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Liquid-Phase Exfoliation of Magnetically and Optoelectronically Active Ruthenium Trichloride Nanosheets

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possesses a range of exotic magnetic, optical, and electronic properties including fractional excitations indicative of a proximate Kitaev quantum spin liquid (QSL). While previous reports have explored these properties on idealized single crystals or mechanically exfoliated samples, the scalable production of α -RuCl₃ nanosheets has not yet been demonstrated. Here, we perform liquid-phase exfoliation (LPE) of α -RuCl₃ through an electrochemically assisted approach, which yields ultrathin, electron-doped α -RuCl₃ nanosheets that are then assembled into electrically conductive large-area thin films. The crystalline integrity of the α -RuCl₃ nanosheets following LPE is confirmed through a wide range of structural and



chemical analyses. Moreover, the physical properties of the LPE α -RuCl₃ nanosheets are investigated through electrical, optical, and magnetic characterization methods, which reveal a structural phase transition at 230 K that is consistent with the onset of Kitaev paramagnetism in addition to an antiferromagnetic transition at 2.6 K. Intercalated ions from the electrochemical LPE protocol favorably alter the optical response of the α -RuCl₃ nanosheets, enabling large-area Mott insulator photodetectors that operate at telecommunications-relevant infrared wavelengths near 1.55 μ m. These photodetectors show a linear photocurrent response as a function of incident power, which suggests negligible trap-mediated recombination or photothermal effects, ultimately resulting in a photoresponsivity of ≈ 2 mA/W.

KEYWORDS: 2D materials, α -RuCl₃, transition metal halide, proximate Kitaev spin liquid, Mott insulator, electrochemical exfoliation, solution processing

Rule trichloride (α -RuCl₃) is a layered transition metal halide, previously identified as a Mott insulator^{1,2} with strong spin-orbit coupling,³ making it a prime candidate for experimentally achieving a proximate Kitaev quantum spin liquid (QSL) that can host Majorana fermionic fractional excitations.^{4,5} Consistent with QSLs, previous work on α -RuCl₃ has demonstrated magnetic signatures of Majorana fermions through Raman scattering,⁶⁻¹¹ inelastic neutron scattering,¹²⁻¹⁵ and terahertz spectroscopy.¹⁶⁻¹⁸ In addition, the observation of the fractional thermal quantum Hall effect in α -RuCl₃ has provided further evidence in support of the existence of Majorana fermions.^{19,20} Although the exact onset of magnetic excitations varies between studies, it has been repeatedly suggested that the atomic structure of α -RuCl₃ is intimately connected with its magnetic properties, with a structural phase change reported between 100 and 180 K that

accompanies a transition from a traditional paramagnetic state to that of a Kitaev paramagnetic state. 7,8,21

Due to the large electron affinity of α -RuCl₃, this material has also been studied in the context of an electron acceptor in van der Waals heterojunctions with various two-dimensional (2D) materials.^{22,23} In particular, α -RuCl₃ effectively *p*-type dopes graphene and WSe₂²⁴ and introduces spin-split band hybridization in graphene-RuCl₃ heterostructures.²⁵ This charge transfer process can further drive α -RuCl₃ to the

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Figure 1. Electrochemical Intercalation of α -RuCl₃. (A and B) Crystal structure of α -RuCl₃ along the (A) in-plane *a*-axis and (B) out-ofplane *c**-axis. α -RuCl₃ adopts a monoclinic structure (a = 5.976 Å, b = 10.342 Å, c = 6.013 Å, $\alpha = \gamma = 90^{\circ}$, $\beta = 108.87^{\circ}$). Models made with VESTA.⁴⁸ (C) Chemical structure of THAB and CHP. (D) Schematic of the electrochemical intercalation setup. A negative bias is applied on the α -RuCl₃ working electrode, which leads to the intercalation of THA⁺ cations, while the counter electrode oxidizes Br⁻. (E) XRD of the α -RuCl₃ crystal prior to intercalation, after intercalation, and after exfoliation. Intercalation with THA⁺ results in expansion of the *c*parameter to 24.9 Å. After exfoliation, the α -RuCl₃ film shows a broad peak corresponding to a *c*-parameter of 16.2 Å, most likely due to CHP intercalation. Photographs of a film of α -RuCl₃ filtered on an AAO membrane, an intercalated crystal, and a pristine crystal are shown in the plot from top to bottom. On the right is a photograph of a dispersion of α -RuCl₃ after exfoliation.

