



OPEN

SUBJECT AREAS:

TOPOLOGICAL
INSULATORS

SPINTRONICS

Received
13 December 2013Accepted
16 April 2014Published
8 May 2014

Correspondence and requests for materials should be addressed to N.T. (ntang@pku.edu.cn); W.K.G. (geweikun@mail.tsinghua.edu.cn) or B.S. (bshen@pku.edu.cn)

Identification of Helicity-Dependent Photocurrents from Topological Surface States in Bi_2Se_3 Gated by Ionic Liquid

Junxi Duan¹, Ning Tang¹, Xin He¹, Yuan Yan¹, Shan Zhang¹, Xudong Qin², Xinqiang Wang^{1,3}, Xuelin Yang¹, Fujun Xu¹, Yonghai Chen², Weikun Ge^{1,4} & Bo Shen^{1,3}

¹State Key Laboratory of Artificial Microstructure and Mesoscopic Physics, School of Physics, Peking University, Beijing 100871, People's Republic of China, ²Laboratory of Semiconductor Materials Science, Institute of Semiconductors, Chinese Academy of Sciences(CAS), Beijing 100083, People's Republic of China, ³Collaborative Innovation Center of Quantum Matter, Beijing 100871, People's Republic of China, ⁴Department of Physics, Tsinghua University, Beijing 100084, People's Republic of China.

Dirac-like surface states on surfaces of topological insulators have a chiral spin structure with spin locked to momentum, which is interesting in physics and may also have important applications in spintronics. In this work, by measuring the tunable helicity-dependent photocurrent (HDP), we present an identification of the HDP from the Dirac-like surface states at room temperature. It turns out that the total HDP has two components, one from the Dirac-like surface states, and the other from the surface accumulation layer. These two components have opposite directions. The clear gate tuning of the electron density as well as the HDP signal indicates that the surface band bending and resulted surface accumulation are successfully modulated by the applied ionic liquid gate, which provides a promising way to the study of the Dirac-like surface states and also potential applications in spintronic devices.

Three dimensional topological insulators are insulators with time-reversal symmetry and strong spin-orbit coupling (SOC)^{1,2}. It is a new quantum phase of matter with insulating bulk states and Dirac-like helical surface states whose spin is perpendicularly locked to its momentum²⁻⁴. The helical surface states reside in the bulk insulating gap, and are protected from backscattering by time-reversal symmetry^{3,4}. That makes the topological insulators potentially promising to serve as a platform for spintronics and quantum computing applications, based on the crucial spin coherence. Bi_2Se_3 is currently most applied one of these fascinating materials, with topologically non-trivial energy gap about 0.3 eV and only a single Dirac cone in the surface energy spectrum⁵. The static electronic properties of the surface states have been comprehensively imaged by angle-resolved photoemission spectroscopy (ARPES) and other surface sensitive techniques⁵⁻⁸. Transport measurements at low temperature have also been carried out to study the new physics of these novel massless two-dimensional electron systems⁹⁻¹¹. However, the reported transport studies have been bothered by its inevitably metallic bulk^{10,11}. ARPES studies have also shown that the cleaved sample surfaces progressively become more electron doped by either gas contamination, or formation/migration of defects, e.g. vacancies^{12,13}. Although it has been reported that the chemical potential in Bi_2Se_3 could be tuned by surface deposits, bulk doping, and back gates, these methods are nevertheless cumbersome or restricted^{10,11,14}.

Spin-polarized helicity-dependent photocurrent (HDP) generated by circularly polarized light in the helical Dirac cone (HDC) is a useful technique to study the novel properties of topological surface states¹⁵. It had been studied theoretically as well as experimentally^{16,17}. Different from and advantaged than transport measurements, the contribution from the bulk states to HDP can be neglected, since the bulk states are spin degenerate^{5,17}. However, clear Rashba spin-splitting of the conduction band in samples cleaved in air or exposure to water vapor has been reported by several groups through ARPES measurements^{18,19}. Furthermore, quantized sub-bands existed in the surface-electron-accumulation layer (SEAL) at the surface of the samples. Thus, one could not directly make the conclusion that the HDP is generated in HDC only. Therefore, it is very important to find a convenient and direct way to modulate the SEAL, and thereby identify the HDP truly stemmed from the HDC.

