Fast and recoverable NO2 detection achieved by assembling ZnO on Ti3C2Tx MXene nanosheets under UV illumination at room temperature†

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Recently, Ti3C2Tx MXenes have begun to receive attention in the field of gas sensors owing to their characteristics of high conductivity and abundant surface functional groups. However, Ti3C2Tx-based gas sensors still suffer from the drawbacks of low sensitivity and sluggish response/recovery speed towards target gases, limiting their development in further applications. In this work, Ti3C2Tx–ZnO nanosheet hybrids were fabricated through a simple sonication method. The Ti3C2Tx–ZnO nanosheet hybrids exhibited a short recovery time (10 s) under UV (ultraviolet) illumination, a short response time (22 s), a high sensitivity (367.63% to 20 ppm NO2) and selectivity. Furthermore, the Ti3C2Tx–ZnO sensor has prominent anti-humidity properties, as well as superior reproducibility in multiple tests. The abundant active sites in the Ti3C2Tx–ZnO nanosheet hybrids, including surface groups (–F, –OH, –O) of Ti3C2Tx and oxygen vacancies of ZnO, the formation of Schottky barriers between Ti3C2Tx and ZnO nanosheets and the rich photogenerated charge carriers of ZnO under UV illumination, together result in excellent gas-sensing performance. Density functional theory calculations have been further employed to explore the sensing performance of Ti3C2Tx and ZnO nanosheets, showing strong interactions existing between the NO2 and ZnO nanosheets. The main adsorption sites for NO2 were present on the ZnO nanosheets, while the Ti3C2Tx played the role of the conductive path to accelerate the transformation of charge carriers. Our work can provide an effective way for improving the gas-sensing performances of Ti3C2Tx-based gas sensors.

Introduction

With the acceleration of industrial production and the continued increasing use of automobiles, a large quantity of toxic and harmful gases, such as NO2, SO2 and NO, etc., is discharged into the atmosphere.1,2 Among these harmful gases, NO2 is a toxic gas that mainly damages the respiratory tract of humans.3,4 When people are exposed to an environment containing NO2 gas for several minutes, they will have symptoms of chest tightness, respiratory distress and cough.5,6 The reported upper exposure limit of NO2 gas concentration for humans is 20 ppm.7 The respiratory tract and nervous system become seriously injured following exposure to NO2 environments above this concentration over long periods of time.8 In addition, the discharge of large amounts of NO2 can lead to the phenomenon of acid rain, which pollutes soil and water environments. Therefore, fast detection of NO2 gas and timely feedback are extremely important for the health of people and of the environment.9–11

In recent years, two-dimensional layered material such as graphene,12–15 transition metal dichalcogenide-based materials,16–19 black phosphorus,20–22 MXene,23,24 etc., have attracted much attention owing to their great promise as gas sensors at room temperature.25–27 Among these materials, MXene has become a promising candidate for gas-sensitive material that can operate at room temperature because of its low signal-to-noise ratio, rich surface functional groups (–OH, –F, –O) and high electron conductivity.28–30 Ti3C2Tx is one of the earliest discovered MXene materials, which exhibits metallic conductivity, and it has been widely studied in recent years. However, it has remained a major challenge to improve the poor sensitivity and response/recovery speed of Ti3C2Tx–based sensors.

Resistance modulation of Schottky barriers can effectively improve current transport efficiency and induce a high NO2
sensing response. In addition, the construction of MXene/metal oxide semiconductor composites has been considered to be an effective method to improve the NO$_2$ sensing properties of Ti$_3$C$_2$Tx MXene-based gas sensors. Since the Ti$_3$C$_2$Tx MXene material displays a layer-like structure, metal oxide semiconductors can easily interact with Ti$_3$C$_2$Tx. For example, Choi et al. developed TiO$_2$/Ti$_3$C$_2$ MXene materials through the in situ oxidation method and tailored the oxidation time to change the number of Schottky barriers. The TiO$_2$/Ti$_3$C$_2$ sensor exhibited higher NO$_2$ sensitivity compared with the bare Ti$_3$C$_2$ MXene material. Sun et al. reported Co$_3$O$_4$ nanoparticle-based polyethyleneimine-functionalized Ti$_3$C$_2$Tx MXene sheets, which showed a high gas response and fast response time (below 2 s) towards NO$_2$ gas at room temperature. Chen et al. reported that the nanohybrid of SnS$_2$ and MXene-derived TiO$_2$ exhibited a large response and ultra-fast recovery towards NO$_2$ gas.

