2D Janus Niobium Oxydihalide NbOXY: Multifunctional High-Mobility Piezoelectric Semiconductor for Electronics, Photonics and Sustainable Energy Applications

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Two-dimensional (2D) niobium oxydihalide NbOXY has been recently demonstrated as an excellent in-plane piezoelectric and nonlinear optical material. Here we show that Janus niobium oxydihalide, NbOXY (X, Y = Cl, Br, I and X ≠ Y), is a multifunctional anisotropic semiconductor family with exceptional piezoelectric, electronic, photocatalytic and optical properties. NbOXY are stable and flexible monolayers with band gap around the visible light regime of ~1.9 eV. The anisotropic carrier mobility of NbOXY lies in the range of 10^3 ~ 10^4 cm^2V^{-1}s^{-1}, which represents some of the highest among 2D semiconductors of bandgap 2 eV. Inversion symmetry breaking in Janus NbOXY generates sizable out-of-plane d_{31} piezoelectric response while still retaining a strong in-plane piezoelectricity. Remarkably, NbOXY exhibits an additional out-of-plane piezoelectric response, d_{32} as large as 0.55 pm/V. G_0W_0 calculation further reveals the strong linear optical dichroism of NbOXY in the visible-to-ultraviolet regime. The optical absorption peaks of 14 ~ 18 % in the deep UV regime (5 ~ 6 eV) outperform the vast majority of other 2D materials. The high carrier mobility, strong optical absorption, sizable built-in electric field and band alignment compatible with overall water splitting further suggest the strengths of NbOXY in solar-to-hydrogen conversion. We further propose a directional stress sensing device to demonstrate how the out-of-plane piezoelectricity can be harnessed for functional device applications. Our findings unveil NbOXY as an exceptional multifunctional 2D semiconductor for flexible electronics, optoelectronics, UV photonics, piezoelectronics and sustainable energy applications.

I. INTRODUCTION

Piezoelectricity is a phenomenon in which electrical (mechanical) signals are generated in a material in response to an external mechanical (electrical) stimuli. Piezoelectric materials, including crystals [1], polymer [2], bi-molecules [3] and 2D materials [4], play a critical role in electromechanical and mechno-electrical device technology, such as sensors and actuators [5–10]. Alongside with solid-state energy conversion strategies, such as solar cell [11], thermoelectricity [12] and triboelectricity [13], piezoelectricity represents another promising contender for salvaging electrical energy from mechanical motion [14]. Materials with simultaneous presence of excellent piezoelectric, electrical, mechanical and optical properties are particularly much sought-after due to their enormous technological usefulness for developing multifunctional devices that synergize piezoelectricity with other functionalities.

Two-dimensional (2D) materials offer an exciting platform for the development of next-generation piezoelectronic technology [1, 16]. The atomically-thin nature of 2D materials and the enormous design space uniquely enabled by van der Waals heterostructure engineering [17, 18] offer a new paradigm for designing ultimately-compact and high-performance piezoelectric devices in the 2D Flatland. Myriads of 2D in-plane and out-of-plane piezoelectric materials have been reported recently [19], including TMDCs [14, 20–24], hBN [25], graphene nitride [26], α-In$_2$S$_3$, doped graphene [27], and multilayer MoS$_2$ on PbTiO$_3$ [28]). The existence 2D materials with simultaneous in-plane and out-of-plane piezoelectricity, such as Janus transition metal dichalcogenides (TMDCs) [29, 30], Janus silicon dichalcogenide [31] as well as III-V [32, 33] and Janus III-VI monolayers [34, 35], further enriches the application potential of 2D piezoelec-
Janus Niobium Oxydihalide Monolayers

(a) to (d) shows the lattice structures of non-Janus NbOI2 and the Janus monolayers of NbOCIBr, NbOClI, NbOBri, respectively, in which the inversion symmetry in the out-of-plane direction is broken due to the nonequivalent halogen atoms. (e) Comparison of electrical mobility of various 2D semiconductors obtained from DFT calculations. The NbOX monolayers mobility is in the range of $10^3 \sim 10^4 \text{cm}^2\text{V}^{-1}\text{s}^{-1}$. (f) Schematic drawings of the $d_{11}$, $d_{31}$ and $d_{32}$ piezoelectric responses. The thin arrows (green) denote the direction of mechanical stress and the thick arrows (black, blue and red) denote the direction of the electric charge polarization ($d_{11}$, $d_{31}$, $d_{32}$). (g) Piezoelectric responses $d_{11}$ and $d_{31}$ (or $d_{32}$) for various 2D materials. (h) Peak optical absorbance of NbOXY in comparison of other 2D materials [15]. The frequency of the peak absorbance are marked in blue font directly below the monolayer labels.

Recent high throughput searches [37, 38] has established niobium oxydihalide monolayers (NbOX2, X = Cl, Br, or I) as an exceptional piezoelectric 2D material family. Monolayer NbO12 – an experimentally [39, 40] fabricated air-stable 2D semiconductors with anisotropic electrical, mechanical and optical properties [41–43] – has an exceedingly large piezoelectric response of $d_{11} \approx 45 \text{pm}/\text{V}$. Out-of-plane piezoelectricity is, however, strictly forbidden in the NbOX2 monolayer family due to the lattice centrosymmetry, which severely limits the potential of NbOX2 in piezoelectric device applications. The absence of out-of-plane piezoelectricity in NbO12 immediately raises the following questions: Can inversion symmetry breaking from Janus phase engineering [29, 30] be used as an efficient way to generate sizable out-of-plane and in-plane piezoelectric response? Apart from the commonly observed $d_{31}$ piezoelectric response, can other types of out-of-plane piezoelectricity, such as $d_{32}$ response, exist in Janus niobium oxydihalide monolayers? Will the electrical and optical properties of Janus niobium oxydihalide monolayers be beneficial for solid-state device applications, in addition to piezoelectricity?

