

Controlled Micro/nano-Dome Formation in Proton-Irradiated Bulk Transition-Metal Dichalcogenides

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At the few-atom-thick limit, transition-metal dichalcogenides (TMDs) exhibit strongly interconnected structural and optoelectronic properties. The possibility to tailor the latter by controlling the former is expected to have a great impact on applied and fundamental research. As shown here, proton irradiation deeply affects the surface morphology of bulk TMD crystals. Protons penetrate the top layer, resulting in the production and progressive accumulation of molecular hydrogen in the first interlayer region. This leads to the blistering of one-monolayer thick domes, which stud the crystal surface and locally turn the dark bulk material into an efficient light emitter. The domes are stable (>2-year lifetime) and robust, and host strong, complex strain fields. Lithographic techniques provide a means to engineer the formation process

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so that the domes can be produced with well-ordered positions and sizes tunable from the nanometer to the micrometer scale, with important prospects for so far unattainable applications.

1. Introduction

The notable transformation of the electronic properties of transition metal dichalcogenides (TMDs) when reduced to a single X-M-X plane (X: chalcogen; M: metal)¹ makes them suitable for flexible, innovative optoelectronic devices^{2,3,4} and transistors⁵. Like graphene, few-layer TMDs can also withstand surprisingly large mechanical deformations^{6,7,8,9}, which, coupled to the material's electronic structure, would enable the observation of non-dissipative topological transport, provided a periodic modulation of strain is attained^{10,11,12,13}. Finally, TMD monolayers (MLs) and nanostructures are also important for their catalytic role in the cost-effective production of hydrogen^{14,15,16}. These examples share the need to achieve spatial control of the material's properties, over sample regions with size ranging from the nano^{14,16} to the micrometer¹⁶ scale lengths.

In this study, we present a route toward the patterning of TMDs based on the effects of low-energy proton irradiation¹⁷ on the structural and electronic properties of *bulk* WS₂, WSe₂, WTe₂, MoS₂, MoSe₂ and MoTe₂. Suitable irradiation conditions trigger the production and accumulation of H₂ just beneath the first X-M-X basal plane, leading to the localized exfoliation of the topmost monolayer and to the formation of spherically shaped domes. Structural and optical characterizations confirm that these domes are typically one ML-thick and contain H₂ at pressures in the 10-100 atm range, depending on their size. Such high

pressures induce strong and complex strain fields acting on the curved X-M-X planes, which are evaluated by means of a mechanical model. The domes' morphological characteristics can be tuned by lithographically controlling the area of the sample basal plane participating in the hydrogen production process. This results in the unprecedented fabrication of robust domes with controlled position/density and sizes tunable from the nanometer to the micrometer scale, that, by virtue of their inherently strained nature and geometry, might prompt a variety of applications.

2. Creation of light-emitting micro-/nano-domes

2.1 Low energy proton-irradiation of bulk TMDs

The samples, consisting of thick (tens to hundreds of MLs) TMD flakes, were obtained by mechanical exfoliation, deposited on Si substrates, and afterwards proton-irradiated using a Kaufman source (see Methods). Differently from the other works in the literature concerning proton-irradiation of TMDs —where beams with energies $\geq 10^5$ eV are used¹⁸, aiming at the controlled formation of defects in the irradiated samples— here we irradiate the flakes with low energy beams ($\lesssim 20$ eV), with the specific goal of suppressing the defect formation process. The top-right inset of **Figure 1a** displays the optical microscope image of a large bulk WS₂ sample after irradiation with an impinging dose $d_H = 8 \times 10^{16}$ protons/cm².

Unexpectedly for indirect-gap bulk WS₂, the sample exhibits strong photoluminescence (PL, see Methods) in the red wavelength region ($\lambda \sim 690$ nm), as displayed in the main part of **Figure 1a** and **Figure S1**, Supporting Information. The bottom-left inset shows that the

luminescence originates from circular spots with diameters varying between less than one (which is an upper limit due to the finite resolution of our optical setup; see Methods) to few microns. As is evident from the atomic force microscopy (AFM, see Methods) image in Figure 1b, these spots signal the presence of dome-shaped features, protruding from the irradiated crystal surface, with virtually perfect spherical shape (see Figure S2, Supporting Information). The average footprint radius of the features displayed in Figure 1b is $R=(715\pm60)$ nm—with maximal height $h_m=(230\pm20)$ nm—but the dome size can be controlled by the irradiated proton dose: with $d_H=1.0\times10^{16}$ protons/cm² we obtained nanometer-sized structures, with average $R=(82\pm20)$ nm and $h_m=(25.6\pm5.6)$ nm (Figure 1c). Figure 1d shows an AFM image encompassing three domes formed on a WS₂ sample analogous to that shown in panel c. The corresponding room temperature micro-PL (μ -PL, see Methods) intensity map, detected at $\lambda_{\text{det}}=689$ nm and displayed in panel e, demonstrates the perfect match between the domes and the light-emitting spots. The μ -PL spectrum of one dome (singled out from the ensemble of panel a) is provided in Figure 1f. The luminescence of an untreated WS₂ ML measured under the same excitation/collection conditions is shown for comparison. The PL intensity of the domes is typically larger than that of the exfoliated WS₂ MLs, indeed suggesting a one-ML thickness for the domes. This hypothesis is confirmed by measuring the μ -PL spectrum and the thickness of the outer layer of *exploded* domes, which are both fully consistent with that of the monolayer (as exemplified for a MoSe₂ dome in Figure S3, Supporting Information). This is further supported by the strong *circular dichroism* measured for the PL emission of the domes (in a WS₂ dome the degree of circular polarization is >50% at 130 K, see Figure S4A, Supporting Information), which is a

property stemming directly from the hexagonal symmetry of the first Brillouin zone of *monolayered* TMDs (see Figure S4B, Supporting Information)¹⁹ and by second harmonic generation measurements, as discussed in the following. Albeit rare, the formation of two-layer thick domes and of Russian-doll-like structures can also be observed, as exemplified and discussed in Figure S5, Supporting Information.

