

Static Electrification of Plastics under Friction: The Position of Engineering-Grade Polyethylene Terephthalate in the Triboelectric Series

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Abstract

There is an emerging trend to replace moving metallic parts, such as bearings or bushes, with plastic components. The electrostatic hazard associated with plastic components subject to mechanical friction is well documented, but the magnitude as well as the physical chemical origin of this phenomenon remains debated. Using atomic force microscopy and Faraday pail measurements we have studied the triboelectrification of Ertalyte®, a commonly used bearing-grade formulation of polyethylene terephthalate, when rubbed against other polymers and metals. We have analyzed the sign and magnitude of the net-charge that Ertalyte® gains in relation to the chemical nature – electron affinity and ionization energy – of the contacting material, concluding that this material should be located towards negative end of the triboelectric series. We also reveal that large charge densities and fast charge decays result

from the contact of Ertalyte® with polymers of a small DMT modulus and unstable ions, suggesting that ion transfer leads to the electrification of a dynamic insulator/insulator contact. These findings have immediate implications in the choice of the material used to manufacture plastic parts subject to friction and wear, and help addressing ongoing fundamental questions over the nature of the charge carriers that lead to static electricity.

Mechanical moving parts, or housing for moving parts, such as bushes or shafts traditionally made out of metals, can now be machined out of plastic materials of sufficiently high resistance to wear, impact and chemical corrosion.^[1] One of the known causes of mechanical damage in moving metallic parts, such as the failure of automotive bearings, is associated to the passage of electric currents in response to voltages developed upon friction.^[2] This type of wear can be prevented by using a material of high electrical resistance, hence, combined with their ease of manufacturing, light weight and the resistance to oxidation in air, plastics offers unique engineering advantages over metals.^[3] On the other hand, being electrical insulators, plastics cannot be effectively grounded. This leads to an electrostatic hazard which is well perceived in industrial settings,^[4] with several reports of incidents and explosions in chemical plants dealing with the processing of liquids and powders.^[5] Furthermore, the build-up and dissipation of static electricity is also known to shorten the life and performance of any added lubricant.^[6]

Ertalyte® is a formulation of polyethylene terephthalate (PET), and one of the best-known examples of bearing-grade plastics routinely used to manufacture precision mechanical parts subject to high loads and wear.^[7] It is one of the hardest industrial plastics, it exhibits high mechanical strength, low thermal expansion, very good sliding properties and high dimensional stability.^[8] It is easily machined, can be glued, it is non-toxic and has FDA approval. However, the material has a large electrical resistivity and is therefore expected to develop static charges

upon contact.^[9] The purpose of this paper is to place Ertalyte® on the triboelectric series for the first time, as well as to clarify whether physical chemical properties of the contacting polymer – namely its hardness and electron affinity – influence the tribocharging of Ertalyte®.

We have quantified the magnitude and sign of the static electricity developed on Ertalyte® when rubbed against the surface of nylon, poly (methyl methacrylate) (PMMA), polycarbonate (PC), polyvinyl chloride (PVC), polytetrafluoroethylene (PTFE) and polydimethylsiloxane (silicone) samples. The choice of these polymers is motivated by their positions covering the entire length of available triboelectric series;^[10] nylon being located towards the top of the series (i.e. positive end), while PMMA, PC, PVC, PTFE and silicone sitting towards the bottom (i.e. negative end). DMT (Derjaguin-Muller-Toporov) moduli of these polymers, as derived by atomic force microscopy (AFM) measurements, together with their computed values of electron affinities, are used to explain the direction of material transfer upon contact and separation of Ertalyte® with other plastics, and to provide predictive power on charging magnitude and decay velocity. Moreover, our findings help clarifying the nature of the charge carriers responsible for the triboelectrification of electric insulators, that is, they help resolving the ongoing electrons versus ions debate.^[11]

The triboelectric series is an ordered list of materials representing their tendencies to gain charges upon contact, but the position of PET in the series is ambiguous,^[12] and most importantly, data for engineering-grade formulations such as Ertalyte® are not yet available. To address this point, we have performed Faraday pail charge measurement on this bearing-grade plastic when it is contacted against polymers whose position in triboelectric charts is established. Faraday pail measurements reveal that Ertalyte® gains a small (ca. 0.95 nC/cm²) net-positive charge after contact with silicone, while it gains a net-negative charge after contact with nylon, PMMA, PC, PVC and PTFE (**Figure 1a**). The magnitude of the negative charging

