Wide-bandgap semiconductor of three-dimensional unconventional stoichiometric NaCl2 crystal

Authors: Siyan Gao, Junlin Jia, Xu Wang, Yue-Yu Zhang, Yijie Xiang, Pei Li, Ruobing Yi, Xuchang Su, Guosheng Shi, Feifei Qin, Yi-Feng Zheng, Lei Chen, Yu Qiang, Junjie Zhang, Lei Zhang, Haiping Fang, Yue-Yu Zhang, Lei Zhang, Haiping Fang

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Abstract

The expanding applications call for novel new-generation wide-bandgap semiconductors. Here, we show that a compound only composed of the ordinary elements Na and Cl, namely three-dimensional NaCl2 crystal, is a wide-bandgap semiconductor. This finding benefits from the breaking of conventional stoichiometry frameworks in the theoretical design, leading to the discovery of three-dimensional XY2 (X = Na, Li, K; Y = Cl, F, Br, I) crystals, with covalent bonds of Y pairs inducing the wide bandgap from 2.24 to 4.45 eV. Crucially, such an unexpected NaCl2 crystal was successfully synthesized under ambient conditions. The unconventional stoichiometric strategy with other chemical elements potentially yields more wide-bandgap semiconductors, offering the capability for bandgap tuning. These unconventional stoichiometric materials may also exhibit superconductivity, transparent inorganic electrides, high-energy-density, and beyond.

Full Text

Wide-Bandgap Semiconductor Based on a Three-Dimensional Unconventional Stoichiometric NaCl2 Crystal

Siyan Gao[1]†, Junlin Jia[1]†, Xu Wang[2]†, Yue-Yu Zhang[3], *Yijie Xiang*[1], *Pei Li*[2], *Ruobing Yi*[4], *Xuchang Su*[4], *Guosheng Shi*[5], *Feifei Qin*[6], *Yi-Feng Zheng*[3], *Lei Chen*[1], *Yu Qiang*[1], *Junjie Zhang*[7], *Lei Zhang*[4], Haiping Fang[1],[8]*

[1]School of Physics and School of Material Science and Engineering, East China University of Science and Technology, Shanghai 200237, China
[2]School of Physical Science and Technology and Department of Microelectronic

Science and Engineering, Ningbo University, Ningbo 315211, China
[3]Wenzhou Institute, University of Chinese Academy of Sciences, Wenzhou 325001, China
[4]MOE Key Laboratory for Nonequilibrium Synthesis and Modulation of Condensed Matter, School of Physics, Xi'an Jiaotong University, Xi'an 710049, China
[5]Shanghai Applied Radiation Institute, Shanghai University, Shanghai 200444, China
[6]GaN Optoelectronic Integration International Cooperation Joint Laboratory of Jiangsu Province, College of Telecommunications and Information Engineering, Nanjing University of Posts and Telecommunications, Nanjing 210003, China
[7]College of Safety Engineering and Emergency Management, Nantong Institute of Technology, Nantong 226002, China
[8]School of Physics, Zhejiang University, Hangzhou, 310027, China

†These authors contributed equally to this work.
*Corresponding authors. Email: fanghaiping@sinap.ac.cn; zhangleio@xjtu.edu.cn; zhangyy@wiucas.ac.cn

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Abstract

The expanding applications of power electronics and optoelectronics call for novel new-generation wide-bandgap semiconductors. Here, we demonstrate that a compound composed solely of the ordinary elements sodium and chlorine—namely a three-dimensional $NaCl_2$ crystal—functions as a wide-bandgap semiconductor. This discovery emerges from breaking conventional stoichiometry frameworks in theoretical design, leading to a family of three-dimensional XY_2 crystals (X = Na, Li, K; Y = Cl, F, Br, I) where covalent bonds between Y pairs induce wide bandgaps ranging from 2.24 to 4.45 eV. Crucially, such an unexpected $NaCl_2$ crystal was successfully synthesized under ambient conditions. This unconventional stoichiometric strategy, extendable to other chemical elements, potentially yields additional wide-bandgap semiconductors with tunable bandgaps. These unconventional stoichiometric materials may also exhibit superconductivity, transparent inorganic electrides, high-energy-density characteristics, and other exotic properties.

