Remarkable surface-enhanced Raman scattering of highly crystalline monolayer Ti_3C_2 nanosheets

Yuting Ye^{1†}, Wencai Yi^{2†}, Wei Liu¹, Yun Zhou³, Hua Bai¹, Junfang Li¹ and Guangcheng Xi^{1*}

ABSTRACT As a powerful non-destructive and label-free detection technology, surface-enhanced Raman scattering (SERS) has been widely used in environmental-pollutant detection, biological-tissue sensing, molecular fingerprint analysis and so on. Different from the traditional SERS substrates represented by noble metals and semiconductors, herein, we report a new highly sensitive SERS substrate material with high stability, biocompatibility, and low cost, namely nucleus-free two-dimensional electron gas (2DEG) Ti_3C_2 monolayer nanosheets. The highly crystalline monolayer Ti_3C_2 nanosheets with clean surface are synthesized by an improved chemical exfoliation and microwave heating method. The unique structure of nucleus-free-2DEG in Ti_3C_2 monolayer provides an ideal transport channel without nuclear scattering, which makes the highly crystalline monolayer Ti_3C_2 nanosheets achieve a Raman enhanced factor of 3.82×10^8 and a 10^{-11} level detection limit for typical environmental pollutants such as azo dyes, trichlorophenol, and bisphenol A. Single-molecule imaging is also realized on the surface of the Ti_3C_2 monolayers, which may be the first time that approximate single-molecule imaging has been achieved on a non-noble-metal SERS substrates. Preliminary toxicological experiments show that the cytotoxicity of this material is very low. Considering the facile synthesis, high biocompatibility, low cost and high chemical stability of carbide nanosheets, these Ti_3C_2 monolayer nanosheets show significant promise for the design and fabrication of flexible SERS substrates for the sensing of trace substances with ultrahigh sensitivity.

Keywords: Ti_3C_2 , nucleus-free 2D electron gas, monolayer nanosheets, SERS, microwave heating quasi-metals

INTRODUCTION

Surface-enhanced Raman scattering (SERS) can greatly

enhance the weak Raman signal of molecules, which makes it an extremely sensitive nondestructive analytical technique at trace levels [1,2]. As a label-free method, SERS has been widely used in various research fields, such as biological and drug sensing [3,4], environmental detection [5,6], molecular fingerprint discriminating [7,8], and catalytic mechanism exploration [9,10]. Since Fleischmann and Van Duyne *et al.* [11–13] discovered SERS on rough silver surface, the search for perfect materials as substrates for SERS is one of the challenges facing material and chemical scientists. An excellent SERS substrate should have the advantages of low cost, high chemical stability, good biocompatibility, and more importantly a vigorous resonance with analytes [14]. In addition, it should be environment-friendly, have abundant reserve, and can be easily processed into desired shape. Various inorganic materials have been developed as substrates for Raman enhancement. The traditional SERS materials are based on noble-metal nanostructures with strong surface plasmon resonance (SPR), in which the electromagnetic mechanism (EM) is regarded as the dominant contribution to the Raman enhancement [15–17]. Although the EM-based noble-metal substrates show superior enhancement factors (EFs) of 10^6 or higher, they inevitably suffer from poor biocompatibility, nearly immobilized band structure, excessive cost and so on. In addition to noble-metals, SERS has also been found in semiconductors [18–22], metal-organic frameworks (MOFs) [23] and amorphous materials [24,25], in which Raman enhancement is thought to be the chemical mechanism (CM) caused by the charge-transfer between the analytes and the substrates. Particularly interesting is the recent discovery of SERS activity in conductive polymer films [26]. These results enrich the types of SERS sub-

¹ Institute of Industrial and Consumer Product Safety, Chinese Academy of Inspection and Quarantine, Beijing 100176, China

² School of Physics and Physical Engineering, Qufu Normal University, Qufu 273165, China

³ College of Science, Chinese Jiliang University, Hangzhou 310018, China

[†] These two authors contributed equally to this work.

* Corresponding author (email: xiguangcheng@caiq.org.cn)

strates and provide valuable directions for finding efficient substrates. Although these CM-based SERS substrates have the advantage of adjustable band-gap, excellent biocompatibility and low cost, they are generally trapped by the low EFs and poor stability compared with noble-metals, which greatly limits their practical applications. Therefore, the discovery of highly sensitive SERS materials with high stability, low cost and environmental friendliness is a major issue to be solved urgently both in academic and practical perspectives.

As a rising star of photoelectric materials, two-dimensional (2D) ultrathin materials have attracted more and more interests [27–30]. Among them, graphene [31], MoS_2 [32], Ti_2N [33], and Mo(W)Te_2 [34] have also joined the SERS substrate family. Because of their uniformity at atomic scale, strong chemisorption, high chemical stability and excellent biocompatibility, these 2D ultrathin nanosheets have been suggested to be promising Raman-enhanced substrates. However, due to the limitation of CM enhancement mechanism, the EFs of 2D SERS substrates are still far less than that of noble-metals. As a most representative member of the 2D metal carbides (MXenes), Ti_3C_2 nanosheets have recently attracted more and more attention due to their high conductivity and high stability as well as very low production costs, showing great potential as high-performance electrode materials, supercapacitors, electrocatalysts, photothermal agents and so on [35–42]. Recently, Sarycheva *et al.* [43] reported that $\text{Ti}_3\text{C}_2\text{T}_x$ ($\text{T}_x = -\text{OH}$, $-\text{COOH}$, $-\text{F}$) monolayers also showed SERS activity and 10^5 – 10^6 EF. Although this EF is relatively high, there is still a big gap of 10^3 times compared with the recently reported W(Mo)Te_2 monolayer nanosheets [34]. Therefore, it is very meaningful to deeply explore the SERS enhancement mechanism of Ti_3C_2 monolayers and improve their sensitivity. Eliminating the surface organic groups and obtaining highly crystalline monolayers with clean substrate/molecular interfaces is an effective way to increase the sensing activity [44]. However, the traditional synthesis method (HF method) often introduces a large number of hydroxyl, carbonyl and other organic functional groups on the surface of Ti_3C_2 monolayers [37,40–42]. How to remove these organic groups without changing the shape and size is a difficult issue, because the common heating method would easily lead to the destruction of its ultrathin structure [45].