Kitaev point without the aid of magnetic fields.^{26,27} Upon electron doping, α -RuCl₃ exhibits an unconventional Mott transition where a distinct band is generated close to the valence band that does not accompany a metal-to-insulator transition but instead reduces the optical bandgap.²⁸ This phenomenon has recently been exploited in a near-infrared (NIR) photodetector based on α -RuCl₃ that was electron-doped following organic cation intercalation.²⁹ In addition, it has been predicted that magnetic phase transitions can be driven optically in α -RuCl₃, providing another degree of freedom in tuning magnetic properties.³⁰

The vast majority of previous research on α -RuCl₃ has focused on idealized single crystals or micromechanically exfoliated samples, with only limited reports investigating fewlayer α -RuCl₃ nanosheets. When exfoliated down to the monolayer or bilayer limit, α -RuCl₃ exhibits significant temperature-dependent Raman spectra, which likely results from enhanced magnetic fluctuations in the ultrathin limit, emphasizing the need for further investigation of few-layer α -RuCl₃ nanosheets.⁶ An exception to single-crystal or micromechanically exfoliated samples is the work of Weber et al.,³¹ where few-layer α -RuCl₃ nanosheets were prepared by lithium intercalation, exfoliation in water, and bromination to oxidize the α -RuCl₃ layers. Since the subsequent property characterization focused exclusively on magnetic measurements on restacked pellets of the α -RuCl₃ nanosheets, the optoelectronic properties of large-area percolating thin films of α -RuCl₃ nanosheets remain unexplored.

In this work, we demonstrate electrochemically assisted liquid-phase exfoliation (LPE) of electron-doped, few-layer α -RuCl₃ nanosheets. Electrochemically assisted LPE facilitates exfoliation using relatively gentle bath sonication and electron dopes the resulting α -RuCl₃ nanosheets, resulting in electrically percolating thin films that have not previously been demonstrated for LPE transition metal halides. These α -RuCl₃ nanosheets are assembled into optoelectronically active large-area thin films that show modified optical properties, namely, a broad optical absorption peak that encompasses energies as low as 0.59 eV, due to the electron doping that arises from electrochemical intercalation. These optoelectronic properties are suitable for NIR applications, particularly for α -RuCl₃ thin-film photodetectors that show a nearly intensityindependent responsivity of ≈ 2 mA/W and rise/fall times of \approx 100 ms when illuminated at telecommunications-relevant wavelengths near 1.55 μ m. The electronically percolating and magnetically active α -RuCl₃ thin films also enable variable

temperature studies via electronic and magnetic probes. These measurements reveal a structural phase transition occurring at 230 K that is linked to the onset of Kitaev paramagnetism and an antiferromagnetic transition at 2.6 K. Overall, this work establishes a methodology for scalable exfoliation and assembly of electron-doped, few-layer α -RuCl₃ nanosheets into magnetically and optoelectronically active thin films with broad utility for fundamental studies and technological applications.

RESULTS AND DISCUSSION

 α -RuCl₃ possesses a layered, monoclinic structure (a = 5.976Å, b = 10.342 Å, c = 6.013 Å, $\alpha = \gamma = 90^{\circ}$, $\beta = 108.87^{\circ}$) with an interlayer spacing of 5.69 Å, as shown in Figure 1A,B.^{32,33} To facilitate LPE, an α -RuCl₃ crystal is first electrochemically intercalated with large quaternary ammonium cations using a previously reported procedure.³⁴ Briefly, the α -RuCl₃ crystal is clipped between pieces of Pt foil and submerged in an electrolyte of tetrahexylammonium bromide (THAB or THA+ Br⁻, Figure 1C) dissolved in acetonitrile, which is chosen due to its wide electrochemical stability window. The large THA⁺ cation is then intercalated by applying a negative bias to the $\alpha\text{-}$ RuCl₃ crystal, with the counter electrode oxidizing the Brcounterion. THAB is chosen as the salt as it has been shown to provide the optimal balance between intercalation efficiency and layer expansion.³⁴ X-ray diffraction (XRD) of the α -RuCl₃ crystal before and after intercalation (Figure 1E) reveals that the c-parameter changes from 6.0 to 24.9 Å, with THA⁺ intercalation successfully expanding the layered structure. In contrast, in-plane XRD of α -RuCl₃ displays only a slight compression along the *b*-axis (Figure S1). One-dimensional (1D) electron density model calculations based on the XRD patterns confirm that the THA⁺ is responsible for the expansion of the Cl-Cl interlayer spacing in α -RuCl₃ from 3.2 to11.9 Å, without appreciably distorting the α -RuCl₃ layers in-plane (Figure S2).

