Quasi-Metal for Highly Sensitive and Stable Surface-Enhanced Raman Scattering

HIGHLIGHTS
- Surface-enhanced Raman scattering (SERS) on quasi-metallic VO$_2$
- High SERS enhancement factor and low limit of detection have been achieved
- Synergistic effect of electromagnetic enhancement and chemical enhancement
Quasi-Metal for Highly Sensitive and Stable Surface-Enhanced Raman Scattering

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SUMMARY
Compared with the noble-metal surface-enhanced Raman scattering (SERS) substrates activated by the surface plasmon resonance (SPR)-induced electromagnetic mechanism (EM), the relative low sensitivity and stability of the chemical mechanism (CM)-based substrates are the biggest obstacles to their applications. Herein, we report that quasi-metallic VO$_2$ nanosheet arrays can be used as a sensitive and stable SERS substrate. The lowest detectable limit of analyte adsorbed on the VO$_2$ nanosheets achieves $10^{-10}$ M and the maximum Raman enhancement factor (EF) reaches $6.7 \times 10^7$, which is comparable with that of the noble metals. The experimental and theoretical results demonstrate that the SERS performance of the VO$_2$ nanosheets comes from the strong interfacial interactions based on charge transfer and the vigorous SPR effects. Our research results demonstrate that quasi-metals are very promising SERS detection platforms and reveal that CM, like EM, contributes significantly to the SERS activity of quasi-metals.

INTRODUCTION
Since Fleischmann and Van Duyne et al. groundbreakingly discovered that weak Raman signals of molecules can be drastically amplified by surface-enhanced Raman scattering (SERS) on rough silver surface (Fleischmann et al., 1974; Jeanmaire and Van Duyne, 1977; Moskovits, 1978), this technology already has become a very important label-free detection method in trace and even single-molecule levels (Nie, and Emory, 1997; Kneipp et al., 1997). As a highly sensitive, non-contact, and non-destructive technology, SERS has been widely adopted in environmental detection (Li et al., 2010; Mulvihill et al., 2008), biological imaging (Palonpon et al., 2013; Kneipp et al., 2008; Qian et al., 2008), medical diagnostics (Schlucker, 2014; Wang et al., 2012), fingerprint molecular distinguishing (Lin et al., 2009; Alvarez-Puebla and Liz-Marzan, 2012), catalytic reaction monitoring, and other fields (Feksa et al., 2015; Li et al., 2015). The traditional SERS substrate materials are based on noble-metal nanostructures with roughened surfaces (Taylor et al., 2013; Zhang et al., 2013; Kanipe et al., 2016; Phan-Quang et al., 2015), which can greatly enhance the Raman signal intensity of analyte adsorbed on the substrate surfaces with a factor of 10$^6$ or higher. Local field enhancement-induced surface plasmon resonance (SPR), especially the emergence of a large number of ‘hot spots’ (high-intensity electromagnetic field regions formed at nanoscale gaps) (Zhu et al., 2016), is considered as a well-known enhancement mechanism of Raman scattering, that is, electromagnetic mechanism (EM). However, EM-based noble-metal SERS substrates are generally subjected to the considerable complex and precise preparation processes, which makes them lack the structural controllability and signal repeatability of the substrates. In addition, they also suffer from the high cost, poor biocompatibility, negligible photocorrosion, and so on. Another universally accepted enhancement mode, chemical mechanism (CM), mainly refers to the process of charge transfer between SERS substrates and molecules adsorbed on their surfaces (Zhang et al., 2015; Quagliano, 2004; Li et al., 2013). Charge transfer will cause molecule resonance, which will greatly increase the polarizability of adsorbed molecules, and the corresponding Raman scattering cross-section will increase, resulting in the enhancement of SERS signal (Qiu et al., 2015; Cong et al., 2015; Zheng et al., 2017). Although researchers have accepted the concept that SERS is a result of EM and CM combining, it is generally believed that CM plays only a minor role since charge transfer is a short-range action.

After the first generation of SERS technology based on the noble-metal materials dominated by EM, the non-noble-metal substrates based on CM have been developed vigorously in the last 10 years, such as semiconductor nanostructures including Cu$_2$O (Lin et al., 2017, 2018), Si (Wang et al., 2011), W$_2$O$_7$ (Cong et al., 2015), TiO$_2$ (Qi et al., 2014), MoO$_3$ (Zhang et al., 2017), conductive polymers (Yilmaz et al., 2017), and metal-organic framework compounds (Sun et al., 2019), which constitute the second-generation...
of SERS substrates. Interestingly, amorphous semiconductors have recently been found to have better SERS performance than crystalline ones (Wang et al., 2019; Wang et al., 2017; Li et al., 2018a, 2018b). Compared with noble-metal SERS substrates, nanostructural semiconductors possess tailorable band structure and more abundant resonance modes, and therefore can controlled detect target analyte with corresponding excitation-wavelength (532, 633, 785 nm, etc.). In addition to these features, semiconductor SERS substrates also have superior biocompatibility, easy-to-control morphology, and more abundant surface states and active sites. However, for the two most important parameters of SERS, Raman enhancement factors (EFs) and lowest detectable limit of analyze, CM-based semiconducting materials are generally much lower than that of noble metals driven by EM. Furthermore, compared with noble metals, the chemical stability and thermal stability of semiconducting materials are often poor, especially when they are exposed to the excitation light of Raman spectrometer; they are often oxidized or decomposed, thus losing their SERS activity. For example, although W18O49 (Cong et al., 2015) and Cu2O (Lin et al., 2017, 2018) have recently achieved excellent EFs of $10^5$–$10^6$ levels, they are easily oxidized by O2 in the air, thus unavoidably losing their SERS capability. Therefore, it is an urgent problem to find low-cost non-noble-metal SERS substrate materials with high sensitivity, stability, and large-area signal uniformity for the practical application.