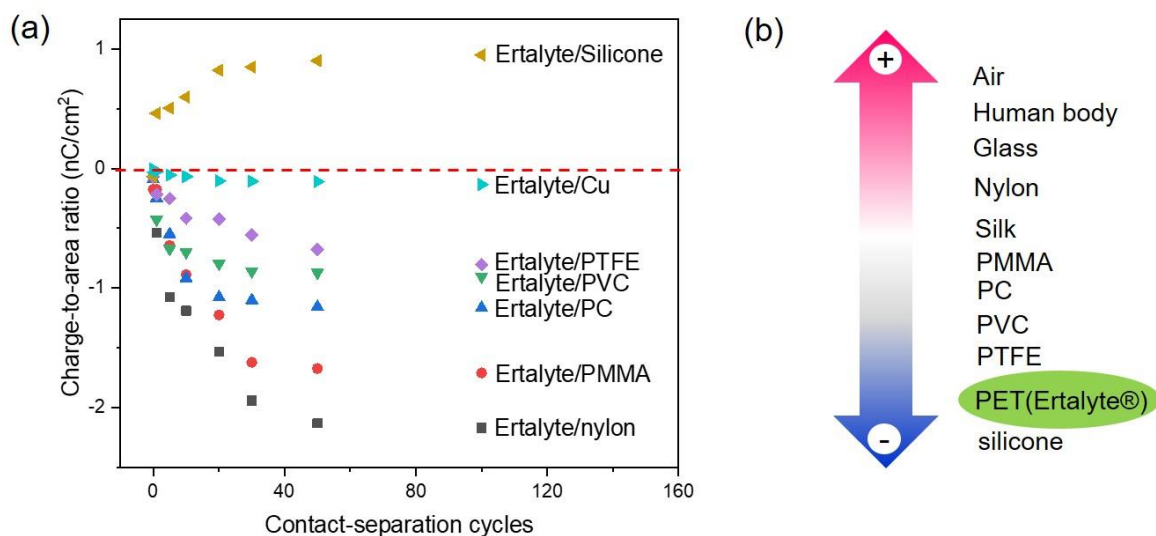


Figure 1. a) Tribocharging of PET (Ertalyte®) against polymer and copper samples. Faraday pail data show Ertalyte® becoming positively charged after contact and separation from a silicone surface, but acquiring an almost zero net charge density after contact with copper sheets. Ertalyte® gained a net negative charge after contact with nylon, PMMA, PC, PVC and PTFE samples. b) Relative position of various dielectric materials in a triboelectric series:^[11c] materials located toward the series bottom (−) tend to acquire a net negative charge upon contact with materials located towards the top (+). The tentative position of PET (Ertalyte®) in the series is between those of PTFE and silicone (green label in (b)).

appears to be a strong function of the chemical nature of the contacting polymer: a large charging is obtained upon

contact with nylon, while the lowest Coulombs are measured for the Ertalyte®/PTFE combination. We therefore suggest that Ertalyte® should be placed towards the negative end of the triboelectric series, most likely between PTFE and silicone (**Figure 1b**). Notably, friction between Ertalyte® and a metal surface, here a copper plate, leads to an almost zero charge density on the polymer.

The net charge on Ertalyte® is small (nC range), yet the total number of negative charges on the sample will be probably much larger, possibly in the order of $10^{15}/\text{cm}^2$ elemental charges.^[11b] A “mosaic” nature for a tribocharged surface is now generally accepted,^[13] and oppositely charged regions of nanoscopic dimension co-exist on the sample surface.^[13-14] We

