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Photo-mechanochemistry: a new paradigm for coupled energy inputs in sustainable chemical processing?

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Mechanochemistry and photocatalysis have independently emerged as powerful, sustainable strategies for driving chemical transformations. Their integration offers new opportunities to modulate reaction pathways, enhance selectivity, and access reactivity regimes unattainable by either stimulus alone. This contribution outlines the fundamental principles governing force-driven solid-state reactions and photon-induced charge dynamics and analyzes how their coupling can enable synergistic activation modes. We discuss key reactor-design considerations for both mechanochemical and photocatalytic systems, emphasizing engineering strategies for incorporating light into mechanically driven environments. Particular attention is devoted to the configurations of these reactors and the technological challenges associated with integrating light delivery and mechanical force within a single operational environment, including the practical constraints that arise when controlling irradiation, heat dissipation, and energy transfer under mechanically dynamic conditions. We highlight emerging application areas and the potential for scale-up *via* extrusion or irradiated milling. Altogether, these insights aim to guide future efforts toward establishing predictive, physics-based frameworks for the design of next-generation photo-mechanochemical reactors and processes.

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1. This Perspective discusses advances in green chemistry arising from coupling mechanochemistry and photocatalysis as complementary. Their integration enables solvent-free or solvent-minimized processing, enhanced selectivity, and access to reactivity regimes not attainable under either individual stimulus alone.
2. The field is of broad interest because it redefines how chemical energy is delivered and controlled, offering intensified, potentially energy-efficient routes relevant to sustainable synthesis, materials design, and scalable manufacturing.
3. Future progress will rely on predictive, physics-based models and reactor designs integrating controlled irradiation (*e.g.* LSRPA, LVRPA) with mechanical force. By identifying mechanistic gaps and engineering challenges, this work helps guide the development of next-generation, multi-energy green chemical processes.

1. Introduction

The origin of mechanochemistry dates back hundreds of years, but it was not until the end of the last century that it began to

establish itself as a recognized method for materials synthesis.¹ Mechanochemistry is defined as the chemical reactions induced by the direct absorption of mechanical energy, such as cutting, stretching, or crushing.² This process can be performed using various techniques, such as a mortar and pestle, planetary mill, mixer mill, or twin-screw extruder,³ or more sophisticated equipment that allows the processing of materials in a more reproducible and scalable manner. Mechanochemistry has become a sustainable and eco-friendly method, based on the principles of green chemistry, improving the atomic efficiency, being solvent-free, and reducing the synthesis time in some cases.^{4,5} This method presents advantages compared to conventional methods of synthesis that can be

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explained by physical effects intrinsic to mechanical processing, such as reduction of particle size, increase of surface area, generation of active interfaces, and breaking of mass transfer barriers, all of which help to obtain accelerated kinetics without the need for a distributed heat input.^{6,7} Some studies confirm that, for the synthesis of certain materials, such as MOFs, electrodes, and functional polymers, mechanochemical routes are more sustainable and cost-effective than traditional methods that use different solvents.^{8,9} However, the implementation of this approach from the laboratory to industrial scale is gaining recognition, establishing it as a sustainable technology. From a scalability perspective, extruders enable continuous control of feed and residence time and are ideal for integration into the value chain (catalyst manufacturing, polymers, biomass recycling). However, the transition to industrial scales requires precise and efficient engineering across various parameters, such as mass transfer, heat transfer, and mechanical energy.^{4,10}

For this reason, light irradiation during milling becomes a valuable tool for selective activation, thermal management, and hybrid processes. Currently, most of the reported photo-mechanochemical systems rely on molecular photocatalysts, most likely due to their higher tolerance to the dynamic mechanochemical environment. Indeed, the use of semiconductors represents a major challenge since mechanochemical processing could alter the material properties, including crystallinity, morphology, particle size and defect density. Such *in situ* modifications during mechanochemical operation could consequently affect the photocatalytic performance, requiring operando studies to get a complete understanding of

the underlying processes and the structure–activity relationships.

