**RESULTS**

1TL MoS$_2$ single crystals were first synthesized on various substrates, followed by depositing Bi$_2$Se$_3$ QLs, both using CVD (36, 38). 1TL...
MoS$_2$ has a very strong PL signature, and we have used it as the starting crystal to grow 1QL and few-QL Bi$_2$Se$_3$ on top of MoS$_2$. Because the heterocrystal unit cell contains dissimilar numbers of MoS$_2$ and Bi$_2$Se$_3$ unit cells, we will refer to the corresponding layers as TL and QL (instead of Mo$_{16}$S$_{32}$, Bi$_{18}$Se$_{27}$, etc.), respectively. By varying the synthesis conditions, it was possible to obtain samples whose overall thicknesses were those corresponding to 1TL$n$QL, where $n$QL denotes the thickness equivalent of $n$ quintuple layers of Bi$_2$Se$_3$.

Figure 1 (A and B) shows typical optical images of 1TL@1QL and 1TL@2QL heterocrystals grown on quartz and SiO$_2$/Si substrates, where the QLS have uniform one- or two-layer coverage, respectively. (Our notation of 1TL@1QL is meant to denote that Bi$_2$Se$_3$ was grown on top of MoS$_2$.) Figure 1C shows a low-magnification transmission electron microscopy (TEM) image of a QL growth-arrested sample, revealing grains formed from multiple QL nucleation sites on the 1TL surface. Despite the multinucleation growth, selected-area electron diffraction (SAED) (Fig. 1D) of the composite structure reveals a single distinct set of points representing a superposition of MoS$_2$-type (39) and Bi$_2$Se$_3$-type (40) diffraction patterns (red and green hexagons, respectively), with perfect crystallographic alignment. Analysis of the diffraction spots leads to MoS$_2$ lattice spacing of 3.1622 ± 0.0276 Å, similar to a previous report on pristine MoS$_2$ (~3.2 Å) (41), and Bi$_2$Se$_3$ lattice spacing of 4.1401 ± 0.0223 Å, very close to previous reports on pristine Bi$_2$Se$_3$ (~4.136 Å) (42, 43). The ratio of these two lattice parameters $d_{\text{MoS}_2} : d_{\text{Bi}_2\text{Se}_3} \approx 3:4$ is within the accuracy of our TEM and suggests a novel lattice matching between 4 × 4 unit cells of MoS$_2$ and 3 × 3 unit cells of Bi$_2$Se$_3$.

Figure 1E shows the atomic force microscopy (AFM) topographic image of a crystal with a QL step edge separating the 1TL@1QL and 1TL@2QL regions, with the QLS being about 0.9 to 1.1 nm in height (see section S1). The geometry-optimized DFT structure of a proposed 1TL@1QL heterocrystal with various atomic dimensions is shown in Fig. 1F (side view) and Fig. 1G (top view). The in-plane lattice parameters were fixed to experimental values while allowing the atoms to relax along the $c$ axis. This resulted in a QL step height of 1.06 nm, which is in excellent agreement with our experimental results. The unit cell of the 1TL@1QL heterocrystals contains 16 MoS$_2$ parent unit cells and 9 Bi$_2$Se$_3$ unit cells; both AA- and AB-type stacking were present within the same unit cell, as shown in Fig. 1F. The parent unit cells are shown in Fig. 1H for comparison. We conclude that MoS$_2$ and Bi$_2$Se$_3$ can form rotationally aligned epitaxial stacks through space filling (along each crystallographic axis) by a ratio of number of unit cells that is the inverse of the ratio of their lattice parameters. To our knowledge, this is the first instance of such a unique 2D crystal structure built from completely incommensurate parent unit cells.

