Controlled one step thinning and doping of two-dimensional transition metal dichalcogenides

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ABSTRACT Two-dimensional (2D) transition metal dichalcogenides (TMDCs) have drawn intensive attention due to their ultrathin feature with excellent electrostatic gating capability, and unique thickness-dependent electronic and optical properties. Controlling the thickness and doping of 2D TMDCs are crucial toward their future applications. Here, we report an effective H_{AuCl}₄ treatment method and achieve simultaneous thinning and doping of various TMDCs in one step. We find that the H_{AuCl}₄ treatment not only thins thick MoS₂ flakes into few layers or even monolayers, but also simultaneously tunes MoS₂ into p-type. The effects of various parameters in the process have been studied systematically, and an Au intercalation assisted thinning and doping mechanism is proposed. Importantly, this method also works for other typical TMDCs, including WS₂, MoSe₂ and WSe₂, showing good universality. Electrical transport measurements of field-effect transistors (FETs) based on MoS₂ flakes show a big increase of On/Off current ratios (from 10² to 10⁷) after the H_{AuCl}₄ treatment. Meanwhile, the subthreshold voltages of the MoS₂ FETs shift from −60 to +27 V after the H_{AuCl}₄ treatment, with a p-type doping behavior. This study provides an effective and simple method to control the thickness and doping properties of 2D TMDCs, paving a way for their applications in high performance electronics and optoelectronics.

Keywords: 2D materials, transition metal dichalcogenides, MoS₂, thinning, doping, field-effect transistor, H_{AuCl}₄

INTRODUCTION

Due to its extraordinary properties including high charge carrier mobility, high thermal conductivity, good mechanical flexibility, and chemical stability, graphene unlocked the door of two-dimensional (2D) materials world [1–3]. Nevertheless, zero band gap nature of graphene is

not desirable for the applications in digital electronics where semiconductors play key roles. Unlike graphene, 2D transition metal dichalcogenides (TMDCs) with sizeable bandgaps are promising candidates and have potentials to redefine next generation electronics and optoelectronics. Among various TMDCs, MoS₂ has received intensive attention and has been shown as a competitive material to fabricate sensors [4], field effect transistors (FETs) [5], light emitting diodes [6], photo-detectors [7,8], energy storage devices [9], and micro-processor [10]. Many TMDCs including MoS₂ exhibit thickness-dependent electronic and optical properties. Taking MoS₂ as an example, with the decrease of thickness, its band gap increases from 1.20 eV in bulk to 1.85 eV in monolayer. In addition, MoS₂ shows a band structure transition from indirect to direct type when its thickness decreases from thick samples to monolayer ones. This feature results in a higher efficiency of photoelectrical conversion in monolayer MoS₂ than thicker ones [11,12]. In addition, only thin TMDC flakes (ca. <10–20 nm) show good flexibility and strong electrostatic gating controllability, which are desired for future flexible electronics [13–15]. Therefore, it is critical to control the thickness of 2D TMDCs and many efforts have been made toward this direction. For instance, Varghese *et al.* [16] have used microwave plasma etching to reduce the thickness of MoS₂ without damage to the basal plane, in which the thickness of MoS₂ is dependent on the etching time. In addition, Wang *et al.* [17] have found that ion bombardment can thin the thickness of chemical vapor deposited MoS₂ films *via* a physical process. In another work, Liu *et al.* [18] have thinned MoS₂ flakes *via* electrochemical ablation where bubble intercalation helps to decouple the interlayer interaction of MoS₂ and realizes its exfoliation into thin flakes.

