



# Selective Decoration of Au Nanoparticles on Monolayer MoS<sub>2</sub> Single Crystals

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We report a controllable wet method for effective decoration of 2-dimensional (2D) molybdenum disulfide (MoS<sub>2</sub>) layers with Au nanoparticles (NPs). Au NPs can be selectively formed on the edge sites or defective sites of MoS<sub>2</sub> layers. The Au-MoS<sub>2</sub> 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<sub>2</sub> layers. Field effect transistors were directly fabricated by placing ion gel gate dielectrics on Au-decorated MoS<sub>2</sub> layers without the need to transfer these MoS<sub>2</sub> layers to SiO<sub>2</sub>/Si substrates for bottom gate devices. The ion gel method allows probing the intrinsic electrical properties of the as-grown and Au-decorated MoS<sub>2</sub> layers. This study shows that Au NPs impose remarkable *p*-doping effects to the MoS<sub>2</sub> transistors without degrading their electrical characteristics.

Due to their unique properties, atomically thin two-dimensional (2D) materials with a layered structure such as graphene<sup>1–3</sup>, hexagonal boron nitride (*h*-BN)<sup>4,5</sup> and transition-metal dichalcogenide (LTMDs)<sup>6–8</sup> have been attracting increasing attention. Molybdenum disulfide (MoS<sub>2</sub>), 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)<sup>9–11</sup>. In recent years, it has been demonstrated that ultra-thin MoS<sub>2</sub> crystals with a typical thickness of ~0.65 nm can be obtained by either physical<sup>6,12</sup> or chemical exfoliation methods<sup>13,14</sup>. MoS<sub>2</sub> layers with uniform thickness can also be synthesized in large scale by chemical vapor deposition<sup>15–19</sup>. The monolayer MoS<sub>2</sub> exhibits excellent electrical<sup>6–8</sup> and optical performance<sup>20,21</sup> compared to its bulky counterpart.

MoS<sub>2</sub> can be seen as an inorganic graphene analogue, similar to graphene and *h*-BN. The structure of MoS<sub>2</sub> is based on a hexagonal crystal<sup>22</sup>, 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<sub>2</sub> is catalytically inactive, and the activity in the HDS and HER is associated with the edge termination of MoS<sub>2</sub> clusters<sup>9–11,23</sup>. Especially for the MoS<sub>2</sub> 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<sup>10,24–27</sup>, which could be a promising clean energy source. The better understanding of catalytical active edge sites of MoS<sub>2</sub> is critical for the advanced catalysts design and developing its practical applications<sup>28</sup>. 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<sup>29,30</sup>, photonics<sup>31,32</sup> and catalysis<sup>33,34</sup>. It can be expected that the noble metal nanoparticles (NPs) anchored on the MoS<sub>2</sub> sheet could potentially extend its functionalities as novel catalytic, magnetic, and optoelectronic nanomaterials<sup>28,35</sup>. Furthermore, compared with graphene, MoS<sub>2</sub> is a semiconducting material with a suitable band gap around 1.2 to 1.9 eV, depending on its thickness<sup>6,20,21</sup>. 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 MoS<sub>2</sub> layers by chemical doping methods are still lack of investigation. It was reported metal NPs can be selectively decorated on carbon nanomaterials by controlling the surface wetting properties<sup>36</sup> and it was also suggested the edges of 2D nanomaterials may favor the anchoring of metal NPs<sup>37</sup>. However, location dependence of metal NPs decoration on MoS<sub>2</sub> layers



