Exploring Dicarboxylic Acid Interactions and Surface Chemistry Through X-ray Photoelectron Spectroscopy

Ghafoor Ahmad [a], Md Wazed Hossan Shehab [b], Hosen Md Sajib [b], Muhmmad Saleem [c], Md Atoar Hossan Siblu [d], Tayyaba Munawar [e], Abu Musa Sarkar [b], Hafiz Mahmood Ul Hasan [a]*

[a] Collaborative Innovation Center of Chemical Science and Engineering, Key Laboratory for Green Chemical Technology of Ministry of Education and School of Chemical Engineering and Technology, Tianjin University, Tianjin 300350, P. R. China.
[b] School of Chemical Engineering and Technology, Tianjin University, Tianjin 300350, P. R. China.
[c] Department of Zoology, Minhaj University, Lahore 54000, Pakistan
[d] School of Environmental Science and Engineering, Tianjin University, Tianjin 300350, P. R. China.
[e] Department of Chemistry, University of Agriculture, Faisalabad 38040, Pakistan
*Corresponding authors: hafizhasan@tju.edu.cn (Hafiz Mahmood Ul Hasan)

Abstract

Dicarboxylic acids have become key players in designing functional surfaces, offering precise control over interactions in catalysis, materials science, and environmental applications. However, understanding their complex chemical states and surface behavior remains a challenge. Advanced X-ray photoelectron spectroscopy (XPS), known for its ability to identify elements and resolve chemical states, is now essential for studying these systems at the molecular level. This review explores recent advancements in cutting-edge XPS techniques, including synchrotron-based, angle-resolved, and ambient-pressure methods, to analyze surfaces modified with dicarboxylic acids. It highlights important findings on metal-ligand interactions, electrical conductivity, and degradation processes in systems like metal-organic frameworks, hydrogels, composite adsorbents, and single-atom catalysts. The discussion focuses on how the shifts in binding energy, peak analysis, and oxidation state mapping connect to functional properties such as adsorption capacity, catalytic performance, and interfacial role. Additionally, the review addresses ongoing challenges, such as beam-induced damage and reactivity under operational conditions, suggesting the integration of operando and multi-modal methods as a way forward. By emphasizing the role of XPS, this review establishes it as a cornerstone technique for unraveling dicarboxylic acid driven surface chemistry, paving the way for the rational design of sustainable and multifunctional materials.

Keywords: Dicarboxylic acids; X-ray photoelectron spectroscopy; Surface modification; Surface chemistry; Binding energy shifts.

1. Introduction

Carboxylic acids are fundamental to modern surface chemistry, with applications spanning catalysis [1,2], bio-sensing [3], battery design [4,5], the pharmaceutical [2,6,7] and environmental remediation [8,9]. Their versatility arises from structural diversity and reactivity, enabling them to act as ligands [10], linkers [11,12], surface modifiers [13,14], and charge mediators through monodentate or multidentate coordination [15]. Dicarboxylic acids and their polyfunctional counterparts are particularly important for tailoring interfacial properties [16]. Despite their widespread use, a detailed mechanistic understanding of how carboxylic acids interact with solid surfaces and influence system performance remains elusive. This gap is being addressed

by advances in surface-sensitive spectroscopies, especially X-ray photoelectron spectroscopy (XPS). XPS provides unmatched capabilities for analyzing elemental composition [17], oxidation states [18], and electronic environments within the top few nanometers of a material's surface. It can distinguish between protonated and deprotonated carboxylic species [19], track metal-oxygen coordination [20-22], and quantify interfacial charge redistribution [23,24], making it essential for studying carboxylic acid systems. Recent innovations, such as ambient-pressure XPS (AP-XPS), synchrotron-based high-resolution XPS, and angle-resolved techniques, have broadened the scope of analysis, enabling in situ and operando studies [25] of dynamic processes under real-world conditions.

Advanced XPS has been instrumental in uncovering the interfacial roles of carboxylic acids [26], offering valuable insights into their behavior and interactions at surfaces [27]. In catalysis, XPS has been instrumental in studying systems like Pd, Pt, and Ru single-atom catalysts [28-30], revealing oxidation state changes [31,32] and ligand-induced shifts [33,34] in metal centers that are vital for reactions such as alcohol oxidation and HMF-to-FDCA conversion. Specific peak shifts, such as Pd $3d_{5/2}$ shifting from ~336.1 to 337.2 eV during oxidation, along with the emergence of shake-up satellites, provide direct evidence of surface-bound intermediates [35]. In biomass valorization, XPS has demonstrated how carboxylates influence redox dynamics [36,37], confirming the regeneration potential of catalysts after multiple cycles [37-39]. For environmental applications, materials modified with carboxylic acids like layered double hydroxides [40], porous polyamides [41], and graphene-based hydrogels [42] exhibit high selectivity for heavy metals like Hg^{2+} and Cu^{2+}. XPS analysis of O 1s and N 1s binding energies has uncovered specific interactions, informing strategies to optimize adsorption sites through ligand engineering [43]. Carboxylic acids also function as molecular adhesives in bio-interfaces [44,45], as observed in DNA-functionalized diamond and peptide-functionalized polymers [46,47]. Despite these strides, challenges remain, beam-induced decarboxylation in thermally sensitive aliphatic acids complicates high-resolution data interpretation. Moreover, many systems lack operando XPS validation under real working conditions, a crucial step for translating laboratory findings into functional designs.

This review tackles these challenges by systematically examining how carboxylic acids influence surface phenomena and how XPS uncovers their mechanistic roles. We contend that XPS is more than just a diagnostic tool as powerful enabler in the molecular engineering of carboxylate-functionalized systems. By integrating high-resolution spectroscopy with multimodal techniques and computational modeling, we foresee a future where carboxylic acid interfaces can be precisely tuned with predictive accuracy to meet the demands of high-performance applications.

2. Surface Interactions and Chemical States of Carboxylic Acids

The investigation of carboxylic acids and their interactions with surfaces plays a critical role across diverse scientific disciplines, including atmospheric science, and materials science. Using advanced techniques such as XPS, researchers have examined how various carboxylic acids, engage with metal surfaces, modulate molecular behavior, and affect material properties. These studies underscore the importance of understanding surface interactions to advance applications in these fields.

