Grain-boundary-rich 2D materials for attomolar-ability biochemical sensors

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Article

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Abstract

Next-generation high-performance biological and chemical sensors based on the emerging multitudinous two-dimensional (2D) layered materials have been attracting great attention in recent years. The performance of 2D biochemical sensors is strongly dependent on the structural defects, which provide indispensable active sites for sensitive and selective adsorption of analytes. However, achieving controllable defect engineering is still a big challenge. In the present work, we propose achieving superior biochemical sensor performance with high-surface-density grain boundaries (GBs), a kind of ubiquitous structural defects, in polycrystalline 2D thin films, which can be controllably synthesized. As a proof-of-concept, by utilizing the high-density GBs in monolayer (1L) WS_2 films, we fabricated a series of surface plasmon resonance (SPR) sensors for mercury ion (Hg^{2+}) detection. Our investigation has demonstrated substantial sensitivity enhancement of Hg^{2+} detection down to trace attomolar-level quantification (detection limit of 1 aM), which is ascribed to the abundance of active sites on high-density GBs. This work provides a promising avenue for the design of ultra-sensitive sensors toward commercialized products based on the GB-rich 2D layered materials.

Introduction

Atomically thin two-dimensional (2D) layered materials are emerging, structurally fascinating materials for biological and chemical sensing. The multitudinous 2D layered materials, such as graphene^{1–3}, transition-metal dichalcogenides (TMDs)^{4–6}, MXene^{7–9}, and black phosphorus^{10–12}, possess an ultra-high specific surface area, guaranteeing superior surface sensitivity, which is a prerequisite and essential characteristic for fabrication of next-generation high-performance sensors for detection of analytes encompassing gases^{10–15}, ions^{16–19} and biomolecules^{20–24}. Theoretical and experimental investigations have demonstrated that the structural defects in 2D layered materials, *e.g.* vacancy, antisite, substitution, edge, grain boundary (GB), *etc.*, are the pivotal factors that ultimately enable and govern the 2D material sensing selectivity and sensitivity.^{3,14,16,25–27} Generally, a pristine defect-free 2D crystal is unfavorable for sensitive and selective detection because it is lack of dangling bonds or dangling-bond-free and relatively chemically inert. The introduction of atomic-level crystallographic defects in 2D materials can significantly alter its physico-chemical properties, including energy landscape, chemical reactivity and chemical selectivity. Therefore, the structural defects as energetically activated, chemically selective sites can promote 2D material sensor capacities, *i.e.* the selective and sensitive low-limit detection of target analyte. In exploitation of biochemical sensors with various 2D layered materials toward superior sensitivity, high selectivity and ultra-low limit of detection (LOD), the controllable and high-throughput production of structural defects is vital but still remains a fundamental challenge.

Notably, structural defects are able to be formed in the preparation process of 2D layered materials, and are strongly dependent on the preparation method.^{28–29} Conventionally, 2D layered materials are produced by using top-down methods such as mechanical and liquid-phase exfoliation and bottom-up methods like solvothermal synthesis and chemical vapor deposition (CVD). Mechanical exfoliation is a