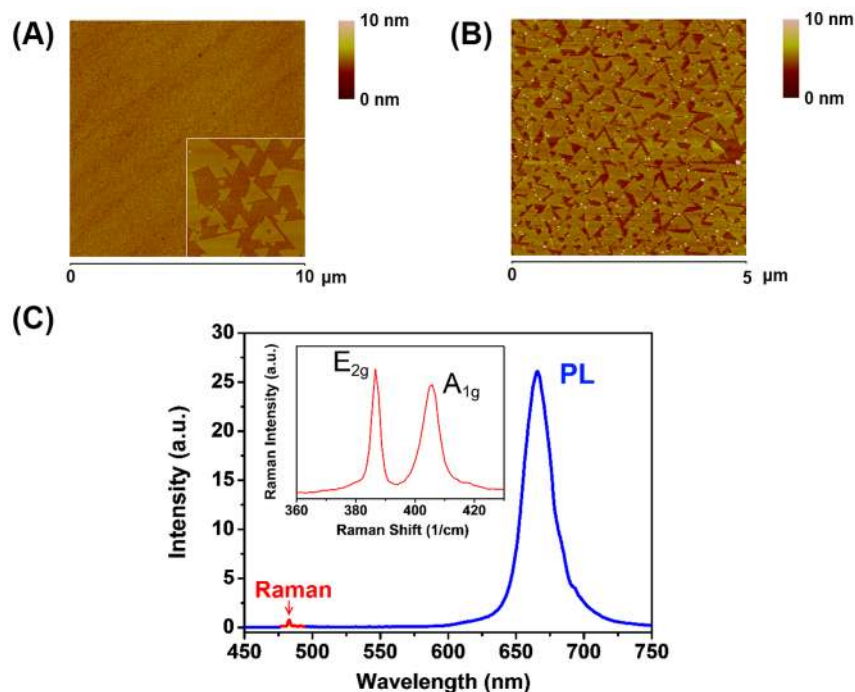
was rarely reported. In this contribution, we study the controllable decoration of isolated MoS<sub>2</sub> single crystal prepared by chemical vapor deposition method (CVD-MoS<sub>2</sub>) by Au NPs. The CVD-MoS<sub>2</sub> layers are in well-defined triangular shapes, providing a perfect template for the nanoparticle decoration. It was found that AuCl<sub>4</sub><sup>-</sup> ions can be reduced to neutral gold atoms selectively on the edge part, or defective sites of MoS<sub>2</sub> layers by a simple solution dip casting method. The quality of MoS<sub>2</sub>-Au NPs composite was evaluated by atomic force microscopy (AFM), transmission electron microscopy (TEM), selected area electron diffraction (SAED), X-ray energy dispersive spectroscopy (EDS), Raman spectroscopy, X-ray photoelectron spectroscopy (XPS) and electrical characterizations.

