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Electrical Tuning of the *SERS* Enhancement by Precise Defect Density Control

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3 **ABSTRACT** Surface-enhanced Raman scattering (*SERS*) has been widely established as a
4 powerful analytical technique in molecular fingerprint recognition. Although conventional noble
5 metal-based *SERS* substrates show admirable enhancement of the Raman signals, challenges on
6 reproducibility, bio-compatibility and costs limit their implementations as the preferred analysis
7 platforms. Recently, researches on *SERS* substrates have found that some innovatively prepared
8 metal oxides/chalcogenides could produce noble metal comparable *SERS* enhancement, which
9 profoundly expanded the material selection. Nevertheless, to tune the *SERS* enhancement of
10 these materials, careful experimental designs and sophisticated processes were needed. Here, it is
11 demonstrated an electrically tunable *SERS* substrate based on tungsten oxides (WO_{3-x}). Electric
12 field is used to introduce the defects in the oxide on an individual substrate, readily invoking the
13 *SERS* detection capability, and further tuning the enhancement factor is achieved through
14 electrical programming of the oxide leakage level. Additionally, by virtue of *in-situ* tuning the
15 defect density and enhancement factor, the substrate can adapt to different molecular
16 concentrations, potentially improving the detection range. These results not only help build a
17 better understanding of the chemical mechanism, they also open an avenue for engaging non-
18 noble metal materials as multi-functional *SERS* substrates.

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41 **KEYWORDS:** surface enhanced Raman scattering, transition metal oxide, chemical
42 enhancement, charge transfer, electrical programming, defect density tuning
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3 The surface-enhanced Raman scattering (*SERS*) technique has been intensively studied since it
4 was first observed on a roughened silver electrode coated with pyridine in 1973.¹ It is known for
5 ultra-high sensitivity and specificity when it is used to detect the molecules adsorbed on the
6 *SERS* substrate. For this reason, *SERS* detection has been extensively utilized as a powerful tool
7 for molecular fingerprint tracing in various biological and chemical applications.²⁻⁷ As the *SERS*
8 performance is usually determined by material selection, surface morphology of the substrate
9 and the adsorbed analytes, developing novel substrate with attractive enhancement factor (*EF*),
10 excellent uniformity and reproducibility, additional bio-compatibility and reusability is keenly
11 demanded.^{8, 9} Conventionally, noble metals with optimized surface nanostructures are
12 implemented as the *SERS* substrates and normally up to 7~8 orders of molecules' Raman
13 scattering signal enhancement can be obtained.¹⁰⁻¹³ The mechanism behind the enhancement
14 observed on noble metal substrates is attributed to the boosted surface electromagnetic field
15 confinement by the surface plasmon, and thus it is termed as the electromagnetic mechanism
16 (*EM*) for the Raman signal enhancement.^{14, 15} However, to make full use of the *EM*, precise
17 control of the metal nanostructures to ensure the strong near-surface electromagnetic field still
18 poses as a significant challenge, especially known for sophisticated experimental design and high
19 costs. In addition, noble metals occasionally show poor stability and biocompatibility when the
20 *SERS* detection is carried in a harsh environment or biological system, which further limits their
21 applications as the prior-selection analysis platforms.¹⁶⁻¹⁹

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24 Recently, studies on transition metal oxides (*TiO₂*, *Cu₂O*, *MoO₃*, *ZnO* and *WO₃* etc.), transition
25 metal chalcogenides (*Cu₂S*, *Cu₂Se*, *MoS₂* and *WSe₂* etc.) and two-dimensional materials
26 (*graphene*, *graphene oxide* etc.) have demonstrated that non-metal surface could also provide
27 noble-metal comparable *SERS* enhancement.²⁰⁻²⁷ In these experiments, the Raman signal
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3 enhancement was mainly ascribed to an increase of charge transfer (*CT*) between the substrate
4 material and molecules, consequently enhancing the molecule polarizability. Thus, the
5 mechanism is named as the chemical mechanism (*CM*) for the Raman signal enhancement.²⁸ In
6 the meanwhile, a series of elegant papers also have reported that materials like *TiO₂*, *MoO₃*, *ZnO*,
7 *WO₃*, *graphene* and *MoS₂* showed excellent biocompatibility, and some of them were highly
8 resistant to degradation in harsh environment, therefore, the potential use of these materials
9 would greatly expand the application of *SERS* detection in many fields, *e.g. in-vivo* health
10 monitoring or chemical reaction tracing.²⁹⁻³⁴ However, essential improvements of the non-metal
11 *SERS* substrates, such as a simple preparing procedure and achievement of high *EF*, are still
12 demanded.
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26 To-date, established strategies for promoting the *CM* in *SERS* lie on the alignment of energy
27 levels between the substrate material and molecules to facilitate the *CT*. Electrochemical *SERS*,
28 as a comprehensively discussed technique, has been implemented to manipulate the surface
29 states and promote the *CT* for *SERS* enhancement, however this method requires constant voltage
30 bias and aqueous electrolyte.^{35, 36} Recently, defect engineering on the solid-state materials has
31 been extensively used to improve the *SERS* performance of materials. Compared to the
32 electrochemical method, the defect states in these solid-state electrolytes are nonvolatile, which
33 means that they are able to support the *CT* even after the removing of the bias. To introduce the
34 defect states in the material, previous reported results have indicated that plasma treatment, ion
35 doping or gas annealing, *etc.* on materials like *TiO₂*, *WO₃* and *ZnO* could be effective
36 approaches.^{22, 37-39} In the meanwhile, high-energy ultraviolet (*UV*) light was also implemented to
37 create the defects in the substrate oxide. A *UV*-exposed *Au*-nanoparticle embedded oxide
38 substrate showed synergetic enhancement effect; the Raman intensity was raised to a much
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3 higher level than the case without *UV* exposure.⁴⁰ Furthermore, optimization of chemical
4 synthesis conditions was another extensively adopted approach for adjusting the surface states
5 and achieving significant Raman signal improvement.^{24, 41, 42} All in all, these experimental
6 practices purposely introduce defects into the material and the *SERS* enhancement subsequently
7 benefits from the trap-assisted *CT* between the substrate material and molecules. Nevertheless,
8 they involve a time-consuming process and some of them even require accuracy control of
9 processing conditions. Besides, the defect density as well as the defect level positions in the
10 substrate material is relatively difficult to control through these methods.

