Symmetry induced phonon renormalization in few layers of 2H-MoTe$_2$ transistors: Raman and first-principles studies

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Understanding of electron-phonon coupling (EPC) in two dimensional (2D) materials manifesting as phonon renormalization is essential to their possible applications in nanoelectronics. Here we report in-situ Raman measurements of electrochemically top-gated 2, 3 and 7 layered 2H-MoTe$_2$ channel based field-effect transistors (FETs). While the $E_{2g}$ and $B_{2g}$ phonon modes exhibit frequency softening and linewidth broadening with hole doping concentration ($p$) up to $\sim 2.3 \times 10^{13}$/cm$^2$, $A_{1g}$ shows relatively small frequency hardening and linewidth sharpening. The dependence of frequency renormalization of the $E_{2g}$ mode on the number of layers in these 2D crystals confirms that hole doping occurs primarily in the top two layers, in agreement with recent predictions. We present first-principles density functional theory (DFT) analysis of bilayer MoTe$_2$ that qualitatively captures our observations, and explain that a relatively stronger coupling of holes with $E_{2g}$ or $B_{2g}$ modes as compared with the $A_{1g}$ mode originates from the in-plane orbital character and symmetry of the states at valence band maximum (VBM). The contrast between the manifestation of EPC in monolayer MoS$_2$ and those observed here in a few-layered MoTe$_2$ demonstrates the role of the symmetry of phonons and electronic states in determining the EPC in these isostructural systems.

Keywords: Raman spectroscopy, field-effect transistor, electron-phonon coupling, MoTe$_2$, first-principles density functional theory, hole doping.

I. INTRODUCTION

The discovery of unique and remarkable properties of graphene has sparked unprecedented interest in other classes of two dimensional (2D) materials like transition metal dichalcogenides (TMDs, MX$_2$, where M= transition metals (Mo, W, Ti, Nb, Ta) and X= chalcogens (S, Se, Te)) for their potential applications in nano and optoelectronics [1]. Optical and electrical properties of these TMDs can be easily manipulated by both changing the layer number and carrier doping. MoTe$_2$ is a member of the group-VI TMD family that crystallizes into three stable phases: Hexagonal ($\alpha$ or 2H) [2], monoclinic ($\beta$ or 1T$'$) [3] and orthorhombic ($\gamma$ or T$_d$) [4]. The 2H phase is semiconducting [5], whereas the 1T$'$ phase is a narrow band gap semiconductor [6]. Similar to other group-VI dichalcogenides, 2H-MoTe$_2$ has a trigonal-prismatic coordinated crystal structure [7], consisting of weakly coupled sandwich layers of Te-Mo-Te units, where Mo-atom layer is enclosed between two Te layers (Fig. 1(a)) [2]. Unlike other TMDs, energy difference between the 2H and 1T$'$ phase is very small (\sim 31 meV per formula unit [8]). This enables easy tuning of the two phases by strain [9, 10], laser irradiation [11, 12] and electron doping [13, 14], making this material an ideal candidate for next generation homojunction devices [15]. From electron doping (n) induced transition from 2H to 1T$'$ phase in multilayer MoTe$_2$, Zakhidov et al. recently suggested that doped electrons by ionic liquid (IL) gating are localized on the top few layers of the nanocrystal [14], consistent with previous theoretical calculations [16].

Bulk MoTe$_2$ has an indirect band gap of \sim 1.0 eV [18, 19] which becomes a direct band gap semiconductor in a monolayer with an emission peak of excitonic photoluminescence (PL) spectrum in the near-infrared range (\sim 1.1 eV) [5]. This enables the material to be a highly sensitive photodetector [20, 21] and light-emitting diode [22, 23]. With device performance at par with its sister compounds MoS$_2$ and MoSe$_2$ [24], MoTe$_2$ shows ambipolar transport properties [25], which has been recently implemented as a p-n homojunction rectifier device with low charge trapping at the junction interface [26]. Since the exploration of these properties has been mostly carried out in monolayer regime, investigation of the charge localization at high gate bias in few layers of the nanocrystal can open up new possibilities in the field of opto-electronics.

Carrier concentration in a semiconductor can be modulated by injecting resonant photons from light emitting diode [27–29], substitutional doping during growth process [30] and application of an electrostatic field on the channel of a FET [31–34]. Electrolyte gating has gained immense interest recently for electrostatic modulation of carrier density up to \sim 10^{15}$/cm$^2$ [35] owing to their large dielectric capacitance. On application of gate voltage, ions move inside the electrolyte to screen the applied electric field to form few Angstroms [36] thick double layers of ions near the device and gate electrode [37, 38]. However electrolyte gating is well known source of electrostatic disorders [39, 40] and is best suited for disorder.