Here we report a study of the topological surface states in HDC by measuring the HDP generated by illumination of circularly polarized light. The SEAL in the samples was modulated by ionic liquid gate (ILG)²⁰⁻²². The clear gate-voltage dependence of the density of electrons and HDP signal shows that the band bending as well as the Rashba spin-orbit splitting of SEAL are successfully modulated by the ILG. These results demonstrate that the



measured HDP has two components with different directions, one of which indeed stems from the HDC while the other from the SEAL. This work provides a promising way to the study of the Dirac-like surface states and also potential applications in spintronic devices.

Results

Photocurrents with different planes of incidence were measured, as shown in Figure 1b–1e. In the measurement, the total photocurrent j_y can be fitted by the formula:

$$j_y(\varphi) = j_c \sin 2\varphi + j_L \sin 4\varphi + j_0 \quad (1)$$

where j_c is the magnitude of the HDP, j_L the photocurrents induced by linear polarized light, and j_0 the background photocurrent which is polarization-independent¹⁵. Only the HDP j_c is of concern in this study. The helicity dependence evidently indicates that j_c here is generated through a spin-related process, as in a spin-orbit coupling system the electrons with spin polarizations aligned or anti-aligned to the wave vector would be preferentially excited by left- or right-circularly polarized light, respectively. The results here show that j_c is extremely small when the light is obliquely incident in the y - z plane, in comparison with that in the x - z plane with the same incident angle. Although no clear signal can be observed when light is normally incident, j_c increases when the incident angle becomes larger in the x - z plane (Figure 1f).

To clarify the origins of the measured HDP, we modulated the surface band-bending curvature by ILG. This is the key advance of this work along with the multiple advantages of ILG over the conventional solid gates^{20–22}. The ionic liquid together with the sample and the gate electrode forms an electric double-layer transistor geometry, where the interfaces could be regarded as nano-gap capacitors with huge capacitance, resulting in very high electron-density tunability²³. Electric charges will accumulate at the interface when a gate

voltage is applied. The electric charge accumulation will then induce an electric field at the interface to modulate the density of electrons and band-bending curvature in the SEAL. As sketched in Figure 2a, when a positive gate voltage is applied, electrons will accumulate at the interface, and the band-bending curvature will increase.

Hall measurements with different gate voltage applied on ILG were carried out to have a quantitative evaluation of the electron accumulation near the surface. From the measurement, the density of electrons in the sample is tuned from $4.94 \times 10^{13} \text{ cm}^{-2}$ to $7.48 \times 10^{13} \text{ cm}^{-2}$ in the gate-voltage range varying from -0.9 V to 1.2 V . Further increase of the magnitude of the gate voltage will cause saturation²⁰. Surface electric field induced by the electron accumulation could be obtained according to the Poisson equation $E_s = qN_s/\epsilon_0\epsilon_{TI}$, where E_s is the surface electric field, q the elementary charge, N_s the surface electron density, ϵ_0 the vacuum dielectric permittivity, and $\epsilon_{TI} \sim 113$ the dielectric permittivity of Bi_2Se_3 ^{20,24}. From the change of the density of electrons given above, the surface electric field is tuned as much as 0.43 MV/cm .

We then measured the HDP with different gate voltages based on the setup shown in Figure 2b. The gate voltage is applied between the Au gate pad and Bi_2Se_3 flake. Figure 2c shows the dependence of the HDP and surface electric field shift on the applied gate voltage measured in one of the samples. The HDP decreases from 154 pA to 5.4 pA with increasing gate voltage from -0.4 V to 1 V . The saturation of the HDP with further increasing of the gate voltage may come from the effective screening of the electric field or saturation of the ILG, as in the case of electron density mentioned earlier^{20–22}. Note that an interesting happening is the decreasing of the HDP with increasing gate voltage.