Based on the above-mentioned analysis, we hope to find highly sensitive non-noble-metal SERS active materials and explore whether CM and EM have comparable contributions to their SERS effects. Transition metal oxides often contain abundant family members with different valences (e.g., WO3, WO2.9, WO2.8, WO2.72, WO2) (Manthiram and Alivisatos, 2012; Xi et al., 2012a, 2012b). Among them, the high-valence species are often insulators or wide-band-gap semiconductors, whereas the low-valence members often have good conductivity and localized-SPR effects owing to their abundant d-orbital free electrons, that is to say, low-valence members often have both certain metallicity and semiconductivity, or quasi-metallicity. It is well known that strong localized SPR and appropriate energy level distribution are the essential conditions for EM and CM enhancements, respectively; therefore, if we can find a quasi-metallic metal oxide that has both strong charge transfer and localized SPR effects as SERS materials, it is possible to obtain high sensitivity due to the combination of EM and CM.

As a very interesting transition metal oxide with intermediate valence state, VO2 nanostructures have been deeply studied and widely applied in fabrication of intelligent temperature-controlled films and electronic devices with ultralow power consumption due to its magical phase transition of insulator-conductor properties (Qazilbash et al., 2007; Strelcov et al., 2009; Morrison et al., 2014). VO2 has also recently been reported as a smart glass and high performance battery material (Hao et al., 2018; Li et al., 2019). However, the SERS properties are seldom studied. Herein, we report that quasi-metallic VO2 nanosheet arrays grown on ordinary glass with 16 cm² scale can be used as an effective SERS substrate material with outstanding Raman enhancement effect. As a result of the dual enhancement of EM and CM of the VO2 substrate, the lowest detectable limit to the typical Raman probe molecule Rhodamine 6G (R6G) on the VO2 nanosheet arrays can be as low as $10^{-10}$ M level and the maximum EF is up to $6.7 \times 10^7$, which are even compared with the commercialized Au SERS substrates. From the perspective of application and fundamental science, our results demonstrate that quasi-metals can be used as ultrasensitive and stable SERS platforms and reveal that CM and EM both contribute equally to the total SERS performance of quasi-metallic materials.

**RESULTS**

**Selection and Structural Design of SERS Substrate Candidate**

As a very interesting transition metal oxide, VO2 has many crystal structures, such as m-VO2 (monoclinic), t-VO2 (triclinic), r-VO2 (rutile), and a-VO2 (tetragonal). Among them, m-VO2 contains a metastable b-VO2 (bronze phase) (Whittaker et al., 2009). We chose b-VO2 as the candidate for a new SERS active material because theoretical calculations forecast that this structure has an obvious quasi-metallic feature, which is different from the most studied m-VO2, which exhibits typical semiconductor characteristics at room temperature. As shown in Figure 1A, the results of simulated density functional theory (DFT) calculations clearly show that b-VO2 present a definite quasi-metallic characteristic. It can be seen that the calculated band gap is about 1.15 eV. At the same time, the highest occupied states of the b-VO2 near the Fermi level are composed of V 3d orbitals and O 2p orbitals. Combined with these characteristics, therefore, b-VO2 can be considered as a typical quasi-metal. Furthermore, the free electron gas distribution, which was achieved by conducting the electron localization functions (ELF) calculation, also suggests that there are non-zero

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*Note: The content includes references which are not fully visible in the image.*
Free electron tunnels between V atoms (Figure 1B). These tunnels of free electrons could form non-polar V-V metallic bonds, giving b-VO₂ conducting properties. From the perspective of SERS, the quasi-metal characteristic of b-VO₂ suggests that it may have the synergistic enhancement effect of charge-transfer-induced CM and localized SPR-driven EM.

It is known that charge transfer between analyte and substrate is a short-range action (Park and Kim, 2010); therefore, the enhancement effect based on CM is closely related to the scale and dimension of substrate materials. Recent studies on two-dimensional (2D) SERS active materials such as graphene and molybdenum disulfide nanosheets show that effective charge transfer between the adsorbed molecules and the substrates requires that the surface of the material be as flat as possible to effectively adsorb the molecules to be measured (Xie et al., 2009; Muehlethaler et al., 2016). At the same time, to obtain strong interactions of analytes and substrates, the thickness of these SERS active materials should be as small as possible to
minimize the loss of charge carriers during the transfer process (Li et al., 2018a, 2018b). On the other hand, the localized-SPR-based EM enhancement generally requires that the surface of the SERS substrate be as rough as possible, preferably containing a large number of nano-scale gaps, to generate a large number of high-intensity electromagnetic “hot spots” (Willetts, 2014). From these two seemingly contradictory aspects, we expect to synthesize b-VO₂ ultrathin nanosheet arrays, which not only meets the structural requirements of charge transfer, but also satisfies the demand of forming a large number of high-intensity electromagnetic “hot spots” among the nanosheet gaps.

Synthesis and Characterizations of VO₂ Nanosheet Arrays

According to the previous analysis, a facile, scalable, and low-cost hydrothermal-assisted chemical vapor decomposition (HCVD) route has been designed for the in situ growth of the large-area b-VO₂ ultrathin nanosheet arrays on glass (16 cm² level). As shown in Figure 1C, an appropriate amount of vanadyl acetylacetonate (VAA) is dissolved in a certain volume of absolute ethanol to form a bright blue transparent solution. The resulting homogeneous solution is then transferred to a Teflon-lined high-pressure reactor, and a common glass sheet is placed above the liquid level as a growth platform for b-VO₂ nanosheets. At 200°C, the closed reaction system is filled with ethanol vapor mixed with VAA molecules. Under this solvothermal condition, these tetravalent vanadium atoms contained in VAA will undergo alcoholysis to form crystal clusters of VO₂, which are then deposited on glass surface and grown into arrayed nanosheets. The key to the success of this method is to maintain a reductive reaction atmosphere in the autoclave; otherwise it is very easy to generate V₂O₅ with a higher valence state. In the reactor, ethanol vapor exactly has a considerable strong reducibility under the heating conditions. Contrast experiments show that, if ethanol is replaced by deionized water, the obtained product is V₂O₅ nanobelts (Figure S1). As shown in Figure 1D, a glass sheet of 4 cm × 4 cm can be completely covered by a layer of black b-VO₂ nanosheets after 12 h of HCVD reaction, which suggests that our method is very suitable for the growing of large-area VO₂ nanosheet arrays.