## Results

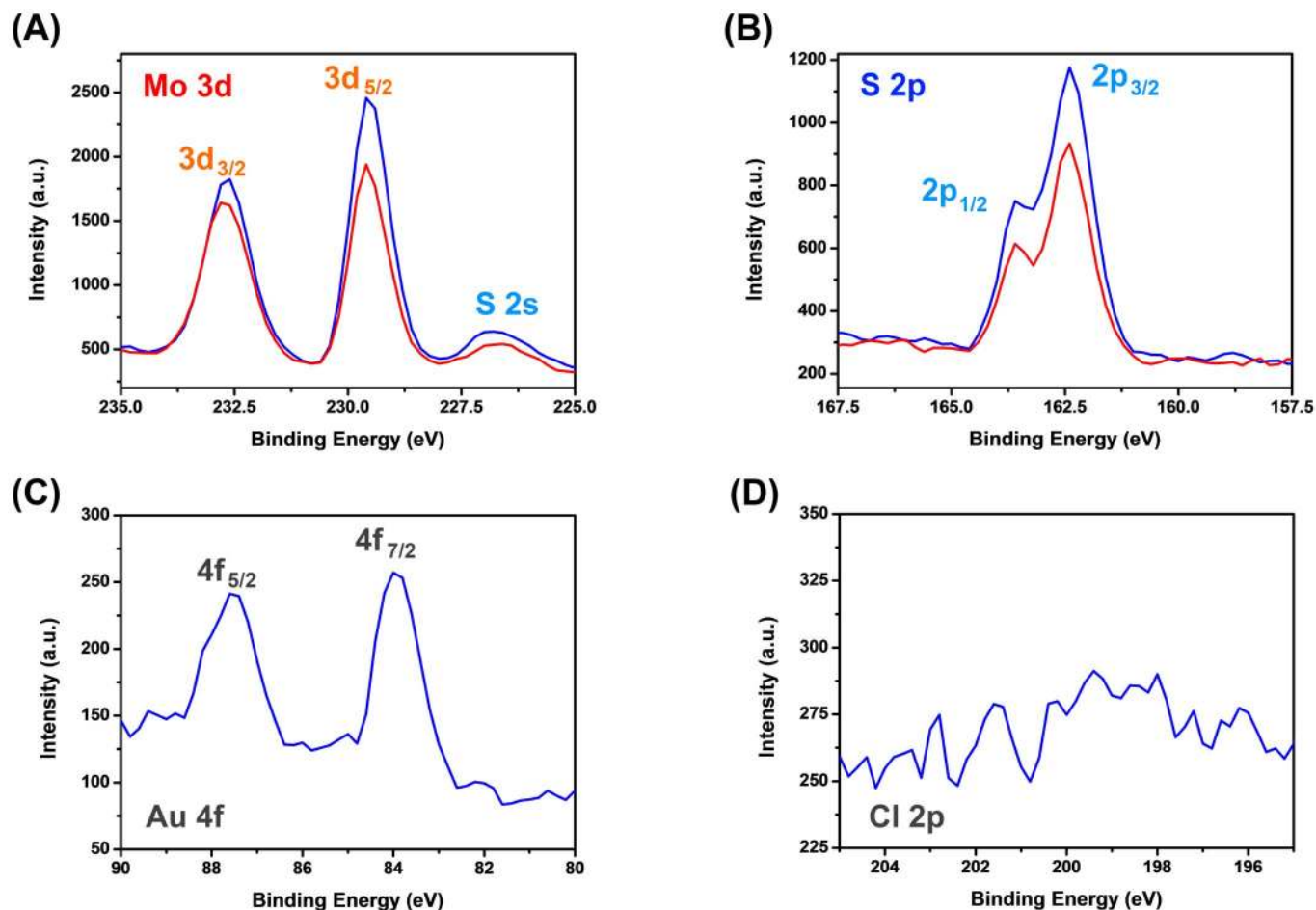
With the recently developed techniques for MoS<sub>2</sub> growth by CVD method, single layer and crystalline MoS<sub>2</sub> can be produced in a large scale on single crystal substrates<sup>16–18</sup> or even an atomically thin graphene layer<sup>15</sup>. These highly crystalline CVD-MoS<sub>2</sub> 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 MoS<sub>2</sub> sheets obtained on the sapphire substrates. Smooth surface morphology of MoS<sub>2</sub> sheet is observed under AFM, which suggests that a layer structure of MoS<sub>2</sub> is formed. These continuous MoS<sub>2</sub> layers are formed by small triangular MoS<sub>2</sub> single crystals with a typical thickness of 0.71 nm (See supporting information Figure S1). According to the previous report<sup>38</sup>, the triangular shape is a unique feature of the single-layer MoS<sub>2</sub> clusters, since the S edge terminations is considerably more stable. The inset in Fig. 1 (A) displays the non-continuous MoS<sub>2</sub> single crystals in a triangular shape, where the well-defined feature allows us to further study the reactivity of MoS<sub>2</sub> edges and basal planes. Fig. 1(B) provides AFM images of the MoS<sub>2</sub> nanosheets with Au NPs grown on them. The AFM images clearly show that small NPs with a diameter around 5 nm were formed after AuCl<sub>4</sub><sup>-</sup> doping and there is no

particles found on the surface of substrate which suggests the selectively reduction reaction of AuCl<sub>4</sub><sup>-</sup> on MoS<sub>2</sub> nanosheets. Interestingly, the Au NPs tend to form on the edge sites of MoS<sub>2</sub> with only few particles on the basal plane of MoS<sub>2</sub> 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 growth<sup>39</sup>. Different from the chemical vapor deposited graphene (CVD-G), there is no obvious wrinkle formation on CVD-grown MoS<sub>2</sub> 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 MoS<sub>2</sub> indicates that the edge site is more reactive than the basal plane region. The edge area could attract the AuCl<sub>4</sub><sup>-</sup> 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<sub>1g</sub> and E<sub>2g</sub> peaks have been found to relate to the number of MoS<sub>2</sub> layers<sup>20,21</sup>. Fig. 1 (C) shows the Raman and PL spectra for the MoS<sub>2</sub> 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<sup>-1</sup> are identified as the A<sub>1g</sub> and E<sub>2g</sub> vibration modes, which are characteristics for MoS<sub>2</sub>. The PL spectrum displays a distinct main emission peak at ~663 nm, which is in good agreement with the MoS<sub>2</sub> thin layer obtained from exfoliation method. The PL and Raman characterizations suggest the good crystallinity of the CVD-MoS<sub>2</sub>.

