Yang, C., Cattelan, M., Fox, N., Huang, Y., Golden, M., & Schwarzacher, W. (2019). Electrochemical modification and characterization of topological insulator single crystals. *Langmuir*, 35(8), 2983-2988. <https://doi.org/10.1021/acs.langmuir.8b03801>

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Link to published version (if available):
[10.1021/acs.langmuir.8b03801](https://doi.org/10.1021/acs.langmuir.8b03801)

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Electrochemical modification and characterization of topological insulator single crystals

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ABSTRACT

We compare electrochemically modified or thiol functionalized single-crystal samples of the topological insulator (TI) $\text{Bi}_2\text{Te}_{0.9}\text{Se}_{2.1}$ to freshly cleaved/air exposed control samples, and use X-ray photoelectron spectroscopy (XPS) to investigate the extent of any surface oxidation. XPS spectra for a TI sample maintained at an appropriate potential for 2 hours demonstrate the feasibility of protecting the TI surface from oxidation while working in an electrochemical environment. Deliberate electrochemical oxidation, in contrast, generates prominent Bi, Te and Se peaks associated with oxidation. However, this change is reversible, as further XPS spectra following electrochemical reduction are similar to those measured for an in-situ cleaved sample. XPS also shows that adsorption of pentanedithiol (PDT) protects the TI surface from oxidation. Cyclic voltammetry shows that PDT adsorption suppresses electrochemical oxidation and reduction, while electrochemical impedance spectroscopy shows that it increases the charge transfer resistance significantly. Our work demonstrate the ability to control and characterize the surface chemistry of single-crystal TIs in an electrochemical environment for the first time.

1. INTRODUCTION

The remarkable properties of topological insulators (TIs) make them one of the most exciting materials discoveries of the twenty-first century¹⁻⁴. A TI behaves as an insulator in the bulk but possesses topologically protected metallic surface states (topological surface states - TSS) due to time reversal symmetry and band structure. In the absence of magnetic impurities, spin and momentum locking in these topological states lead to new ways of generating a spin polarized current⁵⁻⁸, which paves the way for novel types of spintronic device. Topological protection means that backscattering is forbidden, so that in appropriate geometries dissipation-less spin currents can be generated in TSSs. Dissipation-free transport of information is a holy grail of modern electronics, as it would avoid the related problems of high energy consumption and the need for cooling. In addition, TSSs are expected to provide a promising platform for surface chemistry and catalysis: both positive and negative effects on the hydrogen evolution reaction (HER) were discovered for different metal clusters supported on Bi_2Se_3 ⁹. Furthermore, many exotic physical phenomena occurred at the

interfaces of heterostructures incorporating TIs surface¹⁰⁻¹³, such as Majorana fermions at a TI/superconductor interface¹⁴⁻¹⁵ or the anomalous quantum hall effect at TI/magnetic material interfaces¹⁶.

The ability to work in air or solution is a precondition for many practical applications. Although there have been several attempts to study the properties of the three-dimensional TIs Bi₂Se₃ and Be₂Te₃ following exposure to air or water, results to date partly disagree. There are some reports that Bi₂Se₃ or Bi₂Te₃ surfaces are inert¹⁷⁻¹⁸. However, the majority of work indicates that exposure to air or water can modify TI surface chemistry, and that this will affect the TI surface electronic properties despite the robustness of surface states. Effects observed include a clear shift of chemical potential after exposure of Bi₂Te₃ to air¹⁹ and the observation of two different reconstructed surfaces for long term air-exposed Bi₂Se₃, one of which had a notable presence of neutral selenium²⁰. Other workers observed strong modification or disappearance of the TSS for Bi₂Se₃ and Bi₂Te₃ after air-exposure²¹⁻²³. Therefore, to make good use of the exotic properties of TIs, there is an urgent need to protect the surface and control its chemistry in air/aqueous solution.