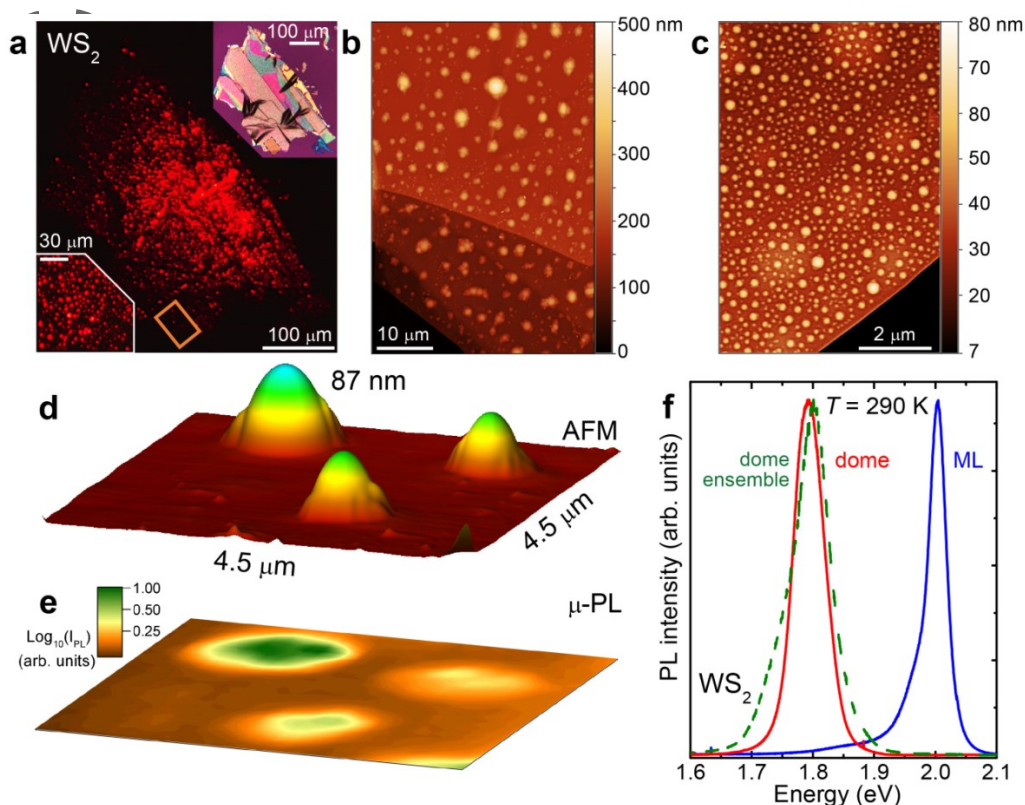


Figure 1. Creation of Light Emitting Domes by proton irradiation. **a**, Optical microscope image showing the laser-excited red luminescence of bulk WS₂ after irradiation with proton dose $d_H = 8 \times 10^{16}$ protons/cm². The top-right inset shows the same flake in absence of laser excitation. The bottom-left inset is a zoomed-in image of the main picture showing the round shape of the emitting spots. **b**, AFM image of the rectangular region highlighted in panel (a). Round-shaped features on the sample surface form after H⁺ irradiation. **c**, AFM image of a bulk WS₂ flake H⁺-irradiated with a dose 8 times smaller than in panels (a) and (b). **d**, AFM image of a limited region of a sample treated like that shown in (c) but on a different flake, where a smaller density of domes was fortuitously found. The maximal height reached by the

domes is 87 nm. **e**, μ -PL mapping (detection wavelength equal to 689 nm) of the same region displayed in **(d)**. The base-10 logarithm of the μ -PL intensity is shown as a false color scale (see color bar). **f**, μ -PL spectrum of a dome (red line) singled out from the ensemble displayed in **(a)**; the blue line is the μ -PL spectrum of a WS₂ monolayer, whereas the green dashed line is the macro-PL spectrum of an ensemble formed by ~ 2500 domes. The spectra are peak normalized for ease of comparison.

Based on the percentage of visible domes that double as strong light emitters (see Figure S1, Supporting Information), at least 85-90% of the domes can be estimated to be one-ML thick. The energy of the PL peak (corresponding to the free-exciton recombination involving electrons and holes at the K point of the first Brillouin zone, named as *A* exciton, as in TMD MLs^{1,2}) of a typical (single-layer) WS₂ dome is 200 meV lower than that of the ML (see Figure 1f), mainly because of the strain exerting on the dome's surface^{7,8}, as we will discuss in more detail in the following. Notably, no significant linewidth broadening is observed when many such domes are measured together, as demonstrated by the PL spectrum of a dome ensemble, displayed in Figure 1f as a dashed line. The spectral homogeneity of the light emitted by the domes suggests that the same average strain is present in each dome, irrespective of the dome size. The evidence shown in Figure 1 demonstrates that indirect-gap *bulk* WS₂ can be turned into an efficient light emitter with no size restrictions, like those typically affecting exfoliated flakes or samples grown by chemical vapor deposition. We point out that the reported phenomenon is substantially independent of the specific MX₂ composition (see measurements on H⁺-treated MoSe₂, MoS₂, MoTe₂, WSe₂ and WTe₂ in Figs. S6-S7) and is exclusively induced by the interaction of the material with protons. No effect was found in samples exposed to molecular hydrogen or ionized helium atoms under the same temperature and gas flow conditions.

2.2 Dome formation mechanism

Clues on the internal make-up of the domes can be derived by following their low-temperature evolution. **Figure 2a** and **Figure 2b** show, respectively, the 300 K and 4 K optical microscope images of a bulk WS₂ sample irradiated with $d_H=8\times10^{16}$ protons/cm². At 300 K, many domes—featuring *iridescence*, as accounted for below—are visible. For $T\lesssim30$ K the domes disappear, and the sample surface looks conspicuously flat. As T is increased, at ~30 K, the domes bulge *suddenly* (within our system resolution equal to 10 mK, see insets of **Figure 2c** and **Movie 1**). As illustrated in **Figure 2c**, the transition temperature distribution was sampled over more than 500 domes obtained on several proton-irradiated flakes deposited on different substrates (see Methods). The resulting average transition temperature is (32.2 ± 2.4) K, a number close to the critical temperature of H₂ (33.18 K) and thus compatible exclusively with the presence of molecular hydrogen inside the domes (see **Supporting Note 1**): when T is sufficiently low/high, H₂ liquefies/boils, and the domes deflate/inflate always in the same position.