Recent studies have shown that, due to the generation of eddy currents, metallic graphene itself will be heated at a very fast rate (2000 K/0.1s) under microwave irradiation, thereby greatly improving its crystallinity and even

decomposing the metal salts adsorbed on its surface [46,47]. Inspired by these work, since Ti_3C_2 also has good electrical conductivity [48,49], can it also achieve an increase in crystallinity and elimination of organic groups through the extremely fast microwave heating? Herein, we developed an efficient chemical exfoliation and rapid microwave heating method for the large-scale synthesis of highly crystalline monolayer Ti_3C_2 nanosheets. Due to the extremely short microwave irradiation time (2 s), the morphology and dimensions of the titanium carbide monolayer were not damaged. Benefiting from its unique structure of nucleus-free 2D electron gas (2DEG), these ultrathin Ti_3C_2 nanosheets have been found to have outstanding SERS properties. The highly crystalline Ti_3C_2 monolayer nanosheets achieve a Raman enhanced factor of 3.82×10^8 and a 10^{-11} level limit of detection (LOD) for typical environmental pollutants such as azo dyes, trichlorophenol, and bisphenol A (BPA), which far exceeds most semiconductor substrates and can even be comparable to noble-metal substrates. Single molecule SERS imaging is also realized on the surface of the Ti_3C_2 monolayers, which may be the first time that approximate single-molecule imaging has been achieved on a non-noble-metal SERS substrates.

EXPERIMENTAL SECTION

Synthesis of highly crystalline monolayer Ti_3C_2 nanosheets

In a typical synthesis, the commercial Ti_3AlC_2 was first pulverized into micron-sized particles by a ball mill. After washing and drying, 0.1 g of the Ti_3AlC_2 particles were put into a mixed solution of perchloric acid (HClO_4 , 2 mol L^{-1}), hydrofluoric acid (HF, 5 mol L^{-1}) in 100 mL of distilled water, and stirred gently in a water bath for 12 h at 50°C. **Note:** HF and HClO_4 are corrosive and should be used with extra care. The acid-etched product was separated by centrifugation (1000 rpm). After being washed with deionized water, 0.1 g of the acid-etched product was poured into 1 mol L^{-1} aqueous solution of ethylenediamine (EN), heated to 60°C in a water bath, and gently stirred for 24 h. Then, 0.1 g of the particles expanded by the EN intercalations were dispersed in 30 mL of deionized water, and ultrasonically shaken for 2 h. The product was collected by centrifugation (5000 rpm). 0.1 g of the product was dispersed in 100 mL distilled water for washing three times. After freeze-drying, 0.1 g of the powders were irradiated in a microwave oven with the power of 700 W for 2 s. Finally, the product was washed three times with deionized water and absolute ethanol, and dried at 50°C for 4 h in a vacuum oven.

Constructing flexible Ti_3C_2 nanosheet SERS substrate

In a typical preparation process, 0.3 g of Ti_3C_2 nanosheets were mixed with 50 mL of ethanol to form a suspension. The suspension was filtered to form a thin layer on the filter paper. After natural drying in air at room temperature, the thin layer of Ti_3C_2 was spontaneously separated from the filter paper to form a flexible SERS substrate.

Characterizations

The obtained samples were systematically characterized by a variety of detection techniques. Powder X-ray diffraction (XRD) patterns of the products were measured on a Bruker D-8 focus X-ray diffractometer by using $\text{CuK}\alpha$ radiation ($\lambda = 1.54178 \text{ \AA}$). Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) observations were completed with a Tecnai G F30 operated at 300 kV accelerating voltage. Scanning electron microscopy (SEM) images and energy-disperse X-ray spectroscopy (EDS) were obtained on a Hitachi S-4800 with an accelerating voltage of 15 kV. The X-ray photoelectron spectroscopy (XPS) measurements were performed in a Theta probe (ESCALab-250Xi Thermo Fisher) by using monochromated Al $\text{K}\alpha$ X-rays at $h\nu = 1486.6 \text{ eV}$. Peak positions were internally referenced to the C 1s peak at 284.6 eV. UV-Vis absorption spectra were detected with a Shimadzu UV-3600. The Fourier transform infrared (FTIR) spectra were measured from a THERMO Iz-10. The specific surface area was detected in a Micro Tristar II 3020. Atomic force microscopy (AFM) image was recorded from Agilent Technologies 5500.

Raman property test

A laser-confocal-micro-Raman spectrometer (Renishaw-InVia Reflex) was used as the measuring equipment to detect the SERS properties of the as-prepared Ti_3C_2 nanosheets. In all the experiments mentioned in this work, if there is no definite indication, the used excitation wavelengths were all 532 nm, the magnification of the objective was $\times 100$ L, and the excitation power was 0.5 mW. A series of standard solutions (R6G) with concentrations of 10^{-2} – $10^{-11} \text{ mol L}^{-1}$ were used as the probe molecules. To improve the signal reproducibility and uniformity of the SERS substrates, the Ti_3C_2 nanosheet flexible substrates were added into a probe molecule aqueous solution to be measured and maintained for 20 min. After 3 min, the obtained flexible substrate was coated on a glass slide, and then dried in air for 5 min under the irradiation of a infrared light (200 W). In all SERS detections, the laser beam was perpendicular to the

top of the sample to be tested with a resultant beam spot diameter of 5 μm . Raman enhanced factor calculation details are provided in the Supplementary information.

Cytotoxicity of the monolayer Ti_3C_2 nanosheets

Human cervix carcinoma cell lines (Hela) used in this study were purchased from the National Infrastructure of Cell Line Resource (Beijing, China). Cells were cultured in RPMI1640 medium and supplemented with 10% fetal bovine serum (Gibco), 2 mmol L^{-1} L-glutamine, 100 U mL^{-1} penicillin and 1 mg mL^{-1} streptomycin (Invitrogen) at 37°C in an incubator with 95% air and 5% CO_2 . For cytotoxicity, cells were seeded in two parallel 96-well cell culture plates at 5000 cells per well and incubated for 12 h. Then the cells were treated with a series of concentrations of Ti_3C_2 nanosheets (0, 7.5, 15, 31, 62, 125, 250, 500 and $1000 \mu\text{g mL}^{-1}$) for 24 and 48 h respectively. The relative cellular viabilities were quantitatively determined by the Alamar Blue® (Thermo Fisher Technology Inc.) assay. For cellular apoptosis detection, cells were seeded in two parallel 6-well cell culture plates at 5×10^4 cells per well and incubated for 12 h. Then three wells of cells were exposed to Ti_3C_2 nanosheets at the concentration of $1000 \mu\text{g mL}^{-1}$ for 48 h. After exposure, one plate of cells were incubated in 55°C water bath for 10 min as the positive control of late apoptosis. All cells were co-stained with 1 mg mL^{-1} acridine orange and ethidium bromide (AO/EB). The cell apoptosis was detected with a micro-confocal and high content screening system (HCA, Image Xpress micro XLS, Molecular Devices Corporation, USA).