Figure 2A shows the calculated first-principles band structures of the 1TL@1QL heterocrystals, superimposed on those of the parent monolayer crystals for comparison (see section S3 for details of band structures for greater clarity). 1TL MoS$_2$ has a direct bandgap located at the K and K’ points of the first Brillouin zone that results in a signature PL peak at $E \sim 1.85$ eV (44), whereas 1QL Bi$_2$Se$_3$ is characterized by an indirect transition gap of ~0.5 eV, with the direct gap being much larger (~0.75 eV), located at the Γ point at the center of the first Brillouin zone. Compared to that of 1TL MoS$_2$, the electronic band structure of the 1TL@1QL heterocrystal displays an indirect DFT bandgap, as seen in Fig. 2A. Figure 2B demonstrates how this gap rapidly decreases further as a function of increasing QL thickness. The significant differences between the band structure of the parent crystals and the daughter heterocrystals are attributed to strong TL-QL interaction despite their incommensurate lattices. Our Raman spectroscopic investigations reveal (see section S2) that in 1QL and 2QL heterocrystals, the interlayer interactions are strong enough to substantially suppress the dominant Raman peaks of both MoS$_2$ and Bi$_2$Se$_3$ in stark contrast with heterolayers of 2D materials with weak, van der Waals interactions, where signature Raman peaks of individual layers are largely undiminished (27, 45–47). Figure 2B shows the band structure of the 1TL@1QL heterocrystal.
Figure 2. Electronic and optical properties of nQL Bi$_2$Se$_3$ grown on 1TL MoS$_2$ (1TL⊕nQL heterocrystals). (A) First-principles band structure of pristine 1TL MoS$_2$, 1QL Bi$_2$Se$_3$, and 1TL⊕1QL heterocrystal (see section S3 for details). This heterocrystal has an indirect bandgap at the $\Gamma$ point in sharp contrast to the direct gap of 1TL MoS$_2$ at the K point of the first Brillouin zone. (B) Band structure of the 1TL⊕2QL and 1TL⊕3QL heterocrystals, showing progressively decreasing gaps between the valence and conduction bands with increasing QL thickness. (C) Signature PL spectrum in a 1TL MoS$_2$ sample (peaks A and B are labeled), which is completely quenched in the heterocrystals, consistent with the formation of an indirect bandgap material. The inset highlights how 99% of the PL was quenched by the addition of 1QL of Bi$_2$Se$_3$ on 1TL MoS$_2$. (D) PL from a 1TL MoS$_2$ sample transferred on a Bi$_2$Se$_3$ flake (random stacking). With growing QL thickness, a substantial decrease in the transmittance is seen over the entire visible range of photon energies, consistent with the increase in their visible light reflectance, as evident from the brighter contrast seen in the optical images of thicker samples shown alongside. (E) Evolution of energy-resolved optical transmittance in samples of progressively increasing thickness ($\sim$1–6 nm). The absorption lines A and B, as well as the transmittance minima $T_{\text{min}}$, are labeled for the 1TL MoS$_2$ sample. With growing QL thickness, a substantial decrease in the transmittance is seen over the entire visible range of photon energies, consistent with the increase in their visible light reflectance, as evident from the brighter contrast seen in the optical images of thicker samples shown alongside. (F) DFT DOS of 1TL⊕nQL ($n = 0$ to 3) heterocrystals, showing that the DOS spectral weight near the bottom of the conduction band shifts to lower energies as QL thickness increases.

Figure 2E shows the energy-resolved optical transmittance ($T$) of pristine MoS$_2$ and heterocrystals with increasing thickness below 6 nm (corresponding to $n = 1$ to 5 QL). The highest transmittance curve corresponds to that of 1TL MoS$_2$, with dips at 1.9 and 2.04 eV, corresponding to the formation of A and B excitons from the two spin-orbit split edges of the valence band at the K points. This is followed by a gradual decrease in transmittance with increasing energy ending in a broad transmittance valley centered around the lowest transmittance ($T_{\text{min}}$) at 2.88 eV, possibly associated with degenerate exciton states near the $\Gamma$ point. The broadband absorbance between $\sim$1.9 and 2.9 eV has been proposed to arise from strong electron-phonon effects that smear out several higher-order excitonic peaks within this region (49). With increasing QL thickness, there is a steady decrease in transmittance over the entire region of the measured spectra. Note that although the PL of these samples is completely quenched, the dip-like A and B excitonic features in the transmittance spectra are retained, suggesting that these excitons can survive in the heterocrystals although the material as a whole becomes an indirect-gap system, in a manner similar to few-layered MoS$_2$ (50). Because of the large size of the heterocrystal supercell, we were unable to carry out a calculation of the absorption spectrum that accounts for electron-hole interactions (49), and hence, we could not theoretically ascertain whether excitonic peaks survive in the heterocrystals. However, our analysis of the projected band structures (see section S3) reveals that despite the overall systematic changes in the band structures with increased QL thickness and dominance of the bandgap near the $\Gamma$ point by the Bi$_2$Se$_3$ bands, the nature of the 1TL⊕2QL and 1TL⊕3QL heterocrystals, according to which the bandgap continues to decrease with increasing QL thickness, which is consistent with the decreasing gap obtained from optical measurements (section S4).