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22 Herein, we report the study of the electrically tunable Raman enhancement phenomenon based
23 on the design and fabrication of tungsten oxides (WO_{3-x}) associated substrate. By electrical
24 programming the defect density in the WO_{3-x} through the oxide leakage current control, the *SERS*
25 detection capability of the novel substrate can be invoked instantaneously and the enhancement
26 factor can be further precisely modulated. Moreover, the advantage of *in-situ* electrical defect
27 density control allows the *EF* of the *SERS* substrate that can be tuned and adapted to different
28 molecular concentrations. This gives the *SERS* substrates a self-adapt capability with potentially
29 improved detection range. The above results not only help affirm the *CM*, they also pave the way
30 towards the implementation of dynamically tunable, self-adaptive non-metal-based *SERS*
31 substrate for multifunctional and high-sensitivity bio-sensing applications.

32 33 34 35 36 37 38 39 40 41 42 43 44 45 **Results and Discussion**

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48 WO_{3-x} was synthesized by a hydrothermal method. Briefly, tungsten hexachloride (WCl_6) was
49 used as the tungsten source. It was dissolved in ethanol, and the solution was transferred to a
50 Teflon-lined stainless steel autoclave and kept at 180 °C for 24 hours.⁴³ Thereafter, the obtained
51 blue products (WO_{3-x}) were collected by centrifugation, washed with ethanol for several times,
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3 and finally dried in the air at 60 °C. The morphology of the synthesized WO_{3-x} was detected by
4 scanning electron microscopy (*SEM*) and transmission electron microscopy (*TEM*) (see Figure
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8 S1, Supporting Information). From the *SEM* images, it could be found that the prepared WO_{3-x}
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10 nanoparticle shows multiple-tentacles growing on the core plate. The tentacles entangle with
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12 each other, and the lengths of these tentacles vary a lot. In the meanwhile, the *TEM* image
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14 reveals more details. For a typical WO_{3-x} nanoparticle, the size of the core plate is 330 nm×577
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16 nm, and high resolution inspection on the single tentacle further evidences that the lattice
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18 constant is 0.378 nm, which belongs to (010) planes of monoclinic WO_3 .³⁷ To realize electrical
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20 tuning of defect density in the WO_{3-x} , the synthesized WO_{3-x} powder was dissolved in ethanol
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22 again, sonicated for 15 min and then spin-coated on a *Si* wafer with prefabricated 100-nm-thick
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24 *Au* planar electrodes. After that, the substrate was annealed at 100 °C for 0.5 hour in the air to
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26 improve the adhesion between the WO_{3-x} and the electrodes (see the Methods). Figure 1a and b
27
28 show the optical image and schematic structure of the prepared *SERS* substrate. Principally,
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30 WO_{3-x} deposited between the gap of the two electrodes constitutes the active *SERS* region, where
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32 the defect density could be electrically modulated by applying voltage on the two electrodes.
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34 Figure 1c shows the atomic force microscopy (*AFM*) topographical image. It can be seen that the
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36 width of the electrodes and the spacing between the two electrodes are both 10 μm. Figure 1d
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38 shows the cross-section *SEM* picture of the *SERS* substrate, it reveals that an 80-nm-thick WO_{3-x}
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40 is deposited between the two electrodes during the spin-coating process. In addition, *XRD* and
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42 *UV-vis* spectroscopy were measured for the WO_{3-x} powder sample before and after 100 °C
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44 annealing in the air (Figure S2, Supporting Information). It can be seen from the *XRD*
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46 spectroscopy that both of the pristine and annealed WO_{3-x} are monoclinic phases (*P2/m*, *JCPDS*
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48 *no. 84-1516*). Besides, *UV-vis* spectroscopy discerns slight blue shift of the absorption curve
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3 after 100 °C annealing in the air, indicating the partial removing of deep defects, whereas the
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5 weak absorption hump is kept at near-infrared region, which reveals the remaining of shallow
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7 defects.
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10 Electrical tuning of the defect density was performed using a *Keithley 4200-SCS*
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12 semiconductor parameter analyzer (see the Methods). A voltage was applied on the left electrode
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14 and the right one was always grounded. The average electric field between the electrodes could
15
16 be evaluated as $\frac{V}{d}$ V·cm⁻¹, where **V** is the applied voltage and **d** is the spacing of the electrodes.
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19 Previous understanding revealed that the oxygen vacancy defect density in the *WO_{3-x}* layer firmly
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21 depended on the leakage current level.⁴⁴ Typically, conductive filaments constituted by oxygen
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23 vacancy chains were created during the voltage sweep phase, and the number of the oxygen
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25 vacancies in the conductive filaments were determined by the current level sneaking through the
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27 oxide; the higher the leakage current, the higher the density.⁴⁵ Therefore, to achieve different
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29 defect densities in the oxide, the leakage current level in the oxide are precisely controlled with a
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31 preset current compliance (*I_C*) during the voltage sweep. When the leakage current reaches the
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33 compliance value, the voltage sweep is immediately aborted, yielding a defect density that
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35 corresponds to the preset *I_C*. Figure 2a shows typical current-voltage (*I-V*) curves obtained on
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37 three similar *SERS* substrates with respective preset *I_C* values. The voltage sweeps were carried
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39 out in steps. For the first step (when the *WO_{3-x}* was in the pristine state), a relatively low *I_C*
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41 (1×10^{-7} A) was chosen to prevent catastrophic breakdown of the *WO_{3-x}* when the voltage
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43 exceeded a certain threshold voltage (> 100 V). Beyond this voltage, the leakage current rose
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45 sharply, signaling a rapid increase of defect generation rate. If this increase was not arrested
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47 quickly, a thermal runaway situation that led to a catastrophic breakdown of the *WO_{3-x}* would
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49 occur. Below the threshold voltage, the leakage current was relatively low (< 1×10^{-12} A @ 1 V)
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3 and was comparable for all three substrates. This showed that the WO_{3-x} fabricated by the
4 hydrothermal method was of good quality (low defect density) and uniformity. After the first
5 step, the leakage current of each individual *SERS* substrate was further programmed to the preset I_C
6 of $1 \times 10^{-7} A$, $1 \times 10^{-5} A$, $1 \times 10^{-3} A$, respectively (inset of Figure 2a). During the entire two-stage
7 electric field programming periods, the *O* atom of the weak *W-O* bond was considered to be
8 outstretched away from its lattice site when the electric field gradually increased in the oxide,
9 leaving the oxygen vacancies behind.⁴⁶ The continuous accumulation of the oxygen vacancies