In this work, we show that Janus-engineered niobium oxydihalide monolayer, NbOX where $X$ and $Y$ are the halogen atoms Br, Cl, I, and $X \neq Y$, is a multifunctional semiconductor with ultrahigh carrier mobility, mechanical flexibility, strong optical dichroism, broadband visible and strong UV light absorption, compatibility with overall photocatalytic water splitting and simultaneous presence of in-plane and out-of-plane piezoelectricity (see Fig. 1 for the crystal structures and a highlight of the electrical, piezoelectric and optical properties of NbOX). Using first-principle density functional theory (DFT) calculations, we show that NbOX is dynamically, thermally and mechanically stable with excellent mechanical flexibility. The band gap of 2 eV, which lies in the visible light regime, and the large anisotropic [44, 45] carrier mobility, ranging from $10^{-1} \sim 10^4 \text{cm}^2\text{V}^{-1}\text{s}^{-1}$ with NbOClI reaching well over $2 \times 10^4 \text{cm}^2\text{V}^{-1}\text{s}^{-1}$ which is higher than most 2D semiconductors of similar band gap [47–56] (Fig. 1(e)), suggest their strong potential in electronics.
and optoelectronics applications [46]. The broken inversion symmetry of NbOXY generates both in-plane and out-of-plane response – an uncommon but much sought-after behavior in 2D materials [4, 31]. Intriguingly, the orthorhombic crystal of NbOXY generates an additional $d_{32}$ response not commonly found in other 2D materials [see Fig. 1(f) for schematic illustrations of $d_{11}$, $d_{31}$ and $d_{32}$ piezoelectric responses]. The simultaneously sizable $d_{11}$ and $d_{32}$ responses [see Fig. 1(g) for a comparison with other 2D piezoelectric materials] suggests that NbOXY is an uncommon 2D semiconductor capable of operating in both in-plane and out-of-plane device settings, thus greatly expanding their practicality in piezoelectric and piezoelectric device applications. We propose a device concept of directional stress sensor to illustrate how the $d_{31}$ and $d_{32}$ of NbOXY responses can be harnessed for complementary piezoelectric functionality not found in their non-Janus counterpart. GoWo-BSE calculations further reveals the strong optical anisotropic, broadband visible light absorption, and sharp absorption peaks in the deep UV regime which are much stronger than other 2D optical materials [15] [Fig. 1(h)], thus unravelling the capability of NbOXY in solar energy harvesting and UV photonics applications [57]. The high-mobility, broadband visible light absorption, presence of built-in electric fields and band edge energies compatible with photovoltaic water splitting [58] further suggest the enormous potential of NbOXY for high-efficiency solar-to-hydrogen conversion. Our findings unveil NbOXY as a compelling multifunctional semiconductor family with promising potential in high-performance flexible electronics, optoelectronics, photonics, sensing and sustainable energy harvesting applications.

II. COMPUTATIONAL METHODS

A. Structural Relaxation, Electronic Structures and Transport Properties

First-principles density functional theory (DFT) calculations are performed using the projector-augmented wave method as implemented in the Vienna ab initio simulation package (VASP) [60–62]. We consider the generalized gradient approximation of Perdew, Burke and Ernzerhof (GGA-PBE) as the exchange-correlation functional [63]. For band structure calculations, we employ the range-separated HSE06 hybrid functionals [64, 65]. An energy cut-off of 500 eV, total energy convergence criterion of $10^{-8}$ eV and a force convergence criteria of less than $10^{-3}$ eV/Å on each atom are adopted. A vacuum region of > 30 Å along the z direction is added to avoid interactions between two neighboring images Γ-centered k-point meshes of $25 \times 13 \times 1$ in the first Brillouin zone is employed to yield well-converged results, i.e. $a$ and $b$ lattice constant, for the unit cells of the Janus monolayers. VASPKIT is used for postprocessing of the DFT calculation data [66]. Bader charge analysis is performed to obtain the net charge transfer between the atoms [67].

The carrier mobility is calculated based on the deformation potential theory of Bardeen and Shockley [68],

$$
\mu_i^{(\nu)} = \frac{e\hbar^2 C_{2D,i} m_i^{(\nu)} m_d^{(\nu)} E_i^{(\nu)^2}}{k_B T m_i^{(\nu)} m_d^{(\nu)} E_i^{(\nu)^2}}
$$

where the superscript $\nu = e, h$ denotes electron and hole, the subscript $i = x, y$ denotes the two orthogonal directions, $m_i^{(\nu)} = \hbar^2 (\partial^2 E_k/\partial k_i^2)$ is the effective mass of $\nu$ carrier, $E_k$ is the energy dispersion around the band edge assuming a parabolic dispersion relation, $k = (k_x, k_y)$ is the 2D wave vector, $m_d^{(\nu)} = \sqrt{m_x^{(\nu)} m_y^{(\nu)}}$ is the density of states effective mass of $\nu$ carrier, $T$ is the temperature, $C_{2D,i}$ is the 2D elastic modulus along $i$ direction and $E_i^{(\nu)}$ is the deformation potential constant [69].

B. Thermal, Dynamical, Mechanical and Piezoelectric Properties Calculations

To assess the dynamical stability of NbOXY monolayers, we calculate the phonon frequencies using density functional perturbation theory (DFPT) calculations [70] through the direct supercell method with the $4 \times 2 \times 1$ supercell. The lattice vector is greater than 15 Å as implemented in the Phonopy code [71]. The phonon dispersion at different $q$ points are obtained by computing the force constants on a sufficiently large supercell and Fourier interpolating the dynamical matrices in the primitive cell. Ab initio molecular dynamics (AIMD) simulations of canonical ensemble (i.e. NVT ensemble) are performed to confirm the thermal stability of NbOXY monolayer at 300 K, for 5 ps with a time step of 1 fs, in a $4 \times 2 \times 1$ supercell configuration. The Nose algorithm is used to control the temperature [72]. The piezoelectric effect is determined by third-rank tensors $e_{ijk}$ and $d_{ijk}$. In the contracted Voigt notation, $e_{ijk}$ and $d_{ijk}$ are reduced to $e_{ij}$ and $d_{ij}$, respectively, where $i, j, k = 1, 2, 3$ denotes the three orthogonal spatial directions, and $l = 1, 2, \ldots, 6$. The elastic stiffness coefficients $(C_{ij}^{SP})$ are calculated using the finite difference method [73] and the piezoelectric stress tensors $(e_{ij})$ are obtained from DFPT in VASP [70], via the following definitions [30, 74],

\begin{align}
\dot{e}_{ijk} &= \frac{\partial P_i}{\partial \sigma_{jk}} = \frac{\partial \sigma_{jk}}{\partial E_i}, \\
\dot{d}_{ijk} &= \frac{\partial P_i}{\partial \sigma_{jk}} = \frac{\partial \sigma_{jk}}{\partial E_i},
\end{align}

where $\sigma_{jk}$, $\varepsilon_{jk}$, $P_i$ and $E_i$ are the stress, strain, intrinsic polarization tensors, and macroscopic electric fields, respectively. The piezoelectric strain coefficient, $d_{ij}$, can then be determined from $e_{ij} = \sum d_{lk} C_{lk}$. For monolayers, the 2D elastic coefficients $C_{ij}$ and the piezoelectric
TABLE I. Summary of DFT calculation data of NbOXY. Lattice constants $a$ and $b$, monolayer thickness $t$, band gap $E_g$, ionization (VBM) energy of the face with $X$ atoms $E_{ip}^{(X)}$ and with $Y$ atoms $E_{ip}^{(Y)}$, electron affinity (CBM) energy of the surface with $X$ halogen atoms $E_{ea}^{(X)}$ and with $Y$ halogen atoms $E_{ea}^{(Y)}$, built-in dipole potential $\Delta V$, charge transfer from Nb atoms to $X$ halogen atoms $\Delta V_{N_{b-x}}$ and to $Y$ halogen atoms to $X$ halogen atoms $\Delta V_{N_{b-y}}$, and the charge differences between the $X$ and $Y$ halogen atoms are listed here.

