Surface-enhanced Raman scattering technique, as a powerful tool to identify the molecular species, has been severely restricted to the noble metals. The surface-enhanced Raman scattering substrates based on semiconductors would overcome the shortcomings of metal substrates and promote development of surface-enhanced Raman scattering technique in surface science, spectroscopy, and biomedicine studies. However, the detection sensitivity and enhancement effects of semiconductor substrates are suffering from their weak activities. In this work, a semiconductor based on Nb2O5 is reported as a new candidate for highly sensitive surface-enhanced Raman scattering detection of dye molecules. The largest enhancement factor value greater than 107 was observed with the laser excitation at 633 and 780 nm for methylene blue detection. As far as literature review shows, this is in the rank of the highest sensitivity among semiconductor materials; even comparable to the metal nanostructure substrates with “hot spots”. The impressive surface-enhanced Raman scattering activities can be attributed to the chemical enhancement dominated by the photo-induced charge transfer, as well as the electromagnetic enhancement, which have been supported by the density-functional-theory and finite element method calculation results. The chemisorption of dye on Nb2O5 creates a new highest occupied molecular orbital and lowest unoccupied molecular orbital contributed by both fragments in the molecule-Nb2O5 system, which makes the charge transfer more feasible with longer excitation wavelength. In addition, the electromagnetic enhancement mechanism also accounts for two orders of magnitude enhancement in the overall enhancement factor value. This work has revealed Nb2O5 nanoparticles as a new semiconductor surface-enhanced Raman scattering substrate that is able to replace noble metals and shows great potentials applied in the fields of biology related.

npj Computational Materials (2017) 3:11; doi:10.1038/s41524-017-0008-0

INTRODUCTION

Surface-enhanced Raman scattering (SERS) has inspired researchers’ great interests because of its highly sensitive, efficient, and nondestructive characters for detection of traces amount of target molecules. This enables promising applications in the fields of surface science, spectroscopy, chemical analysis, and biochemical detection.1–5 Generally, the noble metals of Au and Ag, because of their unique and remarkable surface plasmon resonance effect, are widely used as SERS sensors with high sensitivity.6–9 However, the SERS technique as a new analytical methodology has not vanished as far as initially predicted.10 It is one of the most profound difficulties that only several limited noble metals possess a significant Raman enhancement capability, but can hardly satisfy the applications involving other non-metal materials. In addition, the noble metal nanostructures are difficult and costly to fabricate with high uniformity.11 They are also poor in stability and reproducibility because of their readily oxidizability and agglomeration.12 These limitations for noble metal SERS substrates seriously hinder the exploitation of SERS technique in practical applications. Accordingly, it is of great significance to explore alternative non-metal SERS substrates for a better applicability.

Recent achievements in the semiconductor SERS-active substrates have endowed semiconductors as potential candidates for new generation of SERS sensors.10, 12–15 Compared with the noble metal SERS substrates, many semiconductor substrates are more stable, reproducible, and biocompatible. Meanwhile, the mature synthesis method also enables to manufacture semiconductors with better uniformity at lower cost, which makes them an immense prospect in the fundamental studies as well as the practical applications. Liu et al. detected the Raman signals of 4-mercaptobenzoic acid at a small concentration of 10−6 M on porous ZnO.16 Qi et al. applied TiO2 inverse opals SERS substrates for sensitive detection of methylene blue (MeB) molecules.16 Islam et al. observed the SERS spectra of 4-mercaptopyridine (4-MPy) from a chemically etched ZnSe surface with the greatest enhancement factor (EF) value for semiconductor substrate up to ~2 x 106.17 Other semiconductors, such as V2O5,18 CuO,19 AgFeO2,20 ZnS,21 CdS,22 CuTe,23 CdTe,22 GaP,24 Si and Ge,25 were also applied as SERS substrates with EF values in the range of 103–106. However, although semiconductors deliver significant advantages in SERS examination, the relatively worse enhancement effect originated from the chemical enhancement (CM) is the most prominent problem that the overwhelming majority of semiconductor SERS sensors are suffering. The electromagnetic enhancement (EM), except when caused by the remote excitation of surface plasmon in MoO3 ribbon 14 and near-field EM in Cu2O nanostructure,19 has been seldom reported in semiconductor SERS materials. Especially for TiO2 and ZnO, the most popular semiconductors that have exhibited excellent performance in many fields, however, the SERS behavior for them is rather unsatisfactory.15, 16 Therefore, it is of great challenge to seek novel
semiconductors instead of noble metals for high-sensitive SERS sensors.

