Large-area synthesis of high-quality and uniform monolayer WS$_2$ on reusable Au foils

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Large-area monolayer WS$_2$ is a desirable material for applications in next-generation electronics and optoelectronics. However, the chemical vapour deposition (CVD) with rigid and inert substrates for large-area sample growth suffers from a non-uniform number of layers, small domain size and many defects, and is not compatible with the fabrication process of flexible devices. Here we report the self-limited catalytic surface growth of uniform monolayer WS$_2$ single crystals of millimetre size and large-area films by ambient-pressure CVD on Au. The weak interaction between the WS$_2$ and Au enables the intact transfer of the monolayers to arbitrary substrates using the electrochemical bubbling method without sacrificing Au. The WS$_2$ shows high crystal quality and optical and electrical properties comparable or superior to mechanically exfoliated samples. We also demonstrate the roll-to-roll/bubbling production of large-area flexible films of uniform monolayer, double-layer WS$_2$ and WS$_2$/graphene heterostructures, and batch fabrication of large-area flexible monolayer WS$_2$ film transistor arrays.

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Atomic thin two-dimensional (2D) transition metal dichalcogenides (TMDCs) have attracted increasing interest because of their unique electronic and optical properties that are distinct from and complementary to graphene\(^1\)–\(^3\). Different from multilayers, monolayer semiconducting TMDCs have sizable direct bandgaps\(^1\)–\(^3\) and show efficient valley polarization by optical pumping\(^4\)–\(^6\), which opens up the possibility for their use in transistors\(^7\)–\(^10\), integrated circuits\(^1\), photodetectors\(^12\), electrochromic devices\(^3\) and valleytronic and spintronic devices\(^5\)–\(^6\). Besides the number of layers, defects\(^14\)–\(^15\) and grain boundaries\(^9\) in 2D TMDCs also have a strong influence on their electronic and optical properties. Therefore, similar to current silicon-based electronics, the availability of wafer-size, defect-free and uniform monolayer TMDC single crystals is necessary for their future electronic, optoelectronic and spintronic applications.

Monolayer WS\(_2\) is a very important example of 2D TMDCs with a direct bandgap, which exhibits many fascinating properties and promises applications in electronics and optoelectronics\(^1\)–\(^3\),\(^16\)–\(^17\). It is a robust platform to study spin and valley physics because of its large spin–orbit interaction\(^4\). Vertical field-effect transistors (FETs) on the basis of graphene/WS\(_2\) heterostructures show an unprecedented high ON/OFF ratio and a very large ON current because of a combination of tunnelling and thermionic transport\(^16\). Chemical vapour deposition (CVD) on inert substrates such as SiO\(_2\)/Si (refs 7,18–23) has shown a potential to grow large-area WS\(_2\), compared with other methods such as mechanical cleavage\(^24\)–\(^25\) and liquid exfoliation\(^3\)–\(^26\). However, as with the growth of graphene on the SiO\(_2\)/Si substrate\(^27\), the material obtained suffers from unsatisfactory structure control and low quality\(^7\)–\(^18\)–\(^21\). The growth of a uniform monolayer of WS\(_2\) over a large area has not yet been achieved, and the domain size of the crystals is usually smaller than 100 \(\mu\)m (refs 7,18,19,21). More importantly, many structural defects exist in 2D TMDCs CVD-grown on inert substrates, including sulphur vacancies, antisite defects, adatoms and dislocations\(^3\)–\(^14\)\(^,\)\(^15\). Such defects introduce localized states in the bandgap, leading to hopping transport behaviour and consequently a dramatic decrease in the carrier mobility\(^15\). Monolayer WS\(_2\) CVD-grown on SiO\(_2\)/Si substrate shows a very low carrier mobility of \(\sim 0.01\) cm\(^2\)V\(^{-1}\)s\(^{-1}\) at room temperature\(^7\), far below that of mechanically exfoliated samples \((\sim 10\) cm\(^2\)V\(^{-1}\)s\(^{-1}\)) measured under similar conditions\(^24\).

