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Correspondence and requests for materials should be addressed to S.F.Y. (Siu.Fung.Yu@ inet.polyu.edu.hk) or H.Y.Y. (yanghuiying@ sutd.edu.sg)

* These authors contributed equally to this work.

Selective Decoration of Au Nanoparticles on Monolayer MoS₂ Single Crystals

Yumeng Shi¹*, Jing-Kai Huang²*, Limin Jin³*, Yu-Te Hsu², Siu Fung Yu³, Lain-Jong Li^{2,4} & Hui Ying Yang¹

¹Pillar of Engineering Product Development, Singapore University of Technology and Design, Singapore 138682, Singapore, ²Institute of Atomic and Molecular Sciences Academia Sinica, Taipei 10617, Taiwan, ³Departments of Applied Physics, the Hong Kong Polytechnic University, Hung Hum, Kowloon, Hong Kong, China, ⁴Department of Physics National Tsing Hua University, HsinChu 300, Taiwan.

We report a controllable wet method for effective decoration of 2-dimensional (2D) molybdenum disulfide (MoS_2) layers with Au nanoparticles (NPs). Au NPs can be selectively formed on the edge sites or defective sites of MoS_2 layers. The Au-MoS_2 nano-composites are formed by non-covalent bond. The size distribution, morphology and density of the metal nanoparticles can be tuned by changing the defect density in MoS_2 layers. Field effect transistors were directly fabricated by placing ion gel gate dielectrics on Au-decorated MoS_2 layers without the need to transfer these MoS_2 layers to SiO_2/Si substrates for bottom gate devices. The ion gel method allows probing the intrinsic electrical properties of the as-grown and Au-decorated MoS_2 layers. This study shows that Au NPs impose remarkable *p*-doping effects to the MoS_2 transistors without degrading their electrical characteristics.

Use to their unique properties, atomically thin two-dimensional (2D) materials with a layered structure such as graphene¹⁻³, hexagonal boron nitride (*h*-BN)^{4,5} and transition-metal dichalcogenide (LTMDs)⁶⁻⁸ have been attracting increasing attention. Molybdenum disulfide (MoS₂), belongs to the layered 2D nanomaterial family, is traditionally used as a solid state lubricant and a catalyst for hydrodesulfurization (HDS) and hydrogen evolution reaction (HER)⁹⁻¹¹. In recent years, it has been demonstrated that ultra-thin MoS₂ crystals with a typical thickness of ~0.65 nm can be obtained by either physical^{6,12} or chemical exfoliation methods^{13,14}, MoS₂ layers with uniform thickness can also be synthesized in large scale by chemical vapor deposition¹⁵⁻¹⁹. The monolayer MoS₂ exhibits excellent electrical⁶⁻⁸ and optical performance^{20,21} compared to its bulky counterpart.

MoS₂ can be seen as an inorganic graphene analogue, similar to graphene and *h*-BN. The structure of MoS₂ is based on a hexagonal crystal²², where Mo atom is six-fold coordinated and hexagonally packed between two trigonally coordinated sulphur atoms. One S-Mo-S quintuple-layer is weakly bonded to another S-Mo-S layer by van der Waals forces. It has been reported that the basal plane of MoS_2 is catalytically inactive, and the activity in the HDS and HER is associated with the edge termination of MoS₂ clusters^{9-11,23}. Especially for the MoS₂ nanocrystals form, it has been investigated as an inexpensive alternative to platinum or other noble metals for the electrochemical or photochemical generation of hydrogen from water^{10,24–27}, which could be a promising clean energy source. The better understanding of catalytical active edge sits of MoS₂ is critical for the advanced catalysts design and developing its practical applications²⁸. However, the precise molecular structure modulation and engineering, especially for a well-defined edge site, is fundamentally challenging and rarely reported. On the other hand, noble metal nanoparticles such as Au, Pt and Ag are a class of materials with unique chemical and physical properties which find great applications in biosensing^{29,30}, photonics^{31,32} and catalysis^{33,34} It can be expected that the noble metal nanoparticles (NPs) anchored on the MoS₂ sheet could potentially extend its functionalities as novel catalytic, magnetic, and optoelectronic nanomaterials^{28,35}. Furthermore, compared with graphene, MoS₂ is a semiconducting material with a suitable band gap around 1.2 to 1.9 eV, depending on its thickness^{6,20,21}. It is possible to form p-n junctions with other semiconducting materials as new type of electronic devices. While substantial research efforts have been paid, the Fermi level engineering of MoS₂ layers by chemical doping methods are still lack of investigation. It was reported metal NPs can be selectively decorated on carbon nanomatierals by controlling the surface wetting properties³⁶ and it was also suggested the edges of 2D nanotmateirals may favor the anchoring of metal NPs³⁷. However, location dependence of metal NPs decoration on MoS₂ layers

