Reviving the "Schottky" Barrier for Flexible Polymer Dielectrics with a Superior 2D Nanoassembly Coating

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The organic insulator-metal interface is the most important junction in flexible electronics. The strong band offset of organic insulators over the Fermi level of electrodes should theoretically impart a sufficient impediment for charge injection known as the Schottky barrier. However, defect formation through Anderson localization due to topological disorder in polymers leads to reduced barriers and hence cumbersome devices. A facile nanocoating comprising hundreds of highly oriented organic/inorganic alternating nanolayers is self-coassembled on the surface of polymer films to revive the Schottky barrier. Carrier injection over the enhanced barrier is further shunted by anisotropic 2D conduction. This new interface engineering strategy allows a significant elevation of the operating field for organic insulators by 45% and a 7× improvement in discharge efficiency for Kapton at 150 °C. This superior 2D nanocoating thus provides a defect-tolerant approach for effective reviving of the Schottky barrier, one century after its discovery, broadly applicable for flexible electronics.

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Polymer-film dielectrics represent the core framework of flexible electronics,^[1-5] serving as insulators,^[3] gate dielectrics,^[1,3-5] and capacitors.^[6,7] To provide charge and energy storage for channel conductance and power conversion, they must be able to withstand enormous and ever-increasing operating electric fields (E).^[4,6] Especially to enable ultra-compact and fast signal and power conversions, substantial effort has been devoted over the past several decades to tailoring materials properties in order to improve the breakdown strength ($E_{\rm BD}$). Often the focus is on improving the bulk properties of polymer dielectrics, with promising progress coming from rational codesigns of new molecular structures,^[6,7] bulk nanostructure engineering,^[8] and processing

optimization.^[9,10] Performance-limiting phenomena related to the organic dielectric–metal electrode interface itself, on the other hand, continue to be debated even a century after Schottky injection was discovered as a principal mechanism of conduction and charge injection for insulators.^[11–16]

Despite great success with junction control in inorganic electronics,^[17,18] an ideal Schottky barrier is simply never achieved for real-world organic devices. For instance, measured current densities are ten orders of magnitude higher than predicted for Au-polyethylene interfaces, which is generally explained with a practical Schottky-barrier height of merely ≈1 eV rather than the theoretically expected 4.5 eV.^[19-24] Under high fields, intense injection over such a strongly reduced barrier-generally explained by the presence of chemical and physical defects near the interface-results in soaring conduction that drains power, raises local temperatures, causes aging, and can culminate in catastrophic breakdown with particular sensitivity to localized compositional, structural, and manufacturing-induced defects. Promising solutions include modifying the metalorganic insulator interface with well aligned inorganics,^[12,25] though they generally employ chemical vapor deposition (CVD) or physical vapor deposition (PVD), typically with relatively high processing temperatures and/or plasma assistance. These are collectively cumbersome and-more problematicallyare prone to defect generation, since, e.g., a single pinhole may lead to complete failure.^[26-28] A scalable, defect-free, and

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defect-tolerant approach, compatible with large-scale manufacturing such as roll-to-roll processing, is therefore crucial for the future implementation of high-performance organic insulators, especially in the rapidly growing field of flexible electronics.

Accordingly, a self-assembled biomimetic nanocoating is reported, comprising a highly oriented organic/inorganic layered structure that enables a significantly elevated Schottky barrier between metal electrode and polymer dielectric. Specifically, a flow-induced facile coassembly technique is implemented to align exfoliated montmorillonite (MMT) single-layer nanosheets on film substrates. This mimics the structure of nacre,^[29] which possesses excellent fracture and impact resistance,^[30,31] but instead the 2D nanoassembly coating imparts a remarkable "defect-free" charge-injection blocking capability originating from the well-aligned multilaminated interfaces. Furthermore, the inherent in-plane conductivity effectively spreads localized surface charges, suppressing hot carriers which have considerable energy and thus could otherwise create defects and degrade the polymers locally. If successful in improving the injection barrier (reviving) and promoting lateral dissipation of injected charges (shunting), breakdown testing should result in a branched surface morphology indicating a surface-arrested Lichtenberg discharge pattern (tree-like patterns of damage that are created by the incontrollable passage of high-voltage electrical discharges along a surface and were already observed in 1778).^[32,33]