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Besides thickness controlling, how to realize controllable doping is another important challenge for TMDCs. It is well known that doping is essential for modern silicon semiconductor industry to modulate types and concentrations of charge carriers, as well as reduce electrical contact resistance in silicon devices. One of the key advantages of silicon is that it can be readily doped into either n-type or p-type, building the foundation for silicon based complementary circuits. However, compared with silicon which is a bulk material, controllable doping of 2D TMDCs is more challenging due to their ultrathin thickness. Recently, Li *et al.* [19] have used AuCl_3 and benzyl viologen as p-type and n-type dopants, respectively and fabricated ultrathin MoS_2 based p–n junctions. In addition, Mouri *et al.* [20] have used organic molecules like 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane and 7,7,8,8-tetracyanoquinodimethane as p-type dopants, and nicotinamide adenine dinucleotide as a n-type dopant, to tune the photoluminescence (PL) properties of MoS_2 . The results show that p-doping generates an increase while n-doping results in a decrease of the PL intensities of MoS_2 . In another work, Tarasov *et al.* [21] have utilized molecules like 2-ferrocenyl *N,N'*-dimethylbenzimidazoline (2-Fc-DMBI) and 2-ferrocenyl-dihydro-1*H*-benzimidazoles (2-Fc-DMBIH) as n-type dopants to modulate the subthreshold voltages (V_{th}) of MoS_2 FETs. The above achievements clearly show the importance of thickness control and doping in TMDCs. Note that some organic molecules exhibit poor doping stability over long times. In addition, most of the reported methods can either thin or tune TMDCs, while they are difficult to achieve simultaneous thinning and doping (Supporting information, Table S1).

Here we report an efficient one-step HAuCl_4 treatment method which achieves simultaneous thinning and doping of TMDCs. Taking MoS_2 as an example, after simply immersing the MoS_2 flakes into HAuCl_4 solution for certain times, the thicknesses of MoS_2 flakes decrease, as evidenced by optical microscopy (OM), atomic force microscopy (AFM), Raman and PL spectroscopy measurements. An Au^{3+} intercalation induced exfoliation and thinning mechanism is proposed based on the X-ray diffraction (XRD), transmission electron microscopy (TEM), and X-ray photoelectron spectroscopy (XPS) studies. Importantly, we find that this HAuCl_4 treatment induced thinning method also works for other TMDCs including MoSe_2 , WS_2 , and WSe_2 , demonstrating its universality. The FETs based on MoS_2 were fabricated. Compared with the devices with original MoS_2 , the On/Off current ratios of the FETs based on the MoS_2 after

HAuCl_4 treatment increased from 10^2 to 10^7 , and the V_{th} shifted from -60 to $+27$ V, showing a p-type doping effect to MoS_2 .

EXPERIMENTAL SECTION

Materials preparation and characterization

Bulk crystals of MoS_2 , MoSe_2 , WS_2 , and WSe_2 were purchased from HQ Graphene. 2D TMDC flakes were mechanically exfoliated from their bulk crystals onto Si/SiO_2 substrates *via* the Scotch tape exfoliation method. The thickness of SiO_2 layer is 300 nm for Si/SiO_2 substrate. After examination under OM, the substrates with exfoliated 2D materials were immersed into HAuCl_4 aqueous solutions with different concentrations ($0.1\text{--}1\text{ mmol L}^{-1}$), immersion times (20–60 min), and temperatures ($20\text{--}90^\circ\text{C}$). Here the aqueous solution of HAuCl_4 was prepared by mixing AuCl_3 and HCl with a molar ratio of 1:1. After HAuCl_4 treatment, the samples were rinsed with deionization (DI) water for several times and dried with pure N_2 before further characterization. OM (Zeiss, Imager A2m, Germany), Raman and PL (with a laser wavelength of 532 nm and a spot size of $\sim 1\text{ }\mu\text{m}$, Horiba LabRAM HR Evolution, Japan), and AFM (tapping mode, Bruker Dimension Icon, USA) were used to characterize the thickness of 2D materials. XRD (Cu $\text{K}\alpha$ X-ray with a wavelength of 0.1541 nm, Bruker D8 Advance, Germany) and XPS (monochromatic Al $\text{K}\alpha$ X-ray with a wavelength of 0.834 nm, Thermo Fisher ESCALAB 250Xi, UK), TEM (FEI Tecnai F30, 300 kV, Netherlands) measurements were performed to study the mechanism of HAuCl_4 treatment induced thinning and doping of MoS_2 .

Device fabrication and measurements

The MoS_2 FETs were fabricated by photolithography. Briefly, a photoresist (AZ 5214) was firstly spin-coated (5000 rpm for 60 s) onto the Si/SiO_2 substrate with MoS_2 flakes. The substrate with photoresist was then baked at 120°C for 1 min. After that, the substrate was exposed in a Direct Laser Writer system to define the patterns (DaLI-A, Germany). After writing, the substrate was dipped into a developer (AZ 340) for 50 s, followed by DI water rinsing. The source and drain electrodes ($\text{Ti/Au}=5\text{ nm}/50\text{ nm}$) were deposited by electron beam evaporation followed by lift-off in hot acetone (80°C). The electrical performance of MoS_2 FETs was measured by using a probe station with a semiconductor property analyzer (Keithley 4200 SCS, USA) under ambient environment. The silicon substrate was used as a global back gate

during the electrical measurements.