Photons introduce additional activation pathways in mechanochemical systems, where light–matter interactions could occur through various mechanisms depending on the material's nature. Molecular photocatalysts undergo photoexcitation to generate reactive excited states, while semiconductors generate electron–hole pairs upon irradiation. Additionally, plasmonic materials can exhibit plasmonic resonances and localized photothermal effects. All these phenomena can improve the synthesis pathway and influence selectivity in photo-mechanochemical transformations.^{11–14}

In this sense, mechanical energy facilitates the formation and exposure of reactive sites, while light provides specific energy that favors the process, thereby eliminating the need for external heat.^{13,15} Furthermore, an optimal design can be found to enhance the efficiency of light radiation and mechanical grinding by synchronizing the mechanical processes (shear, impact, extrusion speed) with the phenomena associated with light (spectrum, intensity, pulse).^{14,15} In this way, the process can be more sustainable if the light source is energy-efficient (*e.g.*, efficient LEDs or renewable sources such as concentrated solar power), in accordance with the principles of green chemistry that promote energy efficiency and the use of renewable resources.¹⁶ However, despite the synergy between photonic and mechanical energy, the reactor design is the primary challenge to scaling this process to industrial levels (*i.e.*, delivering and distributing the photonic energy and controlling the temperature).^{13,17} There are some critical limitations such as: (i) incomplete reproducibility and metrology since most studies do not report some data that are important for the process, such as the applied mechanical energy, geometry and material of which the screws and spheres are made, the incident photons on the material, the temperature distribution, this limits the scalability and the replication of the process;^{9,17} (ii) spatial heterogeneity and hotspots in some processes such as mills and extruders generate temperature and shear variations; light radiation adds complexity to the system when there are opaque materials that absorb light, affecting the selectivity and stability of the product;^{12,13} (iii) complex construction materials, requiring high optical transmittance but at the same time high resistance to wear and impacts, therefore it becomes a great challenge for materials science and engineering;^{8,18} (iv) control over the process: by not having sensors to monitor the internal temperature and light intensity, they limit automation, safety and traceability to take it to industrial scales.^{13,17} For this reason, we propose that the best route to take this process to an industrial level is to prioritize the design of reactors with illumination and thermal dissipation zones, develop materials with the required optical properties, and, at the same time, be mechanically resistant, have control and instrumentation in the production line that allow reproducibility and safety. In the following sections, we focus on the system design, integrating the light source, and the critical control parameters, as well as scaling this process up to an industrial level.



Mario J. Muñoz-Batista

Mario J. Muñoz-Batista is a Professor in the Department of Chemical Engineering at the University of Granada. His research has focused on the development of advanced catalytic materials and innovative catalytic processes, with a strong emphasis on sustainability concepts and process intensification. He has made significant contributions to the design of environmentally responsible catalytic technologies for chemical,

environmental, and energy-related applications. This perspective article highlights one of the main research lines of his scientific career, focused on the combined use of multiple external stimuli, such as thermo-photo-catalysis and mechanochemical approaches, to develop novel catalytic processes with strong potential for scalability and industrial implementation. It also reflects his strong interest in multidisciplinary approaches and collaborative research.



2. Fundamentals

2.1. Mechanochemistry: force-driven transformations in the solid state

As briefly mentioned in the Introduction section, mechanochemistry utilizes mechanical energy to promote chemical transformations in the solid state, eliminating or drastically reducing the amount of solvent required.^{5,19} In some reactions, the possibility of using small amounts of solvent, while still reducing the overall consumption, could play a critical role in tuning, for instance, the product selectivity.^{20–26} But to what extent is a small amount of solvent truly small and still compatible with mechanochemical processes? To answer this question, it is necessary to consider that mechanochemical processes can be classified according to the η parameter, which is defined as the volume of liquid in μL per milligram of solid. For $\eta = 0$, hence in the absence of solvents, the process is referred to as Neat Grinding. Instead, for $0 < \eta \leq 2 \mu\text{L mg}^{-1}$, the process is denoted as Liquid-Assisted Grinding (LAG). In turn, when the liquid content increases to values between 2 and $12 \mu\text{L mg}^{-1}$, the system is considered a slurry, and finally, the η value higher than $12 \mu\text{L mg}^{-1}$ refers to a conventional solution. Typically, mechanochemical reactions are performed either under neat grinding ($\eta = 0$) or under LAG conditions ($0 < \eta \leq 2$).²⁶

By varying not only η , but also the chemical properties of the employed liquid, it is possible to access additional control of the reactants/catalysts interface, the solid-state reactivity and thus the product distribution. Besides the enhanced diffusion and surface mobility expected under LAG conditions, the physicochemical properties of the chosen liquid, particularly its polarity and hydrogen-bonding ability, can significantly modify the reaction pathways, often enabling the targeted formation of specific products.^{27,28} In this regard, there are several examples in the literature, for instance the work of Mack and colleagues on the dimerization of alkynes, which interestingly lead to the formation of the alkyne–alkene product using polar solvents like ethanol, while conducting to the alkyne–alkyne product using non-polar solvents like cyclohexane.²⁹ In other cases, the employed solvent could also have a stabilizing effect on the catalytic species, for example the use of 1,5-cyclooctadiene as a liquid additive for palladium catalyzed reactions.³⁰ On the other hand, the possibility of working in the complete absence of solvents could allow the formation of improbable/unusual products or materials. For instance, trimethylsilylated tetraallyltin(IV), which decomposes in solution, could be assessed *via* ball-milling under neat grinding conditions.³¹ Particular attention should be given to the potential of mechanochemistry for polymer processing and valorization schemes. Recent studies demonstrate that polymers such as poly(styrene) (PS) and poly(ethylene terephthalate) (PET) can be efficiently depolymerized under mechanochemical conditions, where factors such as surface generation, shear-induced cohesive states, and the formation of reactive interfaces critically govern the reaction rates, selectivity, and overall process efficiency, highlighting a promising

