Nanopatterning of room-temperature localized excitons in MoS$_2$

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We demonstrate a simple approach to pattern a novel localized excitonic state in monolayer MoS$_2$. We raster an electron beam over pristine monolayer MoS$_2$ with a resolution down to 20 nm. In the exposed areas we observe new narrow (1 meV) peaks near 1.72 eV in the photoluminescence (PL) spectrum. We investigate the nature of the state responsible for the peaks using AFM and STEM microscopies, PL spectroscopy, and by examining the response of the state to AFM mechanical cleaning. All these techniques indicate that the state is not associated with structural defects in MoS$_2$, as commonly assumed for irradiation-induced states, and results neither from strain nor from local dielectric screening. Instead, we suggest that this state is a charge transfer exciton associated with the organic substance deposited onto the MoS$_2$ during the e-beam exposure. We show that this new state is well-resolved, easy-to-generate via conventional EBL, and its emission is visible at room temperature. It can be used to study localized excitons, to enable chemical sensing, and to generate new many-body excitonic states.

Localized (or bound) excitons in transition metal dichalcogenides (TMDs, e.g. MoS$_2$, MoSe$_2$, WS$_2$, WSe$_2$) arise when photoexcited electron-hole complexes are trapped in an external potential strong enough to spatially confine that complex. Localized excitons typically feature long ($\mu$s) lifetimes, high brightness, and inherit spin-valley coupling of free excitons in TMDs$^1$–$^4$. These properties ignited interest in multiple applications of localized excitons. First, they can be used as bright, wavelength-tunable, and gate-controlled single quantum emitters for quantum communication technologies$^5$–$^7$. Second, they may preserve spin-polarized carriers for times longer than a microsecond, which is of prime interest for the field of TMD spintronics$^1$,$^8$. Third, regular arrays of localized excitons can form excitonic solids exhibiting a wide range of behaviors from metal-insulator-superconductor transitions to ferromagnetism$^9$–$^{11}$. Such systems may find potential uses as quantum simulators$^{12,13}$. Finally, localized excitons coupled to functionalization molecules can be used as sensitive nanoscale sensors of local chemical environment$^{14,15}$.

To study new physical phenomena and to enable potential applications of the localized excitons, several key requirements must be met. The localization potential should ideally be controlled with high spatial resolution and its strength should be tunable. Additionally, signatures of the localized state should be observable at room temperature and the fabrication technique should be simple and scalable. The required potential can be produced by inducing lattice defects, combining monolayers in heterostructures, or through the interaction with external molecules$^8$,$^{16–23}$. These
approaches only partially meet the requirements outlined above. First, excitons can be localized by controlled structural defects in TMDs that have been induced with high (< 20 nm) spatial resolution using e.g. Helium Ion Beam microscopy\textsuperscript{24}. However, the technique does not allow the control over potential depth, reduces the quality of the TMD material, and is relatively complex. Second, a controlled localized potential in TMDs can be induced by combining monolayers into heterostructures\textsuperscript{12,25–28}. The resulting Moiré lattice induces a periodic potential for excitons with a periodicity controlled by the rotation angle between the lattice vectors of the TMDs. While multiple recent breakthroughs emerged from this system\textsuperscript{9–13,19}, it remains challenging to fabricate such devices. In addition, the localized states are only visible at cryogenic temperatures. Finally, excitons in TMDs can be localized due to the presence of molecules on the surface of TMDs\textsuperscript{22,29}. The resulting charge-transfer excitons (e.g., electron in TMD, hole at the molecule) are localized at the position of the molecule. However, spatial control of such states has not been achieved so far.

Here, we report a simple approach to controllably pattern bright localized excitons in MoS\textsubscript{2} that are visible at room temperature. To produce the localizing potential, we use ubiquitous electron beam lithography (EBL) technique achieving spatial resolution down to 20 nm. We use a combination of photoluminescence spectroscopy (PL), scanning transmission electron microscopy (STEM), and atomic force microscopy (AFM) to show that EBL does not produce structural defects in TMDs under used conditions. Instead, we suggest that the new localized state is a charge transfer exciton between a TMD and organic deposits on its surface induced during EBL.

