Optoelectronic crystal of artificial atoms in strain-textured molybdenum disulphide

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The isolation of the two-dimensional semiconductor molybdenum disulphide introduced a new optically active material possessing a band gap that can be facilely tuned via elastic strain. As an atomically thin membrane with exceptional strength, monolayer molybdenum disulphide subjected to biaxial strain can embed wide band gap variations overlapping the visible light spectrum, with calculations showing the modified electronic potential emanating from point-induced tensile strain perturbations mimics the Coulomb potential in a mesoscopic atom. Here we realize and confirm this ‘artificial atom’ concept via capillary-pressure-induced nanoindentation of monolayer molybdenum disulphide from a tailored nanopattern, and demonstrate that a synthetic superlattice of these building blocks forms an optoelectronic crystal capable of broadband light absorption and efficient funnelling of photo-generated excitons to points of maximum strain at the artificial-atom nuclei. Such two-dimensional semiconductors with spatially textured band gaps represent a new class of materials, which may find applications in next-generation optoelectronics or photovoltaics.
training two-dimensional (2D) materials\textsuperscript{1–8} with a spatially varying ‘designer’ strain can lead to new artificial materials with exotic properties. Assembling such tuned artificial materials in condensed matter is an emerging field and has employed tools such as atomic manipulation\textsuperscript{9} and lithographic techniques\textsuperscript{10}. Here we focus on monolayer molybdenum disulphide (MoS\textsubscript{2}), a direct band gap semiconductor that shows promise for applications in photonics and optoelectronics due to its extraordinary physical properties\textsuperscript{11–18}. Elastic strain offers a novel and exciting opportunity to tune the band gap of monolayer MoS\textsubscript{2} (refs 1–4) since it can sustain very high elastic strain before rupturing compared with its bulk counterpart\textsuperscript{19,20}. For instance, uniaxial strain has been shown to modulate the electronic structure\textsuperscript{5–7} and reduce the optical band gap (OBG) of monolayer MoS\textsubscript{2} up to 100 meV\textsuperscript{6}.

Besides pushing the magnitude of the strain, the ability to apply a spatially controllable strain is even more crucial because it enables the realization of a graded band gap semiconductor eagerly sought for wider photonic, optoelectronic and photovoltaic applications\textsuperscript{21,22}. It has been calculated that indenting monolayer MoS\textsubscript{2} creates a tensile strain field that reduces the local quasiparticle band gap (QBG). The resulting modified electronic potential falls off inversely with distance from the indentation, playing the role of an effective electronic potential centred on a mesoscopic ‘artificial atom’\textsuperscript{8}. This electronic potential funnels photogenerated excitons from larger band gap regions into smaller band gap regions, resulting in potential broader spectrum light absorption and more efficient photocarrier concentration. The exciton funnel concept has been successfully employed to interpret the OBG of wrinkled few-layer MoS\textsubscript{2}. However, the indirect band gap of few-layer MoS\textsubscript{2} prevents the distinctive photoluminescence (PL) intensity enhancement expected from the exciton funnelling process from being directly observed\textsuperscript{23}. Assembly of the aforementioned artificial atoms would result in a large-area functional ‘artificial crystal.’ Currently there exists no fundamental proof-of-principle of this idea, neither at the single ‘artificial atom’ level nor at a more practical macroscopic scale.

In the following, we apply spatially modulated biaxial tensile strain in monolayer MoS\textsubscript{2} using a patterned nanocone substrate to realize the optoelectronic crystal consisting of ‘artificial atoms.’ MoS\textsubscript{2} on top of the nanocones experiences high strain, which gradually decreases from the tip to the perimeter of the nanocones (Fig. 1a). Since the band gap decreases with increasing tensile strain, the nanocone apex marks the ‘nucleus’ of the ‘artificial atom’. The strain profile has been optimized for maximum exciton solar funnel collection by controlling the geometry and dimensions of the nanocones.

