Selective Decoration of Au Nanoparticles on Monolayer MoS₂ Single Crystals

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We report a controllable wet method for effective decoration of 2-dimensional (2D) molybdenum disulfide (MoS₂) layers with Au nanoparticles (NPs). Au NPs can be selectively formed on the edge sites or defective sites of MoS₂ layers. The Au-MoS₂ 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 MoS₂ layers. Field effect transistors were directly fabricated by placing ion gel gate dielectrics on Au-decorated MoS₂ layers without the need to transfer these MoS₂ layers to SiO₂/Si substrates for bottom gate devices. The ion gel method allows probing the intrinsic electrical properties of the as-grown and Au-decorated MoS₂ layers. This study shows that Au NPs impose remarkable p-doping effects to the MoS₂ transistors without degrading their electrical characteristics.

Due to their unique properties, atomically thin two-dimensional (2D) materials with a layered structure such as graphene¹⁻³, hexagonal boron nitride (h-BN)⁴⁻⁶ and transition-metal dichalcogenide (LTMDs)⁷⁻¹⁰ 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 physical⁶,¹² or chemical exfoliation methods¹³,¹⁴. 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 performance²⁰,²¹ 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 MoS₂ is catalytically inactive, and the activity in the HDS and HER is associated with the edge termination of MoS₂ clusters⁹⁻¹¹,¹³⁻¹⁵. 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 water¹⁰,²⁴⁻²⁷, 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 biosensing²⁹,³⁰, photonics³¹,³₂ and catalysis³³,³⁴. 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 nanomaterials²⁸,³⁵. Furthermore, compared with graphene, MoS₂ is a semiconducting material with a suitable band gap around 1.2 to 1.9 eV, depending on its thickness²⁶,²⁸,³⁶. 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 nanomaterials by controlling the surface wetting properties²⁶ and it was also suggested the edges of 2D nanomaterials may favor the anchoring of metal NPs²⁶. However, location dependence of metal NPs decoration on MoS₂ layers

SUBJECT AREAS:
- NANOPARTICLES
- TWO-DIMENSIONAL MATERIALS
- ELECTRONIC DEVICES
- DESIGN, SYNTHESIS AND PROCESSING

Received 18 March 2013
Accepted 24 April 2013
Published 14 May 2013

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DOI: 10.1038/srep01839

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was rarely reported. In this contribution, we study the controllable decoration of isolated MoS₂ 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 AuCl₄⁻ ions can be reduced to neutral gold atoms selectively on the edge part, or defective sites of MoS₂ layers by a simple solution dip casting method. The quality of MoS₂-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 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 MoS₂ 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 A₁₈g and E₂g peaks have been found to relate to the number of MoS₂ layers²⁰,²¹. 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 A₁₈g and E₂g vibration modes, which are characteristics for MoS₂. The PL spectrum displays a distinct main emission peak at ~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 nano-sized particles. Fig. 2 shows the XPS spectra of the Au doped MoS₂ 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 3d₅/₂ and Mo 3d₃/₂. The binding energy for S 2p₃/₂ and S 2p₁/₂ 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 MoS₂, and the MoS₂ monolayer.

Figure 1 | MoS₂ nano-flakes on c-face sapphire substrate substrates. (A) Typical AFM height images of MoS₂ flakes grown on c-face sapphire substrates. Inset shows a non-continuous MoS₂ 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-MoS₂ layers, inset shows the Raman spectra of the CVD-MoS₂. Both Raman and PL experiments were performed using a confocal spectrometer with 476 nm excitation laser.
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 MoS₂ layers and understand the tendency of the epitaxial stacking manner of Au NPs on MoS₂ nanosheets, the Au NPs/CVD-MoS₂ 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 MoS₂ (Au NPs/CE-MoS₂) 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).

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 MoS₂ layers after Au nanoparticles decoration. The red cure in (A) and (B) display the corresponding spectrum taken from the pristine CVD-MoS₂ sample.

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 nano-size 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 distance is about 0.23 nm which is in good consistency with the Au (111) spacing. We also noticed that 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 leave 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 images 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 (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 MoS2 [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 formation of Au NPs is associated with the defects of MoS2. The edge parts or defects in MoS2 layers could interact with the AuCl4− 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) shows 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 template 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 surface. 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 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, 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. 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 modes while p-doping in MoS2 layers should cause relative shifting of the Raman-active 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 ~404 and 386 cm−1, corresponding to the A1g and E2g modes respectively. It was reported oxygen in the ambient may attack Mo-S-Mo bands and cause the shift of Raman vibrations modes. 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. To further evaluate doping effect of Au NPs on CVD-MoS2, the 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) 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. 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-V curves plotted in log scale.

**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 (~2 nm) located on the CE-MoS2 films; (D) HRTEM image of large Au particle (~10 nm) located on the CE-MoS2.
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-doping 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 doping is around 3.54 × 10^3, which is around 50 times larger than that of the pristine MoS2 EDLTs. 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 Id = \( \mu WV_D(C_i/L)(V_G-V_{th}) \) for the linear region. Where \( I_d \) is the drain current, \( \mu \) 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 cm^2/(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 MoS2. The Au NPs exhibited a remarkable p-doping effect to the MoS2 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. 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 before. 0.5 g of natural MoS2 crystals from Sigma-Aldrich were 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_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 μm 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 by chemical vapor deposition method inside a horizontal tube furnace. The detailed fabrication procedure can be found elsewhere. 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.

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prepare Au NPs/CE MoS2 samples, the CE MoS2 film was firstly delaminated on water surface by the previously described method.[9] 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 aquarums (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 μm. 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 spectroscopy (XPS, PHI 5000). 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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**Acknowledgements**
This work is supported by SUTD-MIT international design center fund to Dr Yang Hui Ying. L.J. Li thanks the support from Academia Sinica (IAMS and Nano program) and National Science Council Taiwan (NSC-99-2112-M-001-021-MY3). S.F. Yu and L.M. Jin thank PolyU grant (Grant No. G-Y773).

**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
Competing financial interests: The authors declare no competing financial interests.

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How to cite this article: Shi, Y. et al. Selective Decoration of Au Nanoparticles on Monolayer MoS2 Single Crystals. Sci. Rep. 3, 1839; DOI:10.1038/srep01839 (2013).