Due to the expanded interlayer spacing, the intercalated α -RuCl₃ crystal is then easily exfoliated via bath sonication in Ncyclohexyl-2-pyrrolidone (CHP, Figure 1C), without the need for additional stabilizers or surfactants. XRD on a film of the exfoliated α -RuCl₃ nanosheets shows a broad peak corresponding to a c-parameter of 16.2 Å, indicating that some guest species remain intercalated even after exfoliation. On the basis of XRD studies on mechanically exfoliated samples intercalated with CHP, we assign these species to CHP intercalated α -RuCl₃ (Figure S3). When compared to other high boiling point solvents such as N-methyl-2-pyrrolidone (NMP) or the electrolyte THAB in acetonitrile, the exposure to CHP results in larger and faster expansion of the interlayer spacing, indicating the suitability of CHP for the high-yield exfoliation of α -RuCl₃ (Figure S3). The absence of other peaks besides the (00*l*) peaks suggests that our film of exfoliated α -RuCl₃ nanosheets is highly oriented, with flakes lying flat on the filter membrane. Atomic force microscopy (AFM) reveals that electrochemically assisted LPE results in an ultrathin, highaspect-ratio α -RuCl₃ nanosheets (Figure 2A). Size histograms generated from AFM analysis of 606 nanosheets show a narrow peak in the thickness distribution with a log-normal mean of ≈ 2 nm (Figure 2B) and a lateral length distribution with a log-normal mean of ≈ 200 nm (Figure 2C).

To confirm that the LPE process does not compromise the crystalline integrity of the α -RuCl₃ nanosheets, multiple spectroscopy and microscopy characterization methods were applied to the exfoliated α -RuCl₃ dispersion and compared to a



Figure 2. AFM size histograms of α -RuCl₃. (A) AFM of α -RuCl₃ nanosheets drop-cast on a SiO₂/Si substrate. A line profile of an exemplar flake shows a thickness of 1.68 nm with a corresponding lateral size of 861 nm. (B) Thickness and (C) lateral size histograms of α -RuCl₃ nanosheets fit to a log-normal distribution with a log-normal mean thickness of 2.00 nm and log-normal mean lateral length of 203 nm.

pristine α -RuCl₃ crystal. For example, optical absorbance spectroscopy of the α -RuCl₃ crystal shows the onset of absorption at 1.14 eV with higher energy absorption peaks at 2.1 and 3.2 eV (Figure 3A), while the LPE α -RuCl₃ sample possesses a broad absorption feature that appears at energies as low as 0.59 eV in addition to the higher energy absorption features being blue-shifted. Photoluminescence (PL) spectroscopy with an excitation laser of 532 nm (2.33 eV) on the α -RuCl₃ crystal reveals a weak response at 2.15 eV, which increases upon electrochemical intercalation and exfoliation (Figure 3B). These optical absorption and PL results agree well with the previous literature for intercalated α -RuCl₃ nanosheets²⁹ and indicate that electron doping persists after exfoliation, leading to a modification of the optical response of