The crystal phase of the obtained product was determined by X-ray diffraction (XRD) technology. The XRD pattern of the black sample can be accurately indexed as the monoclinic b-VO₂ with the lattice parameters of a = 4.5968, b = 5.6844, c = 4.9133, and β = 89.39° (JCPDF No. 65-7960), and no other crystalline phase was found (Figure 1E). Energy dispersive spectrum (EDS) reveals that these samples contain only V and O elements, and the O/V ratio is about 2.08, which further proves that this sample is indeed VO₂ (Figure 1F). The morphology and crystallographic orientation of the sample were investigated by field-emission scanning electron microscopy (SEM) and high-resolution transmission electron microscope (HRTEM). Overall, the black products are a lay of very uniform sheet-like nanostructures, which are vertically distributed on the glass surface (Figure 1G). High-magnification SEM images show that the thickness of these b-VO₂ nanosheets are only 3–15 nm (inset in Figure 1G). Interestingly, there are many thin nanosheets interspersed between these thick nanosheets, a feature that is very helpful to adsorb more molecules on the surfaces and strongly promote charge transfer between nanosheets and analytes. Furthermore, the clear lattice fringes recorded in the HRTEM image demonstrate that these b-VO₂ nanosheets possess a high crystallinity (Figure 1H). The lattice fringes with the interplanar spacing of 0.37 and 0.35 nm can be accurately referred to as the (201) and (110) crystal faces, respectively, which are also confirmed by the corresponding selected area electron diffraction pattern (inset in Figure 1H). Based on the information of the HRTEM image, it can be reasonably calculated that the exposed crystal face of the nanosheets is (112). Interestingly, this exposed crystal surface can interact strongly with the probe molecule R6G of SERS, which will be further demonstrated below. The specific BET (Brunauer-Emmett-Teller) surface area of the b-VO₂ nanosheets was determined to be 44.8 m² g⁻¹ (Figure S2). In addition, Fourier transform infrared spectroscopy and Raman spectroscopy characterizations suggest that the surfaces of these nanosheets are very clean (Figures S3 and S4) and there was no signal of reaction residues except b-VO₂, which is very important for trace detection because it can reduce the interference of the substrate itself.

Localized SPR Effect and Stability

X-ray photoelectron spectroscopy (XPS) was used to identify the binding states and chemical compositions of these b-VO₂ nanosheets. The XPS survey spectrum shows that these detected peaks at 515.2 and 631.3 eV can be identified as V 2p and V 2s of V⁴⁺, respectively (Figure 2A), which is characteristic of vanadium dioxide (Nethravathi et al., 2013). The peak at 529.6 eV can be assigned to O 1s of the O²⁻. The high-resolution XPS of V 2p, as shown in Figure 2B, could be well fitted into two spin-orbit doublets, corresponding to V⁵⁺ and V⁴⁺ oxidation states, respectively. The two characteristic strong peaks at 516.03 and 523.35 eV can be indexed to V⁴⁺, whereas the other two weak shoulder peaks at 517.38 and 524.61 eV can be
attributed to $V^{5+}$. According to the size of the peak areas, the concentration of $V^{4+}$ on the sample surface is much higher than that of $V^{5+}$, which confirms that the vanadium ion in the sample is basically tetravalent. At the same time, the strong electron paramagnetic resonance (EPR) spectrum signal directly demonstrated that the $b$-VO$_2$ nanosheets have a large number of free electrons in its $d$-orbital (Figure 2C). In contrast, V$_2$O$_5$ nanosheets (morphology see Figure S5) obtained by oxidizing the VO$_2$ nanosheets at 400°C in air were not detected by the effective ESR signals. These XPS and EPR results are highly consistent with the theoretical results mentioned earlier, which together prove that these $b$-VO$_2$ nanosheets contain a high concentration of $d$-orbital free electrons.

Importantly, these abundant $d$-orbital free electrons make the $b$-VO$_2$ nanosheets exhibit strong localized-SPR effect from visible to near-infrared (NIR) regions (Figure 2D), which provides the possibility for EM enhancement of SERS to take place. In contrast, V$_2$O$_5$ nanosheets without free $d$-orbit electrons did not exhibit SPR behavior. Many intermediate valence transition metal oxide nanomaterials with strong localized-SPR are easy to be oxidized by oxygen in air, thus losing the SPR behavior and the corresponding SERS activities, which is another major obstacle to the practical application of semiconductor SERS substrates in addition to their low sensitivity. For example, plasmonic W$_{18}$O$_{49}$ nanostructure has been reported to have excellent SERS performance, and its Raman EF ($10^5$) is comparable with that of noble metals. However, for W$_{18}$O$_{49}$, even if heated at 100°C for 5 h in air, its SPR activity quickly disappears owing to oxidation (Figures S6 and S7). In contrast, the $b$-VO$_2$ nanosheets show a high oxidation resistance (Figure 2E). Even if heated at 300°C in air for 1 h, the intensity and position of the plasma resonance absorption of these nanosheets did not change significantly, which is rare in transition metal oxides with intermediate valence states. This strong oxidation resistance has also been demonstrated by its high thermal stability (Figure S8).

Considering that SERS substrates are exposed to the laser irradiation of Raman spectrometer, the high
stability of the substrate materials is extremely important. In addition to the strong oxidation resistance, these b-VO₂ nanosheets also exhibit long-term environmental and irradiated stability (Figure 2F). Even after exposure to air for 6 months, their SPR peaks did not change noticeably, which provides an opportunity for the commercialization of this material. The stability of these b-VO₂ nanosheets was also confirmed by XRD and XPS characterization (Figures S9 and S10).