pathway toward solvent-free and energy-efficient polymer upcycling.^{32–34}

Mechanical input can both induce/modify molecular motion or generate intramolecular strain, which could determine the reaction performance.³⁵ Mechanical energy can reduce the particle size, generating defects and reactive sites that increase the likelihood of effective collisions between reactants and lower activation barriers, thus promoting the reactivity. Moreover, efficient mechanical mixing could also ensure the homogeneity of the reaction environment.

For a long time, mechanochemical transformations were directly linked to a thermal effect related to the temperature rise during grinding. It was not until 1866 that Matthew Carey Lea, considered the father of mechanochemistry, reported the first systematic investigation, correlating mechanical energy and chemical transformations. It is, indeed, fundamental to distinguish mechanical and thermal effects in mechanochemical reactions. While mechanical energy can generate heat, not all observed reactivity arises from temperature increases. Instead, direct bond deformation and stress-induced changes to the molecule's potential energy landscape can independently drive chemical transformations.³⁶ Specifically in extrusion, both thermal and mechanical effects can be precisely combined, controlling the temperature and torque. In some recent studies, for example for the preparation of amides and amines *via* the Leuckart reaction, it has been demonstrated that different product distributions can be achieved by heating or extrusion, respectively.³⁶

The kinetics of mechanochemical processes could be described using the Arrhenius equation, where the reaction rate depends on both the activation energy and the pre-exponential factor. Mechanical energy effectively reduces activation barriers, yielding faster, cleaner, and more sustainable reactions. Moreover, it is well-known that the pre-exponential factor reflects the frequency of effective molecular collisions and, therefore, the probability of correct molecular orientation. When it comes to mechanochemistry, the applied mechanical forces (impact, friction, shear, acoustic vibration, *etc.*) can enhance this factor by increasing the contact between the reactant or catalyst surfaces, exposing reactive sites, and thereby accelerating reactions beyond what thermal effects alone would achieve.³⁷

While a mortar and pestle are known as the most common and historically known mechanochemical instruments, a concern arises regarding reproducibility. In this sense, modern approaches employ advanced technologies such as planetary mills, vibratory mills, resonant acoustic mixers (RAM) and twin-screw extruders that enable both batch and continuous operations, under precise and reproducible conditions.¹ Typically, planetary ball mills employ rotating jars, which have translational and rotational motions. This dual motion, mimicking planetary movement patterns, generates high-energy impacts and shearing forces, effectively breaking down particles, increasing the surface area and creating defects, which could enhance effective molecular collisions and the surface interaction with catalytically active sites. On



the other hand, vibratory mills rely on rapid oscillatory motion to transfer the kinetic energy to the powders and milling media. The vibrations produce repeated collisions and friction between particles and balls, promoting efficient mixing and comminution.

Furthermore, in RAM instruments, the sample chamber is placed on a plate connected to a bed of springs, which oscillate at a desired frequency. The resulting acoustic vibrations enable efficient and intimate mixing between reactants without the need for milling media (such as stainless steel or zirconia balls or beads), which helps avoid metal contamination, an important advantage when preparing materials for pharmaceutical applications.

Finally, twin-screw extruders are continuous mechanochemical reactors in which reactants are fed into co-rotating screws within a barrel. The screws could be configured with conveying and mixing zones, allowing solventless reactions to be performed in a continuous flow, and promoted by shear and compressive forces. In addition, twin-screw extrusion provides precise control over the residence time, temperature, and mechanical input (torque monitoring), making it particularly suitable for scalable, continuous mechanochemical processes such as polymer processing, co-crystal formation, solvent-free organic synthesis or more recently nanometric catalytic materials preparation. These methods position mechanochemistry, particularly *via* extrusion, as a central pillar of Green Chemistry, recognized by IUPAC among the Top Ten Chemical Innovations 2019.^{38,39}