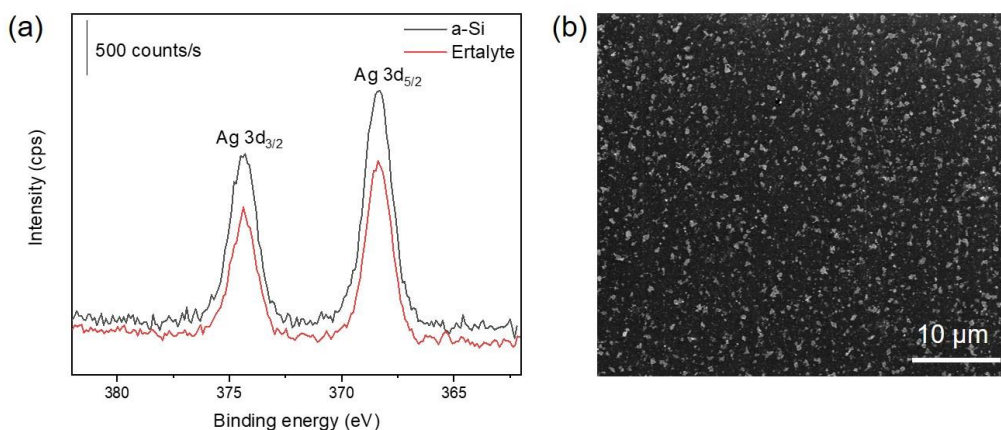


Figure 2. a) XPS analysis of tribocharged Ertalyte® and intrinsic amorphous silicon (a-Si) samples discharged in aqueous solutions of silver nitrate. Narrow scans of the Ag 3d region indicate a spin-orbit-split emissions of binding energy consistent with literature values for metallic silver (Ag 3d_{3/2} and 3d_{5/2} signals are located at 374.4 eV and 368.4 eV, respectively). b) SEM image of silver particles reduced on tribocharged intrinsic amorphous silicon samples.

have tentatively clarified on this point by discharging aqueous solutions of silver nitrate on charged Ertalyte® and then running XPS measurements to quantify the elemental silver deposited on the polymer surface upon reduction of the silver ions (**Figure 2a**). In an attempt to convert the XPS atomic percentage into a surface density number, we have compared the XPS-derived elemental silver atomic percentage obtained on Ertalyte® with that measured on tribocharged intrinsic amorphous silicon samples that underwent the same charging/discharging procedure. Silver elemental intensities are roughly of the same order of magnitude on both samples (**Figure 2a**), with the advantage that intrinsic amorphous silicon is a perfect insulator in the dark, can be tribocharged,^[15] but still allows for SEM measurements of sufficiently high quality (**Figure 2b**). Using a previously reported procedure,^[11b] we estimate that approximately $10^{15}/\text{cm}^2$ atoms of silver were discharged on the Ertalyte® sample.

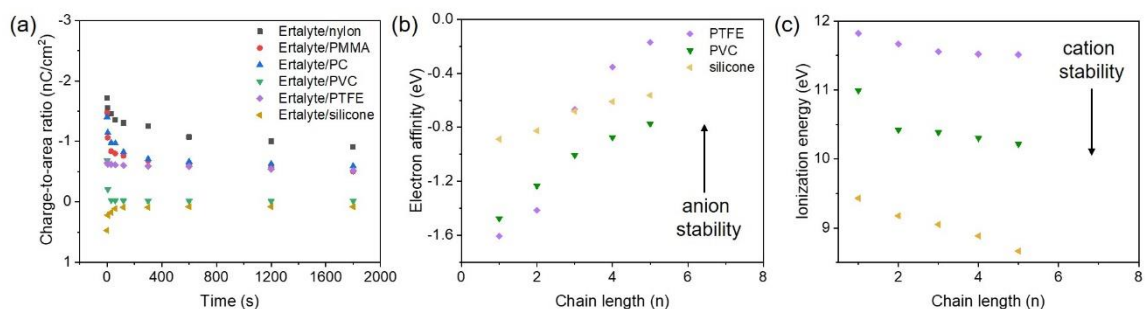


Figure 3. a) Decay in air of the static charging (Faraday pail measurements) of Ertalyte® (engineering-grade PET) tribocharged against various polymer samples. For the Ertalyte/PTFE pair, the static charging is stable and the samples lose only about 19% of their net charging after 2000 s. For Ertalyte/PVC and Ertalyte/silicone pairs the decay is significantly more rapid, and these samples lose about 98% and 83% of their net charging over the same time scale. b) Literature computed values of electron affinities (EA) and c) ionization energies (IE) for oligomers of PTFE, PVC and silicone as a function of the oligomer chain length.^[11b]