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As Raman spectroscopy does not require any sample preparation, it has been extensively used as a non-invasive, contact-less, fast and accurate tool to determine strain [43], doping effects [13], layer number [17, 44], crystal orientation [45], structural transitions between different polytypes [9, 11–14, 46–48] in fewlayer MoTe₂ devices in ambient as well as different sample environments. Furthermore, Raman scattering has been employed in various 2D materials to measure electron-phonon coupling (EPC) that governs electronic transport properties [31, 32]. For n-type semiconducting MoS₂, symmetry of the conduction band minimum (CBM) determines EPC of the A₁g and E₂g modes [33]. In ambipolar phosphorene transistor, electrons and holes couple differently to phonons as CBM and valence band maximum (VBM) possess different orbital symmetries [34]. Although the electronic band structure of monolayer MoTe₂ is similar to MoS₂ [16], the VBM of the former remains at the K-point from single to three layers [16, 49]. Thus a study of the EPC in few layer MoTe₂, an intrinsic p-type semiconductor [50, 51], will reveal asymmetry of phonon coupling with holes and electrons in these hexagonal polytypes of TMDs.

Bulk MoTe₂ belongs to D₆h point-group [52] having six Raman active modes (A₁g + 2B₂g + E₁g + 2E₂g) [17]. A₁g and E₂g modes have vibrations perpendicular to and along the basal plane of the lattice, respectively [17]. The in-plane E₁g mode is absent in backscattering configuration [17]. Notably, the translation symmetry along the z-direction is broken in a few layer nanocrystal, reducing the symmetry to D₃h and D₃d for odd and even layers of MoTe₂, respectively [52]. Thus, the out-of-plane inactive mode B₂g in bulk becomes Raman active in few layers and shows highest intensity in a bilayer nanocrystal [53]. For odd layer nanocrystal, the inversion symmetry breaks, making some modes both Raman and infrared active [17]. For simplicity, the Raman modes of even and odd layers of MoTe₂ in this paper are represented by the bulk phonon symmetry group of equivalent atomic displacements (see table-S1 of the supplemental material (SM)).

In the present study, we measure in-operando optical phonons in a few layers of 2H-MoTe₂ based field-effect transistors (FETs) as a function of hole doping concentration (p) up to ∼ 2.3×10¹³ cm⁻². The modes involving both metal and chalcogen atom vibrations, E₂g and B₂g [17] show phonon softening and linewidth broadening while the A₁g mode with out-of-plane vibrations of only the chalcogen atoms [17], shows in contrast, relatively smaller phonon hardening and linewidth sharpening. The frequency renormalization comparison of E₂g mode from 2, 3 and 7 layer devices indicate that the doping is confined to only two top layers of the nanocrystal. We have carried out first-principles density functional theory (DFT) calculations on a bilayer MoTe₂ transis-
tor for understanding the experimental results. We show that the holes couple weakly with the A$_{1g}$ mode as compared to E$_{2g}$ and B$_{2g}$ modes and demonstrate that different orbital symmetries of the VBM and CBM at the K-point of MoTe$_2$ and MoS$_2$, respectively, contribute to their contrasting EPC.

II. RESULTS AND DISCUSSION

A. Experimental results

Bulk MoTe$_2$ crystals were mechanically exfoliated and transferred to a clean Si/SiO$_2$ (285 nm) substrate. Device contacts were fabricated by first patterning them in electron-beam lithography followed by thermal evaporation of 5 and 50 nm thick chromium and gold respectively. The optical image of the two-probe device is shown in Fig. 1(b). Atomic force microscope (AFM) measurement in tapping mode (inset graph of Fig. 1(b)) confirms the nanocrystal thickness to be ∼2.5 nm (∼3 monolayers). A drop of 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMIM-TFSI) IL was drop casted on top of the device channel for electrochemical top gating. Electrical measurements were done using a Keithley 2400 source meters. Conductivity ($\sigma$) as a function of gate voltage ($V_g$) shows hole transport (Fig. 1(c)) due to unintentional doping from the environment. Previous experiments done on few layer MoTe$_2$ show formation of Mo-O bonds on tellurium vacancy sites which shift the Fermi level towards the VBM, making MoTe$_2$ intrinsically hole doped [50, 51]. To determine hole doping, $p$, from $V_g$, we use parallel plate capacitor formula, $p = C_G(V_g - V_{Th})$, where $V_{Th}$ is the current threshold voltage, and the gate capacitance of the IL, $C_G$ is taken to be ∼5.9 $\mu$F/cm$^2$ [54]. Consistent with previous reports [55, 56], the device shows field-effect mobility ∼1.85 cm$^2$/V.s and current on/off ratio ∼10$^5$.

