ion conductivity could be neglected after such a long time, indicating that the as-exfoliated LDH nanosheets have excellent stability in terms of hydroxyl ion conduction. In addition, previous studies (52–54) on using exfoliated LDH nanosheets as electrode materials for fabricating supercapacitors showed that the charge-discharge performances of LDH-based supercapacitors did not undergo an obvious degradation even after several thousand cycles, indicating that LDH nanosheets have an excellent stability in strong alkaline environments (for example, 1 to 6 M KOH).

Cross-nanosheet or cross-plane hydroxyl ion–conducting properties were studied on lamellar membranes of restacked LDH nanosheets prepared by vacuum filtration (figs. S10 and S11). The cross-membrane conductivities increased with increasing temperature and RH, but the values for both Mg-Al and Co-Al LDH nanosheets were on the order of \(10^{-6} \text{ S cm}^{-1}\) even at 80% RH (fig. S11). Notably, reducing the lateral dimension of LDH nanosheets from micrometers to several hundred nanometers yielded a proportional increase in cross-membrane conductivities, indicating that more inter-edge channels formed by reducing the lateral size of LDH nanosheets may be beneficial in contributing to cross-plane hydroxyl ion conduction.

Under a humidified environment, the adsorbed water molecules on LDHs underwent a self-dissociation process to generate protons and hydroxyl ions (55). This self-dissociation increased with temperature. Therefore, at elevated temperature, a higher concentration of hydroxyl ions (with an equal concentration of protons) would be generated. Because of the positive charges of LDH host layers, hydroxyl ions were attracted and propagated along the hydrogen bond networks of adsorbed water molecules and hydroxyl slab surface (nearest neighboring distance of OH–OH centers, ~0.3 nm) through high-frequency hydrogen bond breaking and reformation. This led to the formation of a space-charge zone with an increased hydroxyl ion concentration around LDH host layers. The generated hydroxyl ions were rapidly conducted, which broke the water self-dissociation equilibrium, leading to the sustaining generation of sufficient flow of hydroxyl ions. Through an isotope effect experiment (fig. S12) in which the ionic conductivities of representative LDH nanosheet samples were measured in \(\text{H}_2\text{O}\) and \(\text{D}_2\text{O}\) atmospheres in both real-time and static states, hydroxyl ions, rather than protons, could be verified to be the vehicle of ion conduction from the negligible variations in ionic conductivities upon replacing the atmosphere from \(\text{H}_2\text{O}\) to \(\text{D}_2\text{O}\). For LDH nanosheets, the charge-balancing anions were distributed on both surfaces. The hydroxyl ion conduction was confined on the 2D slab surfaces without serious restraint from adjacent layers (because of the larger interlayer spacing of single- and multilayer assemblies, as compared in figs. S2 and S13). Electrostatic repulsion from the interlayer hydrated anions might also be relieved to some extent because of the presence of abundant spacing for hydroxyl ions to choose their conduction pathways. Hydroxyl ions might propagate through the fully hydrated covalently bonded hydroxide surfaces following the Grotthuss mechanism (45), that is, rapid hydrogen bond formation/cleavage with the aid of adsorbed water (Fig. 1B), yielding extremely high in-plane ion conductivities (Fig. 3 and figs. S7 to S9). However, the propagation may be slowed down in limited interlayer galleries of crowded anions, leading to decreased conductivities for lamellar platelets. In addition, the cross-plane
hydroxyl ion conduction should rely on interlayer hopping, which may be severely impeded by the interlayer anions and a large gallery spacing (~1 nm) (fig. S13), resulting in much slower transport than the in-plane case.

**Ionic conduction of lamellar LDH platelets**
To distinguish the ion transport behavior of single-layer nanosheets from lamellar platelets, we evaluated the hydroxyl ion conductivity of LDH platelets with the assistance of comb electrodes. Through an oil/water interfacial self-assembling procedure by Ma et al. (56), closely packed films of LDH platelets with a typical thickness of several tens of nanometers and a lateral dimension of several micrometers were assembled on comb electrodes. Figure 4 (A and B) shows SEM and AFM characterizations of the representative packing of LDH hexagonal platelets. Figure 4C depicts the representative variations of impedance changes of restacked LDH nanosheets. It is noteworthy that the measured conductivities of LDH nanosheets (Fig. 3 and figs. S7 to S9 and S11) seemed more sensitive to humidity change than those of LDH platelets (fig. S15), inferring that the surface of LDH nanosheets might be more accessible to water molecules than the interlayer galleries of LDH platelets. This may be rationalized as an important merit of exfoliating lamellar LDHs into single-layer nanosheets for significantly exposing more accessible surface area, adsorbing more water content, and accordingly improving hydroxyl ion transport properties.