Mocellin et al. [48] examined the surface interactions of zwitterionic amino acids, including glycine, alanine, valine, and methionine in aqueous solutions. Hydrophobic amino acids, like valine and methionine tend to concentrate at the surface as evidence by their significant higher XPS signal intensities while hydrophilic ones like glycine and alanine remain in the bulk solution showing lower surface intensities. The behavior, governed by hydrophilic-hydrophobic interactions, has implications for aerosol dynamics and cloud formation, as these amino acids may influence surface tension. Additionally, Abyazisani et al. [49] investigated the adsorption and reactivity of 3,5-pyridinedicarboxylic acid (PDC) on Cu(111) surfaces using synchrotron radiation XPS. XPS spectra of the C1s, O 1s and N 1s regions revealed the PDC undergo deprotonation at 160 ˚C and decarboxylation at 270 ˚C and showed the heating induced changes in molecular orientation and fragmentation. These transformations are critical for surface-based polymerization

processes, emphasizing the importance of temperature control when utilizing dicarboxylic acids in material synthesis (**Figure 1**).

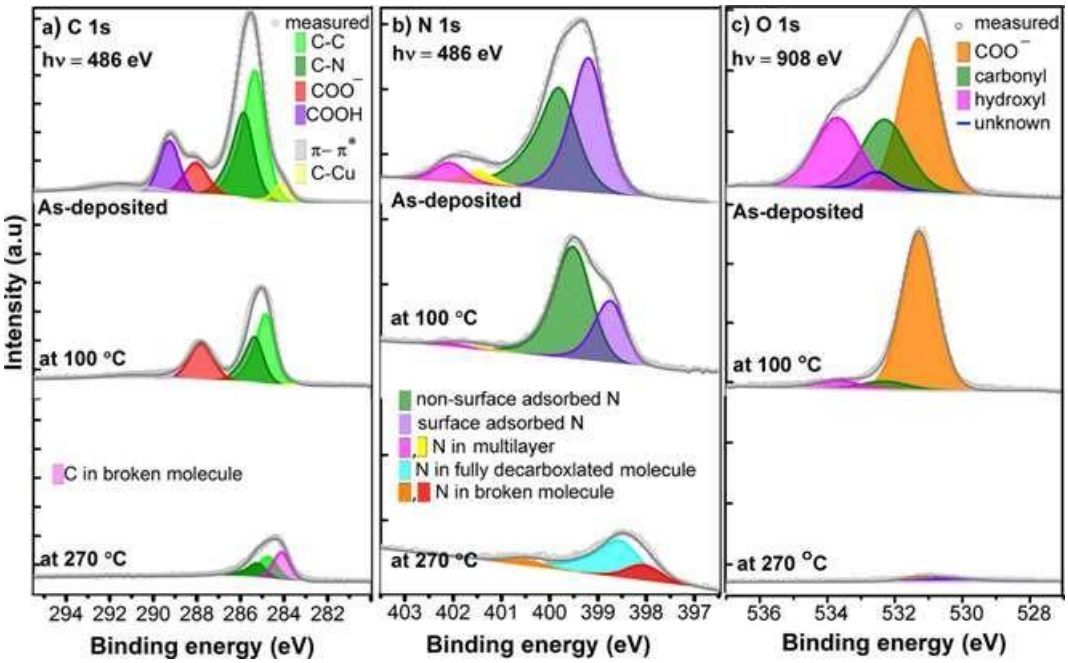

Figure 1. The C 1s, O 1s, and N 1s spectra of PDC deposited on Cu(111) at room temperature and subsequently annealed to 270 ˚C are shown. The experimental data is displayed as a line graph with black circular markers, and the fitted peak envelopes are indicated by solid gray lines. Reused with permission from Ref [49]. Copyright © 2018, American Chemical Society.

In another study, Yang et al. [50] investigated the use of carboxylic acid-based additives in water-based synthetic cutting fluids, demonstrating through molecular dynamics simulations that longer alkyl chains significantly reduce wear and friction on metal surfaces while enhancing corrosion resistance and antibacterial properties. The results underscored the potential of carboxylic acids in improving industrial lubricants and fluid formulations. Similarly, Xiong et al. [51] explored thiophene-2,5-dicarboxylic acid (TDA) derivatives for environmental applications, showing their effectiveness in removing Hg^{2+} from aqueous solutions. XPS analysis highlighted the critical role of carboxyl groups in the adsorption mechanism, emphasizing the utility of surface-modified materials for heavy metal removal and environmental cleanup. In a related study, Zheng et al. [52] examined how aliphatic dicarboxylic acids influence the properties of reduced graphene hydrogels (rGHs). Using XPS, they fond that shorter-chain acids enhance surface area and reducing capabilities, while longer-chain acids improve dispersibility in polar solvents, offering insights into tailoring rGHs for energy storage, sensors, and biomedical uses.

Gao et al. [53] investigated the development of bimetallic metal-organic frameworks (MOFs) for environmental applications, focusing on Ce/Fe MOFs for efficient phosphate removal. XPS analysis provided critical insights into the oxidation states of cerium, highlighting the importance of Ce(III)/Ce(IV) ratios in phosphate binding. This study demonstrated how carboxylate ligands in MOFs can be tailored to optimize adsorption processes for environmental remediation. In a related effort, Zeraati et al. [54] synthesize a zinc-based MOF using 2,6-pyridine dicarboxylic acid as a ligand. XPS confirmed the successful formation of the MOF, which exhibited antimicrobial properties against both Gram-positive and Gram-negative bacteria, showcasing the potential of carboxylate-containing materials in biomedical applications such as infection control in medical devices. Meanwhile, Kim et al. [55] explored the use of dicarboxylic acids, including oxalic, succinic, and phthalic acids, to modify Ag-coated Cu particles, aiming to enhance the

electrical conductivity of sintered films. XPS investigation revealed the coordination between carboxylate groups and the Ag surface, confirming the formation of chemical bond that improved conductivity but also prevented oxidation (**Figure 2)**.