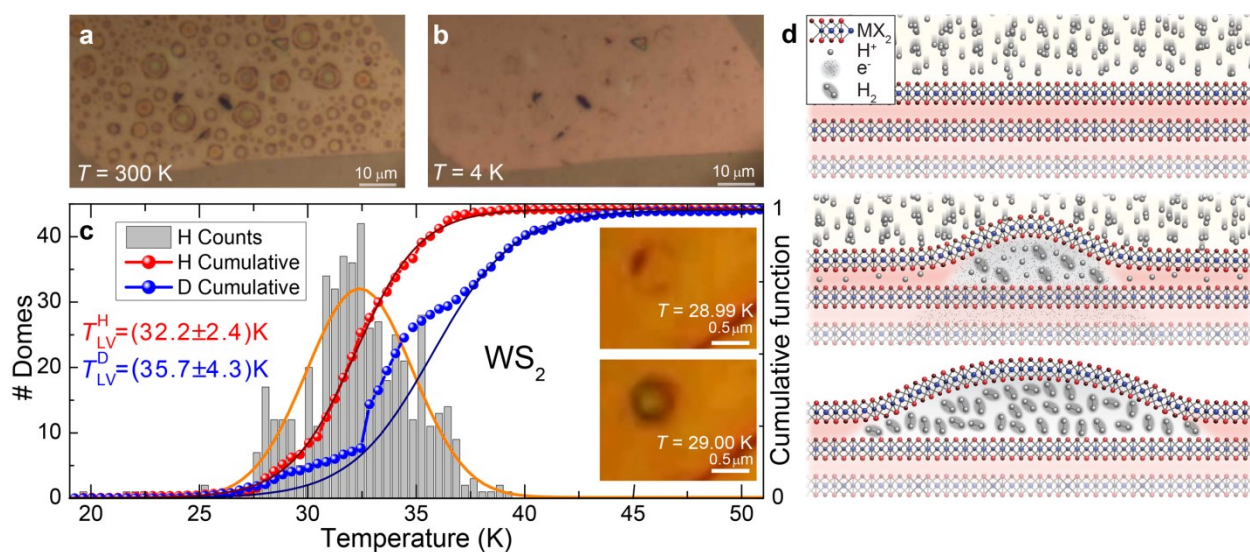


Figure 2. Dome inflating/deflating process. **a**, Optical microscope image of an H^+ -irradiated ($d_H=8 \times 10^{16}$ protons/cm²) WS_2 sample at $T=300$ K. **b**, Same as **(a)** at $T=4$ K. **c**, Histogram of the transition temperature at which domes appear (left axis). The orange line is a Gaussian fit to the data. The red point-line is the cumulative function of the histogram (right axis). The solid wine curve superimposed is a fit to the cumulative function providing the average transition temperature T_{LV}^H of proton-irradiated flakes. The blue point-line is the cumulative function of the histogram derived from deuteron-irradiated WS_2 flakes and the corresponding navy fit providing T_{LV}^D is performed only on the part of the cumulative function in which H effects are negligible (see Supporting Note 1). The insets are two optical microscope pictures of the same dome, recorded immediately before (top) and after (bottom) the transition temperature. **d**, Sketch of the process leading to the formation of domes caused by the local blistering of atomically thin material membranes.

The fluctuations observed in the liquid-vapor transition temperature (T_{LV}^H) are chiefly due to the spread in the size (and hence in the internal pressure) of the domes. To reinforce our hypothesis, we considered the study of isotopic effects in our system and we repeated our analysis on 500 more WS_2 domes, obtained by *deuteron irradiation*. The (p - T) phase diagrams of hydrogen and deuterium²⁰ show an isotopic shift in the temperature at which the liquid-vapor phase transition occurs of about 2.9 K (the exact value depending on the pressure of the gas). The details of our measurements are discussed in Supporting Note 1.

The cumulative function of deuteron-irradiated samples is displayed in Figure 2b (see Figure SN1A for the histogram, Supporting Information): differently from proton-irradiated samples, the behavior is in this case characterized by a composite shape, corresponding to the three different steps that are apparent in the cumulative function. We ascribe empirically these three steps to the presence of H₂, HD and D₂ molecules²¹ within the domes. There are several possible explanations why H may be present also in deuterium-treated samples: 1) even the highest purity deuterium bottles contain a 0.25% of H₂ and HD molecules; 2) it has been reported that deuterons permeate through graphene and BN monolayers much slower than protons: At room temperature the areal conductivity of deuterons results to be 1/10 of that of protons²². This effect could be even much stronger in the case of TMDs, whose single layer is constituted by three atomic planes; 3) the hydrogen evolution reaction is expected to be remarkably faster with respect to the deuterium evolution reaction because of the high mass difference between the two isotopes^{23,24}. For deuteron-irradiated samples, a sigmoidal fit was thus performed only to the high-temperature data of the cumulative function shown, where no effect from hydrogen is expected. The fit estimates a transition temperature of $T_{LV}^D = (35.7 \pm 4.3)$ K, resulting in a difference between the centers of the distributions equal to (3.5 ± 0.7) K, consistent with the (p - T) diagram of the two isotopes. Indeed, the measured transition temperatures are consistent only with the presence of H₂ (or its isotopes) within the domes (see Figure SN1B, Supporting Information). We can therefore hypothesize that, during irradiation, accelerated protons penetrate through the top MX₂ basal plane (Figure 2d top), becoming confined in between two X-M-X layers. The penetration process is indeed ruled by the potential barrier met by protons at the interface with the bulk flake, which should be

determined by both the binding energy profile of protons²⁵ and electric fields/charges establishing at the sample surface²⁶. Therein, likely triggered by the catalytic activity of TMDs^{14,15,16}, the following reaction takes place:



with electrons e^- being supplied from the ground contact or possibly also from the bulk flakes themselves (Figure 2d middle). This hypothesis is supported by the fact that the formation of domes is strongly quenched in flakes deposited on an insulating substrate (Kapton tape). The subsequent build-up of H_2 molecules, stored just beneath the top surface, leads to the local blistering of one X-M-X plane, and eventually to the formation of the domes (Figure 2d bottom). The above scenario is supported by theoretical studies, which showed that thermal protons remain trapped in the metal plane of X-M-X layers and do not diffuse, thus favoring the accumulation of H_2 molecules in the interlayer regions²⁵. An estimation of the number of molecules accumulated after irradiation (via AFM measurements and the mechanical model described in the following) indicates that $< 3\%$ of the impinging protons penetrate and lead to the formation of molecular hydrogen, the remaining part likely being rejected by the potential barrier met at the sample surface, in agreement with previous studies concerning proton irradiation of solid matrices²⁷. The formation of localized nucleation sites (*i.e.*, the domes), rather than the establishment of a uniform H_2 distribution underneath the top layer, is due to the van der Waals (vdW) forces existing between adjacent planes, which prevent H_2 molecules from moving freely. The shape of the domes itself—*i.e.*, their height-to-radius ratio—results from the interplay between: (i) the vdW forces that tend to keep the TMD layers together, thus minimizing the dome radius; (ii) the stiffness of the top TMD layer,

which limits the dome height; and (iii) the tendency to expand of the trapped gas, which results in the application of a constant pressure on the dome's walls⁶. We estimate such pressure to be about 10 atm for $R \gtrsim 500$ nm, given the average $T_{LV}^H = 32.2$ K and the H₂ phase diagram (see Supporting Note 1 and Ref. 28). Therefore, the multi-colored appearance of the large domes in Figure 2a can be ascribed to *Newton's rings* caused by the interference of the light reflected inside the H₂-filled spherical volume²⁹.

3. Domes' strain fields

3.1 Domes' profile and strain tensor modeling

As noted earlier and shown in Figure 1f, the average PL peak energy of the domes is about 200 meV lower than that of the corresponding material in the ML form (see also Figure S7, Supporting Information). This is ascribable to the presence of tensile strain, ε , which reaches its maximum ε_m at the domes' summit. As predicted by Hencky's model^{7,30,31},

$$\varepsilon_m = f(\nu) \cdot (h_m/R)^2, \quad (2)$$

where f only depends on the material's Poisson ratio, ν , while R and h_m are the dome footprint radius and maximum height, respectively; see Supporting Note 2. As reported in Ref. 6, the dome's height-to-radius ratio is largely independent of the dome's dimensions: h_m scales linearly with R , and the value of ε_m in a given material can be estimated by Eq. (2). As shown in **Figure 3a**, wherein the experimental (*i.e.*, obtained by AFM) values of h_m are plotted as a function of R for six different chemical compositions, the expected linear dependence is

verified over a wide span of dome sizes (R between 100 nm and $\sim 3 \mu\text{m}$). The average values of h_m/R estimated for each of the investigated materials are: 0.16 ± 0.02 (MoS_2), 0.18 ± 0.02 (MoSe_2), 0.17 ± 0.02 (MoTe_2), 0.16 ± 0.02 (WS_2), 0.15 ± 0.01 (WSe_2) and 0.13 ± 0.02 (WTe_2) yielding the values of ε_m shown in Figure 3a and in Supporting Note 2.

The height profile of the dome and the evolution of the strain tensor across the dome's surface can both be computed via Finite-Element Method (FEM) calculations, performed within the framework of nonlinear membrane theory (see Supporting Note 3)³⁰. As an illustrative case, Figure 3b (left) shows the comparison between these calculations and the AFM profile of a MoS_2 dome with $R = (3.76 \pm 0.12) \mu\text{m}$ and $h_m = (618 \pm 15) \text{ nm}$, formed after irradiation of a flake with $8 \times 10^{16} \text{ protons/cm}^2$.

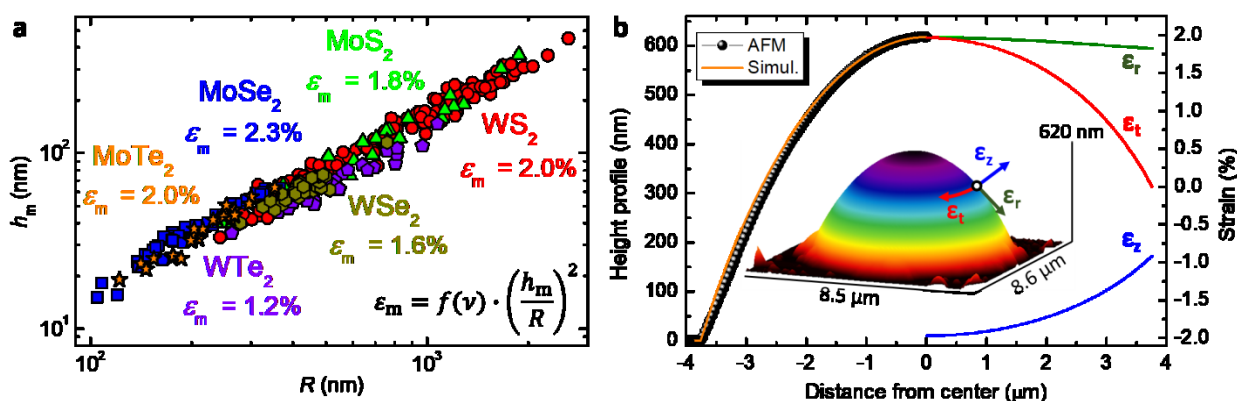


Figure 3. Dome's shape, strain, and size distribution. **a**, Maximum height h_m vs footprint radius R of MX_2 domes. The average h_m/R provides the average dome biaxial tensile strain at the dome apex ε_m , according to the equation reported in the figure. **b**, Left side: Comparison between the height profile of a MoS_2 dome measured by AFM (black dots), and the profile obtained by Finite Elements calculations (solid orange line; see Methods). The dome footprint radius and height, as estimated by AFM measurements, are $3.76 \mu\text{m}$ and 618 nm , respectively. Right side: Components of the strain tensor along the three principal axes of the dome, *i.e.*, in the radial (ε_r , solid olive line), circumferential (ε_t , solid red line), and perpendicular (ε_z , solid blue line) directions. These components are represented as color-coded arrows in the inset, showing a three-dimensional AFM image of the dome.