Figure 3. Spectroscopic characterization and microscopy of α -RuCl₃ nanosheets. (A) Optical absorbance spectroscopy of α -RuCl₃ micromechanically exfoliated on a sapphire substrate and an α -RuCl₃ dispersion in CHP. The micromechanically exfoliated α -RuCl₃ shows an absorption onset at 1.14 eV, followed by higher energy peaks at 2.1 and 3.2 eV. Following liquid-phase exfoliation, a much larger absorption feature appears down to energies as low as 0.59 eV, while the high energy peaks shift to higher energies compared to the micromechanically exfoliated samples. (B) PL spectroscopy of a bulk α -RuCl₃ crystal and a film of LPE α -RuCl₃. The film shows an enhanced PL response at 2.15 eV. (C) Raman spectroscopy of a bulk α -RuCl₃ crystal and an LPE α -RuCl₃ film. The Raman peaks are broadened after LPE as expected for few-layer α -RuCl₃ nanosheets. (D) TEM micrograph of LPE α -RuCl₃ nanosheets with corresponding (E) high-resolution TEM and (F) SAED. The atomic structure and diffraction agree well with α -RuCl₃ oriented along the *c**-axis. (G) Ru 3d and (H) Cl 2p XPS scans of an α -RuCl₃ crystal and an LPE α -RuCl₃ film. The Ru 3d core scan shows Ru³⁺ levels overlapping with adventitious carbon. After LPE, one Ru³⁺ peak doublet shifts to lower binding energies, corresponding to Ru²⁺. The Cl 2p shows a similar shift to lower binding energies, further suggesting a reduction of α -RuCl₃ due to intercalation-induced electron doping.

LPE α -RuCl₃. Raman spectroscopy reveals broadening of the E_g and A_{1g} vibrational modes upon solution-phase exfoliation (Figure 3C), which can be attributed to quantum confinement in the nanosheets, since similar broadening has been reported for mechanically exfoliated few-layer α -RuCl₃.⁶ In addition, high-resolution transmission electron microscopy (TEM) and selected-area electron diffraction (SAED) show atomic resolution and diffraction patterns (Figure 3D–F) consistent with micromechanically exfoliated α -RuCl₃ (Figure S4), which further emphasizes the high crystalline integrity of the LPE α -RuCl₃ nanosheets.

Chemical characterization via X-ray photoelectron spectroscopy (XPS) on a pristine α -RuCl₃ crystal reveals three major doublets attributed to Ru³⁺ in the Ru 3d core level scan (Figure 3G) with Ru 3d 5/2 peaks centered at 281.2, 281.9, and 282.7 eV (the aquamarine dashed line is a visual aid to see the Ru contribution to the spectra after C 1s peak subtraction). Upon electrochemical intercalation and exfoliation, the lowest energy doublet shifts toward lower binding energy, with the Ru 3d 5/2 peak moving from 281.2 to 280.2 eV, indicative of a reduction of Ru³⁺ to Ru²⁺, as expected for electron doping and as reported in previous α -RuCl₃ intercalation studies.^{29,35} Cl 2p scans show a similar reduction in the binding energy in Figure 3H, with the Cl 2p 3/2 peaks centered at 198.6 and 198.8 eV shifting to 198.0 and 198.6 eV, respectively.

Electrochemical intercalation allows for high yields of exfoliation through mild bath sonication that imparts ultrasonic intensities a factor of 1000 lower than tip sonication,³⁶ which accordingly reduces the amount of sonochemical degradation that occurs in typical LPE procedures using pyrrolidone-based solvents (e.g., tip sonication in NMP).³⁷⁻³⁹ Control experiments on MoS₂ thin films obtained by a similar exfoliation procedure demonstrates that bath sonication of MoS₂ results in films that are on average an order of magnitude more conductive, indicating that bath sonication contributes to higher conductivity in films when using pyrrolidone-based solvents (Figure S5). Consequently, we anticipate that our LPE α -RuCl₃ should be well-suited for charge transport measurements in percolating thin films. Toward this end, a thin film of α -RuCl₃ nanosheets (thickness \approx 200 nm as measured by cross-sectional scanning electron microscopy) was formed on anodized aluminum oxide (AAO) by vacuum filtration and then patterned using a polydimethylsiloxane (PDMS) stamp. Cr/Au contacts were then evaporated directly onto the AAO membrane through shadow masks, as depicted in Figure 4A,B. Linear current-voltage (I-V) curves were



Figure 4. Electrical characterization of α -RuCl₃ films. (A) Schematic of the α -RuCl₃ thin-film device. Au contacts are evaporated on top of a film of α -RuCl₃ that is patterned using a PDMS stamp on top of the AAO membrane. (B) Optical image of the α -RuCl₃ device (channel length 225 μ m, channel width 790 μ m). (C) Four-probe output curves as a function of temperature. The curves are linear down to 120 K. (D) Resistance plotted as a function of $T^{-1/3}$. By fitting to a variable range hopping model, a phase transition temperature of 230 K is extracted.