| Monolayer | $a$ (Å) | $b$ (Å) | $t$ (Å) | $E_g$ (eV) | $E_{ip}^{(X)}$ (eV) | $E_{ip}^{(Y)}$ (eV) | $E_{ea}^{(X)}$ (eV) | $E_{ea}^{(Y)}$ (eV) | $\Delta V$ (eV) | $\Delta V_{N_{b-x}}$ (eV) | $\Delta V_{N_{b-y}}$ (eV) | $\Delta \Delta \Delta$ (eV) |
|----------|---------|---------|---------|------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|
| NbO12    | 3.97    | 7.59    | 4.60    | 1.87       | -6.00         | -6.00         | -4.14         | -4.14         | 0.00           | 0.72           | 0.72           | 0.00           |
| NbOCIBr  | 3.96    | 6.94    | 4.07    | 1.98       | -6.86         | -6.42         | -4.88         | -4.44         | 0.44           | 1.09           | 0.91           | 0.17           |
| NbOCII   | 3.96    | 7.23    | 4.25    | 1.89       | -6.87         | -5.83         | -4.98         | -3.94         | 1.04           | 1.10           | 0.70           | 0.41           |
| NbOBrI   | 3.96    | 7.36    | 4.41    | 1.91       | -6.53         | -5.91         | -4.62         | -4.00         | 0.62           | 0.94           | 0.70           | 0.24           |

stress coefficients $e_{ij}$ are normalized by the slab thickness of the simulation cell along the $z$ direction ($L_z$) via $C_{ij} = L_z e_{ij}^{(3D)}$ and $e_{ij} = L_z e_{ij}^{(3D)}$, where $C_{ij}^{(3D)}$ and $e_{ij}^{(3D)}$ are the 3D elastic stiffness and piezoelectric stress coefficients, respectively. Unlike NbO12 ($mm2$ point group symmetry), NbOXY structures only have $m$ point group symmetry. Consider only the in-plane strain and stress for 2D systems [30, 74–76], we obtain,

$$
e^{(2D)} = \begin{pmatrix} e_{11} & e_{12} & 0 \\ 0 & 0 & e_{23} \\ e_{31} & e_{32} & 0 \end{pmatrix}, \quad (3a)$$

$$
C^{(2D)} = \begin{pmatrix} C_{11} & C_{12} & 0 \\ C_{12} & C_{22} & 0 \\ 0 & 0 & C_{33} \end{pmatrix}, \quad (3b)
$$

$$
d^{(2D)} = \begin{pmatrix} d_{11} & d_{12} & 0 \\ 0 & 0 & d_{23} \\ d_{31} & d_{32} & 0 \end{pmatrix}. \quad (3c)
$$

where $d_{11} \neq d_{12}$ and $d_{31} \neq d_{32}$ represent two distinctive in-plane and out-of-plane piezoelectric responses, respectively, and $d_{23}$ is a shear piezoelectric response. The elastic properties (i.e. Young’s modulus and Poisson’s ratio) are averaged by the Voigt-Reuss-Hill schemes [77] and evaluated using the ElasticPOST code (https://github.com/hitliaomq/ElasticPOST) [78–80].

C. Optical Properties Calculations

For the optical properties, random phase approximation (RPA) [81, 82] with $G_0W_0$ are employed with $6 \times 6 \times 1$ k-point mesh, 300 eV cutoff energy, and the number of bands was tripled. Beyond the RPA approach which considers only the dipole transition, single-shot $G_0W_0$ approximation [83] is used with the Bethe-Salpeter equation (BSE) [84, 85] within the Tamm-Dancoff approximation which captures the electron-hole interactions. The complex dielectric function $\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$ are computed by considering the electromagnetic wave polarization along both $x$ and $y$ directions. The optical absorption coefficient is obtained as [15],

$$
\alpha(\omega) = \frac{\text{Re}[\tilde{\sigma}(\omega)]}{1 + \frac{\tilde{\sigma}(\omega)^2}{2 \varepsilon_0 \varepsilon_2 \varepsilon_2}} \quad (4)
$$

where $\tilde{\sigma}(\omega) \equiv \sigma_{2D}(\omega)/\varepsilon_0 c$, $\sigma_{2D}(\omega) = i\varepsilon_0 \omega L_z \left[1 - \varepsilon(\omega)\right]$ is the frequency-dependent complex optical conductivity of a 2D system, $\varepsilon_0$ is the permittivity of free space, $c$ is the speed of light, and $L_z$ is the slab thickness of the simulation supercell.

III. RESULTS AND DISCUSSIONS

A. Structural Properties and Monolayer Stability

The lattice structure of NbOXY takes an orthorhombic form with a rectangular network lattice [Fig. 1(a) to (d)]. The Janus nature of NbOXY arises from the two outer sublayers of nonequivalent halogen atoms ($X \neq Y$) sandwiching the central Nb atoms. The rectangular lattice are highly anisotropic with $x$ and $y$ directions composed of O-Nb-O and X-Nb-Y networks, respectively. The lattice constants of the fully relaxed NbOXY are 6.93 Å, 7.22 Å, and 7.36 Å, respectively, along the $a$-axis ($x$ direction), and about 3.96 Å along the $b$-axis ($y$ direction) for all Janus monolayers (see Table I for a summary of DFT calculation data). The monolayer thicknesses ($t$) are 4.067 Å, 4.250 Å and 4.409 Å for NbOClBr, NbOClI, and NbOBrI, respectively, which are comparable to that of the NbO12 (4.405 Å).