Here we show firstly that the surface chemistry of a Bi₂Te_{0.9}Se_{2.1} single crystal can be controlled in an electrochemical environment with considerable precision, and secondly that electrochemical methods can be used to study the effects of TI exposure to organic molecules. Bi₂Te_{0.9}Se_{2.1} was chosen for surface chemical study as a representative of the family of TIs that includes Bi₂Se₃ and Bi₂Te₃. Single-crystal Bi₂Te_{0.9}Se_{2.1} has previously been shown to possess topological surface states despite the metallic nature of the bulk conductivity²⁴. We use X-ray photoelectron spectroscopy (XPS) to obtain element-specific information on any surface oxidation. An in-situ cleaved TI sample shows no evidence of oxidation, whereas air-exposed samples show different degrees of oxidation depending on the exposure duration. Interestingly, a sample that was immersed in electrolyte at a potential where neither oxidation nor reduction was expected, shows much greater similarity to the in-situ cleaved sample rather than those exposed to air, establishing the feasibility of electrochemical protection. To verify the feasibility and reversibility of electrochemical modification, we electrochemically oxidized a sample by applying a positive potential, and as expected, the Bi, Te and Se XPS peaks changed significantly. The changes took place at approximately the same binding energies as for air exposure, but were much more extensive. However, applying a negative potential to reduce the sample removed the effects of oxidation and generated spectra that were remarkably similar to those from the in-situ cleaved sample.

Electrochemical methods were also used to study the effects of exposing the TI surface to 1,5'-pentanedithiol (PDT), a molecule that can form an organic capping layer. Comparing the cyclic voltammograms (CVs) and electrochemical impedance spectroscopy (EIS) before and after PDT adsorption, we find many changes: the redox peaks associated with the TI are strongly suppressed, while the charge transport resistance increases significantly. The XPS of a PDT functionalized sample exposed to air for 2 days shows no oxidation peaks for Bi, Te and Se, whereas clear oxidation peaks for those elements are observed in XPS of a sample exposed to air for the same time.

2. EXPERIMENTAL METHODS

Single crystals of $\text{Bi}_2\text{Te}_{0.9}\text{Se}_{2.1}$ were grown by a modified Bridgman method. The starting materials were high purity (99.9999%) elements of Bi, Se and Te. The desired components were mixed and sealed in an evacuated cone-ended quartz ampoule, which was heated up to 900°C , held for 24 hours, and then cooled down to 600°C at a rate of 2°C per hour, followed by furnace cooling. Surfaces were prepared for study by sticking carbon tape to a single-crystal surface, then pulling the tape away to leave a freshly cleaved surface. Samples were cleaved in air or (in the case of the in-situ cleaved surface) under high vacuum in the XPS load-lock chamber.

The reagents 1,5'-pentanedithiol (PDT), pentanethiol, ethanol, Na_2SO_4 , H_2SO_4 were purchased from Aldrich and used as received. For electrochemical measurements without subsequent XPS characterization, the crystal was mounted on a gold substrate using carbon paste, and then insulated with nail polish (Essie brand) and Kapton tape. For XPS measurements, the crystal was mounted on copper foil using conductive silver epoxy (EPO-TEK). To permit electrochemical modification, the copper foil was covered with Kapton tape, and insulating epoxy (MG Chemicals) was used to insulate the gap between the crystal and the Kapton tape.

CVs and EIS measurements were performed using an Autolab PGSTAT302 potentiostat with FRA2 electrochemical impedance spectroscopy module, while electrochemical modifications were performed using a Biologic SP-150 potentiostat. We used a conventional three-electrode set-up with a mercury-mercurous sulfate reference electrode (MSE) and a platinum foil counter electrode. The electrolyte used for all the electrochemical experiments was 0.05M Na_2SO_4 in MilliQ water at pH3 (adjusted by H_2SO_4 addition). Thiol functionalization was achieved by placing a freshly cleaved sample in a small beaker and then putting the small beaker in a large beaker which contains thiol. This procedure avoids direct contact between the sample and liquid thiol. The large beaker was sealed with parafilm and left in a fume cupboard for 48 hours before the sample was removed. The sample was rinsed in copious amounts of ethanol before XPS measurements.

XPS analyses were carried out at the Bristol NanoESCA Facility working at a base pressure of 4.0×10^{-11} mbar. XPS high-resolution spectra were collected using an ARGUS analyser and monochromatic Al K_α source (1486.7eV). The binding energy scale is calibrated with the Au 4f $7/2$ at 84 eV. The analysis area is of few mm^2 spot size and the pass energy is 20 eV, with an overall energy resolution of about 600 meV.

