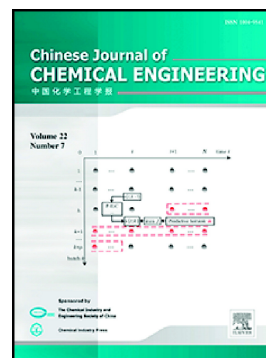


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## Interfacial Potassium Induced Enhanced Raman Spectroscopy for Single-Crystal TiO<sub>2</sub> Nanowhisker

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**Abstract:** Structural control and element doping are two popular strategies to produce semiconductors with surface enhanced Raman spectroscopy (SERS) properties. For TiO<sub>2</sub> based SERS substrates, maintaining a good crystallinity is critical to achieve excellent Raman scattering. At elevated temperatures (> 600 °C), the phase transition from anatase to rutile TiO<sub>2</sub>, could result in a poor SERS performance. In this work, we report the successful synthesis of TiO<sub>2</sub> nanowhiskers with excellent SERS properties. The enhancement factor, an index of SERS performance, is  $4.96 \times 10^6$  for methylene blue molecule detecting, with a detection sensitivity around  $10^{-7}$  M. Characterizations, such as XRD, Raman, TEM, UV-vis and Zeta potential measurement, have been performed to decrypt structural and chemical characteristics of the newly synthesized TiO<sub>2</sub> nanowhiskers. The photo absorption onset of MB adsorbed TiO<sub>2</sub> nanowhiskers was similar to that of bare TiO<sub>2</sub> nanowhiskers. In addition, no new band was observed from the UV-vis of MB modified TiO<sub>2</sub> nanowhiskers. Both results suggest that the high enhancement factor cannot be explained by the charge-transfer mechanism. With the support of *ab initio* density functional theory calculations, we reveal that interfacial potassium is critical to maintain thermal stability of the anatase phase up to 900 °C. In addition, the deposition of potassium results in a negatively charged TiO<sub>2</sub> nanowhisker surface, which favours specific adsorption of methylene blue molecules and significantly

improves SERS performance via the electrostatic adsorption effect.

**Keywords:** TiO<sub>2</sub> nanowhisker; SERS; potassium induced

## 1. Introduction

Surface-enhanced Raman spectroscopy (SERS) is one of the most sensitive spectroscopic techniques to detect molecules that have a strong Raman response at a single-molecule resolution [1]. In recent years, TiO<sub>2</sub> semiconductor-based SERS has attracted much attention due to the advantages of low cost, good stability and excellent reproducibility [2-4]. TiO<sub>2</sub> SERS performance is mainly tuned via the preparation protocol where element doping (hydrogen and oxygen), morphology manipulation and band structure engineering are beneficial. Compared with traditional coinage metal substrates such as gold, silver and copper, TiO<sub>2</sub> photocatalytic properties enable an environment-friendly removal of adsorbed molecules and a reuse of the SERS substrate [5].

Despite the promise, semiconductor-based SERS substrates are generally limited by the inferior enhancement factor (EF), an index of how sensitive the detection is. The theoretical maximum EF for semiconductor-based SERS [4], based on charge-transfer (CT) mechanism, has been estimated to be around  $10^6$ . However, reported experimental EF values for TiO<sub>2</sub> substrates are only in the range of  $10\sim10^3$ . Generally, there are two options to improve the SERS performance. The first one is to change the semiconductor morphology and thus enhance the interactions between the laser and the substrate. Under this guideline, Alessandri synthesized TiO<sub>2</sub> shell-based spherical resonators and reported a remarkable Raman scattering enhancement [6]. The improvement is ascribed to the synergistic effects of high refractive index of TiO<sub>2</sub> shell layer and multiple light scattering through spherical geometries. Similarly, Zhang and co-workers used a sol-gel method and prepared TiO<sub>2</sub> inverse opal photonic microarrays [7]. They reported that the morphology change results in the photonic band gap change, which in return promotes multiple light scattering and the resulted EF is about  $10^4$ . Recently, we adopted a two-step anodic oxidation process and prepared TiO<sub>2</sub> nanofoam–nanotube array [8], which shows a remarkable Raman scattering enhancement for methylene blue ( $EF = 2.3 \times 10^5$ ). The second option is to

manipulate interactions between the substrate and adsorbed molecules. For example, Cong and co-workers engineered oxygen vacancy at tungsten oxide nanowire surfaces [9]. It was observed that the new interfacial oxygen vacancies can enrich tungsten oxide surface states, strengthen adsorbent-adsorbate interactions, and eventually produce an improved EF value of  $3.4 \times 10^5$ . Inspired by Cong's work, hydrogen or oxygen doping has been adopted to treat other semiconductors [5]. It is generally accepted that quasi-amorphous interfacial thin layers and hydrogen or oxygen doping effectively facilitate charge transfer, enhance vibrational scattering of adsorbed molecules and improve the SERS performance.

It is worth pointing out that defect engineering is a double-edged sword. A poorly designed defective interface can severely degrade SERS performance. For example, it was reported that the excess amorphous structure at interface can decrease the refractive index, which could weaken the interactions between the SERS substrate and the laser [4]. Also, interfacial defects can induce the transformation and recombination of electron/hole pairs, which will degrade SERS performance [10]. For instance, Zhao and co-workers investigated the crystallinity effect of anatase  $\text{TiO}_2$  nanoparticles on SERS performance [11]. They concluded that both high degree of crystallinity and high concentration of surface defects are critical for a superior SERS performance. However, the challenge is that the two factors do not come together very easily for  $\text{TiO}_2$  materials: using a high-temperature treatment (normally above  $600^\circ\text{C}$ ) to improve anatase  $\text{TiO}_2$  crystallinity, one can easily witness the intrinsic phase transformation from anatase to rutile  $\text{TiO}_2$ . The as-synthesized  $\text{TiO}_2$  substrate has an inferior SERS performance.

