Surrounding Sensitive Electronic Properties of Bi$_2$Te$_3$ Nanoplates—Potential Sensing Applications of Topological Insulators

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Significant efforts have been paid to exploring the fundamental properties of topological insulators (TIs) in recent years. However, the investigation of TIs as functional materials for practical device applications is still quite limited. In this work, electronic sensors based on Bi$_2$Te$_3$ nanoplates were fabricated and the sensing performance was investigated. On exposure to different surrounding environments, significant changes in the conducting properties were observed by direct electrical measurements. These results suggest that nanostructured TIs hold great potential for sensing applications.

Topological insulators (TIs) are materials with gapped insulating bulks and metallic conducting surfaces\cite{1,2}. The strong spin-orbit coupling in TIs reduces the probability of the electrons being backscattered by surface defects, which lowers the surface resistivity and leads to the formation of topologically protected surface states\cite{3,4}. This special spin helical Dirac transport regime makes TIs promising for a number of novel applications such as spintronics and quantum computing\cite{4,5,6}. The recently discovered three-dimensional (3D) TIs such as Bi$_2$Se$_3$ and Bi$_2$Te$_3$ which are referred to as the second generation of TIs open up new possibilities for device applications\cite{2,7,8}. This is because these 3D TIs are composed by layered structures in which the adjacent layers are bonded together by weak van der Waals forces, thereby enabling mass production by both top-down mechanical exfoliation\cite{9,10} and bottom-up chemical synthesis\cite{11,12,13,14}. But nowadays the substantial bulk carrier density is still a major challenge, hence enhancing the surface conduction is critical. Making TIs into nanostructures is a simple but effective strategy because the large surface to volume ratios of nano-scaled materials can maximize the surface contribution to the total conduction\cite{15,16}. So nanostructured TIs may have wider potential applications than bulk single crystals due to the reduced bulk conduction\cite{15,17,18}.

Device applications do require detailed investigation on the electric and dielectric properties of the material under different conditions, as the practical operating environment can be quite diversified. The chemical doping effect of gas molecules on TIs has drawn much attention because of its potential applications in tuning the transport properties of TI based devices. It has been demonstrated that the energy position of the Dirac point (E_D) in TIs can be tuned by dosing with certain gas molecules\cite{4,19,20}. Reducing gases such as H$_2$ and CO serve as n-type doping agents\cite{20} while oxidizing ones such as O$_2$ and NO$_2$ serve as p-type doping agents\cite{4}. All these experimental evidences are obtained using non-transport, surface sensitive techniques such as angle resolved photoemission spectroscopy (ARPES) and scanning tunneling microscopy (STM)\cite{21}. However, these techniques are difficult to be used in portable applications because of the large size and high cost of the equipment. Therefore, investigating the material properties by direct electrical measurement is of fundamental importance for device development and innovation.

In this work, single-crystalline Bi$_2$Te$_3$ nanoplates (NPs) are synthesized through a solvothermal route. The crystal structure and growth orientation are analyzed by high resolution transmission electron microscopy (HRTEM) and selected area electron diffraction (SEAD) patterns. We have performed two-terminal measurements for the Bi$_2$Te$_3$ nanostructures in different surroundings with the purpose of inspecting whether they are sensitive to the external changes. Interestingly, exposing to different chemical environment dramatically...
influences the conduction and polarization properties of this material. What’s more, we show that these parameters can be reversibly tuned, demonstrating that Bi$_2$Te$_3$ may find use as multifunctional sensing materials.