**Enhanced Raman Scattering**

Then, we tested the SERS properties of the b-VO₂ nanosheet array substrate. As shown in Figure 3A, in all SERS measurements, the Raman exciting light is incident from above the substrate plane. In the experiments, the prepared probe molecule (R6G) solutions with specific concentrations (10⁻⁷–10⁻¹⁰ M) was added dropwise into the b-VO₂ nanosheet arrays and dried at room temperature for 10 min before SERS measurement (see the Transparent Methods section for the specific process). Figure 3B shows that the b-VO₂ nanosheet arrays exhibit excellent SERS activity for R6G with a concentration of 10⁻⁷ M (blue spectrum in Figure 3B). All Raman scattering peaks

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**Figure 3. SERS Measurements of R6G with the as-Prepared b-VO₂ Nanosheets**

(A) SERS measurement schematic diagram.
(B) Raman spectra of 10⁻⁷ M R6G aqueous solution obtained on b-VO₂ nanosheets, bare glass, and V₂O₅ nanosheets.
(C) Gradually weakened Raman scattering signals recorded from Rh6G aqueous solution at four different concentration levels (10⁻⁷, 10⁻⁸, 10⁻⁹, 10⁻¹⁰ M), suggesting that the b-VO₂ nanosheets have greatly enhanced Raman scattering, with a lowest detection limit of 10⁻¹⁰ M for analytes.
(D) These b-VO₂ nanosheets still have high Raman enhancement effects even after 300°C of high-temperature heating in air.
(E) SERS mapping near an edge of a R6G/b-VO₂ film.
(F) The average Raman EFs obtained by counting the peak intensities (R₁ and R₂) at three different concentration levels.
are clearly visible and highly consistent with the standard Raman spectrum of R6G reference material (Figure S11). The strongest four Raman scattering peaks at 612 (R1), 773 (R2), 1,363 (R3), and 1,652 cm$^{-1}$ (R4) can be clearly observed, in which R1 and R2 can be indexed with the in-plane and out-of-plane bending motions of C and H atoms of the xanthenes skeleton, respectively; R3 and R4 can be referred to the C-C stretching vibrations of aromatic nucleus (Hildebrandt and Stockburger, 1984). To eliminate the contribution of glass to the properties of SERS since the nanosheets are grown on them, the R6G probe solutions were directly dripped onto the bare glass and tested for Raman signals. The results showed that no Raman signals were detected (black spectrum in Figure 3B), which definitely excludes the contribution of the glass in the SERS. When the quasi-metallic b-VO$_2$ nanosheets were completely oxidized to the semiconducting V$_2$O$_5$ nanosheets without localized SPR effect (Figure S5), no effective SERS signals of probe molecules was detected except for the fluorescence background (red spectrum in Figure 3B), which further confirms that the enhanced Raman signals come from the quasi-metallic b-VO$_2$ nanosheet arrays. On the other hand, contrastive experiments revealed that the bare b-VO$_2$ nanosheet arrays without R6G solution only showed the typical Raman scattering peaks of themselves (Figure S12), indicating the enhanced Raman scattering peaks represented by R$_1$, R$_2$, R$_3$, and R$_4$ really originate from R6G molecules.

Figure 3C shows the SERS spectra of a series of R6G samples with different concentrations ($10^{-7}$, $10^{-8}$, $10^{-9}$, $10^{-10}$ M). It can be seen that the b-VO$_2$ substrate exhibits excellent SERS performance in a large concentration range. Even when the concentration of R6G is only $10^{-10}$ M, the distinguishable Raman signals still can be detected (signal-to-noise ratio greater than 5). Such a low detection limit allows this new SERS substrate to be used to trace even single-molecule detection of compounds with ultrahigh sensitivity. More importantly, this new SERS substrate based on the b-VO$_2$ nanosheets has considerable high stability. As mentioned earlier, these b-VO$_2$ nanosheets will not lose their localized-SPR effect even if heated at 300$^\circ$C in air; accordingly, after the b-VO$_2$ nanosheets were treated at 300$^\circ$C for 5 h, it can be seen that their SERS intensities did not decrease noticeably and even $10^{-10}$ M analytes could still be detected (Figure 3D). For the practical applications of SERS, high stability of the SERS substrates is very important, because when transition metal oxides-based SERS substrates with intermediate valence state are exposed to the laser irradiation of Raman spectroscopy, they could often easily be oxidized or deformed, thus losing SERS activity or the reproducibility of the signals.

Raman scattering EF is generally considered to be the most important factor in evaluating the performances of SERS substrates. To visualize the EF of the VO$_2$ nanosheet arrays, Figure 3E shows the Raman mapping image recorded from the edge of a R6G/VO$_2$ layer. The obtained Raman mapping is clearly separated into two regions: the area covered with VO$_2$ nanosheets showed strong Raman signals of R6G, whereas the R6G directly placed on the glass did not show any signals, suggesting the high uniform and strong SERS enhancement originated from the densely arranged VO$_2$ nanosheets. To evaluate the Raman EF of the VO$_2$ nanosheets more accurately, contrastive experiments were carried out. In these experiments, on the VO$_2$ nanosheet arrays, the SERS signal intensity of R$_1$ and R$_2$ scattering peaks of R6G with $10^{-8}$, $10^{-9}$, and $10^{-10}$ M was measured (integration time is 10 s). As references, on the bare glass, the normal Raman signal intensity of R$_1$ and R$_2$ scattering peaks of R6G with a much higher concentration ($10^{-2}$ M) and integration time (4,000 s) was also measured under the same excitation light and operating mode. The calculated maximum EF is more than $6.7 \times 10^7$ (Figure 3F), which can be compared with the EFs of noble-metal substrates and is sufficient for single-molecule detection. As far as we know, the EF and detection limit of the quasi-metallic b-VO$_2$ nanosheet arrays in various reported non-noble-metal SERS substrates (Table S1) are only lower than that of Mo(W)Te$_2$ nanosheets with atomic layer thickness (Li et al., 2018a, 2018b). But considering the difficulty of synthesis and quality control of the Mo(W)Te$_2$ monatomic layers, these large-scale VO$_2$ SERS substrates, which are easy to synthesize, have great advantages in practical applications.