3. RESULTS AND DISCUSSION

We start by showing the electrochemical behaviour of a freshly cleaved $\text{Bi}_2\text{Te}_{0.9}\text{Se}_{2.1}$ TI sample. Figure 1 presents a set of cyclic voltammograms (CVs) in which the turning points are extended to successively more positive and more negative potentials. The CV for which the positive turning point is 0.1 V and the negative turning point -0.9V is the first to show evidence of a redox reaction, starting at 0.1 V. The presence of an oxidation peak starting at around 0.1 V is confirmed by the appearance of a small reduction peak at around -0.6V in the first cycle (red trace) of the following CV that covers the range between 0.2 V and -1.0V. The red trace also shows a significant oxidation current above 0.1V, and this additional oxidation

current means that in the following cycle (blue trace) the reduction peak at -0.6V is much more pronounced. The CVs were used to define potentials for subsequent electrochemical oxidation and reduction experiments (see later).

Figure 1. Cyclic voltammograms for a freshly cleaved $\text{Bi}_2\text{Te}_{0.9}\text{Se}_{2.1}$ single crystal as the scan range is extended. The green traces are for the ranges (-0.6V, -0.2V), (-0.7V, -0.1V), (-0.8V, 0.0V), and (-0.9V, 0.1V) successively. The red trace is the first cycle for the range (-1.0V, 0.2V), while the blue one is part of the second cycle for the same range. The black arrow shows the scan sense, while the purple squares mark the potentials at which the electrochemical oxidation and reduction experiments described later were performed. All experiments were carried out in an aqueous 0.05M Na_2SO_4 electrolyte at pH3, and all potentials are stated relative to a mercury-mercurous sulfate reference electrode.

The CVs also suggest that because no oxidation or reduction currents are observed at -0.3 V the TI sample should be protected from both oxidation and reduction at this potential. This is confirmed by Figure 2, which compares a sample maintained in the aqueous 0.05M Na_2SO_4 electrolyte for 2 hours (2h) with an in-situ cleaved sample, and one that was exposed to air for 2h. Although a sample exposed to air for a shorter time of 20min did not show obvious signs of oxidation (see Figure S1), such signs are clearly seen in the XPS data for the 2h air exposed sample (middle row). Interestingly, different elements show very different sensitivity to air exposure. The Bi 4f (Figure 2a) and Se 3d (Figure 2c) indicate bismuth and selenium are little affected by exposure to air for 2 hours, whereas in the Te 3d an additional doublet appears, labelled Te-O at 576.1 and 586.5eV, respectively, consistent with previous measurements on TeO_2^{25} (Figure 2b).

Bi_2Se_3 and Bi_2Te_3 consist of strongly-bonded quintuplets with the layer structure chalcogenide - Bi - chalcogenide - Bi - chalcogenide. These quintuplets are weakly bonded to each other via

van der Waals interactions²⁶. Calculations suggest that a Bi_2TeSe_2 structure with the outermost layers of each quintuplet consisting of 50 % Te and 50% Se would have a very low energy²⁷. If our $\text{Bi}_2\text{Te}_{0.9}\text{Se}_{2.1}$ also has approximately 50% Te and 50% Se in the outermost layers, this would facilitate Te oxidation as observed.

Comparison of the top curves of Figure 2 with the remaining curves shows that the XPS data for the electrochemically protected sample is much closer to the XPS data for the in-situ cleaved sample than for the sample exposed to air for the same length of time. This shows the feasibility of electrochemical protection. XPS data for Bi 5d, Te 4d and Se 3s (see Figure S3) lead to the same conclusions.

Figure 2. Bi 4f (a), Te 3d (b) and Se 3d (c) XPS for in-situ cleaved (bottom), 2 hour (2h) air exposed (middle) and 2h electrochemically protected - see text - (top) samples. The Te 3d XPS of the 2h air exposed sample shows oxidation peaks (middle curve in Figure 2(b)), whereas the in-situ cleaved sample and the electrochemically protected sample show no evidence of oxidation. NB the small peak in the top curve of Figure 2 (c) is due to Na 2s rather than oxidized Se, and may be attributed to residual electrolyte (Na_2SO_4).