**Summary and comparison of ionic conductivities for LDH nanosheets and lamellar platelets**
Typical hydroxyl ion conductivities of LDH nanosheets and hexagonal lamellar platelets are compared and summarized in Fig. 5. All the in-plane conductivities of Mg-Al and Co-Al LDH nanosheets were extremely high, which were on the order of 10⁻² S cm⁻¹ and approaching 10⁻¹ S cm⁻¹ for single-layer sheets, whereas the cross-plane values were ultralow, which were only on the order of 10⁻⁶ S cm⁻¹. The highly

As control experiments, lamellar LDH platelets were cold-pressed into pellets. Within the pellets, LDH platelets were randomly oriented to the specimen surface. The measured conductivities, which also increased with temperature and RH (figs. S14 and S15), thus reflected bulk and average characteristics of LDH compounds. As shown in fig. S15, there was a significant enhancement in ion conductivities after anion exchange from CO₃²⁻ to monovalent (Cl⁻, Br⁻, and NO₃⁻) forms. Compared to CO₃²⁻ LDHs (10⁻⁶ to 10⁻⁴ S cm⁻¹), the conductivities of Cl⁻/Br⁻ and NO₃⁻ LDHs increased to the order of 10⁻⁴ and 10⁻³ S cm⁻¹, respectively. Accordingly, the activation energy E values decreased in the same order. The change tendencies of ion conductivity and related E value with respect to interlayer anionic species resonated well with the variation of gallery spacing (fig. S2), indicating that the increase in the interlayer spacing of LDHs might favor hydroxyl ion conduction in host layers. Notably, the measured conductivities of LDH platelets assembled on comb electrodes were close to those of pellet samples. This could be attributed to the bulk nature of LDH platelets in both cases, which reflected the overall conduction characteristics, in stark contrast to the ultimate 2D anisotropic feature of single-layer nanosheets.

The above results have proven that the hydroxyl ion conduction was affected by the water content/hydration behavior and interlayer species-spacing of LDHs. A higher RH resulted in more water molecules being adsorbed and a higher hydration degree of hydroxide host layers, which could provide faster channels for hydroxyl ion propagation. A larger interlayer spacing might accelerate ion mobility and hydrogen bond breaking/reformation process, which was beneficial for achieving higher in-plane ion conductivities. When migrating into and through the interlayer galleries of lamellar LDH platelets, hydroxyl ions were electrostatically repulsed by the confined anions in the much narrower spacing, which would weaken the highly anisotropic ion conductivities, as compared to single-layer nanosheets (presumably through an enhanced electrostatic repulsion from the interlayer anions in the narrower spacing for decreasing in-plane ion conductivities and a shortened hopping distance for increasing cross-plane ion conductivities). In particular, divalent CO₃²⁻ might impart stronger electrostatic repulsions to the propagated hydroxyl ions than those of monovalent anions (Cl⁻, Br⁻, and NO₃⁻), which was confirmed by the increased activation energy E values (fig. S15). Therefore, the hydroxyl ion conductivities of bulk LDHs were orders of magnitude lower than the in-plane values of single-layer nanosheets.

**Fig. 5. Comparisons of hydroxyl ion conductivity values.** (A) Schematic diagrams for the measurements of hydroxyl ion conductivities in different directions for both LDH nanosheets and hexagonal lamellar platelets. (B) Summary and comparison of the measured values at 60°C and 80% RH.
anisotropic hydroxyl ion conductivities were attributed to the morphological and structural anisotropy originating from the exfoliation of LDH crystals to ultimate 2D nanosheets. By contrast, pellet samples containing randomly orientated LDH platelets yielded values in the same order of magnitude as the platelets measured along the plate plane direction on comb electrodes. In general, the conductivities of unexfoliated LDHs were one to three orders of magnitude lower than the in-plane values of LDH nanosheets, demonstrating the possibility of exploiting the 2D full-exposure effects arising from dimensionality reduction for superior ion/mass transport properties. This highly anisotropic ion-conducting characteristic of LDH nanosheets should be taken into full account for fabricating hydroxyl ion conductors or AEMs, that is, the ultrafast in-plane conduction should be maximized, whereas the ultralow cross-plane transport should be minimized. Here, we propose two possible routes: One might be to perpendicularly align and immobilize LDH nanosheets in a matrix to create ultrafast ion conduction pathways along nanosheet planes, similar to the reports on anisotropic hydrogels of cofacially aligned oxide nanosheets (57, 58); the other might be to first assemble LDH nanosheets into large-area lamellar membranes (fig. S10), then scroll into Archimedean spiral fibers, similar to the preparation of layered and scolled graphene-based nanocomposites (59), and finally cut along the direction perpendicular to the axis of the fiber to produce thin membranes with spiral ultrafast in-plane conduction pathways. Taking into account that various liquid-phase membrane formation techniques (for example, drop casting, vacuum filtration, and spin coating) are available, such technological innovations could enable the promises of LDH nanosheets as an inorganic anion exchange conductor for practical electrochemical devices.