**Uniformity and Repeatability of SERS Signals**

In addition to the high sensitivity and EF, the large-range homogeneity and reproducibility of Raman signals is another important index to evaluate the performance and practicability of SERS substrate. The premise of obtaining uniform and repeatable signals is the uniformity of the substrate surface. As shown in Figure 4A, the optical photographs of one glass sheet covered with b-VO$_2$ nanosheets show that the surface of the substrate is very uniform, which is highly consistent with the SEM characterizations described earlier. In the area shown in Figure 4A, 100 points are selected randomly for SERS detection, and the results show that the Raman spectra obtained by these points are highly consistent (Figure 4B), indicating that the present SERS substrate has excellent signal uniformity and reproducibility. The Raman mapping result of R$_1$ scattering peak at 612 cm$^{-1}$ recorded from 5,000 measuring points displays a uniform intensity distribution.
By counting the distribution of the intensity values of the 5,000 R1 peaks, the acquired relative standard deviation (RSD) is only 5.1% (Figure 4D). Similarly, the Raman mapping and statistical results of R2 scattering peak at 773 cm\(^{-1}\) also demonstrated the high signal uniformity of the b-VO\(_2\) substrate (Figure 4E), with RSD of about 5.3% (Figure 4F). Such high signal reproducibility makes it possible for the practical application of this new SERS substrate.

Universality as SERS Detection Platform

In addition to exhibiting the high sensitivity for the probe molecule of R6G, this quasi-metallic b-VO\(_2\) SERS substrate also exhibits very low detection limits for several other common dye molecules, such as methyl blue, methyl orange, and Rhodamine B. From 10\(^{-8}\) to 10\(^{-10}\) M, the resolvable Raman signals of the dye molecules can be measured from the nanosheet arrays (Figures 5A and S13). More importantly, the quasi-metallic VO\(_2\) substrate also exhibits excellent sensitivity to a range of highly concerned risk
substances. Dichlorophenol, a common environmental hormone, has been proved to be highly carcino-
genic and has attracted much attention from environmental monitoring departments in various countries. On this b-VO2 nanosheet arrays, the 2,5-dichlorophenol (2,5-DCP) molecules can be sensitively detected even if its concentration is only $10^{-10}$ M (Figure 5B). Another hazardous environmental hormone, bisphenol A (BPA), has been banned in the United States, the European Union, Canada, China, and so on. It is reported that BPA is an endocrine disruptor, which can mimic human hormones and may lead to adverse health effects. Like 2,5-DCP, BPA also can be sensitively detected at $10^{-10}$ M level on the b-VO2-based SERS substrate (Figure 5C). In addition, as a powerful antioxidant, butyl hydroxy anisd (BHA) has long been used to prevent food spoilage. However, recent studies have shown that it may have strong carcinogenicity and has been banned from food industry in Japan, China, and other countries. It is found that this VO2 SERS substrate also responds well to BHA (Figure 5D). These experimental results showed that the quasi-metallic b-VO2 nanosheet arrays are a versatile SERS active substrate to a series of chemicals.

Raman Enhancement Mechanism of the Quasi-Metallic VO₂

Traditionally, the Raman enhancement of noble-metal SERS materials can be explained by EM based on the well-known localized-SPR effect, whereas the enhancement of semiconductor SERS materials can be attributed to the CM resulting from the charge transfer between the adsorbed molecules and the substrates (Li et al., 2010; Qian et al., 2008). Although it is now accepted that both enhancement mechanisms may take place together in one substrate, it is generally believed that the enhancement effect of CM is far less than that of EM owing to the short-range effectiveness of CM. However, our present research results break this traditional view, revealing that CM, like EM, also plays an important role in the enhancement of the total SERS performances when the substrate is quasi-metal. First, UV-vis absorption spectra are to used to examine whether there is charge transfer between the analyte molecule and the VO₂ nanosheets. We measured the absorption spectra of pure R6G solution, clean VO₂ nanosheets, and VO₂ nanosheets adsorbed with R6G molecules, respectively. As shown in Figure 6A, compared with those of the pure R6G,
the main absorption peaks of R6G adsorbed on VO2 nanosheets took place at a significant redshift (marked with color bar), suggesting the strong interaction and charge transfer probability between R6G and VO2. SERS based on CM is very sensitive to the wavelength changes of exciting light, and lasers of different wavelengths often lead to different molecular vibration modes, which are typical characteristics of CM enhancement. As shown in Figure 6B, the experimental results showed that the intensity of Raman scattering signals of R6G decreases obviously when the wavelength of exciting light changes from 532 to 633 nm, which can be reasonably attributed to the fact that the energy of 633-nm exciting light is obviously less than that of 532 nm. When the exciting power is increased by 20 times (633 nm), the Raman signal...
The interactions between the adsorbed R6G molecules and the VO2 nanosheets and subsequent charge transfer were investigated by DFT simulation (Figures 6C and 6D). The DFT calculations revealed that the binding energy of R6G and VO2 with exposed (112) crystal plane is 1.15 eV, whereas the binding energy of R6G and graphene is only 0.67 eV. At the same time, the results also show that the electron transfer from R6G to VO2 is 0.679 e/molecule, whereas that for graphene and R6G is only 0.015 e/molecule (from graphene to R6G). The obvious difference in the values of the binding energy and electron transfer demonstrated that the coupling effect of VO2 and R6G is much stronger than that of graphene and R6G. At the same time, from the charge density iso-surfaces, the DFT simulations also showed that the electrons and holes generated by charge transfer form a strong dipole at the interface of R6G and VO2, which would strengthen the Raman scattering of R6G molecules on VO2 nanosheets. As a contrast, the forming dipole between VO2 and R6G is much stronger than that of graphene and R6G owing to the greater charge transfer, which further proves the strong coupling effect between VO2 and R6G. Furthermore, owing to the relatively high surface activity of VO2 nanosheets, the generated charge carriers are concentrated at the interface of VO2 and R6G, forming so-called quasi-covalent bonds (Li et al., 2018a, 2018b), which would further enhance the coupling of VO2 and R6G in addition to the electrostatic force of dipole. Thus, the strong dipole effect and the consequent quasi-covalent bonds lead to the impressive SERS capability of the quasi-metallic VO2 nanosheets together.