The effect of electrochemical oxidation and reduction on the $\text{Bi}_2\text{Te}_{0.9}\text{Se}_{2.1}$ surface chemistry was also examined by XPS (Figure 3). The applied potentials (i.e. 0.1V and -0.6V) were chosen as they correspond to the oxidation and reduction peaks respectively in the CV of the clean surface (Figure 1). The curves at the bottom of Figure 3 show that electrochemical oxidation has a significant effect on our sample. The Bi, Te and Se oxide peaks are even more prominent for the electrochemically oxidized sample than for the 2-day air exposed sample. The Bi $4f_{7/2}$ oxide peak is shown in yellow in Figure 3a. The centre of this peak is at 159.2eV for the electrochemically oxidized sample while it is at 158.8eV for the 2-day air exposed sample which could indicate that electrochemical oxidation and air oxidation give rise to different oxide species²⁸⁻³⁰. Any other peak shifts are much smaller. The small shoulder on the Bi $4f_{7/2}$ peak that is shown in purple in Figure 3a is not associated with oxide³¹. XPS data for the electrochemically oxidized sample after subsequent electrochemical reduction are shown in the curves at the top of Figure 3. There is evidence for at most minimal oxidation in the Bi 4f spectra and Se 3d spectra, although very small Te oxide peaks are apparent. Tellurium is the most sensitive of the three elements to oxidation, and it is possible that some oxidation took place while the sample was being washed and transferred to the vacuum system.

Nevertheless, the electrochemically reduced surface resembles the in-situ cleaved surface (Figure 2 bottom curves) much more than the electrochemically oxidized surface.

Figure 3. Bi 4f (a), Te 3d (b) and Se 3d (c) XPS for electrochemically (EC) oxidized (bottom), 2-day air exposed (middle) and EC reduced (top) samples. The EC oxidized sample shows greater evidence of oxidation than the sample exposed to air for 2 days, which reflects the high efficiency of electrochemical surface modification. The reversibility of this EC modification is confirmed by the similarity of the EC reduced and the in-situ cleaved (Figure 2 bottom curves) data. For a discussion of the peak deconvolution (coloured lines in Figure 3a), see main text.

Another interesting phenomenon is shown in Figure 4. The current and charge recorded during electrochemical oxidation and reduction show significant differences. The current during oxidation was stable at around 0.05mA for approximately 50 seconds after which it fell rapidly. The total charge passed was approximately 3mC. Assuming that 6 electrons are released per oxidized Te or Se atom (from -2 to +4), and the density of $\text{Bi}_2\text{Te}_{0.9}\text{Se}_{2.1}$ is 7.6g per cm^3 , this charge corresponds to an oxidized thickness of 15nm if we take the sample surface area (0.1 cm^2) into account. During reduction, the current was significantly smaller than during oxidation, decreasing monotonically to around 10^{-4} mA . The total charge passed during reduction was also much less than during oxidation: approximately 0.08mC after 10 minutes. This mismatch of oxidation and reduction current/charge could be explained if significant dissolution takes place during oxidation. We hypothesize that the fall in the oxidation current after around 50 seconds corresponds to the termination of dissolution following passivation of the surface by insoluble oxide species. During reduction, only enough current/charge is required to reduce these surface oxide species, since the other oxidation products have passed into solution. However, exactly what causes any transition between dissolution and passivation is still not clear.

As an alternative to electrochemical protection, previous work has shown that self-assembled monolayers of organic molecules such as alkanethiols can protect reactive surfaces e.g. Ni or Co from oxidation³²⁻³⁶. We therefore investigated how adsorbing a layer of 1,5'-pentanedithiol (PDT) affects the electrochemical response and XPS signal from the $\text{Bi}_2\text{Te}_{0.9}\text{Se}_{2.1}$ TI. Figure 5a compares CVs for a freshly cleaved surface and one on which PDT

Figure 4. Current (blue lines) and charge (red lines) versus time for the electrochemical oxidation (a) and reduction processes (b).