DISCUSSION
In summary, we have demonstrated that the in-plane hydroxyl ion conductivities of single-layer LDH nanosheets, approaching $10^{-3}$ S cm$^{-1}$, were four to five orders of magnitude higher than those of cross-plane transport and one to three orders of magnitude higher than the measured values of corresponding bulk LDH precursors. The present study has unveiled the 2D confinement-induced highly anisotropic hydroxyl ion conduction in LDH nanosheets, which may be considered an intrinsic characteristic of this peculiar 2D material. The superionic conductivity of LDH nanosheets may endow them with great potential, albeit technological innovations are needed, for high-performance hydroxyl ion conductors and AEMs useful in electrochemical energy storage and conversion, catalysis, sensing, and chemical filters.

**MATERIALS AND METHODS**

**Preparation of LDH platelets and nanosheets**

Mg$_{2/3}$-Al$_{1/3}$-CO$_3^{2-}$ LDH hexagonal platelets were synthesized by hexamethylenetetramine (HMT; C$_6$H$_{12}$N$_4$) hydrolysis of a mixed solution of Mg(NO$_3$)$_2$·6H$_2$O and Al(NO$_3$)$_3$·9H$_2$O (Mg/Al ratio of 2) under hydrothermal treatment (24). For comparison, commercial samples of Mg$_{2/3}$-Al$_{1/3}$-CO$_3^{2-}$ LDHs were also used, which were synthesized by coprecipitation of Mg(NO$_3$)$_2$·6H$_2$O and Al(NO$_3$)$_3$·9H$_2$O mixed solution (Mg/Al ratio of 3) in the presence of Na$_2$CO$_3$. Co$_{2/3}$-Al$_{1/3}$-CO$_3^{2-}$ LDH hexagonal platelets were synthesized from a mixed solution of CoCl$_2$·6H$_2$O and AlCl$_3$·9H$_2$O using urea [CO(NH$_2$)$_2$] as a hydrolysis agent (25).

Co$_{2/3}$-Co$_{3+}$-Br$^-$ and Co$_{2/3}$-Ni$_{1/3}$-Br$^-$ LDH hexagonal platelets were synthesized on the basis of a topochemical oxidative intercalation technique by Ma et al. (26) and Liang et al. (27). In this procedure, brucite-like β-Co(OH)$_2$ and Co$_{2/3}$Ni$_{1/3}$(OH)$_2$ hexagonal platelets were first synthesized via HMT hydrolysis of CoCl$_2$·6H$_2$O solution and CoCl$_2$·6H$_2$O/NiCl$_2$·6H$_2$O mixed solution (Co/Ni ratio of 2), respectively. Subsequently, they were transformed into Co$_{2/3}$-Co$_{3+}$-Br$^-$ and Co$_{2/3}$-Ni$_{1/3}$-Br$^-$ LDHs through partial oxidation of Co$_{2/3}^{+}$ into Co$^{3+}$ with Br$_2$/CH$_3$CN. Simultaneously, Br$_2$ itself was reduced to Br$^-$ and intercalated between resultant LDH host layers.

Anion exchange was performed via a salt-acid treatment (24–27). Briefly, by treating Mg$_{2/3}$-Al$_{1/3}$-CO$_3^{2-}$ and Co$_{2/3}$-Al$_{1/3}$-CO$_3^{2-}$ LDH hexagonal platelets in a salt-acid mixed solution (for example, NaCl-HCl, NaNO$_3$-HNO$_3$, and NaBr-HBr), CO$_3^{2-}$ LDHs could be exchanged into Cl$^-$, NO$_3^-$, and Br$^-$ forms, respectively. By dispersing Co$_{2/3}$-Co$_{3+}$-Br$^-$ and Co$_{2/3}$-Ni$_{1/3}$-Br$^-$ LDH hexagonal platelets in a Na$_2$CO$_3$ solution, they could be converted into CO$_3^{2-}$ forms.