In contrast to solution-phase chemistry, where reaction rates are limited by diffusion or molecular affinity, solid-state mechanochemistry forces reactants to come into direct contact, overcoming these limitations and in some cases allowing to access chemistries not achievable in solution. However, a full understanding of how mechanical energy translates into chemical reactivity and how parameters such as η modulate mechanochemical reactions and product distribution remains a central challenge to design reproducible protocols, which could be translated from one type of mechanochemical reactor to another. In this sense, *in situ* characterization approaches have become increasingly important and are present in the literature. Techniques such as Raman spectroscopy and X-ray diffraction (XRD) can monitor structural changes and reaction progress directly during milling or extrusion, allowing us to track the formation of intermediates and phase transitions and to unravel the interplay between mechanical forces, molecular structure, and reaction pathways.^{17,40–42}

2.2. Photocatalysis: photon-induced charge dynamics

Photocatalytic reactions, defined by the IUPAC as chemical reactions initiated or promoted by light irradiation, in the presence of a photocatalyst, represent also an opportunity to move towards a more sustainable chemistry.^{43–48} There is a wide range of materials which could be used as photocatalysts, including molecular systems, pure semiconductors and doped or composite systems.^{44,49,50}

Molecular photocatalysis mechanisms are based on the light-promoted generation of electronically excited states, which lead to activation pathways typically inaccessible under thermal conditions.⁵¹ Under light-irradiation, photocatalytic systems are promoted to excited singlet states, which may subsequently undergo intersystem crossing, resulting in the generation of longer-lived triplet excited states.⁵² Triplet-state reactivity has a critical role in many visible-light photocatalytic processes, since such excited species can interact with substrates through single electron transfer (SET), energy transfer (EnT), or hydrogen atom transfer (HAT) pathways, and at the same time, limit fast excited-state deactivation.^{53–56}

Fundamental studies on photoinduced electron transfer (PET), rationalized through Marcus theory,⁵⁶ established the basis for understanding charge-transfer dynamics in excited-state catalytic systems.⁵³ Among the principal mechanistic pathways in molecular photocatalysis, SET processes have been extensively explored in photo-redox processes.⁵⁷ In this scenario, the excited photocatalysts can act as either oxidants or reductants, leading to the formation of reactive radical intermediates through oxidative or reductive quenching cycles, respectively. In addition, EnT photocatalysis has emerged as a complementary activation mode that takes place *via* transfer of electronic excitation energy, instead of electrons. Unlike SET pathways, EnT mechanisms are not constrained by substrate redox potentials, therefore allowing the activation of electronically challenging substrates through triplet sensitization or excited-state energy exchange.⁵³

In heterogeneous photocatalytic processes, semiconductors are employed due to their characteristic moderate band gap, which enables the excitation of electrons from the valence band (VB) to the conduction band (CB) upon thermal activation or light irradiation of a suitable wavelength. Consequently, when electrons are excited from the VB to the CB, holes are generated in the VB. Such photo-generated pairs of electrons and holes are highly reactive, and thus actively participate in chemical transformations at the photocatalyst surface. Photocatalysis has become relevant for several relevant reactions, including water splitting,^{58,59} reforming schemes,^{60,61} CO₂ reduction,^{62,63} or other organic reactions under mild conditions.^{64,65}

As just mentioned, the band gap is a key parameter of photocatalytic materials, as it determines the operating wavelength and, consequently, whether the material can be activated under specific illumination conditions. But the overall efficiency of a photocatalytic sample is also determined by many other factors, among which two intrinsic factors stand out, namely the absolute positions of the CB and VB and the charge carrier dynamics. In particular, the CB and VB positions define the reduction and oxidation potentials of the electrons and holes, respectively.^{49,50} Furthermore, the dynamics of photogenerated carriers, including their mobility, lifetime and recombination, are a crucial aspect of optimization to maximize the photocatalytic efficiency. In this sense, the engineering of defects, the use of co-catalysts, and amorphization strategies to improve charge carrier separation have also



been central to the research in the field. Balancing all factors together, light absorption, redox properties and reduced recombination, is a central challenge in photocatalyst design.¹¹

Pure semiconductors often suffer from fast electron–hole recombination, limiting their photocatalytic activity. To overcome this limitation, the formation of heterojunction materials has been widely described in the literature. For example, type-II heterojunctions between two semiconductors lead to a staggered band alignment, where electrons move to the lower energy CB and holes migrate to higher VB, achieving spatial separation.⁶⁶ However, in this case, recombination can still occur due to the intrinsic energy alignment of the materials. On the other hand, the S-scheme heterojunction between two semiconductors, combining an oxidation photocatalyst and a reduction photocatalyst, leads to a bending band alignment, thereby facilitating the selective recombination of the lower energy carriers, while the higher energy pairs and thus the redox properties are preserved.^{62,66,67}

In summary, although photocatalysis is inherently complex, extensive specialized literature has systematically analyzed and categorized its phenomena, established robust methods for quantification,⁶⁸ and provided a broad spectrum of *in situ* and operando studies,^{69–72} alongside intrinsic kinetic analyses and advanced models of light–matter interactions,^{44,68,73,74} offering a solid foundation for understanding and further exploration of this multifaceted process.