was adsorbed. The difference in oxidation peaks between the first and subsequent cycles for the clean surface is evidence that the first cycle has already modified the surface. After thiol functionalization, the current decreases significantly, and the oxidation peaks around 0.1V-0.4V and reduction peak around -0.6V disappear, indicating that the adsorbed PDT has passivated the surface. Figure 5b plots the imaginary part of the measured electrochemical impedance Z'' versus the real part Z' (Nyquist plot) for the clean surface and the surface following PDT adsorption. The low Z' part of the Nyquist plot is approximately a semicircle, which is the shape expected for a simple circuit consisting of a resistor R_s , representing the uncompensated solution resistance, in series with a parallel capacitor and resistor R_{ct} , representing the charge transfer resistance. The low Z' intersection of the semicircle with the real axis is equal to R_s , and is measured at high frequencies, while the high Z' intersection is equal to $R_s + R_{ct}$, and is measured at low frequencies. Since this intersection is significantly larger following PDT adsorption, so too is the charge transfer resistance, as expected if the surface is passivated.

Figure 6 compares XPS spectra from a $\text{Bi}_2\text{Te}_{0.9}\text{Se}_{2.1}\text{TI}$ following PDT adsorption with equivalent spectra for an unprotected sample after each was exposed to air for 2 days (the data for the unprotected sample was previously presented in Figure 3). In contrast to the clear evidence

Figure 5. Electrochemical data for a $\text{Bi}_2\text{Te}_{0.9}\text{Se}_{2.1}$ TI sample before (blue) and after pentanedithiol (PDT) adsorption (red). Cyclic voltammograms (a) and electrochemical impedance data (b) change significantly after PDT functionalization, which is a clear indicator that the surface is passivated. 1st and 2nd in (a) refer to the cycle number. Z' and Z'' are respectively the real and imaginary parts of the electrochemical impedance. The green semicircles are fits to the data and the insert is a magnification of the EIS before PDT functionalization.

Figure 6. Bi 4f (a), Te 3d(b) and Se 3d (c) XPS for an unprotected sample (bottom - the same data as the middle curves of Figure 3) and one on which PDT was adsorbed (top) after each was exposed to air for 2 days.

of oxidation in the XPS from the unprotected sample, the XPS peaks for the sample on which PDT was adsorbed resemble those for the in-situ cleaved sample. This means PDT can protect the surface from oxidation for a relatively long period. For comparison, we also investigated the effect of exposing the TI to pentanethiol (PT) vapour. As can be seen from Figure S2, PT is much less effective at protecting the surface from oxidation than PDT. Alkanedithiols can polymerize spontaneously in vapour³⁷⁻³⁸, hence the reason that PDT is so effective in preventing oxidation may be that it forms a relatively thick layer on adsorption due to polymerization.

4. SUMMARY AND CONCLUSIONS

We demonstrated using XPS that $\text{Bi}_2\text{Te}_{0.9}\text{Se}_{2.1}$ topological insulator (TI) single crystals exposed to air will undergo oxidation on a time scale of hours. We further showed that this oxidation could be avoided, enhanced or even reversed when the sample was immersed in an aqueous electrolyte under potential control. In the case of electrochemical oxidation we observed evidence for a transition from dissolution to passivation. We also used electrochemical methods to show that pentanedithiol adsorption can passivate the TI surface, suppressing redox currents and greatly increasing the charge transfer resistance measured by electrochemical impedance spectroscopy. Pentanethiol shows only limited effectiveness in this respect, possibly because unlike the dithiol, it does not polymerize. Our work shows that electrochemical methods provides a simple and highly controllable means of modifying and characterizing TI surface chemistry.

SUPPORTING INFORMATION DESCRIPTION

XPS for short time air exposed sample; XPS for pentanethiol functionalized sample; Bi 5d, Te 4d and Se 3s XPS for in-situ cleaved, air exposed and EC modified samples; SEM images of the $\text{Bi}_2\text{Te}_{0.9}\text{Se}_{2.1}$ crystal; Cyclic voltammograms of clean and PDT functionalized samples with different potential ranges.

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ACKNOWLEDGEMENTS

The authors acknowledge the Bristol NanoESCA Facility (EPSRC Strategic Equipment Grant EP/K035746/1 and EP/M000605/1).