Discussion

First of all, we should check whether or not the band bending near the surface could be effectively tuned by the ILG. From the Hall mea-

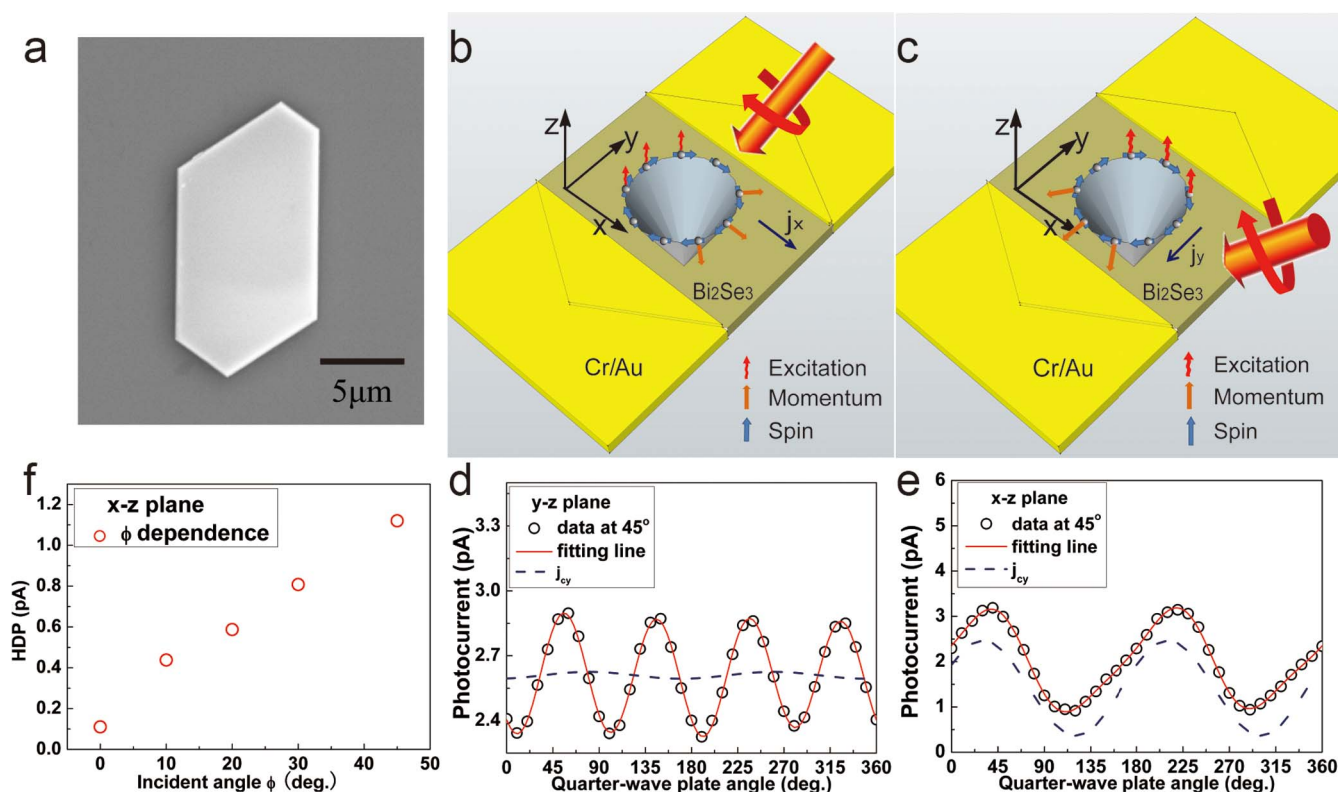


Figure 1 | (a) SEM image of the sample. (b) Sketch of HDP measurement at oblique incidence (45°) with y - z the plane of incidence. (c) Sketch of HDP measurement at oblique incidence (45°) with x - z the plane of incidence. (d) HDP measured at the setup of (b). (e) HDP measured at the setup of (c). In (d) and (e), solid line is a fit to equation (1), and dashed line indicates j_c . (f) HDP measured at different incident angles.