Niobium pentoxide (Nb$_2$O$_5$), one of the most important transition metal oxides, has always been an interesting research subject due to its potential applications in gas sensors, catalysts, electrochemistry, lithium batteries, microelectronics, and optoelectronics.$^{25, 26}$ It is known that there are rich adsorption sites on Nb$_2$O$_5$ surface, including complexible Lewis sites and charged Brønsted sites, which could promote a strong interaction with dye molecules carrying nucleophilic groups or opposite charges.$^{27, 28}$ All the effective adsorption of analyte molecules on the surface of Nb$_2$O$_5$ would further change the electron density distribution of the molecules and result in an increased Raman scattering cross section. Therefore, we expected that the semiconductor of Nb$_2$O$_5$ would exhibit excellent SERS activity.

In this work, the Nb$_2$O$_5$ nanoparticles (NPs) were used as active SERS substrate to detect dyes of MeB, methyl violet (MV), and methyl blue (MB) (SchemeS1). The greatly enhanced SERS effects on the Nb$_2$O$_5$ semiconductor substrate were observed with the SERS EF values over 10$^7$ under the excitation waves of 633 and 780 nm for MeB detection. It is of great interest that the SERS activity of Nb$_2$O$_5$ is even comparable to the noble metal substrate with “hot spots”, foreseeing a substitution of metal substrate by semiconductors for various applications, especially in the fields of biological diagnosis and treatment.

**RESULTS**

Characterization of Nb$_2$O$_5$ NPs

The X-ray diffraction (XRD) pattern of Nb$_2$O$_5$ NPs (Fig. 1a) indicates that all the peaks can be indexed to orthorhombic Nb$_2$O$_5$ (PDF #71-0336).$^{29}$ The Nb$_2$O$_5$ powder was found consistent with irregular NPs with an average size of 104 nm (Fig. 1b). The high resolution transmission electron microscope (HRTEM) micrograph in Fig. 1c further indicates the spacing of adjacent lattice fringes as 0.391 nm, which is corresponding to the (001) lattice planes. The selected area electron diffraction (SAED) pattern in Fig. 1d from one nanoparticle shows a single diffraction pattern corresponding to a single nanocrystal. The calculated lattice parameters were also well matched with the orthorhombic Nb$_2$O$_5$ phase.

SERS enhancement for dyes detection

The MeB is a well-known dye with applications in biotherapy and medical treatment. It is not only a good phenothiazine photosensitizer with high quantum yields of singlet oxygen production, but also a common cationic dye for histological and bacteriologic staining because of its prominent blue color.$^{28}$ It can also be used as a therapeutic drug to treat methemoglobinemia, urinary tract infections, and malaria infection, and as an effective antagonist against heat-shock response gene expression in cancer cells.$^{30-32}$ Therefore, it is of crucial importance to seek more biocompatible substrate materials instead of noble metals to detect and record the track of MeB molecules and make an insight into its functionality in organisms.