Figure 2C shows the PL spectrum of 1TL⊕nQL ($n = 1$ to 4) samples, compared to that of pristine 1TL MoS$_2$. We find a marked (near-100%) suppression of the PL spectrum of the 1TL⊕1QL sample, which suggests a direct-to-indirect bandgap transition (44), in agreement with our DFT results. Addition of further QLs completely quenches the PL, as shown in the inset to Fig. 2C. To ascertain whether interlayer charge transfer (46, 48) could be responsible for the PL suppression, we also performed PL measurements on structures where CVD-grown 1TL MoS$_2$ samples were mechanically transferred (with random position and orientation) onto freshly cleaved Bi$_2$Se$_3$ layers (see section S5). Figure 2D compares the PL spectra from such a “transferred” heterolayer sample, where only a partial PL modification is observed, suggesting that directly grown heterocrystal formation is necessary for the observed complete PL suppression. We will show later on that disrupting the interface alignment of TLs and QLs in the heterocrystals immediately recovers the PL, providing further evidence that the observed PL suppression is not merely an outcome of thermodynamic charge transfer—a mechanism that is sometimes responsible for PL quenching in other heterosystems (46, 48). The charges in heterocrystals appear to redistribute into periodic layers of electrons and holes at the interface in the heterocrystals, as discussed in section S3.
of the valence band peaks at the K and K’ points, which are responsible for the A and B excitons, is mostly MoS2-type, analogous to how the A and B excitons are sensitive to the QL thickness. Although increased reflectance is evident (changing the density of states (DOS)) with increasing QL thickness, the decreasing reflectance values and the comparatively lower reflectance near the exciton DOS near the Fermi level from these curves, approximate transmittance edges of the heterocrystals could be estimated using a modified Tauc plot approach (see section S4). A clear, monotonically decreasing thickness dependence of transmittance edge values is observed in the heterocrystals, ranging from ~1.1 to 0.75 eV, saturating at the higher thickness values. These values are consistent with all PL spectra of heterocrystals that show no detectable indirect peak above 1.2 eV (detection limit of our PL spectrometer). We note that these values are significantly distinct from the energy gaps in either of the participating parent crystals.

The DFT DOS of 1TL MoS2 and representative heterocrystals are plotted in Fig. 2F, which shows that as QL thickness increases, the DOS spectral weight near the bottom of the conduction band also shifts to lower energies, which is in excellent agreement with our experimental observation of red-shift of transmittance spectral weight with increased QL thickness. Detailed analysis of A and B excitons in our heterocrystals (presented in Discussion) also reveals gradual decrease in peak amplitude and peak shift toward lower energies (red-shift) with increasing QL thickness (S0). We thus conclude that heterocrystal formation is responsible for giving rise to several fundamentally new and functionally attractive observed electronic and optical properties.

We next discuss another attractive feature of our heterocrystals. We have discovered that application of a high-intensity laser spot on the heterocrystals results in nearly complete reversal of their optical properties. Figure 3A schematically depicts the laser treatment process on a heterocrystal sample supported on a substrate. Typically, samples were exposed to a 488-nm laser focused onto a spot size down to <1 μm with an intensity of 76 μW/μm². Figure 3B shows a scanning electron microscopy (SEM) image of a sample that has been exposed to spots of various sizes, the affected areas of which are highlighted. The inset to Fig. 3B is an AFM topographic image of one of the “treated” spots, denoted by the submicrometer outlined area. The laser-treated area typically undergoes a small increase in height and surface roughness (discussed later), suggesting that the laser treatment is not “etching/sublimating out” the materials but possibly induces structural changes, whereas the lighter SEM contrast suggests modified electronic properties. The most remarkable outcome of the laser treatment is the recovery of the MoS2 PL peak. Figure 3C summarizes this rather surprising result, where a sample was laser-treated for various time intervals. A strong PL peak (measured using low-intensity laser) is recovered at nearly the same photon energy as that of the parent 1TL MoS2 crystal, indicating that the laser treatment results in the reversion of the electronic structure to that of a pristine 1TL MoS2. In addition to the PL recovery, prolonged laser treatment of the heterocrystals results in a complete change of their color (as seen in the optical image inset to Fig. 3C), further indicating the marked change in their electronic properties. PL spectra were also measured in samples of different QL thicknesses after identical, 10-min laser treatment (Fig. 3D). The degree of PL recovery was found to be inversely related to the QL thickness, confirming that most of the changes observed occurred in the Bi2Se3 region. As discussed later, the recovered PL slightly red-shifted compared to the pristine PL, possibly because the Bi2Se3 layers were still attached to the MoS2 layer.