We examine the (i) dynamical stability; (ii) thermal stability; and (iii) mechanical stability of Janus NbOXY via phonon spectra calculation, AIMD simulations and elastic coefficients analysis based on the Born-Huang criteria [86], respectively (Fig. 2). As shown in Fig. 2(a), the absence of significant soft modes in the phonon spectra confirms the dynamical stability of NbOXY in the freestanding form. The AIMD simulations of NbOXY reveals minute energy fluctuation less than 2 meV after 5 ps at 300 K, with only minimal lattice distortion [Figs. 2(b) and 2(c)], thus confirming the thermal stability of NbOXY at room temperature [87]. To achieve mechanical stability, the Born-Huang criteria requires the elastic coefficients to fulfill the inequalities [86],
FIG. 2. Dynamical, thermal and mechanical stability of NbOXY monolayers. (a) Phonon spectra of the monolayers reveal the absence of significant soft modes around the Γ point; (b) Ad initio molecular dynamics (AIMD) simulations of NbOXY monolayers for a duration of 5000 fs at 300 K. The energy of the 2D systems fluctuate less than 2 meV; (c) Lattice structure of the NbOXY after 5000 ps showing minimal distortions; (d) the elastic coefficients of $C_{11}$, $C_{33}$, $C_{11}C_{12}$ and $C_{22}^2$ of NbOXY fulfill the Born-Huang criteria [86] of $C_{11} > 0$, $C_{33} > 0$ and $C_{11}C_{22} > C_{12}^2$. The $C_{11}$ and $C_{33}$ are in the unit of N/m while $C_{11}C_{22}$ and $C_{12}^2$ are in the units of $10^2$ N$^2$/m$^2$ and N$^2$/m$^2$, respectively.

B. Electronic structures and electrical properties

1. Electronic Band structures

The band structures and projected density of states (PDOS) of NbO12 and NbOXY calculated via HSE06 method are shown in Fig. 3(a). The band gap is 1.98, 1.89 and 1.90 eV for NbOClBr, NbOClI and NbOBrI, respectively, which are comparable to that of NbO12 (1.87 eV) [41]. Around the CBM, the bands dispenses more sharply along the $x$ direction (i.e. $\Gamma \rightarrow X$) the dispersion around the $y$ direction (i.e. $\Gamma \rightarrow Y_+$ and $\Gamma \rightarrow Y_-$) are relatively flatter, which leads to sharply contrasting transport behaviors along these two orthogonal directions. For non-Janus NbOXY, the electronic states around the conduction band minimum (CBM) valence band maximum (VBM) are predominantly from the Nb atoms whereas the VBM also has a sizable contribution from the halogen atoms [see PDOS in Fig. 3(a)] [41]. Janus NbOXY has a similar electronics structures with CBM and VBM states being dominated by the Nb atoms. However, the VBM has a significantly lower contributions from the halogen atoms [see PDOS in Figs. 3(a)].

2. Band alignment, interface potential difference and overall photocatalytic water splitting

The CBM and VBM energies of NbO12 and NbOXY are shown in Fig. 3(b). Interestingly, the CBM (VBM) of NbO12 is higher (lower) than the water reduction (oxidation) potential of $E_{H^+/H_2} = -4.44$ eV ($E_{O^-/H_2O} = -5.67$ eV) [88, 89] for hydrogen (oxygen) molecule production, thus suggesting the potential of NbO12 in photocatalytic overall water splitting application [90].
to the inversion symmetry breaking of Janus NbOXY, unequal charge transfer to the X and Y halogen atoms [see Table I for a summary of the Bardar charge analysis] leads to a built-in intrinsic electric field along the out-of-direction of the lattice [91, 92]. Correspondingly, a sizable interface potential difference (ΔV) arises across the two surfaces of NbOXY, causing the CBM and VBM to offset by ΔV on the X and Y planar surface as illustrated in the band alignment diagram in Fig. 3(b) as well as the plane-averaged electrostatic potential profile in Fig. 3(c). Here ΔV signifies a work function difference on the two opposite planar surface of NbOXY and is directly proportional to the charge transfer difference between Nb→X and Nb→Y (see Supplementary Materials). While NbOClBr is incompatible for hydrogen evolution reaction (HER) due to the close proximity of the CBM to $E_{H^+/H_2}$, NbOCII and NbOBrI are compatible with both HER and oxygen evolution reaction (OER) with sizable energy differences, $\Delta E_1 \equiv E_{CBM} - E_{H^+/H_2}$ and $\Delta E_2 \equiv E_{O^-/O_2} - E_{VBM}$, which are critically needed for enhancing the HER and OER activities [88]. The ($\Delta E_1, \Delta E_2$) of NbOCII and NbOBrI are (0.50, 1.20) eV and (0.44, 0.86) eV, respectively, which significantly outperforms that of the non-Janus NbOI2, i.e. ($\Delta E_1, \Delta E_2$) = (0.30, 0.28) eV. In addition, the presence of a built-in electric field in NbOXY enables the efficient spatial separation of photoexcited electron-hole pairs onto the two opposite surface [89], with electron (hole) preferentially migrates towards the surface with X (Y) halogen atoms upon photoexcitation. Importantly, the combined factors of (i) sizable ($\Delta E_1, \Delta E_2$) that is beneficial for enhancing HER and OER activities; (ii) built-in electric field that is beneficial for photoexcited electron-hole pair separation; (iii) strong optical absorption covering visible and ultraviolet regimes that is beneficial for optimal coverage of solar spectrum (discussed below); and (iv) large carrier mobility reaching well over $10^4$ cm$^2$V$^{-1}$s$^{-1}$ (discussed below), suggest the capability of NbOXY monolayers in photocatalytic water splitting applications [93, 94].
TABLE II. Electrical transport properties of NbO\textsubscript{I} and NbOXY. The effective masses, \( m_i^{(e)} \), are in the unit of \( m_0 \) where \( m_0 \) is free electron mass. The deformation potential constants, \( E_{ij}^{(o)} \), are in the unit of eV. The elastic moduli, \( C_{2D,i} \), are in the unit of Jm\(^{-2}\). The carrier mobilities, \( \mu_i^{(o)} \), are in the unit of cm\(^2\)V\(^{-1}\)s\(^{-1}\). The band edge position, i.e. \( \Gamma, Y_\pm \) and \( X \), are marked directly after the numeric values as superscript for simplicity.

| Material | \( m_x^{(e)} \) | \( m_y^{(e)} \) | \( m_z^{(e)} \) | \( E_{1}^{(e)} \) | \( E_{1}^{(o)} \) | \( E_{2}^{(e)} \) | \( E_{2}^{(o)} \) | \( E_{3}^{(e)} \) | \( E_{3}^{(o)} \) | \( E_{4}^{(e)} \) | \( E_{4}^{(o)} \) | \( E_{5}^{(e)} \) | \( E_{5}^{(o)} \) | \( E_{6}^{(e)} \) | \( E_{6}^{(o)} \) | \( C_{2D,x} \) | \( C_{2D,y} \) | \( \beta_x^{(o)} \) | \( \beta_y^{(o)} \) | \( \beta_z^{(o)} \) | \( \mu_x^{(o)} \) | \( \mu_y^{(o)} \) | \( \mu_z^{(o)} \) |
|----------|--------------|--------------|--------------|---------------|---------------|---------------|---------------|---------------|---------------|---------------|---------------|---------------|---------------|---------------|---------------|---------------|---------------|---------------|---------------|---------------|---------------|---------------|---------------|
| NbO\textsubscript{I} | 0.916±0.797± | 8.082± | 1.210± | 4.404± | 1.811± | 0.32± | 1.33± | 75.61 | 61.87 | 106.609± | 593.647± | 621.010± | 195.035± |
| NbOCl\textsubscript{I} | 0.334±0.622± | 33.688± | 0.782± | 9.857± | 1.977± | 0.28± | 0.76± | 168.440± | 29.218± | 92.31 | 64.26 | 52.733± | 4836.536± | 2.397± | 0.252± | 0.048± | 0.050± |
| NbOCl\textsubscript{II} | 0.578±1.090± | 11.395± | 0.695± | 9.309± | 0.28± | 1.64± | 1.96± | 85.83 | 66.41 | 46.15± | 20888.791± | 7.17± | 7.26± | 0.240± | 6.457± |
| NbOBr\textsubscript{I} | 0.614±1.014± | 9.899± | 0.210± | 9.010± | 0.46± | 1.00± | 1.88± | 83.17 | 63.40 | 45.11± | 8094.971± | 36.206± | 32.366± | 1.770± | 39.153± |