**Results**

The hexagonal Bi$_2$Te$_3$ NPs were synthesized by a solvothermal method at 180°C. The XRD patterns of the as-grown Bi$_2$Te$_3$ NPs are shown in Fig. S1, all of the detected peaks are indexed to the rhombohedral Bi$_2$Te$_3$ crystal system (space group: R-3m) with hexagonal cells (JCPDS card No.089-2009). Fig. 1a and b show the typical low-magnification scanning electron microscopy (SEM) images of the as-grown Bi$_2$Te$_3$ NPs. They display regular hexagonal shapes with edge lengths ranging from 300 to 450 nm. An enlarged SEM image of a representative individual Bi$_2$Te$_3$ NP is shown in the inset of Fig. 1b, where a hexagonal-shaped NP can be clearly identified. The maximum diagonal length which is twice the length of the edge is 708 nm and the interior angle is 120°. A typical transmission electron microscopy (TEM) image is shown in Fig. 1c in which the NPs exhibit flat surfaces and sharp edges. A defective NP with one ragged edge was chosen for element mapping by energy dispersive X-ray (EDX) spectroscopy on a scanning transmission electron microscope (STEM). The element maps of the overlapped areas show higher color intensities while that of the other areas are uniform. So the ripple-like patterns in the upper image are most likely resulted from bend of the NP but not overlap or thickness variation. The crystal structure of the as-prepared Bi$_2$Te$_3$ NPs was investigated by high-resolution transmission electron microscopy (HRTEM) and SAED patterns. The single-crystalline nature is revealed by the continuous lattice fringes oriented in the same direction in Fig. 1e and the sharp diffraction pattern in Fig. 1g. Bulk Bi$_2$Te$_3$ has a hexagonal primitive cell with parameters $a = 4.384$ Å and $c = 30.45$ Å at room temperature. The d-spacing of 0.22 nm is in good agreement with the {1210} interplaner spacing of Bi$_2$Te$_3$. The diffraction pattern indicates that $<1210>$ is the dominate growth direction and the six side surfaces of the NP belong to the {1210} family of crystallographic planes. The top and bottom surfaces are identified as the {0001} facets, which is also the mainly exposed facet. This result is consistent with the layered structure of Bi$_2$Te$_3$, in which the quintuple layer (QL) [Te$_1$-Bi-Te$_2$-Bi-Te$_1$] is the fundamental building block as shown in Fig. 1f. It is considered that the bonding within one QL is covalent while that between adjacent QLs is the van der Waals forces and $<0001>$ is the slowest growth direction.

We performed both two-probe and four-probe measurements on the device and the contact resistance between the probe and the Au electrode was found to be negligible (Fig. S2 in supporting information).

**Figure 1** Synthesis and characterizations of the hexagonal single-crystalline Bi$_2$Te$_3$ NPs exposed with {0001} facets. (a, b) Scanning electron microscopy images of the as-grown NPs. The inset in (b) is a representative individual NP. (c) TEM image of the as-grown NPs. (d) TEM image of a defective Bi$_2$Te$_3$ NP (top) and its element maps (bottom). (e) HRTEM image of the Bi$_2$Te$_3$ NP in (d) taken along the [0001] direction, revealing a high quality crystalline structure. The inset is the corresponding fast Fourier transform (FFT) image. (f) Side (left) and top (right) views of the crystal structure of Bi$_2$Te$_3$. A quintuple layer (Te$_1$-Bi-Te$_2$-Bi-Te$_1$) is indicated by a double-headed arrow. (g) Selected area diffraction pattern taken along the [0001] direction.
tion). So two-probe measurements were conducted for the Bi$_2$Te$_3$ NPs under controlled environments in a metal shielded chamber (Fig. 2a and b) using a semiconductor parameter analyzer (Agilent 4156C with 1 fA current measurement resolution). A schematic of the measurement configuration is sketched in Fig. 2c and a typical photograph of the interdigital electrode is shown in Fig. 2d. The device showed nearly symmetric and linear current-voltage (I–V) characteristics, as shown in Fig. 2e. The conductance (I/V) of the device increased from 5.7 to 10.2 pS as air pressure increased from 10 to 1 \times 10^3 \text{ Pa}. Afterwards, the chamber was evacuated until the pressure was less than 1 \times 10^{-8} \text{ torr} and then refilled with high purity nitrogen (99.999%, Linde Gas Co. Ltd.). The above operation was repeated 3 times to drive away the residual air. Under the same pressure of 1 \times 10^3 \text{ Pa}, the conductance decreased from 10.2 pS in air to 0.67 pS in pure N$_2$. Similar results were obtained as the pressure was set to 10 or 100 Pa, that the conductance of the device in air was over 10 times larger than that in N$_2$ under the same pressure. This result indicates that the conducting property of the Bi$_2$Te$_3$ NPs is sensitive to the chemical content of the surrounding gas atmospheres.