Chaolong Yang acknowledges China Scholarship Council for financial support.

REFERENCES

1. Qi, X.-L.; Zhang, S.-C., Topological insulators and superconductors. *Reviews of Modern Physics* **2011**, *83* (4), 1057-1110.
2. Ando, Y., Topological Insulator Materials. *Journal of the Physical Society of Japan* **2013**, *82* (10), 102001.
3. He, L.; Kou, X.; Wang, K. L., Review of 3D topological insulator thin-film growth by molecular beam epitaxy and potential applications. *physica status solidi (RRL) – Rapid Research Letters* **2013**, *7* (1-2), 50-63.
4. Fu, L.; Kane, C. L., Topological insulators with inversion symmetry. *Physical Review B* **2007**, *76* (4), 045302.
5. Li, C. H.; van 't Erve, O. M. J.; Robinson, J. T.; Liu, Y.; Li, L.; Jonker, B. T., Electrical detection of charge-current-induced spin polarization due to spin-momentum locking in Bi₂Se₃. *Nature Nanotechnology* **2014**, *9*, 218.
6. Rojas-Sánchez, J. C.; Oyarzún, S.; Fu, Y.; Marty, A.; Vergnaud, C.; Gambarelli, S.; Vila, L.; Jamet, M.; Ohtsubo, Y.; Taleb-Ibrahimi, A.; Le Fèvre, P.; Bertran, F.; Reyren, N.; George, J. M.; Fert, A., Spin to Charge Conversion at Room Temperature by Spin Pumping into a New Type of Topological Insulator: α -Sn Films. *Physical Review Letters* **2016**, *116* (9), 096602.
7. Ando, Y.; Hamasaki, T.; Kurokawa, T.; Ichiba, K.; Yang, F.; Novak, M.; Sasaki, S.; Segawa, K.; Ando, Y.; Shiraishi, M., Electrical Detection of the Spin Polarization Due to Charge Flow in the Surface State of the Topological Insulator Bi_{1.5}Sb_{0.5}Te_{1.7}Se_{1.3}. *Nano Letters* **2014**, *14* (11), 6226-6230.
8. Pesin, D.; MacDonald, A. H., Spintronics and pseudospintronics in graphene and topological insulators. *Nature Materials* **2012**, *11*, 409.
9. Xiao, J.; Kou, L.; Yam, C.-Y.; Frauenheim, T.; Yan, B., Toward Rational Design of Catalysts Supported on a Topological Insulator Substrate. *ACS Catalysis* **2015**, *5* (12), 7063-7067.
10. Hirahara, T.; Bihlmayer, G.; Sakamoto, Y.; Yamada, M.; Miyazaki, H.; Kimura, S.-i.; Blügel, S.; Hasegawa, S., Interfacing 2D and 3D Topological Insulators: Bi(111) Bilayer on. *Physical Review Letters* **2011**, *107* (16), 166801.
11. Liu, X.; Guo, W., Intrinsic Rashba-like splitting in asymmetric Bi₂Te₃/Sb₂Te₃ heterogeneous topological insulator films. *Applied Physics Letters* **2014**, *105* (8), 082401.
12. Yilin, W.; Yeping, J.; Mu, C.; Zhi, L.; Canli, S.; Lili, W.; Ke, H.; Xi, C.; Xucun, M.; Qi-Kun, X., Scanning tunneling microscopy of interface properties of Bi₂Se₃ on FeSe. *Journal of Physics: Condensed Matter* **2012**, *24* (47), 475604.
13. Zhang, J.; Triola, C.; Rossi, E., Proximity Effect in Graphene--Topological-Insulator Heterostructures. *Physical Review Letters* **2014**, *112* (9), 096802.
14. Koren, G.; Kirzhner, T.; Lahoud, E.; Chashka, K. B.; Kanigel, A., Proximity-induced superconductivity in topological Bi₂Te₂Se and Bi₂Se₃ films: Robust zero-energy bound state possibly due to Majorana fermions. *Physical Review B* **2011**, *84* (22), 224521.
15. Wang, M.-X.; Liu, C.; Xu, J.-P.; Yang, F.; Miao, L.; Yao, M.-Y.; Gao, C. L.; Shen, C.; Ma, X.; Chen, X.; Xu, Z.-A.; Liu, Y.; Zhang, S.-C.; Qian, D.; Jia, J.-F.; Xue, Q.-K., The Coexistence of Superconductivity and Topological Order in the Bi₂Se₃ Thin Films. *Science* **2012**, *336* (6077), 52.
16. Jiang, H.; Qiao, Z.; Liu, H.; Niu, Q., Quantum anomalous Hall effect with tunable Chern number in magnetic topological insulator film. *Physical Review B* **2012**, *85* (4), 045445.
17. Atuchin, V. V.; Golyashov, V. A.; Kokh, K. A.; Korolkov, I. V.; Kozhukhov, A. S.; Kruchinin, V. N.; Makarenko, S. V.; Pokrovsky, L. D.; Prosvirin, I. P.; Romanyuk, K. N.; Tereshchenko, O. E., Formation of Inert Bi₂Se₃(0001) Cleaved Surface. *Crystal Growth & Design* **2011**, *11* (12), 5507-5514.
18. Yashina, L. V.; Sánchez-Barriga, J.; Scholz, M. R.; Volykhov, A. A.; Sirotina, A. P.; Neudachina, V. S.; Tamm, M. E.; Varykhalov, A.; Marchenko, D.; Springholz, G.; Bauer, G.; Knop-Gericke, A.; Rader, O., Negligible Surface Reactivity of Topological Insulators Bi₂Se₃ and Bi₂Te₃ towards Oxygen and Water. *ACS Nano* **2013**, *7* (6), 5181-5191.