In addition to the CM induced by the electrostatic coupling between R6G and VO2 discussed earlier, the outstanding SERS performance of the VO2 substrate also can be attributed to the photo-induced charge transfer (PICT) caused CM, as shown in Figure 6E. The energy levels of the highest occupied molecule orbital (HOMO) and the lowest occupied molecule orbital (LOMO) of R6G are $-5.7$ and $-3.4$ eV, respectively (Hildebrandt and Stockburger, 1984), whereas the Fermi level of b-VO2 nanosheets is 4.55 eV according to the characterization results of Kelvin probe force microscope as illustrated in Figure S15. The distribution of the levels is allowed to both the PICT transfer from the HOMO of R6G to the Fermi level of b-VO2, and the Fermi level of VO2 to the LOMO of R6G, which are beneficial to the SERS due to the wide energy range of charge transfer resonance. Therefore, the resonances greatly enhance the polarization tensor of the R6G molecule according to the well-known Herzberg-Teller vibronic coupling (Lombardi et al., 1986). It should be noted that the Fermi level of VO2 is almost a symmetrical match to the HOMO and LUMO of R6G (Figure 6E), which further promotes the PICT process, and the interference of fluorescence background of R6G is greatly reduced.

In addition to the CM-based Raman enhancement mentioned earlier, EM enhancement also contributes significantly to the overall SERS performances of the quasi-metallic VO2 substrate. As illustrated in Figure S16, when these VO2 nanosheets were heated in air for a period of time, their colors changed dramatically. Accordingly, their plasma resonance absorption significantly reduced and ultimately became imperceptible (Figure 6F). Obviously, this is because the VO2 sample is gradually oxidized to V2O5 (Figures S17 and S18), thus losing a large number of d-orbital free electrons, and correspondingly its localized SPR is also weakened and eventually disappeared. As a direct result, the SERS performance of these oxidized samples is greatly reduced (Figure 6G). The Raman mapping results also show that the SERS effect of the sample weakens with the decrease of the SPR intensity (Figure 6H). On the contrary, when we increase the concentration of oxygen vacancies in the VO2 nanosheets by the chemical reduction method (by immersing the VO2 sample in strongly reducing NaBH4 aqueous solution), the corresponding SPR absorption increases gradually (Figure S19) and the corresponding SERS signal also increases gradually (Figure S20). Based on the results, we believe that the regular relationship between the localized-SPR strength and the corresponding SERS performance demonstrated that EM enhancement also exists in the quasi-metallic b-VO2-based SERS. To further prove the existence of EM, these nanosheets are coated with amorphous SiO2 (named as SiO2/VO2) to block charge-transfer-based CM enhancement by an ingenious synthesis experiment (Figure S21). Compared with bare VO2 nanosheets, the SERS signal intensity of analyte on the VO2/SiO2 still can be detected, as shown in (Figure S22), which undoubtedly proves the existence of...
EM. Conversely, this result also further verified the existence of CM. For the total Raman enhancement, by calculating the peak area of $R_1$ recorded on VO$_2$ and VO$_2$/SiO$_2$, respectively, it can be concluded that the contributions of CM and EM are about 57% and 43%, respectively, which reveals that both CM and EM play an important role in enhancing the Raman scattering.

Conclusions
In summary, we demonstrate that quasi-metallic b-VO$_2$ nanosheet arrays can be used as a highly sensitive and stable SERS substrate material. The lowest detectable limit of R6G probe on the VO$_2$ substrate can achieve picomole levels and the optimal Raman EF is up to $6.7 \times 10^7$, which obviously outstrips the previously reported CM based solely on SERS active materials represented by semiconducting nanostructures, graphene, metal organic frameworks, and so on. The ultrasensitive SERS performances achieved on the quasi-metallic VO$_2$ nanosheet arrays can be attributed to the strong analyte-substrate interactions and the vigorous localized-SPR effects of the VO$_2$. The present research results indicate that the quasi-metallic VO$_2$ nanosheet array is a very promising SERS detection platform and demonstrates that CM and EM together play a key role in the overall SERS performance of quasi-metals.

Limitations of the Study
At present, it is difficult to accurately evaluate the contributions of EM and CM in quasi-metal. Although we use a thin layer of amorphous SiO$_2$ to isolate charge transfer, it may also affect EM and introduce new interface effects. A more perfect evaluation method needs to be established in the future to accurately identify the contribution of EM and CM to the properties of quasi-metal SERS.

METHODS
All methods can be found in the accompanying Transparent Methods supplemental file.

SUPPLEMENTAL INFORMATION
Supplemental Information can be found online at https://doi.org/10.1016/j.isci.2019.08.040.

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AUTHOR CONTRIBUTIONS

DECLARATION OF INTERESTS
The authors declare no competing interests.

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Supplemental Information

Quasi-Metal for Highly Sensitive and Stable Surface-Enhanced Raman Scattering

Zheng Tian, Hua Bai, Chao Chen, Yuting Ye, Qinghong Kong, Yahui Li, Wenhao Fan, Wencai Yi, and Guangcheng Xi
Supplemental Information

1. Transparent Methods

Synthesis of b-VO$_2$ nanosheets

All chemicals used in the experiments are of analytical purity. In a typical synthesis, 0.1 g of vanadyl acetylacetonate (VAA) is dissolved in 30 mL of absolute ethanol to form a bright blue transparent solution. The resulting homogeneous solution is then transferred to a Teflon-lined high-pressure reactor, and a common glass sheet is placed above the liquid level as a growth platform for b-VO$_2$ nanosheets. The Teflon-lined stainless steel autoclave was sealed and heated for 20 h at 200 °C. After the reaction is completed, the glass sheet covered with black products was taken out. Finally, the black glass was washed with ethanol and distilled water for three times and dried at 50 °C in a vacuum drying oven.