collected over a range of temperatures from 300 K ($\rho \approx 20 \ \Omega$ cm) to 120 K (Figure 4C), demonstrating ohmic contacts between the metal electrodes and the α -RuCl₃ nanosheets. Using a four-probe geometry, the sheet resistance was measured and fitted to a variable range hopping (VRH) model, with the relation

$$R = R_0 \exp\left(\frac{T_0}{T}\right)^{1/n+1}$$

where *R* is the resistance, T_0 is the characteristic temperature, and *n* is the transport dimensionality (n = 2 for α -RuCl₃ nanosheets). A semilogarithmic plot of *R* versus $T^{-1/3}$ measured upon cooling down reveals two distinct conduction regimes with slightly different slopes in Figure 4D. The extracted transition temperature of ≈ 230 K is slightly higher that previously reported phase transition temperatures for α -RuCl₃, presumably due to enhanced electron–electron correlations resulting from intercalation-induced electron doping and/or thickness-dependent effects for LPE few-layer α -RuCl₃.^{7,21} It should be noted that the warming up data shown in Figure S6 reveal a similar transition temperature of ≈ 240 K.

To further probe this phase transition in LPE α -RuCl₃ nanosheets, we measured four-probe magnetoresistance on the same large-area device. The measurements employed an out-of-plane magnetic field, and the magnetoresistance (MR) was calculated as MR = $\Delta R/R = (R_{\rm H} - R_0)/R_0$ (Figure 5A). At 130 K, the MR is positive, but as the temperature increases, the MR monotonically decreases and ultimately changes sign. Plotting the maximum MR (measured at an effective applied magnetic field of 1 T) as a function of temperature (Figure 5B) reveals a clear transition from positive MR to negative MR, with the transition temperature occurring between 210 and 230 K, agreeing well with the phase transition temperature extracted from the VRH model.

SQUID magnetometry provides additional insight into the low-temperature magnetic transitions in LPE α -RuCl₃. Bulk α -RuCl₃ crystals exhibit an antiferromagnetic transition with $T_{\text{N\acute{e}el}} = 7-14 \text{ K.}^{40}$ In contrast, when the magnetic moment, m, is measured for an LPE α -RuCl₃ film (thickness \approx 900 nm, area $\approx 0.145 \text{ cm}^2$) with an in-plane and out-of-plane magnetic field (Figure 5C and Figure S8), we observe a clear peak at $T_{\text{N\acute{e}el},\parallel} = 2.6$ K, which is lower than the value reported for bulk crystals. This suppression in $T_{\text{N\'eel}}$ can be attributed to electron doping and a relative increase in the interlayer spacing between α -RuCl₃ monolayers due to CHP intercalation, as also observed in lithium-intercalated α -RuCl₃.⁴¹ Specifically, the reduction of Ru³⁺, which is a paramagnetic ion, into Ru²⁺, which has negligible magnetic response, results in a decrease of $T_{\text{N\'eel}}$. In addition, the LPE α -RuCl₃ thin film also shows an antiferromagnetic transition when the magnetic field is applied in the out-of-plane direction at $T_{\text{N\acute{e}el},\perp} = 2.4 \text{ K}$ (Figure S8), which can be attributed to the turbostratically restacked film morphology having some in-plane orientation with the applied magnetic field.

Our electrochemical intercalation and LPE process also favorably modifies the optoelectronic properties of α -RuCl₃. Unlike pristine α -RuCl₃ that exhibits negligible NIR response due to the bandgap being larger than 1 eV, intercalationinduced electron doping produces electronic states near the valence band, which effectively reduce the energy threshold for optical absorption. The net effect is that a large photocurrent



Figure 5. Magnetic characterization of α -RuCl₃ films. (A) Magnetoresistance as a function of the applied magnetic field and temperature. (B) Magnetoresistance versus temperature at an effective magnetic field of 1 T. The magnetoresistance changes signs from positive to negative between 210 and 230 K, agreeing well with the observed phase transition temperature extracted from the variable range hopping model. (C) In-plane magnetic moment as a function of temperature. Left inset: cross-sectional scanning electron microscopy image of a film of α -RuCl₃ on AAO used to measure the in-plane magnetic moment. Right inset: magnetic moment between 1.8 to 10 K reveals that the Néel temperature is \approx 2.6 K.