ZnO, a typical n-type metal–oxide–semiconductor material, with a wide bandgap of 3.37 eV, excellent chemical stability and rich oxygen vacancies has emerged as a promising gas-sensitive material. In particular, ZnO or ZnO composite materials have been widely applied as NO$_2$ sensors at room temperature in recent years. This is because of the abundant defects and the feasibility of shape control of ZnO. For example, Moon et al. reported that nanohybrid materials of reduced graphene oxide and ZnO nanorods exhibited ultra-high sensitive detection to 40 ppb of NO$_2$ and a short response/recovery time. Hung et al. prepared biaxial p-SnO/n-ZnO nanowire heterostructures with enhanced performance for detection of ppb-level NO$_2$ at room temperature. Song et al. produced ZnO nanoflowers by a hydrothermal method, and the fabricated sensor displayed an improved NO$_2$ sensing property (response of 128 to 1 ppm NO$_2$) and a low detection limit (50 ppb). To facilitate the recovery speed of the gas sensors, UV illumination has been widely applied and recognized as an effective way to enhance the properties of the recovery characteristics of gas sensors. The main reason for this is that photogenerated barriers can clean the surface of materials, which can accelerate the desorption process. Zheng et al. reported that the InSe nanosheet sensor can achieve rapid and full recovery to NO$_2$ gas within 169 s under UV illumination. Zhou et al. presented the Au-MoS$_2$ gas sensor, which achieved better sensitivity properties, including three times the response and full recovery under illumination compared with that in the dark. Wu et al. found that the recovery rate of the p-type MoTe$_2$ gas sensor to different concentrations of NO$_2$ was significantly improved under UV illumination. In addition, many studies have shown that ZnO exhibits outstanding NO$_2$ sensing performances under UV illumination because of its excellent optoelectronic properties.

As a result, construction of the Ti$_3$C$_2$T$_x$–ZnO Schottky junction with the assistance of UV illumination can combine the excellent properties of these two materials, which is expected to result in further enhancement of the NO$_2$ sensing properties.

To the best of our knowledge, most Ti$_3$C$_2$T$_x$ MXene-based NO$_2$ sensors are still unable to achieve the properties of fast response and recovery speed at the same time. Few researchers have reported Ti$_3$C$_2$T$_x$–ZnO nanosheet hybrid NO$_2$ sensors. Herein, we propose Ti$_3$C$_2$T$_x$–ZnO nanosheet hybrids with Schottky barriers for NO$_2$ sensing and recovery under UV illumination. The Ti$_3$C$_2$T$_x$ nanosheets were synthesized using the conventional method of HF solution etching of the Al layer of Ti$_3$AlC$_2$ (MAX). ZnO nanosheets were prepared by hydrothermal and calcination methods, with Zn (CH$_3$COOH)$_2$·2H$_2$O, urea and polyvinylpyrrolidone (PVP) as the precursors. The porous morphology for the ZnO nanosheets was successfully obtained, which is helpful for the adsorption of NO$_2$ gas. With the assistance of UV irradiation in the recovery process, the Ti$_3$C$_2$T$_x$–ZnO nanosheet-based gas sensor exhibited better NO$_2$ sensing properties, including high sensitivity (367.63% to 20 ppm NO$_2$), shorter response/recovery time (22 s/10 s), excellent repeatability and superior humidity resistance properties, in comparison to pristine Ti$_3$C$_2$T$_x$ and ZnO materials. Density functional theory (DFT) calculations indicated that the main adsorption sites were on the surface of the ZnO nanosheets, with Ti$_3$C$_2$T$_x$ mainly playing the role of the conductive pathway, which can accelerate the transfer efficiency of carriers between Ti$_3$C$_2$T$_x$ and ZnO materials.

**Experimental**

**Synthesis of Ti$_3$C$_2$T$_x$ MXene**

Ti$_3$C$_2$T$_x$ MXene nanosheets were fabricated using the previously reported methods. Typically, 0.5 g of Ti$_3$AlC$_2$ powder was dispersed in 20 mL HF solution and stirred for 24 h at room temperature. The solution after etching was washed with deionized (DI) water and centrifuged at 8500, 5500 and 3500 rpm, for 5 min each, until the pH of the supernatant reached 6.0. Subsequently, the obtained material was dried at 60 °C overnight in a vacuum drying oven.
Synthesis of ZnO nanosheets

ZnO nanosheets were synthesized through a simple hydrothermal and calcination approach. Typically, 1.1 g of Zn (CH₃COOH)₂·2H₂O was dissolved in 40 mL DI water by vigorous stirring for 10 min. Then, 0.6 g urea and 0.2 g PVP (Mₘ = 58,000) were added into the solution with stirring for 20 min. Afterwards, the solution was transferred into a 50 mL Teflon-lined autoclave, which was then heated at 120 °C in a furnace for 6 h. Finally, the solution was washed with DI water and ethanol and centrifuged at 8000 rpm for 10 min. After drying in the vacuum furnace at 60 °C for 12 h, the collected powder was calcinated at 450 °C for 2 h with a heating rate of 5 °C min⁻¹.

Synthesis of Ti₃C₂Tx-ZnO nanosheet hybrids

The Ti₃C₂Tx-ZnO nanosheet hybrids were prepared via a facile sonication method. First, 25 mg of Ti₃C₂Tx was dispersed in 50 mL DI water and sonicated for 30 min. After that, 10 mg of ZnO nanosheets were added into the above dispersion, followed by sonication for another 30 min at a power of 100 W. Finally, the dispersion was centrifuged six times at 8500 rpm for 5 min with DI water. After drying in a vacuum furnace at 60 °C for 12 h, the Ti₃C₂Tx-ZnO nanosheet hybrids were collected. The samples of ZnO nanosheets and Ti₃C₂Tx-ZnO nanosheet hybrids were labeled as ZnO NS and Ti₃C₂Tx-ZnO NS, respectively.