2.3. Bridging the two worlds: mechano-photochemical coupling

Both mechanochemistry and photocatalysis represent sustainable approaches to promote chemical reactions, one driven by mechanical force and allowing to reduce solvent use, and the other one harnessing light, including sunlight irradiation which is a renewable energy source. Bridging mechanical energy and light irradiation together, through photo-mechanochemistry, could open new possibilities for reactions' selectivity control and efficiency (Fig. 1).^{12,13,75,76} As previously men-

tioned, mechanical forces can increase surface areas, generate defects and promote amorphization, enhancing the molecular proximity and reducing the solvent amount, while light provides additional energy to promote photochemical activation in molecular systems, or trigger structural defect formation and the generation of highly reactive electron–hole pairs, in the case of semiconductors. The combination of these two methodologies can lead to synergistic effects, such as activation of photocatalysts under solid-state conditions, accelerated reaction rates, access to new reaction pathways, or improved product selectivity, as well as improved light absorption and interfacial charge transfer.⁷⁷

In this context, synergy should not be misinterpreted as the mere coexistence of mechanical and photonic energy inputs, but rather as a distinct kinetic and mechanistic response relative to their isolated application. Accordingly, synergy in photo-mechanochemical systems is defined as the emergence of reactivity regimes and reaction pathways that cannot be rationalized through a simple linear superposition of individual contributions, such as photothermal heating.

From a quantitative standpoint, an initial framework to assess this behavior can be established through a rate-based comparison. For a given reaction leading to a target product X, the reaction rate under combined photo-mechanochemical conditions (r_{pm}) can be evaluated against the sum of the individual rates obtained under purely photochemical (r_p) and mechanochemical (r_m) conditions. Based on this, a dimensionless interaction factor can be defined as: $r_{pm}/(r_p + r_m)$. This descriptor provides a first approximation to characterize the nature of the coupling. Values close to unity indicate an additive regime, values below unity suggest antagonistic or inhibitory interactions, and values above unity are indicative of synergistic behavior, where the combined system exceeds the sum of the individual contributions.

At the physicochemical level, the interplay between mechanical activation, photon absorption, and localized thermal effects can give rise to coupled photo-tribo-thermal regimes with distinct behavior. However, it is essential to

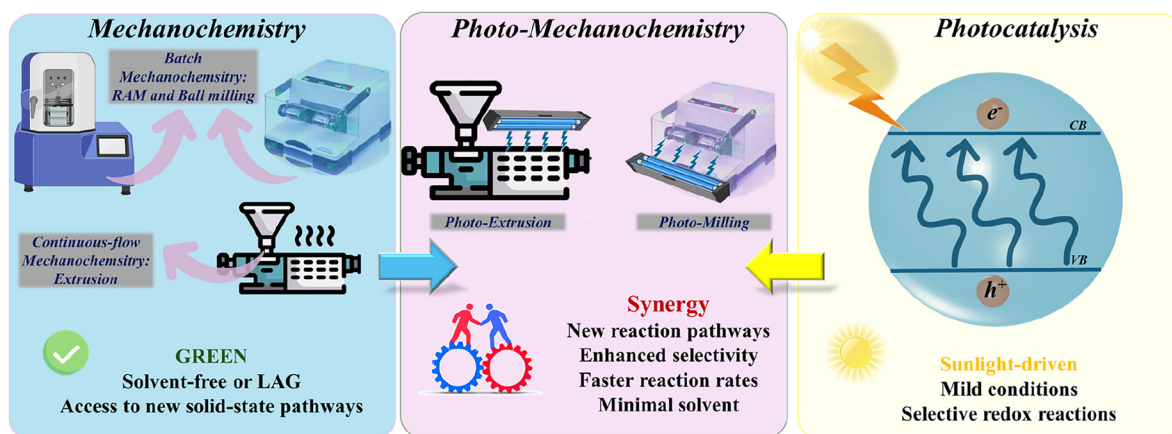


Fig. 1 Conceptual framework of photo-mechanochemistry: synergistic integration of mechanical force and light irradiation.



emphasize that such synergy must be experimentally demonstrated rather than assumed. This requires carefully designed control experiments, including milling in the absence of light, static irradiation without mechanical input, and temperature-matched conditions to decouple purely thermal contributions, complemented by quantitative descriptors such as the one proposed above.

