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Tribocatalysis: a successful marriage of triboelectricity and heterogeneous catalysis

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Tribocatalysis is an emerging and promising approach that integrates triboelectric effects with heterogeneous catalysis to drive chemical reactions through mechanical energy input. In contrast to conventional catalytic methods that rely on thermal, photonic, or electrical stimuli, tribocatalysis utilizes friction-induced charge generation as a sustainable and energy-efficient means of activating catalytic processes. This article discusses the underlying principles of tribocatalysis, with particular emphasis on the dual function of mechanical stirring in facilitating catalyst–substrate interactions and promoting catalyst activation. Key materials and activation mechanisms are reviewed, highlighting their potential in applications such as environmental remediation and chemical energy storage. Despite recent advances, significant challenges remain, including limited mechanistic insight, issues of material durability, and difficulties in scaling up. This work aims to provide a comprehensive perspective on the current state of tribocatalysis, identify critical knowledge gaps, and encourage continued research to advance the field toward practical implementation.

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1. Introduction

Tribocatalysis integrates triboelectricity with catalysis, using frictional forces to drive chemical reactions. It provides an alternative to conventional catalytic processes, which are often energy-intensive. In tribocatalysis, friction generates reactive sites, localized charges, or electron–hole pairs.[1] Unlike traditional catalytic systems that depend on external energy sources such as heat, light, or electrical bias, tribocatalysis harnesses mechanical energy, an abundant yet underutilized resource, offering a more environmentally friendly and cost-effective approach.[2]

Tribocatalysis is based on the principles of triboelectricity. Triboelectricity, also known as the triboelectric effect, refers to the generation of electric charge when two materials come into contact and are subsequently separated.[3,4] This phenomenon arises from the transfer of electrons between the materials, driven by differences in their electron affinities. When materials are rubbed, pressed, or otherwise brought into contact, the resulting charge imbalance can be harnessed for various purposes. As a fundamental phenomenon in tribology, which is the study of friction, lubrication, and wear, the triboelectric effect has gained increasing attention in the development of energy harvesting technologies.[4]

Triboelectric materials are classified based on their tendency to gain or lose electrons.[5] Materials such as glass and wool tend to lose electrons and become positively charged, whereas materials like rubber, Teflon, and polyvinyl chloride are more likely to gain electrons and become negatively charged. The effectiveness of triboelectric materials in generating electricity depends on their relative positions in the triboelectric series and their ability to create a charge difference when paired with another material. The triboelectric series ranks materials according to their tendency to gain or lose electrons through friction. When two materials come into contact and then separate, one becomes positively charged (by losing electrons) and the other negatively charged (by gaining electrons). The series helps predict which material will become charged and in which direction. Materials higher in the series tend to lose electrons, while those lower in the series tend to gain them.

Designing efficient triboelectric materials requires an understanding of their molecular structure and surface properties. Key factors for optimization include surface area, roughness, and the dielectric constant of the materials.[5] Increasing the surface roughness, for example, enhances the contact area and therefore the charge generation.[6] Chemical modifications, such as introducing functional groups that increase electron affinity or donating capability, can also improve performance.[7] Meanwhile, pairing materials with large

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differences in their positions on the triboelectric series maximizes charge transfer.[8] Multilayer or composite materials can also be engineered to combine the desirable properties of different substances, such as flexibility, durability, and high charge density.[9]

Triboelectric materials transform mechanical energy into electrical energy by producing reactive charges that can drive chemical reactions *via* redox processes, assuming the redox potentials are thermodynamically favorable.[2,10] Thus, mechanical energy is ultimately stored as chemical energy in the bonds of the target products or used to chemically convert the substrate into other chemical entities, as in the case of total oxidation or mineralization of recalcitrant organics. Materials are considered tribocatalysts only when they drive such reactions. However, not all triboelectric materials qualify as tribocatalysts, as many lack the catalytic activity necessary to facilitate thermodynamically unfavorable or kinetically sluggish redox reactions. By definition, tribocatalysts are materials that enable chemical reactions through frictional forces.[10] This field combines tribology, which is the study of friction, wear, and lubrication, with catalysis, examining how mechanical forces activate or enhance chemical reactions.

Mechanistically, the application of frictional energy to a material can induce localized changes in its structure or surface, thereby lowering the energy barrier for chemical reactions.[10,11] In tribocatalysis, mechanical forces can generate reactive species, such as free radicals or ions, to drive chemical reactions. The mechanisms of tribocatalysis involve several key factors. Friction can break or activate surface bonds, enhancing material reactivity, and generate electric charges through triboelectric effects, further promoting chemical reactions.[11] In some cases, friction induces localized heating, accelerating reactions without bulk heating.[2] Friction can also expose new reactive surfaces or create defects in the material, both potentially serving as catalytically active sites. Together, these processes make tribocatalysts a versatile tool for chemical transformations.

Although still in its infancy, tribocatalysis shows promising potential, as it can harness even small amounts of mechanical forces from the surrounding environment, which are ubiquitous yet barely exploited, such as water flow. This potential arises from the sensitivity of tribocatalysts to low-frequency mechanical forces in the form of friction. To advance the field and stimulate further discussion, this perspective discusses the state of the art, key achievements, prospects, and challenges of tribocatalysis. We cover several issues that have not yet been explicitly discussed in earlier review articles on tribocatalysis,[2,11–15] including comparative features of different mechanisms, potential techniques for characterizing charge carrier behavior in triboelectric materials, and key design considerations.

2. Tribocatalytic materials

The overall performance of tribocatalysis relies on the selection of catalyst materials. Various classes of materials have exhibited tribocatalytic responses, each offering distinct advantages.

(i) Metal oxides: oxide materials such as TiO_2 are widely utilized for their ability to generate reactive oxygen species (ROS) under frictional forces.[16] These materials are generally robust, chemically stable, and capable of enduring repeated cycles of frictional forces.

(ii) Piezoelectrics: piezoelectric compounds, such as $BaTiO_3$, ZnO, and lead zirconate titanate (PZT), are effective at converting mechanical energy into electrical charges under external mechanical stress, such as pressure and vibration.[17] This property enables piezoelectric materials to facilitate redox reactions in processes like water splitting, CO_2 reduction, and nitrogen fixation.

(iii) Polymers: polymers like polytetrafluoroethylene (PTFE) and fluorinated ethylene propylene (FEP) exhibit strong triboelectric effects, acting as electron acceptors or donors in chemical reactions.[18,19] These materials are lightweight, cost-effective, and capable of generating triboelectric charges under low-frequency mechanical forces, expanding the scope of tribocatalysis to diverse settings.

(iv) Composites: hybrid materials that combine the properties of two or more functional components to form junction composites are applicable for improving tribocatalytic performance. For example, creating heterojunctions such as $Ba_{1.4}Sr_{3.6}NdNb_7Ti_3O_{30}$–$N_2$/g-$C_3N_4$ (ref. 20) and $Cu_{1.8}S/CuCo_2S_4$ (ref. 21) enhances the generation of reactive species, including $^{\bullet}OH$ and $^{\bullet}O_2^-$ radicals. Improved tribocatalytic performance is also observed in $BaTiO_3$ (ref. 22) and CdS[23] when coated with metals, particularly metallic Ti, due to the transfer of excited electrons to the metallic coatings, which then restricts their recombination with holes.

(v) Semiconductors: semiconductor-based materials (other than metal oxides), such as CdS and g-C_3N_4, use their well-defined energy band structures to generate electron–hole pairs under mechanical forces, being relevant to tribocatalytic processes.[24]

Semiconducting metal oxides are generally regarded as an effective class of materials for tribocatalysis. Their widespread use stems from a combination of well-understood electronic properties that allow for relatively straightforward engineering, chemical stability, and adaptability to surface modification. TiO_2 and ZnO are leading examples, owing to their strong mechanical robustness and favorable band structures that support the generation and separation of electron–hole pairs under mechanical stress. The intrinsic piezoelectricity of ZnO is particularly advantageous, as it generates an internal electric field under mechanical deformation, promoting rapid charge separation. These spatially separated charges then become available for redox reactions at the surface. This characteristic has made ZnO one of the most extensively studied tribocatalysts in recent years, especially for environmental applications.[25] ZnO is especially effective in the degradation of organic pollutants due to its strong piezoelectric properties, high surface activity, and non-toxic nature. Under mechanical stress, the internal electric fields generated by ZnO facilitate charge separation, leading to the formation of ROS, which are essential for breaking down organic contaminants in water. Its chemical

stability and relatively low cost further contribute to its widespread adoption in pollution control technologies.

For energy-oriented applications, such as H_2 production *via* water splitting, other transition metal oxides like NiO and Co_3O_4 are favored.[26] These materials offer superior redox activity, with Ni^{2+}/Ni^{3+} and Co^{2+}/Co^{3+} transitions facilitating O_2 evolution and water oxidation under mechanical activation. Their ability to participate directly in surface redox reactions, coupled with high electrical conductivity and stability in alkaline environments, makes them ideal for tribocatalytic water splitting.[27] Moreover, these oxides could be paired with carbonaceous supports or conductive frameworks to enhance electron mobility and surface reaction rates, which is crucial for efficient H_2 evolution. Such application-dependent selection reflects the nuanced material-performance relationship that defines the evolving field of tribocatalysis.

Another key advantage of metal oxides is their ease of modification. Metal oxides can be doped with noble metals or non-metal elements to fine-tune their electronic structure and elongate the lifetime of the generated charge carriers. Forming heterojunctions between different oxides or combining them with carbon-based materials may further enhance charge separation and surface activity.[28] These engineered composites potentially show improved efficiency, even under low-energy friction conditions where maximizing electron utilization is critical.

Despite emerging interest in materials like 2D layered semiconductors and carbon-based nanostructures, they often require more sophisticated synthesis and surface functionalization to achieve the same level of catalytic efficiency observed in oxide systems. Their long-term mechanical durability under repeated frictional contact is also not always guaranteed, limiting their scalability. Thus, metal oxides remain the benchmark for tribocatalytic applications due to their balanced combination of durability, electronic functionality, and surface chemistry, making them the most versatile class of tribocatalytic materials in current research.

3. Mechanistic insights

In considering the so-called tribocatalytic reaction, a fundamental question arises: How can the simple act of stirring catalyst particles be sufficient to drive often thermodynamically demanding reactions, such as water splitting, which generates H_2 and O_2 gas bubbles? This mechanistic question needs to be addressed to establish a proper research direction for tribocatalyst design.

In their early work, the Domen group investigated the mechanism of H_2 production *via* overall water splitting using metal oxides such as Cu_2O, NiO, and Co_3O_4, driven solely by mechanical stirring at room temperature.[26] Vigorous mechanical rubbing between the catalyst and the Pyrex glass vessel, rather than simple stirring or collision, was essential to initiate the reaction, which yielded both H_2 and O_2 in a near-stoichiometric 2 : 1 ratio. Mechanical energy, rather than light or electricity, was converted into chemical energy, enabling continuous gas evolution in the dark. Metallic states (Cu^0, Ni^0, Co^0) formed transiently during the reaction, suggesting a redox mechanism in which metals are oxidized by water to produce H_2, and then reoxidized back to oxides, enabling cyclical activity. While this proposed mechanism is consistent with observed results, they acknowledged unresolved questions. Isotope labeling evidence implies O_2 originates from water, not the oxide lattice. Thus, although the redox cycling of metal/metal oxide pairs appears central, the full mechanism remains partly speculative and likely involves additional tribochemical or electrostatic phenomena.

Later in the 2004 commentary, David S. Ross challenged the interpretation that these reactions occur *via* catalytic cycles at low temperatures, with emphasis on the implausibility of the proposed endoergic mechanisms based on established thermodynamic principles.[29] The volume of gas produced, along with the observed stoichiometric H_2/O_2 ratio, suggests not a low-temperature catalytic process but rather water splitting driven by transient high temperatures, likely produced by localized friction. Thermodynamic data and equilibrium calculations support a reinterpretation showing that the reported gas pressures and product ratios can only occur at temperatures near or above 1500 °C. This implies the reactions occur not *via* proposed catalytic redox cycles but through thermal decomposition of water in microscale high-temperature regions. The analysis of copper-based systems further reinforces this scheme, showing that metallic copper formation and the absence of CuO are consistent with high-temperature conditions. The phenomenon may be more accurately explained as thermally driven water splitting facilitated by frictional heating, possibly enhanced by the catalytic activity of certain oxides.