Electronic structure calculation

All density functional theory (DFT) calculations were performed by using Vienna *ab initio* Simulation Package (VASP). The calculation details are provided in the Supplementary information.

RESULTS AND DISCUSSION

Synthesis and characterization of the highly crystalline Ti_3C_2 monolayers

Compared with the products prepared by the physical vapor deposition (PVD), the ultrathin nanosheets prepared by chemical exfoliation often inevitably have poor crystallinity due to strong acid corrosion and ultrasonic damage. In order to obtain high crystallinity, these monolayer Ti_3C_2 nanosheets were prepared by an improved chemical exfoliation method. Compared with the previous methods, this method greatly enhanced the

crystallinity of the obtained Ti_3C_2 monolayer, which is very beneficial to the formation of strong SPR effect and interface charge-transfer effect. In a typical synthesis, as shown in Fig. 1, firstly, commercial Ti_3AlC_2 powders were ground into micron-sized particles (Fig. 2a) by ball milling; then, these Ti_3AlC_2 microparticles were corroded in a mixture of HClO_4 and HF to remove the Al layer (Fig. 2b); and the Al-removed microparticles were injected into the EN solution for molecular-intercalation. The expanded samples were then dispersed into a monolayer of Ti_3C_2 by ultrasonic vibration; finally, the crystallinity of these Ti_3C_2 nanosheets was rapidly improved by microwave heating. In particular, it should be pointed out that the addition of a small amount of HClO_4 is a key to obtain the high-quality monolayer Ti_3C_2 nanosheets, because without HClO_4 , it is difficult to completely remove the Al component. However, the concentration of HClO_4 should not exceed 3.5 mol L^{-1} , otherwise the Ti_3C_2 layer will be corroded due to the strong oxidation of HClO_4 [49]. In addition, microwave heating is also a key step to obtain the highly crystallized Ti_3C_2 nanosheets. Without this rapid heating process, the crystallinity of the obtained nanosheets is poor, and the EF of the nanosheets would be reduced by two orders of magnitude.

By the method described above, we have obtained a well dispersed sample of monolayer Ti_3C_2 nanosheets, which can be stored in water and ethanol stably (Fig. S1). XRD patterns show that these samples can be accurately indexed as Ti_3C_2 monolayers, and no diffraction peaks of

Ti_3AlC_2 are detected (Fig. S2). The SEM image shows that the prepared Ti_3C_2 samples are indeed composed of a large number of flexible nanosheets (Fig. 2c). It is noteworthy that the thickness of these nanosheets is very thin, and the electron beam can easily penetrate these nanosheets. TEM further demonstrates that these samples contain soft and ultrathin Ti_3C_2 nanosheets (Fig. 2d). The EDS obtained on the copper microgrid shows that the atomic ratio of Ti to C in the sample is about 1.53, which is basically consistent with the theoretical value of titanium carbide (Fig. S3). In order to accurately characterize the thickness of these nanosheets, AFM was used to measure these nanosheets. The results show that the thickness of these nanosheets is about 1.22 nm (Fig. 2e). Compared with the theoretical calculation of the thickness of Ti_3C_2 monolayer (0.98 nm) [40], the thickness of the nanosheet obtained in our experiment increases by 0.24 nanometer, which may be caused by the adsorbed water molecules and carbon dioxide molecules on the surface of the nanosheet [41]. Furthermore, HRTEM image reveals that these monolayer Ti_3C_2 nanosheets have clear lattice fringes (Fig. 2f). The corresponding fast Fourier transform (FFT) pattern also proves this high crystallinity (inset in Fig. 2f). All the above results indicate that highly crystallized monolayer Ti_3C_2 nanosheets have been successfully prepared by the present method.

XPS was performed to further explore the composition and surface chemistry of the monolayer Ti_3C_2 nanosheets.

Figure 1 Schematic diagram for the synthesis of highly crystalline monolayer Ti_3C_2 nanosheets. Note: HF and HClO_4 are corrosive and should be used with extra care.

Figure 2 Morphology and structure characterizations of the Ti_3AlC_2 precursor and the monolayer Ti_3C_2 nanosheets. (a) The commercial Ti_3AlC_2 powders after grinding. (b) The multilayer Ti_3C_2 nanosheets obtained by HClO_4 and HF etching. (c) The SEM image of the monolayer Ti_3C_2 nanosheets. (d) TEM image of the monolayer Ti_3C_2 nanosheets. (e) AFM image of the Ti_3C_2 nanosheets. (f) HRTEM image of the monolayer Ti_3C_2 nanosheets, inset: FFT pattern of the nanosheet.

The data were calibrated based on the peak of C–C bond located at 284.8 eV. A survey spectrum of Ti_3C_2 nanosheets indicated the presence of Ti, C, and O atoms (Fig. S4). The high-resolution XPS spectrum for Ti 2p is shown in Fig. 3a. The peaks located at 453.8 and 461.7 eV prove the presence of Ti–C bonding in the Ti_3C_2 nanosheets, whereas the low peak at 457.1 eV can be attributed to the Ti–O bond. It is worth pointing out that such well-defined XPS spectrum is rarely seen in Ti_3C_2 nanosheets prepared by traditional chemical exfoliation. In sharp contrast, the Ti_3C_2 monolayers that have not been subjected to microwave heating show multiple Ti–O bonds at 455.20, 456.52, 458.42, 460.31 and 461.42 eV (Fig. 3b). Obviously, they originate from the Ti–O bonds with different oxidation states of Ti, and their strength is significantly increased compared with that of Ti–C bonds, which is highly consistent with the results of $\text{Ti}_3\text{C}_2\text{T}_x$ monolayer nanosheets reported earlier [37,41]. The two distinct XPS spectra prove that microwave heating is an effective method for removing groups introduced by

synthetic processes such as hydroxyl groups on the surface of Ti_3C_2 monolayers.