Material characterizations

The morphologies of Ti₃C₂Tx MXene nanosheets, ZnO NS and Ti₃C₂Tx-ZnO NS were observed by scanning electron microscopy (SEM, Ultra Plus, Carl Zeiss, Germany), transmission electron microscope (TEM, JEM-2100, JEOL, Japan) and scanning transmission electron microscopy (STEM, JEM-2100, JEOL, Japan). The elemental analysis of Ti₃C₂Tx-ZnO NS was obtained by energy-dispersive X-ray spectroscopy (EDX) attached to TEM (JEM-2100, JEOL, Japan). The X-ray diffraction (XRD) patterns of samples were analyzed by an X-ray diffractometer (Bruker, Germany) with CuKα radiation (λ = 0.154056 nm) and the 2θ range was 0° to 80° with a scan speed of 5° min⁻¹. The element composition and internal bonding were collected by X-ray photoelectron spectroscopy (XPS, Japan Kratos Axis Ultra DLD, AlKα, 1486.6 eV). Raman spectral results were obtained using a Raman spectrometer with a 532 nm laser as the excitation source (inVia Reflex, RENISHAW, England). The specific surface areas were analyzed by the Brunauer–Emmett–Teller (BET) method based on the nitrogen adsorption–desorption isotherms at 77 K (Micromeritics ASAP 2460, USA).

Gas sensor fabrication and sensing measurements

The gas sensor was composed of interdigital electrodes and a thin layer of gas-sensing material. The interdigital electrode consisted of 180 nm Au layer and 20 nm Ti layer on the Si/SiO₂ substrate, as shown in Fig. S1.† In the fabrication process of the layer of gas-sensing material, Ti₃C₂Tx-ZnO NS were first dispersed in DI water and sonicated for 10 min. Then, 5 μL DI water dispersion-contained materials were dropped onto the electrodes and dried at 60 °C for 2 h in the furnace. SEM images of the bare interdigital electrode and of the electrode covered with gas-sensing materials are shown in Fig. S2a and b.† For the sensing measurements, the gas sensor was put into a chamber and the gas-sensing performance was tested through the gas-sensing system. The signal was obtained using an Agilent 4156 C, which maintained a voltage of 0.5 V during the testing process. The flow rate of the gas was adjusted by the mass flow controllers (MFCs). The concentration of gas was changed using the mixer, which can mix the target gas with carrier air. For selectivity tests of the gas sensor, the standard NO₂ gas cylinder was replaced by a corresponding standard gas cylinder, including CO₂, H₂, NH₃, and hexanal. The effect of humidity on the gas sensor was tested on a simple homemade gas-line system as shown in Fig. S3† ranging from 0% to 80% relative humidity (RH). The response of the gas sensor is defined as Rg = |Rg – Rs|/Rs × 100%, where Rs is the resistance value of the gas sensor after stabilization in air and Rg is the resistance value of the gas sensor after exposure in NO₂ for a time. In the experiments, the wavelength of UV light-emitting diode (LED) light adopted was 365 nm. The distance between the gas sensor and UV LED light was 4 cm and the power of the UV LED light was 0.15 W. The selected light intensity was fixed at 3 mW cm⁻².

DFT calculations

The interactions between electrons and ions were examined using the projector augmented wave pseudopotentials. The geometry relaxation, electronic calculations and the self-consistent field calculations of the Ti₃C₂Tx and ZnO nanosheets were completed using DFT and operated in the Vienna ab initio simulation package. The DFT-D3 correction method was considered to describe the van der Waals interactions between the gas molecules and the substrate. The Perdew–Burke–Ernzerhof function within the generalized gradient approximation analysis was conducted to assess the exchange–correlation function. A plane-wave basis set with a cut-off energy of 450 eV was used to expand the one-electron wave function. The periodic structure of a 3 × 3 × 1 supercell of Ti₃C₂Tx and ZnO with a vacuum thickness of 15 Å was used to simulate the interface of Ti₃C₂Tx and ZnO. A 3 × 3 × 1 k-grid mesh sampling was used for geometry optimization, which was used for calculating the electronic structure to obtain a more precise result. All the calculations were carried out until the energy and the Hellmann–Feynman force reached the convergence criteria of 10⁻⁶ and 0.01 eV Å⁻¹, respectively. The Bader charge analysis developed by Henkelman was used to analyze the charge transfer between the gas molecule and the substrate materials.

Results and discussion

The schematic diagram displayed in Fig. 1 illustrates the etching and subsequent sonication process for preparing...
Ti$_3$C$_2$Tx–ZnO NS and the corresponding gas sensor. Briefly, the Ti$_3$C$_2$Tx was produced by etching the Ti$_3$AlC$_2$ (MAX) in a 20 mL HF solution at room temperature. Hydrothermal and calcination methods were employed to synthesize the ZnO nanosheets. Finally, the obtained Ti$_3$C$_2$T$_x$ nanosheets were hybridized with ZnO NS by sonication treatment. The materials were dispersed in DI water and dropped onto the interdigital electrode to fabricate the gas sensor.

