

Perspective towards atomic-resolution imaging of two-dimensional polymers

Haoyuan Qi^{1,2}  | Baokun Liang¹ | Ute Kaiser¹

¹Central Facility of Electron Microscopy, Electron Microscopy Group of Materials Science, Universität Ulm, Ulm, Germany

²Center for Advancing Electronics Dresden (cfaed), Faculty of Chemistry and Food Chemistry, Technische Universität Dresden, Dresden, Germany

Correspondence

Dr. Haoyuan Qi and Ute Kaiser, Central Facility of Electron Microscopy, Electron Microscopy Group of Materials Science, Universität Ulm, Ulm 89081, Germany.

Email: haoyuan.qi@uni-ulm.de and ute.kaiser@uni-ulm.de

Funding information

Deutsche Forschungsgemeinschaft, Grant/Award Numbers: SFB1415, 417590517; GrapheneCore3, Grant/Award Numbers: 881603, 785219

Abstract

Recent years have witnessed the rise of an emerging class of synthetic two-dimensional (2D) materials-2D polymers. The combination of organic chemistry and rational design of polymeric crystals has stimulated tremendous research efforts in the controlled synthesis of 2D polymers. However, despite the advancement in synthetic methodologies, the structural characterization of 2D polymers remains a significant challenge. Although aberration-corrected high-resolution transmission electron microscopy (AC-HRTEM) is capable of direct imaging of atomic structures with sub-Ångström resolution, electron radiation damage poses a substantial limit on the achievable image resolution due to instant decomposition of the molecular framework. In this Perspective, we will briefly discuss radiation damage mitigation strategies, which may eventually result in AC-HRTEM imaging of 2D polymers down to the atomic scale.

KEYWORDS

covalent organic frameworks, transmission electron microscopy, two-dimensional polymers

1 | CHALLENGES

Two-dimensional (2D) polymers, comprising covalently bonded repeating units with well-defined periodicity along with two orthogonal directions, have attracted great interest in recent years.^{1,2} Due to the structural and functional diversity of monomers and their linkage chemistry, the fabrication of 2D polymers opens up an appealing route to the rational design of 2D materials tailored for future applications in catalysis, adsorption and separation, and energy conversion and storage.^{1,2} Recently, extensive efforts have been devoted to synthesizing highly crystalline 2D polymers and covalent organic frameworks (COFs).¹⁻⁴ The single-crystal-to-single-crystal approach has led to the successful synthesis of highly-crystalline 2D polymer particles with

typical sizes ranging from tens to hundreds of micrometers, allowing for structural elucidation via single-crystal X-ray diffraction (SC-XRD) even down to atomic scale.⁵⁻⁷ Subsequent liquid-phase exfoliation gives rise to dispersions of 2D polymer nanosheets.⁸ However, the homogeneity in their thickness and lateral size, as well as the exfoliation yield, remain to be improved, posing potential limitations on the device integration of the top-down fabricated 2D polymer nanosheets. Alternatively, a bottom-up synthetic route has emerged in the last few years. Air-water,^{9,10} surfactant-assisted air-water,¹¹⁻¹⁴ as well as liquid-liquid interfaces¹⁵ have been explored for the fabrication of 2D polymer thin films. The interfaces could act as efficient templates for 2D-confined polymerization, affording thin films with the controlled thickness (from a monolayer to a few tens of

This is an open access article under the terms of the Creative Commons Attribution License, which permits use, distribution and reproduction in any medium, provided the original work is properly cited.

© 2021 The Authors. *SmartMat* published by Tianjin University and John Wiley & Sons Australia, Ltd

nanometers) and defined crystallographic orientations. The thin films can be readily transferred onto arbitrary substrates, greatly facilitating their device integration. Nonetheless, the thinness (thus limited bulk volume) of 2D polymer thin films renders them unamenable to SC-XRD or single-crystal electron diffraction as in the case of bulk 2D polymer and COF particles.^{5-7,16} It is, therefore, necessary to probe the molecular structures using microscopic techniques. Table 1 summarizes the comparison between several structural characterization methods.