In addition to conventional rigid device applications, transparent and flexible electronic and optoelectronic devices have been widely considered to be one of the most appealing applications of all 2D materials because of their high transparency and good flexibility\(^1\)–\(^16\). To this end, the low-cost fabrication of large-area monolayer WS\(_2\) films on flexible substrates is highly desired. For CVD-grown 2D WS\(_2\) materials on inert substrates, however, the growth substrates usually have to be etched away by acidic or basic solutions such as concentrated HF, KOH and NaOH before they are transferred to flexible substrates\(^7\)–\(^18\)–\(^21\). This transfer method not only leads to inevitable damage to the WS\(_2\) but also produces substrate residues and serious environmental pollution, and increases production cost. Moreover, the rigid nature of inert substrates is not compatible with the cost- and time-effective roll-to-roll production technique, which has been used for the fabrication of large-area graphene-transparent conductive films as well as of high-throughput printed flexible electronics\(^28\)–\(^29\).

Here we develop a scalable ambient-pressure catalytic CVD method on the basis of the self-limited surface growth mechanism, using flexible Au foils as substrate, to grow high-quality uniform monolayer WS\(_2\) single crystals of the order of millimetres and large-area continuous films. These WS\(_2\) monolayers can be transferred from Au foils to arbitrary substrates without damage to either the WS\(_2\) or the Au foils by using an electrochemical bubbling method because of the weak interaction between monolayer WS\(_2\) and the Au substrate in this unique growth process. The WS\(_2\) domains show optical and electrical properties comparable or superior to those of mechanically exfoliated samples, and their carrier mobility and ON/OFF ratio are 100 times higher than those of CVD-grown samples on SiO\(_2\)/Si substrates measured under similar conditions\(^7\). Using the good flexibility of Au foils and the electrochemical bubbling method, we also demonstrate the roll-to-roll/bubbling production of large-area, transparent, flexible monolayer WS\(_2\) films and their heterostructures with graphene films without sacrificing the Au foils, and batch fabrication of large-area flexible monolayer WS\(_2\) film transistor arrays with electrical performance comparable to those on SiO\(_2\)/Si substrates.

**Results**

**Growth and transfer of uniform monolayer WS\(_2\).** As described in Methods (Fig. 1 and Supplementary Fig. 1), we grew monolayer WS\(_2\) single crystals and films on the Au foil by ambient-pressure CVD at 800 °C using WO\(_3\) and sulphur powders as precursors. The reasons why we chose Au as the growth substrate are as follows: Au is the only metal that does not form any sulphide when reacting with sulphur at high temperature (500 °C or even higher); Au is a commonly used catalyst for the growth of different materials including graphene and carbon nanotubes\(^30\)–\(^32\), and it can lower the barrier energies for the sulfuration of WO\(_3\) through the formation of sulphur atoms (Supplementary Fig. 2 and Supplementary Fig. 3), which allows the use of a very low concentration of WO\(_3\) and sulphur and thus is beneficial for the formation of monolayer WS\(_2\) with much higher quality than would be produced using inert substrates; and the solubility of W in Au is extremely low (below 0.1 atomic% at 800 °C), which makes the segregation and precipitation processes for multilayer growth impossible\(^33\). These three features make it possible to grow uniform high-quality monolayer WS\(_2\) on Au by a self-limited surface-catalytic process similar to that used for the growth of graphene on Cu (ref. 34). In addition, the good flexibility of the Au foil is compatible with the large-area roll-to-roll production process\(^28\).

As shown in Fig. 1 and Supplementary Fig. 4, all the isolated WS\(_2\) domains have a regular triangular shape, a typical characteristic of single-crystal WS\(_2\) prepared by CVD\(^7\)–\(^18\)–\(^21\). Atomic force microscopy (AFM) measurements show that the thickness of the WS\(_2\) obtained is \(\sim 0.95\) nm (Supplementary Fig. 5), indicating that they are monolayers. Moreover, the domain size is increased by increasing the growth time, lowering the heating temperature of the sulphur powder and increasing the Ar flow rate in the reaction zone (Supplementary Fig. 4 and Supplementary Fig. 6). Under optimized conditions, millimetre-size single-crystal monolayer WS\(_2\) domains were obtained (Fig. 1b), and these are much larger than the samples CVD-grown on inert substrates and mechanically or liquid-exfoliated samples\(^7\)–\(^18\)–\(^21\)–\(^24\)–\(^26\), which are typically smaller than 100 \(\mu\)m. It is needed to point out that all the WS\(_2\) domains obtained under the above conditions are monolayers despite their different domain size, indicating a broad window for monolayer WS\(_2\) growth on Au. By increasing the growth time, adjacent domains expand, join and eventually form a continuous monolayer WS\(_2\) film (Supplementary Fig. 7), a typical characteristic of surface growth. It is important to note that no additional layers were formed on the film even by further increasing the growth time (Supplementary Fig. 7). Moreover, there were still enough WO\(_3\) and sulphur source for the growth of WS\(_2\) in the reaction system.
after the growth of a monolayer WS2 film, which was confirmed by the growth of monolayer WS2 domains on a newly loaded bare Au foil (Supplementary Fig. 8). These facts confirm the self-limited surface growth behaviour of monolayer WS2 on Au substrates.