was rarely reported. In this contribution, we study the controllable decoration of isolated MoS_2 single crystal prepared by chemical vapor deposition method (CVD-MoS₂) by Au NPs. The CVD-MoS₂ layers are in well-defined triangular shapes, providing a perfect template for the nanoparticle decoration. It was found that $AuCl_4$ ions can be reduced to neutral gold atoms selectively on the edge part, or defective sites of MoS_2 layers by a simple solution dip casting method. The quality of MoS_2 -Au NPs composite was evaluated by atomic force microscopy (AFM), transmission electron microscopy (TEM), selected area electron diffraction (SAED), X-ray energy dispersive spectroscopy (ZPS) and electrical characterizations.

Results

With the recently developed techniques for MoS₂ growth by CVD method, single layer and crystalline MoS₂ can be produced in a large scale on single crystal substrates¹⁶⁻¹⁸ or even an atomically thin graphene layer¹⁵. These highly crystalline CVD-MoS₂ layers serve as good model 2D material systems for us to investigate the growth mechanism of Au NPs on 2D materials. Fig. 1 (A) shows the AFM images of the MoS₂ sheets obtained on the sapphire substrates. Smooth surface morphology of MoS2 sheet is observed under AFM, which suggests that a layer structure of MoS₂ is formed. These continuous MoS₂ layers are formed by small triangular MoS₂ single crystals with a typical thickness of 0.71 nm (See supporting information Figure S1). According to the previous report³⁸, the triangular shape is a unique feature of the single-layer MoS₂ clusters, since the S edge terminations is considerably more stable. The inset in Fig. 1 (A) displays the non-continuous MoS_2 single crystals in a triangular shape, where the well-defined feature allows us to further study the reactivity of MoS₂ edges and basal planes. Fig. 1(B) provides AFM images of the MoS₂ nanosheets with Au NPs grown on them. The AFM images clearly show that small NPs with a diameter around 5 nm were formed after AuCl₄⁻ doping and there is no

particles found on the surface of substrate which suggests the selectively reduction reaction of AuCl₄⁻ on MoS₂ nanosheets. Interestingly, the Au NPs tend to form on the edge sites of MoS₂ with only few particles on the basal plane of MoS₂ layers. Previously we report the Au NPs tend to nucleate on the graphene wrinkles due to the morphology change which could trap the precursor and act as the initial nucleation centers for Au particle growth³⁹. Different from the chemical vapor deposited graphene (CVD-G), there is no obvious wrinkle formation on CVD-grown MoS2 nanosheets. The atomically flat surface morphology excludes the influence of different surface energy induced by surface smoothness. In this case, the preferential formation of Au NPs on the edge sites of MoS₂ indicates that the edge site is more reactive than the basal plane region. The edge area could attract the AuCl₄⁻ precursor at the initial stage, and act as the first nucleation center for Au growth. The intensity of photoluminescence (PL) peak and the energy separation between the Raman $A_{1\sigma}$ and $E_{2\sigma}$ peaks have been found to relate to the number of MoS₂ layers^{20,21}. Fig. 1 (C) shows the Raman and PL spectra for the MoS₂ layer, where the excitation light source is a continuous laser with a wavelength of 473 nm. The Raman peaks at 405 and 385.6 cm⁻¹ are identified as the A1g and E2g vibration modes, which are characteristics for MoS₂. The PL spectrum displays a distinct main emission peak at \sim 663 nm, which is in good agreement with the MoS₂ thin layer obtained from exfoliation method. The PL and Raman characterizations suggest the good crystallinity of the CVD-MoS₂.