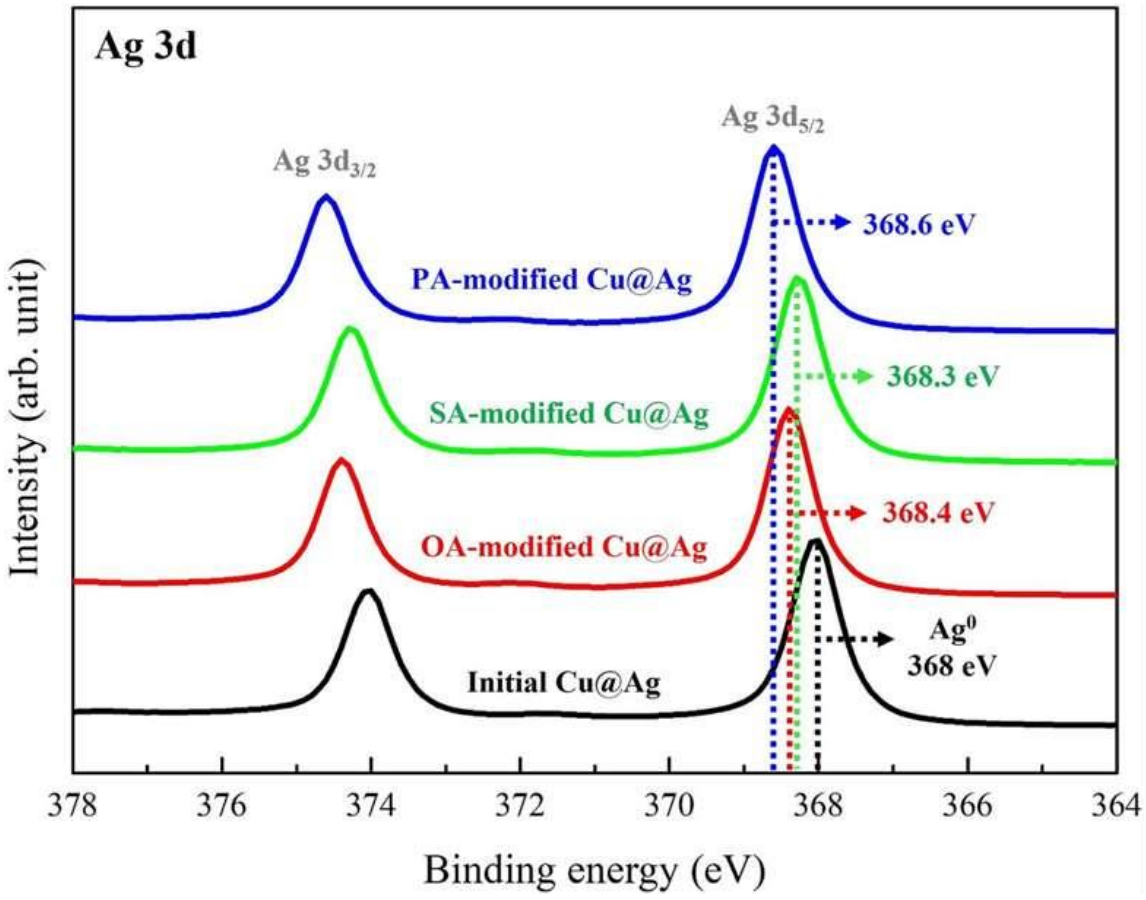

Figure 2. XPS Ag 3d spectra of the original and surface-treated 1.5 Cu-Ag nanoparticles. Reused with permission from Ref [55]. Copyright © 2023 Elsevier B.V. All rights reserved.

In the field of catalytic processes, carboxylic acids and their derivatives play a pivotal role in enhancing performance and understanding reaction mechanisms. Maciulis et al. [56] explored the modification of platinum (Pt) single-atom catalysts (SACs) on ceria using carboxylic acid ligands. XPS analysis revealed that these ligands significantly influence metal loading and catalytic activity in the hydrosilylation of olefins, with the PDO-C ligand demonstrating superior performance. This highlighted the ability of carboxylate ligands to fine-tune catalytic properties for industrial applications. Similarly, Takeda et al. [57] investigated the hydrogenation of dicarboxylic acids (succinic, glutaric, and adipic acids) into diols using a Re-Pd/SiO^2 catalyst. XPS analysis uncovered changes in the oxidation states of rhenium and palladium, which were critical for catalytic efficiency, providing deeper insights into hydrogenation mechanisms and the role of carboxylic acids in shaping catalytic behavior.

However, Carboxylic acids also find application in mineral processing, as demonstrated by Chang et al. [58] who examined the use of phthalic acid in the flotation separation of fluorite and rare earth ores. XPS confirmed strong interactions between carboxylate groups and fluorite surfaces, improving separation efficiency and contributing to advancements in ore processing techniques. In energy storage, Li et al. [59] studied dicarboxylic acids as electrolyte additives in magnesium (Mg) anodes for Mg-air batteries. XPS showed that these acids form soluble complexes with Mg^{2+}, inhibiting corrosion product formation and

enhancing discharge performance, underscoring their potential to improve battery efficiency and lifespan. Moreover, Jeong et al. [60] utilized AP-XPS to investigate the dehydration mechanism of formic acid dissociation on Pt(111) surface. XPS spectra of C 1s and O1s regions showed distinct peaks corresponding to adsorbed CO (Coad) at bridge and non to sites, confirming the formation of CO during the dehydration process. The study offered critical insights into the electrocatalytic oxidation of formic acid, a process with significant implications for fuel cell technologies (**Figure 3)**.