3. Transport properties

The electrical mobilities of NbO\textsubscript{I} and NbOXY are calculated at room temperature (\( T = 300 \) K) [see Fig. 3(d) and Table II]. From the deformation potential theory of Bardeen and Shockley [68] in Eq. (1), the electrical mobility follows the proportionality, \( \mu_i^{(o)} \propto C_{2D,i}/m_i^{(o)}E_{ij}^{(o)} \). As \( \mu \) has a second order dependence on \( E_l \), which is sensitively influenced by the wave function distribution of the band edge states, the spatial extend of the band edge states thus play an important role in governing carrier transport. We first consider electron mobility in the conduction band. For NbO\textsubscript{I}, as the conduction band edge at the \( \Gamma \) and the \( Y_\pm \) points are separated by only about 26 meV, both valleys are expected to contribute to the electron conduction current. The electron mobilities of both valleys are calculated, i.e. \( \mu_{x,Y_\pm} \) and \( \mu_{y,Y_\pm} \), respectively, where \( i = x, y \) represents the two orthogonal crystal directions. In contrast, the \( \Gamma \) valley in NbOXY is energetically well-separated from the actual CBM at \( Y_\pm \) valley by a substantial energy, we thus consider only \( \mu_{x,Y_\pm} \) for NbOXY. The electron mobility is highly anisotropic in both NbO\textsubscript{X} and NbOXY with \( \mu_{x,Y_\pm}/\mu_{y,Y_\pm} \ll \mu_{x,Y_\pm}/\mu_{y,Y_\pm} \) [Fig. 3(d)]. The larger electron mobility in the \( y \) direction (\( \mu_{x,Y_\pm}/\mu_{y,Y_\pm} \)) is a direct consequence of the weak orbital overlap along the \( y \) crystal direction [see the band-decomposed density distributions of the CBM states of NbOCl\textsubscript{II} as a representative example in Fig. 3(e)]. Lattice distortion along the \( y \) direction does not generate significant CBM energy shifting, thus resulting in small \( E_{1,2}^{(CBM)} \). Since \( \mu_{x,Y_\pm}/\mu_{y,Y_\pm} \), the electron mobility is significantly enhanced, leading to high mobility values of \( \mu_{x,Y_\pm}/\mu_{y,Y_\pm} = 10^3 \approx 10^4 \) cm\(^2\)V\(^{-1}\)s\(^{-1}\) in NbOXY. Particularly, NbOCl\textsubscript{II} has an exceedingly large mobility \( \mu_{x,Y_\pm} = 2 \times 10^4 \) cm\(^2\)V\(^{-1}\)s\(^{-1}\), which is considerably higher than the vast majority of 2D semiconductors with band gap \( E_g \geq 2 \) eV.

For the hole conduction in valance bands, because of the close energetic proximity of the \( \Gamma \) point and the CBM at \( X \) point with minute energy separation \( \approx 40 \) meV, we calculate the hole mobility at both \( X \) and \( \Gamma \) point, i.e. \( \mu_{x,X} \) and \( \mu_{y,X} \), for all monolayers. Interestingly, the wave function distribution of the VBM states is contrary to that of the CBM states, i.e. strong orbital overlap strongly (weakly) along the \( x \) (\( y \)) crystal direction. The larger electron mobility of \( \mu_{x,Y_\pm} \) and \( \mu_{y,Y_\pm} \) thus oc-
4. Transport anisotropy and effective mobility

We summarize the mobility and effective mass anisotropy in Fig. 4(a) where the anisotropy ratios are defined as,

\[
\Lambda^{(\mu)} = \frac{\max\left[\mu_{x}^{(\nu)}, \mu_{y}^{(\nu)}\right]}{\min\left[\mu_{x}^{(\nu)}, \mu_{y}^{(\nu)}\right]}, \quad (5a)
\]

\[
\Lambda^{(m)} = \frac{\max\left[m_{x}^{(\nu)}, m_{y}^{(\nu)}\right]}{\min\left[m_{x}^{(\nu)}, m_{y}^{(\nu)}\right]}, \quad (5b)
\]

\[\text{max} [\cdots] \text{ and } \text{min} [\cdots] \text{ are the maximum and minimum functions, respectively. The electron mobility of NbOXY exhibits the enormous mobility anisotropy in the order of } 10^2 \text{ whereas the } \Gamma\text{-point hole effective mass exhibits strong anisotropy in the order of } 10 \sim 10^2. \text{ Such exceptionally anisotropic transport properties of NbOXY suggests new avenues for nanoelectronics device engineering in which the carrier mobility can be tuned over two orders of magnitude by selectively aligning the electrodes along different crystal directions.}