Recent work has shown that the transfer of polymer fragments is the main cause of insulators gaining an electrical charge upon contact and separation,^[11b, 16] it is therefore likely that the electrification of Ertalyte® is also rooted in the rupture of chemical bonds and movement of charged polymer fragments. Measurements of charge decay kinetics were performed to substantiate this hypothesis. Time-resolved Faraday pail data show that for Ertalyte® only about 19% of its tribocharges have dissipated 2000 s after being separated from a PTFE surface (**Figure 3a**). A significantly faster charge decay is found when Ertalyte® samples are rubbed against silicone or PVC, with about 83% and 98% of the net charge, respectively, dissipating over the same period of time (**Figure 3a**). The speed of charge dissipation is probably linked to the electron affinity and ionization energy of the material transferred on the Ertalyte® surface. In line with our previous reports, a fast charge decay is observed for materials with unstable anions (high electron affinity) and stable cations (low ionization energy).^[11b] As the anion stability is in the order PTFE > silicone > PVC, and the stability of cations is in the order silicone > PVC > PTFE (the electron affinities are -0.17, -0.56 and -0.77 eV for PTFE, silicone and PVC, while ionization energies are 11.51, 10.22 and 8.66 eV,^[11b] at the longest

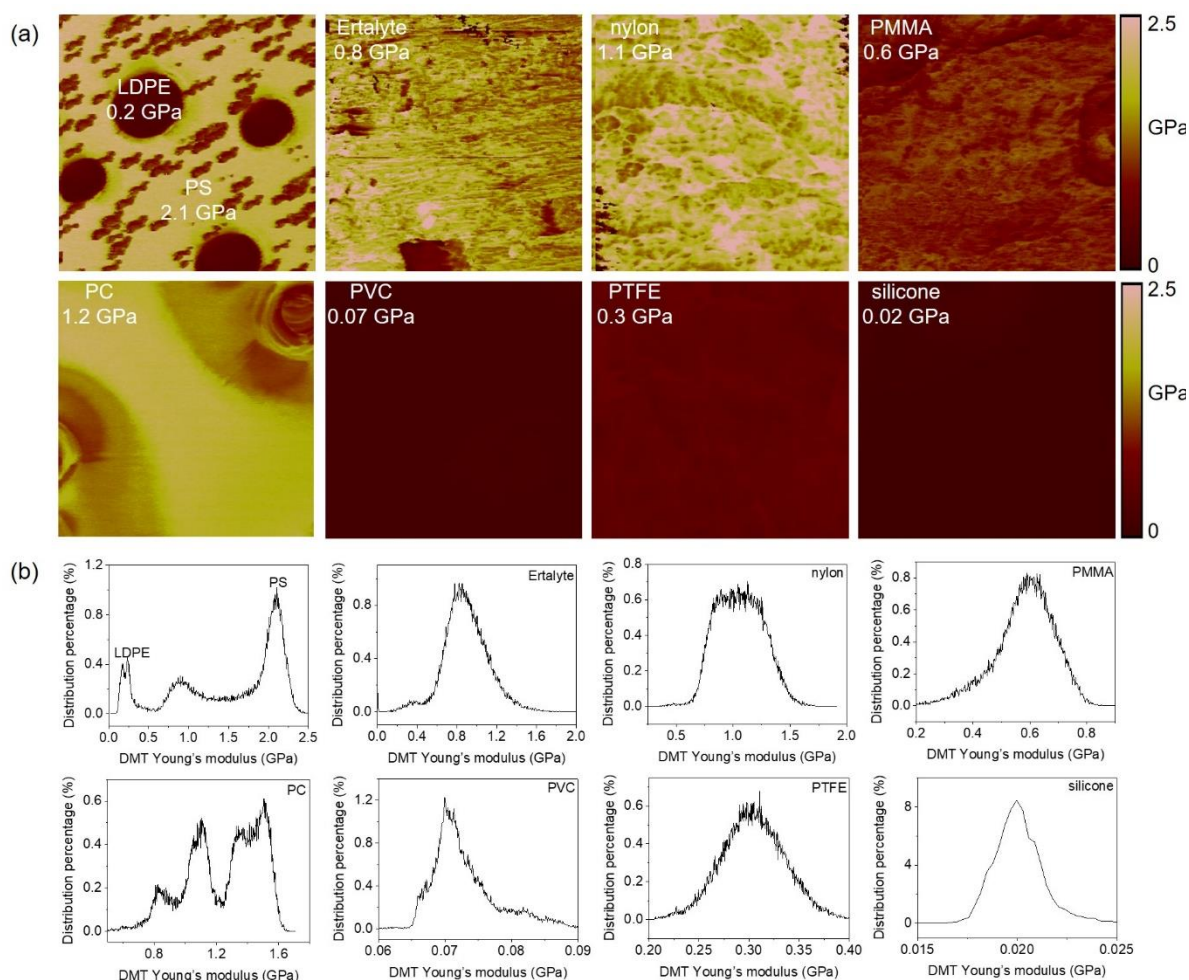


Figure 4. a) Atomic force microscopy QNMTM measurements of surface hardness (DMT modulus) for standard samples of polystyrene and low density polyethylene (PS/LDPE), Ertalyte®, nylon, PMMA, PC, PVC, PTFE and silicone. b) Experimental distribution of the DMT Young's modulus across the samples. Imaged areas are $5 \times 5 \mu\text{m}$ for all samples.