(defined as $I_{\rm pc} = I_{\rm light} - I_{\rm dark}$) is observed when the device is illuminated with a 1546 nm (0.8 eV) laser. The photocurrent varies linearly with applied voltage at all intensities (Figure 6A), revealing ohmic contacts and the relative importance of the channel compared to the contacts in photogeneration. The rise/fall times of these thin-film photodetectors are within the

measurement resolution of ≈ 100 ms, which is a factor of 10 longer than single nanosheet devices due to the larger device area and relatively disordered film morphology (Figure 6B and Figure S10). To further understand the photodetection mechanism, the photocurrent is plotted as a function of illumination intensity, P (Figure 6C), which shows a nearly linear relationship: $I_{\rm PC} \sim P^{0.97}$. This linear relationship indicates the absence of an internal gain mechanism, such as trap-mediated photoconductivity that typically accompanies bimolecular recombination and results in a sublinear relationship at higher intensities. This linear relationship also rules out photothermal effects that show a superlinear intensity dependence. Instead, the linear relationship is attributed to the dissociation of doublon-holon pairs as observed in a variety of Mott insulators including α-RuCl₃, Nd₂CuO₄, Sr₂CuO₂Cl₂, and La₂CuO₄.^{29,42-45} The responsivity, plotted in Figure 6D, shows a nearly intensity-independent value of ≈ 2 mA/W, which is an order of magnitude larger than the responsivity reported on single-flake α -RuCl₃ devices. To further quantify the linearity of these photodetectors, the linear dynamic range (LDR) is calculated to be 23 dB, serving as a lower estimate for the linearity of the photodetectors (see Note 2 in the Supporting Information for a detailed calculation of the LDR). Notably, these photodetectors are stable in ambient conditions, which is a distinct advantage over other NIR 2D photodetectors such as black phosphorus.46,47 The role of intercalation-induced charge transfer in the photocurrent generation process points to future opportunities of tuning the photoresponse by controlling the nature and density of the intercalated species.

CONCLUSIONS

In conclusion, we have demonstrated an electrochemically assisted LPE procedure for obtaining dispersions of ultrathin, electron-doped α -RuCl₃ nanosheets. The resulting nanosheets possess high crystalline integrity and maintain the intrinsic properties of α -RuCl₃. The absence of surfactants or stabilizers and the low ultrasonic intensity of bath sonication relative to tip sonication result in electrically percolating films following vacuum filtration. Sheet resistance and magnetoresistance measurements both reveal a phase transition at 230 K for LPE α -RuCl₃ that is accompanied by the onset of Kitaev paramagnetism. In addition, magnetic susceptibility measurements show an antiferromagnetic transition for LPE α -RuCl₃ at $T_{\text{N\acute{e}el}}$ = 2.6 K. The intercalation-induced electron doping in the LPE α -RuCl₃ nanosheets broaden the optical absorption wavelength range, thus enabling large-area NIR photodetectors to be fabricated from α -RuCl₃ films. These NIR photodetectors show highly linear photocurrent with respect to incident laser intensity, indicating negligible trap states and suggesting a photocurrent generation mechanism that is consistent with a doped Mott insulator. Overall, this work establishes a scalable means of producing magnetically and optoelectronically active α -RuCl₃ nanosheets and electrically percolating thin films that are suitable for both fundamental studies and technologically relevant applications.

METHODS

Crystallization and Purification of α -**RuCl₃.** Two grams of anhydrous ruthenium chloride (99.95%, Mateck) was placed in a quartz glass ampule (30 mm × 160 mm, 3 mm wall thickness) and sealed under a vacuum (10⁻³ Pa) using an oxygen—hydrogen welding torch. The ampule was then placed horizontally in a muffle furnace



Figure 6. α -RuCl₃ Mott insulator thin-film near-infrared photodetectors. (A) Current-voltage (I-V) characteristics of a α -RuCl₃ thin-film Mott insulator photodetector under various illumination intensities at 1546 nm. Photocurrent (I_{PC}) is obtained by subtracting the current measured in dark conditions (I_{dark}) from the current measured under illumination (I_{light}) : $I_{PC} = I_{light} - I_{dark}$. All I-V curves show a linear power-law behavior. The dark current is plotted separately in Figure S9. (B) Time-resolved photocurrent of the α -RuCl₃ thin-film photodetector showing rise and decay times of 100 ms (Figure S10). (C) Photocurrent (V = 10 V) as a function of intensity (P) showing a nearly linear response $I_{PC} \sim P^{0.97}$ as expected for a Mott insulator photodetector. (D) Responsivity as a function of intensity. The responsivity shows a weak response to the illumination intensity ($R \sim P^{0.03}$), indicating that photothermal effects are negligible contributors to the photoconductivity.

and heated at 800 $^{\circ}$ C for 100 h with a heating and cooling rate of 5 $^{\circ}$ C/min. The ampule was opened in an argon glovebox to ensure no ambient exposure prior to use.