The presence of multiple valance band valleys in NbOXY can co-contribute to hole conduction current. However, the electrical current from different valleys cannot be directly distinguished from typical transport measurement. It is thus important to determine the effective hole mobility of the total transport current that includes the current conduction in multiple valleys \[95, 96\]. We consider a drift current transport picture in which the total hole current density is given by

\[\mathcal{J}_{\text{d}}^{(h)} = \epsilon n_{T}^{(h)} \mu_{\text{d,eff}}^{(h)} \mathcal{E}, \quad (6)\]

where \(\mathcal{E}\) is the applied electric field along the \(i = x, y\) direction, \(\mu_{\text{d,eff}}^{(h)}\) is the effective hole mobility inclusive of both \(X\) and \(\Gamma\) valleys, and \(n_{T}^{(h)} = n_{X}^{(h)} + n_{\Gamma}^{(h)}\) is the total 2D carrier density inclusive of both \(X\) and \(\Gamma\) valleys, i.e. \(n_{X}^{(h)}\) and \(n_{\Gamma}^{(h)}\), respectively. Since the total hole current density is contributed by both valleys, we can equivalently write

\[\mathcal{J}_{\text{d}}^{(h)} = \mathcal{J}_{\text{d},X}^{(h)} + \mathcal{J}_{\text{d},\Gamma}^{(h)}, \quad (7)\]

where \(\mathcal{J}_{\text{d},X}^{(h)} = \epsilon n_{X}^{(h)} \mu_{\text{d,eff}}^{(h)} X\) and \(\mathcal{J}_{\text{d},\Gamma}^{(h)} = \epsilon n_{\Gamma}^{(h)} \mu_{\text{d,eff}}^{(h)} \Gamma\) are the \(X\) and \(\Gamma\) valley current component, respectively. The 2D carrier densities are

\[n_{\lambda}^{(h)} = \frac{2}{(2\pi)^{2}} \int_{-\infty}^{\epsilon_{\lambda}} dk_x dk_y \left[ 1 - f(\epsilon_{k}, \varepsilon_{F}, T) \right], \quad (8)\]

where \(\lambda = X, \Gamma\) denotes the band edge position, \(f(\epsilon_{k}, \varepsilon_{F}, T)\) is the Fermi-Dirac distribution function and \(\varepsilon_{F}\) is the Fermi level. Consider the non-degenerate regime with \(\varepsilon_{F}\) several times larger than \(k_{B}T\) which is well achievable at room temperature, the Fermi-Dirac distribution function reduces to the semiclassical limit of \(f(\epsilon_{k}, \varepsilon_{F}, T) \approx \exp \left[ - (\epsilon_{k} - \varepsilon_{F}) / k_{B}T \right] \). Equations (6) to (8) can be combined to yield

\[\mu_{\text{d,eff}}^{(h)} = \frac{\mu_{\text{d,X}}^{(h)} + \mu_{\text{d,\Gamma}}^{(h)}}{1 + n_{\Gamma}^{(h)} / n_{X}^{(h)}}, \quad (9)\]

where the hole density ratio is

\[\frac{n_{\Gamma}^{(h)}}{n_{X}^{(h)}} = \frac{m_{\text{d,\Gamma}}^{(h)}}{m_{\text{d,X}}^{(h)}} \exp \left( - \frac{\Delta X - \Gamma}{k_{B}T} \right), \quad (10)\]
We now examine the Young’s modulus and Poisson’s ratio of NbOXY (Fig. 5). Table III summarizes the mechanical properties of NbOXY. NbOXY exhibits mechanical anisotropy in terms of Young’s modulus [Fig. 5(a)]. The Young’s modulus peaks along x and y directions, with values lying between 20 GPa and 25 GPa along the x direction, and between 18 GPa and 20 GPa along the y direction. The anisotropy ratio of the Young’s modulus is only \( \leq 2 \) for NbOXY, which is less profound when compared to other 2D materials with giant mechanical anisotropy [97, 98]. It is noteworthy that the Young’s modulus of NbOXY is significantly smaller than many other 2D materials, such as graphene, boron nitride and TMDC [99], thus suggesting their excellent mechanical flexibility useful for flexible electronics applications. Unlike auxetic 2D materials [100], the Poisson’s ratio of NbOXY is entirely positive and exhibits directional dependence with maximum values of \( \sim 0.45 \) along the directions 45° to the x and y axis [Fig. 5(b)].

2. Piezoelectric coefficients

The 2D piezoelectric stress coefficients \( e_{ij} \) and the piezoelectric strain coefficients \( d_{ij} \) are summarized in Table III. In contrast to the centrosymmetric NbOI\(_2\) with \( d_{32} = 0 \), the broken inversion symmetry in NbOXY generates two distinctive out-of-plane piezoelectric responses, as characterized by \( d_{31} \) and \( d_{32} \). Janus NbOXY monolayers retain the large \( d_{31} \) of 35.05, 29.62 and 36.49 pm/V for NbOClI, NbOClBr and NbOBrI, respectively.
TABLE III. Mechanical and piezoelectric properties of NbOXY. The piezoelectric stress coefficients \( e_{ij} \) in the unit of \( 10^{-10} \text{C/m} \), elastic stiffness coefficients \( C_{ij} \) in the unit of \( N/m \), and the piezoelectric strain coefficients \( d_{ij} \) in the unit of \( \text{pm/V} \).

| Monolayer         | \( e_{11} \) | \( e_{12} \) | \( e_{31} \) | \( e_{32} \) | \( e_{23} \) | \( C_{11} \) | \( C_{12} \) | \( d_{11} \) | \( d_{12} \) | \( d_{31} \) | \( d_{32} \) | \( d_{23} \) |
|-------------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|
| NbOCl\(^{a}\)     | 31.60       | -1.00       | 0.00        | 0.00        | 0.70         | 75.60       | 5.30        | 42.20       | -5.10       | 0.000       | 0.00        | 5.20        |
| NbOBr\(^{a}\)     | 31.70       | -1.11       | 0.00        | 0.00        | 0.71         | 73.31       | 4.91        | 43.60       | -5.40       | 0.000       | 0.00        | 5.21        |
| NbOClBr\(^{a}\)   | 25.91       | -1.29       | 0.07        | 0.19        | 0.86         | 88.11       | 6.01        | 29.62       | -3.90       | 0.070       | 0.26        | 5.80        |
| NbOClI            | 28.76       | -1.28       | 0.09        | 0.38        | 0.90         | 82.66       | 4.80        | 35.05       | -4.37       | 0.074       | 0.55        | 6.29        |
| NbOBrI            | 29.34       | -1.22       | 0.02        | 0.22        | 0.75         | 81.18       | 5.57        | 36.49       | -5.11       | 0.002       | 0.34        | 5.31        |

\(^{a}\) DFT calculation data from Ref. \([38]\)