Mg$_{2/3}$-Al$_{1/3}$-NO$_3^-$ and Co$_{2/3}$-Al$_{1/3}$-NO$_3^-$ LDH hexagonal platelets were chosen for exfoliation to yield single-layer nanosheets. The samples (100 mg) were dispersed in (200 mL) formamide (HCONH$_2$). Treating the suspensions with mechanical shaking for 2 days could yield single-layer LDH nanosheets with typical lateral dimensions of several micrometers. Sonication for 3 hours resulted in nanosheets with reduced lateral sizes to several hundred nanometers.

**Deposition of LDH nanosheets and platelets on comb microelectrodes**

The deposition of LDH nanosheets on comb electrodes was performed using a drop-casting method previously proposed (31–33). For discrete single-layer nanosheet assembly, a droplet (0.5 µl) of diute LDH nanosheet suspension (0.05 mg/ml) was drop-casted onto comb electrodes, followed by quickly swabbing the droplet away and drying the electrodes at 60°C for 12 hours.

An oil/water interfacial self-assembling procedure was used for the deposition of closely packed films of LDH platelets on comb electrodes (56). Co$_{2/3}$-Al$_{1/3}$-CO$_3^{2-}$, Co$_{2/3}$-Al$_{1/3}$-NO$_3^-$, and Co$_{2/3}$-Ni$_{1/3}$-Br$^-$ LDH hexagonal platelets (100 mg) were uniformly dispersed in 50 mL of water under sonication. Subsequently, hexane (4 mL) was added to form a hexane/water interface, followed by dropwise addition of isopropanol (2 mL). After most hexane was evaporated, a continuous film floating on the interface was visible, which was transferred onto comb electrodes using the vertical lifting method, followed by drying at 60°C for 12 hours.

**Preparation of lamellar membranes of LDH nanosheets**

A vacuum-assisted filtration method was used to prepare lamellar membranes. Briefly, 30 mL of Mg-Al (Co-Al) LDH nanosheet formamide suspension (0.5 mg/ml) was vacuum-filtered through a piece of polyvinylidene difluoride microfilter (pore diameter, ~0.2 µm; porosity, ~80%), followed by drying at 60°C for 12 hours. Consequently, the LDH nanosheet membrane could be easily detached from the microfilter for freestanding operation. Both membrane surfaces were evaporated with Pt (6 mm in diameter), followed by attaching to silver wires with silver paste as the electrodes for cross-plane ionic conductivity measurements.

**Preparation of LDH platelet–based pellets**

LDH platelet samples were cold-pressed into disc-shaped pellets under a pressure of ~500 MPa. The diameter and thickness of the pellets

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Measurement of ion conductivity

Ionic conductivities were determined from AC impedance spectra measured with an LCR meter (6500P, Wayne Kerr) in a frequency range from 20 Hz to 10 MHz at a constant temperature and humidity (IVV 223, Yamato Scientific Co., Ltd.). The impedance data were then transferred to the ZPlot/ZView software package (Scribner Associates). Nyquist plots usually displayed a compressed semicircle in the high-frequency range and an inclined straight line in the low-frequency range. The low-frequency end of the semicircle and the high-frequency end of the straight line generally coincided and represented the bulk resistance ($R$) (46). In plots where the semicircles were not well discerned, the intersection of the high-frequency tail of the straight line with the real axis was extracted as the resistance, which was cross-checked by equivalent circuit analysis (46). The details of the calculation of ionic conductivity ($\sigma$) from measured values of resistance $R$ were provided in the Supplementary Materials.

**SUPPLEMENTARY MATERIALS**

Supplemental material for this article is available at http://advances.sciencemag.org/cgi/content/full/3/4/e1602629/DC1

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Acknowledgments
Funding: The work was supported in part by the World Premier International Research Center Initiative, International Center for Materials Nanoarchitectonics, Ministry of Education, Culture, Sports, Science and Technology, Japan. R.M. acknowledges support from Japan Society for the Promotion of Science Grants-in-Aid for Scientific Research (KAKENHI) (grants 15H03354 and 15K13296). Author contributions: R.M. conceived the research project. R.M. and P.S. designed the experiments. P.S. and H.Z. performed the experiments. R.M., H.Z., and T.S. supervised the project. K.W. contributed to the interpretation of experimental data. P.S. and R.M. drafted the manuscript. All authors discussed the results and reviewed the manuscript. Competing interests: The authors declare that they have no competing interests.

Data and materials availability: All data needed to evaluate the conclusions in the paper are present in the paper and/or the Supplementary Materials. Additional data related to this paper may be requested from the authors.

Submitted 25 October 2016
Accepted 13 February 2017
Published 14 April 2017
10.1126/sciadv.1602629

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Sci Adv 3 (4), e1602629.
DOI: 10.1126/sciadv.1602629

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