XPS was applied to reveal the chemical composition of the nano-sized particles. Fig. 2 shows the XPS spectra of the Au doped MoS<sub>2</sub> 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<sub>5/2</sub> and Mo 3d<sub>3/2</sub>. The binding energy for S 2p<sub>3/2</sub> and S 2p<sub>1/2</sub> 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 value<sup>40</sup>, indicating that the doping of Au does not severely change the crystallinity of MoS<sub>2</sub>, and the MoS<sub>2</sub> monolayer



**Figure 1** | MoS<sub>2</sub> nano-flakes on *c*-face sapphire substrate substrates. (A) Typical AFM height images of MoS<sub>2</sub> flakes grown on *c*-face sapphire substrates. Inset shows a non-continuous MoS<sub>2</sub> 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<sub>2</sub> layers, inset shows the Raman spectra of the CVD-MoS<sub>2</sub>. Both Raman and PL experiments were performed using a confocal spectrometer with 476 nm excitation laser.



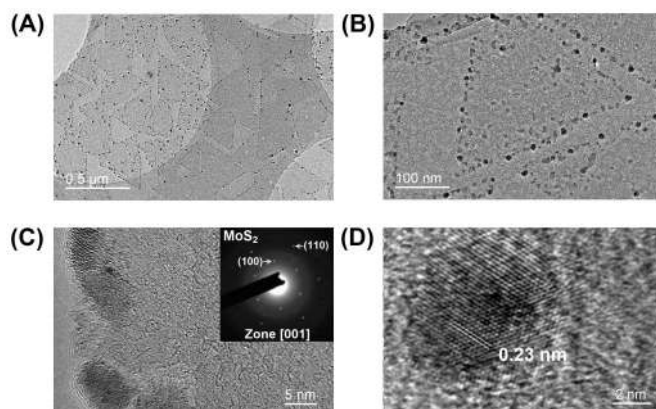
**Figure 2** | Chemical composition analysis by X-Ray photoemission spectroscopy (XPS) for (A) Mo, (B) S, (C) Au and (D) Cl binding energies of the MoS<sub>2</sub> layers after Au nanoparticles decoration. The red curve in (A) and (B) display the corresponding spectrum taken from the pristine CVD-MoS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

is chemically stable in HAuCl<sub>4</sub> aqueous solutions. The XPS scans for the MoS<sub>2</sub> samples after AuCl<sub>4</sub><sup>-</sup> doping confirm the chemical bonding states of the MoS<sub>2</sub> 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 AuCl<sub>4</sub><sup>-</sup> on MoS<sub>2</sub> surface and AuCl<sub>4</sub><sup>-</sup> 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<sub>2</sub> layers and understand the tendency of the epitaxial stacking manner of Au NPs on MoS<sub>2</sub> nanosheets, the Au NPs/CVD-MoS<sub>2</sub> 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<sub>2</sub> (Au NPs/CE-MoS<sub>2</sub>) which has a higher defect density.

Fig. 3 (A) and (B) are the TEM images of Au NPs/CVD-MoS<sub>2</sub>, 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 MoS<sub>2</sub> nanosheets. We noticed that due to the low content of gold in the CVD-MoS<sub>2</sub> nanosheets, no Au element can be obviously detected in Au NPs/CVD-MoS<sub>2</sub> according to EDS (see supporting information Figure S2). Fig. 3 (C) displays a HRTEM image taken from the edge part of Au NPs/CVD-MoS<sub>2</sub>. The inset shows the SAED pattern from the surface of CVD-MoS<sub>2</sub>, which can be attributed to the 2H-MoS<sub>2</sub> single crystal<sup>15,16,18,19</sup>. For the SAED analysis, in order to avoid cover

more than one piece of triangular MoS<sub>2</sub> flake, the aperture in TEM analysis was set to be 10 μm (with the electron beam size of 150 nm), which is a bit smaller than that of the Au decorated MoS<sub>2</sub> flakes. Fig. 3 (D) depicts the HRTEM image of an Au NP which



**Figure 3** | TEM images of the Au NPs decorated CVD-MoS<sub>2</sub> nano-flakes. (A) Low magnification TEM image of isolated single crystal MoS<sub>2</sub> flakes in triangular shape. (B) A zoomed-in TEM image of MoS<sub>2</sub> flakes with nano-size particles mostly adsorbed on the edge parts. (C) A typical HRTEM image taken from the edge of a MoS<sub>2</sub> flake. Inset shows the SAED pattern from the surface of CVD-MoS<sub>2</sub>. (D) Shows an enlarged HRTEM image of Au NPs on MoS<sub>2</sub> edge, the measured d spacing is around 0.23 nm.



