Substantially Enhanced Properties of 2D WS₂ by High Concentration of Erbium Doping against Tungsten Vacancy Formation

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Doping in 2D materials is an important method for tuning of band structures. For this purpose, it is important to develop controllable doping techniques. Here, we demonstrate a substitutional doping strategy by erbium (Er) ions in the synthesis of monolayer WS₂ by chemical vapor deposition. Substantial enhancements in photoluminescent and photoresponsive properties are achieved, which indicate a tungsten vacancy suppression mechanism by Er filling. Er ion doping in the monolayer WS₂ is proved by X-ray diffraction (XRD) and X-ray photoelectron spectra (XPS), fluorescence, absorption, excitation, and Raman spectra. 11.5 at% of the maximum Er concentration is examined by energy dispersive X-ray spectroscopy (EDX). Over 6 times enhancement of intensities with 7.9 nm redshift in peaks are observed from the fluorescent spectra of Er-doped WS₂ monolayers compared with their counterparts of the pristine WS₂ monolayers, which agrees well with the density functional theory calculations. In addition, over 11 times of dark current, 469 times of photocurrents, photoresponsivity, and external quantum efficiency, and two orders of photoresponse speed are demonstrated from the Er-doped WS₂ photodetector compared with those of the pristine WS₂ device. Our findings prove rare-earth doping in 2D materials, the exciting and ideal technique for substantially enhanced photoluminescent and photoresponsive properties.

1. Introduction

The study of photoluminescent and photoresponsive properties in two-dimensional (2D) semiconductors has attracted remarkable scientific and technological interests [1–5]. Among which, transition metal dichalcogenides (TMDs) with over 40 types of metal and chalcogen combinations is one of the mostly focused family due to their thickness-dependent band gaps from visible to near-infrared [6, 7], theoretically high switching ratios [8, 9], carrier mobilities [10, 11], and photoresponsive for applications in photoelectric and electric fields [12–16]. As the first representative TMDs, 2D MoS₂ is the mostly characterized material. Besides MoS₂, WS₂ is possibly more attractive due to its 20 times higher of photoluminescent efficiency, better thermal stability, larger valence band splitting, and theoretically reduced effective carrier masses [17–19]. However, a huge gap exists between the theoretical predictions and the experimental performances [20]. For instance, the measured mobilities and photoresponse time of monolayer WS₂-based field-effect transistors (FETs) are typically in the range of 1-50 cm²/V·s and 5-2000 ms, respectively [21–25], which are far less than the predicted mobility of >500 cm²/V·s and photoresponse time of <100 ns, respectively [17, 26–29]. The reduced performances are partly attributed to the unoptimized device fabrications and structural designs [30]. The essential reason may due to the defect-induced trap states that produced in the synthesizing process [31], since electronic states at energy band edges and defects in 2D WS₂ are significantly more active and especially fatal to its photoluminescent and photoresponsive performances compared with their bulk counterparts. 2D WS₂ prepared by top-
down approaches usually have better crystalline quality but with uncontrollable thicknesses and small sizes [32]. For practical applications, wafer-scale synthesis of homogeneous monolayer WS2 is required. In this regard, chemical vapor deposition (CVD) is extensively employed [22, 23, 33, 34]. Nevertheless, from the perspective of the second law of thermodynamics, a variety of defects are inevitably generated during CVD synthesis. The typical type of intrinsic defects comes from the missing atoms, including transition metal vacancies and chalcogen vacancies, which has been observed in many kinds of 2D TMDs [35–38]. The photoluminescence quantum yields of CVD-grown TMDs are only 0.01–6% of the mechanically exfoliated samples due to the high density of vacancy defects [39]. As the most defective CVD grown 2D TMDs, WSe2 shows 1.48 at% of Se vacancy, but the density of transition metal vacancies in TMDs and the corresponding influences on their photoelectric performances are still unknown [40]. Many methods, including high-temperature treatment, chemical reduction, and ultra-violet irradiation, have been proposed to reduce the chalcogen defects, while approach to lower the transition metal vacancies and similar ion radii between Er and W ions in the WS2 monolayer with a high concentration of 11.5 at% [16–19], then, the argon gas is fed at a rate of 300 sccm to reach a standard atmospheric pressure in the quartz tube. The temperature curve of the synthesis process is shown in Figure 1(b). In the meantime, the second temperature zone is heated to 200°C at a rate of 5°C/min, and then held for 5 min. The CVD chamber is vacuumed again during the heating process (<5 Pa), and then, the argon gas is fed at a rate of 300 sccm to reach a standard atmospheric pressure in the tube. The purpose of this step is to remove the impurity gases and desorbed dusts generated by heating of the quartz chamber. Subsequently, the first and second temperature zones are heated to 200°C and 850°C (Tg) in 40 minutes, respectively. The synthesis of WS2 is finished in 10 min in an argon-hydrogen mixture gas (UHP, Ar 90%, H2 10%) flow at a rate of 60 sccm. Finally, the samples are naturally cooled to room temperature in a 60 sccm of argon flow.

