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Raman analysis of gold on WSe₂ single crystal film

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Abstract

Synthesis and characterization of high-quality single-crystal tungsten diselenide (WSe₂) films on a highly insulating substrate is presented. We demonstrate for the first time that the presence of gold (Au) nanoparticles in the basal plane of a WSe₂ film can enhance its Raman scattering intensity. The experimentally observed enhancement ratio in the Raman signal correlates well with the simulated electric field intensity using both three-dimensional electromagnetic software and theoretical calculation considering layered medium coupled-dipole approximation (LM-CDA). This work serves as a guideline for the use of Au nanoparticles on WSe₂ single-crystal thin films for surface enhanced Raman scattering (SERS) applications in the future.

In recent years, transitional metal dichalcogenide (TMD) materials have attracted tremendous attention due to their potential applications in valleytronics, flexible and low-power electronics, optoelectronics and sensing devices [1–7]. One of the TMD materials, tungsten diselenide (WSe₂), has a structure of Se-W-Se covalently bonded in a hexagonal quasi-2D network configuration that is stacked by weak Van der Waals forces. It is a group VI TMD that exhibits a trigonal prismatic structure with an indirect band gap of 1.21 eV in the bulk form and that increases to 1.25 eV (direct) at monolayer thickness [8]. Besides having excellent electrical properties, WSe₂ shows great promise for optical sensing applications [2–4, 9]. Due to its exceptional optical properties, WSe₂ yields strong Raman signal compared to other TMD materials. Nevertheless, no work has been reported that explores the potential of enhancing its Raman signal to render it a surface-enhanced Raman spectroscopy (SERS) substrate. In view of SERS being a topic of growing research interest, substrate materials with a strong Raman signal are being sought for sensing applications in analytical, biological and surface sciences.

In this work, we synthesize large triangular/hexagonal WSe₂ single-crystal films on c-face sapphire substrates via chemical vapor deposition (CVD) techniques. We demonstrate that the Raman signal of WSe₂ films can be enhanced easily by Au decoration, which might be applicable to use as a SERS substrate for sensing applications in future. An electromagnetic wave simulation and theoretical calculations utilizing the layered medium coupled-dipole approximation (LM-CDA) method were performed to quantitatively explain the experimentally observed enhancement in Raman scattering of our WSe₂ film arising from the Au decoration.

Results and discussion

We have been able to synthesize [5, 6, 10] single-crystal WSe₂ film continuously over a length of more than 170 μm. Figure 1(a) illustrates the experimental setup that was used to grow the WSe₂ films on the c-face sapphire substrate via a CVD approach (see experimental methods for details). Figure 1(b) shows a