At the dawn of the century, spherical-aberration-corrected high-resolution transmission electron microscopy (AC-HRTEM) has been proven a powerful technique revealing inorganic material structures with sub-Ångström resolution at relatively high voltages between 200 and 300 kV.^{17,18} Recently, in the framework of the sub-Ångström low-voltage electron microscopy project SALVE (www.salve-project.de), atomic resolution imaging has been achieved down to low voltages between 80 and 20 kV, which is enabled by the successful implementation of a novel spherical and chromatic aberration corrector.¹⁹ To date, AC-HRTEM imaging has been extensively applied in resolving the atomic structures of a broad spectrum of inorganic 2D materials, such as graphene and transition metal dichalcogenides (TMDCs).^{20,21} Furthermore, in situ observation of dynamic processes in inorganic 2D materials, including crystallization, defect formation and evolution, catalysis, is readily achievable.²²⁻²⁴ Nonetheless, the structural elucidation of organic 2D materials, such as 2D polymers and COFs, remains a challenging task even on the unit-cell level. The main difficulty originates from electron radiation damage.^{25,26} During TEM imaging, the incident electrons transfer kinetic energy to atoms of the molecules. The impact of the incident electrons triggers atomic displacement, bond scission, and various chemical reactions, degrading the structural integrity of the specimen. The extremely high sensitivity of the organic materials towards electron radiation leads to a substantial gap between the instrumental resolution and achievable image resolution. Put differently, the quality

of TEM data is not limited by the resolution of the TEM optics but rather by the stability of the specimens under the electron beam.

We envisage that the difficulty in elucidating molecular/atomic structures in 2D polymers and COFs may pose multifold limitations on the further development of this emerging class of materials. A few important aspects are listed below.

- (1) Establishment of robust structure–property correlations.

With the rapid advancement of synthetic methodologies, featuring ever-growing crystallinity and larger single-crystalline grain size, the overall functionality of 2D polymer thin films will be substantially affected by local structural variations, such as defects and grain boundaries (Figure 1A). In their inorganic counterparts, for example, graphene and TMDCs, defects have been found to predominate the materials' electronic, mechanical, and magnetic properties.^{27,28} Subsequent elucidation on the defect–property correlation has even stimulated vigorous efforts in defect engineering, in which specific types of defects have been introduced intentionally to modulate the functionalities of inorganic 2D materials and to enhance device performance.²⁹ For 2D polymers and COFs, however, probing defect structures alone is already a formidable task,³⁰⁻³² hindering the investigation of defect–property relationship in these materials.

- (2) Understanding of pore interfaces and their functionalization.

Due to the enormous selection of monomers and linkage types from organic chemistry, the pore size and shape of 2D polymers and COFs can be rationally designed and constructed. On top of that, the pore interface can be further functionalized by incorporating specific side groups to fulfill a broad spectrum of application needs (Figure 1B).³³ Yet, since changing the side groups on an identical framework skeleton could not generate distinct powder

TABLE 1 Comparison between structural characterization techniques

Method	Resolution	Averaged or local information	Typical specimen size	Radiation damage
SC-XRD	sub-Å	Averaged	>50 μm	Low
STM	sub-Å	Local	Monolayer	None
SEM	>10 Å	Local	Bulk	High
AC-TEM	sub-Å	Local	<100 nm	High

Abbreviations: AC-TEM, aberration-corrected transmission electron microscopy; SC-XRD, single-crystal X-ray diffraction; SEM, scanning electron microscopy; STM, scanning tunneling microscopy.

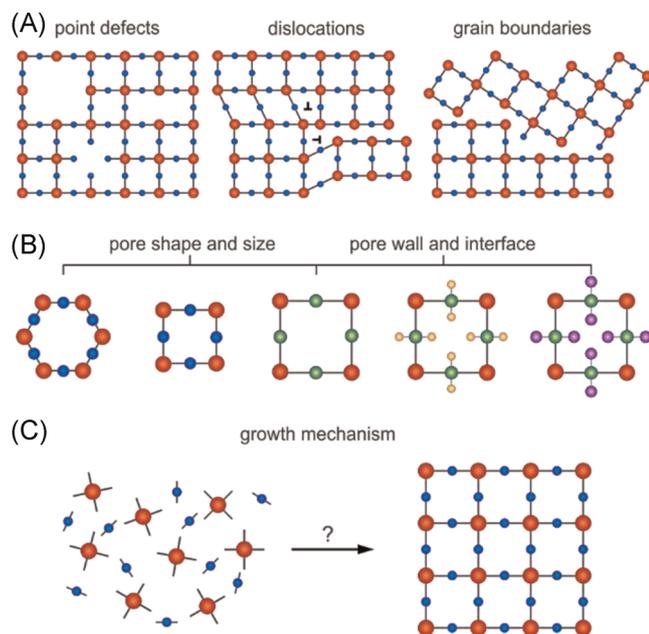


FIGURE 1 (A) Crystal defects in a 2D polymer lattice with square symmetry, for example, missing nodes and missing linker defects, edge-type dislocations, boundary between misoriented grains. (B) Pore engineering in 2D polymers and COFs, rendering framework structures with variant pore shapes, sizes, and side functional groups. (C) Schematic of 2D polymer formation from monomers, which bears further scrutiny. 2D, two-dimensional; COF, covalent organic framework

X-ray patterns. Thus the pore structure characterization is typically reliant on infrared spectroscopy.^{34,35} To date, direct imaging of the functional groups and guest molecules remains mostly unexplored, inhibiting a deeper understanding of host-guest interactions.