Electrochemical Intercalation and Liquid-Phase Exfoliation. Two hundred milligrams of tetrahexylammonium bromide (>99%, Sigma-Aldrich) was dissolved in 40 mL of acetonitrile (99.8%, Sigma-Aldrich) yielding a 5 mg/mL electrolyte. An α -RuCl₃ crystal was clamped with Pt foil as the working electrode, and a second Pt foil was used as the counter electrode. A voltage of -7 V was applied for 6 min, then -10 V for 54 min using a potentiostat (VSP Potentiostat, Biologic). The intercalated α -RuCl₃ crystal was then placed in 20 mL of N-cyclohexyl-2-pyrrolidone (99%, Sigma-Aldrich) in a glass vial and bath sonicated (Branson 5800, 40 kHz, 160 W) for 3 h at 10 °C. After exfoliation, the dispersion was centrifuged at 5 krpm for 90 min (Avanti J-26 Xi, Beckman Coulter), with the supernatant being collected for further characterization.

Materials Characterization. Optical Absorbance Spectroscopy. Optical absorbance spectra were collected using an Agilent Cary 5000 UV–vis–NIR spectrophotometer. α -RuCl₃ crystals were micromechanically exfoliated onto a sapphire substrate using Scotch tape, while α -RuCl₃ dispersions were diluted with CHP (0.1 mL dispersion with 2.4 mL of CHP) and placed in a 1 cm path length quartz cuvette (Thorlabs).

Atomic Force Microscopy. AFM samples were prepared using a drop-casting method. Prior to deposition, SiO_2/Si (300 nm thermal oxide) substrates were cleaned by bath sonication (15 min of acetone, acetone, isopropanol, ethanol, and DI water, with solvent exchange after each step). Next, the clean substrates were transferred into a

beaker containing 2.5% vol (3-aminopropyl)triethoxysilane (APTES, 99%, Sigma-Aldrich) in water (1 mL APTES in 40 mL DI water) and left for 30 min. The APTES solution was gently decanted, ensuring a thin layer of the solution remained on the substrate, and then replaced with approximately the same volume of DI water. Subsequently, the substrates were individually rinsed with DI water and blow-dried. Next, 50 μ L of the α -RuCl₃ dispersion in CHP was distributed evenly on the substrate with a pipet and left for 40 s before being rinsed with ~5 mL of DI water and blow-dried. AFM height measurements were performed in tapping mode using an Asylum Cypher S AFM with Si cantilevers (~300 kHz resonant frequency) at a scan rate of ~1 Hz and resolution of 512 pixels per line.

Transmission Electron Microscopy. TEM samples for the α -RuCl₃ dispersion were prepared by drop-casting 5–10 drops of the α -RuCl₃ dispersion onto a 300 mesh lacey carbon TEM copper grid with holes >250 nm (Ted-Pella) and blotted with qualitative filter paper after each drop. TEM samples of the pristine α -RuCl₃ crystals were prepared by micromechanical exfoliation of α -RuCl₃ on polydimethylsiloxane (PDMS) using Scotch tape, followed by transfer of the flakes onto a PELCO holey silicon nitride support film (5 μ m pores). High-resolution TEM and SAED measurements were performed using a JEM-ARM300F microscope with an accelerating voltage of 300 keV.

Vacuum Filtration. To generate thin films, 1-5 mL of the α -RuCl₃ dispersion was vacuum filtered onto an anodized aluminum oxide filter membrane (diameter 25 mm, pore size 20 nm, Whatman).