chain length studied, $n = 5$ in **Figure 3b**), for both the Ertalyte/silicone and Ertalyte/PVC pairs, relatively unstable anions and stable cations transferred onto Ertalyte® are likely to account for the experimentally observed fast discharge.^[17]

Atomic force microscopy (AFM, **Figure 4**) was then used to probe surface hardness, and Ertalyte® is found to be significantly harder (Young's modulus of 0.8 GPa, Derjaguin–Muller–Toporov model^[18]) than PVC, PTFE and silicone (DMT modulus of 0.07, 0.3 and 0.02 GPa, respectively). The DMT modulus was quantitatively determined with respect to standard samples of polystyrene and low-density polyethylene (PS/LDPE, left top panels in **Figure 4**).

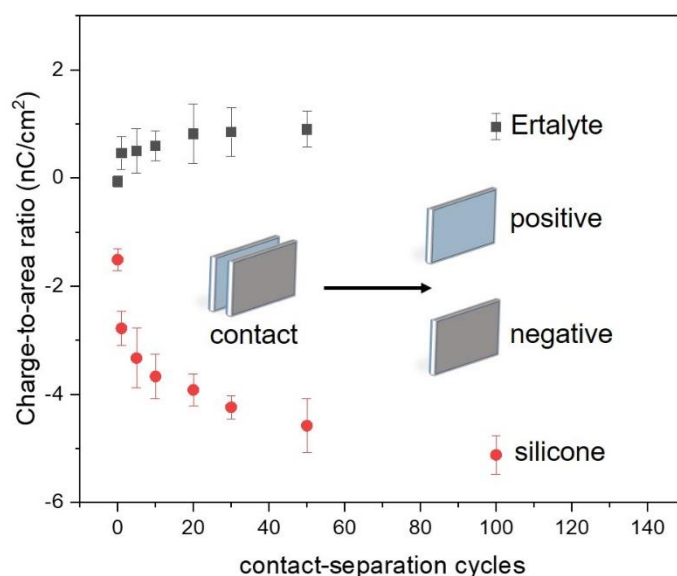


Figure 5. Tribocharging of Ertalyte® against silicone, with error bars showing one standard deviation of uncertainty obtained from the analysis of three independent replicates. Faraday pail data in figure show Ertalyte® samples becoming positively charged, and silicone gaining a large negative charge density, after consecutive contact and separation cycles.

Theoretical data of material transfer rate between dielectrics are limited, but a relationship exists between the hardness of a polymer and the ease of transferring charged fragments: upon contact, softer polymers lose material to harder ones.^[11c] Therefore it is probable that charged fragments of PVC, PTFE and silicone transfer onto the relatively harder Ertalyte® surface (DMT modulus of 0.8 GPa) to a greater extent than the reverse transfer of Ertalyte® onto them. This is also in line with our charge decay data (vide supra) where we highlighted an experimental relationship between the electron affinity (anion stability) of PVC, PTFE and silicone and the velocity of the charge dissipation on Ertalyte® samples charged against these polymers. The cation stability of silicone fragments also explains why Ertalyte® tends to gain a positive charge upon charging against silicone.