**Fig. 1: EBL Nanopatterning.**

a) AFM topography of 1L-MoS\textsubscript{2} on hBN sample (D1) after EBL patterning. The period of the lines seen in the image, 80 nm, matches the EBL pattern. The height profile along the blue line in the image is shown in the bottom panel (linear background was subtracted).

b) Transmission electron microscopy (TEM) of a suspended MoS\textsubscript{2} sample (D2) after EBL along with a line section is taken along the blue line in the image. The deposits in e-beam treated regions of the suspended bilayer MoS\textsubscript{2} are also visible. The width of the stripes, about 20 nm (top panel), and their period, 80 nm, match the parameters of EBL patterning.

c) Local EBL exposure of MoS\textsubscript{2} results in a new peak in photoluminescence from the exposed areas (inset).
From the family of TMD materials, we chose the most studied material, MoS\textsubscript{2}. Native defects and defect-related excitonic states manifested in the PL spectrum of this material are largely understood\textsuperscript{29-34}. A monolayer flake is mechanically exfoliated onto SiO\textsubscript{2} or hBN substrate (Methods) and loaded into the EBL tool (Raith Pioneer II) where an electron beam is rastered across the MoS\textsubscript{2} surface. Unless stated otherwise, acceleration voltage is 10 keV and the dose is varied in the range 0.5÷14 mC/cm\textsuperscript{2}\textsuperscript{2}. We produce a pattern consisting of stripes with spacing of 80 nm (Methods). This pattern is clearly visible in the AFM topography images (Fig. 1a) of the surface of MoS\textsubscript{2} device (D1) after exposure and without any additional treatment (see details on devices in Supplementary Note 1). The exposed regions are about 0.3 nm higher (top panel in Fig. 1a) than unexposed ones while the observed period matches patterning parameters. A similar pattern is observed using STEM of suspended bilayer MoS\textsubscript{2} (D2) exposed to a higher electron dose, 14 mC/cm\textsuperscript{2} (Fig. 1b). The single stripe has a width of 23 nm (top panel in Fig. 1b), close to the resolution limit of EBL with used parameters. The appearance of an extra layer of material after EBL is expected and signals EBL-assisted deposition of organics onto the surface of MoS\textsubscript{2}\textsuperscript{35-37}.

Surprisingly, PL spectra feature a new peak at around 1.7 eV in the e-beam modified region of MoS\textsubscript{2} (D1) even in ambient conditions (blue curve in Fig. 1c). This feature was absent in the device before patterning (red curve in Fig. 1c) as well as in other studied pristine MoS\textsubscript{2} samples. This peak is well-separated from native neutral (1.86 eV) and charged (1.83 eV) excitons in MoS\textsubscript{2}\textsuperscript{38,39}. While excitons localized on TMD defects are known to emit in the same spectral region; every study reporting these excitons shows that their emission is only visible well below room temperature\textsuperscript{20,29-31,40}, unlike in our observations. We tentatively label this new feature “E peak” and turn to the investigation of its properties and origin.

To gain insights of the E peak, we study low-temperature PL spectra of e-beam patterned MoS\textsubscript{2} device (D3). Figure 2a shows PL spectra of the sample at 15 K under excitation power of 50 nW – 2.8 mW focused into a spot with ~0.6 \mu m diameter. The spectrum at high fluence consists of a 40 meV wide E peak centered at 1.735 eV and a shoulder of another peak at 1.77 eV (Supplementary Fig. S1). The latter peak is traditionally interpreted as due to native defect-bound excitons in MoS\textsubscript{2}\textsuperscript{29-31}. At lower excitation fluencies, all other excitonic emission is suppressed (Fig. S2) while sharp features around 1.72 eV emerge (vertical dashed lines). The FWHM of these features, around 1 meV, is much smaller compared to the FWHM of free excitons, 8 meV (Fig. S1). This feature is not observed across the unexposed areas of the flake. Previous studies on localized photon emitters observed similar emission with narrow spectral linewidth and similar power dependence\textsuperscript{2,8,16,20,41,42} which indicates emission due to localized states\textsuperscript{43,44}. The asymmetric lineshape of E peaks is due to a phonon sideband\textsuperscript{20,45,46}.