We also compared the growth of WS2 on the Au foil and the commonly used SiO2/Si substrate under the same experimental conditions. It is worth noting that no WS2 domains were formed on the SiO2/Si substrate when we used the same growth conditions as those for WS2 growth on Au (Supplementary Fig. 9). However, a few WS2 domains can be formed if the concentration of sulphur in the reaction system was greatly increased (the evaporation area of sulphur powder was increased by ~10 times, and its heating temperature was increased by 30 °C; Supplementary Fig. 10a). In contrast, many multilayer WS2 domains were formed on the Au foil under the same conditions (Supplementary Fig. 10b and Supplementary Note 1). These results give strong evidence that the Au helps the growth of WS2, which is consistent with the barrier energy decrease for the sulphurization of WO3 by sulphur atoms on Au compared with the direct sulphurization of WO3 in sulphur atmosphere based on density functional theory (DFT) calculations (Supplementary Fig. 2 and Supplementary Fig. 3). Therefore, a low concentration of WO3 and sulphur that is insufficient for spontaneously sulphurization reaction can be used for WS2 growth on Au. Actually, it has been demonstrated that a very low concentration of precursors is essential for growing monolayer graphene35. Although Cu has a very low solubility for carbon, increasing the concentration of methane in the reaction system can lead to the formation of bi-, tri- and tetra-layer graphene films35. This is also the reason why multilayer WS2 was formed on the Au foil when the concentration of sulphur in the reaction system was greatly increased (Supplementary Fig. 10b). It is worth noting that, when the Au substrate was fully covered by WS2 film, the formation of sulphur atoms and the sulphurization of WO3 were suppressed, and consequently no additional layers were formed even further extending the growth time under the same conditions as those for WS2 growth on Au. Therefore, the barrier energy decrease for the sulphurization of WO3 on Au compared with that in sulphur atmosphere plays an important role for the self-limited growth of monolayer WS2 on Au.

Actually, Au has also been reported as a substrate for the growth of monolayer to few-layer MoS2 (refs 36–40). However, it is worth noting that the solubility of Mo in Au (~0.34 atomic% at 300 °C and ~0.9 atomic% at 800 °C) is significantly higher than that of W (below 0.1 atomic% at 800 °C), which makes the growth of MoS2 on Au and its subsequent transfer completely different from those of the monolayer WS2 reported here. During the two-step growth process of MoS2 on the Au substrate, it has been confirmed that Mo–Au surface alloys are first formed and then transformed to MoS2 on exposure to H2S. In this case, only few-layer MoS2 was obtained by ambient-pressure CVD, and
there are still a certain portion of Mo–Au alloys left after the formation of MoS₂. In contrast, no WS₂ domains were formed when the Au substrate first reacted with WO₃ without the presence of sulphur and then the obtained substrate reacted with sulphur without the presence of WO₃ (Supplementary Fig. 11), and no W–Au alloy signals were detected after the growth of monolayer WS₂ (Supplementary Fig. 12). On the basis of the above analyses, we suggest that the growth of MoS₂ on Au (ref. 39) is similar to the growth of graphene on Ni (ref. 41), and it is difficult to control the number of layers of MoS₂ by ambient-pressure CVD39. Two to three layers of MoS₂ with a very low carrier mobility of \(~0.004\) cm² V⁻¹ s⁻¹ were obtained in this case39. To grow monolayer MoS₂ on the Au substrate, ultrahigh vacuum deposition39 or low-pressure CVD36–38 has to be used to reduce the supply of Mo and S for the deposition reaction, similar to the growth of monolayer graphite on Ni (ref. 42). In contrast, similar to the graphene growth on Cu (ref. 34), the low solubility of tungsten in Au makes the segregation and precipitation processes for multilayer growth impossible, which is another important reason for the self-limited growth of monolayer WS₂ on Au substrates. In the catalytic surface growth process, the passivation of surface imperfections in Au foils by polishing and annealing before CVD growth play an important role in the growth of millimetre-size WS₂ domains (Supplementary Fig. 13 and refs 43,44).