(3) Unraveling the growth mechanism of interfacial synthesis.

Although the growth mechanisms of 2D polymer and COF particles under solvothermal conditions have been investigated via spectroscopic and diffraction techniques,⁴ a systematic study of the interfacial growth mechanism, including nucleation, grain expansion and coalescence, Ostwald ripening, and so forth, is still missing (Figure 1C). Liquid-cell TEM has been applied to reveal the reaction dynamics in situ, offering significant insights into the formation mechanisms of materials, for example, nucleation and growth of nanoparticles, assembly of inorganic and organic matters, biomineralization.^{36,37} Notably, recent advancements and implementation of graphene liquid cells have brought liquid-cell TEM into an atomic-resolution era.³⁸ However, for 2D polymers and COFs, the exceedingly high proneness towards electron radiation renders in

situ observation extremely challenging, if not impossible, precluding detailed analysis of interfacial growth mechanisms.

2 | FIGHTING AGAINST ELECTRON RADIATION DAMAGE

Depending on whether the electron beam interacts with the valence electrons of the atoms or atomic nuclei, radiation damage in TEM can be categorized into two groups.²⁶

First, ionization damage (i.e., radiolysis). This type of electron radiation damage originates from the inelastic interaction between the beam electrons and the electrons of the atoms in the specimen. Upon collision, the incident electron transfers a fraction of its kinetic energy to the valence or inner-shell electrons, giving rise to electron excitation and ionization. As valence electrons play a central role in covalent bond formation (seen in 2D polymers and COFs), ionization leads to bond weakening and even direct bond scission. In addition, when the atom relaxes from the excited state to the ground state, the energy released from electron-hole pair recombination may generate secondary electrons. Since ionization energy is fairly low, ranging from a few to a few hundred eV, the secondary electrons may cause a cascade of radiolysis damage events before exiting the specimen. In a theoretical study considering 100-nm-thick polymethyl methacrylate, 80% of the ionization damage has been attributed to secondary electrons with an incident electron energy of 100 keV.³⁹ The atomic ionization leads to not only radiolysis damage but also positive charging within the illuminated area. The electrostatic charging could lead to mechanical vibration/rapture of the specimen. Furthermore, due to energy loss and chromatic aberration of the objective lens, inelastically scattered electrons will no longer be focused onto the Gaussian image plane, causing imaging noise. Inelastic scattering thus leads to not only beam damage but also reduced signal-to-noise (S/N) ratio. Organic materials are extremely prone to ionization damage because of their low electrical conductivity (i.e., longer lifetime of electron-hole pairs and thus weakened bonds) and relatively high specimen thickness (i.e., more damage induced by secondary electrons). As a result, radiolysis is the predominant damage mechanism in conventional organic materials.⁴⁰

How to circumvent ionization damage? Since the cross-section of inelastic scattering is inversely proportional to $1/\beta^2$, where β is the ratio between beam electron velocity and the speed of light, radiolysis can be effectively reduced by operating the TEM under higher

acceleration voltages (e.g., 300 kV). The low-dose imaging technique is simultaneously applied to reach the desired resolution with the minimum amount of incident electrons. Recently, the implementation of a novel type of camera, that is, direct electron detector, has significantly enhanced the detective quantum efficiency (DQE) and S/N ratio. When comparing to conventional charged-couple device cameras, the same resolution can be achieved now with a much lower amount of incident electrons (thus reduced radiation damage).⁴¹ With the novel detection technique, a resolution revolution has started in cryo-TEM imaging on biological specimens a few years ago.⁴² Moreover, by utilizing direct electron detection with monochromator and energy filtering (to remove inelastic noise) and spherical aberration correction, atomic resolution in cryo-EM single-particle analysis has been achieved.^{43,44} For imaging beam-sensitive crystals, direct electron detection and aberration correction have also led to a quantum leap in attainable resolution. For instance, Zhang et al.⁴⁵ have obtained structural information of various metal-organic frameworks (MOFs) down to the atomic scale. The authors successfully identified individual Zr atomic columns and benzene rings in UiO-66, providing significant new insight into MOF surface termination, as well as subtle Zr cluster distortions upon heating. However, despite the remarkable advances in imaging biological specimens and beam-sensitive crystals, sophisticated postimage processing, such as contrast transfer function correction and real-space averaging (or single-particle analysis), is necessary to retrieve the high-resolution information contained in the raw images.⁴⁶ The retrieval of local structures, for example, defects and boundaries, however, is extremely challenging. Because defect structures occur with low frequency thus could not be readily averaged in real space. Furthermore, although systematic optimization of imaging conditions and techniques has resulted in a significant enhancement of image resolution, the intrinsic stability of typical organic crystals remains extremely low,⁴⁵⁻⁴⁷ setting a physical bottleneck on the low-dose approach.