RESULTS AND DISCUSSION

The HAuCl_4 treatment induced thinning and doping of TMDCs is illustrated in Fig. 1a. We first exfoliated TMDCs onto Si/SiO_2 substrate. After the initial characterization of the samples by OM, the Si/SiO_2 substrates with MoS_2 flakes were immersed into HAuCl_4 aqueous solution for different times, followed by DI water rinsing to remove the residue of HAuCl_4 . Based on the contrast of the OM images (Fig. 1b versus c, Fig. 1d versus e, and Fig. S1 in the Supporting information), one can clearly see that after the HAuCl_4 treatment, the MoS_2 flakes become much thinner. AFM images (Fig. 1f, g) show that the thickness of MoS_2 flake is 1.7 nm after HAuCl_4 treatment (Fig. 1g), which is smaller than the same flake before treatment with a thickness of 3.1 nm (Fig. 1f). We measured the thicknesses of 20 MoS_2 flakes before and after the HAuCl_4 treatment, and found that the flakes were thinned down by an average of 1.5 nm and some of them were thinned down by more than 5 nm (Fig. S2).

We used Raman and PL spectroscopy to further verify such thinning phenomenon. Typically, there are two Raman peaks (E_{2g}^1 and A_{1g}) in MoS_2 in our experimental configuration [14]. According to the previous report [22], the differences between the two Raman peaks in MoS_2

will increase as the thickness of flakes increases. Specifically, Raman peak distance in monolayer MoS_2 is around 19 cm^{-1} , while it gradually increases to 25 cm^{-1} for thick samples [13,23–25]. In addition to peak distance, we found that the Raman intensity ratios of the MoS_2 peaks (either E_{2g}^1 or A_{1g}) to the Si peak (520.7 cm^{-1}) can be another indicator to evaluate the thickness of MoS_2 flakes. When the thickness of MoS_2 increases, its Raman intensity will increase, while the intensity of the Si peak will decrease because more incident light will be absorbed and scattered by thicker MoS_2 flakes than thinner ones. As a result, thicker MoS_2 flakes will have larger E_{2g}^1/Si and A_{1g}/Si Raman intensity ratios than the thinner ones [26]. Fig. 2a presents the Raman spectra of the MoS_2 flakes before and after the HAuCl_4 treatment. Comparing with the spectrum of the original sample, the Raman intensity ratio between MoS_2 and Si becomes much smaller after the HAuCl_4 treatment, indicating a reduced thickness of the MoS_2 flake. In addition, the distance between the E_{2g}^1 and A_{1g} peaks of MoS_2 decreases from 23.0 to 20.5 cm^{-1} , showing the formation of a bilayer MoS_2 after the HAuCl_4 treatment. Taken together, the Raman results confirm a thinning effect of MoS_2 after HAuCl_4 treatment. The corresponding PL spectra of the samples before and after the HAuCl_4 treatment (Fig. 2b) show an obvious increase of PL intensity, stemming from the reduced thickness of

Figure 1 HAuCl_4 treatment induced thinning and doping of 2D MoS_2 flakes. (a) Schematic of the thinning and doping process of TMDCs upon HAuCl_4 treatment. (b, d, f) OM and AFM images of as-exfoliated MoS_2 flakes before treatment, while (c, e, g) show the corresponding images of the same flakes after treatment.

Figure 2 Raman and PL characterization of MoS₂ flakes before and after HAuCl₄ treatment. (a, b) Typical Raman and PL spectra of a MoS₂ flake before and after HAuCl₄ treatment. Statistics of Raman intensity ratios of E'_{2g} (c, e) and A_{1g} (d, f) peaks in MoS₂ versus Si peak (520.7 cm⁻¹) before and after HAuCl₄ treatment, respectively. Evolutions of Raman intensity ratios of E'_{2g} (green) and A_{1g} (purple) peaks in MoS₂ versus Si peak (520.7 cm⁻¹) when changing temperatures (g), times (h), or concentrations (i) of HAuCl₄ during treatment.