Indeed, the mechanism by which tribocatalysis activates catalysts is not fully understood at present. It is generally believed that the process primarily involves (1) electron transfer across atoms and (2) electron transitions (Fig. 1).[2] Electron transfer mechanism is driven by mechanical friction between the catalyst and its surroundings, facilitating electron migration to generate reactive species important for chemical reactions. This mechanism is particularly relevant in polymer-based materials known for their efficient electron gaining capabilities. In contrast, the electron transition mechanism involves the excitation of electrons from the valence band (VB) to the conduction band (CB) under mechanical force, leading to the formation of reactive species such as free radicals or valuable products like H_2. In this context, electron transition is not equivalent to electron excitation, but rather includes it as one component of the overall process. The term "electron transition," as defined within the research community, refers to a whole mechanism that encompasses excitation, de-excitation, and electron hopping or charge transfer between different atoms or materials. Thus, while all electron excitations are electron transitions, not all electron transitions are excitations. Excitation here specifically refers to the transition of electrons from the VB to the CB, triggered by frictional energy activation. Closely related to the energy band theory in piezocatalysis, which in fact, originally comes from photocatalysis, this mechanism is frequently observed in semiconducting materials

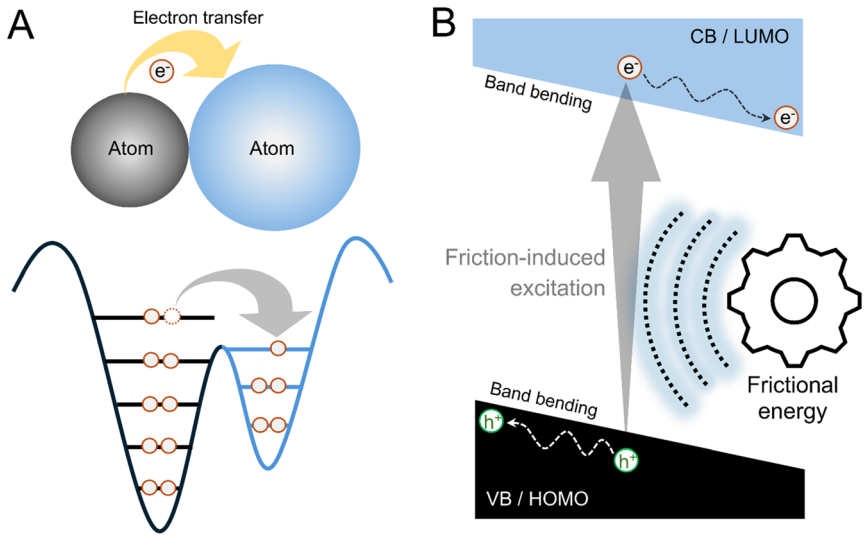

Fig. 1 Schematic of the mechanisms of tribocatalysis: (A) electron transfer and (B) electron transition. Band bending is expected in a semiconducting catalyst (B), especially near its surface, when exposed to frictional forces.

with well-defined energy band structures. Both mechanisms rely on the interaction between the catalyst and its environment to induce reactivity *via* frictional forces. The two proposed mechanisms of tribocatalysis are comparatively summarized in Table 1.

Recall that piezocatalysis refers to a reduction and/or oxidation reaction driven by mechanical stress applied to piezoelectric materials. This stress generates an electric field, which in turn facilitates chemical reactions. Piezoelectric materials are crystalline substances that lack a center of symmetry, allowing the displacement of ions within the material to generate an electric potential. Readers are referred to explore our recent articles on piezocatalysis for more details.[31–33]

The mechanism based on electron transfer across atoms assumes overlapping electron clouds between two atoms or molecules, with friction affecting the strength of this overlap. Thus far, tribocatalysis mostly involves electron transfer between catalysts and environmental materials during friction,

Table 1 Comparative features of two tribocatalytic mechanisms[2,11–15,30]

Feature	Electron transfer	Electron transition
Basic principle	Electrons are transferred directly from one atom to another across contacting surfaces, typically during friction	Electrons in a solid are excited from a lower energy state (*e.g.*, VB) to a higher energy state (*e.g.*, CB) due to friction
Energy source	Mechanical force induces bond breaking and promotes charge exchange at interfaces	Mechanical energy induces electronic excitation, similar to photoexcitation but *via* mechanical means
Key driving force	Contact electrification or triboelectric effect due to atomic interactions	Friction-induced excitation of electrons (*e.g.*, *via* mechanoluminescence or mechanochemical bandgap excitation)
Material dependence	Strongly depends on the work function difference and chemical nature of contacting surfaces	Depends on the electronic structure and bandgap of the material
Example materials	Metal/semiconductor interfaces, triboelectric pairs (*e.g.*, TiO_2–graphite)	Semiconductors and dielectrics with well-defined bandgaps (*e.g.*, ZnO, g-C_3N_4, TiO_2)
Reaction type	Often leads to redox reactions at the interface	Can promote photocatalysis-like reactions (*e.g.*, ROS generation, water splitting)
Notable observations	Generation of charge carriers due to friction, typically measured *via* triboelectric signals	Similarity to photochemical processes; often shows bandgap-dependent activity
Experimental evidence	Kelvin probe force microscopy (KPFM), tribopotential measurements	Electron spin resonance (ESR), photoluminescence-like emissions during friction
Advantages	Works even at low bandgap or metallic systems	Selective excitation possible; parallels to well-studied photocatalysis
Limitations	Highly dependent on contact conditions and atomic-scale interface	Limited to materials with suitable band structures; may require high friction

enabling redox reactions to degrade model pollutants such as synthetic dyes. In solid–solid friction, such as between a catalyst and a PTFE magnetic bar, strong electron cloud overlap enables tribocatalysis. For instance, ZnO nanorods rubbing against a PTFE bar can degrade rhodamine B dye through electron transfer, generating hydroxyl radicals.[34] Similarly, $NiCo_2O_4$ catalysts in friction with PTFE produce superoxide radicals for dye degradation, with efficiency increasing as contact areas expand.[35] Friction between a catalyst and its container also contributes to tribocatalysis. Optimizing friction surfaces and the energy band structures of catalysts, such as switching containers from glass to polypropylene, can further improve degradation rates by enhancing free radical generation.[36]

An early study by Hiratsuka and co-workers suggested that friction enhances the tribocatalytic oxidation of ethylene on a Pd catalyst through an electron transfer mechanism.[37] Two types of reactions, fast and slow, were attributed to near-contact and out-of-contact interactions on the friction surfaces. The near-contact reaction is driven by tribo-electron emission, while the out-of-contact activity is attributed to the formation of nascent surfaces. Friction-induced electron transfer causes Pd to lose electrons, which then react with CO and O_2 to form CO_2. Tribo-electron emission here refers to the release of electrons from a material surface caused by frictional contact. These emitted electrons can drive interfacial chemical reactions.

Hu and co-workers investigated the tribocatalytic degradation of tightly-bound extracellular polymeric substances (T-EPS) using Fe-doped ZnO (Fe–ZnO) nanorods under mechanical friction in dark conditions, focusing on the mechanism of electron transfer across atoms.[38] Tribocatalysis is initiated when physical contact and friction between ZnO and a material like PTFE induce electron transfer across atomic interfaces (Fig. 2). This process results in charge separation, where electrons accumulate on the PTFE surface and holes remain on the ZnO, enabling catalytic activity without the need for light or external electric fields. The introduction of Fe into ZnO enhances this mechanism by introducing impurity levels, which lower the material's work function and facilitate more efficient electron mobility and charge separation. As a result, the tribocatalytic degradation efficiency significantly increases, with Fe–ZnO achieving a 75.8% degradation of T-EPS within 12 min, compared to only 32.2% with pure ZnO. The separated charges participate in redox reactions at the catalyst interface: the holes oxidize surface terminal hydroxyl groups (OH_t) to form highly reactive $^{\bullet}OH$ radicals, while the electrons reduce molecular oxygen to generate $^{\bullet}O_2^-$ radicals, both of which actively degrade

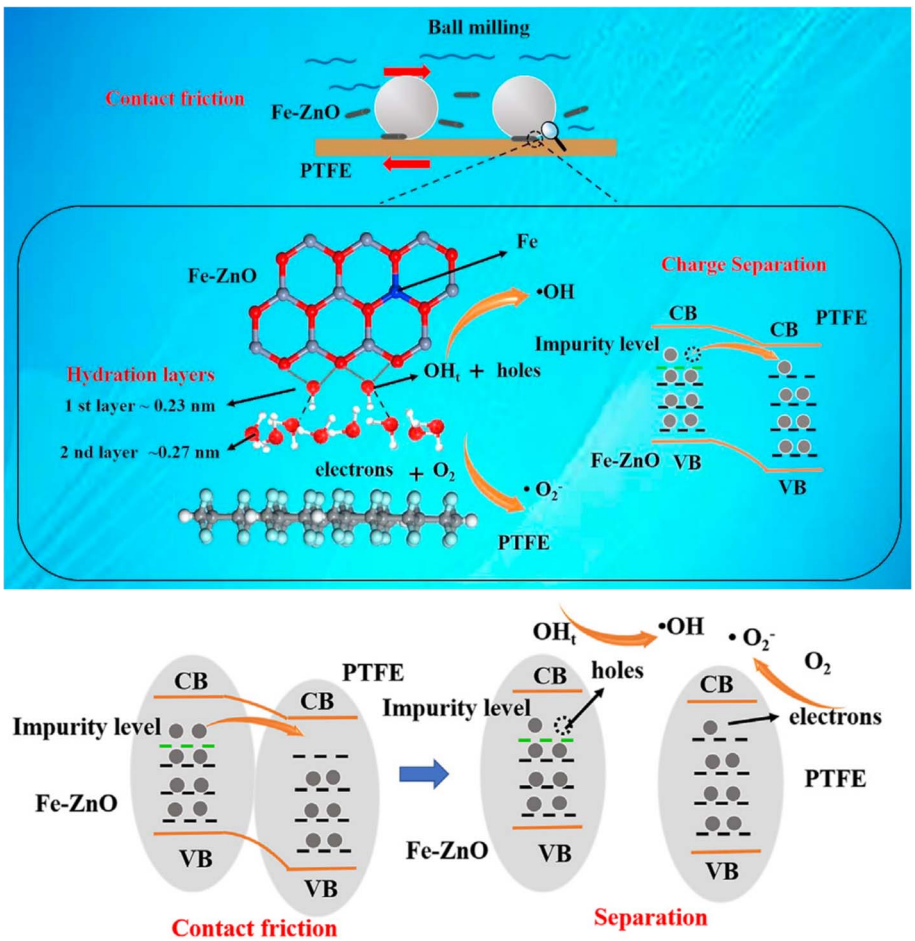

Fig. 2 Schematic of the tribocatalytic degradation of recalcitrant organics by Fe–ZnO through ball milling in a PTFE reactor. Reproduced with permission.[38] Copyright 2021, Elsevier.

organic pollutants. Mechanical friction not only promotes electron transfer but also transforms less reactive bridge hydroxyl groups (OH_{br}) into more reactive OH_t, especially within the structured hydration layers at the catalyst interface.