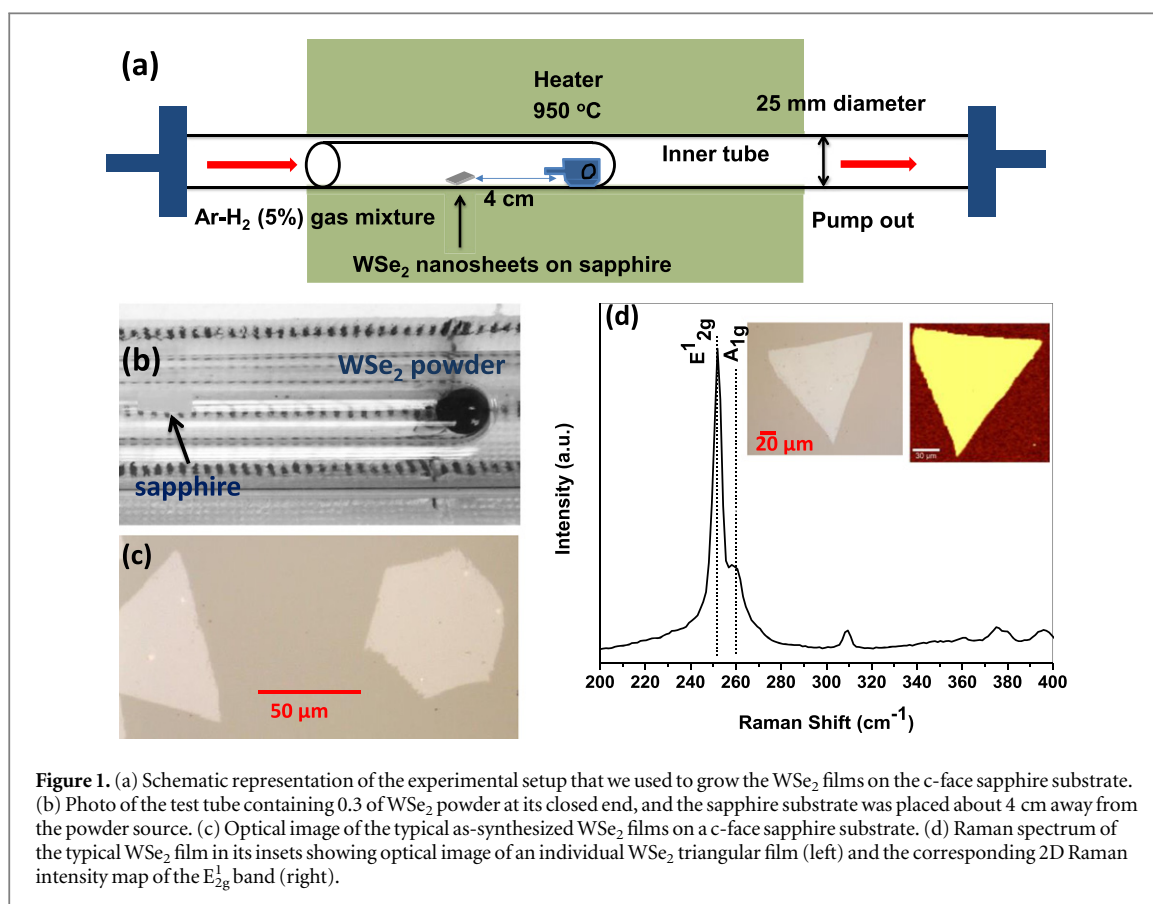
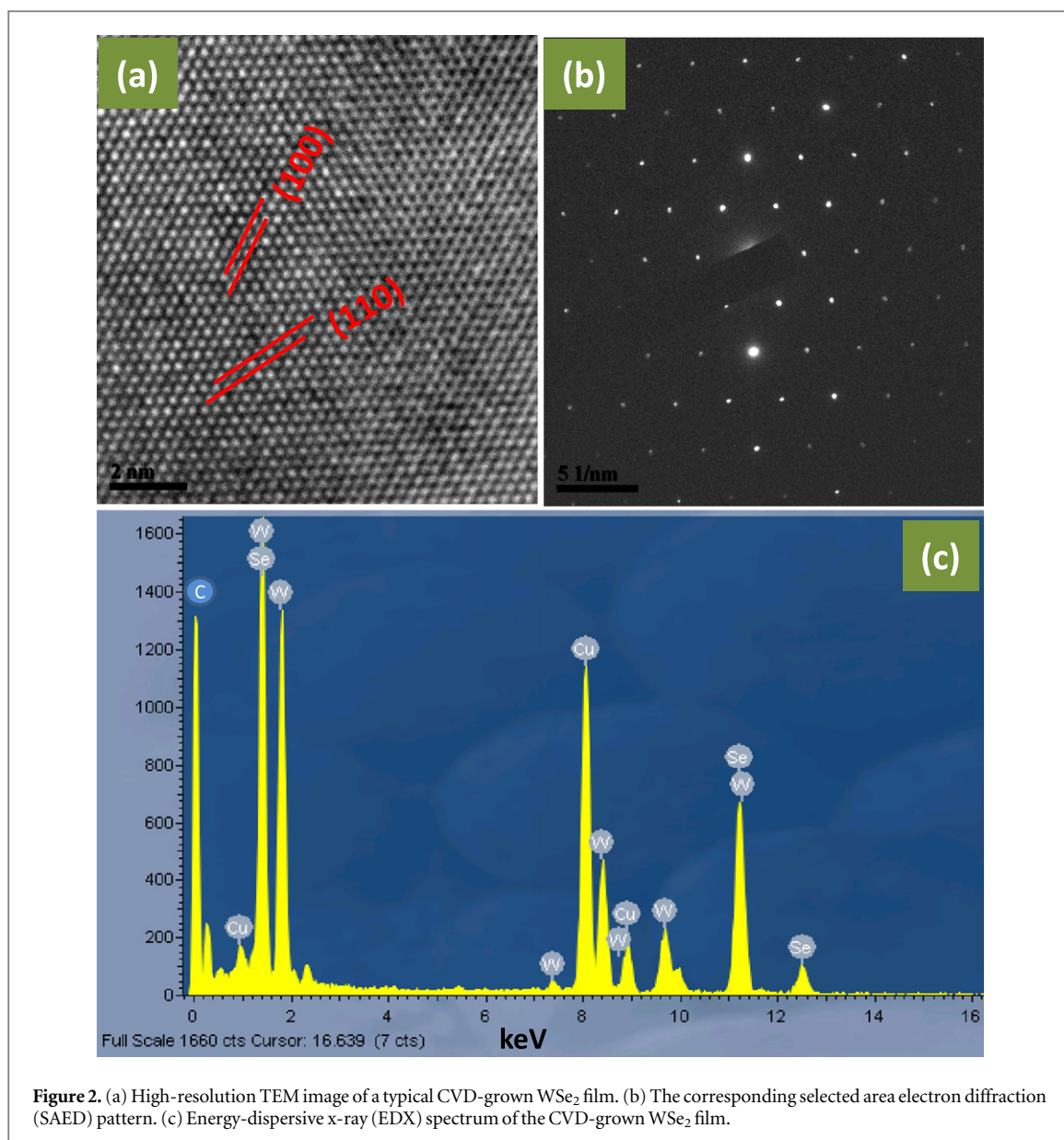