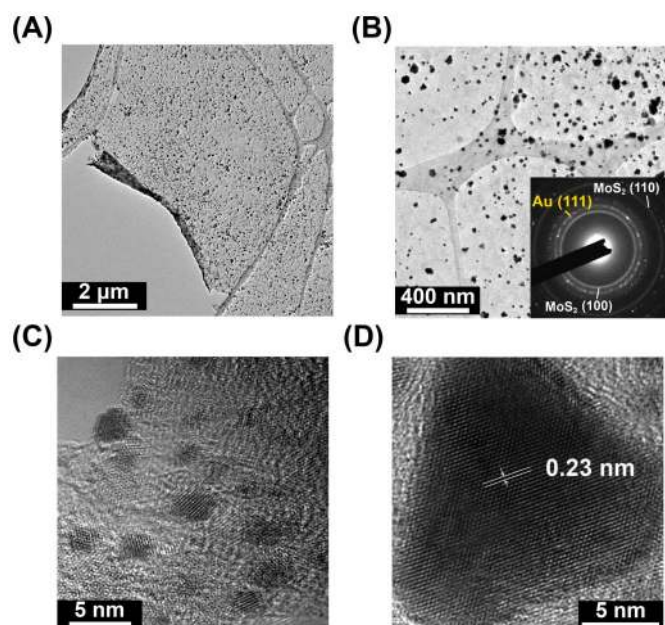
clearly reveals a single crystal nature of Au nano-domain. The measured  $d$  spacing is around 0.23 nm which is in good consistence with the Au (111) spacing<sup>41</sup>. We also noticed although it is hard to indicate the grain boundaries of continuous CVD-MoS<sub>2</sub> layer, after Au decoration and rinsing process, part of the MoS<sub>2</sub> film could break and left mechanically formed MoS<sub>2</sub> edges (See supporting information Figure S3). The Au NPs tend to form on the exposed MoS<sub>2</sub> edges rather than on the basal plane region of MoS<sub>2</sub>. These observations align well and suggest that the MoS<sub>2</sub> 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 MoS<sub>2</sub>, MoS<sub>2</sub> films were also prepared by chemical exfoliation (CE-MoS<sub>2</sub>) method and characterized by TEM. The chemical exfoliation method involves lithium ion intercalation between MoS<sub>2</sub> layers and ultra-sonication was applied to assist the further exfoliation of MoS<sub>2</sub> layers and forming few layer or monolayer MoS<sub>2</sub> nanosheets, therefore CE-MoS<sub>2</sub> was expected to possess more defects than the CVD-MoS<sub>2</sub>. The HRTEM taken for CE-MoS<sub>2</sub> suggest that the CE-MoS<sub>2</sub> films exhibit poor crystallinity compared to the CVD-MoS<sub>2</sub> as expected. (See supporting materials Figure S4). Fig. 4 (A) and (B) displays the TEM image of the chemically exfoliated MoS<sub>2</sub> film after Au doping. Dramatically different from the CVD-MoS<sub>2</sub>, both large and small Au NPs can be found on CE-MoS<sub>2</sub> as shown in Fig. 4 (A) and 4 (B). The particle density is also much higher than that observed from CVD-MoS<sub>2</sub>. The inset images in Fig. 4 (B) shows the corresponding SAED images. The SAED image of a typical Au NPs decorated CE-MoS<sub>2</sub> film exhibits three distinguished rings which can be assigned to the MoS<sub>2</sub> {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-MoS<sub>2</sub> strongly suggests that the forming of Au NPs is associated with the defects of MoS<sub>2</sub>. The edge parts or defects in MoS<sub>2</sub> layers could interact with the AuCl<sub>4</sub><sup>-</sup>