19. Hoefler, K.; Becker, C.; Rata, D.; Swanson, J.; Thalmeier, P.; Tjeng, L. H., Intrinsic conduction through topological surface states of insulating Bi₂Te₃ epitaxial thin films. *Proceedings of the National Academy of Sciences* **2014**, *111* (42), 14979.
20. Edmonds, M. T.; Hellerstedt, J. T.; Tadich, A.; Schenk, A.; O'Donnell, K. M.; Tosado, J.; Butch, N. P.; Syers, P.; Paglione, J.; Fuhrer, M. S., Stability and Surface Reconstruction of Topological Insulator Bi₂Se₃ on Exposure to Atmosphere. *The Journal of Physical Chemistry C* **2014**, *118* (35), 20413-20419.
21. Chen, C.; He, S.; Weng, H.; Zhang, W.; Zhao, L.; Liu, H.; Jia, X.; Mou, D.; Liu, S.; He, J.; Peng, Y.; Feng, Y.; Xie, Z.; Liu, G.; Dong, X.; Zhang, J.; Wang, X.; Peng, Q.; Wang, Z.; Zhang, S.; Yang, F.; Chen, C.; Xu, Z.; Dai, X.; Fang, Z.; Zhou, X. J., Robustness of topological order and formation of quantum well states in topological insulators exposed to ambient environment. *Proceedings of the National Academy of Sciences* **2012**, *109* (10), 3694.
22. Kong, D.; Cha, J. J.; Lai, K.; Peng, H.; Analytis, J. G.; Meister, S.; Chen, Y.; Zhang, H.-J.; Fisher, I. R.; Shen, Z.-X.; Cui, Y., Rapid Surface Oxidation as a Source of Surface Degradation Factor for Bi₂Se₃. *ACS Nano* **2011**, *5* (6), 4698-4703.
23. Ngabonziza, P.; Heimbuch, R.; de Jong, N.; Klaassen, R. A.; Stehno, M. P.; Snelder, M.; Solmaz, A.; Ramankutty, S. V.; Frantzeskakis, E.; van Heumen, E.; Koster, G.; Golden, M. S.; Zandvliet, H. J. W.; Brinkman, A., In situ spectroscopy of intrinsic Bi₂Te₃ topological insulator thin films and impact of extrinsic defects. *Physical Review B* **2015**, *92* (3), 035405.
24. Shrestha, K.; Marinova, V.; Lorenz, B.; Chu, P. C. W., Shubnikov-de Haas oscillations from topological surface states of metallic Bi₂Se_{2.1}Te_{0.9}. *Physical Review B* **2014**, *90* (24), 241111.
25. Bahl, M. K.; Watson, R. L.; Irgolic, K. J., X-ray photoemission studies of tellurium and some of its compounds. *The Journal of Chemical Physics* **1977**, *66* (12), 5526-5535.
26. Shu, G. J.; Liou, S. C.; Karna, S. K.; Sankar, R.; Hayashi, M.; Chou, F. C., Dynamic surface electronic reconstruction as symmetry-protected topological orders in topological insulator Bi₂Se₃. *Physical Review Materials* **2018**, *2* (4), 044201.
27. Wang, L.-L.; Johnson, D. D., Ternary tetradymite compounds as topological insulators. *Physical Review B* **2011**, *83* (24), 241309.