The weak interaction between the monolayer WS₂ and the Au substrate is another very important feature of the samples prepared by ambient-pressure CVD method (Supplementary Fig. 14). We can also obtain monolayer WS₂ on a Au foil by low-pressure CVD (Supplementary Fig. 15); however, the monolayers MoS₂ and WS₂ grown by low-pressure CVD have a strong interaction with the Au substrate (Supplementary Fig. 14 and refs 36–38). As a result, the 2D TMDC cannot be separated from the Au substrate by a nondestructive bubbling method (Supplementary Fig. 15) and have to be transferred by etching away the Au substrate36–39. This makes the fabrication of monolayers MoS₂ and WS₂ on the Au substrate by low-pressure CVD too expensive to be used for large-scale production. We also studied the electrochemical bubbling transfer of the WS₂ samples grown by ambient-pressure CVD followed by low-pressure CVD-successive growth or annealing (Supplementary Fig. 16). It is interesting to find that the ambient-pressure CVD-grown samples cannot be separated by bubbling any more once they are subjected to low-pressure treatments. Moreover, we can clearly see the contrast and roughness difference between the regions grown under ambient-pressure and low-pressure CVD condition in the same domain. These indicate that there are probably some gases trapped between the 2D TMDC and the Au substrate in ambient-pressure CVD process, and these gases tend to be expelled under low-pressure conditions, which lead to remarkable difference in the interaction between the 2D TMDC and the Au substrate for the samples prepared by ambient-pressure and low-pressure CVD processes.

The weak interaction between the monolayer WS₂ and the Au substrate for our samples enables the intact transfer of WS₂ from the substrate using the electrochemical bubbling method45. After CVD growth, therefore, we used an electrochemical bubbling method on the basis of the water electrolysis reaction to transfer the monolayer WS₂ from Au foils to SiO₂/Si substrates (the thickness of the SiO₂ layer is 290 nm), polyethylene terephthalate (PET) and transmission electron microscopy (TEM) grids for further characterizations (Figs 1a,c–e and 2a). Notably, all the transferred domains perfectly preserved their original structure on the Au substrates (Supplementary Fig. 17), and no optical contrast difference was found for all domains and within a single domain on SiO₂/Si substrates (Fig. 1c,e), which indicates the highly uniform thickness of the sample. The Au substrate is chemically inert to the electrolyte used and was not involved in the water electrolysis reaction during transfer. As a result, it was not destroyed and could be used repeatedly (Fig. 1a, Supplementary Fig. 12 and Supplementary Fig. 18). So far, one Au foil has been reused ~700 times, and most of the Au foils have been reused more than 300 times. Moreover, the monolayer WS₂ domains grown on reused Au foils showed a similar structure to those grown on the original ones (Supplementary Fig. 19). The nondestructive transfer makes the CVD method using Au as a substrate suitable for the scalable production of monolayer WS₂ at a low cost.

Structure and optical/electrical properties. We used selected-area electron diffraction (SAED), high-resolution TEM (HRTEM) and atomic resolution scanning TEM (STEM) to characterize the crystal structure of the large WS₂ domains (Fig. 2). Figure 2a shows an optical image of a 400-μm WS₂ domain transferred on a TEM grid. Similar to monolayer MoS₂ (ref. 9), monolayer WS₂ shows a hexagonal structure with threefold symmetry in terms of the two sets of spots in its diffraction pattern (Fig. 2bc and Supplementary Fig. 20), bright k₁ spots (indicated by green arrows) and dark k₂ spots (indicated by blue arrows). To identify whether this domain is a single crystal, we carried out a series of SAED measurements on 12 different regions by carefully moving the sample without rotation or tilting. Figure 2c is a superimposed image of the 12 SAED patterns. The perfect coincidence of all the diffraction patterns confirms the single-crystal nature of this large WS₂ domain. Similar measurements and analyses of dozens of samples show that all the triangular WS₂ domains are single crystals.