The submicrometer-resolution laser treatment could be advantageously used to demonstrate proof-of-concept 2D sheets with laser-patterned or laser-written optical/electronic properties. Figure 3E shows two such examples: (i) In the top panel, a moving laser spot was used to define rectangular windows and arrays of parallel lines on the 2D heterocrystals with modified properties. These laser-written patterns are highly attractive for optoelectronic circuits or photonic/plasmonic crystals. (ii) In the bottom panel, a moving laser spot was periodically chopped to mimic “bit-writing,” where the alternating submicrometer “laser-treated, light-emitting” and “pristine, dark” regions could code 1’s and 0’s, respectively. This represents an interesting new way of optical information storage in atomically thin materials. Figure 3F shows the spectral transmittance curves of two heterocrystals before and after laser treatment along with that of pristine 1TL MoS2. After treatment, the transmittance curves of the heterocrystals look markedly similar to those of 1TL MoS2 over the entire spectrum of energies tested, suggesting that the laser treatment results in near-complete reversal of band structure to that of pristine 1TL MoS2. Similar recovery is also seen in Raman spectroscopy (see section S2) after laser treatment for A1g (~385 cm⁻¹), E1g (~405 cm⁻¹), and 2LA(M) (phonons at the Brillouin zone edge) modes (450 to 460 cm⁻¹). Moreover, by annealing the laser-treated samples at 175°C in argon environment, partial PL quenching and recovery can be repeated a few times, proving that the “reconfiguration” is reversible (as discussed later). To our knowledge, this is the first instance of such a laser-induced optical/electronic property reconfiguration/reversal demonstrated in atomically thin crystals. We next investigate the mechanism underlying this laser-induced reversal.

Figure 4 (A and B) shows AFM images of two laser-treated areas of a 1TL@3QL heterocrystal. Analysis of the surface heights reveals that the laser-treated areas have a slightly greater mean height and surface roughness, indicating that the material under the laser spot has become more uneven or granular. Figure 4 (C and D) shows optical and TEM images of another heterocrystal sample, part of which was laser-treated, as shown. Higher-magnification TEM images from representative regions of this crystal reveal that whereas the pristine heterocrystal retains its planar, homogenous topology (Fig. 4E), spatially distinct nanoscale domains appear in the laser-treated sample (Fig. 4H). It appears that the laser treatment provides sufficient energy to the Bi2Se3 layer to rotate away from their original direction. As we have shown in previous reports (36, 37), markedly different from its bulk
**Fig. 3.** Laser-induced recovery of “1TL MoS2”–like optical properties and designer 2D crystals. (A) Schematic depicting the laser treatment procedure: exposure of a heterocrystal to a focused laser spot ($I = 76 \mu W/mm^2$). (B) SEM image showing laser-treated areas (lighter contrast) on a heterocrystal, with the inset showing an AFM image of one of the treated spots. (C) and (D) The laser treatment results in the recovery of 1TL MoS2–like PL, shown as a function of exposure time in (C) and samples of different QL thickness in (D). (E) 2D materials by design. Top: Schematic and optical image of a laser-written heterocrystal showing a rectangular “window” and an array of lines drawn with submicron spatial resolution. Bottom: An SEM image of a heterocrystal exposed to an optically chopped moving laser, intended to represent an alternating sequence of 1’s and 0’s in a proof-of-concept optical storage device. (F) Variation of energy-resolved transmittance before and after laser treatment in the heterocrystals. The insets show optical images of a 1TL MoS2 and two post–laser-written heterocrystals with different thicknesses, from which the spectra were collected, before and after the laser treatment. A near-complete recovery to pristine MoS2–like behavior is obtained in the posttreated samples.