A recent study by Peet et al.⁴⁸ has been focusing on the efficient usage of the incident electrons, such that more information can be extracted per unit damage. In HRTEM imaging, elastically scattered electrons contribute to the image signal. Therefore, S/N ratio can be enhanced by increasing the proportion of elastic scattering. Since the elastic scattering cross-sections are also reversely proportional to $1/\beta^2$, but with a higher slope as compared to that of inelastic scattering, the elastic-inelastic ratio σ_e/σ_i increases logarithmically with decreasing acceleration voltage.²⁶ This rationale seems to favor the use of lower voltages to obtain an optimal S/N

ratio. However, decreasing the voltage leads to reduced scattering mean free path, giving rise to more scattering events and secondary electron production. In other words, the specimen needs to be extremely thin to benefit from the S/N ratio boost.²⁶ Taking into account the σ_e/σ_i ratio and thickness effect, Peet et al.⁴⁸ has defined a new quantity called information coefficient: $\xi = e^{-t/\lambda}\sigma_e/\sigma_i$, where t is the specimen thickness and λ the total mean free path. Figure 2A shows the optimum acceleration voltage for maximum information coefficient as a function of specimen thickness. It appears that, in a low thickness range (which is typically the case for 2D polymers and COFs thin films), using very low acceleration voltage should be beneficial for HRTEM imaging. In addition, the radiolysis damage can be further mitigated by encapsulating the thin specimens in

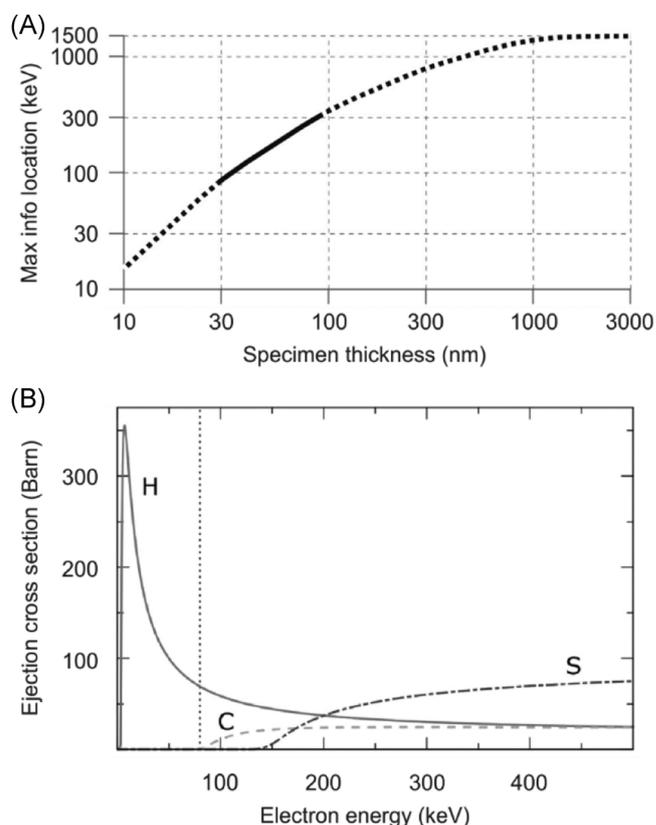


FIGURE 2 (A) Acceleration voltage for maximum information coefficient as a function of specimen thickness. Adapted from Algara-Siller et al.⁵¹ Copyright 2019, Elsevier. (B) Ejection cross-sections as a function of the kinetic energy of the electron beam. For protium isotope of hydrogen (solid line), carbon (dashed line), and sulfur (dashed-dotted line), calculated for sulfur- and hydrogen-terminated graphene nanoribbons as example structures. Notice that upon reduction of the electron beam energy, the stability of carbon and other elements within a molecule increases while the stability of hydrogen atoms decreases sharply. Adapted from Chamberlain et al.⁵² Copyright 2015, Wiley-VCH

graphene.⁴⁹⁻⁵¹ Due to the delocalized π electrons, graphene can as an electron reservoir, scavenging the ionization and charging effects.⁵¹ Yet, another difficulty arises when imaging organic materials under low voltage (*vide infra*).