XPS was applied to reveal the chemical composition of the nanosized particles. Fig. 2 shows the XPS spectra of the Au doped MOS_2 nanosheets on Sapphire substrates. As shown in Fig. 2 (A) and (B), the Mo 3d shows two peaks at 229.2 eV and 232.3 eV, which can be attributed to the doublet of Mo $3d_{5/2}$ and Mo $3d_{3/2}$. The binding energy for S $2p_{3/2}$ and S $2p_{1/2}$ are 162.0 eV and 163.3 eV, shown in Fig. 2 (B). The Mo and S binding energies are in good agreement with reported value⁴⁰, indicating that the doping of Au does not severely change the crystallinity of MOS_2 , and the MOS_2 monolayer



Figure 1 | MoS_2 nano-flakes on *c*-face sapphire substrate substrates. (A) Typical AFM height images of MoS_2 flakes grown on *c*-face sapphire substrates. Inset shows a non-continuous MoS_2 layers formed in triangular feature; (B) AFM image of the corresponding regions after Au nano particles decoration. For these samples, the Au precursor adsorption time was 20 seconds and rinsed with DI water after dip casting; (C) photoluminescence spectra for the obtained CVD- MoS_2 layers, inset shows the Raman spectra of the CVD- MoS_2 . Both Raman and PL experiments were performed using a confocal spectrometer with 476 nm excitation laser.





Figure 2 | Chemical composition analysis by X-Ray photoemission spectroscopy (XPS) for (A) Mo, (B) S, (C) Au and (D) Cl binding energies of the MoS_2 layers after Au nanoparticles decoration. The red cure in (A) and (B) display the corresponding spectrum taken from the pristine CVD- MoS_2 sample.

is chemically stable in HAuCl₄ aqueous solutions. The XPS scans for the MoS₂ samples after AuCl₄⁻ doping confirm the chemical bonding states of the MoS₂ layers and Au as displayed in Fig. 2 (C). No detectable Cl signal within the bonding energy ranging from 196 eV to 204 eV has been observed in Fig. 2 (D). This suggested that there is no physical adsorption of AuCl₄⁻ on MoS₂ surface and AuCl₄⁻ has been fully reduced to Au. The calculated atomic concentration of Mo, S and Au from XPS are 33.9%, 64.6% and 1.5% with a ratio of 1 : 1.90 : 0.044.

To explore the location dependency of Au NPs growth on MoS_2 layers and understand the tendency of the epitaxial stacking manner of Au NPs on MoS_2 nanosheets, the Au NPs/CVD- MoS_2 was investigated by analyzing the high resolution TEM (HRTEM) and the corresponding fast Fourier transform (FFT) images. The results were also compared with the Au doped chemical exfoliated MoS_2 (Au NPs/CE- MoS_2) which has a higher defect density.

Fig. 3 (A) and (B) are the TEM images of Au NPs/CVD-MoS₂, triangular nanosheets with well-proportioned NPs along the edge and sporadic ones on the surface region which is in good consistence with the AFM results. As observed in Fig. 3 (B), NPs appeared to be darker in contrast when compared to that of the MoS₂ nanosheets. We noticed that due to the low content of gold in the CVD-MoS₂ nanosheets, no Au element can be obviously detected in Au NPs/CVD-MoS₂ according to EDS (see supporting information Figure S2). Fig. 3 (C) displays a HRTEM image taken from the edge part of Au NPs/CVD-MoS₂. The inset shows the SAED pattern from the surface of CVD-MoS₂, which can be attributed to the 2H-MoS₂ single crystal^{15,16,18,19}. For the SAED analysis, in order to avoid cover

more than one piece of triangular MoS_2 flake, the aperture in TEM analysis was set to be 10 μ m (with the electron beam size of 150 nm), which is a bit smaller than that of the Au decorated MoS_2 flakes. Fig. 3 (D) depicts the HRTEM image of an Au NP which



Figure 3 | TEM images of the Au NPs decorated CVD-MoS₂ nano-flakes. (A) Low magnification TEM image of isolated single crystal MoS₂ flakes in triangular shape. (B) A zoomed-in TEM image of MoS₂ flakes with nanosize particles mostly adsorbed on the edge parts. (C) A typical HRTEM image taken from the edge of a MoS₂ flake. Inset shows the SAED pattern from the MoS₂ surface. (D) shows an enlarged HRTEM image of Au NPs on MoS₂ edge, the measured d spacing distance is around 0.23 nm.

clearly reveals a single crystal nature of Au nano-domain. The measured d spacing is around 0.23 nm which is in good consistence with the Au (111) spacing⁴¹. We also noticed although it is hard to indicate the grain boundaries of continuous CVD-MoS₂ layer, after Au decoration and rinsing process, part of the MoS₂ film could break and left mechanically formed MoS₂ edges (See supporting information Figure S3). The Au NPs tend to form on the exposed MoS₂ edges rather than on the basal plane region of MoS₂. These observations align well and suggest that the MoS₂ defects, especially for the edge area, may be more reactive than the basal surface.