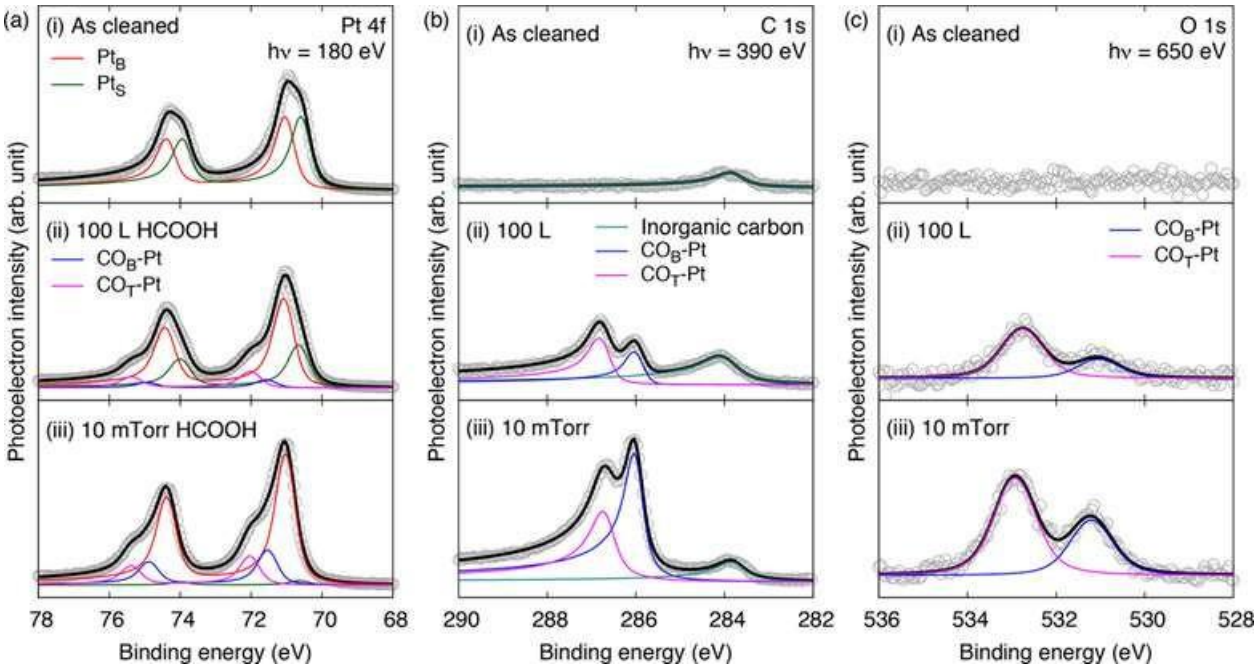

Figure 3. XPS spectra of (a) Pt 4f, (b) C 1s, and (c) O 1s recorded at room temperature for the Pt(111) surface in three states: (i) clean, (ii) after exposure to 100 L (1 Langmuir = 1 Torr) of HCOOH, and (iii) under a background pressure of 10 mTorr HCOOH. Reused with permission from Ref [60]. Copyright © 2018, American Chemical Society.

The above studies presented offer a detailed perspective on the surface interactions and chemical states of carboxylic acids, with a particular focus on dicarboxylic acids, and their significance in a wide range of scientific and industrial applications. Across various fields like material synthesis, mineral processing, environmental remediation, electrochemical systems and energy storage. By providing insights into oxidation states, binding mechanisms, and interfacial dynamics, XPS has not only deepened our understanding of these systems but also paved the way for innovative advancements and optimized designs. This underscores the critical role of carboxylic acids in driving progress across multiple disciplines, highlighting their versatility and importance in addressing contemporary scientific and technological challenges.

3. Dicarboxylic Acid Applications and Catalysis

In recent years, XPS has emerged as a highly effective technique for analyzing surface characteristics, chemical makeup, and shifts in oxidation states of catalysts, adsorbents, and materials used in carboxylic acid-based catalytic systems. The studies highlighted below illustrate the significance of XPS in unraveling the performance of these materials in catalytic reactions, environmental remediation, and sustainable chemical processes.

XPS has gained significant attention for its role in advancing efficient and sustainable catalytic processes. Kirdant et al. [61] introduced a Pd@Glu-HTC catalyst for the direct oxidation of alcohols to

carboxylic acids, utilizing XPS characterization to confirm the presence of Pd and track changes in its oxidation states during the reaction. Derived from biomass based D-glucose, the catalyst demonstrated remarkable catalytic activity under mild conditions, achieving high yields (92-99%) for a variety of alcohols. The study highlighted the catalyst's reusability, with XPS analysis confirming the stability of Pd over multiple reaction cycles further underscoring its potential for sustainable bio based chemical transformations.

In the field of biodegradable materials, Yijie Jin et al. [62] developed polyesters derived from lignin based 2-pyrone-4,6-dicarboxylic acid (PDC) for application as wood adhesives. XPS analysis showed the surface structural changes, particularly at the C1s core level, providing insights into the crosslinking between the polymer and the wood surface (**Figure 4)**. These polyesters exhibited strong adhesion, biodegradability, and outstanding performance under wet conditions, positioning them as promising eco-friendly alternatives for wood adhesives. In another study, Zheng et al. [63] designed a composite adsorbent, PAN@LDH-Hpdc, for the selective removal of Cu^{2+} ions from contaminated water. XPS analysis verified the coordination of metal ions with intercalated Hpdc anions, providing evidence to support the adsorption mechanism. The adsorbent achieved an impressive removal efficiency of 99.6% for Cu^{2+} ions within just 25 minutes. Its high selectivity, stability and reusability highlight its potential for large scale applications in water purification.