**Results**

**Creation of the artificial-atom crystal in strain-textured MoS\textsubscript{2}**

The as-grown MoS\textsubscript{2} sheet (Supplementary Fig. 1) is transferred onto the SiO\textsubscript{2} nanocones (Fig. 1b) assembled using nanosphere lithography\textsuperscript{24,25} (Supplementary Fig. 2). The as-transferred MoS\textsubscript{2} is soaked in ethylene glycol to remove the trapped air bubbles and optimize the strain (Supplementary Fig. 3b). The evaporation of ethylene glycol that fills the gap between the MoS\textsubscript{2} and nanocones generates capillary force that pulls down the MoS\textsubscript{2} sheet, causing it to conform to the topography of the nanocones and accomplishing the nanoindentation. The clearly visible wrinkles between nanocones (Fig. 1c) indicate the presence of deformation and strain in the MoS\textsubscript{2} sheet, which is also verified by atomic force microscopy (AFM; Fig. 1d). A scanning tunnelling microscopy (STM) topograph (Fig. 1e) shows the details of a single MoS\textsubscript{2} artificial-atom element. We note that a similar attempt for templating strain has been carried out in graphene with limited strain magnitude due to a not-yet optimized process\textsuperscript{25,26}.

**Scanning Raman spectroscopy of the artificial-atom crystal**

The spatially varying strain distribution is verified by micro-Raman spectroscopy. Figure 2a shows the typical Raman spectra of the most strained-MoS\textsubscript{2} (on tip of nanocones), less strained-MoS\textsubscript{2} (between nanocones) and unstrained-MoS\textsubscript{2} (on flat SiO\textsubscript{2}}
The unstrained-MoS2 has the typical Raman spectrum of monolayer MoS2 with two dominant peaks at 385.6 (E2g) and 404.9 cm⁻¹ (A1g)²⁷,²⁸. The strained MoS2 samples show significant redshifts for both E2g and A1g peaks: 0.8 and 0.3 cm⁻¹ for less strained-MoS2, and 2.4 and 0.6 cm⁻¹ for most strained-MoS2. From an overall fit to the redshift magnitudes and the unstrained values, we estimate that (0.230 ± 0.035)% and (0.565 ± 0.025)% biaxial tensile strains are sampled on average by the 450-nm diameter laser beam in less strained-MoS2 and most strained-MoS2 according to our theoretical calculation discussed later. The Raman mappings of the E2g (Fig. 2b) and A1g (Fig. 2c) peak frequencies show that the periodically varying strain is consistent over the entire scanned artificial crystal (25 μm)². The darker (lower frequency) and brighter (higher frequency) colours (Fig. 2b,c) indicate that tensile strain is highest on the tips of nanoncenes—at ‘artificial atom’ nuclei—and gradually decreases to a minimum towards the perimeters of the nanoncenes.

**Figure 2 | Scanning Raman spectroscopy of the MoS2 strain crystal.** (a) Raman spectra of most strained-MoS2, less strained-MoS2 and unstrained-MoS2. Symbols are measurement data; curves are fitting data. Inset: schematic atomic displacement of the in-plane E2g and out-of-plane A1g modes. (b,c) Scanning Raman spectroscopic maps plotting (b) E2g peak frequency and (c) A1g peak frequency of strain-textured MoS2 on the nanocone substrate. Scale bars are 1 μm.