In order to further examine the assumption regarding the relationship between Au NPs and the defects in MoS₂, MoS₂ films were also prepared by chemical exfoliation (CE-MoS₂) method and characterized by TEM. The chemical exfoliation method involves lithium ion intercalation between MoS₂ layers and ultra-sonication was applied to assist the further exfoliation of MoS₂ layers and forming few layer or monolayer MoS₂ nanosheets, therefore CE-MoS₂ was expected to possess more defects than the CVD-MoS₂. The HRTEM taken for CE-MoS₂ suggest that the CE-MoS₂ films exhibit poor crystallinity compared to the CVD-MoS₂ as expected. (See supporting materials Figure S4). Fig. 4 (A) and (B) displays the TEM image of the chemically exfoliated MoS₂ film after Au doping. Dramatically different from the CVD-MoS₂, both large and small Au NPs can be found on CE-MoS₂ as shown in Fig. 4 (A) and 4 (B). The particle density is also much higher than that observed from CVD-MoS₂. The inset images in Fig. 4 (B) shows the corresponding SAED images. The SAED image of a typical Au NPs decorated CE-MoS₂ film exhibits three distinguished rings which can be assigned to the MoS_2 {100}, {110} and Au {111} planes with lattice spacing of 0.27, 0.16 and 0.23 nm respectively. The characteristic electron diffraction ring assigned to the {111} planes of the face-centred-cubic (fcc) lattice of Au is much sharper and stronger in comparison with the other planes, revealing the predominant orientation of the Au {111} planes. The increase of Au NPs density on CE-MoS₂ strongly suggests that the forming of Au NPs is associated with the defects of MoS₂. The edge parts or defects in MoS₂ layers could interact with the AuCl₄⁻



Figure 4 | TEM images of the Au NPs/CE-MoS₂ film. (A) Low magnification TEM image of Au NPs/CE-MoS₂ film. (B) Enlarged TEM image of Au NPs/CE-MoS₂ film with various Au NPs size. The inset shows the SAED pattern from the film.) (C) A typical HRTEM image of small particle (\sim 2 nm) located on the CE-MoS₂ films; (D) HRTEM image of large Au particle (\sim 10 nm) located on the CE-MoS₂.

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precursor at the initial stage, and act as the first nucleation center for Au NPs growth, therefore the results suggest the Au NPs could effectively work as a defect marker for MoS₂ layers. HRTEM images were taken to further investigate the orientation relationship between MoS₂ film and Au particles Fig. 4 (C) and (D) show the HRTEM images of typical Au NPs on CE-MoS₂ with different particle sizes ranging from ~ 2 nm to ~ 10 nm. The HRTEM image in Fig. (D) displays an in plane lattice spacing of 0.23 nm which is in good agreement with the number of Au (111). Although it is not easy to determine the accurate lattice of CE-MoS₂ due to its defective polycrystalline nature, the SEAD and HRTEM results suggest that the defective sites in MoS₂ layers could effectively attract Au NPs precursor and serve as nucleation sites and the surface plane of MoS₂ serves as a growth temple for Au NPs along its {111} plane. It was previously reported single layer MoS₂ nano-islands can form on crystalline Au (111) surfaces with their (0001) basal plane oriented parallel to the Au (111) substrate surface³⁸. In this study, we propose at the very beginning, the AuCl₄⁻ ions adsorb onto the defective sites in MoS₂ layers and reduced to Au atoms which subsequently form Au nanoclusters, therefore the density of Au NPs depends on the defect density of MoS₂ layer. Meanwhile, the Au {111} has the lowest surface energy^{42,43} and small lattice mismatch with MoS₂ (0001), which promotes the preferential orientation of Au (111) crystal planes on MoS₂ surface.