2. Methods

2.1. Synthesis of WS2 via CVD Process. The preparation of 2D WS2 is carried out in quartz tubes with 2-inch diameter in double temperature furnaces, as is schematically shown in Figure 1(a). 3 × 3 cm2 of SiO2/Si wafers with 300 nm thickness of SiO2 is used as the substrates. 150 mg sulfur powder (>99.5%) is weighed as the precursor, tungstic acid (H2WO4) powder (>99.5%) with the dosage of 65 mg is used as the tungsten source, and 4-8 mg of sodium chloride (NaCl) powder (>99.9%) is used as the growth promoter. 13 mg of Er2O3 powder (>99.9%) is used as the RE dopant for the preparation of Er-doped WS2 membranes (WS2(Er)). The H2WO4, Er2O3, and NaCl powders are mixed sufficiently before being placed in the quartz boats. The SiO2/Si substrates are put directly face down above the quartz boat with a distance of 10 mm between the substrate and the powder. In the beginning, the CVD chamber is vacuumed (<5 Pa), and argon gas (UHP, >99.999%) is fed subsequently at a rate of 300 sccm to reach a standard atmospheric pressure in the quartz tube. The temperature curve of the synthesis process is shown in Figure 1(b). In the meantime, the second temperature zone is heated to 150°C at a rate of 5°C/min, and then held for 5 min. The CVD chamber is vacuumed again during the heating process (<5 Pa), and then, the argon gas is fed at a rate of 300 sccm to reach a standard atmospheric pressure in the tube. The purpose of this step is to remove the impurity gases and desorbed dusts generated by heating of the quartz chamber. Subsequently, the first and second temperature zones are heated to 200°C and 850°C (Tg) in 40 minutes, respectively. The synthesis of WS2 is finished in 10 min in an argon-hydrogen mixture gas (UHP, Ar 90%, H2 10%) flow at a rate of 60 sccm. Finally, the samples are naturally cooled to room temperature in a 60 sccm of argon flow.

2.2. Characterization of the Pristine and Er-Doped WS2 Membranes. The surface morphologies of the pristine and Er-doped WS2 samples are characterized by optical microscope (50i POL, Nikon) and energy dispersive spectrum...
(EDS) in SEM (JSM-7800F, JEOL), and the roughness and thickness of WS₂ samples are characterized by atomic force microscope (AFM, Dimension EDGE, Bruker). The Raman spectra of WS₂ and WS₂(Er) samples are measured by a laser confocal Raman spectrometer (InVia Reflex, Renishaw) with a continue wave (cw) laser wavelength of 532 nm. X-ray diffraction spectra (XPERT3 Powder) of the samples are performed to confirm the diffracted characteristic peaks of the doped erbium ions. Photoluminescence (PL) spectra are measured by a laser scanning confocal microscope system excited at 532 nm. A spherical aberration correction TEM (Titan Cubed Themis G2 300) is used for the measurement of HAADF-STEM and energy dispersive X-ray spectroscopy (EDX) to characterize the crystalline structures and elemental compositions of the WS₂(Er) samples.