10 along the oxide ultimately induced the dielectric breakdown, which brought the current to the
11 compliance of $1 \times 10^{-7} A$, $1 \times 10^{-5} A$ and $1 \times 10^{-3} A$, respectively.
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24 The *SERS* performance of the substrates was evaluated by using the *Rhodamine B* (*RhB*) as the
25 Raman reporter (the *RhB* molecular structure is shown in the inset of Figure 2b). However,
26 before collecting the *RhB* Raman spectra on the substrates, the Raman spectra of the bare WO_{3-x}
27 were first discerned (see Figure S3 in Supporting Information). For the WO_{3-x} powder, Raman
28 peaks that correspond to *O-W-O* bending and *W-O* stretching modes are clearly observed,⁴⁷
29 whereas no evident peak are found on the 80-nm WO_{3-x} film (same thickness as that on the
30 prepared substrate). This discrepancy could be ascribed to fewer number of *O-W-O* bending and
31 *W-O* stretching that responses to the laser excitation when the film thickness reduces. Thereafter,
32 in a typical experiment of measuring the *RhB* Raman spectra, after the successful electrical
33 programming of the defect in the oxide, the bias was removed, and then 10 μL of *RhB* ethanol
34 solution ($10^{-4} M$) was drop-casted on the substrate surface, drying in the atmosphere. The Raman
35 spectra were collected on the WO_{3-x} region between the two Au electrodes under a 532-nm laser
36 excitation (see the Methods). Figure 2b shows the Raman spectra with the WO_{3-x} pre-programmed
37 to different leakage current levels. Interestingly, no Raman peaks that related to *RhB* are detected
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3 on the pristine WO_{3-x} within the electrodes gap, implying that the chemical interaction between
4 the substrate material and molecules are very weak under defect deficient condition. On the other
5 hand, for the substrate with the leakage current programed to 1×10^{-7} A, it shows that weak
6 Raman signals at 612, 1360, 1507 and 1650 cm^{-1} (named as P1, P2, P3 and P4) are observed. All
7 of these four Raman peaks are off the WO_{3-x} ones, confirming the Raman enhancement capability
8 of the substrate for the *RhB* Raman reporters. Thereafter, with the further increase of the pre-
9 programed leakage current to 1×10^{-5} A and 1×10^{-3} A, it could be found that the intensities of the
10 above Raman peaks are correspondingly increased. Since the defect densities in the oxide are
11 built upon the leakage current level, the increase of Raman intensity with the arising of the
12 leakage current manifests the magnified *CT* between the substrate material and molecules.
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26 At this stage, it is worth noting that the Raman intensity enhancement of P4 vibrational mode
27 is obviously higher than those of P1, P2 and P3 vibrational modes (Figure S4, Supporting
28 Information). According to earlier studies, this selective enhancement of specific vibrational
29 mode under the *CM* condition is determined by the nature of the particular atoms or groups that
30 contributes to the vibrational mode.⁴⁸ And for a large molecule like *RhB*, it contains a few
31 vibrational units, thus one vibrational mode always associates with the motions of several
32 vibrational units. In order to uncover the contribution of different vibrational units to a single
33 vibrational mode, previous research works based on density function calculation has been
34 conducted (contribution < 10% is omitted).^{49, 50} Based on the comprehensive discussion in ref 49
35 and 50, it can be understood in *RhB* that P1 vibrational mode (612 cm^{-1}) comprises two main
36 components, in which 49% comes from the motion of the xanthene ring and 48% belongs to the
37 motion of the phenyl ring with the COOH group. Similarly, for P2 vibrational mode (1360 cm^{-1}),
38 70% is contributed by the motion of the xanthene ring and the NHC_2H_6 group provides another
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3 17% contributions. For P3 vibrational mode (1507 cm^{-1}), the motion of the xanthen ring
4 produces 69% contributions and NHC_2H_6 group gives another 25% contributions. Lastly, the
5 motion of the xanthen ring delivers 98% contributions to the P4 vibration mode (1650 cm^{-1}). On
6 the other hand, as the *CM* is intuitively induced by the *CT* between the molecular orbitals
7 (ground state \rightarrow excited state), and it can be derived from the simulation work indicates that,
8 under the excitation of 532 nm laser, two-electron transition paths usually happen in the *RhB*.
9 The first major one happens from the highest occupied molecular orbital to the lowest
10 unoccupied xanthen π orbital, resulting in the geometry change on the xanthen ring. The
11 second minor one happens from the lowest unoccupied xanthen π orbital to an unoccupied
12 phenyl π orbital, resulting in the geometry change on the xanthen ring and the phenyl ring.
13 During the Raman measurement, the vibrations of the atoms or groups prefer to mimic the
14 molecular geometries change, consequently bringing in the significant enhanced Raman
15 intensity. Therefore, considering the nature of these four Raman vibrational modes observed on
16 *RhB*, the intensity of P4 vibrational mode is promoted much more than the other ones. Other than
17 that, the statistical data for the substrates prepared in the same batch are also collected and shown
18 in the Figure S5 of the supporting information. Obviously, substrates with similar leakage levels
19 produce comparable Raman intensities, indicating relatively good performance in uniformity of
20 the *SERS* intensity. In general, the above observations evidently show the viability of electrically
21 tuning the Raman enhancement through defect density control. Besides, the Raman *EFs* of the
22 substrate were calculated based on the integrated peak intensity at 1650 cm^{-1} (details in the
23 Supporting Information), and shown in the Figure 2c. It could be found that the preliminary *EF*
24 for the substrate with $1\times 10^{-7}\text{ A}$ leakage current can reach 3.01×10^5 . With the further raising of
25 the leakage current levels, the *EF* can be tuned to higher level, *e.g.*, 3.97×10^5 at $1\times 10^{-5}\text{ A}$ and
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3 1.14×10⁶ at 1×10⁻³ A. Furthermore, to approximate the lower limit of detection (*LOD*) for the
4 substrates with 10⁻³ A leakage current (substrate with highest *EF*) were also evaluated by
5 decreasing the *RhB* concentration from 10⁻⁴ to 10⁻⁷ M (see Figure S6 in Supporting Information).
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7 Clearly, P1 and P4 peaks are discernible even the molecular concentration reaches 10⁻⁷ M,
8 indicating the superior performance of the programmed substrate for detecting low trace analyst.
9
10 Additionally, the *SERS* spectra of the other Raman reporters such as *Rhodamine 6G (R6G)*,
11 *Crystal Violet (CV)* and *Methylene Blue (MB)* were also collected and shown in Figure S7 of the
12 supporting information. Obviously, the substrate developed in this work also show admirable
13 Raman signal enhancement capability for the above different molecules.
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24 The retention of the *EF* for the substrate is also evaluated. To achieve this, the programmed
25 substrate (10⁻³ A) with *RhB* (10⁻⁴ M) was kept in the dry box (atmospheric condition, room
26 temperature and 20% humidity) for 14 days, and after that, the Raman spectra were collected
27 again. Unfortunately, it could be observed in the Figure 3a and b that there are 42 % drop of P1
28 peak intensity and about 32% drop of P4 peak intensity, respectively. In an effort to identify the
29 root cause of these evident Raman peak intensity drop, the leakage current of the substrates were
30 measured, and it revealed in the Figure 3c that it reduced significantly. In other words, large
31 components of the defects in the oxide were eliminated by redoxing reaction during the rest
32 period in the air (Figure S8, Supporting Information), therefore the *CT* efficient was weakened,
33 resulting in the drop of the Raman peak intensities. However, relying on the flexible electrical
34 tuning ability of the designed *SERS* substrate based on *WO_{3-x}* material, it was convenient to re-
35 programming the substrate to the pre-defined current level, as shown in the Figure 3c. The Raman
36 spectra were collected for the refreshed substrate, and the peak intensities (P1 and P4) were
37 extracted as shown in Figure 3a and b again. Apparently, it could be found that P1 and P4 peak
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3 intensities resume as the leakage current level recovers, which confirms the role of defects in
4 enhancing the Raman signal. At this stage, it is worth noting that the Raman intensity not only
5 can be *in-situ* recovered to the original intensity through elevating leakage current level, but it
6 also can be electrically tuned down. Nowadays, progress in *SERS* technology usually can achieve