Discussion

Various research methods have been developed aiming at tuning the electronic properties of 2D materials. According to our previous report^{39,44}, the work function of graphene layer can be effectively controlled by immersing graphene film in AuCl₄⁻ solution, due to the spontaneous reduction of Au³⁺ to Au⁰. Raman spectroscopy is a powerful nondestructive characterization tool to reveal the level of doping in single-layer MoS₂ due to the strong electron-phonon interaction^{45,46}. It has been reported that *n*-doping results in softening of the A1g phonon which results in decrease of relative intensity and peak frequency difference between A1g and E2g modes46 while pdoping in MoS₂ layers should cause relative shifting of the Ramanactive modes in opposite direction. Figure 5 (A) shows typical Raman spectra for a single layer MoS₂ sheet before and after Au NPs decoration. The MoS₂ layer exhibits two Raman characteristic bands at ${\sim}404$ and 386 cm $^{-1}\!,$ corresponding to the A_{1g} and E_{2g} modes respectively. It was reported oxygen in the ambient may attack Mo-S-Mo bands and cause the shift of Raman vibrations modes⁴⁵. To reduce the influence from the ambient oxygen, the Raman spectra were taken right after the CVD synthesis and/or Au NPs decoration. It was also noticed that the Raman spectra shows some variation across the sample surface, therefore to reveal the doping effect of Au NPs a set of data points were taken and statistical analysis were carried out as shown in Figure 5 (B) and (C). Figure 5(B) and (C) compare the relative peak intensity and frequency difference shift of A1g and E2g Raman modes, respectively. The results showing a detectable upshift of A1g frequency and an increase of A1g/E2g peak intensity ratio, which suggest distinct p-doping caused by Au NPs decoration^{45,46}. To further evaluate doping effect of Au NPs on CVD-MoS₂ electrically, top-gate transistors were fabricated by evaporating Au/Ti electrodes directly on top of the MoS₂ layers on sapphire substrate. The MoS₂ electric double-layer transistors (EDLTs)^{47,48} were formed with an ionic gel film which works as dielectric layer for the transistor. Details of device fabrication can be found in the previous report⁴⁸. It is worthy to mention, since the devices are directly fabricated on the growth substrates and no transfer process is involved, the intrinsic transport properties of CVD-MoS₂ layers and the effect of Au NPs on the transistor performance can be directly accessed. Fig. 5 (D) shows the transfer curve of CVD-MoS₂ EDLTs before and after Au NPs decoration. Supporting information Figure S5 shows the I-Vg curves plotted in log scale.





Figure 5 | (A) Typical Raman spectra of MoS_2 sheets before and after Au NPs decoration; (B) and (C) show the statistical analysis of the relative intensity and frequency change in E_{2g} and A_{1g} vibration mode induced by the Au NPs decoration; (D) Thin-film MoS_2 EDLT constructed with an ion gel dielectric layer. Black and red lines correspond to the transfer characteristics of the MoS_2 EDLT before and after Au NPs decoration. The inset schematically illustrates the device structure, the source and drain electrodes were electrically isolated from the ion gel by a thin PDMS layer.

The pristine CVD-MoS₂ EDLTs show typical transfer curves of n-typed behavior which is consistent with the other reports. Au/Ti (80 nm and 5 nm, respectively) were used as the source/drain electrodes. The work function of Ti is closer to the conduction band edge of MoS₂ and results an expected *n*-typed behaviors. After Au NPs decoration, the threshold gate voltage changes from 0.47 V to 1.29 V and the transfer curve shifts to the right hand side which indicates that a p-doing effect has been introduced by the Au NPs. The electrical results are consistent with the Raman characterizations confirming that the AuCl₄⁻ ions in solution can strongly withdraw electrons from MoS₂ layers and reduces to Au NPs, therefore, it is anticipated for a down shift of Fermi level in MoS₂ layers. It is found that the on/off ratio for the device after Au NPs doing is around 3.54×10^3 , which is around 50 times larger than that of the pristine MoS₂ electric double-layer transistors (EDLT). The measured maximum current for the doped and pristine MoS₂ EDLT is 13.7 mA and 22.5 mA, respectively. The mobility of the MoS₂ EDLT can be derived from the slope of the transfer characteristics using the standard equation $I_d = (\mu W V_D C_i / L) (V_G - V_{th})$ for the linear region⁴⁸. Where I_d is the drain current, μ is the field-effect mobility, W is the channel width, V_D is the drain voltage, C_i is the specific capacitance of the dielectric, L is the channel length, V_G is the gate voltage, and V_{th} is the threshold voltage. From the calculation, the mobility for Au NPs doped MoS₂ is around 2.44 cm²/(Vs), which is 2 times smaller than the pristine MoS₂ EDLT.

In conclusion, we have proposed a simple method to decorate the CVD-MoS₂ and CE-MoS₂ thin layers with Au NPs. AFM, TEM, XPS characterization methods were carried out to investigate the growth

mechanism and epitaxial stacking manner of Au NPs and MoS_2 . The Au NPs exhibited a remarkable *p*-doping effect to the MoS_2 transistors . Hence, the proposed Au NPs decoration method can provide promising nanomaterials hybrids for the application of future optoelectronics devices.