3. Results and Discussion

By slightly adjusting the weight of NaCl, up to 1 mm of triangular shape and even centimeter-scale of Er-doped WS₂ membranes can be synthesized by the CVD method. Typical optical micrographs of the WS₂ samples are shown in Figures 1(c) and 1(e), and their corresponding thicknesses are measured to be nearly 1 nm by AFM, which is consistent with the reported thickness of monolayer WS₂, as shown in Figures 1(d) and 1(f) [53, 54]. The pristine WS₂ are synthesized under the same conditions without Er₂O₃ as a dopant. Relevant experimental details can be found in S1 (Supporting Information).

Compared with surface chemical doping approaches, substitutional doping involves covalent bonding and is a more stable doping technique. Caption substitutional doping in TMDs, including niobium, rhenium, erbium, and holmium, has been demonstrated to tune their electronic properties in recent report [45, 52, 54, 55]. However, the doping concentrations are usually low (typically ≦ 1 at%), and the PL intensities even decreased. To get the maximum Er doping concentration, excessive dosage of Er₂O₃ is added into the tungsten source with a weight ratio of 1 : 5 to the H₂WO₄ powder, but the exact concentration of Er ion in the WS₂ film is still unknown. SEM and EDS are firstly used to evaluate the [Er] concentration. Figure 2(a) and Figure 2(b) show the SEM image and selected area elemental analysis by EDS of the Er-doped WS₂ film. The insert chart in Figure 2(b) shows the elemental type, weight, and atomic ratio of the WS₂ film on SiO₂/Si substrates measured by EDS in SEM. Besides high contents of [O] and [Si] from SiO₂ substrates, there are still tiny amount of [S], [W], and [Er] which are examined from the EDS spectrum. Compared with the atomic ratio of [W], the atomic percentage of [Er]
Figure 2: Microscopic analysis of WS$_2$(Er) monolayer by SEM and TEM. (a) SEM and (b) EDS image of a WS$_2$(Er) membrane synthesized on a SiO$_2$/Si substrate. The inserted table in (b) shows the atomic ratio measured by EDS in a selected rectangular region in (a). (c) WS$_2$(Er) membrane on Cu grid characterized by HAADF-STEM with the correction of spherical aberration. (d) EDX image of the WS$_2$(Er) membrane measured in (c). (e) SAED pattern of the same WS$_2$(Er) membrane. (f), (g), and (h) are the elemental mapping image of [S], [W], and [Er] in the WS$_2$(Er) membrane measured by the HAADF-STEM system, respectively. (i) Atomic fraction of [S], [W], and [Er] elements in the WS$_2$(Er) matrix analyzed by the HAADF-STEM system.
to [W] is close to 10%. The high content of [C] may come from the remnant of organic cleaning. To further confirm the concentration of erbium ions in the WS$_2$ film, the WS$_2$(Er) sample is characterized by high-angle annular darkfield scanning transmission electron microscopy (HAADF-STEM) with the correction of spherical aberration, as shown in Figure 2(c). A crystalline plane spacing of 0.267 nm can be measured between two immediate lines along the (1010) direction, which is consistent with the results of monolayer WS$_2$ [22]. Because the atomic number of [Er] (No. 68) is close to but a little smaller than [W] (No. 74), and their ion radius in WS$_2$ crystalline is similar, it is difficult to distinguish [Er] locations from the HAADF-STEM image of WS$_2$ film by brightness or ion size. But for the same reason, it is also reasonable to infer that minimal crystalline distortions are induced in the WS$_2$ monolayer by Er doping. Substitutional doping of caption ions with large differences in ion radius usually induces large lattice distortions, which in principle leads to additional surface defects. Surface trapping states caused by these defects will further degenerate material properties, including quantum yields, carrier mobilities, photoresponse speed, and especially fatal for 2D materials. Figure 2(d) shows the EDX image of the WS$_2$(Er) sample on TEM Cu grid; a weak Er-M peak implies the existence of doped [Er] atoms with the Er atomic ratio of about 11.5 at% in WS$_2$ analyzed by the system, as shown in Figure 2(i). This atomic ratio is close to the result of about 10 at% measured by the EDS-SEM for the sample on SiO$_2$/Si substrate. A strong [O] peak is also found in the EDX image, which may come from the residue of PMMA or organic contaminations from organic cleaning of the substrates, since PMMA is used to transfer the WS$_2$(Er) membrane onto the TEM Cu grid. The selective area electron diffraction (SAED) diagram of the Er-doped WS$_2$ film shows six diffraction points on the diffraction pattern, which corresponds to tungsten and sulfur sublattices, respectively, indicating the intact hexagonal symmetry of the present WS$_2$ film after high concentration of Er doping (Figure 2(e)). Additionally, elemental mapping images (Figures 2(f)–2(h)) show the homogeneous distribution of [S], [W], and [Er] in the sample, which also suggests that Er atoms are successfully doped into the WS$_2$ matrix.