The tribocharging of Ertalyte® against silicone is of particular practical relevance, as common lubricants are silicone-based. Increasing the number of contact-separation cycles (**Figure 5**)

increases the magnitude of charging on both Ertalyte® and silicone, but the increase is steeper on the latter (**Figure 5**; after 100 cycles the charge density on the silicone surface is -5.12 nC/cm^2 against 0.95 nC/cm^2 for Ertalyte®). The use of silicone-based lubricants with moving parts made of Ertalyte® is therefore likely to generate a large amount of electrostatic charges, our findings suggest opting for readily available conductive greases to minimize charge build-up.^[19]

In summary, we have studied the electrification of a widely adopted engineering-grade PET formulation (Ertalyte®) and defined for the first time its correct location in the triboelectric series. We have defined the molecular details of the Ertalyte® electrification process and highlighted the electrostatic hazard associated with its lubrication using silicone-based products. The kinetics of charge decay for statically charged Ertalyte® samples depends on the electron affinity and ionization energy of the contacting polymer, which is strong evidence for the movement of charged polymeric fragments causing the electrification of a dynamic insulator/insulator contact. Further, our findings indicate that the electrification of this bearing-grade PET formulation is kept to a minimum when contacted against metals instead of polymeric dielectrics.

Experimental section

Materials. Redistilled solvents and Milli-QTM water ($>18 \text{ M}\Omega \text{ cm}$) were used for substrate cleaning procedures. Samples of polyethylene terephthalate (PET, Ertalyte®, Dotmar Engineering Plastic Products, Australia), polytetrafluoroethylene (PTFE, McMaster-Carr, CAT# 8545K26), poly(dimethylsiloxane) (silicone, McMaster-Carr, CAT# 87315K65), polyvinyl chloride (PVC, McMaster-Carr, CAT# 87545K521), nylon (nylon-66, 514-607, RS Components Australia®), acrylic (PMMA, McMaster-Carr, CAT# 8560K358) and

polycarbonate (PC, McMaster-Carr, CAT# 85585K102) were cut to sheets of 2×2 cm in size and approximately 0.3 cm in thickness. Deposition of a 1 μm thick layer of intrinsic amorphous silicon on prime grade 100-oriented ($(100) \pm 0.5^\circ$, n-type, 8–12 Ω cm) silicon wafers (Siltronix, S.A.S, Archamps, France) followed a previously reported procedure.^[15b] Amorphous silicon samples were cut to 1×1 cm in size and cleaned using the same procedures as for the plastic samples.

Contact electrification procedure. Prior to contact charging, polymer and amorphous silicon samples were washed with water, methanol, dichloromethane, and then dried under a stream of nitrogen. Copper plates were mechanically polished with emery paper, washed with water, methanol, dichloromethane, and then dried under nitrogen. The charge on the polymers was measured using a Faraday cup connected to an electrometer (JCI 140 static monitor and JCI 147 charge measurement units) operating on the 10^{-9} Coulomb scale. Charging data are reported as charge-to-geometric area ratios. Amorphous silicon, nylon, PMMA, PC, PTFE, PVC and silicone sheets were charged by rubbing them against a clean Ertalyte® surface using a spring (spring constant of 4.8 N/m) to control the contact force. The number of the contact–separation cycles was varied between 0 and 100.

Surface characterization. Mechanical properties (DMT moduli) of the plastic samples were measured by atomic force microscopy (AFM) using a Bruker Dimension FastScan (Bruker Corporation, Santa Barbara, CA, USA). AFM data were obtained in QNM™ imaging mode, by tapping in air at room temperature and using NCHV-A Bruker probes with a spring constant of 42 N m^{-1} . The imaging resolution was set to 256 points/line, the scan rate to 2 Hz and the peak force to 500 nN. Standard harmonic samples of polystyrene (PS) and low density polyethylene (LDPE), with discrete domains of 2.1 (PS) and 0.2 GPa (LDPE) moduli, were supplied by Bruker.

Metal ions discharge experiments and spectroscopic surface characterization.

Tribocharged Ertalyte® (against Ertalyte®) and silicon (against PVC) samples were transferred to a 50 Mm aqueous solution of AgNO₃ (99.999%, Sigma), rested for 3 h in the liquid under dark, washed with Milli-Q™ water, and then dried under a stream of nitrogen before X-ray photoelectron spectroscopy (XPS) analysis. XPS experiments were performed on a Kratos Axis Ultra DLD spectrometer fitted with a monochromated Al K α source. The pressure in the analysis chamber during measurement was <10⁻⁸ mbar. Scanning Electron Microscopy (SEM) images were obtained on a Zeiss Neon 40EsB FESEM equipped with a Schottky field emission gun operating at 5 kV and a chamber pressure of approximately 4 × 10⁻⁶ mbar.

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Conflict of Interest

The authors declare no competing financial interest.

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