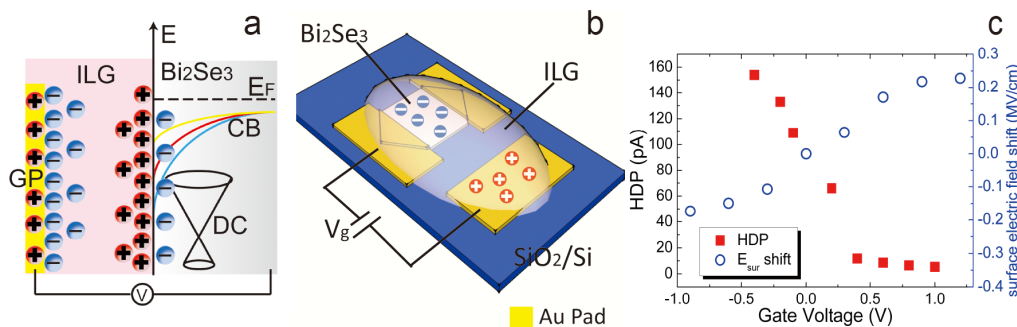


Figure 2 | (a) Sketch of electric double-layer transistor geometry formed by using ILG. (b) Oblique drawing diagram of the setup for gate modulation of the HDP with ILG. Gate voltage is applied between the flake and a gate pad nearby. (c) The dependence of the HDP and surface electric field shift on the gate voltage applied.

measurements, the bulk density of electron in the sample at zero gate voltage is $4.8 \times 10^{18} \text{ cm}^{-3}$, taking the thickness of the sample into account. It is an upper limit since we assume that there is no contribution from the surface during the calculation. The Fermi level of the bulk is about 71 meV above the bottom of the conduction band (CB), where the effective mass of Bi_2Se_3 is $0.13 \sim 0.15m_e$. Then, electrons in the HDC and the SEAL are considered. From the formula in Ref. 24, the depth of the SEAL is estimated to be 10 nm. The total surface density with electrons in HDC and SEAL all included could be expressed as $n_\sigma = 7.4 \times 10^{13} \cdot (x + 0.2)^2 + 13 \times 10^{13} \cdot x^3 (\text{cm}^{-2})$, where x is the distance between the Fermi level and the bottom of CB at the surface in the unit of eV, assuming the SEAL forms a triangle quantum well. If we reasonably suppose that the difference of the bottom of CB between the surface and bulk is 0.1 eV, the range of x modulated in our measurements is from 0.053 eV to 0.253 eV^{18,19}. The tuning range is then 0.2 eV, which is in agreement with the tuned surface electric field considering the depth of the SEAL and screen effect. Thus, the surface band bending and the Rashba spin-splitting in the surface could indeed be effectively modulated by the ILG as shown in the references^{18,19}.

We now consider the possible source to the HDP j_c , i.e. the spin of electrons in the HDC, which is locked perpendicular to their linear momentum, and lies in the plane with slight warping^{5,14,25}. Generally, the HDP can be quantitatively described by $j_{c\mu} = \sum_{\nu} \chi_{\mu\nu} \hat{e}_\nu E_0^2 P_{circ}$,

where $j_{c\mu}$ is the HDP, χ the second-rank pseudotensor, E_0 the complex amplitude of the electric field of the incident light, and P_{circ} the degree of circular polarization of the incident light¹⁵. In the presence of a [111] surface, the symmetry of the crystal is reduced from D_{3d} to C_{3v} . From the view of group theory, the nonzero items of the second-rank pseudotensor χ in HDC are χ_{xy} and χ_{yx} , with $\chi_{xy} = -\chi_{yx}$ which indicates that the HDP is always perpendicular to the plane of incidence. When x - z plane is taken as the plane of incidence, the HDP could be expressed as $j_{cy} = \chi_{yx} \hat{e}_x E_0^2 P_{circ} \propto \gamma \sin \theta \sin 2\varphi$, where γ is the SOC coefficient, θ the incident angle. It is also obvious that j_{cy} should become larger when incident angle of the light increases, due to the enhanced in-plane spin polarization component. As such, the results in Figure 1 (d) to (f) reveal that the HDP j_c indeed arises from the asymmetric optical excitation of the HDC.

To understand the interesting decrease shown in Figure 2c, contributions from other possible origins should be checked carefully. HDP has been observed on many systems with SOC^{26,27}. As a system with strong SOC, there could be additional sources of HDP in the Bi_2Se_3 flakes. Firstly, the photon energy of 1.17 eV for the used laser light is greater than the band gap of the Bi_2Se_3 flakes (~ 0.3 eV). Interband absorption is thus possible, which means that the bulk may have a prominent contribution to the measured photocurrent. However, the contribution from the bulk should be helicity-independent, since