Subsequently, Raman, X-ray diffraction, X-ray photoelectron, photoluminescence, and absorption spectra of the prepared WS$_2$(Er) samples are performed, and the results are compared with the counterparts of the pristine WS$_2$ samples. Figure 3(a) presents Raman spectra of the prepared WS$_2$ and WS$_2$(Er) films under 532 nm laser excitation. The WS$_2$(Er) sample shows almost equal peak intensity in the out-of-plane vibration mode ($A_{1g}(T)$), but two times intensity of the in-plane vibration mode ($E_{2g}(T)$) compared with that of the pristine WS$_2$ sample. Besides, 1.82 cm$^{-1}$ and 1.2 cm$^{-1}$ of redshifts are observed in the $E_{2g}(T)$ and $A_{1g}(T)$ from the WS$_2$(Er) sample, respectively. Both of these phenomena indicate the possible effects of Er doping in WS$_2$ matrix. Because intensity of the $A_{1g}(T)$ mode strongly depends on the layer thickness, the nearly equal intensities of the $A_{1g}(T)$ mode indicate little thickness difference between these two samples. On this basis, higher defect density usually leads to the lower crystalline symmetry and thus to the lower of $E_{2g}(T)$ intensity. Two times intensity enhancement of the $E_{2g}(T)$ mode possibly indicates the lower defect concentration in the WS$_2$(Er) sample. In addition, a Raman peak located at 384.9 cm$^{-1}$ is obviously seen from the WS$_2$(Er) sample but nonexistent in the WS$_2$ sample. This peak is very likely contributed from the Tg mode of Er ion [56].

X-ray diffraction spectra are measured on WS$_2$ and WS$_2$(Er) films to qualitatively confirm the successful doping of Er ions. Because Bragg diffraction effect is weak on a monolayer sample, thick films with large sizes are required in this measurement. In the meantime, concentration of Er ions in the WS$_2$ matrix is not dependent on the thickness and size of the films. Thus, WS$_2$ and WS$_2$(Er) samples with about 10 nanometer in thicknesses and several millimeter in sizes are used in this measurement. Figure 3(b) shows the X-ray diffraction spectra of the WS$_2$ and WS$_2$(Er) samples. The WS$_2$ (101) and WS$_2$ (104) diffraction peaks are observed in both of the two type of samples. Meanwhile, a strong extra peak is discovered in the WS$_2$(Er) sample located at the position of $2\theta = 14.4^\circ$, which is highly consistent with the X-ray diffraction peak of Er$_x$S$_y$(201). The strength ratio between this peak and WS$_2$(101) peaks is 0.51, further indicating the high concentration of Er doping in the WS$_2$(Er) sample.