Main Text

Introduction

Compared to conventional silicon-based semiconductors, new-generation wide-bandgap semiconductors such as GaN [**?**], Ga_2O_3 [**?**, **?**], SiC [**?**], and perovskites [**?**, **?**] exhibit superior thermal conductivity, enhanced resistance to high temperature and radiation, lower on-state resistance, and greater capacity for high-

voltage applications. These advancements have garnered significant attention due to substantial—sometimes orders-of-magnitude—improvements in various performance metrics. However, the development of wide-bandgap semiconductor devices has long been hindered by the scarcity of certain constituent elements, particularly the rare precious metal gallium, and by challenges associated with material extraction and manufacturing processes [**?**, **?**].

In the quest for new wide-bandgap semiconductors and materials with other unusual properties, conventional stoichiometry frameworks—particularly for main-group elements—have greatly restricted our thinking. Stoichiometry, proposed in the early nineteenth century, elegantly explains compound formation. For instance, NaCl, a crystal composed solely of sodium and chlorine with a 1:1 stoichiometry, has long served as a guiding principle for materials design.

The discovery of three-dimensional crystals with unconventional stoichiometry for main-group elements, such as H_3S [**?**, **?**], CaH_6 [**?**], and $Na_3Cl/Na_3Cl_2/NaCl_3$ [**?**], sheds new light on the nature of matter. These materials exhibit distinctive properties unlike those of conventional stoichiometric compounds, including transparent inorganic electrides [**?**, **?**] and even near-room-temperature superconductivity [**?**] and high-energy-density characteristics. However, to date, such materials have predominantly emerged and remained stable only under extremely high pressure.

Recently, unconventional stoichiometric two-dimensional crystals—including Na_2Cl, Na_3Cl, $CaCl$, Li_2Cl, and K_2Cl—have been observed on graphene and metal surfaces under ambient conditions [**?**]. These structures are stabilized by hydrated cation-π [**?**] and cation-metal interactions [**?**]. However, the short-range nature of cation-surface interactions inherently limits material growth in the third dimension and generally induces metallic properties due to enhanced delocalization of unpaired valence electrons. Despite these limitations, unconventional stoichiometric 2D crystals represent a promising avenue toward synthesizing 3D materials with unconventional stoichiometry under ambient conditions, which may exhibit intricate electronic and optical properties that can be designed and tailored, including electronic band structure and optical response.

Here, by transcending the constraints imposed by conventional stoichiometry frameworks in materials design, we have theoretically predicted that stable 3D XY_2 crystals (X = Na, Li, K; Y = Cl, F, Br, I) composed solely of ordinary elements function as wide-bandgap semiconductors with bandgaps ranging from 2.24 to 4.45 eV . These 3D XY_2 crystals hybridize ionic and covalent bonding, with covalent bonds between Y pairs contributing to both stability and wide-bandgap semiconductor properties. The electron and hole carrier mobilities of the 3D $NaCl_2$ crystal are 105 and 2,820 $cm^2\ V^{-1}\ s^{-1}$, respectively, comparable to those of GaN, Ga_2O_3, and SiC, demonstrating its potential for wide-bandgap semiconductor applications. Crucially, the 3D $NaCl_2$ crystal has been successfully synthesized under ambient conditions, and its wide-bandgap semiconductor properties have been experimentally confirmed. Notably, the methodology

employed for constructing such 3D unconventional stoichiometric crystals can be extended to other elements and magic elemental ratios, yielding not only more wide-bandgap semiconductors with tunable bandgaps but also holding vast potential for advancing materials design, including room-temperature superconductivity, transparent inorganic electrides, and high-energy-density materials, mirroring the behavior of 3D unconventional stoichiometric crystals previously obtained only at extremely high pressure.