the symmetry of the bulk Bi_2Se_3 is D_{3d} indicating that the items in the second-rank pseudotensor are all zero. Some recent papers revealed the existence of new unoccupied topological states located in bulk band gap above the Fermi level^{28,29}. This new topological states locates about 1.5 eV above the HDC with quite small band gap and small momentum. Although the new topological states are similar to the HDC, they actually contribute quite little to the HDP comparing with the HDC. Secondly, due to the high thermoelectric power of Bi_2Se_3 , laser generated heat gradients in the sample might induce a bulk thermoelectric current in addition to the photocurrent¹⁷. We argue however that this bulk thermoelectric current should be small and have nothing to do with the circular polarization of the incident light. The light spot used in the experiments is much larger ($\sim \text{mm}^2$) than the sample itself, which means that the light intensity can be considered to be even in the whole area of the sample. Thus no significant heat gradient could be generated. On the other hand, as discussed above, the absorption of the light mainly takes place in the bulk and is therefore helicity-independent also, so that the induced thermoelectric current should contribute to the background current only, but not to the HDP.

Recent reports demonstrated that the magnitude and sign of the surface dichroism of the insulating topological insulator may be oscillatory with the energy of the incident photon^{30,31}. However, the energy of the incident photons is the same in all of our measurements. According to the reports, surface dichroism depends significantly on the photon energy. What is more, the period of the oscillation indicated by this report is about 10 eV, which is almost a hundred times larger than the modulation range in our study. We thus could take the magnitude and the sign of the surface dichroism as the same in our analysis. The change of HDP from the HDC should mainly rely on the density of electron.

Another possible source of HDP is the Rashba spin-splitting states in the SEAL^{12–14,32}. The Hamiltonian of the Rashba SOC can be expressed as $H_{SO} = \alpha \vec{\sigma} \cdot (\vec{E} \times \vec{p})$, where α is the parameter of the SOC, $\vec{\sigma}$ the Pauli spin metrics, \vec{E} the electric field, and \vec{p} the electron momentum^{15,20}. It is noticed that the only nonzero component of the electric field in the SEAL is along z direction, which means that the spin of the electrons over there must lie in x - y plane. The nonzero items of the second-rank pseudotensor in the SEAL are also χ_{xy} and χ_{yx} . HDP stemmed from the SEAL would then have the same relationship with the plane of incidence and incident angle as that for the HDC. We thus cannot rule it out from our previous experimental results. The magnitude of HDP from SEAL depends on the strength of the SOC and electron density, hence it will increase (decrease) when a positive (negative) gate voltage is applied. The total HDP therefore has two components at oblique incidence and can be expressed as $j_c = j_{HDC} + j_{SEAL}$, where j_{HDC} and j_{SEAL} denote the HDP stemmed from the HDC, and SEAL, respectively.



As stated previously, the magnitude of the HDP from the SEAL (j_{SEAL}) has a positive correlation with the applied gate voltage. Obviously, the magnitude of HDP from HDC should also become larger with increasing gate voltage, since the number of electrons in HDC increases. As such, the decreasing of HDP indicates that the two components must have different directions. Actually, by considering the band structure of Bi_2Se_3 , the HDP from HDC is determined to be in opposite direction with the one from the SEAL. Thus, the measurements here make the identification that the total HDP comes mainly from the HDC in our measurements when no gate voltage is applied. The present technique thus provides an effective approach to determine which component accounts for the major part of the HDP by the direction of the HDP in a single measurement.

To summarize, we measured the HDP stemmed from the topological HDC, using generation by circularly polarized light in Bi_2Se_3 . The observed HDP has two components. Besides the one from the HDC, the other one from the Rashba spin-splitting states in the SEAL is also significant. Fortunately, these two components in HDP have opposite directions, and can be distinguished from each other by the ILG modulation. HDP from the HDC dominate the total HDP in our measurements if no gate voltage is applied. In our study, the surface band-bending was successfully modulated by ILG, and the topological surface states as one of the sources was unambiguously identified from the total HDP. Both of the above results might be important for further study and possible applications in optical-spintronics³³.

Methods

Materials. In our study, Bi_2Se_3 single crystals were grown by chemical vapor deposition (CVD)^{34,35}. The samples were fabricated by transferring Bi_2Se_3 flakes from the substrate onto a SiO_2 surface. Suitable ones with smooth surface were picked up by using optical microscope and scanning electron microscope (SEM) (Figure 1a). The Bi_2Se_3 flakes were typically 5 μm wide and 10 μm long, and thicker than 150 nm. Electrodes were patterned by standard electron beam lithography procedures. Perfect Ohmic contacts with 50 nm Cr/100 nm Au were made by electron beam evaporation.