Figure 1. (a) Schematic representation of the experimental setup that we used to grow the WSe₂ films on the c-face sapphire substrate. (b) Photo of the test tube containing 0.3 g of WSe₂ powder at its closed end, and the sapphire substrate was placed about 4 cm away from the powder source. (c) Optical image of the typical as-synthesized WSe₂ films on a c-face sapphire substrate. (d) Raman spectrum of the typical WSe₂ film in its insets showing optical image of an individual WSe₂ triangular film (left) and the corresponding 2D Raman intensity map of the E_{2g}¹ band (right).

photograph of the test tube containing 0.3 g of WSe₂ powder at its closed end, while the sapphire substrate was placed about 4 cm away from the powder source. It is worth noting that the growth of WSe₂ films on the c-face sapphire substrate is highly dependent on the substrate position and temperature. Apart from this, we also attempted to grow WSe₂ films on both a- and r-face sapphire substrates, but there was no sign of growth on both types of the sapphire substrates. The uses of 5% H₂ in the carrier gas might help in reducing the surface oxide layer of the WSe₂ precursor powder. Figure 1(c) and the inset of figure 1(d) show the optical images of our synthesized WSe₂ films, which appear reasonably uniform and exhibit either triangular or hexagonal shapes with a lateral dimension of ~100–200 μm. In order to check the uniformity of the synthesized WSe₂ films, we performed a large area Raman scan using a WITec alpha 300R system with a 532 nm (2.33 eV) laser excitation source and a step size of 160 nm. As can be seen from the inset of figure 1(d), the intensity map of the E_{2g}¹ band is uniform throughout the large triangular WSe₂ film with a lateral size of more than 170 μm. In short, we have synthesized large triangular/hexagonal WSe₂ films on c-face sapphire substrates that are of uniform thickness.

In order to examine the number of layers of our CVD-grown WSe₂ films, we further characterized them through Raman analysis and atomic force microscopy (AFM). It has been reported that monolayer WSe₂ nanosheets on the sapphire substrate show A_{1g} mode vibration at 264 cm⁻¹ and two dominant peaks are observed around 250 cm⁻¹ in various samples from monolayer to bulk on SiO₂ (300 nm)/Si substrate [5, 11], while bulk WSe₂ exhibits two distinct Raman characteristic signals at 248 and 250.8 cm⁻¹ theoretically as well as experimentally [12, 13]. Our as-synthesized WSe₂ film on the sapphire substrate has two characteristic Raman peaks located at ~252 and ~260 cm⁻¹, which can be assigned to the in-plane vibrational E_{2g}¹ mode and the out-of-plane vibrational A_{1g} mode, respectively (figure 1(d)). In addition, another prominent Raman band was detected at ~309 cm⁻¹ for our as-synthesized WSe₂ film, which is an indication of interlayer interaction for layered 2D material [6]. Furthermore, the thickness of our WSe₂ film is measured to be 1.6 nm (figure S1), and hence we believe that our CVD-grown film is a bilayer WSe₂ film.