Theoretical Prediction of 3D $NaCl_2$ Crystal Structure and Bandgap

Through global optimization searches, we investigated the phase diagram of Na–Cl crystals composed solely of sodium and chlorine without external pressure—a condition approximating ambient but distinct from high-pressure scenarios. Figure 1B [Figure 1: see original paper] shows the convex hull diagram of 3D Na–Cl crystals explored using the IM2ODE package [**?**] at the first-principles level, revealing a stable 3D $NaCl_2$ crystal (Fig. 1A). The formation energy of this 3D $NaCl_2$ crystal is -0.03 eV/atom, calculated using Equation (1):

$$E_f^{NaCl_2} = \frac{E(NaCl_2) - E(NaCl) - E(Cl_2)}{3} \quad (1)$$

where $E_f^{NaCl_2}$ is the formation energy, and $E(NaCl_2)$, $E(NaCl)$, and $E(Cl_2)$ represent the total energies of the 3D $NaCl_2$ crystal, 3D NaCl crystal, and Cl_2 molecule, respectively. It should be noted that, according to conventional stoichiometry frameworks, Na in Na–Cl crystals should exhibit a $+1$ oxidation state and Cl should exhibit -1, and the 1:1 Na:Cl ratio in the 3D NaCl crystal is the only known stable structure under ambient conditions. However, our calculations provide clear theoretical evidence for a stable 3D $NaCl_2$ crystal with an unconventional 1:2 Na:Cl ratio and negative formation energy, which is unexpected.

The key to this stability lies in the crystal structure, where horizontal NaCl layers intercalate with vertical Cl pairs, forming a periodic layer-by-layer structure along the [001] direction. Within the NaCl layer, each Na bonds with six Cl atoms, while each Cl atom (designated Cl_1) bonds with only five Na atoms. In the Cl layer, each Cl atom (designated Cl_2) forms two bonds: one to Na and one to another Cl_2. The optimized lattice parameters are $a = 5.63$ Å, $b = 5.63$ Å, $c = 11.07$ Å, and $\alpha = \gamma = 90°$, $\beta = 116.89°$. The 3D $NaCl_2$ crystal possesses $C2/m$ symmetry (space group No. 12), a configuration unprecedented in the literature for Na–Cl crystals [**?**, **?**].

We employed the electron localization function (ELF) [**?**] to analyze the electronic structure of Cl_1 and Cl_2, with results depicted in Fig. 1C. The analysis confirms that electrons are strongly localized around Cl_1 within the NaCl layer, indicating ionic bonding between Na and Cl_1. Conversely, electrons in the Cl_2

layer occupy the space between Cl_2 pairs, indicating covalent bond formation. Bader charge analysis [**?**] shows that each Na loses 0.84 electrons, while each Cl_1 and Cl_2 atom gains 0.76 and 0.08 electrons, respectively (Table S2). Minor charge transfer occurs between Na and the Cl_2 pairs to form ionic bonds, which stabilizes both the NaCl ionic layer and the Cl pairs. Natural bond orbital analysis [**?**, **?**] reveals the formation of sp^3 orbitals between Cl_2 pairs (fig. S14), resembling the covalent bond in Cl_2 molecules. This further confirms that the specific configuration of the 3D $NaCl_2$ crystal, featuring both ionic and covalent bonding, ensures electrical neutrality and stability despite its unconventional stoichiometry.

The 3D $NaCl_2$ crystal demonstrates energetic, dynamical, thermal, and chemical stability through formation energy calculations, phonon dispersion analysis, ab initio molecular dynamics (AIMD) simulations, and chemical potential calculations (figs. S15 and S16). These results underscore the significant potential for stable 3D $NaCl_2$ crystals exhibiting mixed ionic-covalent bonding.