PL spectra of the two types of monolayers are performed under 532 nm laser excitation. Interestingly, over 6 times enhancement of the PL intensity and 7.9 nm redshift of the peak wavelength are achieved in the WS$_2$(Er) monolayer. No obvious broadening is observed by comparing FWHM of the PL peaks from WS$_2$(Er) and WS$_2$ monolayers, indicating that very slight energy transfer occurs after doping. To better identify the spectral change, the same experiments are carried out on 20 WS$_2$ and WS$_2$(Er) triangles, respectively, and similar results are obtained as shown in Figure 3(c). Their statistical variations of the PL intensities and peak positions are shown in Figure 3(d). The small variations in the intensities and peak positions of the same type of samples may due to the fluctuation of laser power densities and slight inhomogeneous thicknesses. However, the significantly enhanced PL intensities and redshifts of the peak positions between the WS$_2$ and WS$_2$(Er) samples should originate from the Er doping. The possible reasons may lie in three factors: Firstly, the formation of tungsten vacancy in the CVD synthesis is probably suppressed by the doped Er ions and thus the suppression of nonradiative recombinations. It is well known that tungsten transition metal sulfides usually have much higher of vacancy density compared with that of the molybdenum transition metal sulfides. The quantum efficiency increases substantially as the tungsten vacancy is effectively reduced by the Er ion filling. Secondly, additional defects caused from crystalline distortion by the introduction of Er ions into WS$_2$ matrix is negligible, which requires similar ion radii between Er and W in the WS$_2$ crystalline. Thirdly, the energy bands become more rich and active by the introduction of Er ions, since complex and rich electronic levels exist in Er ions. The 7.9 nm of photoluminescent redshift between WS$_2$ and WS$_2$(Er)
samples implies the occurrence of shallow impurity level transitions in the PL process. Figure 3(e) shows the absorption spectra from 1300 nm to 2000 nm of the WS$_2$(Er) and pure WS$_2$ films on SiO$_2$/Si substrates measured by an infrared spectrum imager (Spotlight, Platinum Elmer). It is obvious that the WS$_2$(Er) film shows peak absorption coefficient at 1314 nm and with much higher of absorption coefficient compared with that of the WS$_2$ film from 1300 nm to 1800 nm. This result is highly consistent with the calculated absorption characteristics based on DFT as shown in Figure 4(d). Furthermore, X-ray photoelectron spectra (Thermo scientific K-Alpha+) are performed on both of the two films. A strong Er 4d peak is seen to be located at 169.34 eV as shown in Figure 3(f), which is assigned to Er$^{3+}$ [57].