**Fig. 4.** Evidence of laser treatment–induced breakdown of rotational alignment. (A and B) AFM topography images comparing the surface morphology of pristine versus laser-treated areas in few-nanometer-thick heterocrystals. Both root mean square surface roughness and the mean height of the laser-treated [denoted with an asterisk (*)] areas are slightly greater than those of pristine areas. (C) Optical and (D) low-magnification TEM image of a few-nanometer-thick heterocrystal grown on a Si$_3$N$_4$ TEM membrane, with part of the crystal being laser-treated as shown. Corresponding higher-magnification TEM images are shown in (E) pristine and (F) laser-treated demarcated areas. The laser-treated area is seen to have lost its homogeneity and becomes polycrystalline with nanoscale grains. SAED patterns from the (G) pristine and (H) laser-treated areas reveal that the Bi$_2$Se$_3$ crystal nanodomains in the laser-treated samples lose their rotational alignment, with the MoS$_2$ crystal resulting in their rotationally spread-out diffraction patterns (outlined by green dashed circles). Note that the MoS$_2$ pattern remains intact. (I) Typical SAED of laser-treated, suspended (see section S5) heterocrystals, revealing rotational reorientation and spread of both Bi$_2$Se$_3$ and MoS$_2$ crystals, suggesting that both form polycrystalline nanodomains. (J) PL in a similar sample before and after [denoted with an asterisk (*)] laser treatment. Laser treatment in suspended samples is seen to result in a characteristic broadband PL, which is different from the sharply defined PL of supported samples (see fig. S11 for a larger version).
form, quantum-confined few-layered Bi$_2$Se$_3$ can have bandgaps $E_g > 2.5$ eV, absorbing little or no light over the range of photon energies investigated here, and thus, heterocrystals after laser treatment become more transparent and similar to 1TL MoS$_2$ (Fig. 3F). Although these nanodomains of Bi$_2$Se$_3$ retain their crystal structure (as evident from the strong diffraction patterns), breakdown of rotational alignment results in the heterocrystals losing their electronic identity. The underlying MoS$_2$ TL hence regains its PL and other optical properties, as summarized in Fig. 3.

The crystallographic and optical modifications are even more marked when the laser treatment is performed on “suspended” heterocrystals (see section S6). The Bi$_2$Se$_3$ and MoS$_2$ layers appear to break down into smaller domains with a range of rotational orientations, resulting in ring-like patterns characteristic of polycrystalline samples, as seen in the SAED pattern in Fig. 4I. Additional diffraction rings appear in between the patterns formed by the Bi$_2$Se$_3$ and MoS$_2$ layers, corresponding to lattice spacings ranging from 3.54 to 3.57 Å (see section S6), which is consistent with the spacing between (201) planes of orthorhombic Bi$_2$Se$_3$ (51), indicating the possible formation of this phase within the laser-treated region. These regions are optically characterized by a broadband PL spectrum ranging from ~1.7 to 2.2 eV, as seen in Fig. 4I. This response is very unlike the PL emission from the 1TL MoS$_2$ or from laser-treated substrate-supported samples (shown in the same graph for comparison), but its presence is consistent with our recent report on broadband, multiplex PL in nanoscale Bi$_2$Se$_3$ (37) and with size-dependent PL in nanoscale MoS$_2$ (52, 53). It appears that laser treatment is a versatile and powerful tool for “designing” a variety of light-emission properties from the same heterocrystal enabled by nanocrystal formation of the parent crystals without any deleterious effects.

**DISCUSSION**

Variation of optical properties of our heterocrystals as a function of layer thickness and laser treatment reveals a number of interesting features. In pristine MoS$_2$, the A and B excitons are known to be localized at the valence band peaks at the K and K’ points of the first Brillouin zone (49). Figure 5A shows a close-up of the associated excitonic “dips” obtained after a polynomial background subtraction from the transmittance curves of Fig. 2E. Going from pure 1TL MoS$_2$ to the indirect bandgap heterocrystals, the excitonic dips are seen to systematically become somewhat smaller and red-shifted. This behavior is remarkably similar to the manner in which excitonic peaks evolve with increasing layer thickness in pure 2D MoS$_2$ samples (50), although the related valence band peaks shift gradually away from the Fermi level (54). By projecting the states with MoS$_2$ and Bi$_2$Se$_3$ characters, our first-principles computations show that the valence band peaks and their nearly pure MoS$_2$ character are retained at the K and K’ points with an increasing number of QLs in the heterocrystals, some mixing with Bi$_2$Se$_3$ bands notwithstanding (see section S3). These results indicate that the effective electronic interactions between MoS$_2$ and Bi$_2$Se$_3$ layers in our heterocrystals are similar in strength to those between pure MoS$_2$ layers, despite the mismatch between the lattice parameters. Notably, red-shift in the excitonic peaks in both MoS$_2$ and our heterocrystals reflects the effects of a decreasing bandgap energy with an increasing number of layers and the associated changes in the screening environment at K and K’.