A series of Raman spectra of MeB molecules with concentrations in the range of 1 $\times$ 10$^{-4}$ to 1 $\times$ 10$^{-6}$ M were collected on the Nb$_2$O$_5$ substrates with the irradiation of 532 nm laser (Fig. 2a) and the detection limitation of as small as 10$^{-6}$ M. The influences of the excitation wavelength on the SERS activity were also studied. Graphs in Fig. 2b–d display the Raman spectra of solid MeB powders and SERS spectra collected on Nb$_2$O$_5$ substrates under the excitation of 532, 633, and 780 nm lasers, respectively. The Raman shifts and assignments of the main vibrational modes observed in the solid MeB powder and SERS spectra collected with different lasers are presented in Table S1.$^{28, 33}$ The main bands at around 1630 and 453 cm$^{-1}$ are attributed to $\nu$(C–C) ring stretching vibration and C–N–C skeletal deformation mode. The asymmetric and symmetric C–N stretches give birth to the bands around ~1445 and 1402 cm$^{-1}$. An extra band at ~250 cm$^{-1}$, which occurs only in SERS spectra, is ascribed to the Nb–N stretching of the Nb–MeB complex. Several of the bands in the SERS spectra revealed significant shifts relative to the corresponding bands in...
solid MeB, which implies some kind of chemical interactions between Nb₂O₅ substrates and analytes. The variety of the irradiation laser also has an important effect on the intensity and position of vibrational band. Because of the fluorescence effect at 660 nm for MeB as well as the weakened and non-resonant excitation by 632 and 780 nm lasers, many bands for solid MeB did not appear in the spectra. Especially, for 780 nm irradiation laser, only two bands located at 1614 and 1394 cm⁻¹ can be recognized for solid MeB. However, the situation has improved greatly as most of the characteristic bands can be clearly identified in the SERS spectra. Thus, the Nb₂O₅ semiconductor substrate could effectively attenuate the fluorescence effects and enormously enhance the Raman signals of MeB molecules.

To reasonably illustrate the superior SERS activity of semiconducting Nb₂O₅, the enhancement ability of anatase TiO₂ and Ag colloids for MeB molecules were further investigated. Fig. S1 presents the SEM images of Nb₂O₅, TiO₂ and Ag NPs respectively. Nb₂O₅ NPs show irregular shapes with an average particle size of ~100 nm, TiO₂ NPs show a unique cage-like nanostructure with ~50 nm in diameter, and Ag NPs have an average particle size of ~27 nm. TiO₂ has similar energy levels as Nb₂O₅ and their isoelectric points have been reported in the range of 2.7–6.0. Therefore, the cationic coloring regents of MeB dye are apt to adsorb onto TiO₂ surface. Fig. 2b–d presents the Raman spectra of MeB collected on TiO₂ and Ag colloid substrates with 532, 633, and 780 nm laser, respectively. TiO₂ substrate delivers three Raman bands at 396, 516, and 638 cm⁻¹ assigned to anatase TiO₂. Only an extremely weak Raman band at 1632 cm⁻¹ assigned to MeB is nearly negligible under the excitation of 532 nm laser. It is noteworthy that the intensity of SERS spectra collected on Nb₂O₅ is even stronger than that collected on Ag colloid substrate (with a calculated EF value of 6.9 × 10⁵ with 532 nm laser) under the excitation of 532 and 780 nm lasers.

It has been reported that Nb₂O₅ provides various adsorption sites, including the coordination adsorption of Nb⁵⁺ ions (Lewis acidic sites) and electro-adsorption of surface hydroxyl species (Brønsted sites). As shown in Scheme S1, both MeB and MV are base dyes that can be dissociated into cationic pigments in aqueous solutions, whereas MB is an acid dye with anionic coloring agents. The characteristic nucleophilic groups (N or S) make the dyes more inclined to bind with Nb⁵⁺. To disclose the adsorption behavior of MeB, MV, and MB molecules on Nb₂O₅ powder, we measured the UV-vis absorption spectra in Fig. S2 of the original analyte solutions with concentration of 5 × 10⁻⁵ M and the centrifugal solutions out of the Nb₂O₅ suspensions. The adsorption ratios reach up to 19.8 and 13.9% for MeB and MV solutions, respectively, whereas it was observed smaller than 2% for MB solution. The data of adsorption ratios for dyes were further used to evaluate the enhancement capability of Nb₂O₅ semiconductor substrates under the excitation of different laser beams. According to the results presented in Fig. 2b–d, the bands centered at 1402 cm⁻¹ were selected to calculate the Raman EFs (details in Supporting Information). The resulted EFs are listed in Table 1, which are incredibly as large as 2.6 × 10⁶, 1.9 × 10⁷, and 7.1 × 10⁷ for 532, 633, and 780 nm laser beams, respectively. The EF values for MeB molecules excited at 633 and 780 nm were