Excitingly, the bandgap energy of this unconventional 3D $NaCl_2$ crystal is 4.22 eV (Fig. 1D), based on Heyd-Scuseria-Ernzerhof (HSE06) functional calculations [**?**]. This value substantially exceeds those of popular wide-bandgap semiconductors such as SiC (~3.20 eV) [**?**] and GaN (3.39 eV) [**?**], and approaches that of Ga_2O_3 (4.20–5.30 eV) [**?**]. Carrier mobility μ was estimated using the deformation potential (DP) model proposed by Bardeen and Shockley [**?**]. The electron and hole carrier mobilities of the 3D $NaCl_2$ crystal are approximately 105 and 2,820 $cm^2\ V^{-1}\ s^{-1}$, respectively, along the c direction—comparable to those of SiC, GaN, and Ga_2O_3 (20–1000 $cm^2\ V^{-1}\ s^{-1}$) [**?**], demonstrating its potential for wide-bandgap semiconductor applications. The projected density of states (PDOS) reveals that both the valence band maximum (VBM) and conduction band minimum (CBM) are primarily contributed by the p orbitals of Cl atoms (Fig. 1D). Further insights into the electronic states were obtained through partial charge densities for the VBM and CBM. As depicted in Figs. 1E and 1F, the VBM is primarily associated with Cl_1 sp^3 orbitals, while the CBM is mainly contributed by Cl_2 sp^3 orbitals, providing strong evidence for inner-layer pairing of Cl atoms.

Figure 1G shows the optical absorption spectra of the 3D $NaCl_2$ crystal along the a, b, and c directions. Isotropy is observed between the a and b directions, with the first absorption peak commencing at the band edge of 4.22 eV and reaching its maximum at 4.62 eV. However, anisotropy is evident between the a (and b) and c directions, with the first absorption peak along the c direction emerging at 4.70 eV. The significant ultraviolet (UV) absorption of the 3D $NaCl_2$ crystal illustrates its potential application in UV photodetectors. Notably, the absorptance along the c direction is much greater than that along the a and b directions, indicating structure-induced anisotropy.

Synthesis and Characterization of 3D $NaCl_2$ Crystals

Positively charged polyethyleneimine (PEI)-modified graphene oxide (p-GO) membranes exhibited relatively smooth, dense surfaces with uniform, appropriate positive charge, which could induce greater aggregation of Cl than Na in NaCl solution near the surface. Multi-layer p-GO membranes prepared by drop-casting were immersed in 1.0 mol/L (M) NaCl salt solution for 12 hours and subsequently dried using filter paper. Additional cleaning and drying steps—including surface washing with 5 mL deionized water, followed by vacuum drying at 70°C for 12 hours—were undertaken to obtain the final samples, denoted as Na–Cl@p-GO membranes.

We utilized transmission electron microscopy (TEM) to examine the detailed morphology and atomic structure of crystals on the membranes. Crystallization and elemental content were analyzed using high-angle annular dark-field scanning TEM (HAADF-STEM) (Fig. 2A [Figure 2: see original paper]). A considerable number of regularly shaped regions with an approximately 1:2 Na:Cl atomic ratio were observed (Fig. 2A). Figure 2B displays a typical region where a clear crystal lattice is visible in high-resolution TEM (HR-TEM), with the area marked by the red rectangle further magnified in Fig. 2C. The fast Fourier transform (FFT) of this region (inset of Fig. 2C) aligns well with our theoretical predictions for the (001) crystal plane (fig. S18A). The estimated lattice spacing of the observed crystals is ~3.87$±$0.12 Å, closely matching the theoretical Na–Na distance (~3.98 Å).