Another issue that merits careful consideration is identifying which of the two mechanisms—disruption of rotational alignment or a possible “delamination” of the Bi$_2$Se$_3$ layers—plays a more dominant role in the recovery of optical properties after laser treatment. As mentioned earlier (Fig. 4, A and B), we noticed a slight increase in sample height after laser treatment. This could partially reflect the fact that the average height of a rough surface appears larger than that of a flat surface, because a continuous sheet of material redistributes into small grains (even smaller than the AFM tip size) of increased heights. On the other hand, the increased height of laser-treated Bi$_2$Se$_3$ could also potentially indicate a certain degree of delamination of the Bi$_2$Se$_3$ from the MoS$_2$ layer. We have analyzed our data to understand which of these two effects is more dominant. Although laser treatments recover the transmittance curve shapes, we find that positions of the excitonic “dips” continue to be red-shifted by about 30 to 45 meV after laser-treated recovery (Fig. 5B). Similarly, the post–laser-treated PL peaks remain red-shifted by 20 to 25 meV compared to those of pristine MoS$_2$ (see Fig. 5C). As discussed earlier, these peak shifts are associated with the immediate dielectric environment of the excitons. That is, the red-shifted excitonic features after laser treatment (transmittance and PL) appear to indicate that the Bi$_2$Se$_3$ layers were still physically adhered to MoS$_2$ and provide a modified dielectric environment, despite their rotational rearrangement. These observations, in addition to the absence of any diffraction patterns (other than pure rotational spots), suggest that after laser treatment, the formation of randomly oriented nanograins that remain attached to the MoS$_2$ surface is the more dominant reason for PL, transmittance, and laser recovery.

In addition, we find that PL quenching and recovery, when measured from the same spot of a heterocrystal, can be partially repeated through annealing of the laser-treated samples, as shown in Fig. 5D. SAED patterns measured from laser-treated areas before and after the annealing process (see section S7) reveal the remarkable fact that upon annealing, the Bi$_2$Se$_3$ sublattice almost completely recovers its original rotational alignment with respect to the MoS$_2$ crystal. This provides clear evidence that annealing of the samples results in rotational realignment and re-formation of the heterocrystals and recovery of their pristine (pre–laser-treated) properties including the re-quenching of the PL. To our knowledge, this is the first demonstration of reconfigurable interface engineering with a functionally attractive outcome in atomically thin materials. Although further fine-tuning of laser treatment and recovery is required to obtain better reproducibility, we conclude that the laser-induced heterocrystal modification is reversible, which makes it attractive for possible rewritable optical storage devices.

Finally, a key question concerns the identification of the driving forces responsible for the formation of heterocrystals presented in this study. Our analysis indicates that a favorable lattice parameter ratio alone is not sufficient for achieving either rotational alignment or heterocrystal formation. Interlayer interactions, which could overcome stresses due to residual in-plane strains needed for heterocrystal formation, likely play an important role in stabilizing the rotational alignment and crystallographic long-range order. For example, although the ratio of lattice parameters of MoS$_2$ and hexagonal boron nitride (hBN) is close to 5:4, past reports reveal no evidence of perfect rotational alignment between heterolayers of this pair of materials, and moreover, the PL spectrum of MoS$_2$ grown on hBN is close to that of freestanding MoS$_2$ (55–58). An important role will also be played in this connection by how the electronic and optical properties are modified through the presence of the interface in a heterocrystal. It is possible that because h-BN is sp$^2$-bonded, its out-of-the-plane interactions with MoS$_2$ might be weak and thus hinder the ability of this
pair of 2D materials to form heterocrystals. Other layered materials that inherently have beyond–van der Waals out-of-plane characteristics may be more suitable for heterocrystal formation. It is clear that further theoretical and experimental efforts are needed to understand the main factors underlying heterocrystal formation.