We also observed crystallinity of our CVD-grown WSe₂ films in a transmission electron microscope (TEM). The TEM image in figure 2(a) shows the periodic atom arrangement of the WSe₂ film, indicating that the WSe₂ film is highly crystalline. Figure 2(b) shows the selected area electron diffraction (SAED) pattern taken on the WSe₂ film with an aperture size of ~200 nm. The high-resolution TEM image and its corresponding SAED pattern indicate a hexagonal lattice structure with a spacing of 0.38 and 0.34 nm that can be assigned to the (100) and (110) planes, respectively. Apart from that, the chemical composition of the synthesized film is determined to be tungsten (W) and selenium (Se) with an atomic ratio of 1:2 by using an energy-dispersive x-ray



spectroscopy (EDX) detector that is attached to the TEM (figure 2(c)). The carbon and copper peaks in the EDX spectrum can be attributed to the thin carbon film and copper mesh of the TEM grid holder, respectively. These findings confirmed that the synthesized film is a single-crystal WSe₂ film.

Thus far, we have confirmed that our CVD-grown WSe₂ film on the *c*-face sapphire substrate is a bilayer and single crystal, and more importantly, it shows prominent Raman characteristic peaks. In order to transform the synthesized WSe₂ film into an enhanced Raman scattering substrate, we decorated it with Au nanoparticles via two simple steps: Au film deposition and annealing. A thin layer of Au film (~5 nm (figure S2)) was first deposited on the CVD-grown WSe₂ film, followed by annealing in an inert environment at 550 °C for 3 h to form Au nanoparticles (NPs) on the WSe₂ films (see methods for details). The size of Au NPs formed using this approach is estimated to be ~9 nm with a spacing of 13–20 nm between particles (figure S3). Figure 3(a) shows a high-resolution Raman intensity map of the E_{2g} band of a typical WSe₂ film that was half-decorated with Au NPs. It is obvious that the Raman intensity of the Au NPs–decorated WSe₂ film is higher compared to that of the bare WSe₂ film. Figure 3(b) shows the Raman spectrum of both Au-decorated and bare WSe₂ films, and its inset shows their relative intensity difference in E_{2g}/A_{1g}. Basically, the main characteristic Raman peak intensity of the WSe₂ film has been enhanced by ~1.14 times by Au NPs under the excitation wavelength of 532 nm. The E_{2g}/A_{1g} peak intensity ratio is increased from 1.15 to 1.2 after Au NPs coating on the WSe₂ film. As can be seen from figure S4 (the respective Lorentz peaks fitting), both A_{1g} and E_{2g} peaks for the Au NPs–decorated WSe₂ film show a blue shift (towards lower frequency number) compared to that of bare WSe₂, which could be due to *p*-doping caused by electron transfer from the WSe₂ film to Au NPs [16–18]. On the other hand, figure 3(c) shows the optical image of a typical hexagonal WSe₂ film fully decorated with Au NPs, while figure 3(d) shows its