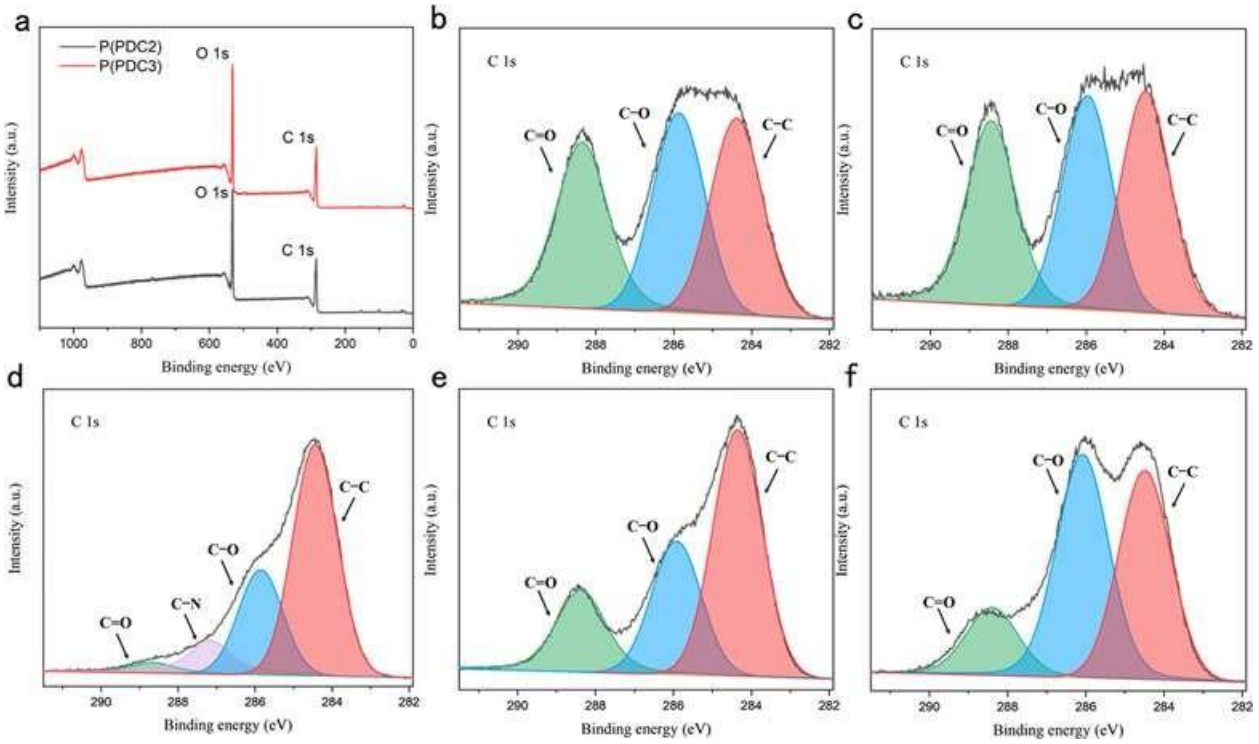

Figure 4. XPS survey spectra of (a) $P(PDC_2)$ and $P(PDC_3)$; C 1s core-level spectra of (b) $P(PDC_2)$, (c) $P(PDC_3)$, and (d) a cypress wood plate; and C 1s spectra of (e) $P(PDC_2)$ and (f) $P(PDC_3)$ after hot-pressing. Reused with permission from Ref [62]. Licensed under CC BY 3.0.

XPS also plays a vital role in material design for environmental applications, as demonstrated by Xiong et al. [64] who synthesized 2,5-furandicarboxylic acid based porous polyamides (FPPA-1 and FPPA-2) for the adsorption of Hg^{2+} ions from aqueous solutions. The XPS analysis revealed notable changes in the N 1s and O1s spectra following Hg^{2+} adsorption, confirming the interaction between the adsorbents and Hg^{2+} ions through coordination with amide and furan groups. The study showed that FPPA-2 exhibited superior adsorption performance, achieving a maximum capacity of 462 mg/g for Hg^{2+}, while maintaining high efficiency even after five cycles.

Moreover, Zhuang et al. [65] explored the role of dicarboxylic acids (DAs) in enhancing the efficiency and stability of perovskite solar cells (PSCs) by modifying the interface between the electron transport layer and the perovskite layer. XPS analysis verified that oxalic acid (OA), along with other DAs, effectively passivated surface defects on SnO_2 leading to improved energy level alignment and enhanced charge extraction. This resulted in superior PSC performance. The study highlighted the potential of DAs in stabilizing PSCs, as the devices retained over 80% of their initial efficiency after prolonged exposure. Rao et al. [66] devised a base free aerobic oxidation method to convert 5-hydroxymethylfurfural (HMF) into 2,5-furandicarboxylic acid (FDCA) using Ru-doped Ni manganite catalysts. XPS characterization of the catalysts revealed high dispersion and stability of the catalysts, with oxygen vacancies and the synergistic interactions between Ru and Mn playing a crucial role in the oxidation process. Especially, the Ru 3p spectra confirmed the presence of Ru-O and Ru-OH species with valencies of +3 and +4 which facilitated catalytic activity. This scalable approach achieved remarkable FDCA yields, offering a promising pathway for the industrial-scale production of bio-based chemicals (**Figure 5)**.

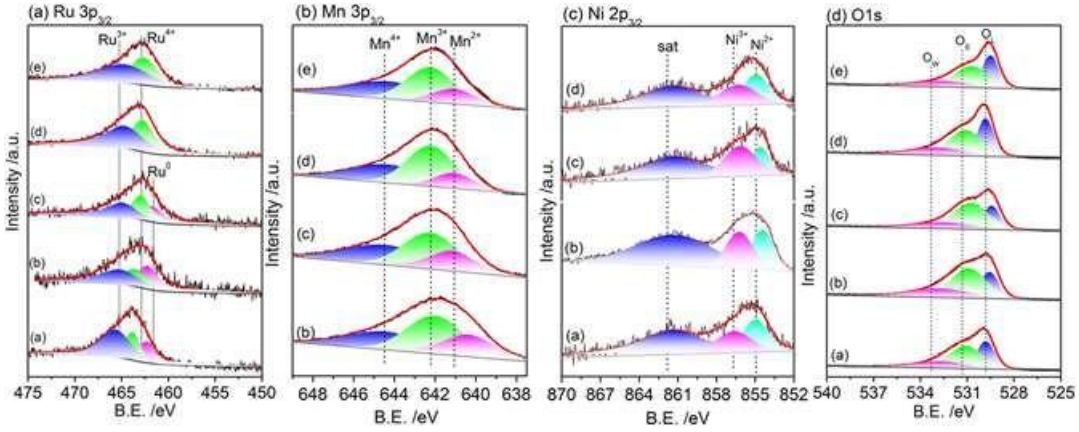

Figure 5. XPS spectra of the Ru 3d core level for the following catalysts: (a) Ru/NiO, (b) Ru/Ni_1Mn_1, (c) Ru/Ni_1Mn_3, (d) Ru/Ni_1Mn_6, and (e) Ru/MnO. Reused with permission from ref [66]. Licensed under CC BY 3.0.