Scanning PL spectroscopy of the artificial-atom crystal. The effect of strain on the OBG of MoS2 strain crystal is examined by micro-PL spectroscopy. Figure 3a compares the representative PL spectra of the most strained-MoS2, less strained-MoS2, and unstrained-MoS2, where the strong PL peaks arise from the direct band gap emissions in monolayer MoS2. First, unstrained-MoS2 shows a typical PL spectrum of monolayer MoS2 with a principal peak at 1.83 eV (A exciton) and a minor peak at 1.95 eV (B exciton)¹¹. Second, the strained MoS2 clearly exhibits redshift of the A exciton energy: 18 and 50 meV for the less strained-MoS2 and most strained-MoS2, respectively, indicating a strain-induced OBG reduction⁶⁻⁷. From the magnitude of the redshift and our theoretical calculation, we estimate approximately 0.2 and 0.5% biaxial tensile strains are optically sampled in less strained-MoS2 and most strained-MoS2, respectively. These values agree well with the strains derived from Raman peak shifts above. Third, the mapping of the PL wavelength (Fig. 3b) shows that spatially varying OBG reduction is consistently observed over scanned areas. Finally and significantly, the A exciton peak intensity is more than doubled in the most strained-MoS2 (Fig. 3a), and the intensity increase is highly reproducible over the scanned region (Fig. 3c). There are a few factors that may affect the PL intensity including strain-modulated oscillator strength, local emission geometry, variation in underlying SiO2 thickness and strain-induced exciton funneling²⁹. First, according to our exciton calculations (see Discussion below), the change of the oscillator strength on elastic strain is relatively small (~6% increase under 1% biaxial strain), which cannot explain the observed >100% PL intensity enhancement. Second, the geometry-dependent PL intensity is expected to be enhanced on a flat substrate as the PL intensity of monolayer MoS2 peaks at normal collection angle³⁰,³¹, which is opposite to our observation. Third, a recent study of PL emission from MoS2 shows a flat dependence on underlying SiO2 thickness in the range of 180–270 nm, corresponding to oxide thicknesses variations in our samples from etching the nanoncenes³². In fact, the PL emission intensity of homogeneously strained monolayer MoS2 was experimentally found to decrease when strain increases due to the increased probability of non-radiative relaxations⁹, again opposite our observations. Finally, we note that enhanced PL intensity due to exciton drifting and concentrating has been observed in strained semiconductor nanowires²⁹,³³,³⁴. Therefore, we rule out alternate factors discussed above and attribute the anomalous enhanced PL intensity to the novel 2D exciton funnel effect⁵. The Raman mappings (Fig. 2b,c) show that the tensile strain increases from the perimeters to the tips of the nanoncenes, so the band gap of MoS2 decreases from the perimeters to the tips of the nanoncenes. Consequently, a built-in electric field pointing...
from the tip towards the perimeter of the nanocone is created (Fig. 3d) and the photogenerated excitons drift towards the funnel center, as can be modelled analytically and numerically\(^\text{39}\). Since the photogenerated excitons in monolayer MoS\(_2\) can drift up to 660 nm before recombination\(^\text{5}\), the majority of photogenerated excitons are able to drift from the valleys to the tips of nanocones (\(\leq 245\) nm from pitch radius) without significant recombination. As a result, excitons are concentrated at the tips of nanocones upon illumination and they eventually recombine, giving rise to the enhanced PL emission localized at the nanocone tips (Fig. 3c,d) and supporting the artificial atom and energy funnel concept.

**STM and STS measurements of the artificial-atom crystal.** The local electronic structure modulation of MoS\(_2\) caused by strain is directly verified by STM. Figure 4a shows an STM topograph (\(V = 2.4\) V, \(I = 18\) pA) in the vicinity of three nanocones with height variations of 80 nm. Scanning tunnelling spectroscopy (STS) is performed in different regions of the area shown, and representative \(dI/dV\) tunnel spectra for unstrained-MoS\(_2\), less strained-MoS\(_2\), and most strained-MoS\(_2\) are shown in Fig. 4b. It is worth noting that these spectra show the Fermi level near mid-gap position due to the electron depletion caused by the gold substrate\(^\text{35}\). The QBG sizes extracted from the \(dI/dV\) spectra (Supplementary Fig. 5) are labelled at each strain level. Unstrained-MoS\(_2\) shows a QBG of 2.29 eV, which is consistent with the OBG of 1.83 eV obtained by PL measurement considering the exciton binding energy \(~\sim 0.5\) eV\(^\text{2}\). The extracted local QBG varies from 2.29 eV down to 1.83 eV from STS measurements acquired from unstrained-MoS\(_2\) (topographic valley), through less strained-MoS\(_2\) (intermediate regions) and to most strained-MoS\(_2\) (topographic peak) locations. This corresponds to a measured local strain approaching \(~\sim 3\)% for most strained-MoS\(_2\). These strains are much higher than the maximum of \(~\sim 0.6\)% measured by Raman spectroscopy, which can be explained by the inherently atomic scale measurement of STM/STS compared with the optical measurements, which average over the finite laser beam size (\(~\sim 450\) nm).