As summarized in Figure SN3A, Supporting Information, FEM simulations correctly reproduce the experimental profile for all the investigated materials. The calculated spatial dependences ($0 \leq r \leq R$) of the principal components of the strain tensor —namely, along the circumferential (ε_t) and radial (ε_r) in-plane directions³⁰ and along the perpendicular (ε_z) out-of-plane direction —are also displayed in Figs. SN3A and 3b (right): interestingly, strain is isotropic biaxial ($\varepsilon_t = \varepsilon_r = 1.97\%$ for the dome in Figure 3b) only at the very top of the dome, gradually becoming uniaxial as the circumferential component goes to zero near the dome's edge. In between these two limits, strain is anisotropic ($\varepsilon_t \neq \varepsilon_r$), with a negative perpendicular component accounting for a compression in out-of-plane direction (as detailed in Supporting Note 3). The complex spatial dependence of the strain tensor across the domes is reflected by the spatial evolution of μ -Raman measurements where, as a general feature, a progressive softening of the in-plane and out-of-plane vibrational modes is observed with increasing strain over the dome. Due to the diffraction-limited size of our laser spot (directly measured and modelled by a Gaussian with standard deviation $\sigma = 0.23 \pm 0.01 \mu\text{m}$, see Methods), the finer details of this evolution can only be appreciated on large ($R > 2 \mu\text{m}$) domes: μ -Raman measurements were therefore performed on WS_2 , MoS_2 and WSe_2 , where large domes were fabricated, giving results in good agreement with the literature⁷ discussed in Figs. S8–S10, Supporting Information. Our results agree well also with Hencky's model^{7,30}, yielding $\varepsilon_m = \varepsilon_t = \varepsilon_r = 1.95\%$ for the MoS_2 dome shown in Figure 3b (the same applies to the other MX_2 compounds investigated; see Supporting Note 3). Moreover, the pressure values used in the calculations match rather well, for μm -sized domes, with the $\sim 10 \text{ atm}$

estimated from the average T_{LV}^H obtained in the previous section (see Figure 2c). For smaller ($R \ll 1 \mu\text{m}$) domes, the model results in internal pressures in excess of 100 atm—as shown in Figure SN3B Supporting Information and reported in Ref. 6—for which H_2 should enter a supercritical fluid phase³².

The strain tensor evolution described by our model and confirmed by Raman measurements allows also to justify the remarkable PL emission intensity characteristic of our domes as well as the PL energy position. The observed redshift is in fact quantitatively consistent with the estimated strain, as discussed for the WS_2 , MoS_2 , WSe_2 , and MoS_2 domes in Figure S7, Supporting Information. Due to the seamless reduction of the excitonic gap with increasing strain, on the other hand, the formation of domes results in the creation of a deformation potential landscape for both electrons and holes, able to funnel the carriers towards the potential minima before recombining and thus giving rise to an enhanced PL emission. Such process, being at the origin of the bright luminescence observed in large electron-hole plasma droplets in locally strained germanium³³, was also similarly observed in TMDs^{34,35}, where excitons were demonstrated to drift for hundreds of nm before recombining³⁵.

4. Engineered creation of TMD domes

The detailed knowledge of the evolution of the strain tensor across the domes' surface is particularly relevant since strain is known to alter profoundly the electronic properties -and hence the optical and transport properties- of TMDs, which can lead to, *e.g.*, the emergence

of giant pseudo-magnetic fields and to the generation of persistent currents^{10,11,12,13}. For this to happen, specific and stable configurations of the strain field need be achieved, and spatial control and durability are therefore necessary. In fact, other methods for the creation of strained TMD bubbles either allow size/position controllability but lack durability (as in Refs. 7, 9) or permit to create durable structures but which lack any spatial ordering (as in Ref. 6), in both cases considerably limiting their potentiality for applications.

As shown in Figure S11A Supporting Information, indeed, the domes created via proton-irradiation remain intact—and keep exhibiting strong light emission—for temperatures up to 510 K. In addition, the shape and size of these nano/micro-structures remain unchanged with time—in the best cases over more than two years—as illustrated by Figs. S11B-F. This confirms the notable absence of gas-permeable, nm-scale pores in TMD materials, as already reported in the literature⁷; moreover, the exceptional durability of our domes is likely also aided by the strong adhesion forces existing between the ML forming the dome and its parent substrate, as well as by the low permeability to H₂ of the latter. In the bulging devices commonly employed to induce strain in TMD membranes^{7,8,9} the ML is usually laying directly on a SiO₂ substrate. As a result, the devices typically deflate within weeks, mostly due to leaks through the substrate and the TMD/SiO₂ interface⁷. Besides durability, the applicative prospects of our MX₂ domes are greatly enhanced by the possibility to precisely control their size and position. The domes' formation process via low-energy proton-irradiation is indeed characterized by a high yield, the domes usually forming over the entire irradiated flakes, as shown in Figure S12, Supporting Information. This allows to engineer the dome formation process, as illustrated in **Figure 4**, which can be achieved by depositing

an H-opaque masking layer prior to proton irradiation. The sample displayed in Figure 4, for example, was patterned by electron-beam lithography with arrays of circular openings with diameter $S=1, 3$, and $5\text{ }\mu\text{m}$ (see Figure S13 Supporting Information and Ref. 36), followed by proton irradiation ($d_{\text{H}}=4\times 10^{16}\text{ protons/cm}^2$) and by the removal of the H-opaque mask (see Methods). Figure 4a displays the AFM image of a WS_2 array of neatly arranged single domes with average $R=(0.93\pm 0.07)\text{ }\mu\text{m}$ and $h_{\text{m}}=(0.13\pm 0.02)\text{ }\mu\text{m}$, obtained for $S=3\text{ }\mu\text{m}$. The $\mu\text{-PL}$ signal emitted by the same array is imaged in Figure 4b (see also the $\mu\text{-PL}$ map in the inset). The ability to fabricate ordered arrays of light-emitting domes is an inherent advantage of our system with respect to, *e.g.*, the bubbles forming because of the accidental incorporation of contaminant gases between monolayers and their supporting substrates^{6,37}, which have been shown to be durable³⁸ but lack any spatial ordering. The dome dimensions can also be engineered by varying the size of the openings in the H-opaque mask.