It should be pointed out that the addition of EN is also a key factor in the formation of the monolayer Ti_3C_2 nanosheets. EN has been used as chelating agent in nanosynthesis for a long time due to its strong coordination ability to guide the formation of special nanostructures [50]. Herein, two N atoms of EN molecule can form Ti–N coordination bond with Ti_3C_2 , which can be easily inserted into the layered structure of Ti_3C_2 to play the role of expansion molecule. After intensive ultrasound treatment, a large number of monolayer Ti_3C_2 nanosheets were formed. In contrast, without EN added, the final sample was a multilayer Ti_3C_2 nanosheets consisting of 3–6 layers (Fig. 3c and Fig. S5). At the same time, we should emphasize the importance of microwave heating. In general, the crystallinity of the Ti_3C_2 nanosheets will inevitably decrease significantly after strong acid corrosion and intense ultrasound treatment, which is unfavorable for their applications in many aspects, especially in photoelectric applications. Fig. 3d shows an HRTEM image of the monolayer Ti_3C_2 nanosheets without microwave heating. It is obvious that many lattice defects exist in the nanosheets, apparently due to corrosion and ultrasound. This difference in crystallinity has a significant effect on their properties. For example, highly crystallized Ti_3C_2 samples show strong localized-SPR effect in the visible region (Fig. S6), while the absorption spectrum of $\text{Ti}_3\text{C}_2\text{T}_x$ monolayer nanosheets with a large number of defects has a significant red shift, showing an obvious lattice defect absorption. Generally, the excitation wavelengths commonly used in SERS experiments are 532 and 633 nm, respectively. It is obvious that high crystallinity Ti_3C_2 nanosheets can more easily resonate with the incident excited light, which is a necessary condition for the formation of strong Raman enhancement.

Enhanced Raman scattering properties of the Ti_3C_2 monolayers

Next, we systematically investigated the SERS properties of these monolayer Ti_3C_2 nanosheets. Unlike those SERS substrates based on nanoparticles prepared by spin-coating method, these ultrathin Ti_3C_2 nanosheets can easily form large-area flexible substrates by simple filtration (Fig. 4a), without glass, silicon and other substrates, which greatly simplifies the substrate preparation process. The detection process is also very simple. After dipping these flexible substrates in the solution to be tested, and then quickly drying under the infrared lamp, they can be placed on the loading table for testing. Without special

Figure 3 (a) XPS spectrum of the monolayer Ti_3C_2 nanosheets. (b) XPS spectrum of the monolayer $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets without microwave heating. (c) HRTEM image of the as-synthesized multilayer Ti_3C_2 nanosheets. (d) HRTEM image of the obtained monolayer Ti_3C_2 nanosheets without microwave heating.

explanation, in all Raman detections, the objective lens used in the experiment was 100 $\times$, the excitation power was 0.5 mW, and the excitation wavelength was 532 nm. The results show that the monolayer Ti_3C_2 nanosheets have a strong SERS effect on the probe molecule R6G (Fig. 4b). It is clear that four typical Raman scattering peaks of R6G, R_1 , R_2 , R_3 , R_4 , are highly consistent with the Raman spectra of R6G reference materials (Fig. S7). Through the detection of a series of R6G samples with different concentrations, we can see that in a large concentration range, the Ti_3C_2 nanosheets have a good response to the probe molecules, and the lowest detection limit can even reach $10^{-11} \text{ mol L}^{-1}$. The Raman EF of the Ti_3C_2 nanosheets was obtained by calculating the signal enhancement multiples of the two scattering peaks R_1 and R_2 of R6G at three concentrations over the Ti_3C_2 nanosheets. As shown in Fig. 4c, compared with the signal intensities obtained over the glass, the calculation results show that the maximum EF of the Ti_3C_2 nanosheets is 3.82×10^8 at $10^{-10} \text{ mol L}^{-1}$, which is comparable to the record of noble-metal substrates, but with much lower cost. These experimental results demonstrate that the monolayer Ti_3C_2 nanosheets have a very high Raman

signal enhancement ability and a very high sensitivity to the analyte.

In addition to sensitivity, the uniformity and reproducibility of signals on the substrates are another important evaluation factor from a practical point of view. For this reason, we randomly detected 20 points in the range of 1 cm^2 on this flexible substrate. The results show that the peak intensities of the 20 Raman spectra of R6G are highly consistent (Fig. 4d). In order to evaluate the signal uniformity of this substrate more accurately, we used Raman mapping technology to scan 10,000 ordered points in 160 mm^2 . Statistical analysis of their R_1 peak intensities reveals that their relative standard deviation is only 5.2% (Fig. 4e), which can be attributed to the uniformity of their atomic level. The corresponding Raman mapping image also demonstrates this high signal uniformity (Fig. 4f). It is precisely because of the high homogeneity of the substrate that a good linear relationship exists between the analyte concentration and the signal intensity (Fig. S8). These excellent properties are very important for actual analysis. As mentioned above, the LOD of these Ti_3C_2 monolayers to R6G is up to $10^{-11} \text{ mol L}^{-1}$, which approaches or reaches single-mole-

Figure 4 SERS properties of the flexible Ti_3C_2 nanosheets. (a) Flexible SERS substrate based on the Ti_3C_2 ultrathin nanosheets. (b) Raman spectra of 10^{-6} – 10^{-11} mol L^{-1} R6G obtained in the flexible SERS substrate. (c) The average Raman EFs obtained by counting the peak intensities (R_1 and R_2) at three different concentration levels. (d) SERS signals collected from 20 randomly selected points on the substrate. (e) The signal intensity distribution at 612 cm^{-1} of 10^{-8} mol L^{-1} R6G recorded from 10,000 sites. (f) The signal intensity distribution recorded by SERS mapping at 612 cm^{-1} of 10^{-8} mol L^{-1} R6G in the substrate. (g) Single-molecule SERS spots recorded from 10^{-11} mol L^{-1} R6G. (h) SERS spectra of Ti_3C_2 ultrathin nanosheets stored in air for 3–12 months. (i) SERS spectra of a series of harmful substances: butyl hydroxy anisole (BHA), melamine, BPA, 2,4,5-TCP, and acid fuchsin (AF).

cule level [26]. Based on such high sensitivity, it is expected to make single molecule SERS imaging. As shown in Fig. 4g, a clear single-molecule (or near single-molecule) SERS imaging of 10^{-11} mol L^{-1} R6G was successfully achieved on the Ti_3C_2 monolayers. To the best of our knowledge, this may be the first time that approximate single-molecule imaging has been achieved on a non-noble-metal SERS substrate. Moreover, due to the inherent high stability of metal carbides, the chemical stability of these Ti_3C_2 nanosheets is considerably high. Even if stored in air for half a year to one year, they still have a high degree of crystallinity (Fig. S9) and their SERS properties do not decrease significantly (Fig. 4h). In addition, for high-risk chemicals, such as BPA, dichlorophenol (DCP), and tetrachlorophenol (TCP), which are widely concerned, these Ti_3C_2 nanosheets also

show high sensitivities (Fig. 4i), showing a good universality as a practical SERS substrate.