2. Results and Discussion

A low-viscosity dispersion containing MMT nanosheets (283 ± 90 nm in lateral dimensions, Figures S1 and S2 in the Supporting Information) and poly(vinyl alcohol) (PVA) binders was prepared and subsequently facilely self-coassembled on polymer films to form a nanostructured coating (Figure 1a-e). The intense X-ray diffraction (XRD) peaks attributed to the nanocoating layers on the various coated polymer films reveal that the MMT nanosheets are highly oriented with an interlayer distance of ≈2.85 nm (Figure 1f). This self-assembly results from both the shear stress during the coating process, and space confinement effects from the high density of MMT nanosheets.^[29] More directly, TEM images from a cross-section of a nanocoating (Figure 1g,h) clearly reveal MMT nanosheets that are densely packed and well aligned parallel to the substrate surface. Greyscale analysis from a magnified region in Figure S3a (Supporting Information) evidences a local interlayer separation of 2.8 ± 0.2 nm (Figure S3b, Supporting Information), while a larger area analysis based on a 2D



Figure 1. Sample preparation and structural characterizations. a) Overall process to fabricate a nacre-like PVA/MMT nanocoating with a well-oriented layered structure containing a high concentration of MMT nanosheets (not drawn to scale). b) Conceptual schematic of a PVA/MMT nanocoating (PVA chains are not shown for better visibility) blocking and dissipating high field electrical discharge. c–e) Photograph of the coated BOPP (c), Kapton (d), and LDPE (e) films. f) XRD patterns of the uncoated and coated polymer films, indicating that the interlayer distance of the MMT nanosheets in the nanocoating is \approx 2.85 nm. g) Low-magnification and h) high-magnification bright-field TEM images of the cross-section of a nanocoating on BOPP. i) The 2D fast Fourier transform of the TEM image in (h) revealing a spatial periodicity (cycles per nm) of 2.7 ± 0.2 nm in accordance with the interlayer spacing.





Fourier transform (Figure 1i) of the 21 025 nm² region (145 nm × 145 nm) exhibits a peak periodicity at 2.7 \pm 0.2 nm (Figure S3d, Supporting Information). Small-angle X-ray scattering (SAXS) was also conducted, with results (Figure S4, Supporting Information) further confirming, within the nanocoating, a very high degree of alignment of the MMT nanosheets. In terms of bonding, the PVA chains and MMT nanosheets were successfully cocrosslinked using glutaraldehyde (verified by infrared spectroscopy, Figure S5, Supporting Information), covalently incorporating the MMT nanosheets into the PVA matrix to form a well-integrated structure (Figure S6, Supporting Information) lead to significant fracture and impact resistance, charge-injection resistance, and energy dissipation.^[34]

To assess the efficacy of the nanocoatings for withstanding electric-field extremes, we studied the dielectric breakdown strengths (E_{BD}) of three industrially relevant polymer films (Table S1, Supporting Information): biaxially oriented polypropylene (BOPP, with a high E_{BD}), Polyimide (PI, Kapton, with an intermediate E_{BD}), and low-density polyethylene (LDPE, with a relatively low E_{BD}). The Weibull statistics plotted in **Figure 2**a–c summarize more than 40 breakdown tests over large areas of 2 cm² per film type (Figure S7, Supporting Information), and identify characteristic values at 63.2% (1 – 1/e), 10%, and 1%

probability of failure, respectively, while the slopes indicate the Weibull shape parameters (β). Notably, the shape factor along with the Weibull 1% failure probability points essentially determines the maximum safe operating fields for practical device designs. The PVA/MMT nanocoatings clearly yield remarkable improvements for all three polymer dielectrics. For instance, while BOPP is the best-known polymer film for capacitive energy storage due to its extremely high breakdown strength,^[35] a 305 nm layer of our novel PVA/MMT nanocoating further increases its breakdown strength (Figure 2a), which has never before been achieved. In fact, the $E_{\rm BD}$ value that corresponds to the critical 1% probability of failure is enhanced by 8% from 636 to 689 MV m⁻¹ (Figure 2a; Table S2, Supporting Information). In addition, the nanocoating enhanced β from 21 to 32, indicating a reduced dispersion and hence improved reliability and scalability (Table S2, Supporting Information, summarizes all Weibull data), outperforming the reported PVD coating approach from a side-by-side comparison.^[27] An equivalent film on Kapton, the most important dielectric material for flexible electronics because of its superior thermal stability and good chemical resistance,^[36] uniformly improves the $E_{\rm BD}$ by 9%, with a consistently high β value beyond 80 (Figure 2b). For the PVA/MMT self-assembly on polyethylene, another key dielectric