Apart from radiolysis damage, the direct elastic collisions between the incident electrons and atomic nuclei lead to the knock-on damage. Upon collision, the beam electrons transfer kinetic energy to the specimen, causing the atoms to shift from their equilibrium positions within the molecule. If the energy transferred exceeds the threshold energy, the atom is knocked out from the molecule causing bond dissociation, and the specimen breaks down during imaging. Since the energy transferred to molecules in electron–nucleus interaction is directly proportional to the electron energy, the knock-on damage can be minimized or even eliminated by operating the TEM with an energy below the knock-on threshold. It has been demonstrated that the knock-on threshold energy for C–C and C=S bonds are 85 and 140 keV (Figure 2B), respectively, which means that for TEM analysis of a specimen containing such C–C bonds, the acceleration voltage should be below 85 kV.⁵² However, unlike C–C or C=S bonds, which are highly stable under low voltages, the likelihood of C–H bond dissociation increases sharply as the electron beam energy decreases below 100 keV (Figure 2B). The instability of C–H bond originates mainly from the exceptionally low atomic weight of hydrogen, causing a large amount of energy to be transferred from the incident electrons to hydrogen (Figure 3A). The exceptionally high knock-on damage cross-section of hydrogen poses a significant challenge in investigating 2D polymers and COFs. Moreover, the removal of hydrogen will create dangling bonds, which further reduces the knock-on threshold on the carbon backbone. Despite the enhanced S/N ratio and reduced knock-on damage on other elements by operating the microscope under lower voltages, hydrogen still poses a severe limitation on the intrinsic stability of 2D polymers and COFs towards electron radiation. Fortunately, this problem can be mitigated via isotope substitution. We found that, by exchanging protium for deuterium, the critical electron dose of coronene molecules can be increased by 2–3 times (Figure 3B).⁵² Replacing protium by chlorine on coronene results in increased stability by two orders of magnitude, reaching a critical dose of $10^6 \text{ e}^-/\text{\AA}^2$, which is comparable to inorganic materials.⁵³

3 | CONCLUSION AND OUTLOOK

Due to the proneness towards electron radiation damage, the achievable image resolution on 2D polymers and COFs remains unsatisfactory. This poses substantial

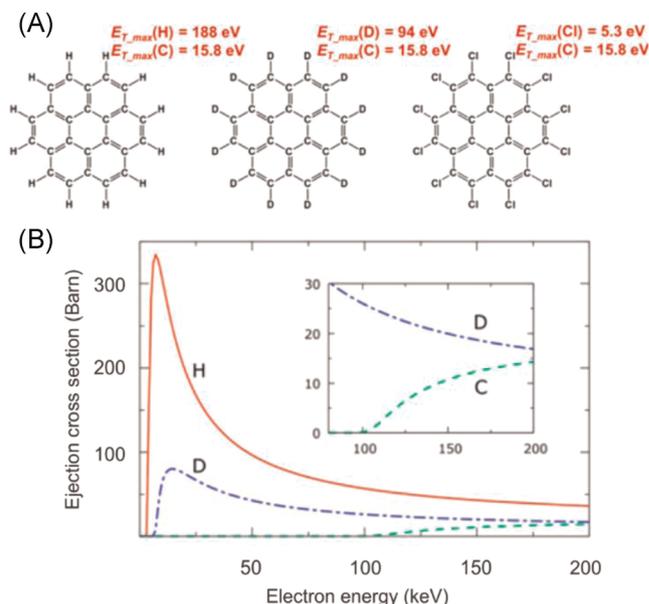


FIGURE 3 (A) Replacing all hydrogen atoms in coronene for deuterium or chlorine atoms reduces the amount of transferred energy, thus improving the stability of molecules. $E_{T,max}$ denotes the maximum transferrable energy from the incident electron beam in a backscattering event (calculated with electron energy of 80 keV). (B) The ejection cross-section quantifies the difference in C–H and C–D bond stabilities under the electron beam. Reproduced with permission: Copyright 2017, American Chemical Society⁵⁴

challenges on the further advancement of this emerging class of organic materials, such as determination of structure–property correlation and direct observation of localized structures, not to mention the investigation of growth dynamics via *in situ* TEM. Recently, vigorous efforts have been devoted to the AC-HRTEM imaging of beam-sensitive materials, including biological specimens and MOFs. The combination of the low-dose technique with direct electron detection has led to a significant improvement in the achievable image resolution. Meanwhile, the optimization of incident electron energy offers another promising revenue for the pursuit of even higher resolution. However, despite the appreciable achievements, the extremely low electron resilience of 2D polymers and COFs still strictly restrict the critical electron dose and thus S/N ratio and resolution.