In-situ transport and Raman measurements in backscattering configuration were done at room temperature using LabRAM HR-800 Evolution spectrometer having 1800 lines/mm gratings and a Peltier cooled CCD detector. Excitation laser of 532 nm wavelength was focused using a 50× long working distance objective with incident power less than 0.5 mW to avoid heating. Raman spectrum of the trilayer nanocrystal is shown in Fig. 1(d). At each gate voltage, the peaks are fitted with a sum of Lorentzian functions to extract the phonon frequency ($\omega$) and linewidth ($\gamma$). Figs. 2(a) and (b) show the change in phonon frequency from zero doped state ($\Delta\omega = \omega_{n\neq0} - \omega_{n=0}$) and linewidth of the trilayer nanocrystal, respectively, with hole doping concentration up to ∼1.1 × 10$^{13}$/cm$^2$. The frequency of the in-plane mode E$_{2g}^1$ decreases and linewidth broadens whereas the out-of-plane mode, A$_{1g}$ shows in contrast, relatively small phonon hardening and linewidth sharpening. We have repeated our experiments for a bilayer nanocrystal. We have used a FET device with both bilayer and multilayer channels in parallel to confirm our doping effect in the electrical transfer characteristic (see Fig. S1(a) of the SM). Electrochemical gating induced ions sit very close (∼few Angstrom [36]) to the semiconductor surface in a FET. Using EMIM-TFSI gating on a hexagonal boron-nitride enclosed strontium titanate (STO), a two-dimensional electron gas system (2DES), Gallagher et al. [40] have shown that disorders induced by the IL reduces the mobility by an order of magnitude. Xia et al. [39] theoretically explained this effect in terms of 2D percolative transport from trapped carriers due to the ions induced by the IL at the semiconductor-electrolyte interface. Hence, the mobility suppression will be higher in monolayer and bilayer channels resulting in negligible transistor performance.

As the intensity of the A$_{1g}$ Raman mode is weak for 532 nm laser excitation for few layers of MoTe$_2$ [5], we have used excitation wavelength of 660 nm (Fig. S1(b) of the SM) for this device. With hole doping concentration up to ∼1.5 × 10$^{13}$/cm$^2$, similar to the trilayer nanocrystal (Figs. 2(a) and (b)), A$_{1g}$ mode shows a trend of phonon hardening and linewidth sharpening to a small extent and the E$_{2g}$ mode shows phonon softening and linewidth broadening (Figs. 2(c) and (d)). The nature of the A$_{1g}$ mode as reported by Grzeszczyn et al. [44], depends on the thickness of the MoTe$_2$ nanocrystal. They have shown that at 633 nm of laser excitation, A$_{1g}$ is a single peak both in monolayer and bilayer nanocrystals [44]. However, the intensity of the peak drops below E$_{2g}$ and splits into multiple peaks in multilayer nanocrystals of 2H-MoTe$_2$ [44]. The single peak of the A$_{1g}$ mode in the observed Raman spectrum at 660nm of laser excitation shown in Fig. S1(b) combined with AFM data in Fig. S1(a), confirm that the doping dependence presented in Figs. 2(c) and (d) are indeed from the bilayer part of the device (Fig. S1(a)). In addition, the observed trend of $\Delta\omega$ and $\gamma$ is similar to the isolated trilayer nanocrystal (Figs. 2(a) and (b)), confirming the effect of hole doping. However, the transfer characteristics shown in Fig. S1(a) is dominated by the multilayer nanocrystal. Furthermore, the threshold voltage for Raman frequency and linewidth shift of the bilayer nanocrystal (Figs. 2(c) and (d)) matches well with the threshold voltage in the transfer characteristics (Fig. S1(a)). It is to be noted that for similar reasons, parallel channels of bulk and monolayer of black phosphorus nanocrystal were used to determine phonon renormalisation with doping [34].