In solid–liquid systems, electron transfer can occur between a polymer (*e.g.*, PTFE or FEP) and water. Ultrasound-induced cavitation facilitates this interaction, enabling the polymer to gain electrons while water molecules lose electrons.[39] These reactions generate reactive species like hydroxyl and superoxide radicals, effectively degrading refractory organics such as dye molecules. In other cases, solid catalysts like zero-valent Fe lose electrons through friction with solutions, enabling dye degradation through reduction reactions.[40]

On the contrary, the mechanism based on electron transition assumes that tribocatalysis involves electron transitions, where mechanical energy excites catalysts to generate electron–hole pairs, initiating redox reactions. This process resembles photocatalysis but relies on mechanical rather than light energy. Semiconductors such as barium strontium titanate (BST) or CdS can harness frictional forces to excite electrons,[41] forming radicals that degrade pollutant molecules. Perovskite-structured materials, such as $PbTiO_3$ and $BaTiO_3$, utilize piezoelectric effects to enhance electron–hole separation, thereby increasing catalytic performance. This phenomenon is evident in the mechanochemical synthesis of organic compounds, where non-piezoelectric materials exhibit little to no formation of the desired products.[33,42] It is to be noted that when assuming an electron transition mechanism to occur, we can expect band bending in the semiconducting catalysts under exposure to mechanical energy including friction, rubbing and sliding. The beneficial effect of this phenomenon is enhanced spatial separation of charge carriers, which leads to reduced charge recombination. However, a detrimental effect is the decreased reduction potential of electrons and oxidation potential of holes (Fig. 1).

Sun and co-workers assume that an electron transition mechanism occurs during dye degradation using a ferroelectric $Ba_{2.5}Sr_{2.5}Nb_8Ta_2O_{30}$ (BSNT) submicron particles under mechanical stirring (Fig. 3).[43] Tribocatalysis here is driven by friction between BSNT particles and materials like PTFE, which induces triboelectric charges due to differences in electron affinity. This charge transfer disrupts the internal electric field of the BSNT particles, creating a non-zero field that promotes the separation of electron–hole pairs. The separated charges then participate in redox reactions: electrons in the CB reduce oxygen to generate $^{\bullet}O_2^-$, while holes in the VB oxidize hydroxide ions to produce $^{\bullet}OH$. These reactive species are responsible for breaking down dye molecules in solution. The BSNT particles exhibit high catalytic performance due to their strong spontaneous polarization and high density of mobile charges. Remarkably, the degradation of Rhodamine B reached 99% efficiency within 1.5 h of stirring at room temperature in the dark. Control experiments using non-ferroelectric materials like Ta_2O_5 showed significantly lower degradation rates, confirming the critical role of BSNT's ferroelectric nature.

Electron transfer and transition may also co-occur during friction, working synergistically to enhance catalytic performance. For instance, materials like ferroelectric $Ba_4Nd_2Fe_2Nb_8O_{30}$ generate internal electric fields upon electron transfer, driving electron transitions and creating reactive radicals.[44] Such interactions suggest that tailoring the energy band

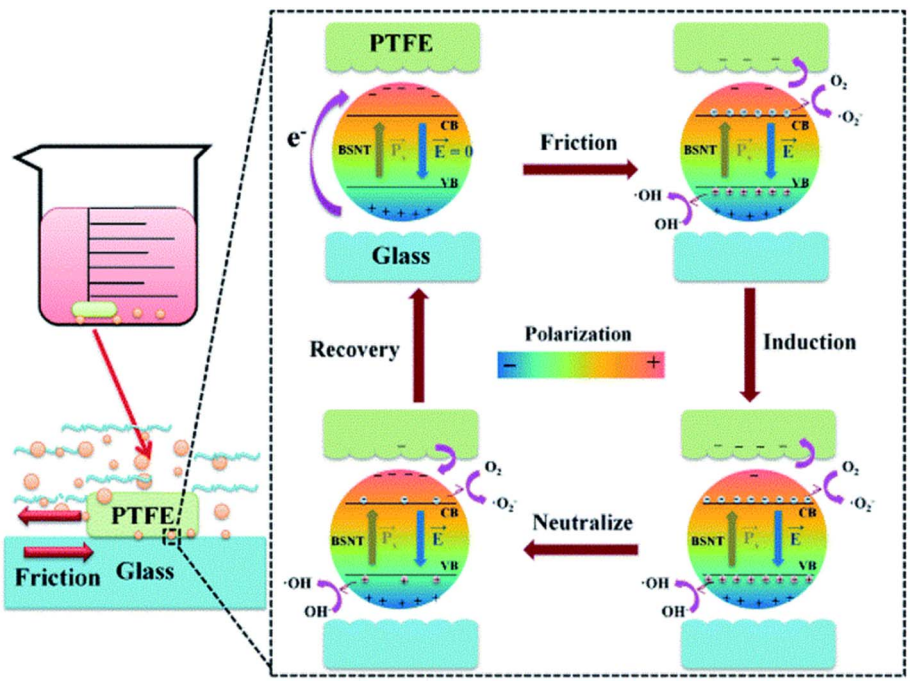

Fig. 3 Schematic of the tribocatalytic mechanism involving ferroelectric BSNT submicron particles. Under frictional force, charge carriers are generated *via* electron transitions from the VB to the CB, followed by charge separation and the formation of reactive species responsible for dye degradation. Reproduced with permission.[43] Copyright 2021, Royal Society of Chemistry.

structures of frictional materials could optimize electron transfer and transition processes, improving catalytic performance. Further research into the specific mechanisms and electric field values (quantification) is necessary to fully understand and exploit these synergistic effects.

Fan and co-workers proposed an alternative perspective on the tribocatalytic process, which is quite similar to the two widely known mechanisms.[11] They hypothesized that when two materials are agitated, their surfaces become highly polarized with opposing charges. Upon separation, the negatively charged surface acts as a reductant, transferring electrons to reaction precursors, while the positively charged surface functions as an oxidant, drawing electrons away. This selective electron transfer closely resembles the principles of redox catalysis.

Very recently, Olson and Marks addressed a longstanding question of why sliding, rather than simple contact, plays a dominant role in the triboelectric generation of static electricity—the "tribo" in triboelectricity.[45] They provide a general explanation rooted in established electromechanical science, specifically highlighting symmetry breaking caused by elastic shear during sliding. As material slides, the front and back of the contact experience different strain gradients, leading to asymmetric polarization and associated bound charges. This charge asymmetry induces a current flow, analogous to how pressure differences across a wing generate lift. Flexoelectricity, the coupling between strain gradients and polarization, is suggested as a key mechanism, moving beyond earlier theories based solely on contact area or heating. The *ab initio* model quantitatively explains the observed dependence of triboelectric charge transfer on sliding velocity, normal force, and contact geometry. It aligns well with experimental trends and provides good agreement with observed currents in nanoscale sliding contacts. Sliding enhances charge transfer due to induced asymmetries, not merely due to increased contact frequency. This reframes triboelectricity as a fundamentally electromechanical phenomenon influenced by material-specific properties, such as doping and surface structure.

4. Factors influencing tribocatalytic performance

Tribocatalytic reactions are influenced by several factors that partially differ from those of traditional catalytic reactions. These factors can be broadly categorized into two groups: (1) the characteristics of the catalyst, such as its electronic structure, morphology, and particle size, and (2) the properties of the reaction system, including the type of stirring bar, choice of solvent, temperature, pH, and the material and configuration of the reactor, as summarized in Table 2.

In terms of catalyst characteristics, the selection depends on which tribocatalysis mechanism is assumed to occur, electron transfer or electron transition. In the electron transfer mechanism, the surface state of the material determines its ability to gain or lose electrons during friction. When materials come into contact, electron clouds overlap, creating an asymmetric potential well that facilitates electron migration and transfer. The Fermi level is a critical parameter for tuning the electron transfer capabilities of metals and polymers. For example, minimizing the Fermi level difference between materials facilitates enhanced electron flow.[2] However, in the case of natural or composite materials with unknown energy band structures, triboelectric charge density measurements can be used to assess their electron transfer tendencies.[2] Selecting materials with pronounced differences in their abilities to gain or lose electrons can significantly improve tribocatalytic performance by promoting efficient electron transfer mechanisms.

In contrast, the electron transition mechanism relies on the energy band structures of materials to influence their redox capabilities,[2] thereby determining the types of chemical reactions that can occur. This mechanism is particularly applicable to

Table 2 Factors influencing tribocatalytic performance[2,11–15,30,46,47]

Category	Factor	Effect on performance
Catalyst	Electronic structure	Fermi level (electron transfer) or band gap & edge positions (electron transition) control charge movement and redox potential
	Particle size and morphology	Smaller size and porous/rough structures increase active sites and friction contact
	Doping and defects	Improve charge separation, reduce recombination, enhance adsorption and reaction selectivity
	Co-catalysts	Promote carrier separation and transfer
	Material type	Semiconductors (electron transition) or metals/polymers (electron transfer) selected based on mechanism
Reaction system	Mechanical force	Higher stirring speed, contact area, and multiple/longer bars enhance friction and charge generation
	pH	Slightly acidic pH promotes charge separation; extremes may reduce catalyst stability (*e.g.*, ZnO in acidic media)
	Solvent	Affects frictional charge generation and redox efficiency depending on polarity and ion mobility
	Temperature	Affects reaction kinetics and charge mobility; moderate heat may boost performance
	Reactor material and surface	PP and modified surfaces enhance triboelectrification; glass and unmodified PTFE perform worse due to low charge generation or nanoparticle adsorption

semiconducting materials, such as metal oxides and conductive polymers. Materials with moderate energy band gaps are preferred, as they require an optimal amount of mechanical energy to excite electrons effectively. If the band gap is too narrow, the mechanically extracted charges may be thermodynamically insufficient to drive the desired redox reactions.[31] Conversely, if the band gap is too wide, a substantial amount of mechanical energy is required for activation, making it difficult to initiate catalytic activity. Equally important is the band edge position, as the edge levels determine the redox potential of the generated charge carriers.[32] The VB edge top must be lower or more positive than the oxidation potential of the target reaction, while the CB edge bottom must be higher or more negative than the reduction potential of the target reaction. Catalysts with improper band-edge positions cannot facilitate the desired reactions. Thus, selecting semiconducting materials with appropriate CB and VB positions is important.

Mechanical force serves as the energy source for friction-driven reactions. In tribocatalysis, primary forces include the impact force from water flow during stirring and pressure from magnetic bar friction (*e.g.*, container-catalyst, magnetic bar-catalyst, and magnetic bar-container contact). Catalytic efficiency is influenced by interaction forces between materials, with increased friction force at higher stirring speeds enhancing performance.[14]

Wu and co-workers investigated the impact of stirring speed, magnetic bar size, and quantity on Rhodamine B degradation.[48] As shown in Fig. 4, increasing the stirring speed from 300 to 500 rpm enhanced degradation efficiency by accelerating dye molecule transfer and increasing PTFE particle friction. However, at 700 rpm, efficiency dropped due to bar instability and catalyst splashing. To emphasize the role of friction, three magnetic bars were tested: Bar I (standard), Bar II (rubber-capped ends), and an overhead stirrer. Bar I achieved nearly 100% degradation, while Bar II and the overhead stirrer showed significantly reduced activity, indicating that direct friction between PTFE powder and the beaker bottom is critical. Given PTFE's hydrophobicity and low density, it tends to float unless stirred. Stirring draws particles beneath the bar, enhancing contact. Thus, in addition to increasing speed, enlarging the contact area (by using larger or multiple bars) also increases activity. Both bar size and number linearly correlate with degradation efficiency.

For electron transfer mechanism, the force magnitude determines electron cloud overlap, requiring stronger forces for solid–solid interfaces compared to solid–liquid interfaces. The extent of this overlap affects the number of transferred electrons and overall efficiency. In the electron transition mechanism, sufficient mechanical force is required to enable electron transitions, especially in catalysts with large band gaps. Hypothetically, the contact area plays a role in tribocatalytic reactions, as larger surfaces provide more chances for frictional interactions. Efficiency can be further improved by using multiple magnetic stirring bars, while longer bars enhance performance by increasing the available frictional surface area.