To summarize, we have presented controlled synthesis of a uniquely new class of vertically stacked 2D heterocrystals with a novel “switchable” PL and widely tunable optical transmittance values and transmittance edges. The range of edge energies is highly attractive for beyond-silicon electronics and optoelectronics, especially for telecommunication wavelengths that require active electronics at the 1550-nm (0.8 eV) standard. Tunable absorbance, reflectance, and photo-emission properties make these crystals potentially important for various photovoltaic and photodetection applications in the visible range. We have also presented a novel laser-induced reversal of the electronic and optical properties, especially the striking manner in which the PL can be reversed and its sharp versus broadband nature can be tuned. To our knowledge, this is the first instance of a 2D material where the optical properties can be tuned very markedly with submicrometer spatial resolution. We have used this laser-writing approach to demonstrate 2D heterocrystals with patterns, arrays, and optical information (bit) storage abilities. It is possible to conceive various photonic, plasmonic, and optoelectronic applications that may benefit from these highly precise optical arrays and circuit-drawing in an atomically thin material. Because the formation of heterocrystals from significantly incommensurate parent crystals is a fundamentally new approach for designing 2D materials, this idea could potentially be explored in a variety of other incommensurate 2D materials, thereby opening up a range of novel electronic, optical, magnetic, thermal, and mechanical properties that are inconceivable through the common van der Waals stacking. We believe that our work represents a significant and important step in furthering fundamental knowledge and potential applications development using 2D materials.

MATERIALS AND METHODS

Growth of MoS$_2$–Bi$_2$Se$_3$ heterocrystals

MoS$_2$ substrates were grown using CVD. The growth setup consisted of quartz tubes [1 inch (2.54 cm) in diameter] in a horizontal tube furnace (Lindberg/Blue M). A quartz boat, containing a thin layer of MoO$_2$ powder (3 mg) with SiO$_2$/Si or polished quartz (MTI Corporation) substrates suspended over the powder with the growth side facing down, was placed in the hot center of the furnace. Sulfur powder (150 mg) was placed near the insulating edge of the furnace. The setup was pumped down and purged with argon gas before it was filled with an Ar atmosphere. Downstream was then opened to atmosphere in addition to a constant 200 standard cubic centimeter per minute (SCCM) Ar flow. The furnace was heated at a rate of 50°C/min to 780°C and then held there for 15 to 25 min. After the elapsed time, the furnace was opened and allowed to cool rapidly.
Bi$_2$Se$_3$ growth was performed in an identical CVD setup. Bi$_2$Se$_3$ powder (50 mg) was placed in the hot center of the furnace. The MoS$_2$ substrate was placed downstream 14 to 16 cm to a temperature range of 315° to 290°C. The system was pumped down to a base pressure of ~10 mtorr before a 20-SCCM Ar flow was introduced, raising the growth pressure to ~350 mtorr. The furnace was heated at a rate of 50°C/min to 480°C and then held there for 10 to 20 min depending on the desired thickness. Once growth was completed, the furnace was opened and allowed to cool rapidly.

Instrumentation
Raman and PL spectra were measured using a Renishaw Raman microscope equipped with a 488-nm laser and a grating of 1800 lines/mm. A ×100 objective focused the laser to diffraction-limited spot size. TEM images and SAED patterns were collected from a JEOL 2010F operated at 200 kV. AFM images were taken from a NanoMagnetics Instruments Ambient AFM. Transmittance spectra of individual heterocrystals were measured by a stepwise schematic describing how the "transferred" samples were prepared with a contamination-free clean interface.

DFT computational details
The ab initio calculations were performed using the pseudopotential DFT computational details (60, 61), where a 7 × 7 × 1 k-point mesh was used under ambient condition.

REFERENCES AND NOTES


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**Competing interests:** At the time of submission, a patent submission was being processed by Northeastern University based on this work (U.S. patent application no. 62/378,345). The authors declare that they have no other competing interests. **Data and materials availability:** All data needed to evaluate the conclusions in the paper are present in the paper and/or the Supplementary Materials. Additional data related to this paper may be requested from the authors.

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Tunable and laser-reconfigurable 2D heterocrystals obtained by epitaxial stacking of crystallographically incommensurate Bi$_2$Se$_3$ and MoS$_2$ atomic layers

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