As the frequency of the Raman mode from the IL (see Fig. S2 of the SM) is close to the B$_{2g}$ mode at ∼290 cm$^{-1}$ (Fig. 1(d)), we did experiments on a seven-layer thick nanocrystal, where the Raman signal (with 532 nm wavelength of laser excitation) is more prominent (Fig. 3(a)). Fig. 3(b) shows the thickness of the nanocrystal to be ∼5 nm (∼seven layers) from AFM measurement (inset graph of Fig. 3(b)). The device transfer characteristics in Fig. 3(b) shows hole field-effect mobility of ∼0.41 cm$^2$/V.s and current on/off ratio ∼10$^2$. Using SiO$_2$ back gate, Pradhan et al. [24], showed similar transis-
charges localize only in the topmost two layers due to the in-plane E$_{1g}$ mode, although having similar vibrational displacements to the A$_{1g}$ mode [17], shows phonon renormalization as the in-plane E$_{2g}$ mode.

Brumme et al. [16] theoretically showed that the charges localize only in the topmost two layers due to screening effects in MoTe$_2$ based FET devices. From electron doping induced 2H to 1T’ phase transition from bulk to monolayer MoTe$_2$, Zakhidov et al. experimentally showed that the gating by IL causes electrons to be confined in the topmost few layers [14]. Consistent with these reports, we observe a smaller change in $\Delta \omega$ and $\gamma$ of E$_{2g}$ mode for a given gate voltage as the layer number increases (Figs. 2, 3(c) and 3(d)). Taking the applied doping ($p$) to be limited to the top two layers rather than the entire nanocrystal, the average doping ($p'$) for a N-layer nanocrystal is scaled as $p' = p \times 2/N$. With $p'$, $\Delta \omega$ of E$_{2g}$ from 2, 3 and 7 layer nanocrystal scale very well with each other (Fig. 4(a)), justifying that the doping is confined to top two layers of the nanocrystal. The scaling of $\gamma$ for the three devices (Fig. 4(b)) is modest with $p'$.

FIG. 2. Change in the frequency ($\Delta \omega = \omega_{n,p} - \omega_{n=0}$) and linewidth ($\gamma$) of the Raman modes with hole doping concentration ($p$) for (a and b) trilayer and (c and d) bilayer nanocrystal, respectively. Gray regions represent the zero doped state ($V_g \leq V_{TH}$). Change in the horizontal axis increments below zero doping is represented by the break symbol.
FIG. 3. (a) Raman spectrum of the seven-layer nanocrystal. (b) Transfer characteristics of the FET device. Similar to the fit on Fig. 1(c), $V_{Th}$ is indicated in the figure. Inset graph shows the AFM height profile of the nanocrystal. (c) $\Delta \omega$ and (d) $\gamma$ versus $p$ of $E_{12g}$ and $B_{2g}$ modes.

FIG. 4. (a) $\Delta \omega$ and (b) $\gamma$ with average doping concentration ($p'$) of the $E_{12g}$ mode in 2, 3 and 7 layer nanocrystal.

**B. Theoretical analysis**

Our first-principles DFT calculations of the bilayer were carried out with Quantum ESPRESSO (QE) pack-

age [57], in which we treat only the valence electrons by effectively replacing the potential of ionic cores with
FIG. 5. (a) Schematic illustration of an FET setup simulated in a periodically repeated unit cell where the layers of 2H-MoTe$_2$ is placed in front of a charged plane mimicking the metallic gate (shown with gray color plate). The layers are doped with holes, such that the charged plane is charged with the same magnitude of opposite charges. To mimic the dielectric separation layer, we include a potential barrier (shown in blue). The length of the unit cell along the z-direction is given by $L$. (b) Electronic structure of bilayer 2H-MoTe$_2$ calculated including the effect of spin-orbit coupling, shows it to be an indirect band gap semiconductor with VBM at K and CBM at Q point (Q point is along Γ-K direction) with a band gap of 0.88 eV. (c) Projected density of states of bilayer 2H-MoTe$_2$ shows a strong coupling between the Mo d orbitals and Te p orbitals evident in their joint contributions to states near the gap.