Measurements. In the measurements, a 1064 nm laser light was illuminated on the samples through a chopper. The induced photocurrent was pre-amplified by a voltage pre-amplifier before being measured by a lock-in amplifier. The circular polarization degree p of the incident light was shifted by rotating a quarter-wavelength plate, varying with the phase difference in terms of the rotation angle φ with a period of π . The polarization modulation is in a series from linearly to left-circular, and linearly again, to right circular, and then back to linearly polarized. The polarization-dependent photocurrents (Figure 1d and 1e) were measured at different polarization degree $P \propto \sin 2\varphi$, where φ is between the polarization direction of the incident light and optical axis of the quarter-wave plate, with a step of $\pi/18$.

- Moore, J. E. The birth of topological insulators. *Nature* **464**, 194 (2010).
- Hasan, M. Z. & Kane, C. L. Topological insulators. *Rev. Mod. Phys.* **82**, 3045 (2010).
- Fu, L., Kane, C. L. & Mele, E. J. Topological insulators in three dimensions. *Phys. Rev. Lett.* **98**, 106803 (2007).
- Fu, L. & Kane, C. L. Topological insulators with inversion symmetry. *Phys. Rev. B* **76**, 045302 (2007).
- Xia, Y. *et al.* Observation of a large-gap topological-insulator class with a single Dirac cone on the surface. *Nature Phys.* **5**, 398 (2009).
- Hsieh, D. *et al.* A topological Dirac insulator in a quantum spin Hall phase. *Nature* **452**, 970 (2008).
- Chen, Y. L. *et al.* Experimental realization of a three-dimensional topological insulator, Bi_2Te_3 . *Science* **325**, 178 (2009).
- Cheng, P. *et al.* Landau quantization of topological surface states in Bi_2Se_3 . *Phys. Rev. Lett.* **105**, 076801 (2010).
- Taskin, A. A. & Ando, Y. Quantum oscillations in a topological insulator $\text{Bi}_{1-x}\text{Sb}_x$. *Phys. Rev. B* **80**, 085303 (2009).
- Checkelsky, J. G. *et al.* Quantum interference in macroscopic crystals of nonmetallic Bi_2Se_3 . *Phys. Rev. Lett.* **103**, 246601 (2009).
- Chen, J. *et al.* Gate-voltage control of chemical potential and weak antilocalization in Bi_2Se_3 . *Phys. Rev. Lett.* **105**, 176602 (2010).
- Park, S. R. *et al.* Quasiparticle scattering and the protected nature of the topological states in a parent topological insulator Bi_2Se_3 . *Phys. Rev. B* **81**, 041405 (2010).
- Hsieh, D. *et al.* Observation of time-reversal-protected single-Dirac-cone topological-insulator states in Bi_2Te_3 and Sb_2Te_3 . *Phys. Rev. Lett.* **103**, 146401 (2009).