7 the *LOD* to 10^{-10} M or even lower. Nevertheless, a high *EF* may induce signal saturation quickly
8 when the molecule concentration increases, thus restricting the whole detection range, especially
9 for molecules with strong Raman activity. Figure 4a and b illustrates the Raman intensity
10 evolution with the lively changing of the leakage current for the designed WO_{3-x} -based *SERS*
11 substrate. First, the initial leakage current level of the substrate was programmed to 1×10^{-3} A
12 (curve 1, Figure 4a) to achieve the maximum *EF*, and then 5 μ L of 10^{-4} M *RhB* ethanol solution
13 was dropped on the substrate surface, drying for Raman measurement. As it shows in Figure 4b
14 that relatively strong signal intensities of P1 and P4 can be clear observed (curve 1, Figure 4b).
15 In this situation, a negative voltage sweep was applied on the substrate (curve 2, Figure 4a),
16 which reset the leakage current of the substrate to 1×10^{-5} A (curve 3, Figure 4a) due to the partial
17 recovery of the defects.⁴⁵ The Raman spectra were re-measured on this substrate. Since the *EF* is
18 adequately determined by the defect density, therefore, in the current condition with fewer
19 defects in the oxide, the intensity of P1 and P4 reduces (curve 3, Figure 4b), which is evidently
20 lower than that when the leakage current is 10^{-3} A. The above procedure demonstrates that by
21 readily adjusting the leakage current through the WO_{3-x} , the same substrate can be adapted to
22 handle different molecule concentrations, thereby potentially extending the detection range that a
23 single substrate can provide. In addition, it is also confirmed that a positive voltage sweep could
24 set the current back to 1×10^{-3} A (curve 4, Figure 4c) and restore the initial high *EF* (curve 4,
25 Figure 4b), enabling its capability to detect the low concentration molecules.
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3 It is well accepted that the Raman enhancement of the semiconductor material is ascribed to
4 the *CM*. The oxygen vacancy, as the main defect morphology in the imperfect semiconductor
5 material, has helped the *CT*.⁴⁴ Herein, to confirm the role of the oxygen vacancy defects for
6 signal enhancement, conductive atomic force microscopy (*C-AFM*) is used to detect the defect
7 distribution in the WO_{3-x} . Since in the Raman measurement, the penetration depth of the laser in
8 the WO_{3-x} material could be several micrometers, thus the electrons could be readily excited to
9 the conduction band by the injected photons even if the defects are situated below the surface,
10 *i.e.* within the bulk of the WO_{3-x} , however a surface-sensitive technique such as the *C-AFM* tip is
11 unable to detect these bulk defects, scanning on the untreated surface only gives the extremely
12 low leakage current (Figure S9, Supporting Information).⁵¹ Therefore, chemical thinning of the
13 WO_{3-x} was necessary to expose the defect clusters. In this work, $NH_3 \cdot H_2O$ etchant was used to
14 remove a top layer of the WO_{3-x} before the *C-AFM* measurement (see the Methods).⁵² After the
15 chemical thinning of the oxide layer, *C-AFM* topography and current mapping were carried out
16 with a 10 V bias applied on the *C-AFM* tip, and the right *Au* electrode grounded (inset of Figure
17 5b). Figure 5a and c show the 3-dimensional topographical profiles of two substrates, one having
18 a pristine WO_{3-x} and the other pre-programmed to a leakage current of 1×10^{-3} A, and Figure 5b
19 and d show the corresponding current maps. The lateral profile of the *SERS* substrates,
20 comprising the left and right electrodes and the sandwiched WO_{3-x} (see Figure 1b), are clearly
21 reproduced by the *C-AFM* topography scan. Additionally, at the right side of the current map of
22 both substrates, a large bright area (corresponding to a saturated leakage current level of 20 nA)
23 representing the highly conductive right electrode, which distinctly confirms the well-grounded
24 electrodes. In addition, at the left side of the current map, no bright area that represents the
25 electrode could be found for the substrate with 1×10^{-12} A leakage current (pristine substrate) on
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3 Figure 3b, this is ascribed to the blocked current path between two electrodes in the defect
4 deficient WO_{3-x} , and thus no leakage current can be detected on the left electrodes. However, this
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7 is not the case for the substrate with 1×10^{-3} A leakage current, area with saturated current level at
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10 the left of the substrate current map still could be clearly observed, indicating the presence of
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12 electric field formed conductive path in the oxide (Figure 5d). Furthermore, in the spacing region
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14 between the electrodes for the substrate with 1×10^{-12} A leakage current, it can be observed that
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17 the peak value of the current map is as low as 100 pA only, which is consistent with the electrical
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19 measurement. On the other hand, bright shades representing strong leakage paths exposed after
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21 chemical thinning could be found on Figure 5d. These high leakage current paths connect the left
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23 and right electrodes, comprising the conductive filaments in the sandwiched WO_{3-x} region, which
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25 unambiguously reveals the high density of oxygen vacancy chains in the spacing region.
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29 To further shed light on the mechanism underlying the Raman signal enhancement, first-
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31 principles simulation was performed. Non-polar WO_{3-x} slabs with oxygen-atom terminated
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33 surfaces were used (Figure 6a). A hybrid density functional that based on the semi-local
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35 approximation developed by Perdew, Burke and Ernzerhof (*PBE*) was implemented to correct the
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37 underestimated band gap (see the Methods). To investigate the energy level alignment between
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39 the WO_{3-x} and *RhB* molecules with the incorporation of oxygen vacancy, the average electrostatic
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41 potential (*AEP*) was calculated and aligned to the vacuum level which was scaled to 0 V, then
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43 the valance band maximum (*VBM*), conduction band minimum (*CBM*) and defect energy levels
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45 were consequently aligned to the *AEP* based on the band diagram.⁵³ It is shown in Figure 6b that
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47 the band gap of the WO_{3-x} given by the simulation is ~ 3.5 eV, which is consistent with the
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49 experimental data and is significantly improved in terms of accuracy as compared to the classical
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51 theoretical calculation.⁵⁴ As for the *RhB* molecules, the highest occupied molecular orbital
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(*HOMO*) is at -4.85 eV and the lowest unoccupied molecular orbital (*LUMO*) is at -1.64 eV. These calculated molecular orbitals also match the reported results.^{55, 56} Since the WO_{3-x} was terminated with un-passivated oxygen atoms, surface states (*SS*) were introduced into the band gap even in the slab without oxygen vacancy. However, both of them were mid-gap states and the energy intervals between the neighboring states were still sizable, resulting in inefficient *CT* under the Raman laser irradiation. On the other hand, the oxygen vacancy brought in an extra level below the *SS* as evidenced in the band diagram of the WO_{3-x} slab with oxygen vacancy. In the meanwhile, the presence of the oxygen vacancy in the oxide also up-shifted slightly the band edges, giving a better alignment between the *CBM* of WO_{3-x} and the *HOMO* level of the *RhB* molecule.⁵⁷ Therefore, it could be expected that those electrons excited under an excitation of 532 nm were more readily transferred to the molecules with the help of the multi-step defect levels. At this stage, it is worth noting that when more oxygen vacancy defects are accumulated in the oxide, additional defect levels are introduced in the band gap. Because of the lower inter-level energy difference, these supplemental energy levels further facilitate the *CT*, resulting in a greater magnification of the Raman scattering signals.