Fig. 2 shows the schematic diagram of the system for the sensing performance tests. The compressed air cylinder was used to provide the carrier gas, which was mixed with the target gas to produce different concentrations of target gas. The main function of the gas mixer was to deliver even levels of target gas with a certain concentration. MFCs were used to control the flow rate of compressed air and NO$_2$ gas. Gas sensors were fixed in a microchamber and connected with the Agilent 4156 C and computer using electric wires. After gas sensor exposure to NO$_2$ gas, UV LED light with 3 mW cm$^{-2}$ light intensity was used to assist in recovery of the gas sensor to the original state. The humidity gas-sensing properties of the sensors were tested through the system shown in Fig. S3.†

Compressed air passed through a flask filled with purified water to produce air with humidity, which was then passed through the chamber where the sensor was located. The humidity conditions were adjusted by changing the flow rate of compressed air via MFCs. The photoelectronic characteristics of Ti$_3$C$_2$T$_x$–ZnO nanosheet hybrids were examined by I–V curves (Fig. S4†). In the dark, the Ti$_3$C$_2$T$_x$–ZnO NS exhibited a linear curve that estimated the ohmic contact between Ti$_3$C$_2$T$_x$–ZnO NS and electrodes. The Ti$_3$C$_2$T$_x$–ZnO NS under UV illumination displayed a nonlinear curve, which is mainly because the production of photogenerated carriers breaks the balance of the built-in electric field at the interface of Ti$_3$C$_2$T$_x$ and ZnO. The photogenerated electrons on the conduction band of ZnO will transfer to the Ti$_3$C$_2$T$_x$ until formation of a new balance. It can be seen that after illumination with UV light, the current varies from 0.99 nA to 9.32 nA. The change in current is caused by the increase in the concentration of photogenerated electrons transferred from ZnO to the Ti$_3$C$_2$T$_x$.

The XRD patterns of Ti$_3$AlC$_2$, Ti$_3$C$_2$T$_x$ and Ti$_3$C$_2$T$_x$–ZnO NS are shown in Fig. 3. The characteristic peaks corresponding to the (002) plane shifted from 9.5° to 8.9° and the intensity of the peak has weakened at the same time. The (104) peak at 38.7° of Ti$_3$AlC$_2$ disappeared, indicating that the Al layer has been fully etched. Meanwhile, some new characteristic peaks appeared, such as for (004), (006) and (110), illustrating the successful fabrication of Ti$_3$C$_2$T$_x$. The XRD pattern shown in Fig. S5† reveals the high crystallinity, and no impurities exist in the ZnO NS. The peaks at 31.8°, 34.3°, 36.2°, 47.5°, 56.6° and 62.8° correspond to (100), (002), (101), (102), (110) and (103) planes, respectively. In the XRD pattern of Ti$_3$C$_2$T$_x$–ZnO NS hybrids, the characteristic peaks of the hexagonal wurtzite ZnO phase (JCPDS No. #36-1451) can be seen. Compared with the XRD results of ZnO NS, the peaks of Ti$_3$C$_2$T$_x$–ZnO NS at 31.3°, 33.9°, 35.7°, 47.2°, 56.3° and 62.6° can be indexed as the (100), (002), (101), (102), (110) and (103) planes, respectively. The 2θ of Ti$_3$C$_2$T$_x$–ZnO NS were shifted by a certain offset to a
small angle, which is because of the bonding effect of Ti$_3$C$_2$T$_x$ and ZnO NS.

Fig. 4 shows the SEM images of Ti$_3$C$_2$T$_x$–ZnO NS, and it is noticeable that the Ti$_3$C$_2$T$_x$ and ZnO nanosheets were well hybridized. ZnO NS covered on the surface of the Ti$_3$C$_2$T$_x$ nanosheets. Due to the ZnO NS being composed of nanoparticles, they are destroyed and decomposed into nanoparticles after violent ultrasonication. Numerous ZnO nanoparticles were distributed on the Ti$_3$C$_2$T$_x$ sheet, which can provide more active sites and promote improvement in the gas-sensing performance. As shown in Fig. S6a and b,† Ti$_3$AlC$_2$ (MAX) displayed a layer-by-layer morphology. The Ti$_3$C$_2$T$_x$ (MXene) nanosheets presented obvious accordion-like morphology after the etching treatment with HF solution, and the spacing between the layers increased significantly. The morphology of the ZnO NS is shown in Fig. S6c and d.† It is worth noting that there are many gaps between the particles of the ZnO nanosheets, which will boost the gas transmission and adsorption in the Ti$_3$C$_2$T$_x$–ZnO NS materials.

To further confirm the structure and element composition of Ti$_3$C$_2$T$_x$ and Ti$_3$C$_2$T$_x$–ZnO NS, TEM and EDX mapping were carried out, as shown in Fig. 5. Fig. 5a shows the TEM image of Ti$_3$C$_2$T$_x$, which presented a clear layer structure. The high-resolution TEM (HRTEM) image of Ti$_3$C$_2$T$_x$ is shown in Fig. 5b. The lattice fringes with a spacing of 0.7 nm can be indexed with (002) of Ti$_3$C$_2$T$_x$. The TEM and HRTEM images of Ti$_3$C$_2$T$_x$–ZnO NS are shown in Fig. 5c and d. The ZnO NS are distributed on the surface of the Ti$_3$C$_2$T$_x$ nanosheets. Lattice fringes with different spacings of 0.25 nm and 0.248 nm correspond to (006) of Ti$_3$C$_2$T$_x$ and (101) of ZnO, respectively. The STEM, EDX mapping images (Fig. 5e) and EDX analysis (Fig. S7b†) demonstrate the uniform distribution of Ti, C, Zn, O and F elements on the Ti$_3$C$_2$T$_x$–ZnO NS, which indicates the close connection between the Ti$_3$C$_2$T$_x$ and ZnO NS. The selective area electron diffraction illustrated in Fig. S7a† indicates that the Ti$_3$C$_2$T$_x$–ZnO NS hybrid material is a composite phase and that these two materials have been successfully hybridized with each other.