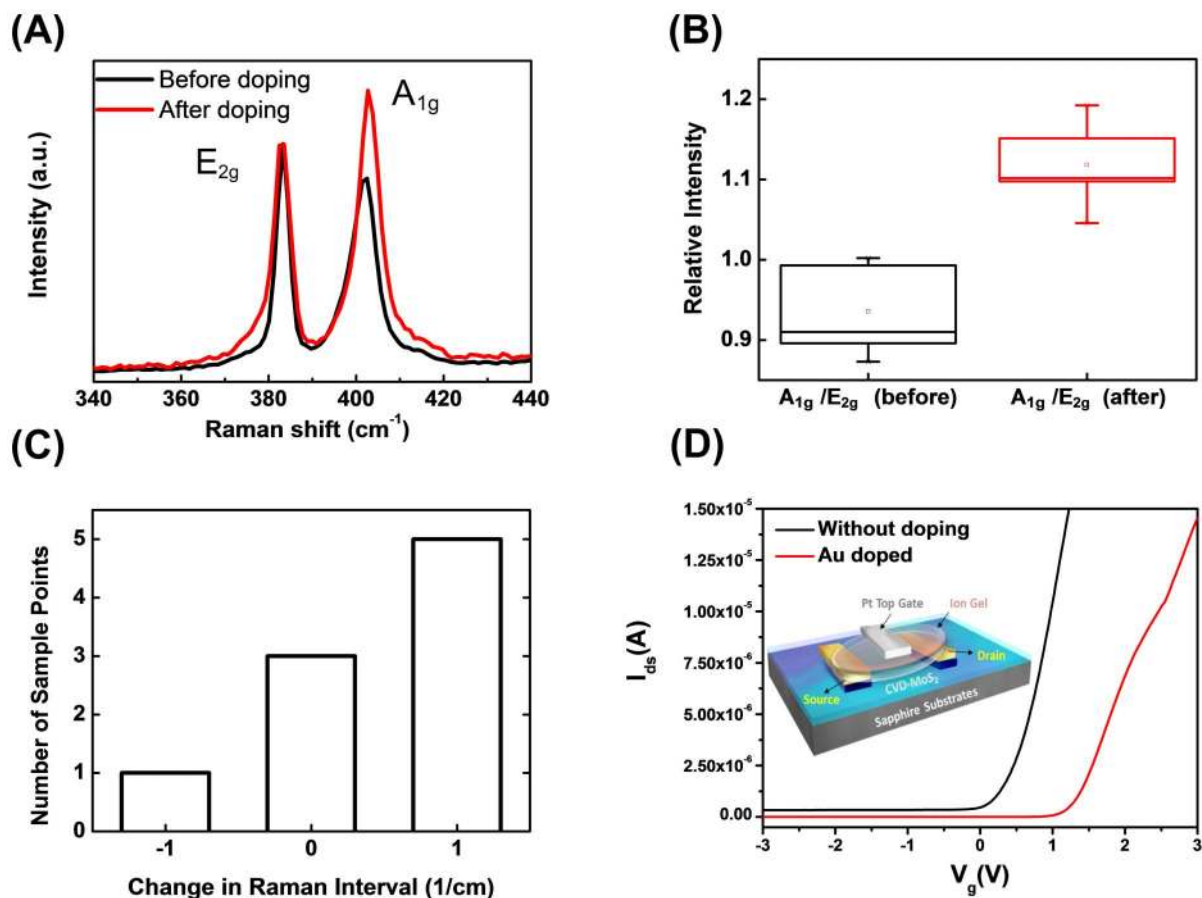
precursor at the initial stage, and act as the first nucleation center for Au NPs growth, therefore the results suggest the Au NPs could effectively work as a defect marker for MoS<sub>2</sub> layers. HRTEM images were taken to further investigate the orientation relationship between MoS<sub>2</sub> film and Au particles Fig. 4 (C) and (D) show the HRTEM images of typical Au NPs on CE-MoS<sub>2</sub> 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-MoS<sub>2</sub> due to its defective polycrystalline nature, the SEAD and HRTEM results suggest that the defective sites in MoS<sub>2</sub> layers could effectively attract Au NPs precursor and serve as nucleation sites and the surface plane of MoS<sub>2</sub> serves as a growth temple for Au NPs along its {111} plane. It was previously reported single layer MoS<sub>2</sub> nano-islands can form on crystalline Au (111) surfaces with their (0001) basal plane oriented parallel to the Au (111) substrate surface<sup>38</sup>. In this study, we propose at the very beginning, the AuCl<sub>4</sub><sup>-</sup> ions adsorb onto the defective sites in MoS<sub>2</sub> layers and reduced to Au atoms which subsequently form Au nanoclusters, therefore the density of Au NPs depends on the defect density of MoS<sub>2</sub> layer. Meanwhile, the Au {111} has the lowest surface energy<sup>42,43</sup> and small lattice mismatch with MoS<sub>2</sub> (0001), which promotes the preferential orientation of Au (111) crystal planes on MoS<sub>2</sub> surface.