Conclusion

In summary, an electrically tunable *SERS* substrate based on the metal oxide is demonstrated. Experimental investigations have shown that the *SERS* enhancement factor, from 3.01×10^5 to 1.14×10^6 , can be conveniently tuned through the electrical programming of the defect density. Moreover, relying on the advantage of *in-situ* defect density tuning, the self-adaption capability of the substrate to different molecular concentrations is also evidenced, which provides a facile way to enlarge the detection range. More importantly, theoretical calculations based on first-principles are also performed, and the results confirm that the defect levels introduced by the

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3 oxygen vacancy defects can be well-aligned to the molecular levels, facilitating the *CT* between
4 the substrate oxide and the molecules. These results not only further enrich the knowledge of the
5 *CM*, they also pave the way towards the implementation of novel, highly flexible non-metal-
6 based *SERS* substrates with variable detection capability.
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11 **Methods**

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16 **Materials:** WCl_6 (99.99 %) was purchased from Macklin. *Ethanol* (99.7 %), $NH_3 \cdot H_2O$ (25 %),
17 H_2SO_4 (95 %), and H_2O_2 (30 %) were purchased from Sinopharm Chemical Reagent Co., Ltd.

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19 All chemicals were used without further purification. In all the experiments, deionized water
20 (resistivity of $18.2 \text{ M}\Omega \cdot \text{cm}$) was used to prepare the solutions.
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26 **Synthesis of WO_{3-x} :** WO_{3-x} was synthesized by implementing a simple hydrothermal method.
27 Basically, WCl_6 (0.099 g) was used as the tungsten source and dissolved in ethanol (30 mL), then
28 the prepared solution was transferred to a Teflon-lined stainless-steel autoclave and kept at 180
29 $^{\circ}\text{C}$ for 24 hours. Thereafter, the obtained blue products were collected by centrifugation (15000
30 rpm), washed with ethanol for several times, and finally it was dried in the air at $60 \text{ }^{\circ}\text{C}$.
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38 **Fabrication of the *SERS* substrate:** The Si wafer was clean by H_2SO_4/H_2O_2 solution (3: 1), and
39 then a 100-nm thermal SiO_2 was grown in a furnace at $1000 \text{ }^{\circ}\text{C}$. *Au* (80 nm)/*Ti* (20 nm)
40 electrodes spaced $10 \text{ }\mu\text{m}$ apart were fabricated on the SiO_2/Si substrate by *UV* photolithography
41 and electron-beam evaporation of *Ti*, *Au* metals, and thereafter followed by a lift-off process. To
42 deposit the synthesized WO_{3-x} powder on the pre-prepared substrate, the dried WO_{3-x} powder (5
43 mg) was dissolved in ethanol (50 mL) again, sonicated for 15 min. Thereafter, $10 \text{ }\mu\text{L}$ of the
44 prepared solution was drop-casted on the substrate center, and spin-coated onto the substrate at
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3 2000 rpm for 30 s. Finally, the substrate was annealed at 100 °C for 0.5 hour in an argon gas
4 ambient.
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7 **Characterization:** Voltage sweep and leakage current measurements were performed using a
8 *Keithley 4200-SCS* semiconductor parameter analyzer system (Tektronix, US). The
9 topographical profile of the substrate and the leakage current map were analyzed by *AFM* and *C-*