The chemical bond composition and surface electronic valence of Ti$_3$C$_2$T$_x$, ZnO nanosheets and Ti$_3$C$_2$T$_x$–ZnO NS were measured by XPS analysis. The XPS full survey spectra illustrated the Ti, C, O and F elements in bare Ti$_3$C$_2$T$_x$ MXene, and the Zn and O elements that existed in the ZnO NS (Fig. 6a). The elements of Ti, C, Zn, O and F were found in the Ti$_3$C$_2$T$_x$–ZnO NS, and the intensity of the peaks assigned to Ti 2p and C 1s decreased on formation of the Ti$_3$C$_2$T$_x$ hybrids with ZnO.
NS. The Ti 2p of Ti$_3$C$_2$T$_x$ showed three bonds, including Ti-C, Ti-X and TiOs.$^{64,65}$ The peaks with binding energy positioned at 455.1 eV can be ascribed to Ti-C, and the peaks located at 455.9 eV and 461.3 eV can be attributed to Ti-X. Other peaks at 457.1 eV and 461.8 eV correspond to TiO$_2$ (Ti$^{4+}$) (Fig. S8a†). As shown in Fig. 6b, the Ti 2p core-level spectrum can be splinted into Ti 2p$_{3/2}$ and Ti 2p$_{1/2}$. The peaks at 454.1 eV and 460.2 eV correspond to the Ti-C bond and other peaks at 454.9 eV and 461.3 eV can be ascribed to the Ti-X bond. The peaks at 458.6 eV can be assigned to the Ti-O bond. Other peaks at 455.8 eV and 463.8 eV can be assigned to Ti$_2$O$_3$ (Ti$^{3+}$).$^{33,66}$ The C 1s core level of Ti$_3$C$_2$T$_x$ displayed in Fig. S8b† can be splinted into C-Ti, C-Ti-O, C-C and C-O peaks, which are located at 281.1 eV, 282.2 eV, 284.8 eV and 284.9 eV, respectively.$^{35,67}$ Meanwhile, the intensity and spacing of peaks corresponding to F 1s decreased in the Ti$_3$C$_2$T$_x$-ZnO NS compared with the pure Ti$_3$C$_2$T$_x$ sheet (Fig. 6a, d and S8c†). The peaks located at 1020.3 eV and 1043.4 eV were assigned to Zn 2p$_{3/2}$ and Zn 2p$_{1/2}$ of pure ZnO NS, respectively. In comparison, the binding energy of the Zn 2p$_{3/2}$ and Zn 2p$_{1/2}$ peaks in Ti$_3$C$_2$T$_x$-ZnO NS both shifted 1 eV and were located at 1021.3 eV and 1044.4 eV, respectively (Fig. 6e).$^{38}$ The O 1s core level of ZnO NS presented in Fig. S8d† can be splinted into O$_{l}$ (lattice oxygen), O$_{v}$ (vacancy oxygen) and O$_{a}$ (adsorbed oxygen) located at 529.8 eV, 530.9 eV and 532.9 eV, respectively.$^{68}$ The vacancy oxygen occupies the majority of the O 1s, which indicates that abundant oxygen vacancies exist in the surface of ZnO. In contrast, the O 1s core level of Ti$_3$C$_2$T$_x$-ZnO NS displayed in Fig. 6f can be deconvoluted into Ti-O and Ti-O-Zn, located at 530.2 eV and 531.7 eV, respectively.$^{69}$

Gas-sensing tests were conducted to explore the sensing performance of Ti$_3$C$_2$T$_x$, ZnO NS and Ti$_3$C$_2$T$_x$-ZnO NS gas sensors. Fig. 7a shows the dynamic response and recovery curves of pure Ti$_3$C$_2$T$_x$ and Ti$_3$C$_2$T$_x$-ZnO NS sensors to 20 ppm NO$_2$ under UV light at room temperature. The resistance of the Ti$_3$C$_2$T$_x$-ZnO NS sensor displayed a rapid increase from 511.8 MΩ to 2395.1 MΩ within a fast response speed (22 s) after exposure to NO$_2$. Meanwhile, the Ti$_3$C$_2$T$_x$-ZnO NS sensor exhibited a higher response (367.63% to 20 ppm NO$_2$) compared with the Ti$_3$C$_2$T$_x$ sensor (10.18% to 20 ppm NO$_2$) in a similar response time. After the resistance remains at a stable value, both gas sensors are unable to recover to the original resistance value. When 365 nm UV illumination was applied to assist the recovery process, the Ti$_3$C$_2$T$_x$-ZnO NS sensor showed an obvious change of resistance and a fast recovery speed (10 s), whereas the Ti$_3$C$_2$T$_x$ sensor still had no change. The NO$_2$ sensing performance of ZnO NS was also examined and is shown in Fig. S9.† The ZnO NS exhibited a large resistance and vibration at room temperature. In addition, the ZnO NS sensor had no significant response after contact with 20 ppm NO$_2$ gas. Fig. 7b illustrates the five cycle tests for the Ti$_3$C$_2$T$_x$-ZnO NS sensor to 20 ppm NO$_2$ at room temperature and recovery under UV illumination, demonstrating an excellent reproducibility without major changes.