Table 1. Calculated EF values for MeB, MV, and MB detection irradiated by different lasers

| Analytes | Peak Position (cm⁻¹) | Laser wavelength |
|----------|----------------------|------------------|
|          | 532 nm | 633 nm | 780 nm |
| MeB      | 1402   | 2.6  × 10⁶ | 1.9  × 10⁷ | 7.1  × 10⁷ |
| MV       | 1382   | 6.7  × 10⁵ | —      | —      |
| MB       | 1617   | 2.3  × 10⁶ | —      | —      |

* The EFs were unable to be calculated because of the undetectable Raman spectra for solid dye powder.
observed as one order of magnitude greater than the largest EF value for all the reported semiconductor SERS materials (Table 2).

The reproducibility of SERS signals for MeB molecule on the semiconductor substrates was further investigated. Eighteen Raman curves were obtained from six Nb$_2$O$_5$ substrates and three spots for each sample were randomly selected to collect the Raman signals (Fig. S3). The calculated relative standard deviation (RSD) values for the main Raman peaks for MeB were observed smaller than 0.1 (Table S2), suggesting an excellent reproducibility. Semiconductor SERS substrates always delivered a much better reproducibility than noble metal SERS substrates, as a uniform adsorption of analyte molecules onto semiconductors was more feasible to realize in comparison to an even distribution of “hot spots” for metal SERS substrates.

MV molecules with positively charged coloring agents were further applied as the analyte to evaluate the SERS performance of Nb$_2$O$_5$ semiconductor substrates. Fig. S4 displays the enhanced Raman spectra of MV molecules with various dye concentrations and lasers. The number as well as the intensity of the bands for solid MV powders decreased with the increase of irradiation laser wavelength due to reduced electronic cross sections. Much more bands were recognized for the SERS spectra of MV molecules collected on Nb$_2$O$_5$ even under the 780 nm laser excitation. The EF values are calculated from Fig. S4b–c and listed in Table 1 (calculation details in Supporting Information) reveal the largest EF value as large as 4.7 × 10^6.

Table 2. Performance of semiconductor SERS active materials from literatures

| Substrates                  | Analyte   | Maximum EF | Detection limit (M)/Analyte concentration | Excited wavelength (nm) | Reference |
|-----------------------------|-----------|------------|------------------------------------------|-------------------------|-----------|
| Porous ZnO nanosheets       | 4-MBA     | 1 × 10^3   | 1 × 10^-6                                | 514.5                   | 15        |
| TiO$_2$ photonic microarrays| MeB       | 2.0 × 10^4 | 6 × 10^-6                                | 532                     | 16        |
| Urchin-like W$_2$O$_4$$_9$  | R6G       | 3.4 × 10^6 | 1 × 10^-7                                | 532                     | 35        |
| Cu$_2$O porous nanowires    | 4-ABT     | 73.8       | 1 × 10^-3                                | 633                     | 36        |
| Chemically etched ZnSe      | 4-MPy     | 2 × 10^6   | 1 × 10^-3                                | 514.5                   | 17        |
| Nb$_2$O$_5$ NPs             | MeB       | 7.1 × 10^7 | 1 × 10^-6                                | 780                     | This work |
| MV                          | 4.7 × 10^6 | 1 × 10^-6  | 633                                     |                         |           |
| MB                          | 2.3 × 10^6 | 1 × 10^-6  | 532                                     |                         |           |