We envisage that, to achieve higher resolution and eventually render *in situ* observation practical, it is vital to enhance the intrinsic electron resilience of the organic specimens. Since for very thin and hydrogen-free materials, S/N ratio and specimen stability can be simultaneously optimized via lower accelerating voltage and graphene encapsulation, hydrogen is becoming the next major obstacle. Although the efficacy of deuteration will still rely on the absolute critical dose, we believe that

using deuterated monomers would be a road worth perusing when synthesizing 2D polymers and COFs. Replacing protium by chlorine could significantly increase the stability, however, due to the steric hindrance, how chlorination affects the polymerization process and the final 2D polymer structure bears further scrutiny. Meanwhile, AC-HRTEM imaging of 2D polymers and COFs will continue to benefit from the rapid instrumentation advancement in TEM hardware (particularly in direct electron detection) as well as acceleration voltage optimization. Note that, the current direct electron detector design offers the best performance under high acceleration voltage, that is, 300 kV. Whereas under lower voltages, the DQE decreases due to increased backscattering, diminishing the advantages of enhanced information coefficient. The improved design will thus be necessary to expand the applicable voltage range of direct electron detection. We also believe that, for beam-sensitive organic and biological specimens, turning the inelastic noise into usable signal via chromatic aberration correction may provide another substantial boost to the S/N ratio and, ultimately, the achievable image resolution.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the funding from the Germany Research Foundation (DFG) in SFB-1415 (Grant No. 417590517) and from the European Union's Horizon 2020 research and innovation programme under Grant Agreement Nos. 881603 and 785291 (GrapheneCore3).

CONFLICT OF INTERESTS

The authors declare that there are no conflict of interests.

ORCID

Haoyuan Qi  <https://orcid.org/0000-0002-6684-7074>

REFERENCES

1. Servalli M, Schlüter AD. Synthetic two-dimensional polymers. *Annu Rev Mater Res*. 2017;47:361-389.
2. Dong R, Zhang T, Feng X. Interface-assisted synthesis of 2D materials: trend and challenges. *Chem Rev*. 2018;118:6189-6235.
3. Lyle SJ, Waller PJ, Yaghi OM. Covalent organic frameworks: organic chemistry extended into two and three dimensions. *Trends Chem*. 2019;1:172-184.
4. Haase F, Lotsch BV. Solving the COF trilemma: towards crystalline, stable and functional covalent organic frameworks. *Chem Soc Rev*. 2020;49:8469-8500.
5. Kissel P, Murray DJ, Wulftange WJ, Catalano VJ, King BT. A nanoporous two-dimensional polymer by single-crystal-to-single-crystal photopolymerization. *Nat Chem*. 2014;6:774-778.
6. Kory MJ, Würle M, Weber T, et al. Gram-scale synthesis of two-dimensional polymer crystals and their structure analysis by X-ray diffraction. *Nat Chem*. 2014;6:779-784.
7. Lange RZ, Hofer G, Weber T, Schlüter AD. A two-dimensional polymer synthesized through topochemical [2 + 2]-cycloaddition on the multigram scale. *J Am Chem Soc*. 2017;139:2053-2059.
8. Yang W, Ling B, Hu B, Yin H, Mao J, Walsh PJ. Enriching and quantifying porous single layer 2D polymers by exfoliation of chemically modified van der Waals crystals. *Angew Chemie Int Ed*. 2020;59:2-15.
9. Sahabudeen H, Qi H, Glatz BA, et al. Wafer-sized multifunctional polyimine-based two-dimensional conjugated polymers with high mechanical stiffness. *Nat Commun*. 2016;7:13461.
10. Müller V, Hinaut A, Moradi M, et al. A two-dimensional polymer synthesized at the air/water interface. *Angew Chemie Int Ed*. 2018;57:10584-10588.
11. Liu K, Qi H, Dong R, et al. On-water surface synthesis of crystalline, few-layer two-dimensional polymers assisted by surfactant monolayers. *Nat Chem*. 2019;11:994-1000.
12. Sahabudeen H, Qi H, Ballabio M, et al. Highly crystalline and semiconducting imine-based two-dimensional polymers enabled by interfacial synthesis. *Angew Chemie Int Ed*. 2020;59:6028-6036.
13. Zhang T, Qi H, Liao Z, et al. Engineering crystalline quasi-two-dimensional polyaniline thin film with enhanced electrical and chemiresistive sensing performances. *Nat Commun*. 2019;10:4225.
14. Park S, Liao Z, Ibarlucea B, et al. Two-dimensional boronate ester covalent organic framework thin films with large single crystalline domains for a neuromorphic memory device. *Angew Chemie Int Ed*. 2020;59:8218-8224.
15. Zhong Y, Cheng B, Park C, et al. Wafer-scale synthesis of monolayer two-dimensional porphyrin polymers for hybrid superlattices. *Science*. 2019;366:1379-1384.
16. Ma T, Kapustin EA, Yin SX, et al. Single-crystal X-ray diffraction structures of covalent organic frameworks. *Science*. 2018;361:48-52.
17. Haider M, Uhlemann S, Schwan E, Rose H, Kabius B, Urban K. Electron microscopy image enhanced. *Nature*. 1998;392:768-769.
18. Jia CL, Mi SB, Barthel J, et al. Determination of the 3D shape of a nanoscale crystal with atomic resolution from a single image. *Nat Mater*. 2014;13:1044-1049.
19. Linck M, Hartel P, Uhlemann S, et al. Chromatic aberration correction for atomic resolution TEM imaging from 20 to 80 kV. *Phys Rev Lett*. 2016;117:76101.
20. Börrnert F, Kaiser U. Chromatic- and geometric-aberration-corrected TEM imaging at 80 kV and 20 kV. *Phys Rev A*. 2018;98:23861.
21. Lehnert T, Ghorbani-Asl M, Köster J, Lee Z, Krasheninnikov AV, Kaiser U. Electron-beam-driven structure evolution of single-layer MoTe₂ for quantum devices. *ACS Appl Nano Mater*. 2019;2:2-3270.
22. Kühne M, Börrnert F, Fecher S, et al. Reversible superdense ordering of lithium between two graphene sheets. *Nature*. 2018;564:234-239.
23. Cao K, Biskupek J, Stoppiello CT, et al. Atomic mechanism of metal crystal nucleus formation in a single-walled carbon nanotube. *Nat Chem*. 2020;12:921-928.
24. Lehnert T, Kinyanjui MK, Ladenburger A, et al. In situ crystallization of the insoluble anhydrite aII phase in graphene pockets. *ACS Nano*. 2017;11:7967-7973.