In the following sections, we further analyze how these phenomena could be decoupled to enable intrinsic kinetic studies and, ultimately, to establish robust criteria for rational scale-up of photo-mechanochemical processes. The efficiency of such coupled systems will depend on several factors, including mechanochemistry-related variables, such as the milling speed, the type of reactor and the liquid-to-solid ratio, and photocatalysis parameters, like the choice of the photocatalytic system, including molecular photocatalysts, semiconductors and heterojunction design. Regarding the selection of the mechanochemical reactor, it is worth mentioning that most of the reports in the literature so far have concentrated on mixer millers employing transparent chambers (of polymethyl methacrylate), leaving a lot of opportunities for the development of photo-extrusion approaches. Overall, photo-mechanochemistry provides a versatile platform for sustainable chemical synthesis, combining the solvent-free advantages of mechanochemistry with the selective, energy-efficient activation provided by light.

3. Reactor design principles for photo- and mechanochemically assisted processes

3.1. Mechanochemical reactors: design parameters

Mechanochemical reactors require a design where the reactants, confined in a solid or semi-continuous state, interact internally with mechanical energy, mass transport, and heat flow. To achieve greater efficiency in this process, the engineering design of these reactors is essential. Key aspects to consider include mechanical energy transfer, scalability depending on the structural arrangement of the equipment, and thermal management and mixing.⁷⁸

Energy transfer in grinding can be different depending on the system: when using the discontinuous system such as ball mills, mixers or planetary mills, energy transfer occurs by collisions between the grinding medium and the powder,²⁷ and due to these internal interactions structural or chemical changes induced by plastic deformations, frictions and fractures generated occur.⁷⁹ These energy transfers have been widely analyzed and discussed, where the kinetics of mechanochemistry depend on the collision frequency.⁵ To determine the effective energy density in the sample, it is important to have control over the intensity and frequency of these phenomena. This is achieved by knowing the variables that can be modified, such as the type of vial, mass, the quantity of balls, angular velocity, and ball/powder ratio.⁸⁰ On the other hand,

in continuous systems such as extrusion, energy is distributed through shear and elongation flows, especially in co-rotating twin-screw extruders. This system offers the advantage of uniform mechanical energy throughout the process, in addition to reducing the dependence on individual impacts.⁸¹ Extrusion allows control of the stress profile in both the feed rate and internal pressure because it operates under sustained stresses. In addition, there is greater control over the process kinetics due to the management of variables such as rotation speed, screw shape, and the configuration of the segments that mix gently, resulting in homogeneous nanoparticles and energy dissipation. For this reason, extrusion promises to be a highly scalable process at the industrial level, even though the point energy level is lower than in milling processes.²⁵ In this sense, it is important to understand how both processes work (knowing that milling generates a higher activation intensity and extrusion prioritizes scalability with time control and stability during the process) to define the conditions and geometry of the initial device in the hybrid process that incorporates light radiation with controlled heat. It is important to mention that the limitations mentioned above are inherent to traditional mechanochemical processes. However, when another variable, such as light incidence, is added to the process, new challenges arise, such as the efficient integration of photonic energy into the system. This includes the penetration of dense and opaque solid materials, the non-uniform distribution within the reactor, and the automation and synchronization of photonic irradiation during mixing. Therefore, scalability also depends on light-assistance factors rather than solely on the mechanochemical system. Consequently, the goal is to achieve optimal coupling between mechanical energy and light transport to ensure a uniform and efficient activation process.

Additionally, other alternatives may also be considered, although they may present greater complexity in their scale-up schemes. One such system is Resonant Acoustic Mixing (RAM). This process has the advantage of avoiding contamination associated with conventional grinding media, enabling efficient and uniform energy transfer.⁸² Similarly, vortex-based mixing systems, especially vortex fluidic devices (VFD), enable improved reaction performance and high process efficiency through high-shear, intense micro-mixing.^{83–86} Another alternative is rod milling, which enables uniform light penetration in heterogeneous systems, thereby improving the reaction efficiency and energy transfer.⁸⁷ These alternatives demonstrate the flexibility and potential of photo-mechanochemical processes, encompassing a wide range of technologies that can be used in these systems.