## Discussion

Various research methods have been developed aiming at tuning the electronic properties of 2D materials. According to our previous report<sup>39,44</sup>, the work function of graphene layer can be effectively controlled by immersing graphene film in AuCl<sub>4</sub><sup>-</sup> solution, due to the spontaneous reduction of Au<sup>3+</sup> to Au<sup>0</sup>. Raman spectroscopy is a powerful nondestructive characterization tool to reveal the level of doping in single-layer MoS<sub>2</sub> due to the strong electron-phonon interaction<sup>45,46</sup>. It has been reported that  $n$ -doping results in softening of the A<sub>1g</sub> phonon which results in decrease of relative intensity and peak frequency difference between A<sub>1g</sub> and E<sub>2g</sub> modes<sup>46</sup> while  $p$ -doping in MoS<sub>2</sub> layers should cause relative shifting of the Raman active modes in opposite direction. Figure 5 (A) shows typical Raman spectra for a single layer MoS<sub>2</sub> sheet before and after Au NPs decoration. The MoS<sub>2</sub> layer exhibits two Raman characteristic bands at ~404 and 386 cm<sup>-1</sup>, corresponding to the A<sub>1g</sub> and E<sub>2g</sub> modes respectively. It was reported oxygen in the ambient may attack Mo-S-Mo bands and cause the shift of Raman vibrations modes<sup>45</sup>. 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 A<sub>1g</sub> and E<sub>2g</sub> Raman modes, respectively. The results showing a detectable upshift of A<sub>1g</sub> frequency and an increase of A<sub>1g</sub>/E<sub>2g</sub> peak intensity ratio, which suggest distinct  $p$ -doping caused by Au NPs decoration<sup>45,46</sup>. To further evaluate doping effect of Au NPs on CVD-MoS<sub>2</sub> electrically, top-gate transistors were fabricated by evaporating Au/Ti electrodes directly on top of the MoS<sub>2</sub> layers on sapphire substrate. The MoS<sub>2</sub> electric double-layer transistors (EDLTs)<sup>47,48</sup> 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 report<sup>48</sup>. 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-MoS<sub>2</sub> layers and the effect of Au NPs on the transistor performance can be directly accessed. Fig. 5 (D) shows the transfer curve of CVD-MoS<sub>2</sub> EDLTs before and after Au NPs decoration. Supporting information Figure S5 shows the I-V<sub>g</sub> curves plotted in log scale.



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



**Figure 5** | (A) Typical Raman spectra of MoS<sub>2</sub> sheets before and after Au NPs decoration; (B) and (C) show the statistical analysis of the relative intensity and frequency change in E<sub>2g</sub> and A<sub>1g</sub> vibration mode induced by the Au NPs decoration; (D) Thin-film MoS<sub>2</sub> EDLT constructed with an ion gel dielectric layer. Black and red lines correspond to the transfer characteristics of the MoS<sub>2</sub> 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-MoS<sub>2</sub> 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 MoS<sub>2</sub> 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 AuCl<sub>4</sub><sup>-</sup> ions in solution can strongly withdraw electrons from MoS<sub>2</sub> layers and reduces to Au NPs, therefore, it is anticipated for a down shift of Fermi level in MoS<sub>2</sub> layers. It is found that the on/off ratio for the device after Au NPs doing is around  $3.54 \times 10^3$ , which is around 50 times larger than that of the pristine MoS<sub>2</sub> electric double-layer transistors (EDLT). The measured maximum current for the doped and pristine MoS<sub>2</sub> EDLT is 13.7 mA and 22.5 mA, respectively. The mobility of the MoS<sub>2</sub> 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 region<sup>48</sup>. Where I<sub>d</sub> is the drain current,  $\mu$  is the field-effect mobility, W is the channel width, V<sub>D</sub> is the drain voltage, C<sub>i</sub> is the specific capacitance of the dielectric, L is the channel length, V<sub>G</sub> is the gate voltage, and V<sub>th</sub> is the threshold voltage. From the calculation, the mobility for Au NPs doped MoS<sub>2</sub> is around 2.44 cm<sup>2</sup>/(Vs), which is 2 times smaller than the pristine MoS<sub>2</sub> EDLT.