10 *AFM* on a Cypher S AFM system (Oxford Instruments, UK). For the *C-AFM* measurement, the
11 substrate was treated with 5 % wt. $NH_3 \cdot H_2O$ at 80 °C for 20 hours in order to remove the surface
12 WO_{3-x} layer and expose the bulk defects. The *XRD* spectra were recorded on a D8 Advance
13 diffraction-meter equipped with a LynxEye XE detector (Bruker-AXS, Karlsruhe, Germany).
14 The SEM images of the substrates were acquired by a Hitachi SU-70 system (Hitachi, Japan)
15 under an accelerating voltage of 5 kV. The *TEM* images were obtained on a JEM-2100F
16 transmission electron microscope (JEOL, Japan). The *UV-vis* spectra were collected with a
17 spectrometer (TU1901, P-General, Samutprakarn, Thailand). *SERS* measurements were made by
18 a Raman microscope equipped with a spectrometer (QE Pro, Ocean Optics, USA). A 532-nm
19 semiconductor laser was used as the excitation source, and the diameter of the spot size of the
20 laser on the substrate is 12.5 μm (100 \times objective lens). The Raman spectra were collected under
21 a laser power of 1mW, and an integration time of 10 s.
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25 **First-principles simulation:** The simulation work was performed by Vienna Ab-initio
26 Simulation Package (*VASP*).⁵⁸ The ultra-soft pseudo-potential and plane-wave expansions of
27 wave functions and potentials were implemented during the calculation.⁵⁹ The exchange
28 correlation energies were treated within the generalized gradient approximation (*GGA*) of
29 Perdew, Burke and Ernzerhof (*PBE*).⁶⁰ Based on the converging tests, the cut-off energy of 400
30 eV for the plane wave basis and k-space grids of 3 \times 3 \times 1 with the Monkhorst Pack scheme were
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3 used to calculate the total system energy. For structure optimization, the conjugate gradient
4 method was used and the ion positions were optimized until the residual force was less than 0.01
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6 $\text{eV} \cdot \text{\AA}^{-1}$. Moreover, the hybrid density functionals based on the semi-local PBE approximation
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8 were implemented by replacing 20 % of *PBE* exchange with the exact exchange to correct the
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10 underestimated band gap.⁶¹ In the simulation work, an oxygen atom terminated non-polar WO_3
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12 slab with 15- \AA thick vacuum layer was used. The size of the WO_3 slab is $7.73 \times 7.67 \times 26.67 \text{\AA}$,
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14 and it contains a total of 12 tungsten atoms and 40 oxygen atoms. To create an oxygen vacancy,
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16 one oxygen atom will be removed and the resultant slab was subjected to the same structural
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18 optimization procedure. As for the calculating of *RhB* molecule, an *RhB* molecule was put in a
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20 cell with the size of $30 \times 30 \times 30 \text{\AA}$.
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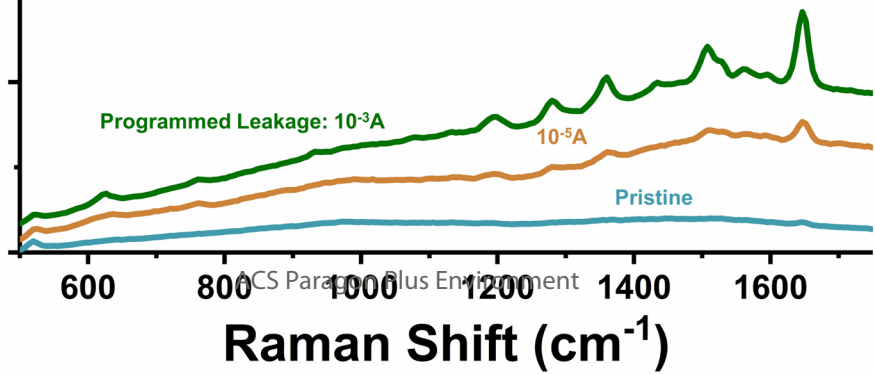
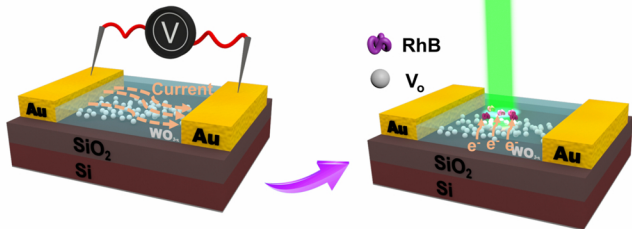
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Intensity (a.u.)



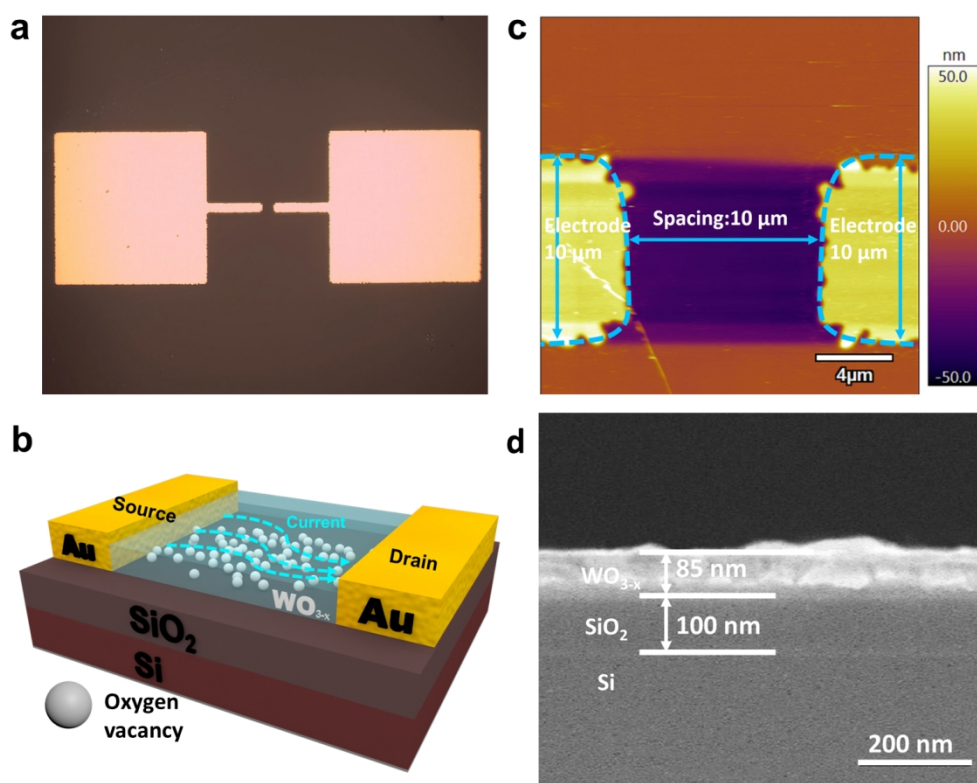


Figure 1. a) Optical image and b) 3D schematic structure of the SERS substrate, c) two-dimensional AFM topographical image, d) cross-section SEM image of the WO_{3-x}-based SERS substrate.