In this work, we report a new semiconductor SERS substrate- $\text{TiO}_2$  nanowhisker with high crystallinity and high thermal stability. The single anatase crystal phase remains intact up to  $900^\circ\text{C}$ , which is mainly due to the interfacial potassium. In addition, potassium binds strongly with  $\text{TiO}_2$  substrate, producing a negatively charged interface for Raman scattering, as well as altering the band gap of anatase  $\text{TiO}_2$ . All three factors, namely, the single-phase crystallinity, the negatively charged interface and the reduced band gap, synergistically enable the synthesized anatase  $\text{TiO}_2$  nanowhisker to be a supreme SERS substrate, with a maximum EF  $4.96 \times 10^6$ . The significance of this work is two-fold: the report of a new SERS performance record from  $\text{TiO}_2$  semiconductor, and the exploration of interfacial potassium doping

effect. We anticipate other alkali elements can also assist engineering  $\text{TiO}_2$  materials to achieve high crystallinity, high thermo stability and high interaction selectivity.

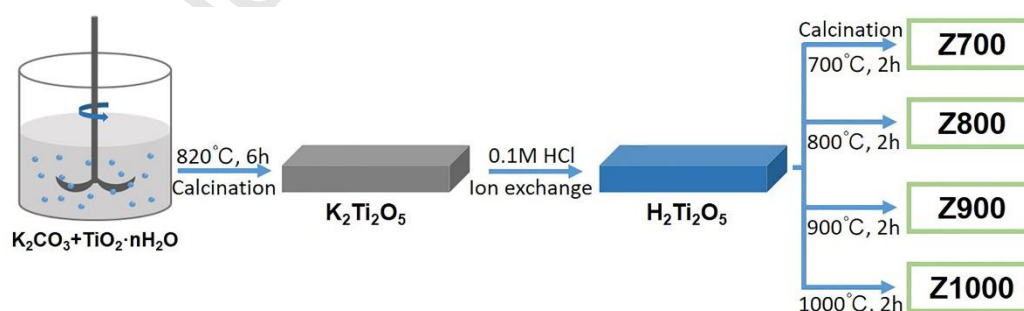
## 2. Experimental

### 2.1 Materials

Metatitanic acid ( $\text{TiO}_2 \cdot n\text{H}_2\text{O}$ ) was from Nanjing oil chemicals Co., Ltd., China. Potassium carbonate ( $\text{K}_2\text{CO}_3$ ) was from Shanghai chemical reagent factory. Methylene blue (MB) was purchased from Tianjin Chemical Reagent Research Institute Co., Ltd. All chemicals were of analytical grade and used as received. Deionized water was used in all experiments.

### 2.2 $\text{TiO}_2$ nanowhisker synthesis

$\text{TiO}_2$  nanowhisker was synthesized by a two-step calcination and ion exchange process, as illustrated in Fig. 1 [12]. Briefly, metatitanic acid ( $\text{TiO}_2 \cdot n\text{H}_2\text{O}$ ) and potassium carbonate were mixed with a 1.9 molar ratio. The mixture was then calcined in the muffle furnace at  $820^\circ\text{C}$  for 6 hrs. After that, the as-obtained potassium dititanate was washed with 0.1 M HCl and deionized water, repeating for three times. Finally, the  $\text{TiO}_2$  nanowhiskers were obtained by calcining the powders at different temperatures for 2 hrs. According to the temperature used in the final calcination step, obtained  $\text{TiO}_2$  samples were named as Z700, Z800, Z900 and Z1000, respectively.



**Fig. 1.** Schematic diagram of  $\text{TiO}_2$  nanowhisker preparation.

### 2.3 Characterizations

The crystal structures of those samples were characterized by X-ray diffraction (XRD, Bruker, Model D8 with Cu K $\alpha$  excitation). In addition, the element composition and chemical states of studied samples were analysed by X-ray photoelectron spectrometer (XPS, Physical Electronics 5600). The UV-vis diffuse reflectance spectra (UV-vis DRS) was obtained by a UV-vis spectrometer (Perkin-Elmer Lambda 950) over a wavelength range of 300~800 nm. Surface morphologies were studied by using field-emission scanning electron microscope (FESEM, Hitachi S-4800) at 5 kV, 10  $\mu$ A. Surface charge of the samples were detected on the Zeta potential analyser (Malvern, ZS90). TEM images were obtained employing JEM-2010 UHR at 200 kV.