Photo-induced charge transfer (PICT) mechanism is one of the most popular CM for semiconductor substrates. Based on the Born-Oppenheimer and Herzberg-Teller theories, the contribution of PICT process to the molecular polarizability tensor in semiconductor-molecule system has been calculated (see Supporting Information), where the vibrational coupling between the semiconductive energy states (conduction band state S and valence state S) and the molecular energy states (excited state K and ground state I) is included. The energy level of highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) should match with the valence band (VB) and conduction band (CB) of semiconductor. Thus thermodynamically allowed charge transfer would be either from semiconductor to molecule or from molecule to semiconductor (see Scheme S3). The HOMO and LUMO of MeB molecule are located at −6.26 and −4.55 eV, and the CB and VB of semiconductor Nb$_2$O$_5$ are located at −4.00 and −7.10 eV, respectively (see Fig. S6a). As a result, the related thermodynamically feasible charge transfer process with the excitation of 532 nm laser includes the photon-induced charge transfer resonance from the HOMO level of MeB to the CB of Nb$_2$O$_5$. The charge transfer process would create a modified polarizability tensor and electron density distribution of the MeB molecules, leading to the observation of non-totally symmetric SERS modes.

It is noted that the theoretical minimum matching photon energy is greater than 2.0 eV for all dyes (see Fig. S6), and the incident lasers with wavelengths of 633 and 780 nm seem unable to induce the charge transfer between molecules and semiconductor. However, different from the PICT mechanism derived from metal-molecule system disregarding of the chemisorption effect, the adsorption effect of analyte molecules for semiconductor-molecule system has to be taken into account. The extra bonding between Nb$_2$O$_5$ and dye molecules through chemisorption would readjust the positions of molecular HOMO and LUMO as well as semiconducting VB and CB, which would allow the PICT process excited by 633 and 780 nm lasers.

Taking the chemical bonding effect between Nb$_2$O$_5$ and MeB into consideration, the density-functional-theory (DFT) calculations were performed to study the chemical enhancement mechanism including charge transfer and light adsorption capacities of MeB-Nb$_2$O$_5$ composite. To reduce computational cost, Nb$_2$O$_{10}$ cluster with H-passivation was used to simulate Nb$_2$O$_5$ nanostructure that further interacts with MeB molecule by Nb-S chemical bonding and the Nb-S bond length (2.45 Å) in MeB-Nb$_2$O$_5$ composite. Therefore, Raman vibrational modes associated with S atom in MeB were considered and compared with experimental values. More interaction modes between Nb$_2$O$_5$ surfaces and adsorbed molecule MeB such as Nb–N bonding were not considered in this work. Fig. 3 displays the optimized structures and computed normal-mode Raman spectra of MeB and MeB-Nb$_2$O$_5$. It is found that several dominant bands located in 1410, 660, and 1445 cm$^{-1}$ in MeB-Nb$_2$O$_{10}$ are obviously

DISCUSSION

Though the exact enhancement mechanism is still a controversial issue, two widely accepted theories have been proposed to interpret the SERS phenomenon in most cases. One is EM, which is based on the enhancement of optical fields at the surface originated from the localized surface plasmon resonance of substrate materials. The other is CM, predicting that the enhancement is introduced by the charge transfer between chemisorbed molecules and substrate. Both the CM and EM mechanisms will be discussed as follows.
MeB-Nb$_4$O$_{10}$ are formed by combining HOMO of MeB with LUMO located in 1630 cm$^{-1}$ for the experimental measurement. The strongest enhancement of Nb$_2$O$_5$ are produced in the basic dye solution with a stronger enhancement owing to the same-charged character between the coloring agents and Nb$_2$O$_5$. Since the Raman spectra of Nb$_2$O$_5$ from the density surface charge as a function of pH and ionic strength were obtained with a high pH of 10 and 12. Little attenuation Raman signal at pH 4 is ascribed to the deceased base sites. There is not any characteristic Raman band at pH 1 and 2 as a result of fully protonated acid sites coverage on Nb$_2$O$_5$ surface. These results demonstrate that the deprotonated sites with one negative charge play a crucial role for the excellent SERS detection of MeB molecules.