MoS₂ flakes. As control experiments, we decorated Au nanoparticles on MoS₂ flakes and found that it quenched the PL intensity of MoS₂ (Fig. S3), suggesting that the increase of PL intensity in Fig. 2b related to the thickness reduction of MoS₂ after the HAuCl₄ treatment. We collected Raman spectra of 50 MoS₂ flakes before and after the HAuCl₄ treatment, and the statistical results of the intensity ratios of E'_{2g}/Si and A_{1g}/Si peaks are shown in Fig. 2c–f. For the E'_{2g}/Si, the ratios center at 3 and most of them are >2 before the treatment (Fig. 2c), while it reduces to be <2 after the treatment (Fig. 2e). The same trend is also observed for the A_{1g}/Si intensity ratios (Fig. 2d, f). In addition, Raman mapping of the intensity of A_{1g} peak for the HAuCl₄ treated MoS₂ flakes shows good uniformity (Fig. S4). Therefore, the results from Raman and PL spectroscopy measurements confirm that the thickness of MoS₂ decreases after the HAuCl₄ treatment, in good agreement with the above OM and AFM

results.

We systematically studied the effects of several experimental parameters on the thinning of MoS₂ during HAuCl₄ treatment including the concentration of HAuCl₄, treatment time, and temperature. We use E'_{2g}/Si and A_{1g}/Si Raman intensity ratios as indicators to evaluate the thickness evolution of MoS₂ flakes upon HAuCl₄ treatment. The thinning process is accelerated with increasing concentrations of HAuCl₄, treatment times, and temperatures (Fig. 2g–i). In addition, the concentration of HAuCl₄ and treatment time are more important factors than the temperature, because E'_{2g}/Si and A_{1g}/Si ratios show smaller change when changing treatment temperature than changing concentration or time. The most profound factor is the treatment time, which shows a sharp initial decrease of E'_{2g}/Si and A_{1g}/Si ratios and enters to a relatively stable state at around 40 min. Prolonging HAuCl₄ treatment time in a certain range

(30 min to 2h) leads to the formation of thinner MoS₂ flakes than short time treatment, while too long time treatment is not desirable because MoS₂ flakes will be partially removed from the substrate (Fig. S5). Likewise, the ratio enters relative stable state when the concentration of HAuCl₄ increases to 0.2 mmol L⁻¹. While the temperature does not show a paramount impact on the thinning effect because it leads to a relatively small decrease of the E_{2g}/Si and A_{1g}/Si ratios. We have studied tens of MoS₂ flakes and found that the HAuCl₄ induced thinning shows very good reproducibility.

We used XPS, XRD and TEM to study the mechanism of the HAuCl₄ treatment induced thinning of MoS₂ flakes. Fig. 3a, b show the XPS spectra of Mo 3d and Au 4f of the samples after the HAuCl₄ treatment. The spectra were collected both from the surfaces of samples (ion etching time is 0 s inside XPS chamber), as well as internal materials (ion etching times are 10 and 20 s before XPS measurements). As shown in Fig. 3a, after the HAuCl₄ treatment, Mo 3d peaks locate at 229.1 and 232.2 eV (black curve), corresponding to Mo⁴⁺ 3d_{5/2} and 3d_{3/2} in MoS₂, respectively. After ion etching, the Mo 3d peaks broaden and shift to low binding energy of 228.7 and