Such \( d_{11} \) values are only slightly lower than that of NbOCl\(^{a}\) and outperforms a large number of 2D in-plane piezoelectric materials [Fig. 1(g)]. The out-of-plane \( d_{31} \) responses are 0.074, 0.070 and 0.002 pm/V for NbOClI, NbOClBr and NbOBrI, respectively. The \( d_{31} \) of NbOCII and NbOCIIBr are more than 2 times larger than that of MoS\(_2\) monolayer (0.030 pm/V) – the top performer in the Janus TMDC family \([30]\) – and several other 2D out-of-plane piezoelectric materials [Fig. 1(g)]. Similarly, \( d_{32} \) coefficient is several times larger than \( d_{31} \), with 0.26, 0.55 and 0.34 pm/V for NbOCII, NbOCIIBr and NbOBrI, respectively. Here NbOCII is a particularly exceptional 2D semiconductor with simultaneously large in-plane (\( d_{11} \)) and sizable out-of-plane (\( d_{32} \)) piezoelectricity. Interestingly, \( d_{32} \) is directly proportional to the interface potential difference \( \Delta V \), exhibiting an excellent linear fit (i.e. \( R^2 \approx 0.999 \)) [Fig. 5(c)] which can be captured by a simple semi-empirical expression,

\[
d_{32} = \lambda \Delta V, \tag{11}
\]

where \( \lambda = 0.5421 \text{ pm/eV}^2 \). Here \( d_{32} \) and \( \Delta V \) are in the units of pm/V and eV, respectively. The linear relationship between out-of-plane piezoelectricity in 2D Janus materials and \( \Delta V \) has not been reported previously. Such linear relationship suggests the importance of having a strong built-in dipole potential in order to achieve strong \( d_{32} \) responses. It should be noted that although other 2D piezoelectric materials have been predicted to exhibit out-of-plane piezoelectric responses stronger than NbOX\(^{a}\), most of these materials have significantly smaller \( d_{11} < 10 \text{ pm/V} \). Figure 5(d) compares NbOX\(^{a}\) with other 2D piezoelectric materials with large out-of-plane response, i.e. \( d_{31} > 0.5 \text{ pm/V} \), in terms of their in-plane and out-of-plane piezoelectricity. It can be seen that \( d_{31} \) or \( d_{32} \) generally decreases with larger \( d_{11} \). Nevertheless, NbOCII still retains a sizable out-of-plane piezoelectricity of \( d_{32} = 0.55 \text{ pm/V} \) despite having an exceedingly large \( d_{11} = 35.05 \text{ pm/V} \). We further calculate the piezoelectric coefficients of \( \text{multilayer} \) NbOCII, which yields significantly amplified piezoelectric coefficients of \( d_{11} = 50.86 \text{ pm/V}, d_{31} = 1.92 \text{ pm/V} \) and \( d_{32} = -1.04 \text{ pm/V} \), thus suggesting that layer number engineering can be used to effectively enhance both in-plane and out-of-plane piezoelectricity.

D. Optical properties

We now investigate the optical properties of NbOX\(^{a}\). The imaginary part of the dielectric function \( \varepsilon_2 \) and the absorption coefficients are shown in Figs. 6(a) and 6(b), respectively, calculated using \( G_0 \text{W}_{0} \text{-RPA} \) and \( G_0 \text{W}_{0} \text{-BSE} \) methods. The optical properties obtained via the \( G_0 \text{W}_{0} \text{-RPA} \) method, which omits the important excitonic effects, differ significantly from that of the \( G_0 \text{W}_{0} \text{-BSE} \) method \([101]\). Especially in the visible regime, \( G_0 \text{W}_{0} \text{-RPA} \) severely overestimates the optical absorption of NbOX\(^{a}\). Since \( G_0 \text{W}_{0} \text{-BSE} \) method exhibit better agreement with experiments \([102]\), we focus our discussion on the \( G_0 \text{W}_{0} \text{-BSE} \) results in the following.

In general, the optical absorption spectra are highly anisotropic and exhibit strong linear optical dichroism between the \( x \) and \( y \) directions \([103]\). The optical absorption in the infrared to red-visible regime for \( x \)-polarized light is stronger than that for \( y \)-polarized light. In contrast, the optical absorption of \( y \)-polarized light is stronger than that of \( x \)-polarized light in the blue-visible to ultraviolet regime. The nearly-full coverage of the infrared-visible-UV spectral regime by \( x \)- and \( y \)-polarization results thus suggests the potential of NbOX\(^{a}\) in solar energy conversion applications, and can complement the conversion efficiency of photocatalytic water splitting in NbOCII and NbOBrI as discussed above.

The strong linear optical dichroism of NbOX\(^{a}\) originate from their anisotropic electronic dispersion. The band structure disperses less in the \( y \) direction when compared to that in the \( x \) direction, thus resulting in an overall stronger optical absorption along the \( y \) direction \([41]\). We quantify the optical anisotropy as \([104, 105]\),

\[
\Lambda^{(\text{opt})}(\hbar\omega) = \max \left[ \alpha_x(\hbar\omega), \alpha_y(\hbar\omega) \right] \div \min \left[ \alpha_x(\hbar\omega), \alpha_y(\hbar\omega) \right], \tag{12}
\]

where \( \alpha_{x,y}(\hbar\omega) \) is the absorption coefficient of \( (x, y) \) direction, respectively, at photon energy \( \hbar\omega \). NbOX\(^{a}\) exhibit significant \( \Lambda^{(\text{opt})} \sim 10 \) in the visible regime (i.e. \( \hbar\omega \gtrsim 2 \text{ eV} \)), thus offering an avenue to straightforwardly determine the crystal direction using polarization optical microscope \([106]\). In the deep UV regime, an exceedingly large \( \Lambda^{(\text{opt})} > 10^2 \) can be achieved. At around 500 nm (i.e. \( \hbar\omega \approx 2.48 \text{ eV} \)), we obtain \( \Lambda^{(\text{opt})} = 1.8, 11.3, 5.5 \) for...
Strong optical absorption and linear optical dichroism in NbOXY monolayers. (a) Imaginary part of the dielectric function. (b) Absorption spectra. (c) Optical anisotropy ratio as a function of photon energy.

E. Proposal of piezoelectric directional stress sensing

Although 2D out-of-plane piezoelectric materials have been extensively studied computationally, how such properties can be harnessed for device applications remain largely unexplored thus far. Here we illustrate how the $d_{31}$ and $d_{32}$ can be harnessed for directional mechanical stress sensing. The operation of the proposed device (see Fig. 7 for a schematic illustration) is analogous to an electromagnetic wave polarizer. Consider an incoming incident linearly polarized electromagnetic wave of unknown polarization angle $\phi$ [see Fig. 7(a)]. The $\phi$ can be determined straightforwardly using two perpendicularly oriented polarizer which selectively reads out the $x$ and $y$ components of the wave intensity, i.e. $I_x$ and $I_y$, and hence $\phi = \tan^{-1}(I_y/I_x)$. Analogously, two NbOXY piezoelectric elements, $\mathbf{A}$ and $\mathbf{B}$, can be stacked onto a flexible substrate with their crystal axis perpendicular to each other [see Fig. 7(b) for the side, back and front views of the proposed device]. Here the elements $\mathbf{A}$ and
FIG. 7. Concept of directional stress sensing based on out-of-plane piezoelectricity in NbOXY. (a) Schematic drawing showing the determination of electromagnetic wave polarization angle $\phi$ using two polarizer measurements. (b) Schematic drawing of the proposed directional stress sensing devices composed of two back-to-back NbOXY sandwiching a flexible substrate. (c) Directional stress sensing mechanism for a mechanical stress applied at angle of $\phi$. (d) $V_{AB}(\phi)$ as a function of $\phi$ shows distinctive value for each $\phi$, thus allowing the direction of the mechanical stress to be determined.