simple and low-cost technique to obtain high-quality, surface-clean, few-layer 2D flakes with uncontrollable size, shape and thickness; and the preferred high-throughput defects can be created via post-treatment defect engineering methods, like plasma, ion/electron beam and laser irradiation.^{28–38} However, the difficulty in scalable production of large-scale few-layer 2D flakes render mechanical exfoliation infeasible in practical applications. Liquid-phase exfoliation is a high-yield method to produce 2D crystals with non-uniform size, shape and thickness. The formation of various structural defects can be induced in large amounts during exfoliation, but it is hard to control. While these structural defects can supply the energetically active sites for enhanced binding of analytes, such uncontrollable defect formation usually results in irreproducible performance of the 2D materials based biochemical sensors. Moreover, liquid exfoliation inevitably produces surface contaminants, which are generally undesirable for 2D material applications.^{25,39–41} Among the bottom-up preparation methods, CVD is well-developed and optimal for controllable and high-throughput synthesis of high-quality, surface-clean, few-layered 2D materials.^{42,43} Motivated by potential applications of 2D layered materials in the fields of optoelectronics, much research efforts are devoted to the CVD growth of large-scale 2D layered crystals, such as TMDs, particularly in wafer-scale.^{44–47} Grain boundaries (GBs) are normally not preferred because their presence leads to sharp drop of carrier mobility and is detrimental to (opto)electronic device performance.^{48,49} However, as revealed in the previous investigations^{48–53}, GBs, the ubiquitous 2D material defects, can induce intrinsic activation of the 2D basal plane, and thus their presence leads to the significant application potential of 2D materials in many other fields including solar cells^{54,55}, electrocatalysis^{52,56,57}, sensors^{26,58,59}, *etc.* Chen *et al.*²⁷ have carried out density functional theory (DFT) calculations to reveal the chemical selectivity at GB dislocations in monolayer $\text{Mo}_{1-x}\text{W}_x\text{S}_2$; Masel *et al.*²⁶ have reported the realization of ~ 50 times higher sensitivity of polycrystalline graphene based organic vapor sensors compared with pristine single-crystalline graphene film based sensors; Bao *et al.*⁵⁹ have showed that polycrystalline graphene film can be selectively functionalized with great amount of Pt nanoparticles along GBs for high-sensitivity H_2 sensing; and Liu *et al.*⁵² recently reported GB-induced superior hydrogen evolution performance of TMD nanograin films. In contrast to the many challenges to synthesize large-area or wafer-scale single crystalline 2D layered films, however, the CVD growth of polycrystalline 2D layered films is easier to implement. Several groups have reported the successful growth of large-area, even wafer-scale, polycrystalline monolayer (1L) TMDs films.^{60–64}

In our previous work, controllable and reproducible CVD growth of wafer-scale polycrystalline 1L $\text{W}(\text{Mo})\text{S}_2$ films has been successfully achieved.^{61,62} The obtained film is composed of grains with an average size of less than 100 nm, implying the presence of GBs at high surface density. Here, we propose the potential application of CVD-grown polycrystalline 1L $\text{Mo}(\text{W})\text{S}_2$ films as biochemical sensors with superior sensitivity, high selectivity and ultra-low limit of detection. As a demonstration, the CVD-grown polycrystalline 1L $\text{Mo}(\text{W})\text{S}_2$ films were transferred onto Au-coated cover glass substrates as SPR sensors for the detection of mercury ions (Hg^{2+}), a common heavy metal pollutant. This work focuses on utilizing GB defects as active sites for analyte detection; and our investigation has indicated that the presence of high-density GBs leads to hugely enhanced detection sensitivity down to trace attomolar-level

quantification (LOD of 1 aM). The observed superior detection sensitivity is ascribed to the inherent reactivity of GB-rich 2D structure, which promotes preferential and efficient adsorption of analyte at the active-S sites along the high-density GBs. Our demonstration of GB-induced exemplary sensor performance can motivate more exciting developments based on GB-rich 2D materials for the advancement of ultra-sensitive sensors towards commercialized products.