Figure 2d,e shows representative HRTEM and aberration-corrected HRTEM images of our single-crystal WS₂ sample, respectively. No point defects or voids are observed over a large area. Moreover, in addition to the commonly observed zigzag edges (Supplementary Fig. 21), we also find that some monolayer WS₂ single crystals have an edge along armchair crystallographic orientation (Fig. 2d, Supplementary Fig. 22 and Supplementary Fig. 23). This is different from the triangular WS₂ or MoS₂ single crystals grown on the SiO₂/Si substrate, in which only zigzag edges have been observed9,20. Actually, different edges have also been observed in the graphene grown on chemically inert SiC substrate (armchair edge; ref. 46) and metal substrates such as Cu and Pt (zigzag edge; refs 47,48). We suggest that this edge difference is probably attributed to the different interfacial interactions for 2D materials grown on metals and inert substrates or on different faces of the same metal substrate. Further experimental studies combined with theoretical calculations are required to elucidate this point in the future.

We then used an aberration-corrected annular dark-field STEM (ADF-STEM), operated at a low voltage of 60 keV, to further identify the atomic structure of our WS₂ samples. The ADF-STEM image intensity scales roughly as the square of the atomic number of the atom, allowing atom-by-atom structural and chemical identification by quantitative analysis of the image intensity. Figure 2f shows a representative ADF-STEM image of our WS₂, which shows a clear hexagonal lattice structure with threefold symmetry. The bright spots correspond to tungsten atoms and the dim spots correspond to carbon atoms. The significant difference in image intensity is attributed to the big difference between the atomic numbers of W and S. The uniform intensity difference between the bright and dim spots indicates that there are no sulphur vacancies (Fig. 2f).

We further used Raman and photoluminescence (PL) spectroscopy to characterize the structure, quality and optical properties...
of the large WS2 domains. Figure 3a–c shows an optical image and the corresponding Raman and PL spectra of an ~100-μm triangular WS2 domain on the SiO2/Si substrate. The Raman spectrum shows typical features of monolayer WS2: the E1g and A1g modes are, respectively, located at ~357 and 418 cm⁻¹, representing an upward shift of ~1 cm⁻¹ and a downward shift of ~3 cm⁻¹ compared with those of bulk WS2; the E1g and 2LA (M) modes are much stronger than the A1g mode; and the absence of the peak at ~310 cm⁻¹ (ref. 49). In addition, it shows a very sharp and strong single PL peak at ~612.6 nm (2.02 eV) in the range of 575–975 nm, which represents an upward shift of ~0.09 eV and is much narrower and ~10² times stronger than the asymmetric peak at ~641 nm of bulk WS2. The strong single PL peak indicates that the WS2 is a direct-gap semiconductor with only one direct electronic transition, further confirming that our WS2 samples grown on Au foils are monolayer. Figure 3d–i shows the intensity, peak position and full-width at half-maximum maps of the Raman and PL spectra of the single-crystal monolayer WS2 in Fig. 3a. It is worth noting that all the maps are very uniform across the whole domain, indicating the high uniformity in the number of layers and crystalline quality of the sample. In addition, the full-width at half-maximum of the PL peak of our samples (33–46 meV) is much narrower than for monolayer WS2 grown by CVD on the SiO2/Si substrate (42–68 meV; ref. 19), further confirming the higher crystalline quality of our samples. Considering the difficulty in laser focusing and time consuming when mapping over a large area, the uniformity of much larger WS2 samples was confirmed by the uniform Raman spectra randomly taken from many positions in a single domain (Supplementary Fig. 24).