## 2.4 SERS measurement

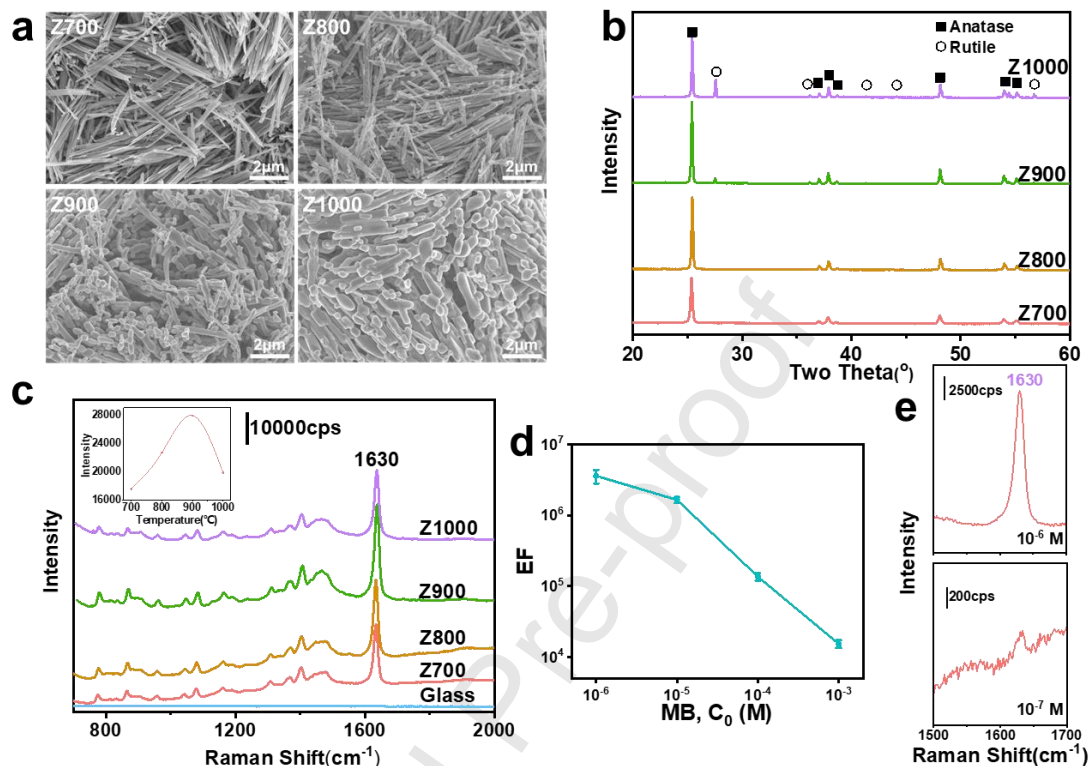
The Raman signal of MB molecules adsorbed on TiO<sub>2</sub> nanowhiskers were obtained using the 514.5 nm laser excitation. Specifically, we obtain the 10<sup>-5</sup> M MB ethanol solution by successively diluting a 10<sup>-3</sup> M MB solution. Then 20  $\mu$ L of the 10<sup>-5</sup> M MB ethanol solution was added to TiO<sub>2</sub> substrate, keeping the sample in the dark for 4 hrs to reach the adsorption equilibrium. Subsequently, the Raman spectra were collected via the high-resolution confocal Raman spectrometer (LabRAM HR-800) using a 50  $\times$  LWD objective lens for 10 s and 0.3 mW powers in all acquisitions. Each sample was collected at least 5 times from different locations of the sample.

## 3. Results and discussion

### 3.1 The characterization of TiO<sub>2</sub> nanowhisker

As shown in Fig. 2a, scanning electron microscopy (SEM) images demonstrate that the four samples possess one-dimensional morphology. For the Z700 sample, the diameter is about 300 nm and the length is a few microns. When the temperature increases from 700  $^{\circ}$ C to 1000  $^{\circ}$ C, all studied samples shrink a little bit and their diameters increase slightly. This indicates that TiO<sub>2</sub> nanowhisker could melt partially at high temperatures. According to XRD characterizations in Fig. 2b, Z700 and Z800 are pure anatase crystalline phase, while Z900 and Z1000 have a small portion of rutile crystalline phase. The content of rutile phase was estimated to be 2 mol % and

10 mol % for Z900 and Z1000, respectively [13]. TEM images of those nanowhiskers are available in Fig. S2, where a crystal phase of nanowhiskers was measured, consistent with XRD results.



**Fig. 2.** Morphology, crystal structure and SERS properties of four TiO<sub>2</sub> nanowhisker samples. (a) SEM images of Z700, Z800, Z900 and Z1000. (b) XRD pattern of four TiO<sub>2</sub> nanowhiskers. (c) Raman spectra of the 10<sup>-5</sup> M MB ethanol solution on four TiO<sub>2</sub> nanowhiskers and bare glass (inset: the 1630 cm<sup>-1</sup> intensity of four nanowhiskers). (d) Raman EFs obtained for MB on the Z900 sample, as a function of MB concentrations at the 1630 cm<sup>-1</sup> peak. (e) The detection limitation test of MB on the Z900 sample.

### 3.2 SERS properties of TiO<sub>2</sub> nanowhisker samples

Methylene blue (MB) was used as the probe molecule to examine the SERS performance of TiO<sub>2</sub> nanowhiskers. As shown in Fig. 2c, the SERS enhancement factor (EF) is calculated at the characteristic peak of 1630 cm<sup>-1</sup>, which is the aromatic C-C stretching vibration mode [9]:

$$EF = (I_{\text{SERS}}/N_{\text{SERS}})/(I_{\text{bulk}}/N_{\text{bulk}}) \quad (1)$$

where  $I_{\text{SERS}}$  and  $I_{\text{bulk}}$  refer to peak intensities of the SERS and non-SERS spectra,