Results And Discussion

Centimeter-scale polycrystalline monolayer (1L) WS₂ films with the presence of high-surface-density grain boundaries (GBs) were successfully synthesized on SiO₂ (300 nm)/Si substrates in a home-made CVD system as reported in our previous works^{61,62}, which are confirmed by measurements of optical microscopy (OM), fluorescence (FL), atomic force microscopy (AFM), Raman and photoluminescence (PL) (see Supplementary Figs. S1, 2, and details about CVD growth and characterization of OM, FL, AFM, Raman and PL). Because of the preferential adsorption of contaminants on GBs in 1L WS₂ film under exposure to air, the GB profiles can be observable even in the OM images⁶⁰. Figures 1a and b show the low and high magnification AFM images of the as-grown polycrystalline 1L WS₂ film on Si substrate after one-week exposure to air for sufficient adsorption on GBs. The GB profiles can be clearly visualized between irregular-shaped WS₂ grains with the lateral dimension of less than 100 nm in average. The nano-scale grain sizes are the direct evidence of high-surface-density GBs in the CVD-grown polycrystalline 1L WS₂ film. The atomic structure of GBs was investigated in detail by using scanning transmission electron microscopy (STEM). The low magnification high angle annular dark field STEM (HAADF-STEM) image of Fig. 1c clearly shows the GBs and the nano-scale grains with lateral sizes of less than 100 nm, confirming the AFM observations. In the corresponding selected area electron diffraction (SAED) of Fig. 1d, the observed diffraction rings instead of individual spots suggest that the nano-scale grains in polycrystalline 1L WS₂ film were grown in nano-scale lateral sizes and without a preferential orientation. Statistical analysis of the grains indicates that the lateral size dominantly lies in the range from 20 to 55 nm, as shown by the inset of Fig. 1c, demonstrating the high grain density (10^{10} - 10^{11} cm⁻²) and high GB surface density. Atomic structure of the GBs on the as-synthesized WS₂ film is distinguished using atomic-resolution HAADF-STEM imaging. After systematic examination of multiple boundary locations (Supplementary Fig. S4), we confirmed that the WS₂ grains in the as-synthesized film are indeed stitched together via GBs. It is established in previous research that the atomic make-up of GBs is diverse. In our sample, GBs are primarily consisted of 5–7 members of rings with a sulfur-rich chemical composition, as illustrated in Fig. 1e.

To demonstrate the application potential of GB-rich 2D layered materials as biochemical sensor materials, we fabricated the SPR sensors based on GB-rich 1L WS₂ film for ultra-sensitive detection of Hg²⁺. The basic setup of our sensor device (fabrication details in Methods) and the SPR imaging system are schematically illustrated in Supplementary Fig. S3. The detection principle of SPR sensors lies in the ultra-sensitivity of SPR signals (i.e. resonance angle of θ in the present work) to minute changes in

refractive index of the sensing surface. In this case, upon Hg^{2+} adsorption onto GB-rich 1L WS_2 film (sensor material), its refractive index changes, thus SPR curve shifts, providing quantitative information of Hg^{2+} on the 1L WS_2 film. By using Snell's Law and the N-layer transfer matrix method, we performed the computational simulation to profile the vertical electric field distribution of Au film before and after the transferring of a 1L WS_2 film (Supplementary Fig. S5). Compared with bare Au, the electric field is significantly enhanced upon the incorporation of GB-rich 1L WS_2 , and it is further increased to a maximum at the interface between 1L WS_2 film and sensing medium. The 1L WS_2 integration induced electric field enhancement between Au film and sensing medium signifies that the proposed SPR sensor is sensitive to slight changes in sensing medium, thus strongly suggests the suitability of 1L WS_2 film for SPR sensor. Generally, SPR signal optimization can be induced via incorporation of many other 2D layered materials onto Au film,^{65,66} which is favorable for detection sensitivity. However, this effect itself is insufficient for high sensor performance, and the fundamentally indispensable key factor is the high analyte adsorption ability of the sensor material.