231.9 eV (red and blue curves in Fig. 3a). Such decrease of Mo 3d peaks binding energies of ~0.5 eV is relatively uniform for samples at different depths (i.e., after ion etching for different times). Previous reports show that decrease of the binding energy of MoS₂ indicates a p-type doping behavior, corresponding to a shift of the Fermi level of MoS₂ toward the valence band edge [27,28]. In addition, Au signals are detected on both the surfaces as well as the samples after ion etching for different times (Fig. 3b), suggesting that Au exists on the surface and in the interlayers of MoS₂ flakes after the HAuCl₄ treatment. AFM characterization shows the existence of abundant nanoparticles on the surfaces and edges of MoS₂ flakes (Fig. 1g), and XPS results show the Au 4f peaks at 87.1 and 83.5 eV on MoS₂ surface (black curve in Fig. 3b), corresponding to metallic Au. Taken together, the above AFM and XPS results indicate that these nanoparticles on surfaces are metallic Au. Importantly, we also observed Au signals in the inlayer of MoS₂ after being etched for 10 and 20 s, with the Au 4f peaks located at 87.7 and 84.0 eV (red and blue curves in Fig. 3b), 0.6 and 0.5 eV larger than metallic Au. The results suggest that the Au in the interlayer of MoS₂ flakes is in the form of Au³⁺ in HAuCl₄. We conducted control experiments by using NiCl₂, CoCl₂, NaCl, and KCl solutions instead of HAuCl₄ to treat the MoS₂ flakes, and did not observe any thinning effect of MoS₂ flakes based on OM and Raman characterization, indicating the importance of strong affinity between Au³⁺ and MoS₂ in the thinning phenomenon (Fig. S6).

According to the above results, we propose an intercalation mechanism for the thinning process. First, when MoS₂ is immersed into HAuCl₄ solution, Au³⁺ combines with the surface and edge of MoS₂ due to high electron concentrations on these positions [29]. According to previous studies, the electron concentration on the surface of MoS₂ is about 10⁴ times higher than that of inner layers [30]. In this step, the Au³⁺ will be reduced into metallic Au and decorate on the surface and edge of MoS₂ flake. Second, with the reduction of Au³⁺ and accumulation of Au nanoparticles on the surface and edge of MoS₂, the interaction between the inter-layers will be reduced gradually. This process would start along the edges followed by block and block exfoliation of MoS₂ flakes (Fig. S7). Meanwhile, more and more solution will fill into the interlayer space of MoS₂, and repeating the above steps leads to thinning of MoS₂ flakes. In short, such behavior is derived from the strong affinity between Au³⁺ and high electron concentrations on the surface and edge of MoS₂, which allows the Au³⁺ to gradually inter-

Figure 3 Mechanism studies of the HAuCl₄ treatment induced intercalation and thinning of MoS₂ flakes. (a) Mo 3d XPS spectra of HAuCl₄ treated MoS₂. The top curve (black) was collected at the surface of HAuCl₄ treated MoS₂ without ion etching before XPS measurements, while the middle (red) and bottom (blue) curves were collected from the same samples after ion etching for 10 and 20 s before XPS measurements. (b) Au 4f XPS spectra of the same sample with different ion etching times of 0, 10, and 20 s. (c) XRD patterns of MoS₂ samples before and after HAuCl₄ treatment. The peak at 38° stems from Au nanoparticles (denoted by ♦), and the peaks at 14.2°, 14.4°, and 39.6° stem from MoS₂ (denoted by Δ).

calate into the interlayer, expand and thin MoS₂ accordingly [31].

During the thinning process, some Au³⁺ will combine with the electrons and be reduced into metallic Au on the surfaces of MoS₂, as supported by XPS results (black curve in Fig. 3b). As a comparison, most Au is still in ion form in the innerlayer of MoS₂ (Fig. 3b) since its reduction needs sufficient contact with the exfoliated interlayers and long times. For MoS₂, such intercalation by Au³⁺ makes the original neutral system positively charged, leading to a p-type doping behavior, consistent with the electrical measurements shown later. This assumption is also supported by the XRD results (Fig. 3c) where a new peak at 38° can be indexed to (110) facet of metallic Au, which appears on MoS₂ samples after H₂AuCl₄ treatment. Moreover, the (002) peak of MoS₂ shifts from 14.4° to 14.2°, indicating a slightly enlarged

interlayer distance, which is a clue for the Au³⁺ intercalation. Based on high resolution TEM characterization (Fig. S8), we do not observe any changes of basal plane lattice structures of MoS₂ after H₂AuCl₄ treatment. This is reasonable because Au³⁺ with radius of ~0.085 nm can enter into the interlayers of MoS₂, but cannot enter into its basal planes.