To further confirm our deduction, the first principle calculations based on the density functional theory (DFT) are performed on the S-vacancy, W-vacancy, and W-vacancy filled by Er of WS$_2$ monolayers, respectively. Electronic band
Figure 4: First principle calculations on the S-vacancy, W-vacancy, and W-vacancy filled by Er of a 3 × 3 × 1 WS₂ supercell. (a) Schematic illustration of the S-vacancy, W-vacancy, and W-vacancy filled by Er of WS₂ matrix. (b) Energy band structures corresponding to the S-vacancy, W-vacancy, and Er-doped conditions of WS₂ supercell described in (a). Weighted bubble chart is used and displayed by the red dotted lines representing the band structures of vacancy and Er-doped WS₂ monolayers, while the black solid curves represent band structure of the protocell WS₂. (c) PDOS of monolayer WS₂ under the S-vacancy, W-vacancy, and Er filled in W-vacancy conditions, respectively. (d)–(i) Dependences of absorption index, refractivity index, extinction index, reflectivity, energy loss, and dielectric constants, respectively, on the incident photon energy (from 0 to 1.8 eV) of the pristine WS₂ and WS₂(Er) monolayers.
structures and partial density of states (PDOS) of these WS₂ monolayers are calculated by generalized gradient approximation (GGA) method. Because 11.5 at% of Er is measured in the EDX spectra, 3 × 3 × 1 supercell is used in the calculation corresponding to 11 at% of [Er] concentration to [W] atoms. Band unfolded technique and weighted bubble chart are applied for the vacancy and Er-filled band structures. The calculation details are described in the supporting information S2. Figure 4(a) shows the schematic images of the S-vacancy, W-vacancy, and Er filled in W-vacancy of monolayer WS₂, respectively. Figure 4(b) shows the energy band structures corresponding to Figure 4(a). The weighted red bubble charts in Figure 4(b) represent the energy bands of the corresponding vacancy and Er-filled WS₂ monolayers, while the black curves represent the energy bands of the WS₂ protocol for comparison. For S-vacancy WS₂ monolayer, the energy bands change slightly compared with the protocol WS₂, except two deep defect energy levels with low weight in the forbidden band. High weight of valance band maximum (VBM) and conduction band minimum (CBM) exist in the high symmetric K point in Brillouin zone, which indicates a relatively small impact of the S-vacancy on the direct transition. For W-vacancy WS₂ monolayer, the energy bands change to more complicated. Multiple valance levels extend to the center of the forbidden band with uniform of low weight, and the VBM shows very small weight in the K point; thus, a very low possibility of carrier exists in the K point, implying that a very low possibility of direct transition occurs in the K point. Furthermore, when W-vacancy is filled by Er ion, the VBM moves upward in the K point with much higher of weight, indicating much higher of possibility for direct transition, and thus the enhancement of the PL efficiency with a redshift. In comparison of these three conditions, S-vacancy in the WS₂ monolayer leads to relatively small impact on the PL efficiency and minute peak shift. W-vacancy degenerates the PL efficiency more seriously than S-vacancy condition. When Er filled in W-vacancy, the PL intensity is enhanced greatly together with a redshift in the PL peak, which well interprets the experimental results as mentioned above. Figure 4(c) shows the PDOS of the S-vacancy, W-vacancy, and Er-filled WS₂ monolayer. Figures 4(d)–4(i) show the dependences of indexes, including refractivity, extinction, reflectivity, energy loss, and dielectric constants, respectively, on the incident photon energy of the pristine WS₂ and WS₂(Er) monolayer. Notably, the WS₂(Er) sample shows much higher of absorption, extinction, energy loss, and imaginary part of dielectric indexes in the infrared region centered at 0.85 eV, while its refractivity, reflectivity, and real part of dielectric indexes show amplitude exchanges in the infrared region centered at 0.85 eV compared with the pristine WS₂ monolayer. To understand the effects of Er doping with lower concentrations, 4 × 4 × 1 and 5 × 5 × 1 supercells of the S-vacancy, W-vacancy, and Er filled in W-vacancy of WS₂ monolayers are also calculated and discussed in detail in supporting information S2.

To understand the effect of Er doping in photoluminescence under different excitations from ultraviolet to infrared, the excitation spectra excited under 250 nm and 850 nm on the WS₂ and WS₂(Er) samples are performed at 77 K, as shown in Figures 5(a) and 5(b), respectively. When the samples are excited at 250 nm, the WS₂(Er) sample exhibits higher fluorescence intensity from 500 nm to 1100 nm. In particular, 11 strong and sharp PL peaks are apparently observed from 761 nm to 1011 nm in the WS₂(Er) sample, but nonexistent in the WS₂ sample. The appearance of these peaks is undoubtedly due to the impurity levels in the forbidden band introduced by the doped Er ions, especially the Er intra-4f levels, which has strong localization characteristics, stable optical excitation, and recombination process. The 11 sharp peaks are probably originated from the transitions from 4F_{9/2} to the ground state of 4I_{15/2} (736 nm), from 4F_{9/2} to 4I_{13/2} (804 nm), and from 4I_{11/2} to 4I_{15/2} (980 nm), respectively. Because of the orbital interactions between the Er-4f and W-4d orbits, the original energy levels split into multiple sublevels, which leads to the present 11 sharp spectra terms at 77 K. This result proves the rich optical characteristics and new features of 2D materials by Er doping. When the excitation wavelength changes to 850 nm, similar result is obtained, and 9 sharp peaks from 881 nm to 1011 nm are observed (Figure 5(b)). The excitation spectra of the WS₂ and WS₂(Er) monolayers by scanning the excitation wavelength and under the monitor wavelength of 1175 nm and 1475 nm for photoluminescence are shown in Figures 5(c) and 5(d), respectively. When the excitation wavelength scans from 600 nm to 900 nm and the photoluminescent intensity is monitored at 1175 nm, both the WS₂ and WS₂(Er) samples show increasing fluorescent efficiency from 600 to 815 nm, but the WS₂(Er) sample shows a higher fluorescent efficiency compared with WS₂ sample. The maximum peak intensities are seen when excited at 849 nm for both of the samples. Similarly, when the excitation wavelength is scanned from 300 nm to 900 nm, and the PL intensity is monitored at 1475 nm, the PL intensities increase in the excitation region from 600 nm to 815 nm for both of the samples, and the WS₂(Er) sample shows over two times of efficiency compared with the counterpart of WS₂ sample. The maximum peak intensity of the two samples also appears at the excitation wavelength of 849 nm. Combined with the PL measurements by a 532 nm laser excitation, the photoluminescent results prove the enhancement of quantum efficiency from ultraviolet to infrared region of the Er-doped WS₂.