To quantify this argument and verify the complete strain profile of the crystal, we simulate the strain induced in a monolayer MoS\(_2\) sheet by applying a constant pressure on the sheet, and Lennard–Jones interatomic interactions between the sheet and substrate (Fig. 4c, Supplementary Fig. 6). To calibrate the mapping between the local tunnelling measurements and the optically averaged Raman/PL measurements, we plot in Fig. 4d the cone-to-cone calculated strain profiles (Fig. 4c) before and after a convolution step. The raw atomic strain \(\epsilon_{bi}\) is convolved...
with a 2D Gaussian of 450-nm 1/e² width, corresponding to the 450-nm diameter Gaussian beam used in our optical experiments. With no fitting parameters, this yields a predicted optically averaged strain sample by scanning Raman/PL; this average strain \( \varepsilon_{\text{bi}} \) ranges from 0.233 to 0.562% and is in excellent agreement with the Raman/PL results from less strained-MoS₂ and most strained-MoS₂ regions presented above. This result provides confirmation that the local atomic strain \( \varepsilon_{\text{bi}} \) is approaching the unprecedentedly high value of 3%.

**Discussion**

We use this calibration to unify all experimental (closed symbols) and theoretical (open symbols) results (Fig. 4e). We calculated Raman spectra under \( \varepsilon_{\text{bi}} \) from 0 to 1% (red and blue triangles in Fig. 4e; Supplementary Fig. 7a). As \( \varepsilon_{\text{bi}} \) increases from 0 to 1%, the \( E_2g \) and \( A_1g \) peaks shift towards lower frequencies. Such Raman peak shifts vary linearly with biaxial strain, and the slopes are \(-4.48 \pm 0.11 \text{ eV per } 1\% \) for the biaxial strain for \( E_2g \) and \( A_1g \) modes, respectively (dashed red and blue lines in Fig. 4e). The fit to all Raman data in unstrained, least strained and most strained regions with respect to these two lines yields \( \varepsilon_{\text{bi}} \) values that are not yet even rupture limited, we anticipate even larger band gap variations and electronic fields can be embedded in such artificial crystals in the future.

We note that this summary shows that our local crystal strain \( \varepsilon_{\text{bi}} \) is sufficiently high to access the indirect band gap of monolayer MoS₂. However, because the Raman/PL measurements are optically averaged, they are dominated by the majority of the points within the laser beam that have direct transition as evidenced by the high PL efficiency. The measurements also confirm a remarkably large exciton binding energy of \( \sim 0.5 \text{ eV} \), only recently verified to be a general feature of dichalcogenides ⁴⁶.

From the STS measurements, a modulation of over 20% in the QBG is directly observed. From the mapping to the optically averaged strain (Fig. 4) and the deduced exciton binding energy, this represents a huge modulation of the QBG, exceeding 25%.

This engineered QBG enables a broadband light absorption by increasing the absorption bandwidth from 677 nm (unstrained-MoS₂) to 905 nm (most strained-MoS₂), which covers the entire visible wavelength and most intensive wavelengths of the solar spectrum. While already without precedent, since these strains are not yet even rupture limited, we anticipate even larger band gap variations and electronic fields can be embedded in such artificial crystals in the future.