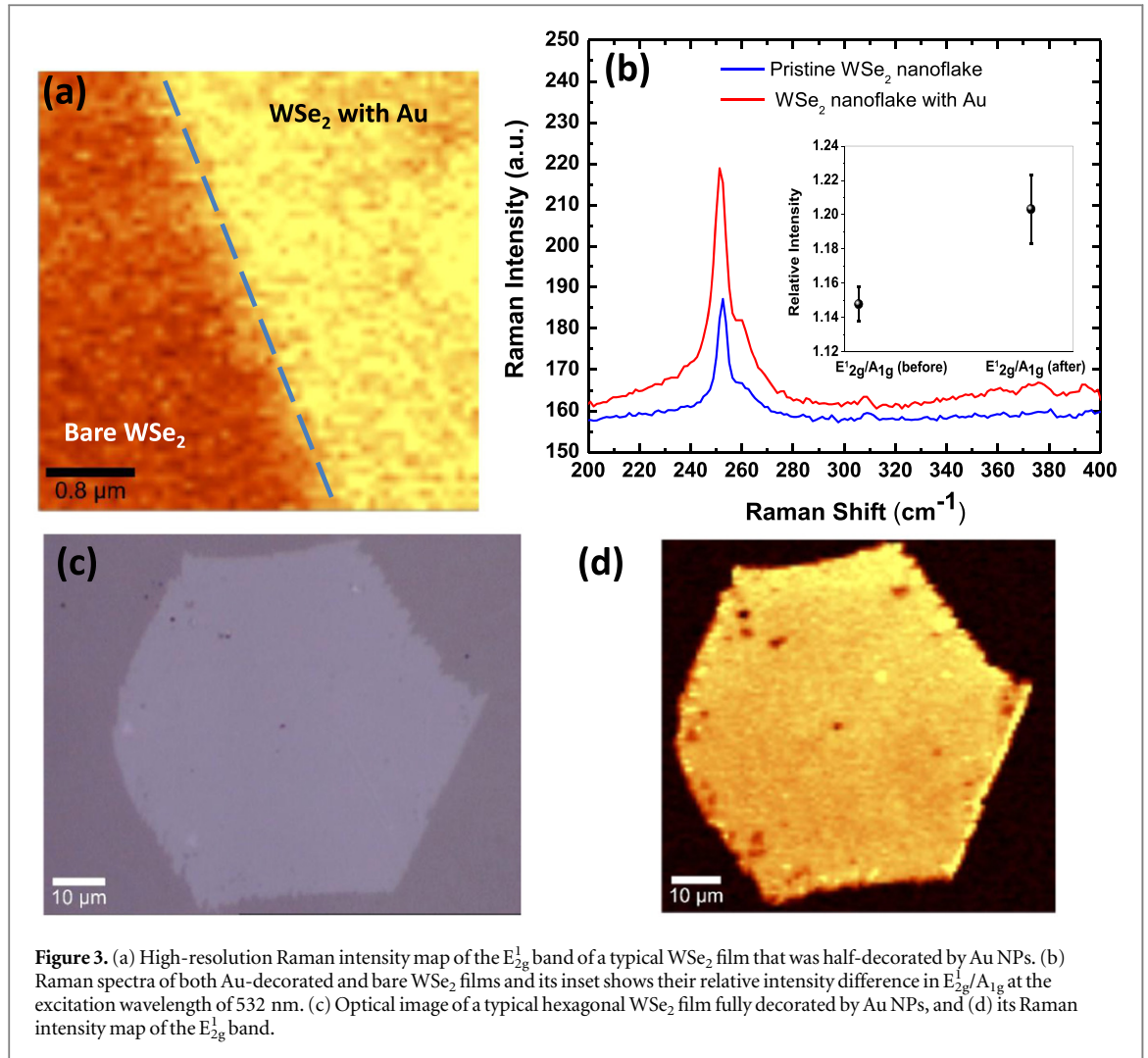


Figure 3. (a) High-resolution Raman intensity map of the E_{2g}^1 band of a typical WSe_2 film that was half-decorated by Au NPs. (b) Raman spectra of both Au-decorated and bare WSe_2 films and its inset shows their relative intensity difference in E_{2g}^1/A_{1g} at the excitation wavelength of 532 nm. (c) Optical image of a typical hexagonal WSe_2 film fully decorated by Au NPs, and (d) its Raman intensity map of the E_{2g}^1 band.

Raman intensity map of the E_{2g}^1 band. It can be clearly seen that the Raman intensity is uniform throughout the Au-decorated WSe_2 film. Besides that, we also characterized the Au-decorated WSe_2 film with different Raman excitation wavelengths (i.e., 488 and 633 nm), as shown in figure S5. The prominent main characteristic Raman peak intensity ratios (I_{Au+WSe_2}/I_{WSe_2}) with and without Au NPs coating on WSe_2 film are 1.01 and 1.04 for an excitation wavelength of 488 and 633 nm, respectively.

To further understand the enhancement in Raman scattering spectra of Au-decorated WSe_2 film and its wavelength-dependent nature, we performed a set of simulations and calculations as follows.