Figure 2. Breakdown strength. a–c) Weibull plots of breakdown strengths of the uncoated and coated polymer films. d–i) Morphology of the breakdown regions for the uncoated (d,f,h) and coated (e,g,i) BOPP, Kapton and LDPE films, respectively (coating thickness: 305 nm).





material with ultralow conduction losses,^[37] the improvement is even more pronounced, with an extraordinary 45% increase in $E_{\rm BD}$ at 1% probability of failure (Figure 2c). With higher fields, for instance at the characteristic Weibull failure level of 63.2%, $E_{\rm BD}$ still increased from 509 to 596 MV m,i.e., an impressive 17% compared to the uncoated control. For the PVA/MMT coated polystyrene, a dielectric with relatively low breakdown strength and high conduction loss at high electric fields, an unprecedented 45% improvement for E_{BD} is achieved at the 63.2% characteristic failure probability (Figure S8, Supporting Information). An important point is that the PVA/MMT coating imparts polymer films with high shape factors β for the Weibull distribution of the E_{BD} . The reduced dispersion and improved reliability reveal the superior defect tolerance of the hundreds of highly oriented organic/inorganic alternating nanolayers, which is impressive compared to the best reported approaches.^[27,38,39]

Importantly, such performance enhancements are also maintained with half the thickness of PVA/MMT (155 nm), including 85 and 102 MV m⁻¹ increases for LDPE in the breakdown strength at the high and low failure rates already discussed (Figure 2c). The high-field discharge efficiency is improved as well, notably for Kapton even at the high temperature of 150 °C (Figure S10, Supporting Information). With a 90% discharge efficiency up from 188 to 314 MV m⁻¹ (+67%), the nanocoating can extend the operating field accordingly for Kapton. These results have significant implications for the reliability and lifetime of advanced polymeric electronics under harsh conditions.

The damage patterns following dielectric breakdown are indicative of the failure mechanism, Figure 2d–i, with significant differences emerging between the uncoated and coated films. Pure films exhibit a single point of failure, while extensive radial traces are apparent for the coated films. The traces result from the tortuous charge-spreading pathways branching along and between the highly aligned inorganic MMT nanosheets^[10,40,41] as illustrated in Figure 1b.

To gain more insight into charge injection at the modified metal–polymer interface, the Schottky-barrier heights of the metal–polymer contacts are determined based on photoinjection currents. Both the bottom and top metal electrodes are aluminum (Al), with a work function of 4.06–4.26 eV, to be consistent with related breakdown measurements that used evaporated Al metalized films as electrodes.^[42] Among the polymers investigated, Kapton exhibits the smallest bandgap arising from the aromatic structure, and thereby provides the lowest interband ionization barrier.^[7] Therefore, any improvement of the Schottky injection barrier is especially significant for Kapton to better suppress charge transport and achieve a higher breakdown strength. Accordingly, the effective Schottky-barrier heights for the Al/uncoated Kapton and Al/coated Kapton interfaces are estimated to be 1.85 and 2.19 eV, respectively, based on photoinjection currents (Figure 3a,c)



Figure 3. Fowler's plots for photo-injection currents in Kapton with negatively biased Al electrodes and the corresponding energy-band diagrams. a,b) Al-uncoated Kapton-Al; c,d) Al-coated Kapton-Al. The coating thickness is 305 nm. The schematic of the photocurrent measurement setup is shown in the insert of (a).





plotted as the square root of the photocurrent against the photon energy, i.e., Fowler's plots.^[43] The results clearly demonstrate that the barrier height of the metal-nanocoating-polymer junction is significantly higher (18%) than that of the original metal-polymer junction; corresponding proposed energy-band diagrams are shown in Figure 3b,d. For the Al-Kapton junction, a relatively low apparent barrier height results from the large number of localized (or surface) states in the polymer, increasing unwanted carrier injection over the reduced barrier. In contrast, the highly ordered PVA/MMT layered nanocoating increases the effective Schottkybarrier height. This effective quantum well structure might be expected to cause increased resonant tunneling which is, however, suppressed by the nonzero imperfections in the MMT-layer periodicity. Therefore, the layered MMT nanocoating at the metalpolymer interface provides an innovative strategy for reviving the Schottky barrier, suppressing charge injection, and limiting tunneling across the metal-insulator heterojunction.