X-ray Diffraction. XRD measurements were performed with a Rigaku SmartLab thin-film diffraction workstation with a 9 kW copper rotating anode. All samples were placed on a Si(911) low background

substrate. X-ray Photoelectron Spectroscopy. XPS characterization was performed using a high vacuum Thermo Scientific ESCALAB 250 Xi⁺ XPS system at a base pressure of $\sim 10^{-8}$ Torr with an Al K α X-ray source (~1486.6 eV). A spot size of 900 μ m was used with a 0.1 eV binding energy resolution, with all core-level spectra being averaged over five scans with a pass energy of 15 eV and dwell time of 100 ms for each scan. All subpeaks were fit with the software suite Avantage (Thermo Scientific), and all core-level spectra were charge corrected to adventitious carbon (284.8 eV).

Cross-Sectional Scanning Electron Microscopy. Cross-sectional SEM samples were prepared by cleaving the vacuum filtered film using a clean razor and mounting the edge that was not pressed pointing up on a cross-sectional SEM stub. All SEM micrographs were obtained on a Hitachi SU8030 field emission SEM with an accelerating voltage of 15 kV and a working distance of 4 mm. Film thicknesses were calculated by taking the average of multiple regions of the film.

Raman and Photoluminescence Spectroscopy. Raman and PL spectra on both the bulk crystal and thin films were collected using a Horiba LabRAM HR Evolution with an excitation wavelength of 532 nm at ~0.06 μ W for 60 s with a 2400/mm grating for Raman measurements and at ~2 μ W for 5 s with a 600/mm grating for PL measurements.

Magnetic Susceptibility Measurements. Magnetic susceptibility measurements were performed on a Quantum Design MPMS-XL. A fragment of the filtered film on the AAO membrane was placed into a sample bucket and cooled down to 1.8 K under zero field before measurements. All measurements were performed under an applied field of $\mu_0 H = 1$ T with the Reciprocating Sample Option in center mode with autotracking enabled. At each temperature, four scans with an amplitude of 4 cm and three cycles with a frequency of 0.5 Hz were collected, and linear drift was subtracted prior to fitting the data to an ideal dipole response using an iterative regression algorithm. Measurements were performed from 1.8 to 10.0 K with 0.2 K step sizes with a ramp rate of 1.0 K/min and 30 s dwell time prior to each measurement and then from 10.0 to 300.0 K (110.0 K for the out-ofplane orientation) with 5.0 K step sizes with a ramp rate of 2.0 K/min and 30 s dwell time. A background scan consisting of just the sample bucket with identical scan conditions was also collected and subtracted to obtain the magnetic susceptibility of the α -RuCl₃ film.

Optoelectronic and Magnetotransport Measurements. Devices were patterned directly on the AAO filter using a PDMS stamp to define channel geometries followed by evaporation of 10 nm Cr/60 nm Au through a shadow mask. Temperature-dependent fourprobe measurements were performed in Lakeshore CRX 4K and Lakeshore CRX VF (magnetotransport) variable temperature probe stations using a Keithley 2400 source meter. The magnetoresistance was measured for both the forward and reverse sweep of magnetic field. Both sweeps were shifted prior to the averaging to compensate for hysteresis, which presumably originated from the large size of the device (Figure S7). Photodetector measurements were performed on the same device, with a channel geometry of approximately 225 μm length and 790 μ m width in ambient conditions. The sample was illuminated with a 1546 nm laser, where the laser power was controlled by setting the diode current (LP520MF100, ThorLabs). Time-dependent measurements were conducted by manually modulating the laser on and off at 10 V with currents being recorded every ≈ 100 ms. Noise measurements were performed in the dark under ambient conditions at 10 V using a spectrum analyzer (Stanford Research SR760) and preamplifier (DL Instruments 1211).

ASSOCIATED CONTENT

5 Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsnano.2c04888.

Figures of in-plane XRD of α -RuCl₃, 1D electron density models, XRD of mechanically exfoliated α -RuCl₃, TEM

of micromechanically exfoliated α -RuCl₃, output curves of MoS₂-based solution-processed films, resistance of α -RuCl₃ film measured upon warming up, raw magnetoresistance data, out-of-plane magnetic moment of α -RuCl₃, dark current of α -RuCl₃ thin-film Mott insulator photodetector, and zoomed-in time-dependent photocurrent of α -RuCl₃ and discussions of exfoliation and characterization procedure for MoS₂ films and calculation of the linear dynamic range of RuCl₃-based photodetectors (PDF)

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Author Contributions

^{\perp}D. Lam and D. Lebedev contributed equally. The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. **Notes**

The authors declare no competing financial interest.

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