In conclusion, we have proposed a simple method to decorate the CVD-MoS<sub>2</sub> and CE-MoS<sub>2</sub> 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<sub>2</sub>. The Au NPs exhibited a remarkable *p*-doping effect to the MoS<sub>2</sub> transistors. Hence, the proposed Au NPs decoration method can provide promising nanomaterials hybrids for the application of future optoelectronics devices.

## Methods

**CVD-MoS<sub>2</sub> synthesis.** CVD-MoS<sub>2</sub> was prepared using the method High-crystal-quality MoS<sub>2</sub> were grown on a sapphire substrates by chemical vapor deposition method inside a horizontal tube furnace. The detailed fabrication procedure can be found elsewhere<sup>17,18</sup>. To be brief, the MoS<sub>2</sub> films were synthesized on c-face sapphire substrates in a hot-wall furnace. High purity MoO<sub>3</sub> (99%, Aldrich) and S powder (99.5, Alfa) were placed in two separated Al<sub>2</sub>O<sub>3</sub> crucibles and the substrates were placed on the downstream side of the Ar carrying gas. The MoS<sub>2</sub> 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 MoS<sub>2</sub>.** The MoS<sub>2</sub> nanoflakes was obtained by lithium intercalation method follow the procedure reported before<sup>20</sup>. 0.5 g of natural MoS<sub>2</sub> crystals from Sigma-Aldrich was dispersed in 5 mL of 1.6 M butyllithium solution in hexane (Sigma-Aldrich) for 48 hours in a flask filled with argon gas. The Li<sub>x</sub>MoS<sub>2</sub> was retrieved by filtration and washed with hexane (60 mL) to remove excess lithium and organic residues. Exfoliation was achieved by ultrasonicing the obtained Li<sub>x</sub>MoS<sub>2</sub> 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 μm pores (Millipore). The film was delaminated on water surface for subsequent transfer onto substrates or TEM Grids.

**Au NPs decoration on CVD-MoS<sub>2</sub> and CE-MoS<sub>2</sub>.** AuCl<sub>3</sub> dissolved in water was used for the growth of Au nano particles (Au NPs) on MoS<sub>2</sub>. To prepare Au NPs/CVD-MoS<sub>2</sub>, the as prepared CVD-MoS<sub>2</sub> on sapphire substrates was directly



immersed in 5 mM AuCl<sub>3</sub> for 20 sec, followed by gently rinsing with DI water. To prepare Au NPs/CE MoS<sub>2</sub> samples, the CE MoS<sub>2</sub> film was firstly delaminated on water surface by the previously described method<sup>29</sup>. Several drops of 5 mM AuCl<sub>3</sub> water solution were added into the water subsequently. Finally, the Au NPs/CE-MoS<sub>2</sub> floating on water surface can be picked up by TEM grids or arbitrary substrates.

**Transfer of the as-grown Au NPs/MoS<sub>2</sub> hybrid to arbitrary substrates.** The CVD-MoS<sub>2</sub> and Au NPs decorated MoS<sub>2</sub> 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/MoS<sub>2</sub> 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 H<sub>2</sub> 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 μm. For the Raman characterization, the Si peak at 520 cm<sup>-1</sup> 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 spectroscopy (XPS, Phi V5000). XPS measurements were performed with an Al Kα X-ray source. The energy calibrations were made against the C 1s peak to eliminate the charging of the sample during analysis.

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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

Supplementary information accompanies this paper at <http://www.nature.com/scientificreports>

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