**Methods**

**Transfer and strain of MoS₂ monolayer.** MoS₂ monolayers grown by chemical vapour deposition were transferred onto the SiO₂ nanocone substrate using the PMMA-assisted wet transfer process. The transferred sample was then baked at 100 °C for 30 min and the PMMA was removed by sequential soaking in acetone at 60 °C for 10 min followed by chloroform at 60 °C for 1 h. Afterwards, the SiO₂ nanocone with transferred MoS₂ was immersed in ethylene glycol in vacuum for 1 h to ensure that both sides of the MoS₂ sheet were wetted by ethylene glycol. Last, the sample was dried in ambient air to completely evaporate ethylene glycol.

**Raman and photoluminescence characterization.** The Raman and PL measurements were performed with the excitation laser line of 532 nm using a WITEC alpha300 Confocal Raman system in ambient environment. The power of the excitation laser was kept below 1 mW to avoid damage of MoS₂. The Raman scattering was collected by an Olympus 100 × objective (N.A. = 0.9) and dispersed by 1,800 grooves/mm for Raman measurements and 600 for PL measurements per mm gratings.

**STM/STS measurements.** STM/STS measurements were performed at 77 K in ultrahigh vacuum. A bilayer of titanium (10 nm) and gold (80 nm) films were deposited onto the silicon oxide nanocone surface, then monolayer MoS₂ flakes were transferred and strained on the metalized nanocone surface. A control sample was prepared alongside the STM sample and characterized using STM and AFM to ensure conformal coating of MoS₂ on the metalized nanocone. The STM sample was annealed in the STM ultrahigh vacuum chamber at 200 °C for 1 h to clean the MoS₂ surface for a reliable STM measurement.

**Modelling of strain distribution of MoS₂ on nanocones.** The MoS₂ sheet was modelled using honeycomb lattice with Tersoff potential and the substrate was modelled as a fcc lattice. A Lennard–Jones potential was employed to include the van der Waals interaction between substrate and the MoS₂ sheet. A constant force was placed on each atom downward to emulate the pressure difference across the MoS₂ sheet (see Supplementary Fig. 6 for more details).

**Theoretical Raman spectra of monolayer MoS₂.** The theoretical biaxial strain-dependent Raman spectra were calculated using first-principles density-functional perturbation theory implemented in the Quantum-ESPRESSO package with a plane-wave cutoff of 120 Rydberg, a Monkhorst-Pack k-point sampling of \( 12 \times 12 \times 1 \), and an exchange correlation functional of the Perdew–Zunger form within the local density approximation. The spin-orbit coupling was not included. In addition, norm-conserving Hartwigsen–Goedecker–Hutter pseudopotentials were used to take into account the core electrons and reduce the computational efforts. All biaxially strained configuration were fully relaxed with a convergence criteria of 0.0001 a.u. for the maximal residual force. The calculation was carried out in a periodic supercell with a vacuum spacing of 20 Å along the \( z \) (plane normal) direction to reduce the spurious interaction between the neighbouring unit cells.

**Theoretical optical absorption spectra of monolayer MoS₂.** The theoretical biaxial strain-dependent optical absorption spectra were calculated by solving the Bethe–Salpeter equation within the Tamm–Dancoff approximation. The key parameters used in the Bethe–Salpeter equation including quasi-particle energies and screened-Coulomb interactions calculated were obtained from many-body perturbation theory with the Hedin’s GW approximation. All the calculations were...
References