pseudopotentials. Exchange-correlation energy of electrons is included within a generalized gradient approximation (GGA) [58] in the functional form parametrized by Perdew, Burke, and Ernzerhof [59]. We include spin-orbit coupling (SOC) through use of relativistic pseudopotentials and a second variational procedure [60]. Kohn-Sham wave functions and charge density were represented in plane wave basis sets truncated at energy cut-offs of 40 Ry and 320 Ry respectively. A vacuum layer of 10 Å has been introduced parallel to MoTe$_2$ layer (perpendicular to z-direction) to weaken the interaction between the layer and its periodic images. Brillouin zone (BZ) integrations were sampled on uniform $24 \times 24 \times 1$ mesh of k-points. The discontinuity in occupation numbers of electronic states was smeared using a Fermi-Dirac distribution function with broadening temperature of $k_B T = 0.003$ Ry. We include van der Waals (vdW) interaction using PBE + D2 parametrized scheme of Grimme [61].

We have used the FET setup [62] as implemented in QE package to treat gating electric field. A 2D charged plate modeling the gate electrode is placed at $z = 0.019$ L. A potential barrier with a height of $V_0 = 0.09$ Ry and a width of $d_b = 0.1$ L is used to model the dielectric layer, preventing ions from moving too close to the gate electrode (Fig. 5(a)). Dynamical matrices were calculated within the Density Functional Perturbation Theory (DFPT) [63] on a $3 \times 3 \times 1$ mesh of q-vectors in the Brillouin zone. Fourier interpolation of these dynamical matrices was done to obtain phonon frequencies at arbitrary wavevectors and dispersion along the high symmetry lines in the Brillouin zone.

Bilayer 2H-MoTe$_2$ has a hexagonal structure, where covalently bonded layers of Te-Mo-Te atomic planes are stacked along c-axis interacting via weak vdW interaction. The periodic unit cell of bilayer 2H-MoTe$_2$ is characterized by a stacking sequence $AbABA$, where Wyckoff positions $A$, $B$ label basal Te atomic planes and $a$, $b$ label Mo atomic planes of the hexagonal lattice (Fig. 1(a)). Our estimate of the lattice parameter $a (= b)$ is 3.53 Å which matches well with previous experimental value [64]. Bilayer 2H-MoTe$_2$ is an indirect band gap semiconductor with VBM at K and CBM at Q point (along Γ-K direction) separated by a gap of 0.88 eV (Fig. 5(b)). From the projected electronic density of states (DOS) (calculated without SOC) (Fig. 5(c)), it is evident that there is a rather strong coupling between the Mo d orbitals and Te p orbitals, contributing to states near the
Electron doping in monolayer MoS\textsubscript{2} has contrasting effects on the frequencies of A\textsubscript{1g} and E\textsubscript{2g} optic modes [33]. While A\textsubscript{1g} mode softens significantly (\(\sim 7\) cm\textsuperscript{-1} at \(\sim 1.8 \times 10^{13}/\text{cm}^2\)), E\textsubscript{2g} remains unaffected [33]. We can understand this contrast as follows: monolayer MoS\textsubscript{2} is a direct band-gap semiconductor with a gap of \(\sim 1.8\) eV with the VBM and CBM at the K-point [49]. The CBM at the K-point of MoS\textsubscript{2} has contribution from the out-of-plane d\textsubscript{z} orbital of Mo atoms [33]. The A\textsubscript{1g} mode has the symmetry of the lattice, hence matrix element \(<\psi_{k+q,i}|\Delta V_{qv}|\psi_{k,j}>\) is non zero [33]. In contrast, matrix element \(<\psi_{k+q,i}|\Delta V_{qv}|\psi_{k,j}>\) of in-plane vibrational mode E\textsubscript{2g} vanishes as it is orthogonal to A\textsubscript{1g} irreducible representation [33]. In comparison, hole doping in bilayer 2H-MoTe\textsubscript{2} leads to occupation of states at the top of the valence band at the K-point, having domi-
nanence of in-plane $d_{xy}$ orbitals (odd symmetry states) of Mo. The crystal symmetry at K-point is point group $C_2$ which is a nontrivial subgroup of $D_{3d}$ and the symmetry of the valence band is $A_{1g}$. The matrix element $<\psi_f|\Delta V_{pp}^{\parallel}|\psi_i>$ (where $i$ and $f$ are the initial and final electronic wavefunctions) for $\nu = A_{1g}, E_{2g}^1$ and $B_{2g}$ modes are non-zero as calculated using direct product table for $C_2$. Hence, changes in occupancy of these states as a function of doping result in renormalization of these modes. Though $A_{1g}$ and $B_{2g}$ modes have different symmetries in bulk, the modes reduce to the same symmetry, $A_{1g}$ in the case of bilayer (symmetry in even layer, odd layer, and bulk MoTe$_2$ has been listed in table S1), softening is stronger for $B_{2g}$ mode as compared to $A_{1g}$. This is consistent with the EPC being slightly higher for the $B_{2g}$ ($0.016$) than the $A_{1g}$ ($0.011$) mode and is also evident in frequency versus hole doping concentration plot (Fig.6(e)).