A series of electrical measurements were performed on the device with an impedance analyzer (Agilent 4294A) under increasing relative humidity (RH). The relationships between the impedance (Z) and the corresponding phase angle of the device and RH are shown in Fig. 3(a,b) obtained under a 500 mV alternating voltage. In the same ambient conditions, the impedance decreased with increasing frequency, indicating that the device acted as a capacitive load. The impedance changed from 100 k\Omega to about 3 k\Omega as the RH varied from 11\% to 98\% at 10 kHz, exhibiting a good sensitivity.

In order to explain the enhanced conductivity under high RH, we consider two possible mechanisms that affect the transport properties of the Bi$_2$Te$_3$ NPs. At relatively low humidities, the change is ascribed to the band bending effect induced by the adsorption of water molecules, which has been experimentally discovered independently using ARPES by several other research groups. The band bending shifts the Dirac point into the occupied states and increases the charge carrier densities at the surface, which results in the decreased impedance. But as the water molecule adsorption progresses, a continuous water layer will be formed at the surface. At this point, proton conduction will play a role in enhancing the total conductivity of the material, which can be written as:

$$H_2O^+(l,x) + H_2O(l,x') \rightarrow H_2O(l,x) + H_3O^+(l,x') \quad (1)$$

Where $l$ denotes the liquid phase, $x$ and $x'$ indicate the different spatial positions. There we neglect the contribution of hydroxide (OH$^-$) because its mobility is much smaller than that of the protons. The relationships between the capacitance and resistance of the device and RH were also measured and shown in Fig. 3(c,d). The results were obtained using the Cs-Rs measurement mode in which the sensor was treated as a two terminal device under test (DUT) composed by a resistor and a capacitor in series. In contrast to the resistance, the capacitance increases with increasing RH. This is because the capacitance reflects the dielectric property (or polarization property) of the Bi$_2$Te$_3$ NPs. Since water molecule is highly polar, the accumulation of water on the surface of the Bi$_2$Te$_3$ film increases the dielectric coefficient, which accounts for the increased capacitance. The transient responding dynamics of impedance and capacitance of the device are shown in Fig. 3(e,f). The response times (the time for the device to attain 90\% of the final value) from 43\% RH to 75\%, 85\% and 98\% RHs are all less than 10 s. The transient responding characteristics at low RHs are also shown in Fig. S3. The impedance and capacitance change curves as the RH decreased step by step from 98\% to 11\% are shown in Fig. S4, showing the device can be used as a full range RH sensor.

To gain further information about the surrounding sensitive properties of the sensors. Ammonia was used as the probe molecule for its explicit n-doping characteristics, which had been widely used to explore the sensing properties of carbon nanotubes, graphene and molybdenum disulfide. The transient response of the sensor to NH$_3$ (0.05\% to 0.4\% in air) is shown in Fig. 4a. The response time $\tau_{\text{res}}$ and recovery time $\tau_{\text{rec}}$ are defined as the time required for the sensor to attain 90\% of the maximum conductance change after a sudden change in the ammonia concentration. And the gas response is defined as $R = R_u/R_a$, where $R_u$ and $R_a$ are the resistances of the sensor in air and in the target gas, respectively.

As shown in Fig. 4b, the response exhibits an almost linear dependence on the NH$_3$ concentration. At relatively low NH$_3$ concentrations, the surface coverage is expected to be much less than a monolayer and the interaction between absorbed NH$_3$ molecules is negligible so it can be described by the Langmuir adsorption model. The fractional coverage $\theta$ depends on the ammonia concentration $C_{NH_3}$, by means of the binding energy $E_\theta$:

$$\theta = \frac{\alpha C_{NH_3}}{1 + \alpha C_{NH_3}} \quad (2)$$

where $\alpha = \exp(E_\theta/k_BT)$, in which $k_B$ is the Boltzmann’s constant and $T$ the absolute temperature. Assuming the number of NH$_3$ gas molecules per unit area under a monolayer coverage is $\rho$ and the charge transfer per NH$_3$ molecule to Bi$_2$Te$_3$ is $\delta$. The number of excess electrons per unit area on the surface of Bi$_2$Te$_3$ is given by $\Delta n = \rho \delta$. The increased conductance can be expressed as:

![Figure 2](https://www.nature.com/scientificreports/4639) Measurement configuration and electrical test results under different gas environments. (a) A photograph showing the two-probe configuration. (b) Enlarged image of the selected area in (a). (c) A simplified schematic of the testing method (applying a variable voltage on the device with the current being monitored by a high resolution source monitor unit). (d) A photograph of the interdigital electrode. (e) I–V curves of the device under different gas environments.
Under low ammonia concentrations, $\alpha C_{NH_3} \ll 1$, so that $\Delta G^*$ exhibits good linear dependence on NH$_3$ concentration. However, this is only a very simplified model to describe the relationship between the change of conductance and gas concentration. As the concentration increases, both the repulsive interactions between the absorbed NH$_3$ molecules and the change in the carrier mobility can’t be neglected$^{19,33,34,35}$. The ultrafast response speed of this model sensor at room temperature is striking. The response time is 1.2 s at 0.05 vol% and becomes less than 1 s as the concentration is higher than 0.1 vol%, which is much faster than most metal oxides based NH$_3$ sensors, even those working at very high temperatures of 300–600 °C$^{36}$. Another interesting thing is that the response time of this sensor is much shorter than its recovery time as shown in Fig. 4c. The long recovery time indicates that NH$_3$ molecules are strongly bound to the Bi$_2$Te$_3$ surface and desorb very slowly. Both response time and recovery time have a tendency to decrease as the concentration of NH$_3$ increases, which can be explained by the higher adsorption/desorption rate resulted from the larger concentration gradients. In addition, we have fabricated another two sensors based on the Bi$_2$Te$_3$ NPs to test the repeatability of this phenomenon. As shown in Fig. 4d, the three sensors named SN-1, SN-2 and SN-3 all exhibit fast and high response to ammonia but the void IDE doesn’t show any response.

**Discussion**

We have shown that the electric and dielectric properties of the Bi$_2$Te$_3$ NPs could be significantly changed by the outside environ-

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**Figure 3 | Humidity sensing properties of the sensor.** (a,b,c,d) The dependence of impedance, phase, capacitance and resistance of the sensor on relative humidity measured at various frequencies. (e,f) Transient response of the impedance and capacitance from 43% RH to the corresponding humidities measured at 1 kHz.

$$
\Delta G^* = \mu_c e \Delta n = \mu_c e \rho \delta \frac{\alpha C_{NH_3}}{1 + \alpha C_{NH_3}}
$$

(3)
The synthesis of Bi₂Te₃ NPs was achieved by a solvothermal method. Typically BiCl₃ (1.0 mmol, 0.315 g), Na₂TeO₃ (1.53 mmol, 0.34 g), NaOH (15 mmol, 0.6 g) and polyvinylpyrrolidone (PVP, 0.5 g) were added to ethylene glycol (EG, 36 mL) under magnetic stirring. After 1 h of stirring, the homogeneous solution was transferred to a 50 mL Teflon-lined stainless autoclave which was then sealed and heated to 180 °C and maintained at this temperature for 36 h. After cooling down to room temperature, the resulting product was collected by centrifugation and washed with distilled water and ethanol each for 3 times.

Device Fabrication. Alumina ceramic was used as the substrate for its high dielectric strength and excellent chemical stability. The IDEs composed of 10 nm of titanium and 80 nm of gold with a line-width of 80 μm were fabricated by sputtering. The devices were fabricated by dropping the Bi₂Te₃ NPs dispersion onto the pre-cleaned interdigital electrodes.

Device Characterizations and Gas Sensing Measurements. The current-voltage (I–V) tests were conducted in a four-probe microscopy cryostat (JANIS ST-500) equipped with a turbo-molecular pump. The chamber pressure could be adjusted by a controlled valve. Electrical measurements were performed on a semiconductor parameter analyzer (Agilent E4156C, 1 fA/2 μV resolution). The impedance and capacitance of the device were obtained with an impedance analyzer (Agilent 4294A, 40 Hz to 110 MHz). Open and short calibration were performed with user defined kit before the measurement to ensure accuracy. The ammonia sensing test was carried out on a ZhongKe NS-4003 smart sensor analyzer under a constant voltage of 5 V.

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Author contributions
B.L., Q.L. and T.W. conceived the experiments. D.W. and L.W. carried out material synthesis. D.C and H.L. carried out material characterizations. Y.L. carried out the device fabrication. B.L. Y.W. and W.X. implemented electrical measurements and analysis. All authors discussed the results and contributed to writing of the manuscript.

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