Other structural factors, such as doping with impurity atoms and the introduction of defective structures, can enhance tribocatalytic performance.[3,4] Doping and defects modify the electronic structure,[49] including the work function and the behavior of friction-generated charges, potentially improving electron transfer. Doping introduces impurity energy levels,[50] which lower the work function, enhance charge separation, and inhibit charge recombination.[51] Defects within the bulk of the catalyst can also create impurity energy levels that facilitate charge separation and further reduce recombination.[13] Surface defects, on the other hand, affect reactant adsorption and conversion into intermediates, enhancing the production and selectivity of target products. Although the role of defects in tribocatalysis remains largely unexplored, they hold large potential for advancing the field. The interaction between frictional forces and defect-rich surfaces may align with the Sabatier principle, potentially enhancing catalytic efficiency. The Sabatier principle suggests that the best catalysts bind reactants with intermediate strength, neither too weak nor too strong. This balance allows efficient activation of reactants and easy release of products, optimizing reaction rates and selectivity. Surface morphology can also influence tribocatalytic performance. Features such as porous structures increase frictional areas, potentially enhancing electron transfer, while metal nanoparticles, nanoclusters or single atoms acting as "co-catalyst" on catalyst surfaces may promote carrier separation and transfer.

In terms of the properties of the reaction system, solution pH is an important factor affecting electron transfer and free radical generation. Acidic environments typically enhance electron transfer by creating positively charged surfaces that attract electrons and reduce recombination of electrons with holes. In contrast, highly alkaline conditions may hinder catalytic performance due to repulsion between catalysts and substrates. Adjusting pH to optimize charge interactions may improve reaction rates and efficiency. However, it should be noted that some potentially efficient materials for tribocatalysis, such as ZnO, are sensitive to low pH conditions. ZnO tends to undergo self-degradation in acidic environments. Therefore, an optimal pH balance should be achieved to maximize performance while maintaining the catalyst stability.

The type of reactor also influences the tribocatalytic performance, with polypropylene (PP) and PTFE reactors generally outperforming glass reactors. Triboelectrification in PP reactors was reported to enhance the generation of positive charges on catalysts like Bi_2WO_6 (ref. 52) and $Bi_{12}TiO_{20}$,[53] improving Rhodamine B degradation. The tendency of PP to become negatively charged amplifies charge separation and catalytic activity. In contrast, PTFE vessels exhibit weaker performance due to nanoparticle adsorption, reducing friction. PP and PTFE reactors, with proper surface enhancements, are more effective for tribocatalytic operations than glass reactors.[13,41] The influence of reaction chamber surface roughness on tribocatalytic performance has also been investigated, given its strong dependence on the friction coefficient between the catalyst and the chamber surface. Material alterations, such as attaching sandpaper or aluminum oxide plates, have been shown to enhance performance compared to unmodified system.[54] This improvement is attributed to the higher friction coefficient between tribocatalyst particles and roughened surfaces, which facilitates greater generation of friction-induced charges.

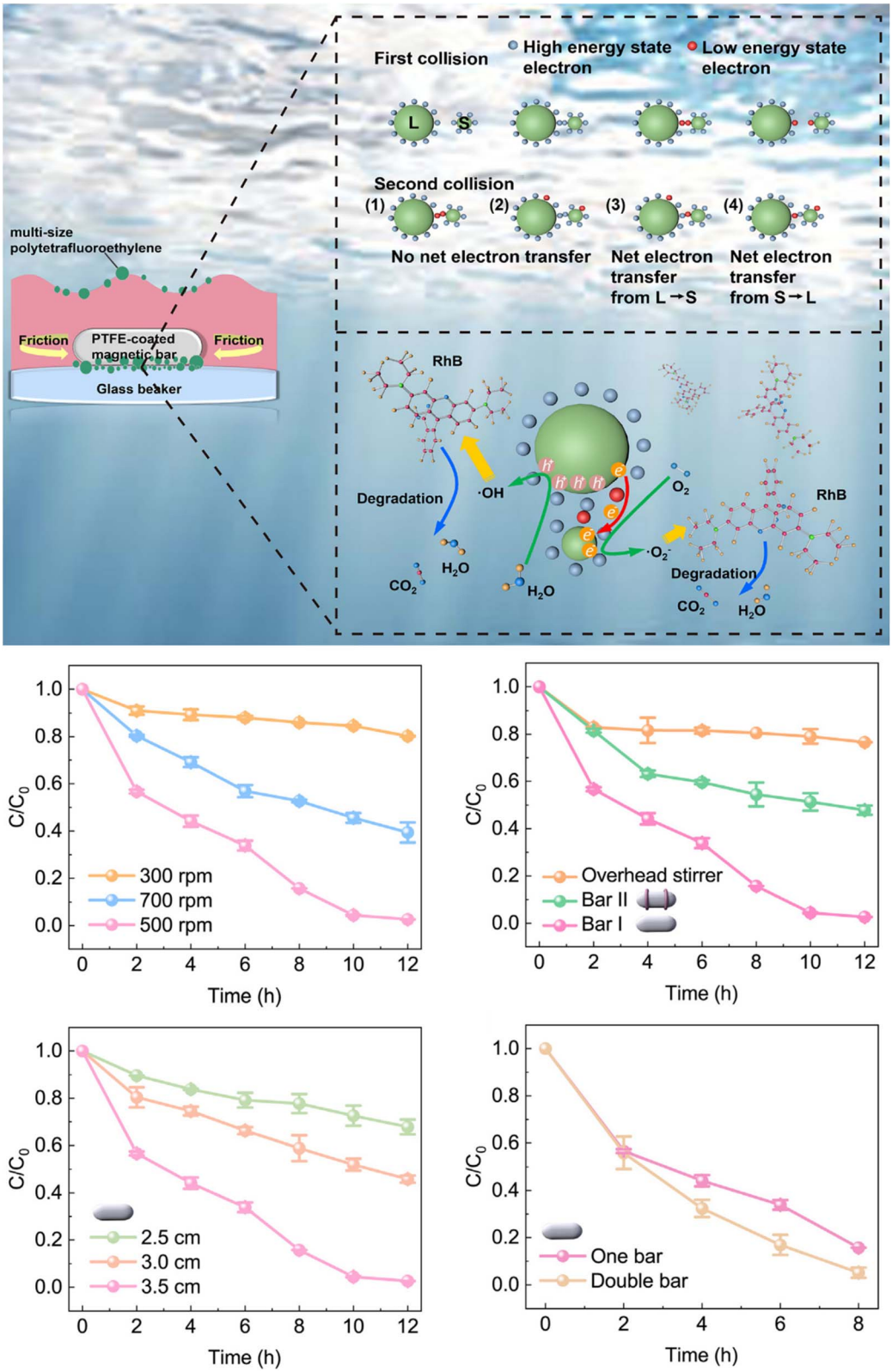

Fig. 4 Effects of key parameters on PTFE-based tribocatalytic Rhodamine B degradation such as stirring speed, contact condition between stirring bar and beaker, stirring bar length, and number of stirring bars. Reproduced with permission.[48] Copyright 2022, Elsevier.

5. Applications of tribocatalysis

Triboelectric materials are being applied for diverse catalytic reactions.[12,55] Thermodynamically, the applications of tribocatalysis can be divided into two categories: (1) exergonic reactions and (2) endergonic reactions. These reactions describe the energy flow in chemical systems, determining whether a reaction can proceed spontaneously or requires external energy input. Exergonic reactions are thermodynamically favorable processes where energy is released, characterized by a negative Gibbs free energy change, making them spontaneous. In contrast, endergonic reactions are thermodynamically unfavorable, requiring energy input, and are characterized by a positive Gibbs free energy change, meaning they are non-spontaneous under standard conditions.

Most tribocatalytic applications focus on exergonic reactions, such as the decomposition of refractory organics, where mechanical energy drives their breakdown in water.[13,14] This is due to the thermodynamic favorability and relatively fast kinetics of exergonic reactions. Conversely, endergonic reactions, including chemical bond formation, are more challenging and kinetically sluggish. For instance, tribocatalysis provides an alternative approach for H_2 generation or CO_2 reduction to C_1/C_{2+} products, utilizing mechanical energy to facilitate water splitting and the activation of small molecules.[26]

The Domen group pioneered research on tribocatalysis for fuel synthesis. They observed an unexpected phenomenon with Cu(I)-containing oxides, *e.g.*, Cu_2O. H_2 and O_2 gases evolved in stoichiometric ratios, even in the dark and far beyond the expected catalytic capacity of the material under study.[27] The reaction also depended significantly on the stirring rate, ceasing entirely without stirring. This led to the conclusion that the reaction mechanism was not photocatalytic but rather tribocatalytic, driven by mechanical energy in the form of friction. The experimental setup involved suspending oxide powders in distilled water and stirring them in a sealed system. Stirring-induced gas evolutions were confirmed using various oxides like Cu_2O, NiO, Co_3O_4, and Fe_3O_4. Photocatalysts like TiO_2 were inert, and tests showed no reverse reaction occurred when H_2 and O_2 were introduced. Notably, the reaction proceeded catalytically, as evidenced by H_2 evolution exceeding the oxide amount used. Isotopic studies confirmed that the oxygen in evolved O_2 originated from water.

Further studies identified specific oxides and their oxidation states as crucial for the reaction.[26] For example, NiO and Cu(I)-containing compounds demonstrated catalytic activity, while other oxides and non-metallic catalysts did not. The role of mechanical energy was investigated, showing that H_2 and O_2 evolution depended on contact between oxide powders and the base of the reaction vessel. Mechanical energy at the interface was hypothesized as the source of chemical energy conversion, achieving an efficiency of up to 4.3% for NiO-based systems. Frictional contact was believed to generate electrostatic charges that drive redox reactions. However, inconsistencies with this model were observed, such as the absence of reactions in water vapor and the selective activity of certain oxides. These findings suggest that oxide powders may have a unique role beyond charge separation in facilitating tribocatalytic water splitting.

CO_2 reduction has also been reported for generating gaseous fuels. For instance, gentle stirring of TiO_2 with a PTFE magnetic bar at 500 rpm in water produces valuable gases like CO, H_2, and CH_4.[56,57] This mechanoreforming occurs through electron transitions initiated by mechanical energy generated from friction between TiO_2 and the PTFE bar. The electrons reduce CO_2 and H_2O to form CO, CH_4, and H_2, while holes oxidize H_2O to produce O_2. Similarly, stirring g-C_3N_4 in methanol with a PTFE magnetic bar at 1000 rpm enables the tribocatalytic conversion of N_2 to NH_3.[58] During friction, g-C_3N_4 loses electrons while PTFE gains them. The resulting electrons reduce N_2 and H^+ to form NH_3, which dissolves in water. As shown in Fig. 5, the addition of methanol as a positive charge scavenger significantly enhances NH_4^+ production, reaching 100.56 μmol L^{-1} g^{-1} h^{-1} (3.91 times higher than without scavengers), while the use of a negative charge scavenger ($KBrO_3$) inhibits the reaction. Negative charges play a vital role in the tribocatalytic nitrogen fixation process. Reduced contact area led to lower NH_4^+ yields, while NH_4^+ production increased with stirring speed. Furthermore, increasing the number of stirring rods enhanced performance due to a larger contact area, though not proportionally, due to uneven catalyst distribution and limited stirring efficiency.

Tribocatalysis demonstrates the conversion of common substances like H_2O, CO_2, and N_2, which are thermodynamically very stable and difficult chemically react with, into valuable products such as CO, H_2, CH_4, and NH_3. By harnessing mechanical energy to drive chemical reactions in an eco-friendly manner, tribocatalysis shows great potential for sustainable fuel production. Different applications of tribocatalysis are highlighted below.

(i) Environmental remediation: tribocatalysis is mostly used to degrade organic pollutants in water, such as synthetic dyes.[12–14] For example, ZnO has demonstrated efficacy in degrading Rhodamine B under stirring-induced friction.[34,59,60] Such self-powered systems provide an alternative approach for treating wastewater.