Raman enhancement mechanism

In order to understand the enhancement mechanism of this highly sensitive quasi-metallic Ti_3C_2 monolayer SERS substrate, we explored it by combining experimental and theoretical calculations. The Ti_3C_2 structure unit can be defined as trilayer Ti-atomic layers being interleaved with two C-atomic layers, forming an edge-shared TiC_6 octahedral structure (Fig. S10). Interestingly, the results of the DFT calculations reveal that the Ti_3C_2 monolayer possesses intrinsic nucleus-free 2DEG in free space, which is similar to the Ga_2N monolayer [51], and the 2DEG distributes among the edge Ti atoms (Fig. 5a), indicating the strong chemical activity of Ti_3C_2 monolayer. It should be

Figure 5 Enhancement mechanism of the monolayer Ti_3C_2 nanosheets. (a) The electronic local function (ELF) of Ti_3C_2 with a scale bar from zero at the low end to one at the high end. (b) The DOS of Ti_3C_2 near the Fermi levels. (c) Side views of the electron density differences for R6G chemisorbed onto the Ti_3C_2 surface, in which the isosurface was set to $2 \times 10^{-3} \text{ e } \text{\AA}^{-3}$, and the Bader charge analysis indicates there are 3.43 e transferring from Ti_3C_2 surface to R6G. (d) The DOS of R6G adsorbed on the Ti_3C_2 surface. (e) Absorption spectra for R6G on the monolayer Ti_3C_2 nanosheets compared with pure monolayer Ti_3C_2 nanosheets and R6G. (f) The measured surface potential difference profiles. (g) Energy level distribution and PICT in the R6G- Ti_3C_2 complex. (h) Structure diagram of the Ti_3C_2 nanosheets and $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets. (i) Comparison of the SERS performance of the Ti_3C_2 nanosheets and $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets.

noted that this unique 2DEG in the surface of the Ti_3C_2 monolayer provides an ideal transport channel without nuclear scattering, which would greatly promote the interface charge-transfer and increase the Raman scattering cross-section of the adsorbed molecules. The further electronic structure calculations show the 2DEG is composed of Ti 3d orbitals, presenting a strong metallic feature rather than semiconducting characteristic (Fig. 5b). Due to the existence of a high density of free electrons, these Ti_3C_2 monolayers exhibit strong SPR in the visible region (Fig. S6). Dravid *et al.* [40] found that high density magnetic field “hot spots” exist between these

ultrathin Ti_3C_2 nanosheets, which suggests that EM enhancement exists in this quasi-metallic 2D SERS substrate.

Importantly, DFT calculations show that the binding energy between R6G and Ti_3C_2 monolayer and the number of electron transport (Fig. 5c) were pretty high. The binding energy is up to 5.07 eV, which is more than seven times that between WTe_2 and R6G reported recently (0.67 eV), and far exceeds that between graphene and R6G (0.24 eV) [34]. This indicates that there is a very strong interfacial interaction between R6G and Ti_3C_2 monolayer. At the same time, by using the Bader’s

quantum theory of atoms in molecules (QTAIM) charge analysis [52], there are 3.43 electrons per unit transferred from the Ti_3C_2 monolayer to R6G, which is about three times that of the WTe_2 and R6G system (1.26 e), and far exceeds that of graphene and R6G (0.46 e) [34]. The high binding energy and the large amount of charge transfer reveal that the coupling of R6G- Ti_3C_2 is much stronger than that of WTe_2 and graphene with R6G. More interestingly, the density of states (DOS) near the Fermi level of Ti_3C_2 monolayer increases significantly after R6G adsorption (Fig. 5d), the d-band center increases from 0.61 to 0.85 eV, which not only demonstrates that the analyte has a strong interfacial-charge-transfer with the substrate, but also indicates that the analyte improves the electron concentration near the Fermi level of the substrate, and further gives rise to the high charge transition probabilities according to the Fermi's golden rule.

Furthermore, due to the relatively high surface activity of Ti_3C_2 monolayer, shown in the charge density difference isosurfaces, the electrons go through a self-charge transfer process and concentrate at the R6G/ Ti_3C_2 interface, forming a quasi-covalent bond, which will enhance the electron coupling between R6G and the Ti_3C_2 monolayer. The electron transfer also forms a strong dipole between the R6G and Ti_3C_2 , which will improve the electrostatic attraction of the dipole and further enhance the Raman scattering of R6G on the Ti_3C_2 monolayer. The results of calculations have also been confirmed by experiments. As shown in Fig. 5e, the main absorption bands of R6G adsorbed on the Ti_3C_2 monolayer have changed significantly, which undoubtedly proves that the charge-transfer behavior occurs at the Ti_3C_2 /R6G interface. Therefore, the strong dipole interaction and the quasi-covalent bond interaction greatly enhance the interface charge-transfer between the analyte and the substrate, and increase the Raman scattering cross-section of the analyte molecule.