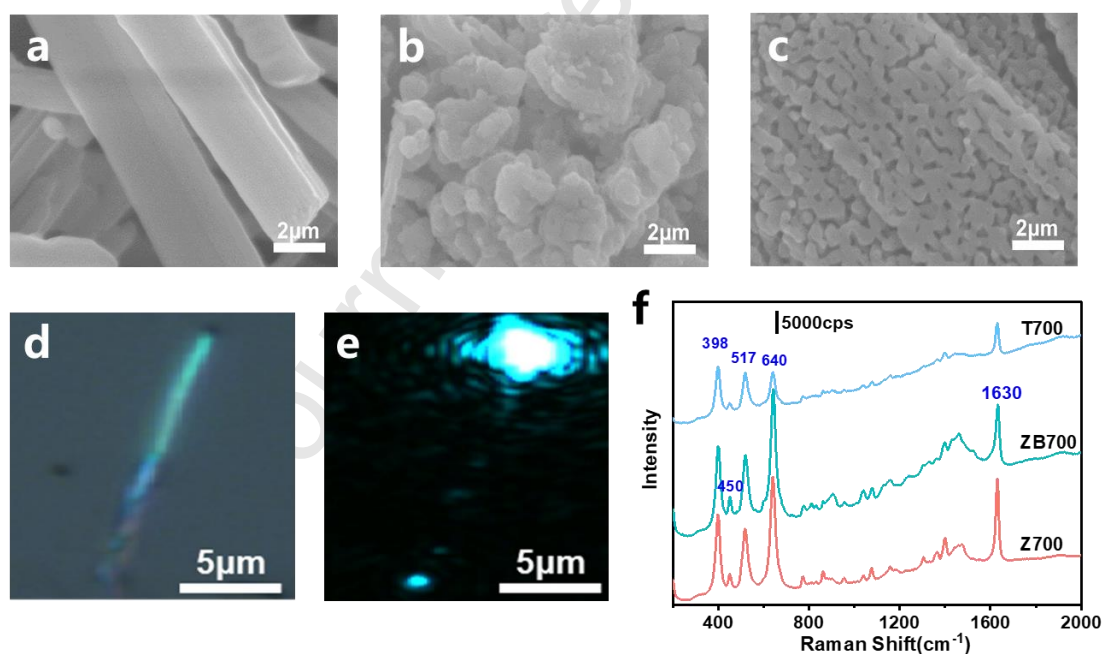
respectively.  $N_{\text{SERS}}$  and  $N_{\text{bulk}}$  correspond to the number of probe molecules in the laser area for the SERS and non-SERS measurements. Calculation details are available in the Section S2 of Supporting Information.

Significant SERS enhancements are observed for all four samples but there is almost no enhancement from the bare glass substrate. The Z900 sample shows the best SERS performance compared with other samples. It is probably because Z900 has a high crystallinity. It is worth pointing out that when the calcination temperature increases to 1000 °C, a significant phase transformation will occur, from the anatase to rutile phase, which will result in a decrease of Raman detecting signal of MB molecules. The trend of anatase phase has a better SERS performance than the rutile phase is also reported by Zhao et al. [14]. As illustrated in Fig. 2d, the calculated EF from the Z900 sample is  $4.96 \times 10^6$  at the  $10^{-6}$  M MB concentration, which is the best performance reported so far for TiO<sub>2</sub>-based SERS substrates (Table S1). In addition, the Z900 sample has an applicable detection of MB molecules even at a very dilute concentration of  $10^{-7}$  M, see Fig. 2e. Such detecting sensitivity is better than most reported results from semiconductor SERS substrates.

### 3.3 TiO<sub>2</sub> morphology and SERS performance

TiO<sub>2</sub> SERS substrates are traditionally polycrystalline materials, with the morphology of nanoparticles or mesoporous membranes. The TiO<sub>2</sub> nanowhisker synthesized in this work is a one-dimensional single crystal. A high crystallinity could improve the SERS performance. For example, Sun and co-workers reported that one-dimensional semiconductor materials with single crystal structures (such as nanowire and nanobelt), are excellent plasmonic waveguides to transfer Raman signals and realize remote SERS properties [15]. Such signal transfer and remote Raman scattering are promising for Raman scattering enhancement. For the Z700 sample, as shown in Fig. 3d and 3e, remote Raman scattering was also observed. In order to further validate the dominating contribution of the single crystal morphology, a new set of three samples has been prepared: Z700 nanowhisker with the one-dimensional morphology (Fig. 3a); ZB700, a sample from ball-milling Z700, where the single crystallinity was destroyed (Fig. 3b); T700, a mesoporous TiO<sub>2</sub> nanowhisker sample prepared with additional water vapor treatment during the Z700 sample preparation

(Fig. 3c). The detailed preparation conditions are provided in the supporting information and see also Fig. S1. The key differences between three samples: ZB700 sample is composed of  $\text{TiO}_2$  nanoparticles with irregular morphologies; T700 has the one-dimensional morphology, similar to that of Z700. But T700 has a significant number of cavities at the surface. SERS performances of the three samples are compared in Fig. 3f. First of all, the Raman scattering at low wavenumbers ( $200\sim 800\text{ cm}^{-1}$ ) supports that all three samples are generally composed of  $\text{TiO}_2$  anatase phase. However, the SERS performance from the three samples is obviously different: at the characteristic  $1630\text{ cm}^{-1}$  peak, the EF has the order of  $\text{T700} < \text{ZB700} < \text{Z700}$  (Table S2). It is important to point out that despite the one-dimensional morphology, the cavities of T700 significantly degrade the SERS performance. In summary, both the single crystallinity and the one-dimensional morphology are important for excellent SERS performance.