(ii) Energy production: mechanical forces harvested through tribocatalysis drive water splitting to produce H_2 or reduce CO_2 to value-added hydrocarbons. Piezoelectric materials like $BaTiO_3$ are particularly effective in these processes, contributing to clean energy production.[31,32]

(iii) Organic synthesis: tribocatalytic systems can potentially provide selective and energy-efficient pathways for the synthesis of pharmaceuticals, polymers, and fine chemicals, adhering to green chemistry principles by eliminating the need for external heating, electrical bias or illumination. In organic synthesis, tribocatalysis seems somewhat equivalent to direct mechanocatalysis which uses milling materials themselves like WC, ZrO_2, Au, Cu, or Pd as catalysts.[61,62] The distinction lies in their activation mechanisms. Mechanocatalysis uses mechanical stress (strain-driven) for direct catalyst activation, while

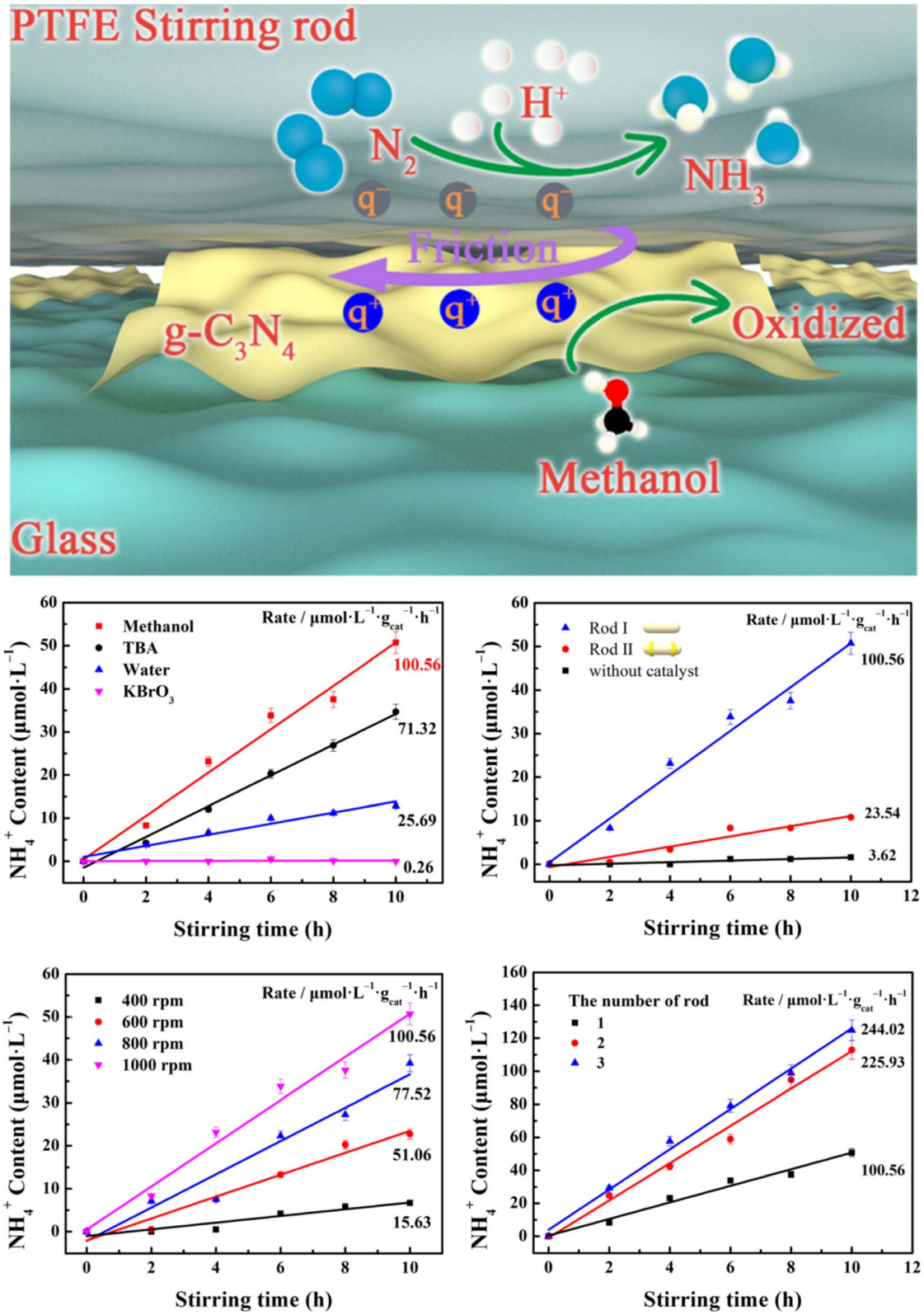

Fig. 5 Tribocatalytic nitrogen fixation of g-C_3N_4 and the effects of operating parameters on performance. Reproduced with permission.[58] Copyright 2022, MDPI.

tribocatalysis uses triboelectric effects (friction-driven) to transform mechanical energy into electric fields, indirectly initiating catalytic processes.

(iv) Wear-resistant coatings: tribocatalysts embedded in wear-resistant coatings enhance machinery durability while catalyzing reactions driven by frictional forces.[63,64] For instance,

TiO_2-coated surfaces facilitate *in situ* reactions that reduce wear while performing secondary catalytic functions.[64]

(v) Self-powered systems: integrating tribocatalysis with natural mechanical energy sources, such as river currents or wind enables autonomous systems for energy harnessing and environmental remediation.[2]

(vi) Lubrication: tribocatalytic materials facilitate the *in situ* generation of lubricating films, reducing friction and wear in industrial applications.[65] For example, molybdenum dithiocarbamate decomposes under friction to form molybdenum disulfide, a lubricant that simultaneously protects surfaces and catalyzes reactions.[66]

6. Tribocatalysis *versus* piezocatalysis

Tribocatalysis and piezocatalysis are distinct phenomena, but they share a common principle: both convert mechanical energy into chemical energy *via* electrical energy (Table 3). Thus, best practices, such as selecting and engineering catalyst materials for improved performance, can be adapted with suitable modifications to the less developed field of tribocatalysis.

Owing to the shared underlying principles of tribocatalysis and piezocatalysis, these approaches have been referred to as "mechano-electrocatalysis" by Tian and co-workers.[11] Mechano-electrocatalysis refers to catalytic reactions in which mechanical forces are applied to reactants and catalysts, with the reaction being driven by the conversion of mechanical energy into electrical energy.

While piezocatalysis is more established, tribocatalysis remains in the early stages of development. Tribocatalysis operates through distinct mechanisms that differentiate it from piezocatalysis and other mechanochemical processes, such as mechano-thermocatalysis and mechano-photocatalysis. A great advantage of tribocatalysis is its ability to generate reactive charges through frictional forces, enabling chemical transformations with simple methods like magnetic stirring or fluid flow in a water stream. Tribocatalysis may outperform piezocatalysis in efficiency under equal mechanical energy, due to the higher sensitivity of triboelectric materials to low-frequency input.

Another distinct advantage of tribocatalysis is its ability to activate catalyst surfaces. Frictional forces can disrupt the surface of a catalyst,[11] and when carefully controlled, this may enhance both catalytic activity and selectivity. Friction induces surface defects by mechanically altering the atomic or molecular structure, creating vacancies, dislocations, or amorphous regions. These defects can have both beneficial and detrimental effects, depending on their nature and extent. On the beneficial side, they can generate active sites that boost catalytic activity, increase surface roughness for greater surface area, and improve charge separation and transfer. Furthermore, defects may lower activation energy, facilitating more efficient reaction pathways. However, excessive defects can compromise the structural integrity of the catalyst, leading to fragmentation or deactivation, and may promote undesirable side reactions, reducing selectivity. Over-abrasion can also shorten the lifespan of the catalyst or result in material loss. Thus, controlled friction that produces moderate defects can significantly enhance catalytic performance, but excessive or uncontrolled friction should be avoided. Optimizing frictional parameters is critical to maximizing these benefits while minimizing damage. This mechanism holds the potential for tribocatalysis to outperform traditional catalytic systems by enabling more efficient interactions between catalysts and reactants. Developing strategies to precisely control frictional forces will be critical for advancing tribocatalytic systems.

Equally importantly, tribocatalysts can operate under low-frequency mechanical forces, a feature not always shared by piezocatalysts. They can be activated mechanically by simply rubbing against the walls of a reaction vessel. This ability makes them particularly well-suited for harnessing ambient or

Table 3 Differences between three emerging catalytic processes that convert mechanical energy into chemical energy[2,11,31–33,68,70][a]

Feature	Tribocatalysis	Piezocatalysis	Flexocatalysis
Energy source	Friction or sliding contact	Mechanical stress or vibration (*e.g.*, ultrasonic waves)	Strain gradients (non-uniform mechanical deformation)
Mechanism	Triboelectric effect: charge separation from friction	Piezoelectric effect: internal electric field from strain	Flexoelectric effect: polarization from strain gradient
Catalyst type	Triboelectric materials (*e.g.*, NiO, Cu_2O)	Piezoelectric materials (*e.g.*, $BaTiO_3$, ZnO)	Flexoelectric materials (usually dielectric oxides)
Key phenomenon	Surface charge generation by rubbing/sliding	Dipole generation under uniform strain	Dipole generation under strain gradient
Dependence on shape/size	Not strongly size-dependent (but area of contact matters)	More effective at nanoscale due to enhanced strain effects	Highly dependent on nanoscale dimensions and geometry
Reaction environment	Usually ambient, requires movement/contact	Often aqueous, under ultrasonic or pressure vibration	Requires bending or inhomogeneous deformation
Applications	Dye degradation, pollutant treatment, H_2 production	Environmental remediation, H_2 production	Novel concept: being explored in nanoscale catalysis
Research stage	Moderately studied, especially in dye degradation	Well-studied in recent years	Emerging, under active theoretical and experimental study

[a] Sonocatalysis is not included in this categorization because it does not always require catalyst particles. Ultrasound itself can induce chemical reactions in liquids through a process called sonolysis.

naturally occurring mechanical energy sources, such as vibrations or fluid flows. By utilizing these readily accessible energy inputs, tribocatalysis offers a self-sustaining and versatile approach to catalysis across diverse fields. For instance, in the near future, tribocatalyst particles could be coated onto the inner walls of pipes in water treatment facilities to decompose dissolved organic pollutants.

The range of materials is also different between the two approaches. Piezocatalysis relies on piezoelectric materials with asymmetric crystalline structures, whereas tribocatalysis can utilize a wider variety of materials. These include conventional polymers, such as PTFE and FEP, as well as semiconducting oxides. This versatility allows tribocatalysis to operate with materials that are more readily available and often cost-effective, expanding its potential applications. Despite its advantages, however, tribocatalysis faces limitations, particularly in aqueous environments. Unlike piezocatalysis, where charges are confined to a single material, triboelectric charges form across two interacting materials, rendering them more susceptible to environmental factors such as humidity.[11] Therefore, when working with tribocatalysis, one must carefully consider the electrochemical properties of the reaction medium. Tribocatalysis is particularly sensitive to reaction pH.