25. Egerton RF. Radiation damage to organic and inorganic specimens in the TEM. *Micron*. 2019;119:72-87.
26. Kretschmer S, Lehnert T, Kaiser U, Krasheninnikov AV. Formation of defects in two-dimensional MoS₂ in the transmission electron microscope at electron energies below the knock-on threshold: the role of electronic excitations. *Nano Lett*. 2020;20:2865-2870.
27. Huang PY, Ruiz-vargas CS, van der Zande AM, et al. Grains and grain boundaries in single-layer graphene atomic patchwork quilts. *Nature*. 2011;469:389-392.
28. van der Zande AM, Huang PY, Chenet DA, et al. Grains and grain boundaries in highly crystalline monolayer molybdenum disulphide. *Nat Mater*. 2013;12:554-561.
29. Hu Z, Wu Z, Han C, He J, Ni Z, Chen W. Two-dimensional transition metal dichalcogenides: interface and defect engineering. *Chem Soc Rev*. 2018;47:3100-3128.
30. Haase F, Troschke E, Savasci G, et al. Topochemical conversion of an imine- into a thiazole-linked covalent organic framework enabling real structure analysis. *Nat Commun*. 2018;9:2600.
31. Qi H, Sahabudeen H, Liang B, et al. Near-atomic-scale observation of grain boundaries in a layer-stacked two-dimensional polymer. *Sci Adv*. 2020;6:eabb5976.
32. Castano I, Evans AM, Reis R dos, Dravid VP, Gianneschi NC, Dichtel WR. Mapping grains, boundaries, and defects in 2D covalent organic framework thin films. *Chem Mater*. 2021;33:1341-1352.
33. Li Z, He T, Gong Y, Jiang D. Covalent organic frameworks: pore design and interface engineering. *Acc Chem Res*. 2020;53:1672-1685.
34. Chen L, Furukawa K, Gao J, et al. Photoelectric covalent organic frameworks: converting open lattices into ordered donor-acceptor heterojunctions. *J Am Chem Soc*. 2014;136:9806-9809.
35. Huang N, Krishna R, Jiang D. Tailor-made pore surface engineering in covalent organic frameworks: systematic functionalization for performance screening. *J Am Chem Soc*. 2015;137:7079-7082.
36. Ross FM. Opportunities and challenges in liquid cell electron microscopy. *Science*. 2015;350:350.
37. de Jonge N, Houben L, Dunin-Borkowski RE, Ross FM. Resolution and aberration correction in liquid cell transmission electron microscopy. *Nat Rev Mater*. 2019;4:61-78.
38. Park J, Koo K, Noh N, et al. Graphene liquid cell electron microscopy: progress, applications, and perspectives. *ACS Nano*. 2021;15:288-308.
39. Wu B, Neureuther AR. Energy deposition and transfer in electron-beam lithography. *J Vac Sci Technol B Microelectron Nanom Struct Process Meas Phenom*. 2001;19:2508-2511.
40. Egerton RF. Mechanisms of radiation damage in beam-sensitive specimens for TEM accelerating voltages between 10 and 300 kV. *Microsc Res Tech*. 2012;75:1550-1556.
41. McMullan G, Faruqi AR, Henderson R. Direct Electron Detectors. In: Crowther R, ed. *Methods in Enzymology—The Resolution Revolution: Recent Advances in cryoEM*. Vol 579. Cambridge, MA: Academic Press; 2016:1-17.
42. Kühlbrandt W. The resolution revolution. *Science*. 2014;343:1443-1444.
43. Nakane T, Kotecha A, Sente A, et al. Single-particle cryo-EM at atomic resolution. *Nature*. 2020;587:152-156.
44. Yip KM, Fischer N, Paknia E, Chari A, Stark H. Atomic-resolution protein structure determination by cryo-EM. *Nature*. 2020;587:157-161.
45. Zhang D, Zhu Y, Liu L, et al. Atomic-resolution transmission electron microscopy of electron beam-sensitive crystalline materials. *Science*. 2018;679:675-679.
46. Zhu Y, Ciston J, Zheng B, et al. Unravelling surface and interfacial structures of a metal-organic framework by transmission electron microscopy. *Nat Mater*. 2017;16:4-9.
47. Aulakh D, Liu L, Varghese JR, et al. Direct imaging of isolated single-molecule magnets in metal-organic frameworks. *J Am Chem Soc*. 2019;141:2997-3005.
48. Peet MJ, Henderson R, Russo CJ. The energy dependence of contrast and damage in electron cryomicroscopy of biological molecules. *Ultramicroscopy*. 2019;203:125-131.
49. Pantelic RS, Meyer JC, Kaiser U, Stahlberg H. The application of graphene as a sample support in transmission electron microscopy. *Solid State Commun*. 2012;152:1375-1382.
50. Lehtinen O, Tsai I-L, Jalil R, et al. Non-invasive transmission electron microscopy of vacancy defects in graphene produced by ion irradiation. *Nanoscale*. 2014;6:6569-6576.
51. Algara-Siller G, Kurasch S, Sedighi M, Lehtinen O, Kaiser U. The pristine atomic structure of MoS₂ monolayer protected from electron radiation damage by graphene. *Appl Phys Lett*. 2013;103:203107.
52. Chamberlain TW, Biskupek J, Skowron ST, et al. Isotope substitution extends the lifetime of organic molecules in transmission electron microscopy. *Small*. 2015;11:622-629.
53. Chamberlain TW, Biskupek J, Skowron ST, et al. Stop-frame filming and discovery of reactions at the single-molecule level by transmission electron microscopy. *ACS Nano*. 2017;11:2509-2520.
54. Skowron ST, Chamberlain TW, Biskupek J, Kaiser U, Besley E, Khlobystov AN. Chemical reactions of molecules promoted and simultaneously imaged by the electron beam in transmission electron microscopy. *Acc Chem Res*. 2017;50:1797-1807.