The selectivity of the Ti$_3$C$_2$T$_x$-ZnO NS sensor to various gases was investigated, including 20 ppm NO$_2$ and 50 ppm of NH$_3$, CO$_2$, H$_2$ and hexanal, as shown in Fig. 7c. The responses to NO$_2$, NH$_3$, CO$_2$, H$_2$ and hexanal were 367.63%, 7.27%, 58.23%, 0% and 4.66%, respectively. The sensor exhibited a high selectivity towards NO$_2$ gas over the other gases. As shown in Fig. 7d, the Ti$_3$C$_2$T$_x$-ZnO NS sensor was exposed to different concentrations of NO$_2$ gas at room temp-
**Fig. 7** (a) Dynamic response and recovery curves under UV irradiation for Ti$_3$C$_2$T$_x$ MXene and Ti$_3$C$_2$T$_x$–ZnO NS sensors to 20 ppm NO$_2$ at room temperature. (b) Repeatability tests of Ti$_3$C$_2$T$_x$–ZnO NS sensor to 20 ppm NO$_2$ at room temperature. (c) Selectivity of Ti$_3$C$_2$T$_x$–ZnO NS sensor to 20 ppm NO$_2$ and various target gases with a concentration of 50 ppm at room temperature. (d) Dynamic response and recovery curves of Ti$_3$C$_2$T$_x$–ZnO NS sensor under UV illumination to 0.5–100 ppm NO$_2$ at room temperature. (e) Dynamic response and recovery tests for the Ti$_3$C$_2$T$_x$–ZnO NS sensor in the RH ranging from 0% to 80% RH. (f) The response values of the Ti$_3$C$_2$T$_x$–ZnO NS sensor at different humidity conditions ranging from 0% to 80% RH.

The sensor were increased with the concentration of NO$_2$ gas varying from low concentration to high concentration. Fig. 7e and f shows the responses of the Ti$_3$C$_2$T$_x$–ZnO NS sensor to 20 ppm NO$_2$ gas at room temperature under different RH conditions. The responses of the sensor decreased with increase in RH, with the responses being 367.63% (0% RH), 339.77% (20% RH), 247.41% (40% RH), 244.96% (60% RH) and 206.26% (80% RH), separately. With RH increasing from 0% to 80%, the response of the Ti$_3$C$_2$T$_x$–ZnO NS sensor to NO$_2$ gas exhibits a decrease, which is mainly because the water molecules covered the active sites and hindered the gas molecules adsorbed onto the surface of the material. More importantly, the sensor can remain at a relatively high response whether in a low-humidity or high-humidity environment, suggesting great potential in further applications. In addition, the long-term gas-sensing performance of the Ti$_3$C$_2$T$_x$–ZnO NS sensor was determined and is displayed in Fig. S10.† Significantly, the gas sensor exhibited a relatively high response (>275% to 20 ppm NO$_2$) after four weeks, indicating that the gas sensor can be used for a long time. To investigate the structural stability of Ti$_3$C$_2$T$_x$–ZnO NS, Raman analysis was carried out and the spectra are displayed in Fig. S11.† Raman peaks located at 156 cm$^{-1}$ and 207 cm$^{-1}$ correspond to the A$_{1g}$ vibration modes of Ti$_3$C$_2$T$_x$.$^{32}$ Meanwhile, the small Raman peaks located at 434 cm$^{-1}$ correspond to the E$_2$ (high) vibration mode of ZnO in the wurtzite structure.$^{13}$ It is notable that after 30 minutes of UV illumination the corresponding Raman peaks show almost no change. The results indicate that the Ti$_3$C$_2$T$_x$–ZnO NS can retain its structure without any destruction after a long period of UV illumination (365 nm, 3 mW cm$^{-2}$). Fig. S13† illustrates the response of Ti$_3$C$_2$T$_x$–ZnO NS towards 365 nm UV light (3 mW cm$^{-2}$) without NO$_2$ gas at room temperature. The Ti$_3$C$_2$T$_x$–ZnO NS exhibited periodic and stable resistance changes under UV light. In terms of the response process of Ti$_3$C$_2$T$_x$–ZnO NS towards NO$_2$ gas, the resistance of Ti$_3$C$_2$T$_x$–ZnO NS was increased when exposed to NO$_2$ gas. Therefore, the UV light illumination cannot provide enhancement to the sensor response, but only acts in the role of assisting the recovery of the sensor after the desorption of NO$_2$ gas. The UV light-induced gas desorption could help to accelerate the recovery process of the Ti$_3$C$_2$T$_x$–ZnO NS gas sensor.$^{70}$ In addition, comparison of the NO$_2$ sensing performances of the various gas sensors under UV illumination, including response/recovery time and sensitivity, are illustrated in Table S1.$^†$ The Ti$_3$C$_2$T$_x$–ZnO NS sensor exhibited better response and recovery properties compared with other reported NO$_2$ sensors. It is important that the Ti$_3$C$_2$T$_x$–ZnO NS sensor only needs a short period of external UV light for a long time during the entire stage.