It is worth mentioning that the scalability of the mechanochemistry process is of utmost importance and presents some limitations, particularly when increasing the production quantity. In this sense, the most significant limitation is that laboratory mills perform very well in obtaining small quantities, ensuring a homogeneous mixture due to the high number of collisions per unit of mass. However, when it comes to obtaining large quantities, the resulting material is usually hetero-



geneous due to the insufficient trajectory of the balls, which generates zones with different collisions and temperatures.⁸⁸ On the other hand, modular extruders offer a transition from laboratory to industrial level, due to the feeding, kneading, reaction, and cooling zones. In addition, screws can be designed with different geometries, and stress gradients and residence times can be adjusted. Parameters such as mass flow density (\dot{m}), specific mechanical energy (SME), and power number (N_p) can also be modified; all of these relate to the transmitted power, the processed mass, and the reactor design.⁸⁹ It is important to mention that successful scalability requires monitoring throughout the process. This can be achieved with the help of sensors that record the torque, temperature, and pressure distributed throughout the reactor. This is essential for controlling the operating conditions of the material being synthesized and is a fundamental step prior to the incorporation of light radiation.

Another important point to consider is the generation of heat during the process. In mills, friction and mechanical impacts generate an increase in internal temperature. This temperature increase can, in some cases, be responsible for phase diffusion and transformation, thus resulting in a loss of process control. To solve this problem, vials with appropriate geometry and materials, such as steel, zirconia, or tungsten carbide, capable of dissipating heat through conduction, are used to improve the heat exchange efficiency.⁹⁰ On the other hand, extruders offer greater thermal control thanks to independent heating and cooling zones. This arrangement contributes to an advanced design where the kneading modules are monitored by sensors to control heat dissipation and ensure process control, avoiding overheating.⁹¹

In grinding systems, mass transfer depends on the direct contact of the material with the balls, which are subject to specific parameters: rotation speed, time, number, size, and material. However, there is a risk of material agglomeration, limiting the reactive surface area.⁹² In contrast, extruders do not have this problem because the mixture is distributed throughout the process, creating solid interfaces and avoiding heterogeneous materials. This behavior is important for designs where light and heat will affect the material during the mechanochemical process.²⁴

In short, efficient energy transfer, thermal and compositional uniformity, and real-time process control are essential. This is the basis for light-assisted mechanochemistry.

3.2. Photocatalytic reactors: design parameters

Photocatalytic reactors have attracted much attention for their excellent performance in photoactivation, thanks to their design and geometry. In these systems, one of the most important parameters to consider is that the irradiation uniformly reaches the entire material, since the stability of the mass and heat transfer during the process depends on it. Thanks to all this, the process can be controlled, increasing the quantum efficiency and decreasing the probability of charge carrier recombination.^{62,73}

Photocatalytic reactors are classified into batch and continuous-flow systems. The continuous flow system is the most promising for scaling this process to large scales, because it provides greater control during illumination and requires a shorter reaction time.⁹³ When there are suspension systems, the reactors are of the slurry or fluidized-bed type; on the other hand, when there are solid-liquid or film systems, catalysts are coated on the walls of the photoreactor. However, in any photoreactor, the important thing is to optimize the light irradiation that interacts with the material.⁹⁴ Among the most used photoreactors are tubular and annular ones, as they offer excellent irradiation uniformity thanks to the perimeter or coaxial design of the light source.⁷³ Beyond conventional tubular photoreactors, systems have recently been developed to overcome limitations in light penetration and mass transfer, as mentioned in section 3.1. Taylor vortex flow reactors exhibit good photon distribution through controlled hydrodynamics, allowing at the same time homogeneous mixing and therefore good process efficiency.⁹⁵⁻⁹⁷ In addition to rotor-stator spinning disk reactors⁹⁸⁻¹⁰⁰ and vortex fluidic devices (VFD),⁸⁴⁻⁸⁶ these systems provide uniform irradiation throughout the reaction. They ensure more efficient photon transport within the material during the process, independent of the light source's intensity.

The choice of materials is crucial for the design of photoreactors. For example, FEP (Fluorinated Ethylene Propylene) or PFA (Perfluoroalkoxy Alkane) offers advantages, including high UV-Vis transmittance and good chemical stability, ensuring illumination homogeneity and good heat dissipation in micro-reactors and capillary reactors.⁹³ Other materials with high efficiency in photoreactors include quartz, sapphire, borosilicate, and PMMA, as they exhibit high transmittance across the UV-Vis-NIR spectrum. Another very important factor to be considered in the design of the photoreactor is the light source, since, as previously discussed, the irradiation must be uniform, avoiding excess or deficit of photons. In addition, the source is sought to have low energy consumption; therefore, the selection of the light source (UV-Vis-NIR) must be adjusted to the geometry of the reactor and the optical properties required by the catalyst.^{73,93,101} LEDs are the most widely used light sources because they meet the spectral requirements, offer high efficiency, and consume little energy. An environmentally friendly alternative could be the use of solar concentrators.^{73,101,102} One of the parameters to be considered is the heat that can be generated in this type of reactor; for this reason, it is of utmost importance to maintain thermal control during the process to avoid hot spots and keep the catalyst stable. However, the photothermal effects generated can be exploited if they are controlled, in order to accelerate the chemical reaction, especially in plasmonic systems.⁶⁴ One strategy for maintaining thermal control in the system is to include cooling, heat sinks, heating jackets, or optical and thermal sensors to maintain control throughout the process and enable reproducibility.¹⁰³