When excited with an incident electromagnetic wave, where the associated electric field intensity is $\mathbf{E} = \mathbf{n}_e E_0 \cos(\omega t)$, the dipole moment induced on an atom (or an NP) is given by $\mathbf{P} = \alpha \mathbf{E}$, where α is the polarizability of the atom, ω is the angular frequency, and \mathbf{n}_e is a unit vector representing the polarization of the electric field. Under such excitation, atoms vibrate around their equilibrium position and the physical displacement can be approximated as $dQ = Q_0 \cos(\omega_v t)$, where Q_0 is the maximum displacement and ω_v is the vibration frequency. Since the displacements for these planarly confined atoms are very short, their polarizability can be well approximated with a Taylor series expansion, such that $\alpha = \alpha_0 + \frac{\partial \alpha}{\partial Q} dQ$, where α_0 is the polarizability of the atom at the equilibrium position. Then the induced dipole moment intensity can be written as

$$P = \alpha_0 E_0 \cos(\omega t) + \frac{\partial \alpha}{\partial Q} \frac{Q_0 E_0}{2} \times \left\{ \cos((\omega - \omega_v)t) + \cos((\omega + \omega_v)t) \right\} \quad (1)$$

Basically, this equation means that all Rayleigh (first term), Stoke (second term), and anti-Stoke (third term) scattering components are proportional to the incident field strength. The experimentally observed Raman peak intensity enhancement informs us that when the WSe_2 layer is decorated with Au NPs, the electric field intensity

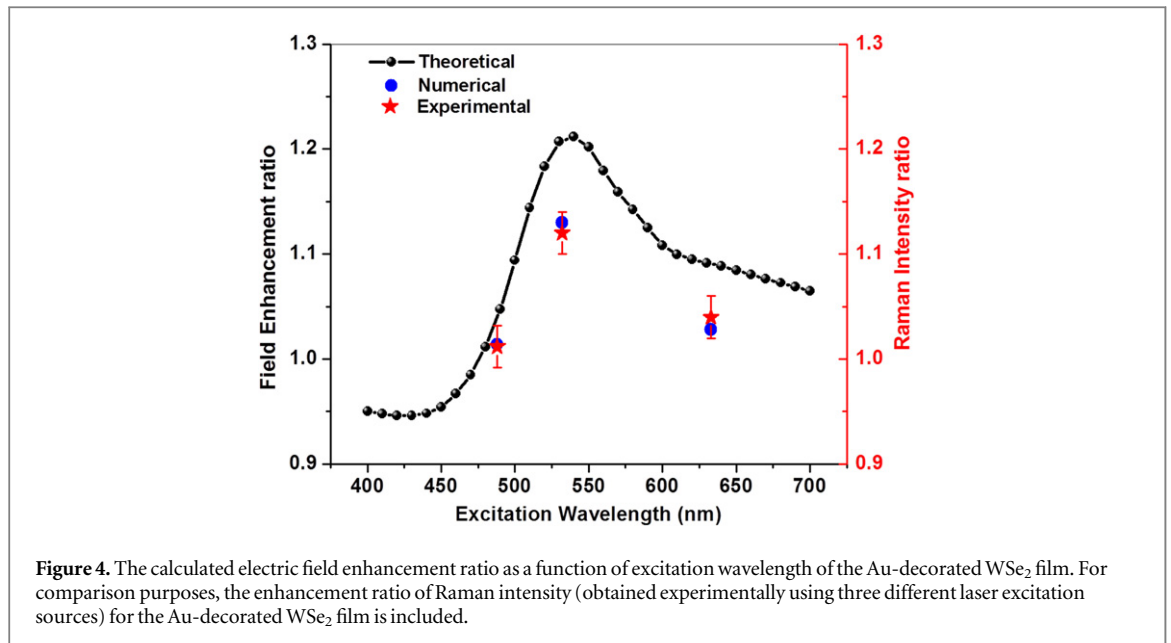


Figure 4. The calculated electric field enhancement ratio as a function of excitation wavelength of the Au-decorated WSe₂ film. For comparison purposes, the enhancement ratio of Raman intensity (obtained experimentally using three different laser excitation sources) for the Au-decorated WSe₂ film is included.