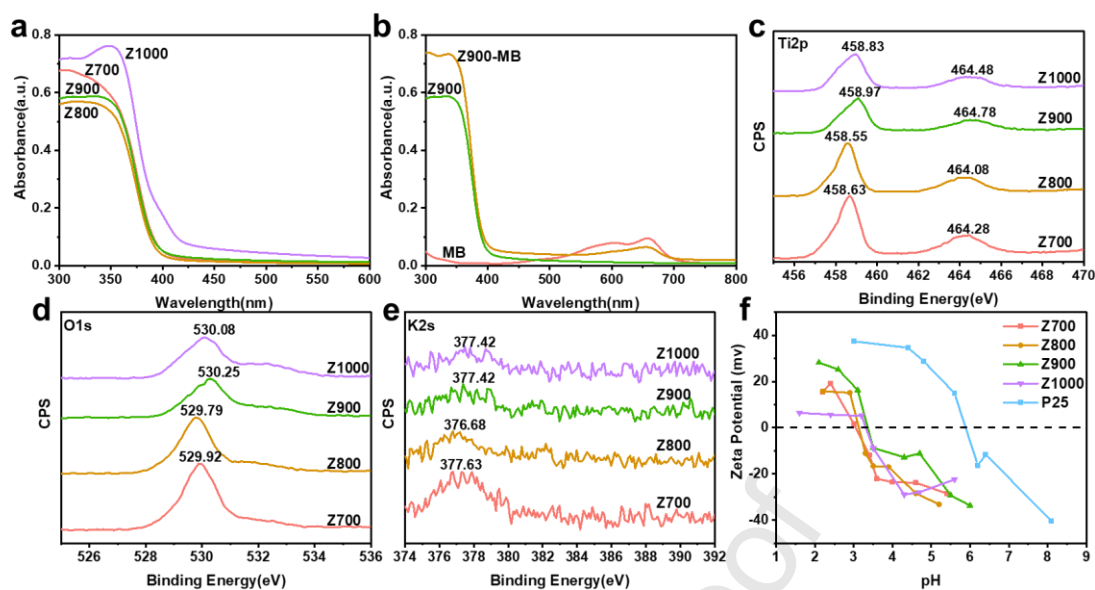
**Fig. 3.** Morphology, Remote SERS and SERS performance of  $\text{TiO}_2$  samples. SEM images of Z700 (a), ZB700 (b) and T700(c). The propagation of light along  $\text{TiO}_2$  nanowhisker (Z700) under visible light (d) and laser (e). (f) Raman spectra of MB ( $10^{-5}\text{ M}$ ) adsorbed on T700, ZB 700 and Z700 samples.

### 3.4 Interfacial potassium and significant SERS improvement

Despite the performance degradation with respect to Z700 and ZB700, the T700

sample still has an EF of  $4.13 \times 10^5$ , higher than other reported TiO<sub>2</sub> semiconductors. Since T700 possesses no single crystallinity nor perfect interfacial morphology, the excellent SERS performance is attributed by other factors. In literature, Zhao et al. reported that the photo absorption threshold to the 4-Mercaptobenzoic acid (4-MBA) adsorbed TiO<sub>2</sub> shows a blue-shift, compared with that of unmodified TiO<sub>2</sub>. It is interpreted due to the interaction between adsorbed molecules and TiO<sub>2</sub> substrate [16]. Similarly, Cong et al. reported their X-ray photoelectron spectroscopy (XPS) results that hydrogen treated W<sub>18</sub>O<sub>49</sub> sample has an increased percentage of W<sup>5+</sup>, from 30.4 mol % (untreated, pristine W<sub>18</sub>O<sub>49</sub>) to 47.5 mol % [9]. Obviously, there are more surface oxygen vacancies of the modified sample. Moreover, they determined UV-vis diffuse reflectance spectroscopy (DRS) spectra of R6G molecules deposited on W<sub>18</sub>O<sub>49</sub> and reported a new band from the hybrid sample, an evidence of the charge transfer between R6G and W<sub>18</sub>O<sub>49</sub>.

Inspired by those studies, UV-vis DRS and XPS were performed in this work to further explore the enhancement mechanism of Raman scattering. As shown in Fig. 4a, the photo absorption spectra for Z700, Z800 and Z900 samples are very similar to each other, with a same onset around 400 nm. Such result is in accordance with the photo absorption onset of TiO<sub>2</sub> anatase phase. A red shift of the absorption edge for Z1000 was observed, which is mainly due to the phase transformation and the resulted rutile phase. Ti2p and O1s peak positions of XPS spectra in Fig. 4c and 4d further confirmed that Z700 and Z800 are in the anatase phase, while Z900 and Z1000 have co-existing anatase and rutile phases [17]. Moreover, as shown in Fig. 4b, we compared UV-vis DRS spectra of MB molecule adsorbed on Z900 with that of pristine MB and Z900. No new band was observed from the spectra of MB modified Z900. In addition, the absorption edge of MB modified Z900 was same as that of the pristine Z900 sample. Those results suggested that the excellent SERS performance of TiO<sub>2</sub> nanowhisker is not from defect states near TiO<sub>2</sub> conduction band.

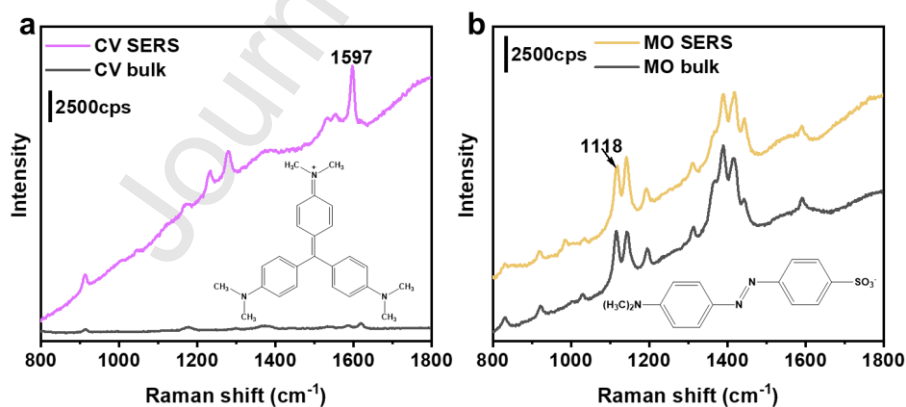


**Fig. 4.** UV-vis DRS spectra of (a) TiO<sub>2</sub> nanowhiskers and (b) Z900 compared with pristine Z900 and MB. XPS spectra and binding energies of (c) titanium, (d) oxygen and (e) potassium. (f) Zeta potential as a function of pH: the comparison between four studied TiO<sub>2</sub> nanowhiskers and the commercial P25 sample.