Synthesis of SiO$_2$/VO$_2$

Open a bottle of analytically pure silicon tetrachloride (SiCl$_4$) in air. Soon, a lot of “white-fog” formed at the mouth of the bottle. Place the glass sheet covered with VO$_2$ nanosheets in a white mist at the mouth of the bottle for 3 min. Then, the glass sheet is placed in a nitrogen-protected tubular furnace and heated to 400 °C for 1 hours. After natural cooling, take out for use.

Synthesis of urchin-like W$_{18}$O$_{49}$ nanostructures

In a typical procedure, 3 g of WCl$_6$ was dissolved in 100 mL of ethanol, and the obtained yellow solution was magnetically stirred for 20 min, and then transferred to a Teflon-lined stainless-steel autoclave and heated at 200 °C for 20 h with a heating rate
of 4 °C/min. The autoclave was cool down naturally and a blue product was collected, washed, and dried in a vacuum drying oven at 50 °C for 4 h.

**Characterization**

These samples were measured by a variety of characterization techniques. XRD patterns of the products were obtained on a Bruker D8 focus X-ray diffractometer by using CuKa radiation (\(\lambda = 1.54178\) Å). SEM images and EDS were obtained on a Hitachi S-4800. TEM and HRTEM characterizations were performed with a Tecnai G F30 operated at 300 kV. Ultraviolet–Vis (UV) absorption spectra were recorded with a Shimadzu UV3600. XPS were recorded on an ESCALab-250Xi of ThermoFisher Scientific. The Fourier transform infrared spectra were measured from THERMO Iz-10. The specific surface area was measured in a Micro Tristar II 3020. The work functions of b-VO\(_2\) nanosheets was detected from Kelvin probe force microscope, Multimode-Picoforce-Veeco. ESR spectrum was obtained from ESP-300.

**Raman tests**

To study the SERS of these b-VO\(_2\) nanosheets, a confocal micro Raman spectrometer (Renishaw-inVia Reflex) is used as the measuring instrument. In all SERS tests, unless specifically stated, the excitation wavelength is 532 nm, laser power is 0.5 mW and the specification of the objective is × 50 L. A series of standard solution (aqueous) of highly risk chemical with concentrations of 10\(^{-7}\)-10\(^{-10}\) M were used as the probe molecules. To improve the signal reproducibility and uniformity, before each test, the glass sheet (1 cm × 1 cm) covered with b-VO\(_2\) nanosheets were immersed into a 20 mL of probe solution with specific concentration for 20 min, then taken out and dried
in air for 20 min. In all SERS tests, the laser beam is perpendicular to the top of the sample to be tested with a resultant beam spot diameter of 5 μm. The calculation of EF are provided in Supplementary Methods.

**Enhanced Factor Calculation**

To calculate the EF of the b-VO₂ nanosheets, the ratio of SERS to normal Raman spectra (NRS) of RH6G was determined by using the following calculating formula 1

\[
EF = \left( \frac{I_{\text{SERS}}}{I_{\text{NRS}}} \right) \times \left( \frac{C_{\text{NRS}}}{C_{\text{SERS}}} \right)
\]

(1)

where \( I_{\text{SERS}} \) and \( I_{\text{NRS}} \) refer to the peak intensities of the SERS and NRS, respectively. \( C_{\text{NRS}} \) and \( C_{\text{SERS}} \) refer to the concentrations of the probe molecules of the NRS and SERS, respectively. In the SERS measurements, two Raman scattering peaks, \( R_1 \) at 612 cm\(^{-1}\) and \( R_2 \) at 773 cm\(^{-1}\) were selected for the calculations of the EF. For comparison, the peak intensities of the R6G (1 × 10\(^{-2}\) M, aqueous solution) directly placed on bare glass slide were detected as NRS data. For the NRS data, the integration time is 4000 s, while for the SERS data, the integration time is 10 s.

**Calculations details**

All the density functional theory (DFT) calculations were carried out using the Vienna Ab initio Simulation Package (VASP)\(^1\)\(^-\)\(^3\). The Perdew-Burke-Ernzerhof (PBE) was used to describe the exchange-correlation\(^4\). The optimization process was performed using a conjugate gradient algorithm with a force tolerance of 0.02 eV/Å, with kinetic energy cutoff set as 500 eV. A Gamma k-point sampling of \( 3 \times 7 \times 5 \) was used to optimize the VO₂ cell parameters. The optimized lattice parameters were 11.99, 3.74, 6.40 Å, and 90.0, 107.0, 90.0°, respectively.
To calculate the VO₂ (112) surface, a 2 × 2 × 1 supercell was built by cut the original cell along (112) facet, with a 20 Å additional vacuum layer in z-direction. Thus, the lattice parameter of the layer slab model was 24.82 Å × 19.68 Å × 26.97 Å. A 2D-shaped graphene layer was calculated to adsorb RH6G molecule as well, containing 200 carbon atoms, with the supercell parameters equal to 24.47 Å × 24.67 Å × 20 Å and 90, 90, 120°, respectively. The structure of RH6G molecule was optimized in the same cell as well. For these simulations, the plane wave cutoff energy set as 500 eV and the k-point mesh set as 1 × 1 × 1.


2. Supporting Figures

Figure S1. SEM image (a) and XRD pattern (b) of the V$_2$O$_5$ nanobelts obtained when ethanol is replaced by deionized water. Related to Figure 1.
Figure S2. N$_2$ adsorption/desorption isotherms of the as-synthesized b-VO$_2$ nanosheets, related to Figure 1.

Figure S3. FTIR spectrum of the as-synthesized b-VO$_2$ nanosheets, related to Figure 1.
Figure S4. Raman spectrum of the b-VO$_2$ nanosheets, related to Figure 1.