To evaluate the electrical quality of our monolayer WS2, we fabricated back-gate FETs (BG-FETs) with transferred WS2 single crystals on SiO2/Si substrates. Both channel length and width are 3 μm in all BG-FETs (Fig. 4a). The devices were measured in vacuum at room temperature. Figure 4c shows the typical electrical transport of a monolayer WS2 BG-FET, indicating that the transferred WS2 is n-type doped. We estimated the field-effect carrier mobility using the equation\[ \mu = \frac{dI_{ds}/dV_{bg}}{I_{ds}/V_{bg}} \times \frac{1}{L (W \times C_i)} \]
where dI/dV is the transconductance, I, W and C are the channel length, channel width and the capacitance between the channel and the back gate per unit area, respectively. The evaluated carrier mobility is 1.7 cm²V⁻¹s⁻¹, and the ON/OFF current ratio is ~10⁷. It is worth pointing out that most of the BG-FETs we measured show the mobilities ranging from 1 to 2 cm²V⁻¹s⁻¹ and ON/OFF ratios ranging from 4 × 10⁶ to 5 × 10⁷ (Fig. 4d). These mobilities are ~100 times larger than those of BG-FETs made by CVD-grown monolayer WS2 on SiO2/Si substrates (~0.01 cm²V⁻¹s⁻¹; ref. 7), and are comparable to those reported for BG-FETs fabricated with mechanically exfoliated WS2 (~10 cm²V⁻¹s⁻¹; ref. 24). Moreover, the ON/OFF ratios are one to two orders of magnitude larger than those reported so far for monolayer WS2 including mechanically
**Figure 3** | Optical properties of monolayer single-crystal WS$_2$ domains. (a) Optical image of an ~100-μm monolayer WS$_2$ domain transferred on a SiO$_2$/Si substrate. (b) Typical Raman spectra of the monolayer WS$_2$ (blue plot) in a and bulk H-WS$_2$ (black plot). (c) Typical PL spectra of the monolayer WS$_2$ (red plot) in a and bulk H-WS$_2$ (black plot). (d–f) Raman maps of the intensity (d), position (e) and full-width at half-maximum (FWHM; f) of $A_{1g}$ peak of the monolayer WS$_2$ domain in a. (g–i) PL maps of the intensity (g), position (h) and FWHM (i) of ~613-nm PL peak of the monolayer WS$_2$ domain in a.

**Figure 4** | Electrical properties of monolayer single-crystal WS$_2$ domains. (a) Optical image of a monolayer WS$_2$ BG-FET. (b) Room-temperature output characteristics of the BG-FET. (c) Logarithmic transfer characteristics of the BG-FET with 5-V applied bias voltage $V_{ds}$. (d) A summary of the room-temperature carrier mobility and the corresponding current ON/OFF ratio of nine monolayer WS$_2$ BG-FETs.
exfoliated samples\textsuperscript{7,24,25}. These results give further strong evidence for the high quality of our samples and confirm the great potential of our samples for applications in transistors and integrated circuits.

**Large-area monolayer WS\(_2\) films and flexible electronics.** Another very important advantage of our method is that the CVD growth and electrochemical bubbling transfer presented here can be integrated in a roll-to-roll technique to produce large-area monolayer WS\(_2\) films on flexible substrates such as PET and polyethylene naphthalate (PEN) at low cost because of the good flexibility and chemical stability of Au foils. Figure 5a shows a schematic of the roll-to-roll/bubbling production of monolayer WS\(_2\) films on PET. First, a monolayer WS\(_2\) film, grown on a flexible Au foil, was attached to a thermal release tape (TRT) by passing between two rollers. Second, the TRT/WS\(_2\)/Au thus obtained was gradually rolled into a 1-M NaOH aqueous solution under a constant current. During this process, the TRT attached to the WS\(_2\) film was separated from the Au foil by hydrogen bubbles generated by water electrolysis. Third, the monolayer WS\(_2\) film was detached from the TRT and was attached to a PET film by thermal treatment, where Cu foils are etched away\textsuperscript{28}. Figure 5b,c shows an \(~2\)-inch monolayer WS\(_2\) film on PET fabricated by our roll-to-roll/bubbling method. It shows no visible cracks and similar Raman features to single-crystal monolayer WS\(_2\) (Supplementary Fig. 25), indicating its intact transfer and high quality. Moreover, this method can be used to produce other 2D materials such as graphene, few-layer WS\(_2\) films and van der Waals heterostructures of monolayer WS\(_2\) assembled with other 2D materials. For example, we have fabricated large-area high-quality transparent and flexible double-layer WS\(_2\) films (Fig. 5d, Supplementary Fig. 25 and Supplementary Fig. 26) and graphene/monolayer WS\(_2\) heterostructures (Fig. 5e) through layer-by-layer transfer. The roll-to-roll/bubbling production of such 2D materials opens up the possibility for the large-scale use of monolayer WS\(_2\) in integrated circuits, vertical FETs and photovoltaic devices for transparent electronics and optoelectronics.