28. Morgan, W. E.; Stec, W. J.; Van Wazer, J. R., Inner-orbital binding-energy shifts of antimony and bismuth compounds. *Inorganic Chemistry* **1973**, *12* (4), 953-955.
29. Debies, T. P.; Rabalais, J. W., X-ray photoelectron spectra and electronic structure of Bi₂X₃ (X= O, S, Se, Te). *Chemical Physics* **1977**, *20* (2), 277-283.
30. Afsin, B.; Roberts, M., Formation of an oxy-chloride overlayer at a Bi (0001) surface. *Spectroscopy letters* **1994**, *27* (1), 139-146.
31. Zhang, G.; Qin, H.; Teng, J.; Guo, J.; Guo, Q.; Dai, X.; Fang, Z.; Wu, K., Quintuple-layer epitaxy of thin films of topological insulator Bi₂Se₃. *Applied Physics Letters* **2009**, *95* (5), 053114.
32. Sadler, J. E.; Szumski, D. S.; Kierzkowska, A.; Catarelli, S. R.; Stella, K.; Nichols, R. J.; Fonticelli, M. H.; Benitez, G.; Blum, B.; Salvarezza, R. C.; Schwarzacher, W., Surface functionalization of electro-deposited nickel. *Physical Chemistry Chemical Physics* **2011**, *13* (40), 17987-17993.
33. Mekhalif, Z.; Laffineur, F.; Couturier, N.; Delhalle, J., Elaboration of Self-Assembled Monolayers of n-Alkanethiols on Nickel Polycrystalline Substrates: Time, Concentration, and Solvent Effects. *Langmuir* **2003**, *19* (3), 637-645.
34. Petrović, Ž.; Metikoš-Huković, M.; Harvey, J.; Omanovic, S., Enhancement of structural and charge-transfer barrier properties of n-alkanethiol layers on a polycrystalline copper surface by electrochemical potentiodynamic polarization. *Physical Chemistry Chemical Physics* **2010**, *12* (25), 6590-6593.
35. Noel, S.; Houze, F.; Boyer, L.; Mekhalif, Z.; Delhalle, J.; Caudano, R., Self-assembled monolayers of alkanethiols on nickel surfaces for low level electrical contact applications. *IEEE Transactions on Components and Packaging Technologies* **1999**, *22* (1), 79-84.
36. Catarelli, S. R.; Higgins, S. J.; Schwarzacher, W.; Mao, B.-W.; Yan, J.-W.; Nichols, R. J., Ionic Liquid Based Approach for Single-Molecule Electronics with Cobalt Contacts. *Langmuir* **2014**, *30* (47), 14329-14336.

37. Zheng, J.; Liu, J.; Zhuo, Y.; Li, R.; Jin, X.; Yang, Y.; Chen, Z.-B.; Shi, J.; Xiao, Z.; Hong, W.; Tian, Z.-q., Electrical and SERS detection of disulfide-mediated dimerization in single-molecule benzene-1,4-dithiol junctions. *Chemical Science* **2018**, *9* (22), 5033-5038.
38. Wang, L.; Li, S.-Y.; Yuan, J.-H.; Gu, J.-Y.; Wang, D.; Wan, L.-J., Electron Transport Characteristics of the Dimeric 1,4-Benzenedithiol Junction. *Chemistry – An Asian Journal* **2014**, *9* (8), 2077-2082.