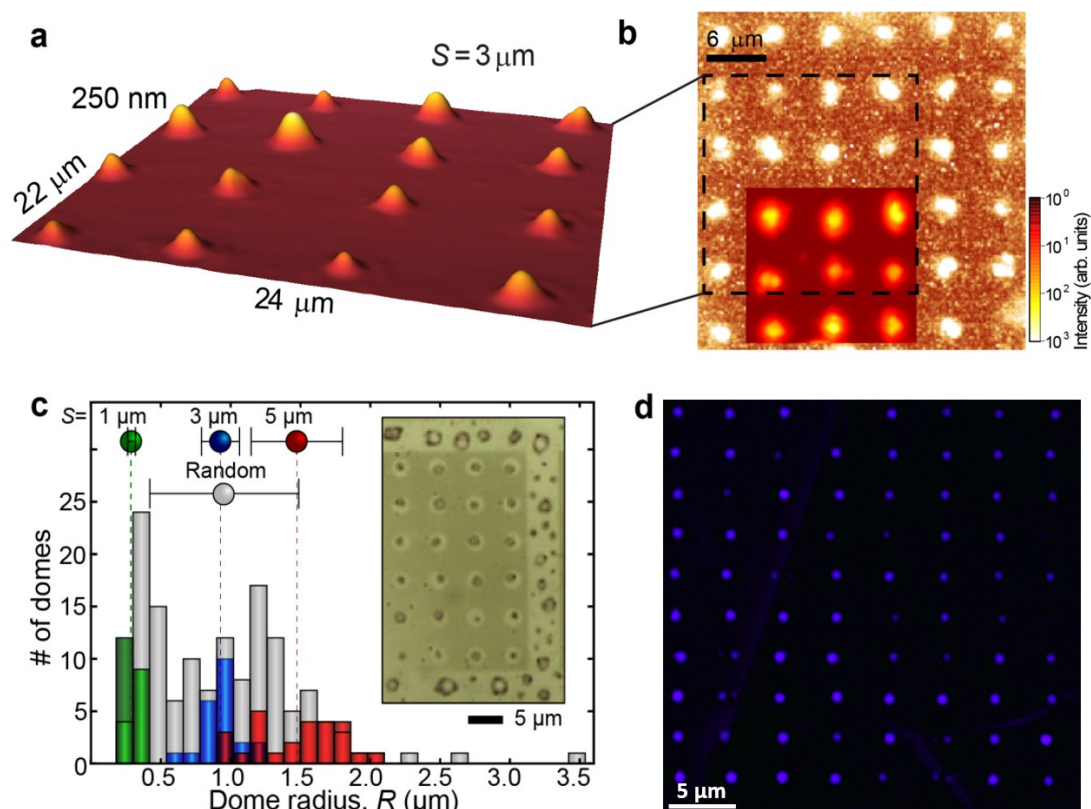


Figure 4. Controlling the dome size and position. **a**, AFM image of an array of WS₂ domes obtained after H⁺ irradiation (dose $d_H = 4 \times 10^{16}$ protons/cm²) of a flake patterned with an H-opaque mask. The mask had openings with diameter $S = 3$ μm and was removed before the AFM measure (see also Figure S13, Supporting Information). **b**, RT PL pan-chromatic imaging of the same array in panel (a) excited by a 532.2 nm laser. The bottom-left inset is a μ-PL mapping (detection wavelength equal to 689 nm) of a portion of the same array. **c**, Distribution of the footprint radius of domes formed in opening arrays with diameter $S = 1$ (green), 3 (blue), and 5 (red) μm. The distribution of randomly formed domes during the same process is given by gray bars. The distribution width is illustrated on top of the figure by horizontal bars. The inset is an optical microscope image comparing random vs ordered ($S = 3$ μm) domes. The much narrower distribution of the ordered domes with respect to the random ones can be appreciated. **d**, Second harmonic generation (SHG) map collected on an array of ordered WS₂ domes obtained after proton irradiation (dose $d_H = 1.5 \times 10^{17}$ protons/cm²) of a flake patterned with an H-opaque mask. The mask had elliptical openings with 2- and 1-μm semi axes and 4-μm center-to-center distance.

In fact, Figure 4c shows the distributions of the dome footprint radii grouped into randomly formed and ordered dome subsets obtained during the *same* proton-irradiation process. It is worth noting that the domes formed using the lithographic approach are characterized by a remarkably narrower size distribution, where the size is clearly determined by the diameter of the aperture. Such distribution gets even narrower with decreasing the dome size. Finally, in the ordered arrays, the average dome volume scales with the surface area ($0.25\pi S^2$) available to the reaction (1) (see Figure S14, Supporting Information), thus supporting the hypothesis of the dome formation as a catalysis-driven process. We point out that controlling the dome position and size over large areas is valuable for the creation of efficient site-controlled photon emitters, as well as in many other situations. For example, TMD MLs have been shown to give rise to efficient second-harmonic generation (SHG), due to their broken inversion symmetry^{39,40}. This property is retained by our domes -as demonstrated in Figure 4d for an ordered array of WS₂ domes excited at 900 nm (see Methods)- which could thus conceivably act as site-controlled SHG “hot spots”, ideal for the integration with specifically designed photonic crystal cavities^{41,42}. One should also notice that the intense second harmonic signal featured by the domes in panel d indicates a > 96% formation yield of one-ML-thick domes.

5. Conclusions and perspectives

ML TMDs have been demonstrated to possess intriguing optoelectronic and mechanical properties, which render them suitable for flexible and innovative optoelectronic devices.