As an example, we fabricated large-area flexible monolayer WS\(_2\) FET device arrays with buried gates on a PEN substrate (Fig. 6). We used the roll-to-roll/bubbling method described above to transfer an \(~2\)-inch monolayer WS\(_2\) film onto the PEN substrate with pre-patterned electrodes made by standard photolithography (Fig. 6c, also see Methods). Note that the photolithography process and roll-to-roll/bubbling method are compatible with the batch fabrication of large-area flexible devices. Figure 6d presents the transfer characteristics of a WS\(_2\) FET on the flexible PEN substrate, showing n-type characteristics. The mobility and ON/OFF ratio were evaluated to be 0.99 cm\(^2\) V\(^{-1}\) s\(^{-1}\) and \(\approx 6 \times 10^5\), respectively, which are comparable to those of the devices on SiO\(_2\)/Si substrates. Moreover, no electrical performance degradation was observed even after repeated bending to a radius of 15 mm for 100 times. These results indicate that our growth and transfer methods have a great

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**Figure 5 | Roll-to-roll/bubbling production of large-area flexible monolayer films and their heterostructures with graphene films.** (a) Schematic of the roll-to-roll/bubbling process. (b–e) Photographs of \(~2\)-inch flexible transparent films of monolayer WS\(_2\) (b,c), double-layer WS\(_2\) (d) and graphene/monolayer WS\(_2\) van der Waals heterostructure (e) on PET fabricated by the roll-to-roll/bubbling method. The insets in b–e show the schematic models of the transferred films. ‘Gr’ represents graphene.
potential for the batch fabrication of large-area WS2 flexible devices. The output characteristics of the same devices show a saturation behaviour at a high source-drain bias (Fig. 6e); however, a nonlinear current at a low source-drain bias indicates a non-ideal ohmic contact between Au electrodes and WS2 channel. We believe that the electrical performance including the carrier mobility and ON/OFF ratio of the flexible WS2 FET presented here can be further improved if given a careful selection of electrode metals with different work functions to decrease the Schottky barrier height at WS2/metal interface.

Discussion
In summary, we report the uniform growth of high-quality monolayer WS2 single crystals of the order of millimetres and large-area continuous films by ambient-pressure CVD using Au foils as the growth substrate. Similar to the CVD growth of graphene on copper, the catalytic activity of gold together with its low solubility for tungsten allow self-limited catalytic growth of a uniform monolayer of WS2 on its surface. Furthermore, the weak interaction between monolayer WS2 and gold enables the intact transfer of the WS2 onto arbitrary substrates without sacrificing the electrical performance after repeated bending to a radius of 15 mm for 100 times. (e) Output characteristics of the same device measured at room temperature.

Methods
Ambient-pressure CVD growth of uniform monolayer WS2 on Au foils. A piece of Au foil (99.95 wt%, 25–100-μm thick) was finely polished and annealed at 1,040 °C for 1 h before the first use, and the polished face was placed face-down above a small quartz boat containing 200 mg WO3 powder (99.998 wt%) and a piece of Au foil (99.95 wt%, 25–100-μm thick) was finely polished and annealed at 1,040 °C in an Ar atmosphere (200 s.c.c.m.) and cooled to room temperature naturally. The Ar gas flow rate remained constant (10–500 s.c.c.m.) during the growth and cooling processes.

Bubbling transfer of monolayer WS2 from Au foils. Similar to the transfer of graphene grown on Pt (ref. 45), the Au foil with monolayer WS2 was first spin-coated with 550-k PMMA (4 wt% dissolved in ethyl lactate) at 3,000 r.p.m. for 1 min followed by curing at 180 °C for 5 min. Then, the PMMA/monolayer WS2/Au was used as the anode in a 1-M NaOH solution with a Pt foil as the cathode. After applying a constant current of 50 mA for 30 s, the PMMA/monolayer WS2 layer was separated from the Au foil by H2 bubbles generated by water electrolysis. After that, the PMMA/monolayer WS2 was immersed in deionized water and collected by a target substrate. Finally, the PMMA layer was removed by warm acetone (50 °C), rinsed with isopropanol and dried by a N2 flow. For TEM samples, the PMMA layer was dissolved with acetone droplets and dried naturally.