Research concerning the doping effects of WS₂ monolayers on the photoresponse characteristics are of interests, and photodetectors based on monolayer WS₂ and WS₂(Er) with similar thickness, morphologies, and sizes are fabricated under the same conditions with Au electrodes for ohmic contacts. Triangular side length of the WS₂ and WS₂(Er) samples are 73 μm and 71 μm, respectively. The length of the channels between two electrodes of these two types of devices is both 40 μm. Their optical micrographs are shown in Figures 6(a) and 6(b). I–V and photoreponse characteristics of the monolayer devices are measured on a shielded probe station connected to a Keithley semiconductor analyzer (SCS4200) by a standard DC technique. Details of the I–V curves in dark condition of the WS₂ and WS₂(Er) devices are discussed in the supporting information (S3). The I–V curves of the WS₂ and WS₂(Er) devices illuminated
by a 635 nm diode laser at different incident intensities from dark to 180 mW/cm² are shown in Figures 6(c) and 6(d), respectively. Compared with the pristine WS₂ monolayer device, the WS₂(Er) device shows 11 times of dark currents at $V_{ds} = 1 \text{V}$, and 469 times of photocurrents at $V_{ds} = 1 \text{V}$, and under 180 mW/cm² of illumination. Photocurrent values of both samples under different illumination power densities are extracted and shown in Figure 6(e) for comparison. Moreover, critical parameters including photoreponsivity ($R_\lambda$) and external quantum efficiency (EQE) are evaluated by the following equations [58, 59]:

$$R_\lambda = \frac{(I_{\text{photo}} - I_{\text{dark}})}{(P \cdot S)}, \quad (1)$$

$$\text{EQE} = \left(\frac{h \cdot c \cdot R_\lambda}{2\pi \cdot e \cdot \lambda}\right), \quad (2)$$

where $I_{\text{photo}}$ and $I_{\text{dark}}$ are photocurrent and dark current, respectively; $P$ is the illumination laser power density; SS is the effective area under illumination; $e$ is the electronic charge; $h$ is the Planck constant; and $c$ is the light velocity.

Based on the experimental data in Figure 6(e), $R_\lambda$ and EQE at different illumination power densities from 2.4 to 180 mW/cm² are calculated for WS₂ and WS₂(Er) devices, and shown in Figures 6(f) and 6(g), respectively. The WS₂ and WS₂(Er) devices show the maximum $R_\lambda$ of 7.8 mA/W and 994.5 mA/W at the $V_{ds} = 1 \text{V}$ and 2.4 mW/cm² of illumination, respectively. Similarly, the WS₂ and WS₂(Er) devices show the maximum EQE of 1.5% and 194.6% at the $V_{ds} = 1 \text{V}$ and 2.4 mW/cm² of illumination, respectively. According to Equations (1) and (2), the $R_\lambda$ and EQE between the two type of devices is also 469 times at $V_{ds} = 1 \text{V}$ and 180 mW/cm² of illumination. This result provides a powerful proof that the doped Er ion contributes to the photoelectric efficiency in a large scale due to its active and rich electronic energy levels.