The excellent Raman enhancement behavior of Ti_3C_2 nanosheets can also be attributed to the CM enhancement caused by photoinduced charge transfer (PICT). As shown in Fig. 5f, considering that the work function of Au reference is 4.8 eV, the work function of Ti_3C_2 monolayers is estimated to be $4.8 - 0.351 = 4.45$ eV according to the work function measurement by Kelvin probe force microscope (KPFM). The Ti_3C_2 thickness dependence of its work function can be neglected. The energy level distribution and the possible PICT process in the R6G- Ti_3C_2 complex are shown in Fig. 5g. μ_{mol} denotes the molecular transition, $\mu_{\text{i-CT}}$ and $\mu_{\text{k-CT}}$ denote the charge transfer transitions from the molecular ground states to

Ti_3C_2 and from Ti_3C_2 to the molecular excited states, respectively. According to early research reports, the energy levels of the highest occupied molecular orbital (HOMO) and lowest occupied molecular orbital (LUMO) of R6G are -5.7 and -3.4 eV, respectively. This energy level distribution makes PICT possible. In this process, the excited electrons can be transferred not only from the HOMO of R6G to the Fermi level of Ti_3C_2 monolayers, but also from the Fermi level of Ti_3C_2 monolayers to the LUMO of R6G. Therefore, according to the well-known Herzberg-Teller vibration coupling law, the molecule resonance caused by the interface PICT greatly enhances the polarization tensor of the R6G molecule. It is particularly noteworthy that the Fermi level of Ti_3C_2 monolayers is almost symmetrically matched to the HOMO and LUMO of R6G (Fig. 5g), which greatly reduces the interference of the luminescence background of the R6G molecule itself.

In addition, our study found that high crystalline and clean surface of the monolayer nanosheets can greatly promote their SERS performances. It is mentioned above that without the final microwave heating, the prepared $\text{Ti}_3\text{C}_2\text{T}_x$ ($T = \text{OH}$) nanosheets have low crystallinity and a large number of -OH radicals on their surfaces. It should be noted that a large number of crystal defects and surface active groups can often promote the catalytic activity of titanium carbide; however, the experimental results show that the SERS effect of the $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets as the substrate is much lower than that of the Ti_3C_2 nanosheets after microwave heating (Fig. 5h, i). This is because a large number of hydroxyl radicals on the surface of $\text{Ti}_3\text{C}_2\text{T}_x$ hinder the charge transfer between the adsorbed molecule and the substrate, while a large number of crystal defects further restrict the charge transfer and SPR. Therefore, microwave heating is a simple and effective way to enhance the SERS performance of these ultrathin nanosheets by improving the crystallinity and eliminating the hydroxyl groups on the surface.

Toxicity of the monolayer Ti_3C_2 nanosheets

The safety and biocompatibility of the active SERS material are essential for its application in the biosensor and detection fields. We evaluated the *in vitro* toxicity of Ti_3C_2 monolayers briefly using Hela cell lines. In order to obtain a more reliable toxicity conclusion, we set the concentration of Ti_3C_2 monolayers used in the toxicity experiment to $1000 \mu\text{g mL}^{-1}$, which far exceeds the amount used in conventional SERS biological imaging experiments. As shown in Fig. 6a, Ti_3C_2 monolayers induced no cellular mortality at such high concentration of

Figure 6 Toxicity of monolayer Ti_3C_2 nanosheets. (a) Cell viabilities after 24 and 48 h exposure to monolayer Ti_3C_2 nanosheets. (b–d) Cell apoptosis in Hela cells exposed to (b) control, (c) positive control (55°C for 10 min), and (d) 1000 $\mu\text{g mL}^{-1}$ Ti_3C_2 nanosheets for 48 h. Live cells were stained with AO (green), late apoptotic and dead cells were stained EB (red) and early apoptotic cells were both stained by AO and EB (orange). Magnification is 200 $\times$ for all panels.

1000 $\mu\text{g mL}^{-1}$ for 24 h exposure. Even if extended to 48 h exposure, the cellular mortality was only $16.9 \pm 2.52\%$. Furthermore, AO/EB assays revealed that the monolayer Ti_3C_2 nanosheets did not trigger apoptosis significantly at the concentration of 1000 $\mu\text{g mL}^{-1}$ and upon exposure for 48 h (Fig. 6b–d). These results indicated that the monolayer Ti_3C_2 nanosheets showed considerably low toxicity at a extremely high concentration for cytotoxicity experiment. Combined with their excellent SERS activity, this low toxicity indicates that the Ti_3C_2 monolayer nanosheets have good application prospects in the field of biological tissue detection.

CONCLUSION

In summary, we have developed an effective chemical exfoliation method for the large-scale synthesis of highly crystalline monolayer Ti_3C_2 nanosheets. Due to the unique structure of nucleus-free 2DEG, the Ti_3C_2 monolayer has an active surface and shows a strong localized-SPR effect in visible region. These ultrathin Ti_3C_2 nanosheets can be easily assembled into flexible SERS substrates with an LOD of 10^{-11} mol L^{-1} and a maximum Raman EF of 3.82×10^8 . The experimental and theoretical results show that the ultrasensitive SERS properties of the Ti_3C_2 monolayers result from the dual functions of strong lo-

calized-SPR and remarkable interfacial-charge-transfer. Moreover, this new material shows very low cytotoxicity. Current research results show that the low cost quasi-metallic 2D metal carbide is a very promising SERS active material.

Received 27 February 2020; accepted 28 February 2020;
published online 25 March 2020

- Nie S. Probing single molecules and single nanoparticles by surface-enhanced Raman scattering. *Science*, 1997, 275: 1102–1106
- Kneipp K, Wang Y, Kneipp H, *et al.* Single molecule detection using surface-enhanced Raman scattering (SERS). *Phys Rev Lett*, 1997, 78: 1667–1670
- Palonpon AF, Ando J, Yamakoshi H, *et al.* Raman and SERS microscopy for molecular imaging of live cells. *Nat Protoc*, 2013, 8: 677–692
- Kneipp J, Kneipp H, Kneipp K. SERS—a single-molecule and nanoscale tool for bioanalytics. *Chem Soc Rev*, 2008, 37: 1052–1060
- Li JF, Huang YF, Ding Y, *et al.* Shell-isolated nanoparticle-enhanced Raman spectroscopy. *Nature*, 2010, 464: 392–395
- Mulvihill M, Tao A, Benjauthrit K, *et al.* Surface-enhanced Raman spectroscopy for trace arsenic detection in contaminated water. *Angew Chem*, 2008, 120: 6556–6560
- Wang M, Meng G, Huang Q, *et al.* CNTs-anchored egg shell membrane decorated with Ag-NPs as cheap but effective SERS substrates. *Sci China Mater*, 2015, 58: 198–203
- Duan C, Ren B, Liu H, *et al.* Flexible SERS active detection from novel Ag nano-necklaces as highly reproducible and ultrasensitive