How tribocatalysis differs from piezocatalysis in mechanochemical synthesis is demonstrated by Wang and co-workers in the context of mechanochemistry.[67] They demonstrated that ball grinding can induce contact-electro-catalysis (CEC) by utilizing inert and conventional triboelectric materials. Exemplified by a liquid-assisted grinding (LAG) setup involving PTFE, ROS are produced, even though PTFE is generally considered catalytically inert. ROS formation is also observed with other polymers such as polydimethylsiloxane (PDMS) and PP, and the quantity of generated ROS closely correlates with the polymers' contact-electrification (CE) abilities. It is proposed that mechanical collision during milling not only maximizes electron wave function overlap at interfaces but also excites phonons that supply the energy needed for electron transitions. This concept is illustrated in Fig. 6, showing the triboelectric

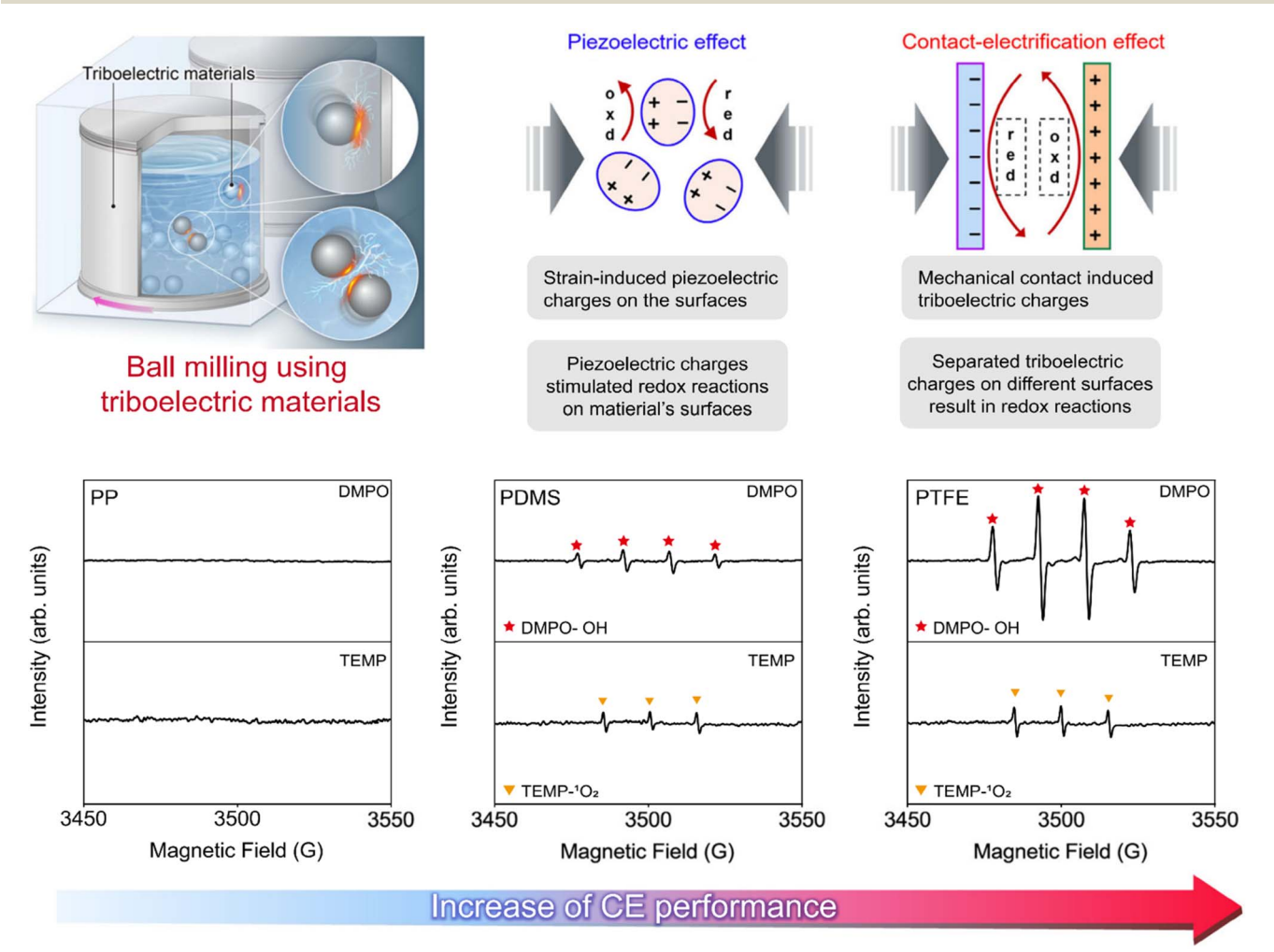

Fig. 6 Schematic of ROS generation *via* CEC in ball mill process utilizing triboelectric materials. A comparison between piezoelectric effects and CE effects suggests that catalyzing reactions through CE charges is feasible. EPR spectra under different conditions show the influence of various triboelectric materials used in ball milling. In these experiments, PP, PDMS, and PTFE serve as the triboelectric materials. The detection of hydroxyl and superoxide radicals is facilitated using 5,5-dimethyl-1-pyrroline *N*-oxide (DMPO) as a spin trap, while singlet oxygen is captured using 2,2,6,6-tetramethyl-4-piperidone hydrochloride (TEMP). Reproduced with permission.[67] Copyright 2024, Springer Nature.

ball milling setup, where both the balls and vials are made from CE-active materials. A comparison between contact electrification and the piezoelectric effect highlights CE's ability to drive redox reactions through mechanically induced charge separation. Electron paramagnetic resonance (EPR) spectra reveal that PTFE generates the highest levels of ROS, followed by PDMS, while PP, due to its low CE capacity, produces minimal ROS. The consistent relationship between CE performance and ROS generation confirms the key role of CEC in this process. These findings reveal a previously untapped catalytic mechanism and suggest that triboelectric materials, due to their abundance and versatility, can serve as universal components in ball milling-assisted mechanochemistry.

7. Tribocatalysis *versus* flexocatalysis

Another similar approach for utilizing mechanical energy to drive chemical reactions is flexocatalysis. Both flexocatalysis and tribocatalysis represent distinct yet conceptually overlapping approaches for converting mechanical energy into chemical energy. While each approach uses mechanical stimuli to drive reactions, particularly the generation of reactive species such as radicals, they operate through fundamentally different physical mechanisms and material requirements.

Tribocatalysis is a friction-driven process that relies on the triboelectric effect. The key to triboelectric charge generation lies not merely in contact but in dynamic actions such as sliding. These motions break symmetry and induce differential strain and polarization between the leading and trailing edges of a moving body.[15] This asymmetry generates a time-varying electric field capable of initiating electrochemical reactions. In contrast, flexocatalysis is a strain gradient-induced catalytic process.[68] It utilizes the flexoelectric effect, an electromechanical phenomenon in which strain gradients induce electrical polarization, even in centrosymmetric (non-piezoelectric) materials. Unlike piezocatalysis, which is limited to non-centrosymmetric crystals, flexocatalysis applies to all insulating and semiconducting materials, expanding the pool of usable catalysts.[69]

Flexocatalysis does not rely on lateral motion or direct contact. Instead, it is activated through dynamic, inhomogeneous deformation. Acoustic waves in liquid media produce alternating compressions and expansions, creating localized strain gradients in suspended nanoparticles. These gradients induce reversible flexoelectric polarization fields that can switch direction with each acoustic cycle. This leads to alternating redox environments on the catalyst's surface, improving reaction uniformity and extending catalytic lifetime. As a result, flexocatalysis is less dependent on surface wear and is more compatible with soft or delicate materials. For example, Du and co-workers demonstrated flexocatalysis using rutile TiO_2 nanoparticles under ultrasonic irradiation.[70] These nanoparticles experience dynamic strain gradients due to acoustic cavitation, resulting in transient flexoelectric polarization fields that separate electron–hole pairs and drive redox reactions in surrounding media. A key technical insight is the size-dependent enhancement of the flexoelectric effect. Strain gradients, and consequently the induced polarization, are significantly amplified at the nanoscale, which increases catalytic efficiency. Smaller TiO_2 particles (as small as 50 nm) exhibited over 70% higher H_2 evolution rates than larger particles under the same ultrasonic conditions. This elegant work illustrates how reducing particle size and optimizing morphology can enhance strain gradients and catalytic performance without relying on rare or hazardous substances.

Tribocatalysis requires that at least one material in the contact pair has a high electron affinity or readily donates or accepts electrons, while flexocatalysis offers broader material flexibility because the flexoelectric effect is intrinsic to all dielectric materials. Even centrosymmetric oxides like rutile TiO_2, which are inactive in piezocatalysis due to their symmetry, become catalytically active under flexoelectric conditions. This universality enables exploration of a wide array of biocompatible, earth-abundant, and eco-friendly materials.

Despite those limitations, however, tribocatalysis has the advantage of operating in dry or ambient environments without the need for a liquid medium, making it suitable for applications like air purification or surface decontamination in the near future. It can function through simple mechanical actions such as rubbing or wind-induced movement, enabling low-cost and passive energy use. Unlike flexocatalysis, which requires ultrasonic stimulation and is limited to specific vibration settings, tribocatalysis can utilize everyday motions and environmental forces. Tribocatalysts are also often simpler to fabricate and deploy, especially using common polymers or ceramic surfaces, and it is better suited for integration with triboelectric nanogenerators, allowing dual-purpose systems for both catalysis and energy harvesting.

Finally, one may ask which is the best among tribocatalysis, piezocatalysis, and flexocatalysis. In our opinion, tribocatalysis indeed shows the most practical promise, primarily due to its higher energy conversion efficiency and scalability under ambient mechanical stimuli. Tribocatalysis exploits friction-induced charge separation, often from simple motions like rubbing, stirring, or flowing liquids, to generate reactive species capable of driving chemical reactions, including pollutant degradation and H_2 evolution. This approach stands out for its operational simplicity and versatility, as it can be activated by a wide range of low-frequency, irregular, and easily accessible mechanical inputs without the need for external electrical or light energy sources. In contrast, piezocatalysis depends on the piezoelectric effect, requiring well-defined crystalline structures and high-frequency ultrasonic vibrations to generate charges, which can limit material selection and increase energy input demands. Flexocatalysis, while promising for nanoscale systems due to its sensitivity to strain gradients, still suffers from limited practical demonstrations and lower energy harvesting efficiency, largely because it relies on nanoscale deformation and is heavily influenced by size effects and material anisotropy. Tribocatalysis, by comparison, has rapidly advanced with the integration of triboelectric nanogenerators (TENGs), which significantly enhance charge generation and transfer to catalytic sites. Moreover, the mechanical durability, low cost, and broad applicability of tribocatalytic systems make them

particularly suitable for environmental remediation and decentralized energy applications. Thus, in our opinion, considering both fundamental mechanisms and real-setting applicability, tribocatalysis is the most promising and adaptable of the three.

8. Design principles

Designing efficient triboelectric materials for catalysis involves optimizing both triboelectric performance and catalytic activity. Tribocatalysis uses mechanical energy (*e.g.*, from friction) to drive chemical reactions *via* electron transfer or transition. Therefore, conceptually, materials must be selected and engineered to (1) efficiently generate charge carriers during friction and (2) effectively transfer or utilize these carriers to drive chemical reactions. Table 4 summarizes essential criteria and guidelines for designing efficient triboelectric materials for catalysis.

Additional design strategies can be employed to enhance performance beyond the basic material selection. Doping is a widely used method to modify the electronic structure and surface reactivity of catalytic materials. By introducing foreign atoms into the crystal lattice, we can tailor the bandgap, create defect sites, and improve charge carrier mobility. These modifications not only enhance the generation and separation of charge carriers under mechanical stimuli but also improve the catalytic activity by providing more active sites or altering reaction pathways.

Another promising approach involves the use of self-assembled films or coatings, which allow precise control over surface thickness and uniformity. This ensures consistent triboelectric and catalytic performance across the material's surface, reducing variability and enhancing reproducibility. Furthermore, coupling with external fields, such as magnetic or electric fields, can be employed to promote directional charge separation and reduce recombination. In piezoelectric or ferroelectric systems, such external stimuli can align dipoles or influence the polarization behavior, leading to more efficient charge transfer during catalytic reactions. Together, these strategies provide a versatile toolbox for optimizing tribocatalytic systems at both the nanoscale and device levels. Example of base materials that can be engineered further or coupled to enhance tribocatalytic performance are shown in Table 5.

9. Key challenges

Tribocatalysis, akin to other branches of catalysis, faces the fundamental challenge of developing high-performance catalysts. As an emerging discipline, its theoretical frameworks remain largely unverified experimentally. Insights from related charge-carrier-driven processes, such as electrocatalysis, photocatalysis, and piezocatalysis, can help establish more reliable design guidelines.