Structure and optical property characterization. The morphology of the monolayer WS2 and Au foils was characterized using an optical microscope (Nikon
Eclipse LV100) and scanning electron microscopy (SEM; Nova NanoSEM 430, 15 kV), and the thickness was measured using AFM (Vecco Dimension 3100 tapping mode). X-ray photoelectron spectroscopy (XPS) was employed to characterize the chemical composition of the Au foils before and after different treatments. HRTEM imaging was performed on a field emission TEM (FEI Tecnai F20, 200 kV); STEM imaging was performed on an aberration-corrected and monochromated TEM (FEI Titan G2 60–300 S/TEM) operating at 60 kV, and SAED measurements were performed on a TEM operating at 120 kV (FEI Tecnai T12). Raman and PL spectra/maps were collected with a confocal Raman spectrometer (Jobin Yvon LabRAM HR800) using a 532 nm laser as the excitation source. The laser spot size was ~1 μm and the laser power on the sample surface was kept below 60 μW to avoid any heating effects. Ultraviolet-visible absorption spectra were collected with a UV-visible NIR spectrometer (Varian Cary 5000).

**Electrical property measurements of monolayer WS2 on SiO2/Si.** BG-FETs were fabricated on n-doped Si substrates with 200-nm-thick SiO2 as the dielectric layer. The monolayer single-crystal WS2 domains were patterned through exposure to electron-beam lithography followed by reactive ion etching (O2 plasma treatment for 50 s at 100 W). Ti/Au (5/30 nm) was used as the source and drain electrodes. The BG-FETs were directly measured after fabrication, without annealing, with a semiconductor analyzer (Keithley 4200) inside a probe station (Lakeshore TTP-4) in vacuum at room temperature.

**Fabrication and electrical property measurements of large-area flexible monolayer WS2 FET arrays.** First, the buried-gate electrodes (Ti/Au; 10/50 nm) were fabricated on PEN substrates (Teijin DuPont Films; thickness, 125 μm) by standard photolithography, electron-beam evaporation, and lift-off processes. A 50-nm Al2O3 insulator layer was then deposited by an atomic layer deposition technique using trimethylaluminum and H2O at 145 °C. Contact windows for the gate electrodes were opened using photolithography and reactive ion etching. The source and drain electrodes were fabricated by the similar processes to the gate electrodes. Second, we used the roll-to-roll-bubbling method to transfer an ~2-inch monolayer WS2 film onto the substrate with patterned electrodes. Third, the WS2 film outside the channel area was removed by photolithography and O2 plasma treatment for 2 min at 200 W. The electrical property measurements of these flexible devices were same as those for the devices on SiO2/Si substrates shown above.

**DFT calculations on the sulphurization of WS2 with and without the presence of Au substrate.** The first-principles calculations were performed using the Vienna Ab initio Simulation Package (VASP) with the projector augmented wave method.54,55 The Perdew–Burke–Ernzerhof functional was exchanged-correlation term was used for all calculations. The projector augmented wave method was used at a plane-wave cutoff of 400 eV to describe the electron–ion interaction. The W3O9 cluster was used to represent the WO3 species for WS2 metal dichalcogenides. The W3O9 cluster was used to represent the WO3 species for WS2 metal dichalcogenides. The W3O9 cluster was used to represent the WO3 species for WS2 metal dichalcogenides. The W3O9 cluster was used to represent the WO3 species for WS2 metal dichalcogenides. The W3O9 cluster was used to represent the WO3 species for WS2 metal dichalcogenides.
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Author contributions

W.R. proposed and supervised the project. Y.G. and W.R. designed the experiments. Y.G. performed growth and transfer experiments and measured Raman, PL and ultraviolet-visible absorption spectra under the supervision of W.R. and H.-M.C. Z.L. performed electron microscopy measurements under the supervision of X.-L.M. D.-M.S. fabricated flexible devices on PEN. L.H. fabricated devices on SiO2/Si, measured electrical properties and analysed the data under the supervision of Z.Z. and L.-M.P. L.-C.Y. performed DFT calculations. L.-P.M. provided graphene films and helped with roll-to-roll transfer. T.M. helped with bubbling transfer. W.R. and Y.G. analysed the data and wrote the manuscript. All the authors discussed the results and commented on the manuscript.

Additional information

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