The chemical bonding induced CM enhancement is closely related to the excellent adsorption ability (uptake of 5.96 $\times$ 10$^{18}$ MeB molecules or 4.18 $\times$ 10$^{19}$ MV molecules per gram of Nb$_2$O$_5$ powder) which was confirmed by the UV-vis adsorption curves shown in Fig. S2. Prado et al. calculated the pK$_1$ and pK$_2$ of Nb$_2$O$_5$ from the density surface charge as a function of pH and observed that Nb$_2$O$_5$ surface was protonated corresponding to Nb–OH$_2^+$ acid sites at pH below 4. At pH greater than 5.4, the surface is covered with fully deprotonated base sites of Nb–O$^-$ (Scheme S2a). For the detection of base dyes, the surface of Nb$_2$O$_5$ is fully deprotonated in the alkaliescent MeB solution (Scheme S2b). The resulting excessive negative charge on the Nb$_2$O$_5$ surface further promotes strong interactions with the coloring agents through the positively charged S or N atom. We collected the Raman spectra of MeB at different pH values (Fig. 5) in which the HCl and NaOH solutions were used to adjust pH of MeB solutions to the target value. As more deprotonated base sites on the surface of Nb$_2$O$_5$ are produced in the basic dye solution with a higher pH value, MeB color regent with positive charges will be more easily bonded to these sites. Therefore, the largely enhanced Raman spectra were obtained with a high pH of 10 and 12. Little attenuated Raman signal at pH 4 is ascribed to the deceased base sites. There is not any characteristic Raman band at pH 1 and 2 as a result of fully protonated acid sites coverage on Nb$_2$O$_5$ surface. These results demonstrate that the deprotonated sites with one negative charge play a crucial role for the excellent SERS detection of MeB molecules.

Similarly, the bonding effect between MV molecules and Nb$_2$O$_5$ also promotes significantly electron transfer, which was revealed by a broader MV adsorption for the MV molecules modified Nb$_2$O$_5$ powder than MV solution (Fig. S7a). However, MB molecule has a poorer adsorption behavior on the surface of Nb$_2$O$_5$ than MeB and MV owing to the same-charged character between the coloring...
agent of MB and Nb$_2$O$_5$ surface. Only one broad peak appears in the curve of MB modified Nb$_2$O$_5$ with respect to the double peaks adsorption of MB aqueous solution (Fig. S7b). Therefore, there is no effective bonding effect to produce the extra hybrid surface states between VB and CB of Nb$_2$O$_5$, and longer irradiation wavelength could not achieve feasible electron transfer between dye molecules and Nb$_2$O$_5$, which also explains the disappearance of the SERS activity with the irradiation lasers of 633 and 780 nm in our experiments.

PICT mechanism could only account for an EF value of smaller than $10^3$, thus, the electromagnetic enhancement here should be investigated using finite element method (FEM). Fig. 6 presents the electric field distribution around a single Nb$_2$O$_5$ crystal with the excitation of 526 nm laser. A quasi-hot spot with the highest electric field amplitude (E) of 5.25 is located around Nb$_2$O$_5$ nanocrystal. As the EF value is proportional to |E|$^4$, EM contributes as high as two orders of magnitude to EF. The calculated results by combining CM and EM are in well consistent with our experimental results. This work has delivered a new semiconductor substrate of Nb$_2$O$_5$ with EFs as high as 10$^7$ that is comparable to noble metal (Ag) substrates with one order of magnitude larger than the largest EF value for all noble metal nanostructures with "hot spots". An excellent roughening pretreatment. The authors gratefully acknowledge the financial support of the National Natural Science Foundation of China (No. 51471182).

Sample preparation
MeB, MV, and MB solutions were diluted with deionized water to various concentrations of $1 \times 10^{-4}$, $5 \times 10^{-5}$, $1 \times 10^{-5}$, $5 \times 10^{-6}$, and $1 \times 10^{-6}$ M. Then 20 mg Nb$_2$O$_5$ powders and 20 ml analyte solutions were mixed thoroughly with ultrasonic dispersion for 30 min. Finally, Nb$_2$O$_5$ was separated from the suspensions by centrifugation and further transferred to the object slice. After dried in a 60 °C oven for 10 min, the Nb$_2$O$_5$ substrate was ready for the Raman measurement.

ACKNOWLEDGEMENTS
The authors gratefully acknowledge the finical support of the National Natural Science Foundation of China (No. 51471182).

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Supplementary Information accompanies the paper on the *npj Computational Materials* website (doi:10.1038/s41524-017-0008-0).