DFT calculations were carried out to explore the sensing properties of Ti$_3$C$_2$T$_x$ and ZnO to NO$_2$ gas. The flat model was constructed by a monolayer MXene and ZnO with a supercell of size of 3 × 3 × 1. The supercell of MXene (Ti$_3$C$_2$T$_x$) and ZnO was relaxed until the energy and the Hellmann–Feynman force reached the convergence criteria of $10^{-6}$ eV and 0.01 eV Å$^{-1}$. The optimized structures of NO$_2$ absorbed on Ti$_3$C$_2$T$_x$ and ZnO are illustrated in Fig. 8a and b. The adsorption energies of...
Ti$_3$C$_2$Tx and ZnO for the NO$_2$ molecule were calculated using the following equation:

$$E_{\text{ads}} = E_{\text{total}} - E_{\text{gas molecule}} - E_{\text{substrate}}$$

(1)

where $E_{\text{total}}$, $E_{\text{gas molecule}}$, and $E_{\text{substrate}}$ represent the total energy of the substrate with gas molecule adsorbed, the gas molecule (which is NO$_2$ here) and the substrate, respectively. The adsorption energies of NO$_2$ on Ti$_3$C$_2$Tx and ZnO were $-0.237$ eV and $-2.956$ eV, respectively. The results revealed that NO$_2$ gas was more easily adsorbed onto the ZnO, which has a higher adsorption energy towards NO$_2$ molecule than does Ti$_3$C$_2$Tx. Meanwhile, the charge transfer ($Q_t$) of the optimized configuration was 0.068e and 0.718e, respectively, for NO$_2$ for Ti$_3$C$_2$Tx and ZnO, with the charge difference density unveiled in Fig. 8c and d. The results demonstrate that the interaction between the NO$_2$ molecule and ZnO is stronger than that with Ti$_3$C$_2$Tx. Furthermore, the results indicate that NO$_2$ mainly extracted electrons from ZnO, and the amount of electrons gained by NO$_2$ from Ti$_3$C$_2$Tx can be neglected. Additionally, the O atom and N atom of NO$_2$ have formed a chemical bond with the Zn atom of ZnO, which means there is a chemical adsorption interaction. The bond lengths of Zn–O and Zn–N were calculated as 2.125 Å and 2.173 Å, respectively. The equilibrium heights of the N atom from the surface of Ti$_3$C$_2$Tx and ZnO were 2.536 Å and 1.88 Å, respectively, as displayed in Table S2.

Fig. 8 Top and side view of the most energetically favorable configuration (a) Ti$_3$C$_2$Tx and (b) ZnO after adsorption of NO$_2$ and the difference charge density plots of NO$_2$ adsorbed on the (c) Ti$_3$C$_2$Tx and (d) ZnO using an isovalue of 0.0001 e Å$^{-3}$ and 0.002 e Å$^{-3}$, respectively. Cyan: charge depletion. Yellow: charge accumulation.

Fig. 9 (a) Schematic diagram of the possible gas-sensing mechanism of Ti$_3$C$_2$Tx–ZnO NS. (b) Energy band structure diagram of Ti$_3$C$_2$Tx–ZnO NS Schottky barriers in air and NO$_2$. 

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BET analysis was carried out to explore the specific area of samples, as displayed in Fig. S12.† Compared with pure Ti3C2Txs, the Ti3C2Txs–ZnO NS exhibits a higher BET specific surface area (9.71 m² g⁻¹) than Ti3C2Txs (1.47 m² g⁻¹). The results illustrate that more active sites exist in the Ti3C2Txs–ZnO NS, which could provide the high sensitivity of Ti3C2Txs–ZnO NS toward NO2 gas. The gas-sensing mechanism of the Ti3C2Txs–ZnO NS sensor can be explained by the charge transfer process. Fig. 9a shows the adsorption process when Ti3C2Txs–ZnO NS is exposed to air. Oxygen molecules are adsorbed onto the surface of ZnO NS and Ti3C2Txs nanosheets, capturing the electrons from the conduction band of the materials and forming the chemisorbed oxygen species (Ox⁻). The specific reaction process is shown in the equations below:

\[
\begin{align*}
O_2 \text{(gas)} & \rightarrow O_2 \text{(ads)} \\
O_2 \text{(ads)} + e^- & \rightarrow O_2^- \text{(ads)}
\end{align*}
\]