To demonstrate the significant role of GBs in physi and/or chemi-adsorption of Hg^{2+} , the CVD-grown 1L WS_2 single crystals (see Supplementary Fig. S6) based SPR sensor for Hg^{2+} detection was also evaluated. Compared with the rich structural defects along GBs in polycrystalline 1L WS_2 film, the 1L WS_2 single crystal has much fewer structural defects on the surface, but possesses edge defects. As revealed in the previous studies,¹⁴ for the biochemical sensors based on 2D layered crystals, preferential adsorption occurs along material edges. Thus, the Hg^{2+} sensing abilities of SPR sensors based on GB-rich 1L WS_2 film and 1L WS_2 single crystal were investigated in detail for comparison. Figure 2a shows the angle-resolved SPR spectra of GB-rich 1L WS_2 film and 1L WS_2 single crystal in ultrapure water and at increasing concentrations of Hg^{2+} aqueous solution (10^{-18} – 10^{-11} M). In contrast to those of the 1L WS_2 single crystal based SPR sensor, the SPR spectra based on GB-rich 1L WS_2 film display much more prominent right-shift with increasing Hg^{2+} concentration, indicating adsorption of more Hg^{2+} ions. Figure 2b shows the determined resonance angle shift ($\Delta\theta$) as a function of Hg^{2+} concentration for the SPR sensors based on GB-rich 1L WS_2 film, in which the extracted one of 1L WS_2 crystal is also included for comparison. Distinctly, at the same Hg^{2+} concentration, the GB-rich 1L WS_2 sensor exhibits a much larger angle shift ($\Delta\theta$) than that of the 1L WS_2 crystal one. The degree of angle shift is proportional to the amount of adsorbed Hg^{2+} . Even at attomolar-level concentration (13 milli-degree for 10^{-18} M), the adsorption of Hg^{2+} by the GB-rich 1L WS_2 film brings about discernible change in SPR resonance angle. Notably, the GB-rich 1L WS_2 sensor displays the wide detectable dynamic range from 10^{-11} to 10^{-18} M, covering 7 orders of magnitude. Compared with that of the 1L WS_2 single crystal sensor, the observed much larger $\Delta\theta$ of GB-rich 1L WS_2 sensor indicates the substantially larger amount of Hg^{2+} ions adsorbed onto GB-rich 1L WS_2 . Thus, this drastic sensor performance difference not only demonstrates the outstanding sensitivity of GB-rich WS_2 sensor device, but, more importantly, reveals the significant role of high-surface-density GBs in sensor performance.

Adsorption or binding sites are energetically active positions, which are widely accepted to exist in structural defects of 2D layered materials, such as vacancy, antisite, substitution, edge, and GB.^{14,26,27,48–58,67–71} Structurally, although 1L WS₂ single crystals contain a certain amount of defects on surface and along edges, the surprisingly high surface-density of GBs in polycrystalline 1L WS₂ film immensely increase the amount of defects per unit area, providing the primary analyte binding sites. Thus, for the SPR sensor based on polycrystalline 1L WS₂ film, the observed superior sensitivity of Hg²⁺ detection is considered to result from the rich GBs.

For fundamental understanding on the role of GBs in Hg²⁺ adsorption of polycrystalline 1L WS₂ film, we performed DFT calculations by considering the chemisorption of Hg²⁺ ions on GBs and GB-free area for comparison, as shown in Figs. 3a, b and supplementary Fig. S7 (also see supplementary for calculation details). The adsorption energies E_{ads} of Hg²⁺ ions on different positions around GBs are listed between Figs. 3a and b. It is evident to find that Hg prefer to adsorb on the pentagon hollow site along GBs. Moreover, the adsorption energies of Hg around the GBs are also lower than that on pristine 1L WS₂ crystal (see Supplementary Fig. S7). This indicates the GBs behave like the Hg traps. From the charge density difference plot shown in Fig. 3b, we can find the apparent charge transfer between Hg and GBs. There are 0.1 negative charge transfer from Hg to neighboring S atoms, indicating the formation of covalent bonds between Hg and S atoms. The formation of Hg-S bond is substantiated by X-ray photoelectron spectroscopy (XPS) measurements of the as-synthesized GB-rich 1L WS₂ film before and after Hg²⁺ detection. Figures 3c-e show the XPS spectra of W4f, S2p and Hg4f core levels before and after Hg²⁺ detection. For the as-synthesized GB-rich 1L WS₂ film, the two deconvoluted W4f peaks at 32.63 and 34.79 eV (Fig. 3c top) and the two deconvoluted S2p peaks at 162.55 and 163.71 eV (Fig. 3d top) are ascribed to WS₂,⁷² while no trace of Hg is observed (Fig. 3e top). For the GB-rich 1L WS₂ film after Hg²⁺ detection in 10⁻⁹ M Hg²⁺ solution and then rinse with ultra-pure water for three times, obvious sign of S-Hg bonds is observable in the XPS spectrum of Hg4f core level (Fig. 3e bottom), and the main deconvoluted peaks of W4f and S2p are slightly shifted toward higher binding energies in contrast to those of the as-synthesized GB-rich 1L WS₂ film. The two deconvoluted W 4f peaks at 33.05 and 35.22 eV can be still related to WS₂. On the XPS spectra of S2p core level, however, in addition to the two strong deconvoluted peaks at 162.55 and 163.71 eV from WS₂, two new weak deconvoluted peaks at 161.67 and 163.11 eV are recognized to be produced by the formation of S-Hg bonds during Hg²⁺ detection. The formation of S-Hg bonds after Hg²⁺ detection, which can induce changes in chemical environment for W and S atoms in the WS₂ film, can also be the underlying origin for the observed slight shift of the XPS W4f and S2p peaks from WS₂ toward higher binding energies. The combined theoretical calculations and XPS measurements provide concrete evidence for the preferential adsorption of Hg²⁺ on the GBs via the formation of S-Hg bonds. Therefore, the rich chemically active sites on GBs in polycrystalline 1L WS₂ film serve as efficient probes for ultra-sensitive detection of Hg²⁺ ions.