Fang et al. [67] developed copper-based metal-organic frameworks (MOFs) for the photocatalytic degradation of tetracycline under visible light. XPS analysis identified critical bonding characteristics of carbon, oxygen, and copper within the MOF, confirming their involvement in the photocatalytic mechanism. The catalyst demonstrated a degradation efficiency of 94% surpassing the performance of other MOFs tested, and highlighting its potential for environmental applications in pollutant removal. Shaikh et al. [68] investigated the surface modification of ferrite nanoparticles using various dicarboxylic acids to catalyze the dehydration of fructose for the production of 5-hydroxymethylfurfural (5-HMF). XPS analysis validated the successful modification of the ferrite nanoparticles, demonstrating that flexible ligands like malic acid significantly enhanced catalytic performance. This study highlights how carboxylic acid-based surface modifications can boost catalytic activity, offering a promising strategy for advancing biofuel production. Xu et al. [69] developed metal-organic frameworks (MOFs) incorporating naphthalenediimide (NDI) derivatives and phenyl dicarboxylic acid ligands for use in sensing and iodine adsorption. XPS analysis verified the interaction between the metal centers and the carboxylate groups of the ligands, highlighting the robust adsorption behavior of these complexes. This work underscores their potential significance in environmental monitoring applications.

Sun et al. [70] fabricated dual-metal ferrocenyl coordination polymer microspheres (M1M2-CPMs) using 1,10-ferrocene dicarboxylic acid as a ligand for hydrogen storage applications. XPS analysis identified metal oxide peaks corresponding to Co, Mn and Cu, confirming the successful formation of the targeted metal coordination structures. Notably the microspheres demonstrated significant hydrogen uptake, with

hollow structured MnCu-CPMs showing particularly promising results. This study emphasizes the critical role of material morphology in enhancing hydrogen storage capacities. Similarly, Ahmad et al. [71] developed a PMA@MIL-53 (Fe) catalyst for the selective nitration of phenol using an ultrasound-assisted method. XPS analysis confirmed the successful encapsulation of phosphomolybdic acid (PMA) within the MIL-53 (Fe) framework. This approach enabled high selectivity and yield under milder and more environmentally friendly reaction conditions. Additionally, Antonyraj et al. [72] investigated the use of Au-Pd alloy nanoparticles supported on anion-exchange resins (AERs) for the oxidation of HMF to FDCA. XPS analysis verified the formation of a well dispersed Au-pd alloy, with the Au 4f and pd 3d spectra indicating strong alloying effects. These interactions contributed to improved FDCA selectivity and excellent reusability over multiple reaction cycles, highlighting the catalyst's stability and efficiency **Figure 6**.

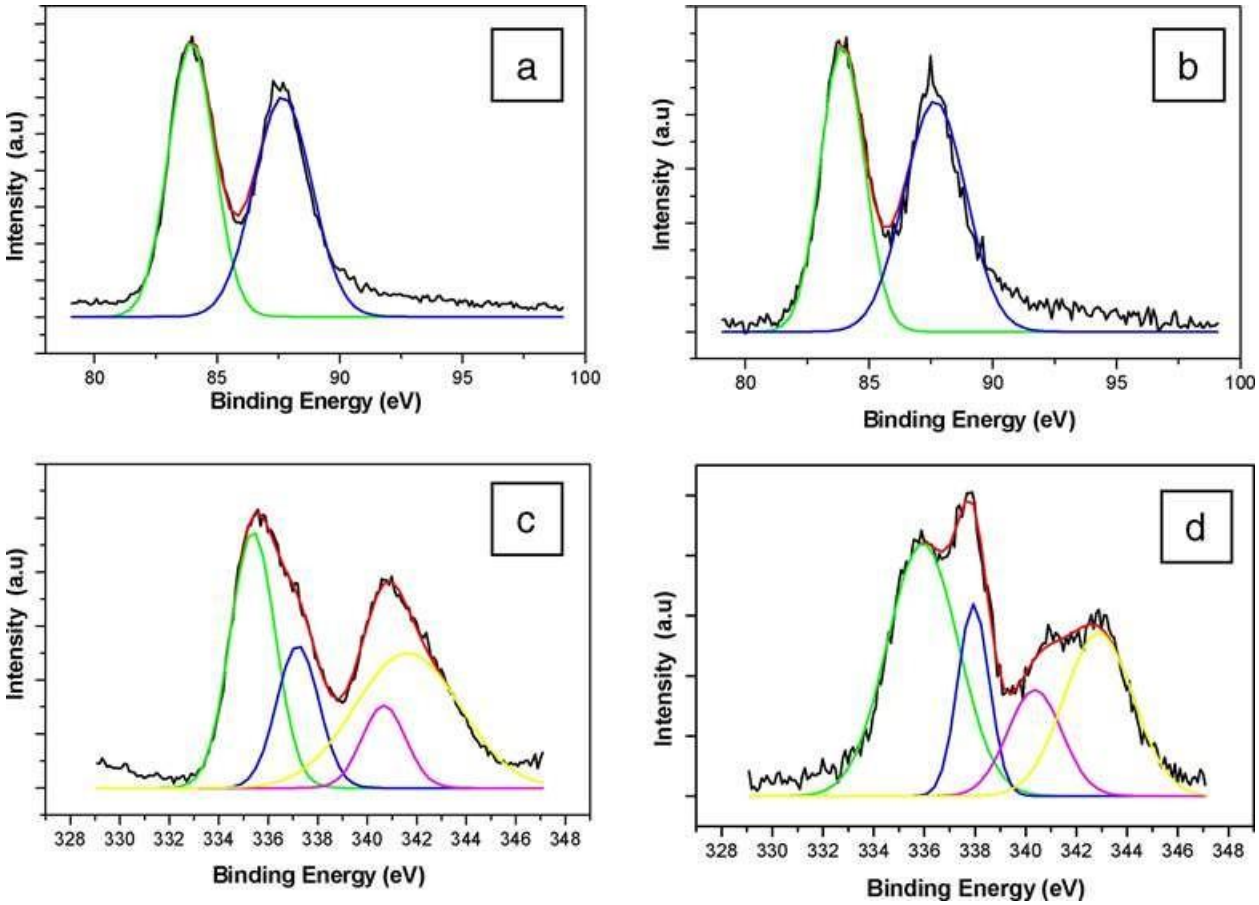

Figure 6. XPS spectra of (A) Au 4f for Au/IRA-743, (B) Au 4f for AuPd/IRA-743, (C) Pd 3d for Pd/IRA-743, and (D) Pd 3d for AuPd/IRA-743. Reused with permission from Ref [72]. Copyright © 2017

The studies collectively underscored the transformative role of carboxylic acids and advanced XPS analysis in driving innovation across catalysis, and sustainable material design. By providing detailed insights into surface interactions, oxidation states, and chemical bonding, XPS enabled the optimization of functional materials for applications ranging from bio-based chemical synthesis to pollutant removal. These advancements highlighted the potential of carboxylic acid-modified systems to address pressing global challenges, offering scalable, efficient, and eco-friendly solutions for industrial and environmental technologies.