We further employed cryo-electron microscopy (cryo-EM) [**?**, **?**] to characterize the structure. Ultra-thin p-GO membranes were prepared for imaging under low-damage, in situ conditions [**?**, **?**]. These membranes were fabricated directly on carbon holey films by dispersing a p-GO solution to a concentration of 0.01 g/mL and depositing 20 L of the dispersion onto the film. Imaging parameters—including high tension, exposure time, total dose, and low-dose techniques—were carefully optimized to balance electron-beam damage against resolution loss. Consequently, crystals with higher crystallographic indices, such as (601) (Fig. 2F), were observed. Upon tilting this same crystal by 5°, the (301) lattice plane became visible (Fig. 2G). This transformation is consistent with our predicted 3D model (figs. S18B and S18C), providing reliable evidence that the $NaCl_2$ crystal indeed forms a 3D structure. Moreover, the (001) plane was also observed by cryo-EM with the presence of a graphene amorphous ring (fig. S7), confirming in situ growth of 3D $NaCl_2$ crystals.

Ultraviolet and Transport Properties of 3D $NaCl_2$ Crystals

We performed ultraviolet-visible-near-infrared (UV-Vis-NIR) spectroscopy to determine the bandgap width of the 3D $NaCl_2$ crystal. The UV-Vis-NIR spectrum (Fig. 3A [Figure 3: see original paper]) was obtained by subtracting the contributions of NaCl solution and p-GO suspension from the mixture of p-GO

suspension and NaCl solution (fig. S9). The 3D $NaCl_2$ crystal exhibits an optical bandgap of 4.27 eV (Fig. 3A), determined using the Tauc equation method [**?**] with x-intercept analysis. This value is in close agreement with the theoretical prediction (4.22 eV).

Additionally, we employed micro-photoluminescence (micro-PL) spectroscopy to measure the PL intensity of NaCl crystal, p-GO, and Na–Cl@p-GO membranes. Samples were mounted on the cold finger of a closed-cycle cryostat and cooled from 300 K to 5 K under flowing helium. As illustrated in Fig. 3B, a minor peak at 3.48 eV (356 nm) and a pronounced PL peak at 2.96 eV (419 nm) were observed at 5 K for Na–Cl@p-GO membranes, while NaCl crystal exhibited two similar peaks at 3.00 eV (414 nm) and 2.74 eV (452 nm) with low intensity. A new PL peak at 2.75 eV (451 nm) was observed for Na–Cl@p-GO membranes, which is smaller than the theoretical bandgap of 3D $NaCl_2$ crystal. We attribute this difference to defect states within the 3D $NaCl_2$ crystal that introduce defect energy levels within the bandgap, resulting in a redshift of the PL peak. Notably, the PL peak intensity showed only minor increases upon cooling to 5 K and fully recovered upon reheating to 300 K (fig. S10), indicating that Na–Cl@p-GO membranes maintain highly stable optoelectronic properties across the 5–300 K temperature range—critical for UV sensor operation.

We performed direct standard four-wire measurements using a physical property measurement system (PPMS-9) to quantitatively assess the transport properties of Na–Cl@p-GO membranes. As depicted in Fig. 3C, the sheet resistance showed exponential decay with increasing temperature, consistent with well-established semiconductor behavior. We also measured the surface resistivity of pure p-GO membranes, which exceeds 100 MΩ, exhibiting inherent insulating characteristics. This confirms that the semiconducting properties observed in Na–Cl@p-GO membranes originate primarily from the 3D $NaCl_2$ crystals.

We subsequently fabricated a photodetector based on the Na–Cl@p-GO membrane. Silver interdigital electrodes were deposited onto the dried membrane to evaluate its UV light response (Fig. 3D). Linear I–V characteristics (Fig. 3E) indicate Ohmic contacts between the Na–Cl@p-GO membranes and Ag electrodes. A notable enhancement in photocurrent under UV illumination compared to the dark current (Fig. 3E) provides further evidence of effective optical absorption by the 3D $NaCl_2$ crystal within the UV spectrum. The photo-switching property of the Na–Cl@p-GO membrane-based photodetector was measured under different bias voltages (Fig. 3F). The current exhibits sharp increases and decreases upon initiation and termination of light illumination, respectively, indicating strong interaction between light and charge carriers. Furthermore, reproducible time-dependent photoresponse under cyclic illumination confirms the stable photo-switching characteristics of the device (Fig. 3F). A transient photocurrent test conducted under 365 nm light exposure at 1 V bias revealed rise and fall times of 237 ms and 248 ms, respectively (fig. S13).