Importantly, we find that the H₂AuCl₄ treatment also thins down other TMDCs like MoSe₂, WS₂, and WSe₂ (Fig. 4). During these experiments, the TMDC flakes were exfoliated from their bulk crystals onto Si/SiO₂ substrates and immersed into H₂AuCl₄ solution, similar to the MoS₂ case. Comparisons of the OM images of the same flakes of these three materials before (Fig. 4a, e, i) and after (Fig. 4b, f, j) H₂AuCl₄ treatment indicate clear thinning effect. In addition, for MoSe₂, the A_{1g} peak in Raman spectra red shifts after the treatment, meaning a de-

Figure 4 Universality of the H₂AuCl₄ treatment induced thinning of TMDCs. OM images of the same MoSe₂ flake before (a) and after (b) the H₂AuCl₄ treatment. Corresponding Raman (c) and PL (d) spectra of the MoSe₂ flake before and after treatment. OM images of the same WS₂ flake before (e) and after (f) treatment. Corresponding Raman (g) and PL (h) spectra of the WS₂ flake before and after treatment. OM images of the same WSe₂ flake before (i) and after (j) treatment. Corresponding Raman (k) and PL (l) spectra of the WSe₂ flake before and after treatment. During these experiments, the samples were treated with 1 mmol L⁻¹ H₂AuCl₄ for 40 min at room temperature.

creased thickness (Fig. 4c) [32]. For WS_2 , it shows a red shift of the A_{1g} mode from 421.7 to 420.0 cm^{-1} with the 2LA peak remaining at around 353.3 cm^{-1} (Fig. 4g). Meanwhile, a reduction of the 2LA/ A_{1g} intensity ratio from 13.8 to 4.8 in WS_2 after the HAuCl_4 treatment indicates a conversion from bulk to a few layer flake [33–36]. Similarly, for WSe_2 , the B_{2g}^1 peak around 308 cm^{-1} , which is a fingerprint for few layer WSe_2 flakes, is absent after the HAuCl_4 treatment, due to the thinning of the WSe_2 flakes to a monolayer (Fig. 4k) [37]. In addition, all the PL spectra show pronounced increase of the intensity after HAuCl_4 treatment, suggesting a reduction of the thickness of WS_2 , MoSe_2 , and WSe_2 flakes (Fig. 4d, h, l). In addition, the PL peaks of WS_2 and WSe_2 after the HAuCl_4 treatment locate at 625 and 755 nm, suggesting the formation of monolayer flakes [38]. Taken together, the above results show that HAuCl_4 treatment is a universal method to thin various TMDCs down to a few layers or monolayer samples.

Later we focused on the effect of HAuCl_4 treatment on device characteristics of MoS_2 FETs. As illustrated in Fig. 5a, we fabricated back gate FETs based on several MoS_2 flakes including pristine and HAuCl_4 treated ones. We find that HAuCl_4 treatment thins down MoS_2 flakes, and increases the On/Off current ratios of FETs. For example, we obtain a large On/Off ratio of $\sim 10^7$ for HAuCl_4 treated MoS_2 flake, which is higher than that of devices based on thick pristine MoS_2 flakes ($\sim 10^2$, Fig. S9). This increase of On/Off current ratios is a direct evidence for the formation of thinner sample, because thick MoS_2 flakes would lead to weak electrostatic gating effect due to the screening of electrical field by bottom MoS_2 [39]. According to the previous report, the effective electronic diffusion length of MoS_2 is ~ 10 nm [30], meaning that only the FETs based on thin MoS_2 flakes (< 10 nm) can be effectively turned off by electrostatic gating. Besides On/Off ratio, another remarkable change of the MoS_2 FETs after the HAuCl_4 treatment is the shift of V_{th} towards more positive voltages. We find that in regardless of the thickness, the V_{th} of FETs based on pristine MoS_2 is around -60 V (Figs S9, S10). After treatment, V_{th} moves along the positive direction to $+27$ V (Fig. 5c). In addition, regarding the stability of the flakes, we find that the PL intensity of the HAuCl_4 treatment produced monolayer MoS_2 is quite stable in hours, and decreases after air exposure for 3 days (Fig. S11), indicating a reasonably good stability. The increased current at negative V_{gs} suggests a p-type doping to MoS_2 upon HAuCl_4 treatment. Such doping and V_{th} shift are due to the reduced Au nanoparticles anchoring on the