4. Material Modification and Surface Engineering Using Carboxylic Acids

Carboxylic acids, including dicarboxylic and polyfunctional variants, have become essential molecular tools for surface engineering due to their rich coordination chemistry, tunable functionality, and environmental compatibility. Their roles are increasingly being validated through advanced surface characterization techniques, particularly XPS. Recent studies have not only utilized carboxylic acids for direct surface modification but have also demonstrated their synergistic integration with metal ions, nanomaterials, and biomolecules. This has led to the development of multifunctional systems with precise interfacial control, further expanding their applications and impact.

At the molecular level, the ability of carboxyl groups to form stable complexes with metal ions has inspired innovative strategies for selective adsorption and sensing. Zhang et al. [73] explored zinc binding to coal-based fulvic acid (FA), identifying carboxyl and carbonyl groups as key coordination sites through XPS analysis and quantum calculations. Their findings emphasized the critical role of dicarboxylic motifs in chelation. Similarly, Hu et al. [74] developed a zirconium-based MOF (MIL-161) using s-tetrazine dicarboxylic acid ligands for the selective uptake of Au(111). In both studies, XPS confirmed metal-ligand interactions, underscoring the significance of carboxylic acid functionality in achieving efficient and selective metal capture. A similar adsorption-driven mechanism is central to the work by Muthu Prabhu et al. [75] who utilized La-MOFs synthesized with various carboxylate ligands (BDC, BTC) for arsenate removal. The identity of the ligand significantly affected performance, and XPS analysis confirmed the formation of $LaAsO_4$ following arsenate adsorption. This variation in behavior, linked to ligand structure, mirrors the findings of An et al. [76] who investigated how different dicarboxylic acids (maleic, succinic, malonic) influence the morphology and mechanical properties of gypsum crystals. XPS analysis illustrated the distinct adsorption behavior across crystal planes. The C 1s spectra highlighted the presence of carboxylic groups adsorbed on specific planes, while O 1s spectra demonstrated interactions between oxygen atoms in the acids and calcium ions on the gypsum surface. Additionally, The Ca 2p spectra showed shifts in binding energy, indicating the formation of coordination bonds between the acids and gypsum surface. These findings underscored the critical role of carboxylic acid structure in determining adsorption strength and crystal growth, providing valuable insights for optimizing gypsum modification processes (Figure 7).

Beyond adsorption, carboxylic acids play a key role in surface passivation and functionalization. Nardi et al. [77] employed 2,6-naphthalene dicarboxylic acid (NDCA) for supersonic molecular beam deposition (SuMBD) onto silicon nitride, creating a clean, covalently bound organic layer well-suited for biosensing applications. This theme of bioconjugation is further advanced by Taylor et al. [78] who used XPS and ToF-SIMS to correlate amino acid content on polymer surfaces with biological responses. Carboxyl functionalized layers showed a strong association with stem cell adhesion, bridging surface chemistry to bioactivity. In a similar vein, Dey et al. [79] developed a Fe-MOF/CNF hybrid sensor using 3,5-pyrazoledicarboxylic acid for the sensitive detection of chlorpyrifos in food samples. The carboxylic functionality was pivotal in facilitating analyte binding and electron transfer, with XPS confirming the structural integrity of the hybrid system. These studies collectively highlight the critical role of carboxyl groups in enhancing both bioactivity and sensing performance.

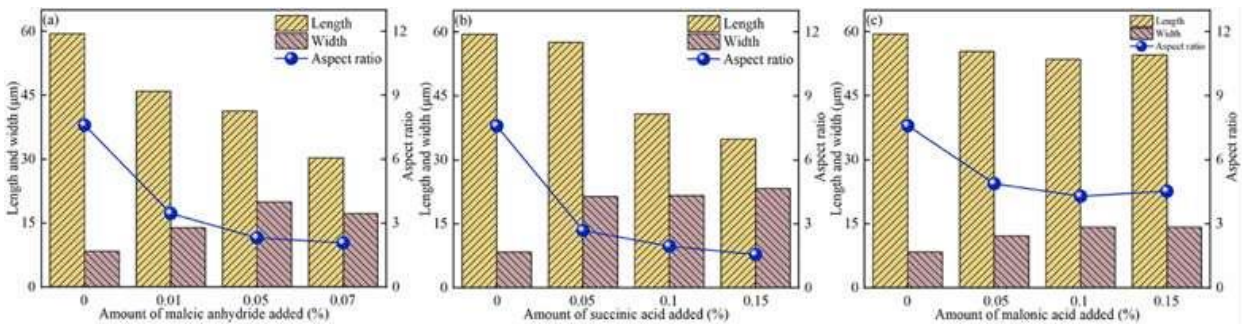

Figure 7. Average length, width, and aspect ratio (AR) of α-HH particles prepared using (a) maleic anhydride, (b) succinic acid and (c) malonic acid at different concentrations. Reused with permission from ref [76]. Copyright © 2025

Surface interactions involving carboxylic acids also play a significant role in flotation chemistry and corrosion processes. Shen et al. [80] introduced mercaptosuccinic acid as a depressant for the selective flotation of chalcopyrite and galena. XPS and molecular dynamics confirmed its adsorption affinity, which altered mineral hydrophilicity. In a separate aqueous system, Dou et al. [81] synthesized fluorescent polyaspartic acid (PASP) derivatives containing carboxyl groups, which effectively inhibited steel corrosion through surface coordination. Despite differing objectives, the underlying mechanism metal ligand bonding at the interface was consistent across both systems, underscoring the versatility of carboxylic acids in mediating surface interactions. Interfacial behavior is further highlighted in catalytic and environmental systems. Safeeda et al. [82] developed an Fe-Mn oxide catalyst supported on zeolite, utilizing sugarcane biomass for the production of 2,5-furandicarboxylic acid (FDCA). XPS analysis revealed the presence of active oxygen species and metal valence states critical to the catalytic process. Similarly, Chen et al. [83] investigated the binding of humic acid to kaolinite, identifying ligand exchange between carboxylate groups and surface hydroxyls. This interaction, influenced by pH, reflects organic-mineral associations that are crucial for understanding soil carbon stability. Together, these studies underscore the importance of interfacial phenomena in both catalytic efficiency and environmental processes.