Next, we investigate low temperature PL of the same feature and study its dependence on electrical doping. For that, we apply a gate voltage ($V_\text{g}$) between the Si backgate and the 1L-MoS\textsubscript{2} sample, D4 (Fig. 2b). We observe that the E peak intensity is strongly $V_\text{g}$-dependent with maximum intensity observed at negative $V_\text{g}$. By examining the intensities of neutral (A) and negatively-charged (T) excitonic peaks at 1.93 and 1.90 eV respectively, we establish that the gate voltage where the E peak is visible corresponds to the Fermi level close to the bottom of the conduction band of MoS\textsubscript{2}\textsuperscript{29}. 
We therefore suggest that the E peak involves a shallow state inside the bandgap of MoS$_2$ close to the conduction band, the occupancy of which changes within the range of applied gate voltage$^{6,47}$. The electrical tunability of this state provides a simple tool for its control$^7$.

Having examined the E peak at low temperatures, we now turn to its room-temperature behavior and study its dependence on the irradiation dose (D5). Unlike the structural defect-related peaks in MoS$_2$ studied elsewhere$^{20,29}$, the E peak is well-resolved at room temperature. Moreover, it is the brightest feature in the PL spectrum above an irradiation dose of 1 mC/cm$^2$ (Fig. 2c). Interestingly, we observe a redshift of the E peak position up to 50 meV between the doses of 0.01 and 1 mC/cm$^2$ (Fig. S3). We suggest that this redshift is related to the statistical distribution of the energy of the states inside the bandgap$^{48,49}$. A decrease in the intensity for higher e-beam doses is likely related to self-quenching$^{50,51}$.

Summarizing our observations so far, the new E peak at about 1.7 eV appearing after electron beam exposure of MoS$_2$ corresponds to a localized excitonic state. This state survives up to room temperature and its gate voltage dependence suggests that shallow-lying midgap states participate in its formation. Several mechanisms could potentially lead to the formation of such a state. First, it can result from localization of a neutral exciton due to e.g., varying dielectric environment of MoS$_2$. However, the observed energy separation between the neutral exciton and the E peak, 165 meV, is too large to be explained by dielectric screening$^{15,52}$. Second, a strongly localized mechanical strain that could be produced, e.g. by the material on top of MoS$_2$ can also induce localization of the excitons$^{27,29,47,53,54}$. However, maximum shift in the PL peak position estimated from AFM topography (Fig. 1a) is two orders of magnitude below the observed peak separation$^{55}$. Third, local patterning can result in structural phase transition (2H → 1T) breaking material into individual quantum dots$^{56,57}$. Our STEM imaging (Fig. 3a) speaks against such scenario, confirming the uniformity of the crystal lattice across pristine and e-beam exposed regions. Finally, the new state may simply be related to the defects produced by e-beam exposure$^{58-60}$. However, the electron energy used in our experiments, 10 keV, is well below the minimal energy needed for displacement threshold in MoS$_2$ for used doses, 70 keV$^{60,61}$.