Figure 5 Device characteristics of MoS_2 FETs upon HAuCl_4 treatment. (a) Schematic of a MoS_2 FET before and after the HAuCl_4 treatment. (b) Transfer curves (I_{ds} - V_{gs}) of a MoS_2 FET after the HAuCl_4 treatment, measured at different V_{ds} . The MoS_2 was treated in 0.2 mmol L^{-1} HAuCl_4 for 40 min at room temperature. (c) Transfer curves of another MoS_2 FET before and after HAuCl_4 treatment, showing a shift of V_{th} . The MoS_2 was treated in 1 mmol L^{-1} HAuCl_4 for 40 min at room temperature. (d) Illustration of the energy band alignment between MoS_2 and Au.

surface of MoS_2 , which subsequently induce charge transfer between Au nanoparticles and MoS_2 . According to the band alignment between the two materials (Fig. 5d), the bottom of the conduction band of MoS_2 is -4.0 eV, which is higher than the work function of decorated Au nanoparticles (-5.1 eV). The mismatch between the two energy levels constructs a potential path for carriers to transport. In order to reach the equilibrium state, the electrons will flow from MoS_2 to Au, leading to a p-type doping effect to MoS_2 .

CONCLUSIONS

In summary, we develop a novel one step thinning and doping method for MoS_2 . We find that the thickness of MoS_2 flakes decreases after controlled HAuCl_4 treatment, and monolayer MoS_2 could be obtained by such thinning method. Various approaches to measure the thickness, including AFM, Raman and PL, have been used to confirm such thinning phenomenon. XPS and XRD studies suggest an Au^{3+} intercalation assisted exfoliation and thinning mechanism. In addition, we find that HAuCl_4 treatment induced thinning method also works for other TMDCs like MoSe_2 , WS_2 , and WSe_2 , suggesting its universality. More importantly, after the treatment, the decoration of Au nanoparticles on MoS_2 turns it to a p-

type fashion, leading to an increase of On/Off current ratios and shift of V_{th} in MoS₂ FETs. This work provides a simple and effective way to control the thickness of TMDCs and tune their electronic and optical properties simultaneously, which lays the foundation for their further electronic and optoelectronic applications.

Received 28 April 2019; accepted 17 June 2019;
published online 9 July 2019

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Acknowledgements We acknowledge the support from the National Natural Science Foundation of China (51722206 and 11674150), the Youth 1000-Talent Program of China, the Economic, Trade and Information Commission of Shenzhen Municipality for the “2017 Graphene Manufacturing Innovation Center Project” (201901171523), Shenzhen Basic Research Project (JCYJ20170307140956657 and JCYJ20160613160524999), Guangdong Innovative and Entrepreneurial Research Team Program (2017ZT07C341 and 2016ZT06D348), and the Development and Reform Commission of Shenzhen Municipality for the development of the “Low-Dimensional Materials and Devices” discipline.

Author contributions Ren J convinced the idea and performed most experiments under the guidance from Liu B. Teng C helped to test the electronic performance of FETs. Cai Z and Liu J helped to conduct some materials characterization. Pan H fabricated devices under guidance of Zhao Y. Liu B directed the research and supervised the project. Ren J and Liu B wrote the manuscript with feedbacks from other authors.

Conflict of interest The authors declare no conflict of interest.

Supplementary information Experimental details and supporting data are available in the online version of this paper.

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一步法可控减薄和掺杂二维过渡金属硫族化合物

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摘要 二维过渡金属硫族化合物(TMDCs)具有超薄结构, 且其电学、光学性质对厚度具有很强的依赖性, 近年来备受研究者的广泛关注. 如何控制TMDCs的厚度和掺杂, 是其未来应用的关键所在. 本文提出了一种简单高效的HAuCl₄处理方法, 实现了TMDCs的一步法可控减薄和掺杂, 可以制备出薄层及单层TMDCs, 同时实现了对MoS₂的可控p型掺杂. 本文系统研究了关键实验参数的影响, 并基于此提出了金插层辅助减薄和掺杂TMDCs的机理. 研究还发现该方法具有普适性, 可以实现对多种TMDCs的可控减薄, 包括MoSe₂, WS₂, WSe₂. 电学测试表明, HAuCl₄处理后的MoS₂纳米片具有更高的场效应晶体管开关比, 其阈值电压向正电压方向偏移. 本工作提出的这种控制二维TMDCs材料厚度和掺杂的方法, 对其未来在高性能电子和光电器件的应用具有一定参考价值.