Other 3D XY_2 (X = Na, Li, K; Y = Cl, F, Br, I) Crystal Structures and Bandgaps

The unique composition of the 3D $NaCl_2$ crystal—featuring NaCl layers with ionic bonding interspersed with layers of covalently bonded Cl pairs—highlights the potential of combining ionic and covalent bonding strategies to stabilize and synthesize novel materials. This methodology can be extended to various Group I–VII ionic materials XY_2 (X = Li, Na, K; Y = F, Cl, Br, I). These materials were demonstrated to be energetically stable through formation energy calculations (Table S6). The calculated bandgaps span a considerable range from 2.24 to 4.45 eV (Fig. 1H and Table S7). Notably, 3D LiF_2 and $LiCl_2$ crystals exhibit bandgaps of 4.42 eV and 4.45 eV, respectively, exceeding that of 3D $NaCl_2$ crystal (4.22 eV), while 3D LiI_2 crystal possesses a moderate bandgap of 2.24 eV, potentially suitable for solar cell absorption. The diverse options offered by this family of 3D XY_2 crystals hold promise for revolutionizing semiconductor development by enabling tunable bandgaps, thereby facilitating their utilization in advanced semiconductor technologies.

Conclusion

In summary, by transcending the limitations of conventional stoichiometry frameworks, we have demonstrated that a 3D unconventional stoichiometric $NaCl_2$ crystal hybridizes ionic and covalent bonds, with covalent Cl–Cl pairs contributing to its stability and wide-bandgap semiconductor properties. Specifically, the 3D $NaCl_2$ crystal exhibits a bandgap of 4.22 eV, with electron and hole carrier mobilities of 105 and 2,820 $cm^2\ V^{-1}\ s^{-1}$, respectively. These bandgap and mobility values are comparable to those of SiC, GaN, and Ga_2O_3 (bandgaps of 3.00–5.00 eV and mobilities of 20–1000 $cm^2\ V^{-1}\ s^{-1}$), demonstrating its potential for wide-bandgap semiconductor applications. Crucially, the predicted 3D $NaCl_2$ crystal has been successfully synthesized under ambient conditions, directly observed via in situ cryo-EM, and its wide-bandgap semiconductor properties experimentally confirmed. Additionally, a functional photodetector based on this $NaCl_2$ crystal has been fabricated.

This hybrid ionic-covalent mechanism universally endows materials composed of various elements with wide-bandgap semiconductor characteristics. We have theoretically constructed a series of 3D unconventional stoichiometric XY_2 crystals (X = Na, Li, K; Y = Cl, F, Br, I) featuring hybrid ionic-covalent bonds, with bandgaps ranging from 2.24 to 4.45 eV. Furthermore, we anticipate that further exploration of unconventional stoichiometry through introduction of other chemical elements will yield additional wide-bandgap semiconductors with an even broader range of bandgaps and carrier mobilities. The diverse options provided by these unconventional stoichiometric crystals potentially make wide-bandgap semiconductors more accessible and enable extensive applications with tunable bandgaps.

Materials featuring both ionic and covalent bonding can be strategically manipulated to harness the benefits of both bonding types. Extension of this bonding paradigm suggests the possibility of applying the Cl-pairing strategy to larger clusters, including metallic clusters with magic numbers and even transition metals. Consequently, a wider array of unconventional stoichiometric materials could be designed under ambient conditions, facilitating the creation of materials with other distinctive properties—such as superconductivity and even near-room-temperature superconductivity, transparent inorganic electrides, and high-energy-density characteristics—previously observed only in 3D unconventional stoichiometric crystals under extremely high pressure. This marks a significant shift toward exploring materials beyond conventional stoichiometries for next-generation technological applications.