**Fig. 2: EBL-related photoluminescence peak and its fluence-, gate-, dose-dependencies.** a) Normalized PL spectrum of hBN encapsulated e-beam exposed 1L-MoS$_2$ (D3) at 15 K measured at excitation powers ranging from 50 nW (solid blue curve, multiplied by x1.5 for better visibility) to 2.8 mW. b) Low temperature PL spectra of the modified MoS$_2$ flake on SiO$_2$/Si substrate (D4) at back gate voltages from -80 V to 20 V. c) Room temperature PL of 1L-MoS$_2$ on SiO$_2$/Si substrate (D5) as a function of EBL exposure dose up to 80 mC/cm$^2$. The E peak is redshifted at higher e-beam doses (Fig. S3) due to increase in lower energy e-beam induced states.
To further confirm the lack of structural defects in our samples, we study their chemical and structural composition via STEM and EELS spectroscopy. We use suspended 2L-MoS$_2$ sample treated with e-beam dose 14 mC/cm$^2$ (D2). The high-resolution STEM image of the patterned region is shown in Fig. 3a. We first note the lack of large area defects, in contrast to what is seen after bombardment with high energy particles$^{24,59}$. Instead, we observe an increased density of foreign material at the e-beam exposed regions on or under the flake. The EELS spectra at those regions (Fig. 3b) reveal almost tripled density of carbon, silicon, and tenfold of oxygen density (Fig. S5 and S6). Therefore, we attribute e-beam deposits to the organics. Maps of Mo and S signal (Fig. 3b) do not show any variation between patterned and not patterned regions, confirming the absence of e-beam induced structural defects.

Having excluded localized strain, dielectric screening, and structural defect contributions as potential mechanisms leading to the E peak formation, we tentatively suggest that the observed excitonic state stems from the interaction of charge carriers in MoS$_2$ with organic materials deposited at its surface during EBL exposure. To test this hypothesis, we use an AFM tip to remove (using the so-called “nano-squeegee” technique$^{62}$) these residues and examine resulting changes in the PL spectra. First,

![Fig. 3: Nature of localized states. a) STEM image of suspended MoS$_2$ on a Quantifoil grid treated with EBL (D2). Dashed blue line shows the border between the pristine and the EBL-modified parts of the flake. The density of structural defects is nearly equal in both regions. The increased density of foreign material in EBL-modified part persists across multiple regions (see Fig. S4). b) Spatial maps of EELS signal for C, O, Si, Mo and S (white – more intense) across the e-beam patterned region D2 (blue dashed line shows region boundaries). While EELS signal is similar for Mo and S atoms across the regions, it surges for C, O, Si. Thus, we attributed deposits to organics. c) Spatial maps of PL (the signal integrated from 1.6 to 1.75 eV, around the E peak) of 1L-MoS$_2$ on hBN (D6) at room temperature before (left) and after (right) mechanical cleaning with AFM (“nanosqueegee”). EBL exposed zones are highlighted with a dashed blue line. PL spectra taken at the same point marked “X” before and after mechanical cleaning are shown in the right panel.](image-url)
the flake (1L-MoS$_2$ on hBN) was treated with doses 0.14 and 1.4 mC/cm$^2$ in two different rectangular areas (D6). These areas are clearly visible in the PL map of the integrated E peak intensity (Fig. 3a, left). Next, we imaged the entire area shown in Fig. 3a in an atomic force microscope while gradually increasing the contact force up to 300 nN over 12 hours. As expected $^{62}$, this procedure squeezed out the deposits produced by EBL outside of the imaging window. We also note that some deposits, especially in high dose regions, are still present (Fig. S7). After the nano-squeegee procedure, the E peak in the low-dose region disappears completely while remaining largely unaffected in the high dose region (Fig. 3a, center and right). This behavior is not expected if structural defects were the mechanism behind the E peak. In contrast, our observations suggest that the E peak is related to the presence of organics deposited on top of MoS$_2$.

Based on all our observations, we suggest that the E peak is related to the interaction between charge carriers in MoS$_2$ and charged foreign impurities on its surface. One possible scenario is that the E peak is a charge-transfer exciton between MoS$_2$ and the organic deposits. Indeed, such excitons have been previously observed between TMDs and organic molecules on TMD surface$^{22,63}$. These excitons are expected to have properties similar to that of E peak: only appear in the presence of and change with the concentration of external material (Fig. 2c)$^{48,49}$, have $\approx$5 meV blueshift at high excitation powers (Fig. 2a and Fig. S8)$^{64}$, and become a ground state at low temperature (Fig. 2b and S9).