- Hsieh, D. *et al.* A tunable topological insulator in the spin helical Dirac transport regime. *Nature* **460**, 1101 (2009).
- Ganichev, S. D. & Prettl, W. Spin photocurrents in quantum wells. *J. Phys. Condens. Matter* **15**, R935 (2003).
- Hosur, P. Circular photogalvanic effect on topological insulator surfaces: Berry-curvature-dependent response. *Phys. Rev. B* **83**, 035309 (2011).
- McIver, J. W. *et al.* Control over topological insulator photocurrents with light polarization. *Nature Nano.* **7**, 96 (2012).
- Benia, H. M. *et al.* Reactive chemical doping of the Bi_2Se_3 topological insulator. *Phys. Rev. Lett.* **107**, 177602 (2011).
- Chen, C. Y. *et al.* Robustness of topological order and formation of quantum well states in topological insulators exposed to ambient environment. *PNAS* **109**, 3694 (2012).
- Yin, C. M. *et al.* Tunable surface electron spin splitting with electric double-layer transistors based on InN. *Nano Lett.* **13**, 2024 (2013).
- Ye, J. T. *et al.* Superconducting Dome in a Gate-Tuned Band Insulator. *Science* **338**, 1193 (2012).
- Zhang, Y. J. *et al.* Ambipolar MoS_2 thin flake transistors. *Nano Lett.* **12**, 1136 (2012).
- Ye, J. T. *et al.* Accessing the transport properties of graphene and its multilayers at high carrier density. *PNAS* **108**, 13002 (2011).
- Analytis, J. G. *et al.* Bulk Fermi surface coexistence with Dirac surface state in Bi_2Se_3 : A comparison of photoemission and Shubnikov-de Haas measurements. *Phys. Rev. B* **81**, 205407 (2010).
- Wang, Y. H. *et al.* Observation of a warped helical spin texture in Bi_2Se_3 from circular dichroism angle-resolved photoemission spectroscopy. *Phys. Rev. Lett.* **107**, 207602 (2011).
- Tang, Y. Q. *et al.* Room-temperature spin-oriented photocurrent under near-infrared irradiation and comparison of optical means with Shubnikov de-Haas measurements in $\text{Al}_x\text{Ga}_{1-x}\text{N}/\text{GaN}$ heterostructures. *Appl. Phys. Lett.* **91**, 071920 (2007).
- Zhang, Q. *et al.* Lattice polarity detection of InN by circular photogalvanic effect. *Appl. Phys. Lett.* **95**, 031902 (2009).
- Eremeev, S. V. *et al.* New topological surface state in layered topological insulators: unoccupied Dirac cone. arXiv: 1303.2472v1 (2013).
- Niesner, D. *et al.* Unoccupied topological states on bismuth chalcogenides. *Phys. Rev. B* **86**, 205403 (2012).
- Scholz, M. R. *et al.* Reversal of the Circular Dichroism in Angle-Resolved Photoemission from Bi_2Te_3 . *Phys. Rev. Lett.* **110**, 216801 (2013).
- Neupane, M. *et al.* Oscillatory surface dichroism of the insulating topological insulator $\text{Bi}_2\text{Te}_2\text{Se}$. *Phys. Rev. B* **88**, 165129 (2013).
- Hsieh, D. *et al.* Nonlinear optical probe of tunable surface electrons on a topological insulator. *Phys. Rev. Lett.* **106**, 057401 (2011).
- Wunderlich, J. *et al.* Spin Hall effect transistor. *Science* **330**, 1801 (2010).
- Yan, Y. *et al.* Synthesis and field emission properties of topological insulator Bi_2Se_3 nanoflake arrays. *Nanotechnology* **23**, 305704 (2012).
- Yan, Y. *et al.* Synthesis and Quantum Transport Properties of Bi_2Se_3 Topological Insulator Nanostructures. *Sci. Rep.* **3**, 1264 (2013).

Acknowledgments

This work was supported by National Basic Research Program of China (Nos.2013CB921901 and 2012CB921304), the National Natural Science Foundation of China (Nos. 61376095, 11174008, 61361166007 and 60990313), and Beijing Higher Education Young Elite Teacher Project (No. YETP0006).

Author contributions

J.X.D., N.T. and B.S. conceived and designed the experiments. J.X.D. and X.H. performed sample fabrication. Y.Y. grew the CVD Bi_2Se_3 . J.X.D. conducted the measurements. S.Z. and X.D.Q. assisted with measurements and data analysis. J.X.D., N.T. and W.K.G. wrote the paper. X.Q.W., X.L.Y., F.J.X., Y.H.C. and B.S. gave scientific advice. All the authors contributed through scientific discussion.

Additional information

Competing financial interests: The authors declare no competing financial interests.

How to cite this article: Duan, J.X. *et al.* Identification of Helicity-Dependent Photocurrents from Topological Surface States in Bi_2Se_3 Gated by Ionic Liquid. *Sci. Rep.* **4**, 4889; DOI:10.1038/srep04889 (2014).



This work is licensed under a Creative Commons Attribution-NonCommercial-NoDerivs 3.0 Unported License. The images in this article are included in the article's Creative Commons license, unless indicated otherwise in the image credit; if the image is not included under the Creative Commons license, users will need to obtain permission from the license holder in order to reproduce the image. To view a copy of this license, visit <http://creativecommons.org/licenses/by-nc-nd/3.0/>