557x445mm (72 x 72 DPI)

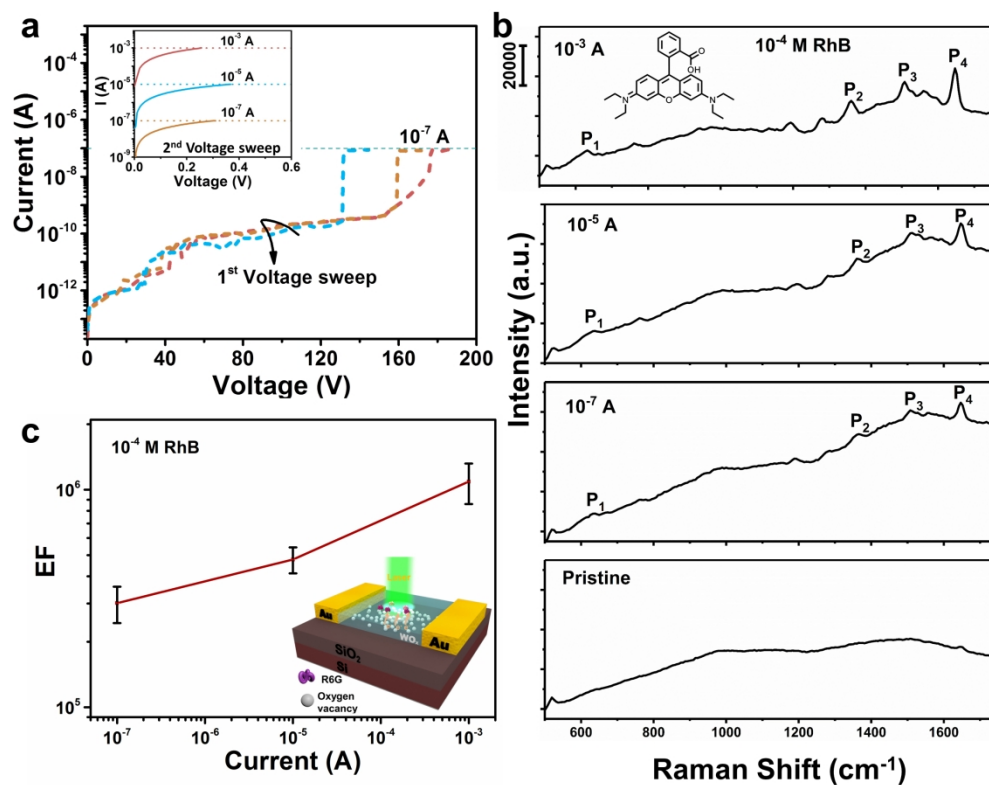


Figure 2. a) Current-voltage (I - V) curves obtained on three similar SERS substrates during the first voltage sweep, b) Raman spectra obtained on a pristine substrate and on the three substrates after programming each of them to a different leakage current, c) SERS enhancement factor as a function of the programmed leakage currents. The inset in (a) shows the second voltage sweep that finally brings the leakage current to the specific compliant current level. The inset in (b) shows the molecular structure of RhB.

916x742mm (72 x 72 DPI)

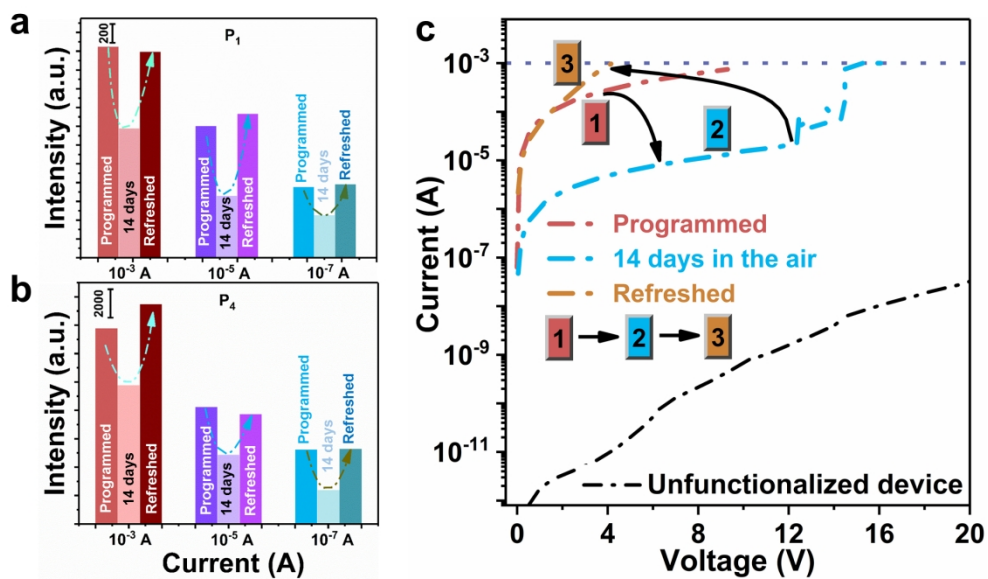


Figure 3. a) The P₁ peak intensities measured on the same substrate with three different conditions, b) the P₄ peak intensities measured on the same substrate with three different conditions, c) the leakage current levels of the substrate that corresponds to the respective peak intensities in (a) and (b).

707x418mm (72 x 72 DPI)