Studies such as that by Ferreira Jr. et al. [84] highlight the analytical implications of XPS itself. Their investigation into dicarboxylic acids (malonic, succinic, glutaric) demonstrated that prolonged X-ray exposure resulted in decarboxylation, revealing the inherent instability of certain acids during surface analysis. This finding underscored the critical importance of carefully controlling measurement conditions to ensure accurate and reliable results. Carboxylic acids also play a pivotal role in advanced nanostructure engineering. Prochazka et al. [85] investigated the phase transformation of biphenyl dicarboxylic acid (BDA) on silver surfaces, uncovering complex surface ordering through XPS. Dietrich et al. [86] investigated the para-aminobenzoic acid (PABA) formed distinct self-assembled monolayers on V_2O_5 surfaces, with configuration varying based on surface coverage. XPS illustration revealed the chemical states of PABA molecules, including peaks for C 1s, N1s and O 1s, which confirmed the molecular orientation and packing on V_2O_5 surfaces (Figure 8). These findings collectively emphasized how the orientation and packing of carboxylated molecules significantly influence interfacial structure and functionality.

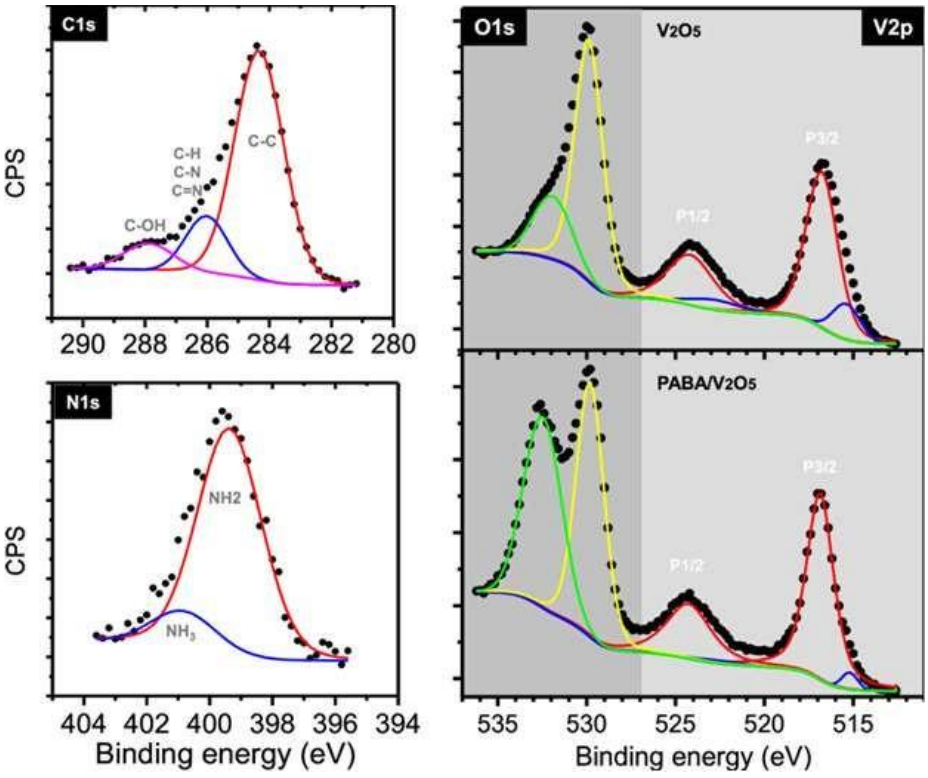

Figure 8. XPS spectra of bare V_2O_5 and PABA-capped V_2O_5 surfaces. Shown are the O 1s and V 2p signals for the bare V_2O_5 surface, and the C 1s, N 1s, O 1s, and V 2p signals for PABA-SAMs/ V_2O_5. Reused with permission from Ref [86]. Copyright © 2021, American Chemical Society

These studies illustrated that carboxylic acids whether employed as surface ligands, linkers, or structural motifs act as a molecular bridge connecting surface chemistry to functional performance. Their versatility is further enhanced by the consistent application of XPS, which not only confirms surface modifications but also provides deeper mechanistic insights across a wide range of applications. This collective body of work highlights how thoughtful molecular design, coupled with precise characterization techniques, continues to push the boundaries of material modification and surface engineering.

5. Conclusion and Perspectives

The strategic incorporation of carboxylic acids in surface chemistry marks a pivotal intersection of molecular design and interfacial control. Advanced XPS methodologies have empowered researchers to obtain quantitative and mechanistic insights into how these acids coordinate, transform, and function at solid surfaces. This review has highlighted how shifts in XPS core-level signals, such as C 1s, O 1s, and metal core lines, have provided profound understanding of binding modes, oxidation states, and degradation processes in carboxylic acid-functionalized systems. Looking ahead, the integration of operando XPS for real-time monitoring under reaction or environmental conditions will unlock deeper insights into dynamic surface phenomena. A key area of focus will be the development of beam-resistant materials and soft X-ray techniques to study fragile organic acids, enabling more robust analyses of delicate systems. Additionally, leveraging machine learning and data science to interpret large XPS datasets will be critical for uncovering meaningful trends and patterns, transitioning the field from observation to predictive modeling. These advancements will pave the way for emerging applications in areas such as perovskite stabilization, antimicrobial coatings, and bioelectronic interfaces, all of which stand to benefit from a deeper mechanistic understanding. XPS is set to remain a cornerstone technique in these innovations, facilitating the rational

design of next-generation surfaces where carboxylic acids serve tailored, multifunctional roles in sustainable and advanced technologies.

CRedit authorship contribution statement

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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