Figure S5. TEM image of the V$_2$O$_5$ nanosheets prepared by heating the b-VO$_2$ nanosheets at 400 °C, related to Figure 2.
Figure S6. XRD pattern (a) and SEM image (b) of the prepared urchin-like $\text{W}_{18}\text{O}_{49}$ nanostructures. Related to Figure 2.
Figure S7. The comparison of oxidation resistance between b-VO$_2$ and W$_{18}$O$_{49}$. The change of color and absorbance before and after heating from two kinds of samples clearly indicated that the oxidation resistance of W$_{18}$O$_{49}$ is much lower than that of b-VO$_2$. Related to Figure 2.

Figure S8. The differential thermal analysis (DTA) curve of the b-VO$_2$ nanosheets. Below 350 °C, the b-VO$_2$ nanosheets are stable. When the temperature continues to rise, they were gradually oxidized to V$_2$O$_5$. Related to Figure 2.
Figure S9. A series of XRD patterns demonstrated that no detectable change in the XRD patterns of b-VO$_2$ nanosheets after the heating, irradiating, and long-term storage. Related to Figure 2.
Figure S10. A series of XPS spectra demonstrated that no detectable change in the valence state of the b-VO$_2$ nanosheets after the heating, irradiation, and long-term storage. The XPS and XRD (Figure S6) results demonstrate that the stability of these b-VO$_2$ nanosheets is extraordinary high. Related to Figure 2.
Figure S11. The standard Raman spectrum of R6G reference material, related to Figure 3.

Figure S12. The bare b-VO$_2$ nanosheet arrays without R6G solution only showed the typical Raman scattering peaks of themself, related to Figure 3.
Figure 13. SERS spectra of the dye molecules of MO (a) and RhB (b). Related to Figure 3.
Figure S14. SERS spectra of $10^{-10}$ M R6G on b-VO$_2$ nanosheets and graphene, respectively, related to Figure 6.

Figure S15. The measured surface potential difference profiles. Considering that the work function of Au reference is 4.8 eV, the work function of b-VO$_2$ nanosheets is estimated to be 4.55 eV. The b-VO$_2$ thickness dependence on its work function can be neglected. Related to Figure 6.
**Figure S16.** When these b-VO$_2$ nanosheets were heated in air for a period of time, their colors have changed dramatically. Related to Figure 6.

**Figure S17.** The XPS spectrum of the sample after heating at 400 °C for 1h in air, which suggests that the VO$_2$ has been transformed into V$_2$O$_5$. Related to Figure 6.
Figure S18. The UV-Vis absorption of the sample after heating at 400 °C for 1h in air, related to Figure 6.

Figure 19. The UV-Vis absorption of the VO₂ samples reduced by NaBH₄ aqueous solution, related to Figure 6.
Figure S20. The obtained SERS signals from the reduced VO$_2$ nanosheet substrates, related to Figure 6.

Figure 21. (a) Schematic illustrating the synthesis of the SiO$_2$/VO$_2$. SiCl$_4$ is easily hydrolyzed into H$_2$SiO$_3$ in air. These formed H$_2$SiO$_3$ species were coated on VO$_2$ nanosheets and formed H$_2$SiO$_3$/VO$_2$. The VO$_2$ nanosheets coated with amorphous SiO$_2$ layers were obtained by heating under N$_2$ protection. (b) The HRTEM image of the obtained SiO$_2$/VO$_2$, revealing the thickness of SiO$_2$ layer is about 2 nm. Related to Figure 6.
Figure S22. (a) The obtained SERS signals from VO$_2$ nanosheet substrate and SiO$_2$/VO$_2$ substrate, respectively. Related to Figure 6.
Table S1: Some of the previously reported EFs for Non-Noble Metal Enhanced Raman Substrate materials, related to Figure 3

<table>
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<th>Substrate</th>
<th>Probe molecule</th>
<th>Excited wavelength (nm)</th>
<th>Author</th>
<th>EF</th>
<th>Detectable Limit (M)</th>
<th>Stability</th>
</tr>
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<td>TiO₂</td>
<td>MB</td>
<td>532</td>
<td>D. Qi et al., 2014</td>
<td>2×10⁴</td>
<td>10⁻⁵</td>
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<td>CdTe</td>
<td>4-Mpy</td>
<td>514.5</td>
<td>Y. F. Wang et al., 2007</td>
<td>10⁴</td>
<td>10⁻³</td>
<td>Liable to oxidation and corrosion</td>
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<td>ZnO</td>
<td>D266</td>
<td>488</td>
<td>H. Wen et al., 1996</td>
<td>50</td>
<td>10⁻⁵</td>
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<td>CdS</td>
<td>4-Mpy</td>
<td>514.5</td>
<td>Y. F. Wang et al., 2008</td>
<td>10²</td>
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<td>α-Fe₂O₃</td>
<td>4-Mpy</td>
<td>514.5</td>
<td>X. Q. Fu et al., 2009</td>
<td>2.7×10⁴</td>
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<tr>
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<td>4-MBA</td>
<td>488</td>
<td>L. Jiang et al., 2013</td>
<td>10⁵</td>
<td>10⁻³</td>
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<tr>
<td>CuO</td>
<td>4-Mpy</td>
<td>514.5</td>
<td>Y. Wang et al., 2007</td>
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<td>W₁₈O₄₉</td>
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<td>532.8</td>
<td>S. Cong et al., 2015</td>
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<tr>
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<td>532</td>
<td>L. Guo et al., 2017</td>
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<td>633</td>
<td>Wang, X. T. et al., 2017</td>
<td>6.6×10⁵</td>
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<td>10⁻⁷</td>
<td>Liable to oxidation</td>
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<th>Sun, H. Z. et al., 2019</th>
<th>10^6</th>
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<td>Organic Semiconductor</td>
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<td>Yilmaz M. et al., 2017</td>
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<td>Nb_2O_5</td>
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<td>532</td>
<td>Shan, Y. F. et al., 2017</td>
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<td>Zhang, Q. et al., 2017</td>
<td>3.75×10^6</td>
<td>10^-7</td>
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<td>b-VO_2</td>
<td>R6G</td>
<td>532</td>
<td>Tian, Z. et al (this work)</td>
<td>6.7×10^7</td>
<td>10^-10</td>
<td>stable</td>
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</tbody>
</table>


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