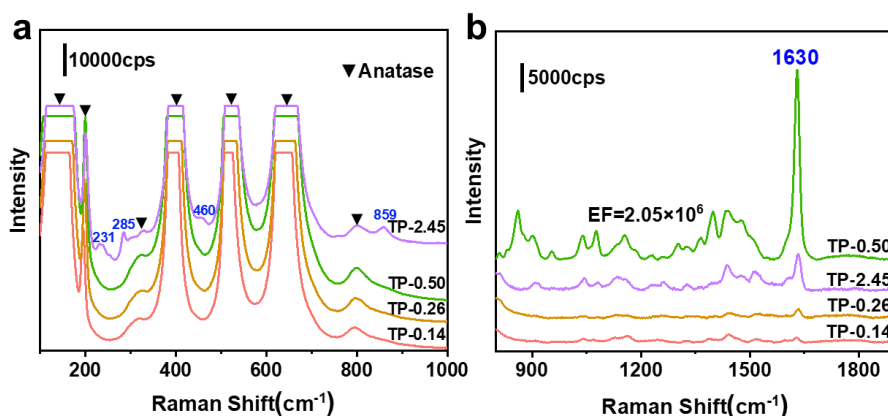
Generally, oxygen vacancy defects of TiO<sub>2</sub> nanoparticles can form surface state energy levels. Zhao et al. observed that defect states favour charge transfer between molecules and TiO<sub>2</sub> substrates. Also, the SERS signal is affected by temperature, which is ascribed to the improved crystallinity and the reduced concentration of surface defects [16]. In this work, the enhanced SERS performance is not dominated by oxygen vacancy defects. Firstly, the SERS signal of MB on Z800 is stronger than that of Z700, despite the fact that Z800 has a lower concentration of oxygen vacancy defects. Secondly, when calcination temperature increases, the XPS spectra peaks of Ti2p (Ti<sup>4+</sup>, ~458.6 eV and 464.2 eV) and O1s (~529.9 eV) are expected to shift towards higher binding energies. However, the results in Fig. 4c and 4d show the opposite. It is worth noting, as suggested by Fig. 4e, that potassium remains at the interface and binds strongly with oxygen sites of studied samples. Although the trace of potassium is negligible to TiO<sub>2</sub> structural characterization, such as XRD results in Fig. 2b, the surface chemistry could have a drastic change due to the trace potassium at interface. The potassium bonded Ti sites could have higher electron densities, which subsequently promote charge transfer between MB and the TiO<sub>2</sub> substrate. For the Z800 sample, the amount of potassium was estimated to be around 0.5 wt % via

XPS and X-ray fluorescence (XRF) experiments.

The Zeta potential measurement in Fig. 4f reveals that the point of zero charge (PZC) for studied TiO<sub>2</sub> nanowhiskers is in the range of pH 3.0 to 3.5, which is remarkably lower than that of the commercial P25 TiO<sub>2</sub> nanoparticles (~pH 6). Such PZC change indicates that the surface of TiO<sub>2</sub> nanowhisker is negatively charged, consequently interacting strongly with MB molecules through positive charged sites (see Fig. S4). The enhancement of electrostatic interactions is beneficial for SERS performance. We note that similar phenomenon has been reported on a Cu<sub>2</sub>O SERS substrate [18]. In order to validate the effect of electrostatic interactions, two molecules with opposite charges, namely, crystal violet (CV) (+) and methyl orange (MO) (-), were used to study their SERS performances on Z700 sample. As shown in Fig. 5, the positively charged CV molecule shows a better SERS performance than the negatively charged MO molecule. See Table S3 of the Supporting Information for the calculated EFs. In conclusion, we contributed Raman scattering enhancement observed in this work to synergistic effects: the interfacial potassium induced charge transfer effect and the electrostatic adsorption effect due to surface negative charges of TiO<sub>2</sub> nanowhiskers.



**Fig. 5.** Comparing Raman spectra of bulk dye and SERS spectra of 10<sup>-5</sup> M dye solution adsorbed on Z700. (a) Crystal violet, insert: CV structure; (b) Methyl orange, insert: MO structure.)