Methods

CVD-MoS₂ synthesis. High-crystal-quality MoS₂ were grown on a sapphire substrates by chemical vapor deposition method inside a horizontal tube furnace. The detailed fabrication procedure can be found elsewhere^{17,18}. To be brief, the MoS₂ films were synthesized on c-face sapphire substrates in a hot-wall furnace. High purity MoO₃ (99%, Aldrich) and S powder (99.5, Alfa) were placed in two separated Al₂O₃ crucibles and the substrates were placed on the downstream side of the Ar carrying gas. The MoS₂ samples were obtained by annealing at 650°C for 15 min with a heating rate of 15°C/min and Ar flow rate was kept at 1 sccm.

Chemical exfoliated MoS₂. The MoS₂ nanoflakes were obtained by lithium intercalation method follow the procedure reported before²⁰. 0.5 g of natural MoS₂ crystals from Sigma-Aldrich were dispersed in 5 mL of 1.6 M butylithium solution in hexane (Sigma-Aldrich) for 48 hours in a flask filled with argon gas. The Li_xMoS₂ was retrieved by filtration and washed with hexane (60 mL) to remove excess lithium and organic residues. Exfoliation was achieved by ultrasonicating the obtained Li_xMoS₂ slurry in DI-water for 1 h. The mixture was centrifuged and re-dispersed in DI water for at least 5 times to remove excess lithium in the form of LiOH and unexfoliated material. Thin films were prepared by filtering through a mixed cellulose ester membrane with 0.025 μ m pores (Millipore). The film was delaminated on water surface for subsequent transfer onto substrates or TEM Grids.

Au NPs decoration on CVD-MoS₂ and CE-MoS₂. AuCl₃ dissolved in water was used for the growth of Au nano particles (Au NPs) on MoS₂. To prepare Au NPs/ CVD-MoS₂, the as prepared CVD-MoS₂ on sapphire substrates were directly immersed in 5 mM AuCl₃ for 20 sec, followed by gently rinsing with DI water. To prepare Au NPs/CE MoS₂ samples, the CE MoS₂ film was firstly delaminated on water surface by the previously described method²⁰. Several drops of 5 mM AuCl₃ water solution were added into the water subsequently. Finally, the Au NPs/CE-MoS₂ floating on water surface can be picked up by TEM grids or arbitrary substrates.

Transfer of the as-grown Au NPs/MoS₂ hybrid to arbitrary substrates. The CVD-MoS₂ and Au NPs decorated MoS₂ films was transferred by coating the film with a thin layer (~100 nm) of Poly[methylmethacrylate] (PMMA). After etching the underlying sapphire substrates with KOH aquariums (with a concentration of 2 M) at 80°C, the PMMA/MoS₂ film was transferred to DI water and was suspended on the surface of water to remove the etchant residue. Subsequently, the film can be transferred to any substrate or TEM grids for analysis and characterization. Finally, the top layer of PMMA can be removed by acetone or by directly annealing the samples in an Ar and H₂ atmosphere at 400°C for 2 hours.

Characterizations. Surface morphology of the samples was examined with commercial atomic force microscope (AFM, Veeco Icon). Raman spectra were collected in a NT-MDT confocal Raman microscopic system with exciting laser wavelength of 473 nm and the laser spot-size is around 0.5 μ m. For the Raman characterization, the Si peak at 520 cm⁻¹ was used as reference for wavenumber calibration. Field-emission transmission electron microscope (JEOL JEM-2010F, operated at 200 keV), equipped with an energy dispersive spectrometer (EDS) was used to obtain the information of the microstructures and the chemical compositions. Chemical composition was determined by X-ray photoelectron spectroscope (XPS, Phi V5000). XPS measurements were performed with an Al K α X-ray source. The energy calibrations were made against the C 1s peak to eliminate the charging of the sample during analysis.