$\text{B}$ serve the same role as that of the orthogonal polarizers in the electromagnetic analogy. Consider a tensile stress applied purely along the $x$-direction, the element $\text{A}$ is mechanically stressed along the ‘2’ axis which produces larger electrical response via $d_{32}$ process, while the element $\text{B}$ is mechanically stressed along the ‘1’ axis with smaller electrical response via $d_{31}$ process. A comparison of these signals generated from $\text{A}$ and $\text{B}$ thus allows the direction of the stress to be determined.

More generally, for a mechanical stress applied along the planar surface of element $\text{A}$ due to the out-of-plane piezoelectric responses, the generated polarization charge density on the planar surface of element $\text{A}$ is $\mathbf{\varrho}_A = d_{31} T \sin \phi + d_{32} T \cos \phi$. Similarly, the polarization charge density generated on the surface of element $\text{B}$ is $\mathbf{\varrho}_B = d_{31} T \cos \phi + d_{32} T \sin \phi$. The voltage generated on elements $\text{A}$ and $\text{B}$ can then be estimated based on a planar diode model, i.e. $V_{AB} = \mathbf{\varrho}_{AB} B/k \varepsilon_0$, where $t$ and $k$ are the thickness and the out-of-plane electrostatic dielectric constant of the 2D piezoelectric material. To assess the performance of the directional stress sensing, we can define the voltage response ratio and the differential voltage response as

$$V_{AB}(\phi) \equiv \frac{V_A}{V_B} = \frac{\sin \phi + \xi \cos \phi}{\cos \phi + \xi \sin \phi}.$$  \hfill (13a)

$$\Delta V_{AB}(\phi) \equiv V_A - V_B = (d_{32} - d_{31}) \frac{T t}{k \varepsilon_0} (\cos \phi - \sin \phi).$$  \hfill (13b)

As $V_{AB}(\phi)$ and $\Delta V_{AB}(\phi)$ are unique functions of $\phi$, measuring one of them allows the mechanical stress direction $\phi$ to be unambiguously determined [e.g. see Fig. 7(d) for the angular plot of $V_{AB}(\phi)$]. Interestingly, Eq. (13b) reveals the importance of having a sizable $d_{32}$ in achieving sensitive directional mechanical stress sensing that is otherwise not achievable in non-Janus NbOX$_2$. Here $\Delta V_{AB}$ should be, ideally, as large as possible so to achieve good signal-to-noise ratio in the measurements. For materials with $d_{32} = 0$, $|\Delta V_{AB}(\phi)| \propto d_{31}$. In this case, a large $d_{31}$ is required to achieve large $\Delta V_{AB}$. In the contrary case of $d_{32} \neq 0$, the magnitude of the differential voltage follows $|\Delta V_{AB}(\phi)| \propto |d_{32} - d_{31}|$, thus suggesting that $d_{32}$ offers an alternative route to achieve large $|\Delta V_{AB}(\phi)|$ for systems in which $d_{31}$ is inherently small, such as Janus TMDC. To illustrate this aspect, we define the maximum differential voltage response per unit stress rescaled by $k$ as $\Delta V_{AB}^{(\text{max})} \equiv k \Delta V_{AB}^{(\text{max})}/T$ where $\Delta V_{AB}^{(\text{max})}$ is the maximum of the magnitude of $\Delta V_{AB}$ evaluated at $\phi = 0$ or $\pi/2$. For NbOCiBr, NbOCIi and
NbOBrI, $\Delta \tilde{\chi}_{\text{AB}}^{(\text{max})} = (0.10, 2.20, 1.63) \times 10^{-2} \text{ V/GPa}$, respectively. These values are significantly larger than the $\Delta \tilde{\chi}_{\text{AB}}^{(\text{max})} = 1.15 \times 10^{-3} \text{ V/GPa}$ of Janus MoSeTe monolayer (thickness $t = 3.405 \text{ Å}$) in which only $d_{31} = 0.030$ pm/V is present. In general, to obtain the same $\Delta \tilde{\chi}_{\text{AB}}^{(\text{max})}$ of a piezoelectric material of thickness $t'$ that possesses only $d_{31}$, a piezoelectric materials with simultaneous $d_{31}$ and $d_{32}$ requires only

$$d_{31} = \frac{t'}{t} \cdot \frac{d_{32}}{\xi - 1}$$

(14)

where $\xi = d_{32}/d_{31}$. The presence of $d_{32}$ (or equivalently $\xi$) relaxes the requirement of $d_{31}$ and offer an alternative way to achieve sensitive directional sensing of mechanical stress. Taking NbOCIII as an example, achieving the same $\Delta \tilde{\chi}_{\text{AB}}^{(\text{max})}$ would require a hypothetical piezoelectric material of the same thickness with a much larger $d_{32} \approx 0.48 \text{ pm/V}$. The above analysis thus highlights the important role of the out-of-plane piezoelectric response $d_{32}$ in supplementing the functionality and performance of 2D piezoelectric and piezoelectronic devices.

### IV. CONCLUSION

In summary, we computationally demonstrated NbOX$\text{Y}$ monolayers as a stable and mechanically flexible 2D semiconductor family with exceptional electronic, piezoelectric, photocatalytic and optical properties. The high carrier mobility and the band gap value lying in the visible light regime of $\sim 2 \text{ eV}$ suggested the strong potential of NbOX$\text{Y}$ in electronic and optoelectronic device applications. The sizable in-plane ($d_{11}$) and two distinctive out-of-plane piezoelectric responses ($d_{31}$ and $d_{32}$) greatly enhances the design flexibility of NbOX$\text{Y}$-based devices. The strong linear optical dichroism in the visible-to-UV regime and the large optical absorption peak response in the deep UV regime revealed the capability of NbOX$\text{Y}$ in photonics device applications, such as polarizer and ultraviolet light photodetector. Finally, the high carrier mobility, sizable built-in electric field, strong optical absorption in the visible light regime, and the appropriate band edge energies that are compatible with overall water splitting suggested the potential of NbOX$\text{Y}$ in achieving high-performance solar-to-hydrogen conversion. Our findings unveiled NbOX$\text{Y}$ as an intriguing multifunctional 2D semiconductor finnaly with strong potential in electronics, optoelectronics, UV photonics, piezoelectronics and sustainable energy applications, and shall form a harbinger for the exploration of the broader 2D oxyhalides family towards next-generation advanced functional device technology.

### DECLARATION OF COMPETING INTEREST

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

### DATA AVAILABILITY

Data will be made available on reasonable request.

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