III. CONCLUSIONS

In FET devices with 2, 3 and 7 layers of MoTe$_2$ as channels, we have demonstrated that hole doping induces phonon softening and linewidth broadening of the $E_{2g}^1$ and $B_{2g}$ modes, while the $A_{1g}$ mode shows relatively small phonon hardening and linewidth sharpening. Due to dielectric screening, we find that holes are induced only in the top two layers of these channels upon electrochemical top gating, as evident in the layer dependent frequency softening of the $E_{2g}^1$ mode. Results of our first-principles density functional theory calculations agree qualitatively with our experiments. Interestingly, effects of EPC in hole doped MoTe$_2$ observed here are in sharp contrast to the trends seen earlier in electron doped monolayer MoS$_2$. We explain this in terms of the difference in symmetry of their frontier states relevant to electron and hole doping. In addition to being relevant to use Raman spectroscopy as a non-invasive tool for characterization of MoTe$_2$-FET devices, our study will be useful in understanding the role of relevant phonon interaction with charge carriers in determining carrier mobility in MoTe$_2$ devices.

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Supplemental Material

Symmetry induced phonon renormalization in few layers of 2H-MoTe₂ transistors: Raman and first-principles studies

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TABLE S1: Irreducible representation of the Raman modes at Γ-point for N-layer and bulk MoTe₂ [1]. The dagger symbols (†) represent silent modes. The E₁g mode is absent in backscattering configuration [1]. The modes with E' symmetry are both Raman and infrared active [1].

| Layer number | Zone-center phonon representation of the Raman modes |
|--------------|-----------------------------------------------------|
| ≤ 30 cm⁻¹ ≤ 40 cm⁻¹ ~120 cm⁻¹ ~ 170 cm⁻¹ ~ 235 cm⁻¹ ~ 290 cm⁻¹ |
| Odd Layer | \( \frac{N-1}{2} E' \) | \( \frac{N-1}{2} A_1' \) | \( \frac{N-1}{2} E' \) | \( \frac{N+1}{2} A_1' \) | \( \frac{N+1}{2} E' \) | \( \frac{N-1}{2} A_1' \) |
| Even layers | \( \frac{N}{2} E_g \) | \( \frac{N}{2} A_{1g} \) | \( \frac{N}{2} E_g \) | \( \frac{N}{2} A_{1g} \) | \( \frac{N}{2} E_g \) | \( \frac{N}{2} A_{1g} \) |
| Bulk | \( E_{2g} \) | \( B_{2g}^\dagger \) | \( E_{1g} \) | \( A_{1g} \) | \( E_{2g} \) | \( B_{2g}^\dagger \) |

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I. Electrical and Raman spectral characterization of the bilayer MoTe$_2$ nanocrystal

Fig. S1: (a) Transport characteristics of the field-effect device with bilayer and multilayer (~9nm) parallel channel. The field effect mobility and current on/off ratio are $\sim 0.21$ cm$^2$/V.s and $10^2$, respectively. The red dashed line indicates linear fit to the transistor off state. The current threshold voltage ($\sim 0.13$V) is indicated in the figure. Inset shows the AFM height profile with the optical image of the device. (b) Raman spectrum of the nanocrystal with 660 nm laser excitation.
II. Raman spectral background from the ionic liquid

![Raman Spectrum of EMIM-TFSI Ionic Liquid](image)

**Fig. S2:** Raman spectrum of EMIM-TFSI ionic liquid. The star symbol marks the Raman modes. The Raman mode at $\sim 520$ cm$^{-1}$ is from the silicon substrate.
III. Output characteristics of the devices at ambient

![Graphs showing linear drain current (I_{DS}) versus drain voltage (V_{DS}) measurement at zero gate bias for (a) three- and (b) seven-layer nanocrystals.]

Fig. S3: Linear drain current (I_{DS}) versus drain voltage (V_{DS}) measurement at zero gate bias for (a) three- and (b) seven-layer nanocrystals.

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