- tips. *Sci China Mater*, 2016, 59: 435–443
- 9 Li J, Liu J, Yang Y, *et al.* Bifunctional Ag@Pd-Ag nanocubes for highly sensitive monitoring of catalytic reactions by surface-enhanced Raman spectroscopy. *J Am Chem Soc*, 2015, 137: 7039–7042
 - 10 Taylor RW, Coulston RJ, Biedermann F, *et al.* *In situ* SERS monitoring of photochemistry within a nanojunction reactor. *Nano Lett*, 2013, 13: 5985–5990
 - 11 Fleischmann M, Hendra PJ, McQuillan AJ. Raman spectra of pyridine adsorbed at a silver electrode. *Chem Phys Lett*, 1974, 26: 163–166
 - 12 Jeanmaire DL, Van Duyne RP. Surface Raman spectro-electrochemistry. *J Electroanal Chem Interfacial Electrochem*, 1977, 84: 1–20
 - 13 Moskovits M. Surface roughness and the enhanced intensity of Raman scattering by molecules adsorbed on metals. *J Chem Phys*, 1978, 69: 4159–4161
 - 14 Lin XM, Cui Y, Xu YH, *et al.* Surface-enhanced Raman spectroscopy: substrate-related issues. *Anal Bioanal Chem*, 2009, 394: 1729–1745
 - 15 Schlücker S. Surface-enhanced Raman spectroscopy: concepts and chemical applications. *Angew Chem Int Ed*, 2014, 53: 4756–4795
 - 16 Li JF, Zhang YJ, Ding SY, *et al.* Core-shell nanoparticle-enhanced Raman spectroscopy. *Chem Rev*, 2017, 117: 5002–5069
 - 17 Zhu C, Meng G, Zheng P, *et al.* A hierarchically ordered array of silver-nanorod bundles for surface-enhanced Raman scattering detection of phenolic pollutants. *Adv Mater*, 2016, 28: 4871–4876
 - 18 Quagliano LG. Observation of molecules adsorbed on III-V semiconductor quantum dots by surface-enhanced Raman scattering. *J Am Chem Soc*, 2004, 126: 7393–7398
 - 19 Qiu B, Xing M, Yi Q, *et al.* Chiral carbonaceous nanotubes modified with titania nanocrystals: plasmon-free and recyclable SERS sensitivity. *Angew Chem Int Ed*, 2015, 54: 10643–10647
 - 20 Lin J, Shang Y, Li X, *et al.* Ultrasensitive SERS detection by defect engineering on single Cu₂O superstructure particle. *Adv Mater*, 2017, 29: 1604797
 - 21 Cong S, Yuan Y, Chen Z, *et al.* Noble metal-comparable SERS enhancement from semiconducting metal oxides by making oxygen vacancies. *Nat Commun*, 2015, 6: 7800
 - 22 Shan Y, Zheng Z, Liu J, *et al.* Niobium pentoxide: a promising surface-enhanced Raman scattering active semiconductor substrate. *npj Comput Mater*, 2017, 3: 11
 - 23 Sun H, Cong S, Zheng Z, *et al.* Metal-organic frameworks as surface enhanced Raman scattering substrates with high tailorability. *J Am Chem Soc*, 2019, 141: 870–878
 - 24 Wang X, Shi W, Wang S, *et al.* Two-dimensional amorphous TiO₂ nanosheets enabling high-efficiency photoinduced charge transfer for excellent SERS activity. *J Am Chem Soc*, 2019, 141: 5856–5862
 - 25 Wang X, Shi W, Jin Z, *et al.* Remarkable SERS activity observed from amorphous ZnO nanocages. *Angew Chem Int Ed*, 2017, 56: 9851–9855
 - 26 Yilmaz M, Babur E, Ozdemir M, *et al.* Nanostructured organic semiconductor films for molecular detection with surface-enhanced Raman spectroscopy. *Nat Mater*, 2017, 16: 918–924
 - 27 Peng X, Peng L, Wu C, *et al.* Two dimensional nanomaterials for flexible supercapacitors. *Chem Soc Rev*, 2014, 43: 3303–3323
 - 28 Wang H, Yang X, Shao W, *et al.* Ultrathin black phosphorus nanosheets for efficient singlet oxygen generation. *J Am Chem Soc*, 2015, 137: 11376–11382
 - 29 Zhang H. Ultrathin two-dimensional nanomaterials. *ACS Nano*, 2015, 9: 9451–9469
 - 30 Xuan J, Wang Z, Chen Y, *et al.* Organic-base-driven intercalation and delamination for the production of functionalized titanium carbide nanosheets with superior photothermal therapeutic performance. *Angew Chem Int Ed*, 2016, 55: 14569–14574
 - 31 Xie L, Ling X, Fang Y, *et al.* Graphene as a substrate to suppress fluorescence in resonance Raman Spectroscopy. *J Am Chem Soc*, 2009, 131: 9890–9891
 - 32 Muehlethaler C, Considine CR, Menon V, *et al.* Ultrahigh Raman enhancement on monolayer MoS₂. *ACS Photonics*, 2016, 3: 1164–1169
 - 33 Soundiraraju B, George BK. Two-dimensional titanium nitride (Ti₂N) MXene: synthesis, characterization, and potential application as surface-enhanced Raman scattering substrate. *ACS Nano*, 2017, 11: 8892–8900
 - 34 Tao L, Chen K, Chen Z, *et al.* 1T' transition metal telluride atomic layers for plasmon-free SERS at femtomolar levels. *J Am Chem Soc*, 2018, 140: 8696–8704
 - 35 Naguib M, Kurtoglu M, Presser V, *et al.* Two-dimensional nanocrystals produced by exfoliation of Ti₃AlC₂. *Adv Mater*, 2011, 23: 4248–4253
 - 36 Xie Y, Dall'Agnese Y, Naguib M, *et al.* Prediction and characterization of MXene nanosheet anodes for non-lithium-ion batteries. *ACS Nano*, 2014, 8: 9606–9615
 - 37 Lipatov A, Alhabeib M, Lukatskaya MR, *et al.* Effect of synthesis on quality, electronic properties and environmental stability of individual monolayer Ti₃C₂ MXene flakes. *Adv Electron Mater*, 2016, 2: 1600255
 - 38 Li R, Zhang L, Shi L, *et al.* MXene Ti₃C₂: an effective 2D light-to-heat conversion material. *ACS Nano*, 2017, 11: 3752–3759
 - 39 Xue Q, Zhang H, Zhu M, *et al.* Photoluminescent Ti₃C₂ MXene quantum dots for multicolor cellular imaging. *Adv Mater*, 2017, 29: 1604847
 - 40 Yasaei P, Tu Q, Xu Y, *et al.* Mapping hot spots at heterogeneities of few-layer Ti₃C₂ MXene sheets. *ACS Nano*, 2019, 13: 3301–3309
 - 41 Yasaei P, Hemmat Z, Foss CJ, *et al.* Enhanced thermal boundary conductance in few-layer Ti₃C₂ MXene with encapsulation. *Adv Mater*, 2018, 30: 1801629
 - 42 Dong Y, Chertopalov S, maleski K, *et al.* Saturable absorption in 2D Ti₃C₂ MXene thin films for passive photonic diodes. *Adv Mater*, 2018, 30: 1705714
 - 43 Sarycheva A, Makaryan T, Maleski K, *et al.* Two-dimensional titanium carbide (MXene) as surface-enhanced Raman scattering substrate. *J Phys Chem C*, 2017, 121: 19983–19988
 - 44 Zrimsek AB, Chiang N, Mattei M, *et al.* Single-molecule chemistry with surface- and tip-enhanced Raman spectroscopy. *Chem Rev*, 2017, 117: 7583–7613
 - 45 Hu S, Wang X. Ultrathin nanostructures: smaller size with new phenomena. *Chem Soc Rev*, 2013, 42: 5577–5594
 - 46 Voiry D, Yang J, Kupferberg J, *et al.* High-quality graphene via microwave reduction of solution-exfoliated graphene oxide. *Science*, 2016, 353: 1413–1416
 - 47 Xu S, Zhong G, Chen C, *et al.* Uniform, scalable, high-temperature microwave shock for nanoparticle synthesis through defect engineering. *Matter*, 2019, 1: 759–769
 - 48 Ghidui M, Lukatskaya MR, Zhao MQ, *et al.* Conductive two-dimensional titanium carbide 'clay' with high volumetric capacitance. *Nature*, 2014, 516: 78–81
 - 49 Lou Z, Chen Q, Zhang Y, *et al.* Diamond formation by reduction of carbon dioxide at low temperatures. *J Am Chem Soc*, 2003, 125:

9302–9303

- 50 Li Y, Liao H, Ding Y, *et al.* Solvothermal elemental direct reaction to CdE (E = S, Se, Te) semiconductor nanorod. *Inorg Chem*, 1999, 38: 1382–1387
- 51 Zhao S, Li Z, Yang J. Obtaining Two-dimensional electron gas in free space without resorting to electron doping: an electride based design. *J Am Chem Soc*, 2014, 136: 13313–13318
- 52 Henkelman G, Arnaldsson A, Jónsson H. A fast and robust algorithm for bader decomposition of charge density. *Comput Mater Sci*, 2006, 36: 354–360

Acknowledgements This work received financial support from the Science Foundation of Chinese Academy of Inspection and Quarantine (2019JK004), the National Key Research and Development Program of China (2017YFF0210003), and the high performance computing center of Qufu Normal University.

Author contributions Ye Y and Xi G designed and performed the experiments; Yi W calculated the electronic structure; Liu W, Zhou Y and Bai H discussed partial experimental data; Li J and Xi G wrote the paper. All authors contributed to the general discussion.

Conflict of interest The authors declare that they have no conflict of interest.

Supplementary information Supplementary methods and data are available in the online version of the paper, including Raman enhanced factor calculation, electronic structure calculation, photograph of the dispersion of the monolayer Ti_3C_2 nanosheets, XRD patterns of the Ti_3C_2 monolayers and Ti_3AlC_2 , XEDS and XPS spectra of the Ti_3C_2 monolayers, UV-Vis absorption spectra of the obtained monolayer Ti_3C_2 nanosheets with high crystallinity and low crystallinity, the standard Raman spectrum of R6G reference material, and the crystal structure of Ti_3C_2 .

Yuting Ye is currently a MSc candidate in material chemistry under the supervision of Prof. Guangcheng Xi at Chinese Academy of Inspection and Quarantine. His research centers on developing the excellent SERS materials for chemical sensing devices.

Wencai Yi received his BSc degree in 2013 from Tianjin Normal University. In 2018, he received his PhD degree from Jilin University, China. Then, he joined Qufu Normal University as a lecturer. His research interests focus on the algorithm of structure prediction, low dimensional gas-sensing materials, SERS and high energy density materials.

Guangcheng Xi received his BSc degree in 2002 from Fuyang Normal University, China. In 2007, he received his PhD degree from the University of Science and Technology of China. Then, he joined Chinese Academy of Inspection and Quarantine as an assistant professor. He became an associate professor in 2011 and a full professor in 2017. Currently, his research interests focus on the SERS, chemical sensing, and the nanostructure-based analysis for harmful substances.

高度结晶 Ti_3C_2 单层纳米片的表面增强拉曼散射

叶雨庭^{1†}, 易文才^{2†}, 刘伟¹, 周云³, 白桦¹, 李俊芳¹, 席广成^{1*}

摘要 表面增强拉曼散射(SERS)作为一种优秀的免标记无损检测技术, 已被广泛应用于环境污染物检测、生物组织传感及指纹级分子分析等领域。与以贵金属和半导体为代表的传统SERS基底不同, 本文报道了一种新型的高灵敏SERS基底材料, 即无核二维电子气(2DEG)结构的 Ti_3C_2 单层纳米片, 其具有高稳定性、生物相容性和低成本等优点。我们通过一种化学剥离和微波加热相结合的方法合成了具有洁净表面的、高度结晶的单层 Ti_3C_2 纳米片。 Ti_3C_2 单层无核2DEG的独特电子结构提供了理想的无核散射传输通道, 使单层 Ti_3C_2 纳米片的拉曼增强因子达到了 3.82×10^8 , 其对典型污染物的检出限高达 $10^{-11} \text{ mol L}^{-1}$ 。初步的毒理学实验表明, 该物质的细胞毒性非常低。考虑到碳化物纳米片合成简单、良好的生物相容性、低成本以及高的化学稳定性, Ti_3C_2 单层对于设计和制造具有超高灵敏度的柔性SERS衬底具有很好的应用前景。