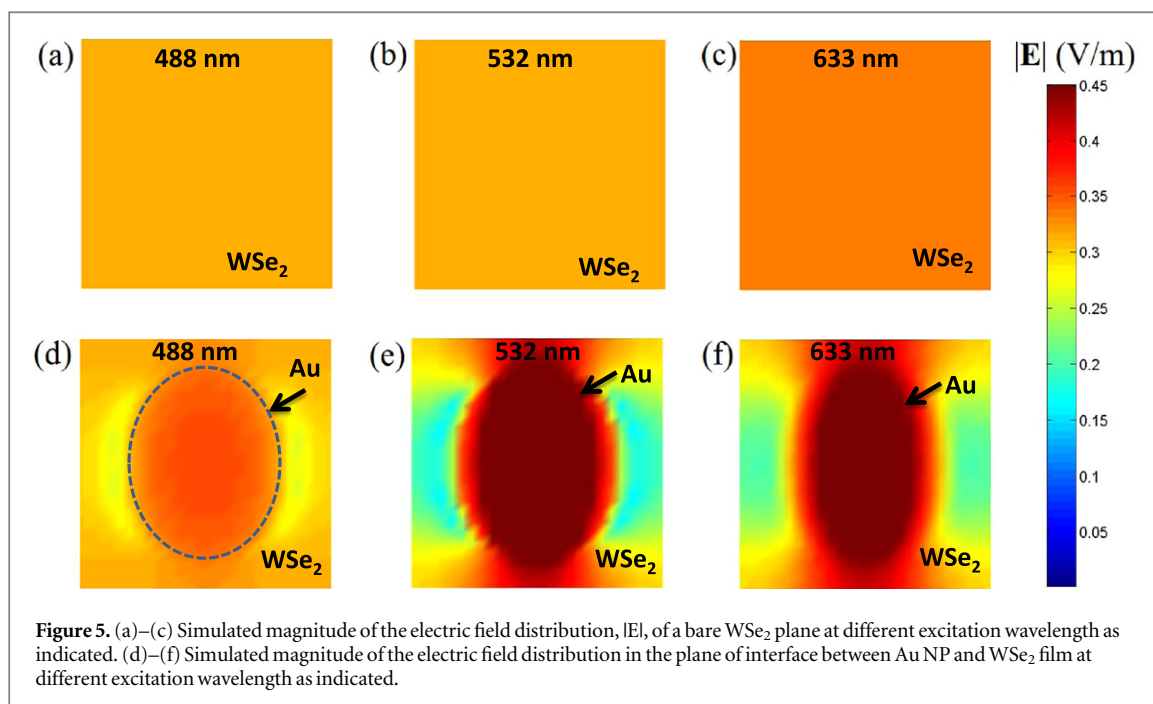
inside the WSe₂ layer changes, and this change is in the positive direction (increase) for the wavelength range of our interest.

The field distribution throughout the WSe₂ thin film-coated sapphire substrates can be calculated analytically. For the Au NP-decorated samples, one can either use the well-known coupled-dipole approximation (CDA) [19] or a commercially available electromagnetic software package [20]. In this work, we followed both approaches assuming Au cylindrical NPs (with a diameter of 9 nm and a height of 6 nm) are periodically aligned on top of a bilayer WSe₂-coated sapphire substrate. The inter-particle spacing is 12 nm along the *x*- and *y*-axes. The frequency-dependent complex permittivity of WSe₂ is taken from [21]; the refractive index of sapphire is assumed to be 1.768. For the optical constants of Au, experimental values are used rather than the Drude model to eliminate any concern regarding the selection of appropriate values for plasmon and relaxation frequencies [22, 23].

For the LM-CDA approach, we first calculate the average electric field intensity, $E_{ave} = \sum_N (E_{LM}^{inc} + E_{LM}^{ind} - E_{LM}^{scat}) / N$, on the WSe₂ surface (at $-6 < X < 6$ nm, $-6 < Y < 6$ nm), where E_{LM}^{inc} is the layered medium incident electric field, E_{LM}^{ind} is the electric field created by the induced dipoles, and E_{LM}^{scat} is the back-scattered electric field. It should be noted that both for E_{LM}^{ind} and E_{LM}^{scat} , the layered medium polarizability factors are used, as explained in [19]. Then, the ratio of E_{ave} to the average layered medium electric field intensity, $E_{ave}^{inc} = \sum_N (E_{LM}^{inc}) / N$, gives the approximate field enhancement ratio. The black line in figure 4 shows this ratio as a function of wavelength for $400 \leq \lambda \leq 700$ nm. This theoretical result suggests that the field is enhanced when the wavelength is 475 nm or higher and the maximum possible enhancement ratio is ~ 1.21 at the wavelength of ~ 540 nm.