Furthermore, they have emerged as a fascinating class of materials for catalysis¹⁵. While irradiation of these materials with energetic (MeV) beams has been shown to modify their properties due to the creation of defects, here we demonstrated that irradiating bulk TMD flakes with a low energy proton flux leads to the formation and accumulation of hydrogen and enables the control of the electronic properties of ML TMDs at the nano- and micro-scale through the creation of light-emitting, highly strained domes. The irradiation process here proposed allows therefore to alter the morphological and optical properties of the flakes without the creation of defects (as demonstrated by the stability of the domes, see Figure S11 Supporting Information, and by optical measurements, see Figure S15 Supporting Information), resulting into relatively large areas characterized by efficient light emission, due to the creation of the domes. These structures can be formed at the desired location and with controllable size on six different compounds. Since we can precisely control the amount of H₂ in single domes, they can act as microscopic calibration gauges for H₂ sensors or for controlled reactive gas delivery (see Figure S16, Supporting Information) in nano-reactors⁴³ with unprecedented accuracies. The engineered formation of domes also allows the creation of arrays of linear and non-linear light emitters and of periodic strain fields, as here demonstrated. Finally, it should be noted that several other 2D crystals—such as graphene, h-BN, and phosphorene—have been found to be virtually transparent to protons, according to both experiments⁴⁴ and theoretical calculations²⁵. Therefore, their deposition on top of bulk TMD samples before proton irradiation should not hinder the dome formation process, and the controlled formation of (ordered) TMD domes could thus be exploited to define a template for modulating strain in a much wider range of two-dimensional materials, leading,

e.g., to the emergence of giant pseudo-magnetic fields in graphene. Thanks to the spatial control enabled by our method, these latter could be created in the desired periodic configurations, which have been predicted to result in the generation of dissipation-less electrical currents^{10,11,12,13}.

Movie 1

Optical microscope movie of a WS₂ sample irradiated with an H⁺ dose $d_H = 8 \times 10^{16}$ protons/cm². The movie (acquired by employing a 50× objective with NA=0.5) was taken as the temperature was raised from $T = 19.75$ K to $T = 45.05$ K. The temperature frame step is 10 mK. The counter visible on the top-right corner of the movie displays the sample temperature. At $T \sim 28$ K the domes start inflating due to the liquid-vapor transition of H₂.

Experimental Section

An extensive description of sample preparation and proton irradiation procedure, of phase transition, optical, and structural measurements, and of sample patterning can be found in the Supporting Information.

Author contributions

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D.T., E.B., M.F. and A.P. fabricated the domes, performed and designed the optical experiments, and conducted the analysis regarding the optical and microscopy data. E.B. performed and analyzed the isotopic shift measurements. G.P. designed and performed the sample lithographic processing and the microscopy measurements. T.Y. and Y.L. made the mechanical modeling calculations. E.P. and S.S. contributed at the initial stages of this work. B.L., C.Z., Y.Z. prepared the samples and performed part of the optical experiments. Y.L. coordinated the work at the Australian National University. A.P. and M.F. wrote the manuscript. A.P. conceived the research and coordinated the work at Sapienza Università di Roma.

All authors discussed the results and commented on the manuscript.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

Davide Tedeschi and Elena Blundo contributed equally to this work.

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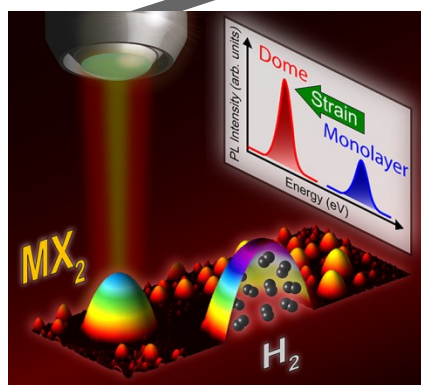
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List of Material in Supporting Information

Figures S1-S17 and Note SN1, SN2, SN3.

Movie 1.

Low-energy proton irradiation of bulk transition metal dichalcogenides leads to the blistering of atomically-thin domes filled by highly pressurized hydrogen. The domes stud the crystal surface and locally turn the dark bulk material into an efficient light emitter. The domes can be produced with well-ordered positions and sizes tunable from the nanometer to the micrometer scale, with important prospects for so far unattainable applications



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References

1. L. Zhang, A. Zunger, *Nano Lett.* **2015**, *15*, 949-957.
2. S. Z. Butler, S. M. Hollen, L. Cao, Y. Cui, J. A. Gupta, H. R. Gutierrez, T. F. Heinz, S. S. Hong, J. Huang, A. F. Ismach, E. Johnston-Halperin, M. Kuno, V. V. Plashnitsa, R. D. Robinson, R. S. Ruoff, S. Salahuddin, J. Shan, L. Shi, M. G. Spencer, M. Terrones, W. Windl, J. E. Goldberger, *ACS Nano* **2013**, *7*, 2898-2926.
3. X. Li, L. Tao, Z. Chen, H. Fang, X. Li, X. Wang, J.-B. Xu, H. Zhu, *Appl. Phys. Rev.* **2017**, *4*, 021306.
4. A. Pospischil, T. Mueller, *Appl. Sci.* **2013**, *6*, 78.
5. F. Schwier, J. Pezoldt, R. Granzner, *Nanoscale* **2015**, *7*, 8261-8283.
6. E. Khestanova, F. Guinea, L. Fumagalli, A. Geim, I. Grigorieva, *Nat. Commun.* **2016**, *7*, 12587.
7. D. Lloyd, X. Liu, J. W. Christopher, L. Cantley, A. Wadehra, B. L. Kim, B. B. Goldberg, A. K. Swan, J. S. Bunch, *Nano Lett.* **2016**, *16*, 5836-5841.
8. R. Yang, J. Lee, S. Ghosh, H. Tang, R. M. Sankaran, C. A. Zorman, P. X.-L. Feng, *Nano Lett.* **2017**, *17*, 4568-4575.
9. D. Lloyd, X. Liu, N. Boddeti, L. Cantley, R. Long, M. L. Dunn, J. S. Bunch, *Nano Lett.* **2017**, *17*, 5329-5334.
10. F. Guinea, M. I. Katsnelson, A. K. Geim, *Nat. Phys.* **2010**, *6*, 30-33.
11. M. Cazalilla, H. Ochoa, F. Guinea, *Phys. Rev. Lett.* **2014**, *113*, 077201 1-6
12. H. Ochoa, R. Zarzuela, Y. Tserkovnyak, *Phys. Rev. Lett.* **2017**, *118*, 026801 1-5.