Efficient tribocatalyst design requires materials that endure mechanical forces, particularly friction, without compromising structural integrity or catalytic performance. Key performance metrics include activity (reactant conversion), selectivity (desired product formation), productivity (rate of product generation), and stability (catalyst reusability). For instance,

Table 4 Key design considerations for tribocatalyst materials

Criteria	Design guideline	Comments
Triboelectric polarity	Select materials with strong electron-donating or -accepting ability	Choose materials far apart on the triboelectric series to maximize charge generation (*e.g.*, PTFE *vs.* Nylon)
Surface roughness and area	Increase surface roughness or nanostructure features	Enhances contact area and friction-induced charge separation; use nanowires, nanosheets, or porous structures
Band structure	Match bandgap and energy levels to the target catalytic reaction	For redox reactions, CB should be more negative than reduction potential (*e.g.*, H^+ to H_2), and VB more positive than oxidation potential of the target reaction
Carrier mobility	Use materials with high electron and hole mobility, especially hole mobility, since oxidation reactions typically have slower kinetics than reduction reactions	Ensures quick transport of charge carriers to surface; examples include graphene composites, doped semiconductors
Stability under mechanical stress	Use mechanically robust materials	Prevents wear and degradation; ceramics like TiO_2, ZnO are good choices
Chemical reactivity	Surface should promote adsorption of reactants	Functionalize or dope surfaces to enhance catalytic sites (*e.g.*, O-vacancies, metal doping)
Dielectric constant	Moderate to high dielectric constants help store triboelectric charges	Enhances electrostatic field effect (*e.g.*, $BaTiO_3$, $SrTiO_3$)
Composite engineering	Combine triboelectric materials with catalytic agents	Synergistic materials (*e.g.*, g-C_3N_4@TiO_2) allow both strong triboelectricity and good catalysis
Interface engineering	Optimize heterojunctions for charge separation	Build p–n or Schottky junctions to suppress recombination of charge carriers
Eco-friendliness and cost	Prefer abundant and non-toxic materials	Important for practical scalability and environmental sustainability

Table 5 Representative materials for potentially efficient tribocatalytic reactions

Material	Role	Comments
g-C_3N_4	Semiconductor catalyst	Moderate bandgap (~2.7 eV), stable, easily modified
ZnO	Tribocatalyst	Piezoelectric and semiconducting, promotes ROS generation
TiO_2	Catalyst support	High surface area, good mechanical and chemical stability
PTFE	Negative triboelectric material	Used in triboelectric pairings to generate electrons; strong electron affinity, chemical stability
$BaTiO_3$	Dielectric enhancer	Enhances charge retention and polarization; high dielectric constant, ferroelectric
Graphene/reduced graphene oxide	Electron transport enhancer	High conductivity, large surface area; improving carrier mobility in composites
CuO/Cu_2O	Redox-active catalyst	Narrow bandgap, good catalytic redox properties
Ag nanoparticles	Plasmonic cocatalyst	Localized surface plasmon resonance (LSPR), electron injection; enhancing charge separation in hybrids
Carbon dots	Sensitizer/electron donor	Energy transfer in hybrid tribocatalysts

studies by the Domen group have shown that tribocatalytically active materials degrade during operation due to surface erosion, which reduces particle size and catalytic activity.[26]

Given that tribocatalytic reactions are surface-driven, surface engineering is crucial. Strategies such as increasing surface area, introducing nanoscale roughness, and creating defects may enhance reactivity and increase the number of active sites. Simultaneously, high mechanical stability, especially at the surface, is essential to resist abrasion and maintain long-term performance under repeated friction.

The rational design of efficient tribocatalytic systems necessitates a comprehensive understanding of the fundamental mechanistic pathways involved. However, the identification and selection of the operative mechanism remain challenging, primarily due to the absence of well-established selection criteria. A thorough elucidation of the electronic structures of both the catalyst and its surrounding matrix is essential to enable informed mechanism selection and system optimization. Current research efforts are increasingly focused on deconvoluting these complex mechanistic interactions and refining methodologies for their accurate evaluation.[39]

Another challenge lies in the fact that triboelectric materials are often insulators, characterized by inherently low electrical conductivity and a lack of mobile charge carriers. To enhance their performance and make them more suitable for catalytic applications, one effective strategy involves surface engineering or functionalization; applying conductive or semiconductive coatings (*e.g.*, graphene, metal oxides, or doped polymers) to the insulating material to facilitate charge transport. Alternatively, introducing defect states or dopants into the bulk material can generate localized energy levels that support limited carrier mobility. Furthermore, integrating triboelectric materials with conductive networks or composite structures may improve charge collection and transport efficiency. These modifications collectively help bridge the gap between the insulating nature of triboelectric materials and the operational requirements of conventional semiconductor-based systems, thereby enabling their more effective use in catalysis and energy-harvesting applications.

Equally important is the fact that tribocatalysis is fundamentally a charge carrier–based process, where mechanical stimuli such as friction generate electrons and holes that drive redox reactions. However, a major gap in current research also lies in the limited understanding of the charge carrier behavior in the triboelectric materials themselves. While these materials are central to tribocatalytic activity, they are barely characterized for properties such as carrier mobility, lifetime, recombination rates, or interfacial charge transfer. This oversight is critical, as the efficiency of tribocatalysis depends directly on how effectively the triboelectric material can generate, separate, and transfer these carriers to catalytic sites. Without such characterization, it is difficult to rationally design or select materials with optimal tribocatalytic performance.

To address this issue, pump–probe spectroscopic techniques such as time-resolved microwave conductivity (TRMC) and transient absorption spectroscopy (TAS) may be applicable to triboelectric materials in tribocatalytic contexts. These tools are well-established in the study of charge dynamics in photocatalysis and semiconductors, offering femtosecond-to-nanosecond resolution of carrier generation and decay. Utilizing them may provide direct evidence of how triboelectric materials respond to mechanical input at the electronic level, revealing crucial parameters such as charge carrier generation rates, spatial separation, and transport behavior. Incorporating these spectroscopic insights into tribocatalysis research is essential to move beyond phenomenological observations and toward a mechanistic, materials-driven understanding of the process. Table 6 summarizes potentially applicable techniques for characterizing charge carrier behavior in triboelectric materials, tailored for applications in tribocatalysis.

With the current understanding of both the fundamental and practical aspects of tribocatalysis, this research direction appears particularly well-suited for downhill or exergonic reactions, such as the decomposition of pollutants in water environment. However, in real-setting wastewater streams, the presence of diverse types of pollutants can complicate the process and reduce overall efficiency. Advances in nanotechnology, materials science, and computational modeling will drive progress in the field, enabling the handling of more challenging endergonic reactions, such as the production of C_{2+} compounds from CO_2 or selective chemical transformations that require precise bond breaking and formation.

Table 6 Techniques for characterizing charge carrier behavior in triboelectric materials for catalysis[71–78a]

Technique	Measured property	Relevance to tribocatalysis	Key advantages	Limitations
Kelvin probe force microscopy (KPFM)	Surface potential, charge distribution	Reveals localized charge accumulation and retention after triboelectric contact	High spatial resolution; direct surface mapping	Only surface-sensitive; may not probe subsurface carrier behavior
Electrostatic force microscopy (EFM)	Electric field strength near surface	Maps charge patterns post-friction, helps identify localized trapping	Non-invasive; nanometer resolution	Cannot quantify absolute charge or mobility
THz time-domain spectroscopy (THz-TDS)	Carrier mobility, lifetime, scattering time	Potential to probe ultrafast carrier motion induced by friction	Ultrafast resolution; widely used in semiconductors	Typically requires optical excitation—mechanical excitation must be adapted
Time-resolved microwave conductivity (TRMC)	Mobility–lifetime product of free carriers	Assesses transient conductivity from tribo-induced carriers; relevant for charge separation efficiency	Non-contact; high time resolution	Generally designed for optically active materials; limited for insulators unless modified
Transient absorption spectroscopy (TAS)	Carrier lifetime, trap states	Probe excited states in semiconducting triboelectric materials under light or hybrid (mechano-optical) excitation	High sensitivity to charge separation and recombination	Less suitable for insulating triboelectrics without optoelectronic activity
Thermally stimulated current (TSC)	Trap depth, charge detrapping dynamics	Useful for analyzing charge retention and release, important for catalytic stability	Good for studying deep traps; provides insight into charge stability	Requires thermal ramping; indirect method
In situ triboelectric–electrochemical measurement	Current, voltage under mechanical stimulus	Links friction-induced charges to catalytic performance (*e.g.*, pollutant degradation, redox reactions)	Real-time monitoring; directly relevant to catalytic output	Does not provide intrinsic material properties like mobility or carrier lifetime
Surface photovoltage spectroscopy (SPV)	Built-in electric fields, carrier diffusion	Can indicate effectiveness of charge separation if photoexcited or coupled with a catalyst	Helps evaluate charge transport and surface potential	Requires light excitation and suitable semiconductor properties
Time-of-flight secondary ion mass spectrometry (ToF-SIMS)	Charge-induced ion distribution, surface chemistry	Reveals chemical effects and migration of charged species during tribocatalysis	High chemical sensitivity; useful for reaction mechanism studies	Destructive technique; low temporal resolution

[a] (1) Triboelectric materials are often insulators, making traditional charge carrier techniques (designed for semiconductors) less directly applicable without modification. (2) Mechanically induced excitation (as in tribocatalysis) is not standard in most spectroscopy setups; custom *in situ* or hybrid systems may be required. (3) A multimodal approach (*e.g.*, combining KPFM with THz-TDS or TRMC) may be used to correlate surface charge behavior with real-time carrier dynamics. (4) Understanding trap states, carrier mobility, and surface charge retention is crucial for improving charge separation efficiency and catalytic lifetime in tribocatalysts.

Altogether, the following issues should be addressed to unlock the potential of tribocatalysis.

(i) Durability: continuous mechanical forces can lead to catalyst abrasion over time. Therefore, developing robust materials capable of withstanding prolonged wear, friction, and pressure is essential to ensure the durability and effectiveness of tribocatalysts. Frictional forces inherently cause surface abrasion between the two contacting materials, gradually reducing the total amount of catalyst. While this phenomenon may initially seem beneficial, since it decreases particle size and increases surface area, studies have shown that these effects are often detrimental to overall catalytic performance.[26] To enhance mechanical reliability under continuous friction stress, the development of wear-resistant tribocatalyst designs is critical. One promising strategy is the integration of ceramic-based oxides such as TiO_2, ZnO, or ZrO_2, which possess high hardness, thermal stability, and intrinsic resistance to abrasive wear.[79,80] These materials could be further engineered into hierarchical or core–shell structures to combine surface activity with robust mechanical resilience. Another effective approach is the application of coatings or encapsulating layers to buffer the core catalyst against repetitive friction-induced damage while preserving charge transport. For example, encapsulating MoS_2 with graphene oxide layers enhanced the tribological performance of the hybrid 2D material.[81] In addition, the doping of oxide and metallic matrices with elements like Zr, Fe, or Nb is also potentially promising to reduce grain boundary weaknesses,[82,83] thus enhancing wear resistance during prolonged operation. Tribocatalysts embedded into tribologically stable supports or flexible films, such as PTFE membranes or polymeric substrates, may further distribute mechanical stress and reduce localized erosion. Future research should emphasize quantitative wear rate analysis under tribocatalytic operating conditions and explore nanoindentation or scratch resistance tests to evaluate long-term structural stability, especially in dynamic, stirred, or flow-through environments. These wear-resistant designs are essential to ensure durability, reusability, and consistent catalytic performance.

(ii) Scalability: scaling tribocatalytic systems requires appropriate and innovative designs to ensure uniform frictional forces and consistent catalytic performance across large reaction areas. The issue of scalability remains a significant obstacle, particularly in the context of synthesizing value-added products. While current laboratory-scale systems typically operate at the milligram-to-gram level, industrial applications demand output at kilogram-to-ton scales. Bridging this gap while preserving catalytic efficiency and mechanical durability under continuous frictional stress represents a formidable challenge that must be addressed for practical deployment.