For the numerical approach, we use Wavenology (from Wave Computation Technologies, Inc. [20]) to calculate the field enhancement ratio by utilizing a mesh setting of 200 points per wavelength. Since Wavenology is a commercial finite-difference time-domain (FDTD) full wave electromagnetic solver, it is expected to provide more realistic results, as it makes no approximation for the polarizability of the NPs. We calculate the electric field distributions with and without NPs for the same physical parameters utilized in the CDA solution by assigning periodic boundary conditions at the $\pm X$ and $\pm Y$ boundaries and perfectly matched layers at the $\pm Z$ boundaries. Figure 5 shows the magnitudes of electric field distributions at three wavelength values (488, 532, and 633) over the WSe₂ surface with and without Au NPs. The ratios of former average field intensities to latter ones yield the enhancement ratios of 1.014, 1.132, and 1.029. These numbers, marked with a blue circular patch on figure 4, show good agreement with the experimental results of the prominent Raman peak intensity ratio, indicated by red stars in figure 4.

In summary, large WSe₂ films were synthesized on a highly insulating sapphire substrate using the CVD technique. We carefully examine the synthesized films using Raman spectroscopy, TEM, EDX and AFM and confirmed that our CVD-grown WSe₂ films on the *c*-face sapphire substrate are single-crystal bilayer WSe₂ films with prominent Raman characteristic peaks. We demonstrate experimentally, theoretically and numerically that the Raman signature of the WSe₂ films can be enhanced by Au decoration due to surface plasmon resonance. To



sum up, Au NPs on WSe_2 single-crystal film holds promise to further enhance Raman scattering, which could be useful for realizing the sensing application.

Experimental methods

Growth and characterization of WSe_2 films

In our experiments, the synthetic route is described as follows. Pure WSe_2 powder (Sigma Aldrich, purity 99.8%) was used as a source material. C-face sapphire substrates were placed inside the one-end open quartz-glass tube, where a small amount (~ 0.3 g) of WSe_2 source powder was loaded at the closed end of the tube as shown in the picture (figure 1(b)). The tube was inserted in a horizontal quartz tube placed in a conventional tube furnace such that the substrate was set at the lower temperature region of the source powders and the distance between them was about 4 cm. Then the quartz tube was evacuated to a base pressure $\sim 10^{-3}$ mbar for 2 h by a vacuum pump and subsequently was filled with the mixture of argon (Ar) with 5% H_2 gas. The gas was allowed to flow for 1 h after flushing the tube 2–3 times. After that, the furnace was heated under the mixture gas of Ar and 5% H_2 at a flow rate of 100 sccm (standard cubic centimeters per minute). When the temperature reached 950°C (heating rate: $30^\circ\text{C min}^{-1}$), the pressure of Ar carrier gas was maintained at ~ 2 mbar during synthesis for 15 min. After the reaction was terminated, the substrates were taken out when the temperature of the furnace cooled down to room temperature.

The morphology, structure and chemical composition of the as-synthesized nanostructures were characterized using AFM (Veeco D3000 NS49 system), TEM (JEOL, JEM-2010 F, 200 kV), and EDX equipped in the TEM and Raman spectroscopy. All Raman analyses in this study were performed using a Raman system (WITec alpha 300 R) with a 532 nm laser excitation source and laser spot size of ~ 320 nm ($\times 100$ objective lens with numerical aperture 0.9). The laser power at the sample was kept below 0.1 mW, which did not give rise to noticeable sample heating [14]. All Raman mappings were conducted with a step size of 160 nm. The spectral resolution was ≤ 1.5 cm^{-1} (using a grating with 1800 grooves mm^{-1}), and each spectrum was an average of 10 acquisitions (0.1 s of accumulation time per acquisition).

Formation of Au NPs on the CVD-grown WSe_2 films

A metal shadow mask was used such that some of the CVD-grown WSe_2 films on the c-face sapphire substrates were partially exposed. Subsequently, Au film was directly deposited on the sample via thermal evaporation at a rate of ~ 0.05 nm s^{-1} for 3–5 s at a chamber base pressure of 3×10^{-6} mbar, and the thickness of the Au film was measured to be ~ 5 nm by AFM (figure S2). The sample was then annealed at 550°C for 3 h in an Ar gas environment to allow formation of Au NPs on the CVD-grown WSe_2 films [15]. As can be seen in figure S3, the size of each Au NP is ~ 9 – 12 nm in diameter with a spacing of 13–20 nm between NPs.

Acknowledgments

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Conflict of interest

The authors declare no competing financial interests.

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