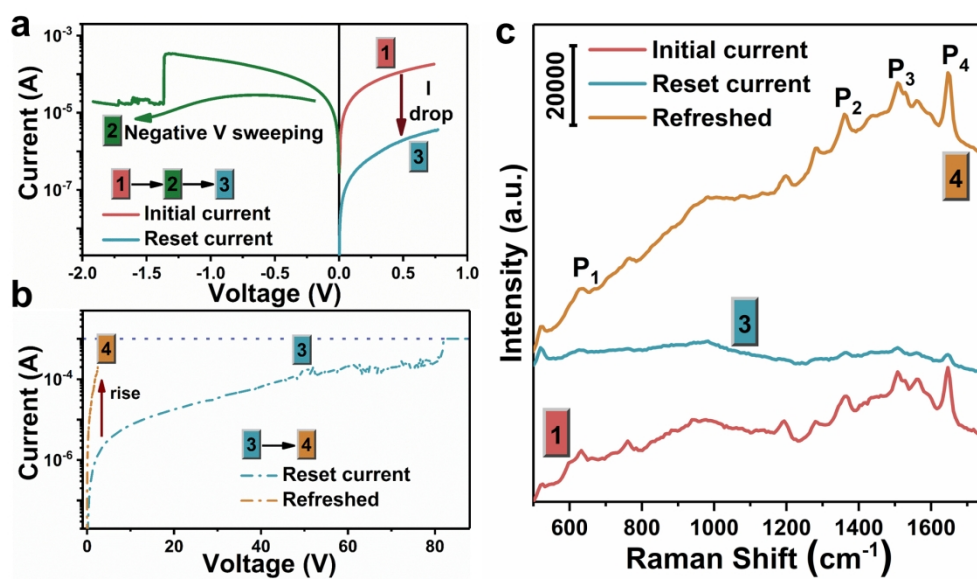


Figure 4. a) Negative voltage sweep that reset the current to lower level. Curve 1 is the initial current level, curve 2 shows the current change when the negative voltage sweep is applied; curve 3 is the current level after negative voltage sweep, b) The evolution of the Raman intensity with *in-situ* change of the leakage current. The numbers labeled on the respective Raman spectra correspond to the current levels in (a) and (c), c) the leakage current level after reprogramming the substrate that has been subjected to the negative voltage sweep.

698x413mm (72 x 72 DPI)

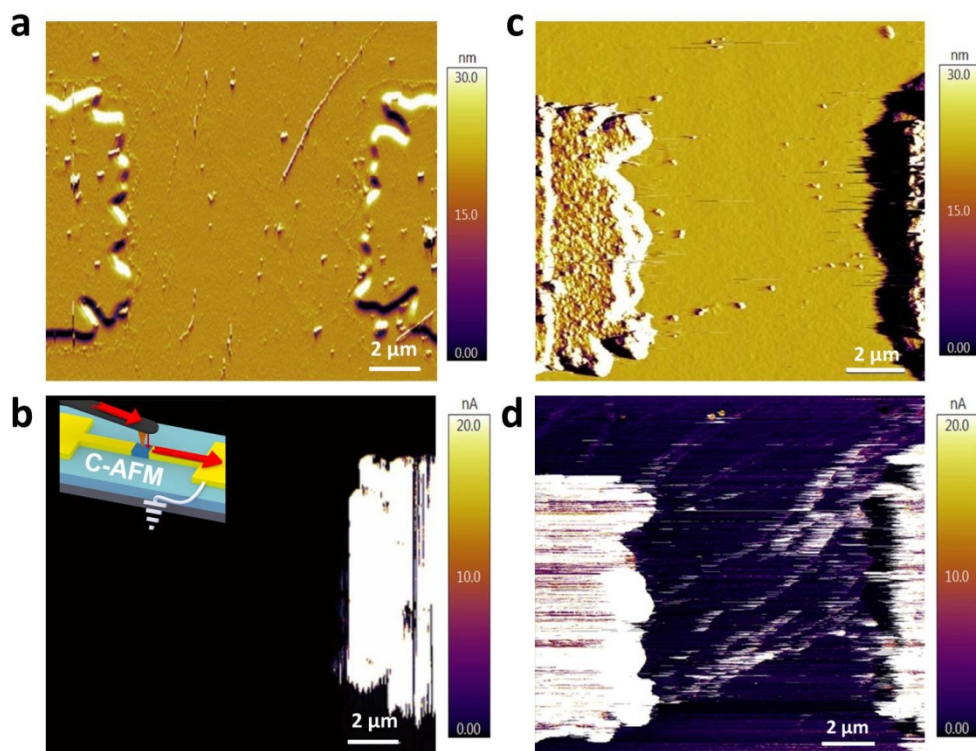


Figure 5. SERS substrate after the chemical thinning. a) The three-dimensional *AFM* topographical image of a *SERS* substrate with 1×10^{-12} A leakage current, b) the corresponding leakage current map obtained on the same substrate in (a), c) the three-dimensional *AFM* topographical image of the substrate with 1×10^{-3} A preprogrammed leakage current, d) the corresponding leakage current map obtained on the same substrate in (c). The inset in (b) shows the schematic diagram of the *C-AFM* measurement. Red arrows show the direction of current flow from the probe towards the grounded right electrode.

533x412mm (72 x 72 DPI)

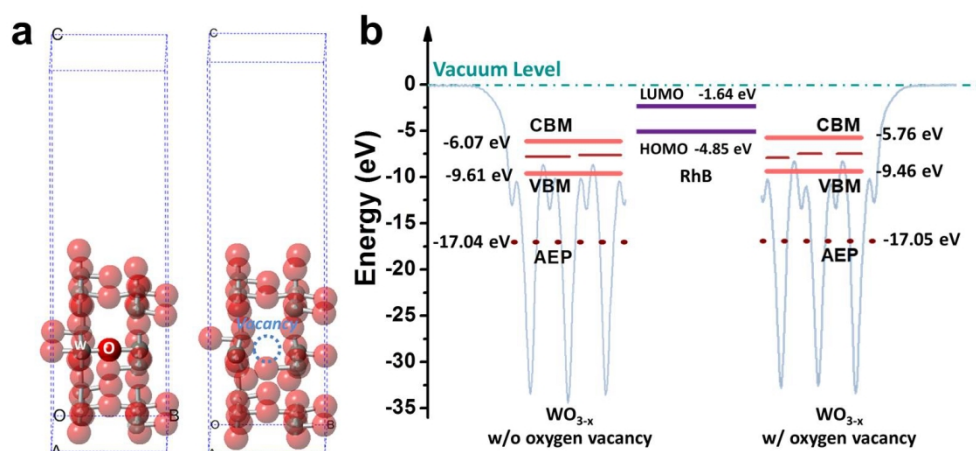


Figure 6. a) Atomic structures of the WO_{3-x} slabs without oxygen vacancy (*left*) and with oxygen vacancy (*right*). In both case, there is a 15-Å thick vacuum layer above the atoms. The large red atoms are oxygen, and the small grey atoms are tungsten, b) alignment of the energy levels of the *RhB* molecule (center), WO_{3-x} slabs with (*left*) and without (*right*) the oxygen vacancy defect. AEP represents the averaged electrostatic potential. CBM means conduction band minimum and VBM means valence band maximum. LUMO represents the lowest unoccupied molecular orbital and HOMO represents the highest occupied molecular orbital.

573x269mm (72 x 72 DPI)