(iii) Mechanistic understanding: the interplay between electron transfer, electron transition mechanisms, and triboelectric effects is still not fully understood. Advanced spectroscopic techniques, computational modeling, machine learning, and *in situ*/*operando* characterizations are crucial. Most of these approaches have yet to be fully implemented. *In situ* triboelectric–electrochemical measurement can potentially monitor current or voltage under friction, directly linking charge generation to catalytic activity. While useful for real-time performance, it does not reveal intrinsic charge carrier properties like mobility or lifetime.

(iv) Catalyst design: engineering triboelectric materials with tailored energy band structures, optimized surface morphologies, and appropriate doping has the potential to enhance catalytic efficiency and expand reaction scopes.

(v) Integration with natural systems: harnessing natural mechanical forces, such as water flow or vibrations, for tribocatalysis offers a transformative approach to developing self-powered, environmentally integrated systems. For instance, coating tribocatalytic particles onto the inner surfaces of water treatment pipes could enable the harvesting of mechanical energy from vortex-induced flow.

(vi) Economic feasibility: ensuring cost-effectiveness and reliability is crucial for the widespread adoption of tribocatalytic technologies. Material synthesis and system design must strike a balance between performance and affordability. Life cycle assessments can help evaluate the economic feasibility in relation to process effectiveness.

10. Future outlook

The future of tribocatalysis is promising, with growing interest in its potential for sustainable energy generation and environmental remediation. Advancements in material science and nanotechnology are enabling more efficient tribocatalysts with higher durability and activity. The key to an efficient tribocatalytic reaction lies in having a highly active catalyst specifically tailored for friction-driven reactions. Achieving a highly active tribocatalyst with sufficient stability beyond lab-scale demonstrations remains a significant challenge. To overcome this bottleneck, catalyst design has emerged as a crucial area of research that warrants thorough exploration.

Designing efficient tribocatalytic materials involves optimizing their physical, chemical, and structural properties to maximize performance in friction-driven reactions. The process begins with the careful selection of base materials that exhibit both catalytic activity and mechanical durability. Commercially available materials are suitable as base candidates, as their widespread availability allows for testing across different laboratories, ensuring reproducibility and broadening reaction scope. Transition metal oxides, sulfides, and noble metals are commonly chosen for their inherent catalytic properties, while materials with complementary triboelectric characteristics are selected to enhance charge transfer during mechanical interactions. The mechanical durability of these materials is important to withstand the mechanical stress on the surface generated by friction. Materials commonly used in direct mechanocatalysis, such as ZrO_2, Cu, Au, and Pd, seem promising options. ZrO_2, for example, is resistant to oxidizers, strong acids, and bases.[61]

In fact, the design parameters for tribocatalytic materials remain unclear at present. Several key aspects need to be considered.

(i) When assuming electron transition mechanism to occur, an optimal energy band gap is crucial. If the band gap is too

narrow, charge separation becomes inefficient, leading to poor redox activity. Conversely, a band gap that is too wide requires excessive mechanical energy for activation, which is not relevant in ambient environment. A moderate band gap (~2.0–3.0 eV) is ideal for balancing charge excitation and catalytic efficiency.

(ii) Tribocatalysts must withstand repeated mechanical stress without significant degradation. Nanostructured materials with high hardness, toughness, and wear resistance (such as metal oxides and perovskites) are preferred. Hierarchical structures could also potentially enhance friction-induced charge generation while maintaining mechanical stability.

(iii) The surface properties of tribocatalysts play a crucial role in charge generation and retention. Materials with high electron affinity, such as fluorinated polymers (*e.g.*, PTFE), facilitate efficient charge transfer. Surface functionalization, such as introducing oxygen vacancies or doping with electronegative elements, can further enhance catalytic performance.

(iv) Tribocatalytic reactions rely on the interaction between the catalyst and contacting surfaces. High-friction surfaces and materials with contrasting work functions enhance electron transfer. For instance, $Bi_{12}TiO_{20}$ (BTO) was paired with four triboelectric polymers (PA-66, PVDF, PP, and PTFE) to form friction pairs (Fig. 7).[84] Small polymer additions initially improved efficiency by enhancing charge transfer, but performance declined when the amount exceeded 3 mg. This decline was due to the polymers' low positions in the triboelectric series, which made them strong electron acceptors and disrupted effective charge flow from BTO. Among the polymers, PTFE demonstrated the highest degradation efficiency, achieving a kinetic constant (k) of 0.68 h^{-1}, 1.26 times higher than BTO alone. PTFE's strong performance is attributed to its high work function (~6.5 eV), which contrasts sharply with BTO's lower work function (~4.4 eV), promoting efficient electron transfer from BTO to PTFE during friction and leaving positively charged sites on the BTO surface. This large work function difference underpins the enhanced tribocatalytic activity.

In addition, integrating tribocatalytic materials with tribological systems should be considered. Materials should be designed to work synergistically with mechanical forces such as vibrations, sliding, or fluid flow. Incorporating these materials into self-powered systems that utilize the triboelectric effect ensures sustained catalytic reactions. Scalability and cost efficiency are also critical considerations. Eco-friendly and cost-effective fabrication methods, as well as the use of abundant and recyclable materials, are essential for widespread applications. Designing efficient tribocatalytic materials indeed requires a comprehensive understanding of electron transfer and transition mechanisms, as well as the interplay between mechanical forces and catalytic activity.

Finally, iterative testing and optimization refine the material design process. Performance evaluations under realistic conditions yield valuable data on catalytic activity, reaction rates, and long-term durability. These insights inform further adjustments to the material's composition and structural features. Tribocatalytic materials are often tailored for specific applications, such as water splitting, CO_2 reduction, or pollutant degradation, to meet the unique demands of each use case. At the same time, expanding the reaction scope is also crucial for enhancing their overall applicability. Unselective

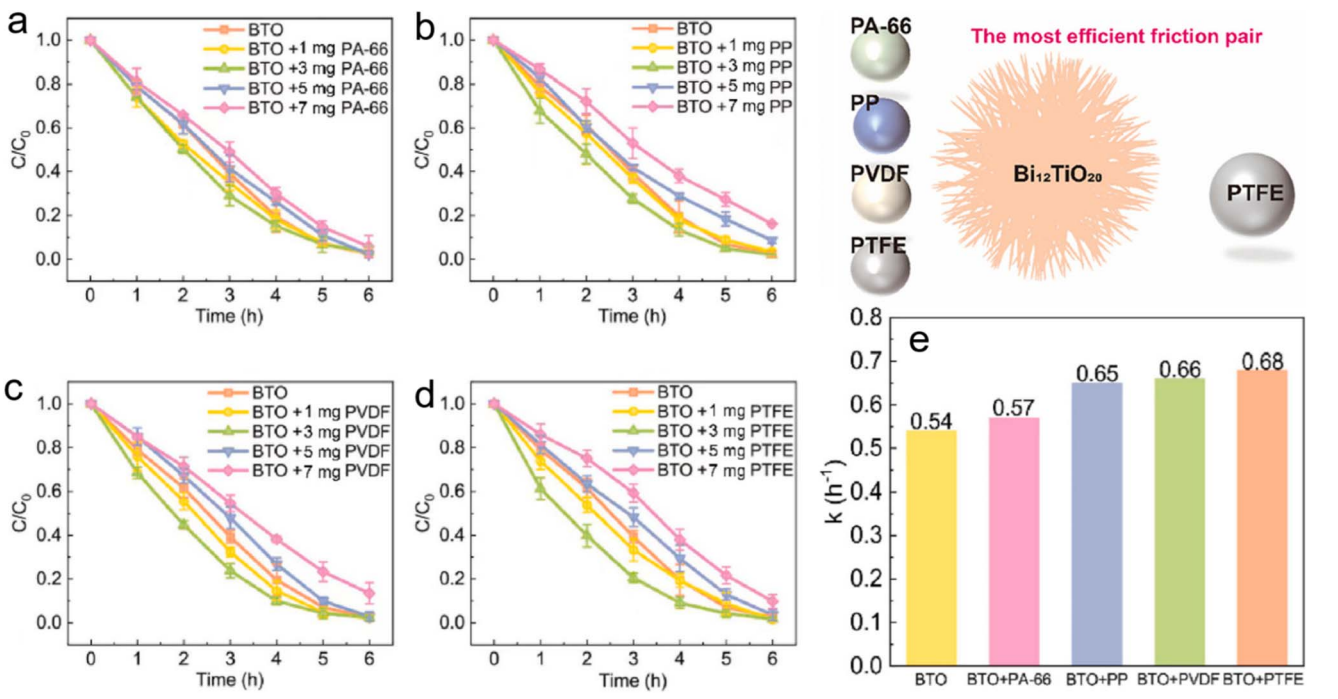

Fig. 7 Rhodamine B degradation by friction pairs of BTO with (a) PA-66, (b) PP, (c) PVDF, and (d) PTFE; (e) corresponding kinetic constants. Reproduced with permission.[84] Copyright 2024, Elsevier.

chemical transformations, such as the degradation of refractory organic compounds in water, are generally easier to accomplish than selective ones. For instance, when coated on the inner walls of water treatment pipes, tribocatalytic particles can facilitate total oxidation, leading to the mineralization of dissolved organics. In contrast, achieving selective transformations, such as the dechlorination of chlorinated aromatic hydrocarbons, is difficult to realize. By systematically addressing these considerations, it is possible to develop highly efficient and versatile tribocatalytic materials for next-generation catalytic processes driven by mechanical forces.

Future important and promising applications of tribocatalysis, which are thermodynamically less demanding than fuel or chemical synthesis, include the degradation of microplastics and pathogenic microorganisms. Tribocatalytic processes have demonstrated effectiveness in breaking down organic pollutants such as dye molecules, suggesting strong potential for treating microplastics due to their similar organic composition and susceptibility to oxidative degradation. The ROS generated through friction-induced charge separation can oxidize and cleave the stable polymer chains in microplastics, leading to their fragmentation and eventual mineralization. A key advantage of tribocatalysis is its ability to operate under ambient conditions without the need for external light or electrical input, relying solely on mechanical energy. This makes it particularly well-suited for environments with inherent turbulence, flow, or agitation, such as water treatment systems. The continuous friction involved not only drives ROS production but also sustains surface activation of the catalyst, enhancing its long-term activity against persistent microplastic particles. In the context of water disinfection, these ROS can diffuse into the water and interact with pathogens, damaging cell membranes, denaturing proteins, and disrupting genetic material, thereby achieving effective microbial inactivation.

11. Summary

Tribocatalysis represents an emerging frontier in catalysis, uniquely driven by mechanical forces and triboelectric charge generation. By harnessing frictional energy, tribocatalysis enables chemical transformations without relying on traditional energy inputs such as heat, light, or electrical bias. Its versatility allows application in environmental remediation, energy production, organic synthesis, and self-powered systems. The underlying mechanisms, electron transfer and electron transition, highlight the complex interplay between material properties and mechanical stimuli. Carefully engineered materials, including metal oxides, polymers, semiconductors, and composites, play a central role in determining catalytic performance. Optimization of electronic band structures, surface morphology, and mechanical durability is essential to enhance activity and selectivity. Although tribocatalysis offers unique advantages, such as compatibility with low-frequency mechanical forces and a broad material scope, it faces significant challenges. These include catalyst degradation under abrasion, limited mechanistic understanding, and the difficulty of scaling reactions for industrial applications. Surface engineering strategies, like introducing defects or nanoscale roughness, can help mitigate durability issues and increase performance. Achieving selective transformations, such as the dechlorination of chlorinated compounds, remains a key obstacle compared to relatively easier unselective degradation processes. Comparisons with related fields like piezocatalysis and flexocatalysis underline tribocatalysis's advantages in simplicity and material flexibility. The development of tribocatalytic materials must also consider compatibility with natural mechanical forces to enable sustainable, real-setting applications. Future research should emphasize precise control of frictional parameters and better integration with tribological systems.

Conflicts of interest

No conflict of interest is to be declared.

Data availability

No primary research results, software or code have been included and no new data were generated or analyzed as part of this article.

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