As one of the crucial performance criteria, the selectivity of Hg^{2+} detection for the SPR sensor based on GB-rich polycrystalline 1L WS_2 film was also assessed. The evaluation was performed by comparing the sensor responses to 10^{-12} M of Hg^{2+} and common interfering ions such as Pb^{2+} , Mn^{2+} , Cu^{2+} , Fe^{3+} , Zn^{2+} , Co^{2+} , Cr^{3+} and Mg^{2+} . The determined resonance angle shifts $\Delta\theta$ in Fig. 4a show that the value of $\Delta\theta$ induced by Hg^{2+} adsorption is at least $\sim 3\text{X}$ higher than those produced by other ions, indicating that the GB-rich WS_2 sensor is highly selective towards Hg^{2+} detection.

To further validate the superior sensing capacity of the GB-rich WS_2 film, we compared its LOD for Hg^{2+} with those of previously reported high-performance Hg^{2+} sensing materials.^{17,73–135} As presented in Fig. 4b, the LOD of GB-rich WS_2 film for Hg^{2+} can reach down to 1 aM ($\sim 600 \text{ ions}\cdot\text{cm}^{-3}$), according to the IUPAC guideline of 3:1 signal to noise ratio, which clearly outperforms the previous ion sensors based on conventional sensor materials.

The superior performance of GB-rich 1L WS_2 based SPR sensor in Hg^{2+} detection relies on the presence of sufficient active sites along the rich GBs for the preferential and efficient adsorption of Hg^{2+} . Therefore, not only the polycrystalline 1L WS_2 film, the GB-rich polycrystalline 1L and few-layer films of any other layered metal sulphides would also be expected to serve as sensor materials for the similar ultra-sensitive detection of Hg^{2+} ions. As a demonstration, the CVD-grown GB-rich polycrystalline 1L MoS_2 film⁶² was used to fabricate the SPR sensor for detection of Hg^{2+} ions. As shown in the SPR spectra and the determined resonance angle shifts of $\Delta\theta$ (Supplementary Fig. S8), the superior sensor sensitivity down to trace attomolar-level quantification (LOD of 1 aM) is also observed for the GB-rich 1L MoS_2 film, comparable to those of the GB-rich 1L WS_2 film, which further demonstrates that the concept of GB-rich 2D layered materials for high-performance sensors is universal and comprehensive.

Conclusion

In summary, we report CVD-grown monolayer 2D films with high-surface-density GBs for biological and chemical sensor applications of attomolar sensing performance. Specifically, as a proof-of-concept, SPR sensor devices based on rich GBs in polycrystalline 1L WS_2 films present superior sensitivity of down to an ultra-low Hg^{2+} LOD of 1 aM. The inherent GB-rich structure is the key factor behind the observed extraordinary sensor performances, because the abundance of active sites in GBs is essential to analyte adsorption. More importantly, DFT calculations confirm that the structural defects on GBs are primary analyte binding sites. Consequently, the discovery of GB-induced exemplary sensor performance motivates more exciting developments based on GB-rich 2D materials and constitutes an extraordinary opportunity for the advancement of ultra-sensitive sensors.