Since the work function of Ti3C2Txs (4.60 eV) is higher than that of ZnO (4.1 eV), the electrons of ZnO flow to Ti3C2Txs until the Fermi energy level reaches equilibrium. Consequently, the Schottky barrier layer is formed at the interface between Ti3C2Txs and ZnO after the electron transfer process, as shown in Fig. 9b. Because the electron affinity of NO2 (2.30 eV) is higher than O2 (0.44 eV),8 electrons will move toward NO2 and yield NO2⁻ ions, as illustrated in eqn (4). The electrons are continuously captured from ZnO nanosheets and flow to the Ti3C2Txs, resulting in enlargement of the Schottky barrier layer at the interface between Ti3C2Txs and ZnO. Meanwhile, as a result of ZnO becoming less doped as electrons are captured by NO2, and large amounts of electron transfer from ZnO to Ti3C2Txs, the Schottky barrier widens at the same time. In addition, the XPS results in Fig. 6e and f provide some important information. In Fig. 6e, the Zn 2p peaks of Ti3C2Txs–ZnO are shifted 1 eV towards higher binding energy compared with the Zn 2p peaks of pure ZnO, which can provide an evidence of the transfer of electrons from ZnO to Ti3C2Txs. In Fig. 6f, the formation of Ti–O–Zn chemical bonds indicates the strong interaction between Ti3C2Txs and ZnO. The Ti–O–Zn chemical bonds that exist in the Ti3C2Txs–ZnO NS can effectively enhance the transfer efficiency of the barriers between these two materials:6

\[
\text{NO}_2 \text{(gas)} + e^- \rightarrow \text{NO}_2^- \text{(ads)}
\]

The enhanced sensing properties can be attributed to the formation of the Schottky barrier layer and the increase in active sites on the surface of Ti3C2Txs–ZnO NS. It can be seen from Fig. 4 that large amounts of ZnO nanoparticles are uniformly distributed on the surface of the Ti3C2Txs nanosheets, which can increase the number of active sites. Apart from these, large surface groups, such as –F, –OH and –O, exist in the Ti3C2Txs nanosheets. Therefore, more gas molecules could easily adsorbed onto the surface of Ti3C2Txs–ZnO NS. The above features of the Ti3C2Txs–ZnO NS all play a role in enhancing the gas-sensing performance. The short recovery time of Ti3C2Txs–ZnO NS is mainly ascribed to the increase in the concentration of photogenerated holes of ZnO when it is under UV illumination (365 nm). The reason is that NO2⁻ could react with the photogenerated holes on the valence band of ZnO and convert into NO2 gas. The specific response and recovery process of Ti3C2Txs–ZnO NS to NO2 gas is shown in Fig. S14† and the reactions of the recovery process are illustrated in eqns (5) and (6). Therefore, the recovery time will decrease significantly. The most important thing is that the light only assists the sensor to recover quickly, rather than the entire response/recovery process, which helps to maintain the stability of the sensor. Therefore, the sensor will not be affected by long-term light illumination, which leads to performance degradation. Nevertheless, NO2 sensing properties can be enhanced through the surface groups (including –F, –O and –OH) on the Ti3C2Txs, and abundant oxygen vacancies act as active sites to adsorb large amounts of NO2 molecules.

\[
\begin{align*}
\text{hv} & \rightarrow h^+ (\text{hv}) + e^- (\text{hv}) \\
\text{NO}_2^- \text{(ads)} + h^+ (\text{hv}) & \rightarrow \text{NO}_2 \text{(g)}
\end{align*}
\]

Conclusions

In summary, Ti3C2Txs–ZnO NS for NO2 detection at room temperature has been prepared by a facile sonication method. The sensor exhibited a 367.63% response, and a short response time (22 s) to 20 ppm NO2 gas at room temperature. Meanwhile, the recovery time was 10 s under 365 nm UV illumination. The sensor also displayed superior reproducibility for five cycles of response tests to 20 ppm NO2. Humidity tests demonstrated excellent anti-humidity properties when the sensor was operated under different humidity conditions. The predominant factor for the gas-sensing performance can be attributed to the abundant active sites in Ti3C2Txs–ZnO NS and the large quantity of photogenerated barriers of ZnO nanosheets under UV illumination. In addition, UV illumination excites the electrons and holes of ZnO, which speeds up the desorption process. The construction of Ti3C2Txs–ZnO NS Schottky junctions not only improves the sensing performance, but also solves the problems of poor sensitivity under humid conditions and easy oxidation. DFT calculations showed that the adsorption energy between NO2 molecules and ZnO was stronger than that with Ti3C2Txs. Moreover, the difference charge transfer density plot illustrated that the NO2 gas mainly extracted electrons from ZnO, indicating the high response of ZnO toward the NO2 gas. Therefore, the combination of the novel Ti3C2Txs material (high conductivity) with conventional metal oxide material (strong absorbability), as well as utilizing the photosensitivity of ZnO to generate photogenerated carriers under UV illumination, can provide new ideas for the further improvement of Ti3C2Txs-based gas sensors.
Author contributions

Chao Fan: Conceptualization, methodology, investigation, formal analysis, visualization, data curation, writing original draft. Jia Shi: Formal analysis, writing-review and editing. Yongwei Zhang: Writing-review and editing. Wenjing Quan: Writing-review and editing. Xiuy Chen: Writing-review and editing. Jianhua Yang: Supervision, conceptualization, methodology, funding acquisition, writing-review and editing. Min Zeng: Resources, writing-review and editing. Zhihua Zhou: Writing-review and editing. Yanjie Su: Writing-review and editing. Hao Wei: Writing-review and editing. Zhi Yang: Resources, supervision, funding acquisition, writing-review and editing.

Conflicts of interest

There are no conflicts to declare.

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