WS₂(Er) monolayer is proved to be photosensitive, and its potential in fast photodetector applications is also demonstrated from the photoswitching characteristics, as shown in Figures 6(h) and 6(i). A high-performance graphic sampling multimeter (Keithley DMM7510) accompanied with a chopper-modulated 635 nm cw laser and a DC voltage supplier is used to measure the photoswitching behavior of the WS₂ and WS₂(Er) devices at $V_{ds} = 1 \text{V}$ and 180 mW/cm² of illumination for on states. 25 ms of rising time and 35 ms of falling time are measured from the WS₂ device. In comparison, the WS₂(Er) device shows over two orders enhancement of the photoresponse speed with the rising
time of 190 μs (1/132 of 25 ms) and falling time of 282 μs (1/124 of 35 ms) from one period of illumination. Notably, this speed is also over 200 times faster than the monolayer MoS₂ device, and 20 times faster than the WS₂ device with 6 nm thickness of WS₂ [60, 61]. More comparisons are provided in the supporting information S4. The photoresponse speed is strongly depended on the density of surface trapping states, since surface states lead to the parasitic capacitance. Two orders enhancements of the photoresponse speed indicate the drastic decrease of the density of surface states in
monolayer WS$_2$(Er). Although multitype of sources including intrinsic defects, impurities, surface dangling bonds, and oxidations will lead to surface states, the main cause is still the intrinsic vacancy defects due to the inert surface feature of 2D materials. Therefore, the present two orders enhancement in the photoresponse speed provides further evidence for the vacancy filling mechanism by Er against the formation of tungsten vacancies in the CVD synthesis process.

4. Conclusion

In summary, high concentration of substitutional Er doping strategy in the synthesis of large scale of 2D WS$_2$ by CVD is achieved experimentally. 11.5 at% of Er concentration in the WS$_2$(Er) monolayer is examined by EDX. The high doping concentration may relate to the nature of high tungsten vacancy density formed during the CVD synthesis process. In addition, strong characteristic peaks contributed from the erbium ions are observed both in the X-ray diffraction spectra, X-ray photoelectron spectra, and the Raman spectra. The photoluminescent, absorptive, and photoresponsive performances are comprehensively and substantially enhanced by the erbium doping compared with the counterparts of the pristine WS$_2$ monolayers synthesized by the same method. Over 6 times of fluorescent intensities are observed from the WS$_2$(Er) spectra. The fluorescent enhancements and redshifts are well agreed with the calculation results by density functional theory (DFT). Eleven excitation peaks from 761 nm to 1011 nm are found from the excitation spectra of WS$_2$(Er) monolayer, and those are nonexistent in the pristine WS$_2$ monolayer. In addition, the WS$_2$(Er) photodetectors show over 11 times of dark current, 469 times of photocurrent, photoresponsivity, and external quantum efficiency, and over two orders of photoresponse speed compared with those of the pristine WS$_2$ photodetectors fabricated and measured under the same conditions. The combined characterizations and theoretical calculations indicate that extra lattice distortions are not obviously introduced by the substitutional erbium doping, but the defect density is effectively reduced, which leads to a reduced density of surface trapping states, and the significantly higher density of carriers are provided by the introduction of substitutional Er ions in the monolayer WS$_2$ matrix.

Data Availability

All data needed to evaluate the conclusions in the paper are present in the paper and/or the Supplementary Materials. Additional data related to this paper may be requested from the authors.

Conflicts of Interest

The authors declare that there is no conflict of interest regarding the publication of this article.

Authors’ Contributions

H. Zhao conceived and administrate this work and write and revised the manuscript. X. Shi supported to administrate this work and data gathering. G. Zhang and Ch. Wang synthesized the materials and performed the material measurements. B. Yan prepared and measured the devices. B. Ning and Y. Zhao performed the simulations.

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Supplementary Materials

S1 Details of the CVD synthesis for large scale of WS$_2$ membranes by Er doping S2. First principle calculations S2.1. 4×4 supercell for S-vacancy, W-vacancy, and Er filled in W-vacancy conditions S2.2. 5×5 supercell for S-vacancy, W-vacancy, and Er filled in W-vacancy conditions S3. Dark current of photodetectors based on WS$2$ and WS$_2$(Er) monolayers S4. Comparison of the photoresponsive characteristics between WS$_2$(Er) photodetector and photodetector based on other 2D materials (Supplementary Materials)

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