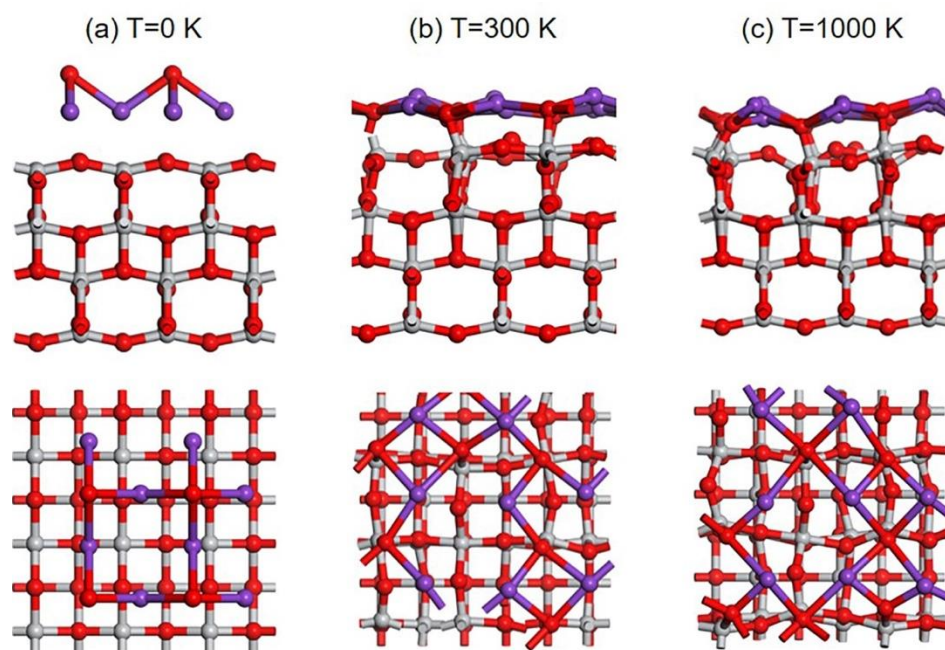
**Fig. 6.** Potassium treated  $\text{TiO}_2$  particles and their SERS performance. (a) Raman spectra of commercial  $\text{TiO}_2$  particles doped with different content of potassium (0.14, 0.26, 0.50 and 2.45 wt %) and (b) SERS spectra of MB ( $10^{-5}$  M) on  $\text{TiO}_2$  particles.

To further verify the effect of interfacial potassium, we design a third set of experiments: use commercially available  $\text{TiO}_2$  anatase particles (TP) with high purity (99.9%) and mix it with  $\text{K}_2\text{CO}_3$  (purity 99%). The mixture was heated at  $800^\circ\text{C}$  for 2 hrs to dope different concentrations of potassium. For the studied samples, “TP-0.14” denotes the TP sample with a content of 0.14 wt % potassium. As shown in Fig. 6, the TP-0.50 sample has the SERS performance of MB molecules. When the potassium content was increased to 2.45 wt %, new Raman peaks appear at 231, 285, 460 and  $859\text{ cm}^{-1}$  of the TP-2.45 sample, see Fig. 6a. Interestingly, If there is a phase transformation from anatase to rutile, characteristic peaks of rutile[13] ( $235$ ,  $445$  and  $612\text{ cm}^{-1}$ ) shall appear. Judging from the results in Fig. 6a, we conclude there is no rutile phase in the studied four samples. Therefore, the new Raman peaks at 231, 285, 460 and  $859\text{ cm}^{-1}$  are attributed to the possible formation of a new potassium titanate compound. Such hypothesis is supported by the literature where similar peaks have been identified from  $\text{K}_2\text{Ti}_2\text{O}_5$  and  $\text{K}_2\text{Ti}_6\text{O}_{13}$  [19]. The DFT calculations in Figure 7 also support the formation of a potassium titanate structure. We also note that while a trace of potassium oxide was applied to  $\text{TiO}_2$  samples, it took a longer time ( $\sim 10\text{ s}$ ) to detect new Raman peaks. Meanwhile, the prolonged collecting time resulted in very strong intensities of characteristic anatase Raman peaks at  $141$ ,  $393$ ,  $514$ ,  $635\text{ cm}^{-1}$ , as shown in Figure 6a. Those peak intensities were beyond the detecting limit of the equipment, therefore were interpreted as plateaus. On the other hand, Figure S6 in the Supporting Information was reported to show the four characteristic anatase peaks,

collected at a typical time window of 1s. We note that it is challenging to distinguish details of possible new crystal phases. This is because there are many potassium titanates and each has complex Raman spectra. Also, results in Fig. 6b reveal that the Raman signal ( $1630\text{ cm}^{-1}$ ) of MB molecules decreases when the content of potassium increases. It suggests that a higher content of potassium significantly downgrades the Raman scattering performance.

The content and existence of interfacial trace potassium have been studied in other systems. Xie et al. reported that at high temperatures trace salts could disperse on oxide surfaces, spontaneously forming a monolayer [20, 21]. In this work, it is hypothesized that trace potassium (0.5 wt %) disperses and stays at the surface of  $\text{TiO}_2$  samples. By a simple sphere model, see Table S5 of the Supporting Information, we estimated the coverage of 0.5 wt % potassium on  $\text{TiO}_2$  particles with different diameters. The analysis shows that when the diameter of  $\text{TiO}_2$  particle is around 100 nm, which is similar to the size of  $\text{TiO}_2$  nanowhiskers in this work, the atomic ratio of potassium/titanium at  $\text{TiO}_2$  surface is around 1. Such analysis suggests that the 0.5 wt % of potassium might form a thin layer at the surface of  $\text{TiO}_2$  samples and show the best SERS performance.