Methods

Device fabrication. SPR sensor devices are constructed of the as-synthesized TMDs films transferred onto a 47 nm Au film-coated cover glass substrate (MATSUNAMI GLASS, Japan; Supplementary Fig. S1a). 2 nm Cr film was deposited prior to Au deposition for enhanced adhesion of Au film to cover glass substrate. The transfer of the as-grown TMDs films were performed via a standard PMMA-based wet transfer method. PMMA was spin-coated onto the as-synthesized film, baked at 150 °C for 180 sec, and immersed in 100 °C H₂O for 10 min to detach the PMMA-coated film from the substrate. The Au-coated substrates were used to pick up the PMMA-coated film. Finally, by dissolving the PMMA coating in acetone, followed by 3X ethanol rinse and 3X DI water rinse, the as-synthesized films were successfully transferred.

Experimental Setup. The adopted SPR imaging system was based on an inverted microscope (Nikon TI2-U, Japan) and a 100× (NA 1.49) oil immersion objective. A 680 nm 10 mW He-Ne laser was used as the light source to excite surface plasmon on the gold surface. The CMOS camera (Zyla 4.2 PLUS, Andor, Belfast, UK) was used to record the SPR image at different incident angles. A stepping motor was incorporated on the optical fiber to translate the incident angle of light beam. The incident angle was synchronized with the corresponding SPR image. The intensity measurement was performed using Image J software.

Sensor characterization. A silicon insert (flexiPERM®8-well reusable silicon insert, Sarstedt, Germany) is placed on the sensor device to hold analyte solutions. Angle-resolved SPR spectra was acquired in ultrapure water and then at increasing concentrations of Hg²⁺ aqueous solution (10⁻¹⁸ – 10⁻¹¹ M). At each measurement, the previous analyte solution is first removed from chamber by pump (Kylin-Bell Lab Instruments), followed by injection of current analyte solution.

Supporting information. Detailed OM, FL, Raman, PL, AFM and TEM characterization of as-synthesized materials and detailed angle-resolved SPR spectra of measured samples are provided.

Declarations

Data availability

The authors declare that the data supporting the findings of this study are available within the paper and its Supplementary Information files.

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Figures

Figure 1

Characterization of GBs in CVD-grown polycrystalline 1L WS₂ films on SiO₂ (300 nm)/Si substrates. AFM images of low (a) and high (b) magnifications. Low-magnification HAADF-STEM image (c) and SAED pattern (d) of as-grown polycrystalline 1L WS₂ films. Inset in (c) is the distribution of grain size. Atomic scale HAADF-STEM image (e) of a typical GB in the polycrystalline 1L WS₂ films.

Figure 2

Hg^{2+} detection of SPR sensor based on GB-rich 1L WS_2 film and 1L WS_2 crystal. SPR spectra at Hg^{2+} concentrations ranging from 10^{-17} M to 10^{-11} M (a) and extracted resonance angle shifts $\Delta\theta$ (b).

Figure 3

DFT and XPS characterization. DFT calculations regarding different adsorption positions of Hg atom on grain boundary labeled out with number 1-6 (a) and charge density difference between Hg atom and WS2 with grain boundaries (b). The calculated adsorption energies of E_{ads} at the 6 different positions are listed between (a) and (b). Yellow, blue and red balls represent S, W and Hg atoms, respectively. There is apparent charge transfer between Hg and nearby S atoms. The isosurface value is 0.0002 e/Bohr³. XPS spectra of W 4f (c), S 2p (d) and Hg 4f (e) core levels for the as-synthesized 1L WS2 film (top) and the 1L WS2 film after Hg₂⁺ detection (bottom). Notably, the XPS peak at 104.54 eV (e) is ascribed to Si from wafer.

Figure 4

Selectivity and LOD. (a) Selectivity of the GB-rich WS₂ based Hg²⁺ sensor. All ion solutions are 10⁻¹² M. (b) Overview of the Hg²⁺-detection limit using different sensor material. 17,73-135

Supplementary Files

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- [EXXXXXXXXXXXXXWS2polycrystalSPRHg detectionXXXXXXXXSupplementaryInformation.docx](#)