- 1. Geim, A. K. & Novoselov, K. S. The rise of graphene. Nat Mater 6, 183-191 (2007).
- 2. Novoselov, K. S. *et al.* Two-dimensional gas of massless Dirac fermions in graphene. *Nature* **438**, 197–200 (2005).
- Novoselov, K. S. et al. Electric Field Effect in Atomically Thin Carbon Films. Science 306, 666–669 (2004).
- Kubota, Y., Watanabe, K., Tsuda, O. & Taniguchi, T. Deep Ultraviolet Light-Emitting Hexagonal Boron Nitride Synthesized at Atmospheric Pressure. *Science* 317, 932–934 (2007).
- Dean, C. R. et al. Boron nitride substrates for high-quality graphene electronics. Nat Nano 5, 722–726 (2010).
- Radisavljevic, B., Radenovic, A., Brivio, J., Giacometti, V. & Kis, A. Single-layer MoS₂ transistors. *Nat Nano* 6, 147–150 (2011).
- Lembke, D. & Kis, A. Breakdown of High-Performance Monolayer MoS₂ Transistors. ACS Nano 6, 10070–10075 (2012).
- Wang, H. et al. Integrated Circuits Based on Bilayer MoS₂ Transistors. Nano Lett 12, 4674–4680 (2012).
- Chang, Y.-H. *et al.* Highly Efficient Electrocatalytic Hydrogen Production by MoS_x Grown on Graphene-Protected 3D Ni Foams. *Adv Mater* 25, 756–760 (2013).
- Li, Y. et al. MoS₂ Nanoparticles Grown on Graphene: An Advanced Catalyst for the Hydrogen Evolution Reaction. J Am Chem Soc 133, 7296–7299 (2011).
- Kong, D. et al. Synthesis of MoS₂ and MoSe₂ Films with Vertically Aligned Layers. Nano Lett 13, 1341–1347 (2013).
- Mak, K. F., Lee, C., Hone, J., Shan, J. & Heinz, T. F. Atomically Thin MoS₂: A New Direct-Gap Semiconductor. *Physical Review Letters* 105, 136805 (2010).
- 13. Coleman, J. N. *et al.* Two-Dimensional Nanosheets Produced by Liquid Exfoliation of Layered Materials. *Science* **331**, 568–571 (2011).
- Gordon, R. A., Yang, D., Crozier, E. D., Jiang, D. T. & Frindt, R. F. Structures of exfoliated single layers of WS₂, MoS₂, and MoSe₂ in aqueous suspension. *Physical Review B* 65, 125407 (2002).
- Shi, Y. et al. van der Waals Epitaxy of MoS₂ Layers Using Graphene As Growth Templates. Nano Lett 12, 2784–2791 (2012).
- Liu, K.-K. *et al.* Growth of Large-Area and Highly Crystalline MoS₂ Thin Layers on Insulating Substrates. *Nano Lett* **12**, 1538–1544 (2012).
- Lin, Y.-C. et al. Wafer-scale MoS₂ thin layers prepared by MoO₃ sulfurization. Nanoscale 4, 6637-6641 (2012).
- Lee, Y.-H. *et al.* Synthesis of Large-Area MoS₂ Atomic Layers with Chemical Vapor Deposition. *Adv Mater* 24, 2320–2325 (2012).
- Zhan, Y., Liu, Z., Najmaei, S., Ajayan, P. M. & Lou, J. Large-Area Vapor-Phase Growth and Characterization of MoS₂ Atomic Layers on a SiO₂ Substrate. *Small* 8, 966–971 (2012).
- Eda, G. et al. Photoluminescence from Chemically Exfoliated MoS₂. Nano Lett 11, 5111–5116 (2011).
- Splendiani, A. *et al.* Emerging Photoluminescence in Monolayer MoS₂. *Nano Lett* 10, 1271–1275 (2010).
- Brivio, J., Alexander, D. T. L. & Kis, A. Ripples and Layers in Ultrathin MoS₂ Membranes. Nano Lett 11, 5148–5153 (2011).
- Laursen, A. B., Kegnaes, S., Dahl, S. & Chorkendorff, I. Molybdenum sulfidesefficient and viable materials for electro - and photoelectrocatalytic hydrogen evolution. *Energy & Environmental Science* 5, 5577–5591 (2012).