Charge dynamics at the polymer surface were also probed using Kelvin probe force microscopy (KPFM, Section S4 and Figure S9, Supporting Information) via non-contact tracking of the surface-potential decay following preliminary DC biasing at a point contact.^[44] This is demonstrated on uncoated and PVA/MMT-coated BOPP, whose highest breakdown strength among the investigated polymers should therefore allow the highest local electric fields and thus the greatest magnitude of injected charge to be considered. As shown in Figure 4, coated BOPP (305 nm coating thickness) leads to a much lower charge magnitude and remarkably faster charge dissipation. The results are similar for opposite polarities, with the charged region dissipating to 80% of the initial local peak (directly measured) within ≈100 s for both positively and negatively charged PVA/MMT coated surfaces (Figure 4b,d). This is in stark contrast to the uncoated BOPP, for which the surface potential shows minimal decay even after 330 s, especially for negative applied voltages (Figure 4a,c). Since there is a 20 s delay between charging and probing (due to unavoidable experimental adjustments between contact-charging and KPFM-imaging), the actual peak potential at t = 0 (i.e., immediately upon charging) is calculated assuming a typical exponential decay according to $V = V_0 \exp(-t/\tau)$. A nanoscale map of the initial peak potential V_0 (Figure 4e,f), representative of the injected-charge magnitude and sign at each image pixel, is produced by properly accounting for the actual instant each scanned pixel is acquired and by fitting the data to the decay model. Comparisons of V_0 for coated and uncoated BOPP over a range of biasing voltages are presented in Figure 4g. The elevated Schottky barrier between the metal and the PVA/MMT nanocoating results in a clear reduction in the magnitude of the injected charge in the coated BOPP as compared to that in the uncoated BOPP. The shorter time constant τ for



Figure 4. Surface charge dissipation analysis. a–d) KPFM scans revealing surface-charge dissipation. The charge spots were written with a ±6 V bias on the surface of uncoated or PVA/MMT-coated BOPP films. e,f,h,i) Calculated initial peak potentials V_0 and time constants τ from (a,b) assuming exponential decay according to $V = V_0 \exp(-t/\tau)$. e) V_0 for uncoated BOPP; f) V_0 for coated BOPP; g) Calculated initial peak potential V_0 under different applied voltages. h) log(τ) for uncoated BOPP; i) log(τ) for coated BOPP. The size of each image frame is 2.0 × 0.5 µm².

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charge decay on coated BOPP (Figure 4h,i) results from the weak, albeit nonzero, in-plane conduction paths for the self-assembled MMT nanosheet layers. Relative to pure BOPP, the combined benefits of a reduced charge injection through the thickness direction, and accelerated in-plane charge dissipation, directly result from the anisotropic characteristics of the PVA/MMT coating.

3. Conclusions

By both blocking and spreading charge injection, our 2D nanoassembly coating can significantly reduce energy losses at electrode/substrate interfaces for high capacitive energy storage even under concurrent harsh conditions. For instance, while the charge-discharge efficiency at 150 °C for uncoated Kapton films is only 40% at 300 MV m⁻¹, this can be improved to 90% after applying a 305 nm PVA/MMT multilaminated coating (Figure S10, Supporting Information). Crucially, the solution-based fabrication of the 2D nanoassembly coating is scalable for large-area roll-to-roll processing. Aside from the "defect-free" nature rendered effective by the massive redundancy of the hundreds of layers of highly oriented organic/inorganic alternating nanolaminates, the 2D nanoassembly coating is also inherently "defect-tolerant" due to its unique anisotropic structure, capable of regulating and laterally dissipating excessive hot carriers. Overall, the superior layered architecture at the metal-dielectric interface thereby unleashes for the first time a practical avenue to engineer an effective injection barrier with wide applicability for flexible electronics and other polymer-dielectric systems.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Author Contributions

B.Z., J.L., M.R. and C.W. contributed equally to this work. L.S. and Y.C. conceived the idea. J.L., S.Z., and A.M.L. prepared the nanocoatings and conducted most of the characterizations of the nanocoatings. B.Z., M.R., C.W., and Z.L. carried out electrical characterizations. T.M. and B.D.H. conducted the KPFM characterizations. S.E.C. and Z.H. performed the

SAXS and XRD characterizations. B.Z., C.W., B.D.H., Y.C., and L.S. wrote the first draft of the manuscript. All authors contributed to revising the manuscript.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

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