1. Johari, P. & Shenoy, V. B. Tuning the Electronic Properties of Semiconductor Transition Metal Dichalcogenides by Applying Mechanical Strains. ACS Nano 6, 5449–5456 (2012).
2. Scalise, E., Houssa, M., Pourtois, G., Afanas’ev, V. & Stesmans, A. Strain-induced semiconductor to metal transition in the two-dimensional honeycomb structure of MoS2. Nano Res. 5, 43–48 (2012).
3. Shi, H., Pan, H., Zhang, Y.-Y. & Yakobson, B. I. Quasiparticle band structures and optical properties of strained monolayer MoS2 and WS2. Phys. Rev. B 87, 155304 (2013).
4. Wang, L., Kutana, A. & Yakobson, B. I. Manifold of indirect-direct band gap transition of strained monolayer MoS2 and WS2. Ann. Phys. 526, L7–L12 (2014).
5. Rice, C. et al. Raman-scattering measurements and first-principles calculations of strain-induced phonon shifts in monolayer MoS2. Phys. Rev. B 87, 081307 (2013).
6. Conley, H. J. et al. Bandgap Engineering of Strained Monolayer and Bilayer MoS2. Nano Lett. 13, 3626–3630 (2013).
7. He, K., Poole, C., Mak, K. F. & Shan, J. Experimental Demonstration of Continuous Electronic Structure Tuning via Strain in Attractically Thin MoS2. Nano Lett. 13, 2931–2936 (2013).
8. Feng, J., Qian, X., Huang, C.-W. & Li, J. Strain-engineered artificial atom as a broad-spectrum solar energy funnel. Nat. Photon. 6, 866–872 (2012).
9. Gomes, K. K., Mar, W., Ko, W., Guinea, F. & Manoharan, H. C. Designer Dirac fermions and topological phases in molecular graphene. Nature 483, 306–310 (2012).
10. Polini, M., Guinea, F., Lewenstein, M., Manoharan, H. C. & Pellegrini, V. Artificial honeycomb lattices for electrons, atoms and photons. Nat. Nanotechnol. 8, 625–633 (2013).
11. Mak, K. F., Lee, C., Hone, J., Shan, J. & Heinz, T. F. Atomically thin MoS2: a new direct gap semiconductor. Phys. Rev. Lett. 105, 136805 (2010).
12. Splendiani, A. et al. Emerging Photoluminescence in Monolayer MoS2. Nano Lett. 10, 1271–1275 (2010).
13. Bernardi, M., Palmumo, M. & Grossman, J. C. Extraordinary sunlight absorption and one nanometer thick photovoltaics using two-dimensional monolayer materials. ACS Nano 13, 3664–3670 (2013).
14. Sundaram, R. S. et al. Electroluminescence in Single Layer MoS2. Nano Lett. 13, 1416–1421 (2013).
15. Radisavljevic, B., Radenovic, A., Brivio, J., Giacometti, V. & Kis, A. Single-layer MoS2 transistors. Nat. Nanotechnol. 6, 147–150 (2011).
16. Butler, S. Z. et al. Progress, challenges, and opportunities in two-dimensional materials beyond graphene. ACS Nano 7, 2898–2926 (2013).
17. Wang, Q. H., Kalantar-Zadeh, K., Kis, A., Coleman, J. N. & Strano, M. S. Electronics and optoelectronics of two-dimensional transition metal dichalcogenides. Nat. Nanotechnol. 7, 699–712 (2012).
18. Mak, K. F., McGill, K. L., Park, J. & McEuen, P. L. The valley Hall effect in MoS2 transistors. Science 344, 14991492 (2014).
19. Bertolazzi, S., Brivio, J. & Kis, A. Stretching and breaking of ultrathin MoS2. ACS Nano 5, 9703–9709 (2011).
20. Castellanos-Gomez, A. et al. Elastic properties of freely suspended MoS2 nanosheets. Adv. Mater. 24, 772–775 (2012).
21. Kuykendall, T., Ulrich, P., Aloni, S. & Yang, P. Complete composition tunability of InGaN nanowires using a combinatorial approach. Nat. Mater. 6, 951–956 (2007).
22. Kim, C.-J. et al. On-nanowire band-graded SiGe photodetectors. Adv. Mater. 23, 1025–1029 (2011).
23. Castellanos-Gomez, A. et al. Local strain engineering in atomically thin MoS2. Nano Lett. 13, 5561–5566 (2013).
Corrigendum: Optoelectronic crystal of artificial atoms in strain-textured molybdenum disulphide

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The original version of this Article contained a typographical error in the spelling of the author Jeffrey M. Weisse, which was incorrectly given as Jeffery M. Weisse. This has now been corrected in both the PDF and HTML versions of the Article.