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Author contributions: H.F. and Y.Z. designed the project. Y.Z., S.G., Y.X., and Y.Z. predicted the existence of three-dimensional crystals with unconventional stoichiometry via the IM2ODE package. Y.Z., J.J., R.Y., L.C., Y.Q., and J.Z. synthesized $NaCl_2$ crystals and p-GO membranes. L.Z., J.J., R.Y., and X.S. characterized the three-dimensional $NaCl_2$ crystal by TEM and cryo-EM. Y.Z. and J.J. performed UV-Vis-NIR spectroscopy to measure the bandgap width. X.W. and F.Q. fabricated a photodetector based on the Na–Cl@p-GO membranes. H.F., Y.Z., L.Z., G.S., S.G., and J.J. co-wrote the paper. All authors discussed the results and commented on the manuscript.

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Supplementary Materials

Materials and Methods
Supplementary Text
Figs. S1 to S18
Tables S1 to S8
References (48–61)

Figure Captions

Fig. 1. Three-dimensional (3D) XY_2 (X = Na, Li, K; Y = Cl, F, Br, I) crystal structures and corresponding bandgap energies. (A) 3D $NaCl_2$ crystal structure. Yellow, green, and blue balls represent Na ions, Cl_1 ions, and Cl_2 ions, respectively. (B) Convex hull diagram of Na–Cl crystals composed solely of

sodium and chlorine obtained from both ground-state structures and structural searches. The 3D $NaCl_2$ crystal structure studied in our work is energetically stable against decomposition into NaCl and Cl_2. (C) Two-dimensional (2D) projection of electron localization function (ELF) at the (110) plane. The unit cell is marked by the black line. (D) Heyd-Scuseria-Ernzerhof (HSE06) band structure, total density of states (TDOS), and projected density of states (PDOS) of 3D $NaCl_2$ crystals. (E) and (F) Partial charge densities for valence band maximum (VBM) (red) and conduction band minimum (CBM) (blue) of 3D $NaCl_2$ crystals. (G) Density functional theory (DFT)-simulated absorption spectra for 3D $NaCl_2$ crystals along the *a*, *b*, and *c* directions. (H) Bandgap energies of 3D XY_2 (X = Na, Li, K; Y = Cl, F, Br, I) crystals.

Fig. 2. Imaging of 3D $NaCl_2$ crystals. (A) High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image of Na–Cl@p-GO membranes. The inset shows the Na:Cl ratio for Na–Cl@p-GO membranes corresponding to the five marked regions. (B) High-resolution transmission electron microscopy (HR-TEM) image of Na–Cl@p-GO membranes. (C) Zoom-in image of the area indicated by the red box in (B). The upper-right inset shows a fast Fourier transform (FFT) image of this area. (D) Background-removed inverse fast Fourier transform (iFFT) image of the selected area in (C). (E) Schematic drawings of the sample preparation process for cryo-electron microscopy (cryo-EM) imaging. (F) Diffraction pattern of the (601) lattice plane from cryo-EM imaging. (G) Diffraction pattern of the (301) lattice plane after 5° tilt of the sample plane from cryo-EM imaging.

Fig. 3. Bandgap properties of 3D $NaCl_2$ crystals measured experimentally. (A) Experimental ultraviolet-visible-near-infrared (UV-Vis-NIR) absorption spectrum for 3D $NaCl_2$ crystals. The experimental optical bandgap obtained from the Tauc plot (4.27 eV) aligns well with the theoretical bandgap (4.22 eV). (B) Micro-photoluminescence (micro-PL) spectra measured at 5 K for NaCl, p-GO, and Na–Cl@p-GO membrane samples. (C) Sheet resistance of Na–Cl@p-GO membrane as a function of temperature. (D) Image of the Na–Cl@p-GO membrane-based photoelectric detector. (E) I–V characteristics of the Na–Cl@p-GO membrane-based photodetector in the dark and under different illumination power intensities. (F) Time-dependent photoresponse of the Na–Cl@p-GO membrane-based photodetector at different bias voltages.

Note: Figure translations are in progress. See original paper for figures.