To conclude, we patterned bright, room-temperature, localized excitons in MoS$_2$ using conventional electron beam lithography. This easy-to-use method features nanoscale resolution along with the wide tunability and scalability potential. We investigated the nature of the localized state using a combination of techniques and concluded that it is not related to intrinsic defects in MoS$_2$. Instead, the state is likely a charge transfer exciton formed between e.g., an electron in MoS$_2$ and a hole in an organic material deposited during the EBL. In the future, the out-of-plane nature of that state could be proven by measuring its Stark shift in the perpendicular electrical field. It will be interesting to controllably pattern closely spaced deterministic arrays of electrically controlled localized excitons. Such systems may be interesting for generating on-demand Hamiltonians to be used as quantum simulators. Moreover, brightly emitting localized states visible at room temperature may be used in various biological and chemical applications involving sensing.

**Methods:**

**Fabrication:** The MoS$_2$ on SiO$_2$ samples were obtained by mechanical exfoliation on the 300 nm SiO$_2$/Si from synthetic crystals (HQ graphene $>$99.9% pure) using scotch tape or PDMS. Samples were washed with acetone and IPA to remove residues of tape. Then samples are loaded in Raith Pioneer II SEM/EBL machine for patterning. We used dose and acceleration voltage specified in the main text with beam current of 0.22 nA and 30 µm apertures. Patterning was done in the dot-by-dot regime with 18.9 nm step between dots in a row and 80 nm step between rows. Afterwards, the presence of E peak in the room temperature PL spectrum of the sample confirms successful modification. Finally, samples were annealed at 230 °C for about 12h in vacuum.
Photoluminescence spectroscopy: The dose dependence and E peak maps (Fig. 2c and 3c) were measured with XploRA™ HORIBA using 532 nm excitation at 16 μW focused in diffraction limited spot (~1 μm diameter). Low temperature experiments (Fig. 2a and 2b) were performed with Witec Alpha confocal spectroscopy setup in an optical cryostat with 532 nm green laser excitation focused in ~0.6 μm diameter spot at various powers. Temperature was monitored by the diode at the sample holder and confirmed by spectral position of MoS$_2$ PL peaks. Low power PL spectra were fitted with four exponentially modified gaussians to account for phononic sidebands.

AFM: Mechanical cleaning (nanosqueegee) and topography scans were performed with NanoWizard® AFM in ambient conditions. For nanosqueegee we used non-contact tips (Tap300Al-G from BudgetSensors) in contact regime applying above 100 nN and contact tips (CONTPt-10 from NanoWorld) below 100 nN. The topography scan (Fig. 1a) was taken in contact mode with 2 nN setpoint, two consecutive scans were always recorded. Afterwards, polynomial background subtraction and line matching were applied to the scan.

STEM and EELS: The 2L – MoS$_2$ sample was mechanically exfoliated on PDMS and transferred onto a Quantifoil grid. Prior to its insertion into the electron microscope, the sample was baked for several hours at an elevated temperature (~130˚C) in high vacuum (~2×10$^{-6}$ Torr). STEM-EELS experiments are carried out using a Nion HERMES microscope. This instrument is equipped with an aberration corrector, a cold-field-emission-gun (cFEG), a monochromator at ground potential, and a hybrid-pixel direct-detection camera (Dectris ELA). For the spectra presented in the main text, an energy dispersion of 0.8 eV/channel was used and the acceleration voltage was 60 keV. The probe convergence and EEL spectrometer aperture semi-angles were both around 36 mrad. To avoid the amorphous carbon film of the TEM grid the spectra is acquired at the freely suspended region, several tens of nanometers away from the film. Model based quantification of the spectra was performed after plural scattering deconvolution, using multi-linear least square (MLLS) fitting. The fitted model contains a power-law background function and Hartree-Slater generalized oscillator strength (GOS) functions for the edges; carbon and oxygen K, silicon and sulfur L3-1 and molybdenum M5-1. In this manner, absolute values for atomic ratios are obtained for the above-mentioned species$^{65,66}$.

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