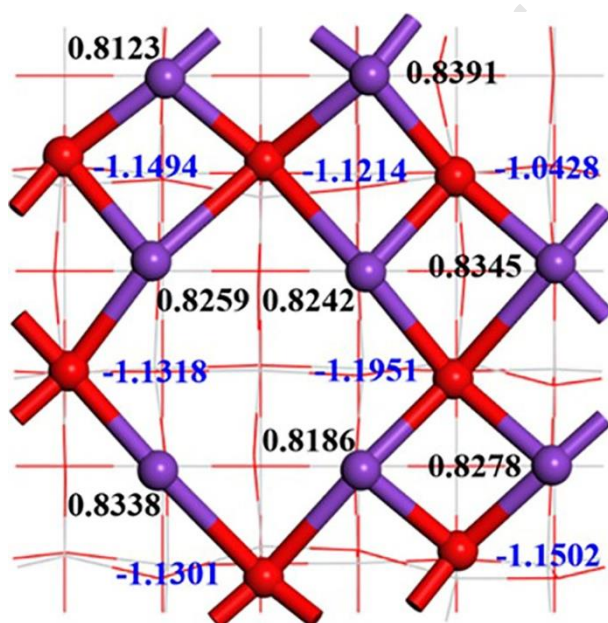
In order to further understand the interaction between potassium and  $\text{TiO}_2$  surface, as well as the potassium/ $\text{TiO}_2$  structural information at elevated temperatures, a series of *ab initio* density functional theory (DFT) calculations and *ab initio* molecular dynamics (AIMD) simulations have been performed via Vienna Ab initio Simulation Package (VASP) of the MedeA computational platform [22]. The ion-electron interactions were described through the projector-augmented wave (PAW) method [23], with the electrons from Ti-pv ( $3p^6 3d^2 4s^2$ ), O ( $2s^2 2p^4$ ) and K-pv ( $3p^6 4s^1$ ). The electron exchange and correlation interactions were represented by generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof (PBE) functionals [24]. Van der Waals interactions were described through Grimme's DFT-D3 semi-empirical method [25]. A cutoff energy of 450 eV was adopted for the planewave basis set and all calculations were performed using a Gaussian smearing with a width of 0.2 eV. The ionic relaxation is considered converged when the atomic force is smaller than  $0.02\text{ eV \AA}^{-1}$ . Self-consistent field (SCF) cycles would stop when successive energy difference is less than  $10^{-5}\text{ eV}$ .



**Fig. 7.** The K-coated  $\text{TiO}_2$  model via  $\text{K}_2\text{O}$  dissociative adsorption at the anatase (001) surface. (a) side and top views of the initial configuration, where a  $2 \times 2$   $\text{K}_2\text{O}$  (001) supercell is placed on top of a 4-layer anatase (001) surface; (b) side and top views of the equilibrium K-coated  $\text{TiO}_2$  model at 300 K; (c) side and top views of the equilibrium K-coated  $\text{TiO}_2$  model at 1000 K. The model has a good thermo stability, due to the stable K/O structure formed at the interface. Color code: purple, potassium; red, oxygen; gray, titanium.

As shown in Fig. 7a, we generated a K-coated  $\text{TiO}_2$  model via  $\text{K}_2\text{O}$  dissociative adsorption at the anatase (001) surface. The initial configuration was constructed by placing a  $2 \times 2$   $\text{K}_2\text{O}$  (001) supercell on top of a 4-layer anatase (001) surface. The anatase (001) surface model had the size of  $a = b = 11.45 \text{ \AA}$ ,  $c = 9.50 \text{ \AA}$ , and a vacuum of  $15 \text{ \AA}$  was added to avoid the interactions between periodic images. During the calculations, the bottom 2 layers were fixed to mimic the bulk behaviour, and all other parts were allowed to relax. It is worth noting that the size of the  $2 \times 2$   $\text{K}_2\text{O}$  (001) supercell was chosen based on the experimental K/Ti ratio of about 1.0. With our  $\text{K}_2\text{O}/\text{TiO}_2$  model, the interfacial K/Ti is 8/9. Fig. 7b shows the equilibrium structure at 300 K, where eight potassium distribute nicely at the interface and each form two bonds with neighbouring oxygen sites. For the interfacial oxygens, 4 were from the  $\text{K}_2\text{O}$  supercell and a few Ti-O bonds would break during the structural optimization to form interfacial K-O bonds. Other than that, there is a negligible  $\text{TiO}_2$  structural

change due to  $K_2O$  adsorption, which confirms the XRD results shown in Fig. 2b. Thermal stability of the K-coated  $TiO_2$  model has been also tested, as illustrated in Fig. 7c, the structure remains stable even at 1000 K. No structural transition was observed for the anatase (001) surface, which is likely due to the stable K/O structure formed at the interface. The excellent thermo stability also explains why the synthesized  $TiO_2$  nanowhisker has a good crystallinity under elevated temperatures up to 900 °C.



**Fig. 8.** Bader charge analysis for the interfacial potassium and oxygen sites: potassium carries a positive while the oxygen sites have negative charges. For clarity, only the interfacial charge information is displayed. The bottom  $TiO_2$  structure is shown by a line model and the charge information is not shown. Color code: purple, potassium; red, oxygen.

The surface charge information was also studied via the Bader charge analysis method [26]. As illustrated in Fig. 8, the interfacial K and O sites were labelled with respective atomic charges. Our calculation agrees with previous DFT results that interfacial potassium would transfer about one electron to neighbouring oxygen sites, therefore carries a positive charge [27]. The summation of all interfacial K and O sites produces an overall negative charge of  $\sim 1.3046$  e. The Bader charge analysis explains the Zeta potential measurements in Fig. 4f, and also supports the experimental hypothesis that the K-coated  $TiO_2$  nanowhisker has a negative surface charge,

therefore favors specific adsorptions of MB and CV molecules via their positively charged groups.

#### 4. Conclusions

In summary, TiO<sub>2</sub> nanowhiskers have been synthesized with excellent surface enhanced Raman spectroscopy properties towards molecules with positive charge groups such as methylene blue and crystal violet. By a combination of experimental characterizations and computational studies, we reveal that the single-layer coated potassium at the TiO<sub>2</sub> nanowhisker helps to achieve a high thermo stability, which in return enables a high crystallinity at elevated temperatures up to 900 °C. In addition, Zeta potential measurements and theoretical Bader charge analysis show that the K-coated nanowhisker carries negative surface charges, which favors specific adsorptions of methylene blue molecules, and promotes the SERS enhancement factor, an index of SERS performance, to be about  $4.96 \times 10^6$  and a detection limit around  $10^{-7}$  M.

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## Graphical Abstract