- Chen, Z. et al. Core-shell MoO₃-MoS₂ Nanowires for Hydrogen Evolution: A Functional Design for Electrocatalytic Materials. Nano Lett 11, 4168–4175 (2011).
- Zong, X. et al. Photocatalytic H₂ Evolution on MoS₂/CdS Catalysts under Visible Light Irradiation. The Journal of Physical Chemistry C 114, 1963–1968 (2010).
- Bonde, J., Moses, P. G., Jaramillo, T. F., Norskov, J. K. & Chorkendorff, I. Hydrogen evolution on nano-particulate transition metal sulfides. *Faraday Discuss* 140, 219–231 (2009).
- Zhou, W. et al. Synthesis of Few-Layer MoS₂ Nanosheet-Coated TiO₂ Nanobelt Heterostructures for Enhanced Photocatalytic Activities. Small 9, 140–147 (2013).
- Jaramillo, T. F. *et al.* Identification of Active Edge Sites for Electrochemical H₂ Evolution from MoS₂ Nanocatalysts. *Science* **317**, 100–102 (2007).
- Dong, X., Shi, Y., Huang, W., Chen, P. & Li, L.-J. Electrical Detection of DNA Hybridization with Single-Base Specificity Using Transistors Based on CVD-Grown Graphene Sheets. Adv Mater 22, 1649–1653 (2010).
- He, S. et al. Graphene-Based High-Efficiency Surface-Enhanced Raman Scattering-Active Platform for Sensitive and Multiplex DNA Detection. Anal Chem 84, 4622–4627 (2012).
- Qian, H., Zhu, Y. & Jin, R. Atomically precise gold nanocrystal molecules with surface plasmon resonance. *Proceedings of the National Academy of Sciences*. DOI 10.1073/pnas.1115307109 (2012).
- 32. Huang, F. & Baumberg, J. J. Actively Tuned Plasmons on Elastomerically Driven Au Nanoparticle Dimers. *Nano Lett* **10**, 1787–1792 (2010).
- Lu, Y.-C. et al. Platinum-Gold Nanoparticles: A Highly Active Bifunctional Electrocatalyst for Rechargeable Lithium-Air Batteries. J Am Chem Soc 132, 12170-12171 (2010).
- Murdoch, M. *et al.* The effect of gold loading and particle size on photocatalytic hydrogen production from ethanol over Au/TiO₂ nanoparticles. *Nat Chem* 3, 489–492 (2011).
- Huang, X. *et al.* Solution-phase epitaxial growth of noble metal nanostructures on dispersible single-layer molybdenum disulfide nanosheets. *Nat Commun* 4, 1444 (2013).
- 36. Yick, S., Han, Z. J. & Ostrikov, K. Atmospheric microplasma-functionalized 3D microfluidic strips within dense carbon nanotube arrays confine Au nanodots for SERS sensing. *Chem Commun* 49, 2861–2863 (2013).
- Rider, A. E., Kumar, S., Furman, S. A. & Ostrikov, K. Self-organized Au nanoarrays on vertical graphenes: an advanced three-dimensional sensing platform. *Chem Commun* 48, 2659–2661 (2012).
- Helveg, S. et al. Atomic-Scale Structure of Single-Layer MoS₂ Nanoclusters. Phys Rev Lett 84, 951–954 (2000).
- 39. Kim, K. K. *et al.* Enhancing the conductivity of transparent graphene films via doping. *Nanotechnology* **21**, 285205 (2010).
- Baker, M. A., Gilmore, R., Lenardi, C. & Gissler, W. XPS investigation of preferential sputtering of S from MoS2 and determination of MoS_x stoichiometry from Mo and S peak positions. *Appl Surf Sci* 150, 255–262 (1999).
- 41. Huang, X. et al. Synthesis of hexagonal close-packed gold nanostructures. Nat Commun 2, 292 (2011).
- 42. Chen, M., Wu, B., Yang, J. & Zheng, N. Small Adsorbate-Assisted Shape Control of Pd and Pt Nanocrystals. *Adv Mater* **24**, 862–879 (2012).
- Wang, A.-J. et al. Melamine assisted one-pot synthesis of Au nanoflowers and their catalytic activity towards p-nitrophenol. New J Chem 36, 2286–2291 (2012).
- 44. Shi, Y. *et al.* Work Function Engineering of Graphene Electrode via Chemical Doping. *Acs Nano* **4**, 2689–2694 (2010).
- Li, H. et al. From Bulk to Monolayer MoS₂: Evolution of Raman Scattering. Adv Funct Mater 22, 1385–1390 (2012).
- Chakraborty, B. et al. Symmetry-dependent phonon renormalization in monolayer MoS₂ transistor. Phys Rev B 85, 161403 (2012).
- Braga, D., Gutiérrez Lezama, I., Berger, H. & Morpurgo, A. F. Quantitative Determination of the Band Gap of WS2 with Ambipolar Ionic Liquid-Gated Transistors. *Nano Lett* 12, 5218–5223 (2012).
- Pu, J. et al. Highly Flexible MoS₂ Thin-Film Transistors with Ion Gel Dielectrics. Nano Lett 12, 4013–4017 (2012).

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Author Contributions

Y. Shi and H.Y. Yang conceived and designed the study. Y. Shi and H.Y. Yang wrote the manuscript. Y. Shi, J. Huang and L. Jin performed the experiments. Y. Hsu helped to do the experiments. L.J. Li and S.F. Yu gave scientific advice. All the authors contributed to discussion and reviewed the manuscript.

Additional information

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