13. M. Taillefumier, V. K. Dugaev, B. Canals, C. Lacroix, P. Bruno, *Phys. Rev. B* **2008**, 78, 155330 1-10.
14. T. F. Jaramillo, K. P. Jørgensen, J. Bonde, J. H. Nielsen, S. Horch, I. Chorkendorff, *Science* **2007**, 317, 100-102.
15. D. Voiry, J. Yang, M. Chhowalla, *Adv. Mater.* **2016**, 28, 6197-6206.
16. D. Kiriya, P. Lobaccaro, H. Y. Y. Nyein, P. Taheri, M. Hettick, H. Shiraki, C. M. Sutter-Fella, P. Zhao, W. Gao, R. Maboudian, J. W. Ager, A. Javey, *Nano Lett.* **2016**, 16, 4047-4053.
17. R. Trotta, A. Polimeni, F. Martelli, G. Pettinari, M. Capizzi, L. Felisari, S. Rubini, M. Francardi, A. Gerardino, P. C. M. Christianen, J. C. Maan, *Adv. Mater.* **2011**, 23, 2706-2710.
18. G.-Y. Zhao, H. Deng, N. Tyree, M. Guy, A. Lisfi, Q. Peng, J.-A. Yan, C. Wang and Y. Lan, *Appl. Sci.* **2019**, 9, 678.
19. G. Sallen, L. Bouet, X. Marie, G. Wang, C. R. Zhu, W. P. Han, Y. Lu, P. H. Tan, T. Amand, B. L. Liu, B. Urbaszek, *Phys. Rev. B* **2012**, 86, 081301(R).
20. A. S. Friedman, D. White, H. L. Johnston, *J. Am. Chem. Soc.* **1951**, 73, 1310.
21. H. J. Hoge, R. D. Arnold, *J. Res. Natl. Inst. Stan.* **1951**, 47, 75-79.
22. M. Lozada-Hidalgo, S. Hu, O. Marshall, A. Mishchenko, A. N. Grigorenko, R. A. W. Dryfe, B. Radha, I. V. Grigorieva, A. K. Geim, *Science*, **2016**, 351, 68-70.
23. T. Green, D. Britz, *J. Electroanal. Chem.* **1996**, 412, 59-66.
24. D. Stolten, B. Emonts, *Hydrogen Science and engineering: Materials, Systems and Technology*, Wiley-VCH, Weinheim, Germany, **2016**, Ch. 24.2.1.2.

25. M. Seel, R. Pandey, *2D Mater.* **2016**, *3*, 025004 1-17.
- 26 C. H. Seager, in *Hydrogen in Semiconductors*, Chapter 2 (Eds.: J. I. Pankove and N. M. Johnson), Academic Press Limited, London UK 1991, pp. 17-34; A. D. Marwick *idibem*, Chapter 9, p. 220.
- 27 R. Trotta, D. Giubertoni, A. Polimeni, M. Bersani, M. Capizzi, F. Martelli, S. Rubini, G. Bisognin, M. Berti, *Phys. Rev. B* **2009**, *80*, 195206
28. A. S. Friedman, D. White, H. L. Johnston, *J. Am. Chem. Soc.* **1951**, *73*, 1310.
29. S. J. Cartamil-Bueno, P. G. Steeneken, A. Centeno, A. Zurutuza, H. S. J. van der Zant, S. Hourri, *Nano Lett.* **2016**, *16*, 6792-6796.
30. P. Wang, W. Gao, Z. Cao, K. M. Liechti, R. Huang, *J. Appl. Mech.* **2013**, *80*, 040906.
31. W. B. Fichter, *NASA Tech. Pap.* **1997**, 3658, 1-24.
32. D. Stolten, B. Emonts, *Hydrogen Science and engineering: Materials, Systems and Technology*, Wiley-VHC, Weinheim, Germany, **2016**, Ch. 24.2.2.
- 33 C. D. Jeffries, *Science* **1975**, *189*, 955-964.
- 34 J. Feng, X. Qian, C.-W. Huang, and J. Li, *Nat. Photon.* **2012**, *6*, 866.
- 35 A. Castellanos-Gomez, R. Roldan, E. Cappelluti, M. Buscema, F. Guinea, H. S. J. van der Zant, and G. A. Steele, *Nano Lett.* **2013**, *13*, 5361.
36. S. Birindelli, M. Felici, J. S. Wildmann, A. Polimeni, M. Capizzi, A. Gerardino, S. Rubini, F. Martelli, A. Rastelli, R. Trotta, *Nano Lett.* **2014**, *14*, 1275-1280.
37. D. A. Sanchez, Z. Dai, P. Wang, A. Cantu-Chavez, C. J. Brennan, R. Huang, N. Lu, *Proc. Natl Acad. Sci.* **2018**, *115*, 7884-7889.

38. A. V. Tyurnina, D. A. Bandurin, E. Khestanova, V. G. Kravets, M. Koperski, F. Guinea, A. N. Grigorenko, A. K. Geim, I. V. Grigorieva, *ACS Photonics* **2019**, *6*, 516-524.
39. N. Kumar, S. Najmaei, Q. Cui, F. Ceballos, P. M. Ajayan, J. Lou, H. Zhao, *Phys. Rev. B* **2013**, *87*, 161403.
40. C. Janisch, Y. Wang, D. Ma, N. Mehta, A. L. Elías, N. Perea-López, M. Terrones, V. Crespi, Z. Liu, *Sci. Rep.* **2014**, *4*, 5530.
41. M. S. Mohamed, A. Simbula, J.-F. Carlin, M. Minkov, D. Gerace, V. Savona, N. Grandjean, M. Galli, R. Houdré, *APL Photonics* **2017**, *2*, 031301.
42. M. Minkov, V. Savona, D. Gerace, *Appl. Phys. Lett.* **2017**, *111*, 131104.
43. Petrosko, S. H., Johnson, R., White, H. & Mirkin, C. A. Nanoreactors: Small Spaces, Big Implications in Chemistry, *J. Am. Chem. Soc.* *138*, 7443 (2016).
44. S. Hu, M. Lozada-Hidalgo, F. C. Wang, A. Mishchenko, F. Schedin, R. R. Nair, E. W. Hill, D. W. Boukhvalov, M. I. Katsnelson, R. A. W. Dryfe, I. V. Grigorieva, H. A. Wu, A. K. Geim, *Nature* **2014**, *516*, 227–230.