AUTHOR BIOGRAPHIES



Haoyuan Qi, By using aberration-corrected transmission electron microscopy, Dr. Qi is devoted to the structural elucidation of organic 2D materials (O2DMs) down to the atomic scale. Understanding and circumvention of electron radiation damage on O2DMs, e.g., 2D polymers, covalent organic frameworks, and metal organic frameworks, take center stage of his research. Dr. Qi received his PhD degree in 2017 from the Electron Microscopy Group of Materials Science in Universität Ulm, and is now working as a joint postdoctoral researcher in Universität Ulm (Prof. Ute Kaiser) and Technische Universität Dresden (Prof. Xinliang Feng).



Ute Kaiser, Born in Berlin, Ute Kaiser studied Crystallography at the Physics Department of the Humboldt University Berlin finishing with the Diploma in 1976, and the doctor degree in 1993. Her habilitation she received from Friedrich Schiller University Jena (Germany) in 2002. Since 2004 she is full professor at Ulm University and head of the Group of Materials Science Electron Microscopy. In 2004, she became full Professor at Ulm University, Germany. From 2008-2018 she was the director of the SALVE (Sub-Ångström Low-Voltage Electron Microscopy) project, where she focuses on the development of low-voltage electron microscopy for application on beam-sensitive low-dimensional materials. Besides applying TEM to battery and semiconductor materials,

her main research interest is to study the properties of functional 2D materials and van der Waals heterostructures and other low-D materials and understand the electron-beam-specimen interactions in 2D organic and inorganic materials on the level of the single atoms. In the center stands unraveling electron-beam-specimen interactions in 2D organic and inorganic materials towards the level of the single atoms.

How to cite this article: Qi H, Liang B, Kaiser U. Perspective towards atomic-resolution imaging of two-dimensional polymers. *SmartMat*. 2021;1-8.
<https://doi.org/10.1002/smm2.1035>