Recently, the trend in photoreactors points toward intelligent systems with automated control, *in situ* monitoring of



internal processes, and measurements using characterization techniques, allowing real-time parameter adjustments.^{104–108} Advances in photoreactors are promising for working in tandem with mechanochemistry, generating a hybrid system in which the synergy of mechanical energy and light would be used.

3.3. Engineering integration of light in mechanochemical systems

The main challenge of light-assisted mechanochemistry lies in designing equipment that ensures efficient photon delivery to the dynamic solid interface while maintaining control over mechanical stress and generated temperature. The following figure shows the proposed designs for light-assisted mechanochemistry.

An important element is the design of light-assisted mechanochemistry models. For example: (a) an agate mortar with direct illumination. This is a straightforward configuration where light is irradiated directly during the grinding process. This process is very artisanal yet efficient, dosing the light and improving grinding times.¹³ (b) Batch mills (mixer/planetary) with integrated illumination. Ball or planetary mills can be modified to irradiate the vials with different light sources, such as lamps, LED rings, laser diodes, or optical fibers. However, it is essential to keep in mind that the jars must be transparent to allow light to pass through, without neglecting their mechanical properties. For this reason, it is a

challenge to search for materials that meet these characteristics, where quartz, sapphire, borosilicate and PMMA are positioned to be used because it is reported that they have been used under low to medium energy conditions and with moderation in frequency and amplitude, in addition to using small balls, giving priority to *in situ* synthesis due to the sound optical transmission that these materials present, allowing UV-Vis irradiation from different sources.^{42,109–111} Another option is to make optical inserts in metallic jars to improve mechanical resistance and optical access. For this, the design is crucial for optimizing the thickness and shape of the appropriate windows, where simulation is essential to improve the efficiency. Additionally, quartz and sapphire are considered the best options for this type of jar.^{12,112} Table 1 shows the advantages and limitations of the different materials that can be used as jars in the light-assisted mechanochemistry process. Another important part of the design is selecting the material for the balls in the mills. Chemical compatibility is sought without neglecting the hardness, which is of utmost importance for grinding, and to avoid contamination and wear. Among the possible materials to be used as balls are zirconia (ZrO₂) and alumina (Al₂O₃) because they are stable ceramics, with high hardness and low contamination, used in the synthesis of nanoparticles.^{27,90,113,114} Stainless steel is also used as balls because it is economical and has high mechanical and corrosion resistance. However, in the long term, contamination by Fe, Cr, or Ni can occur.^{90,115} WC (tungsten

Table 1 Advantages and limitations of jar materials used in light-assisted mechanochemistry

Jar material	Advantages	Limitations	Applications	Ref.
Quartz (crystalline SiO ₂)	<ul style="list-style-type: none"> • High UV-Vis transmittance (200 to 800 nm) • Chemically inert • No autofluorescence 	<ul style="list-style-type: none"> • Brittle under high impacts • Expensive • Difficult to manufacture in complex geometries 	<ul style="list-style-type: none"> • Photo-mechanochemistry; hybrid photoreactors • UV-C/UV-A photocatalysis 	111
Sapphire (Al ₂ O ₃)	<ul style="list-style-type: none"> • Ideal for UV radiation • High hardness and mechanical strength • High UV-Vis-NIR transmittance • Suitable for <i>in situ</i> Raman measurements • Good thermal conductivity 	<ul style="list-style-type: none"> • Used for low-energy milling • Very expensive • Difficult to manufacture in complex geometries • It emits its own Raman bands • It is more commonly used as an optical window than as a complete jar 	<ul style="list-style-type: none"> • Used for <i>in situ</i> Raman or fluorescence measurements • Reactors with high-energy and high-pressure environments 	125 and 126
Borosilicate glass	<ul style="list-style-type: none"> • Economical • Chemically inert • High visible and UV-A (365 nm) transmittance. • Easy to seal and handle. • Compatible with different grinding configurations 	<ul style="list-style-type: none"> • Low UV-C transmittance • Possible leaching during prolonged aging • Less complex than sapphire or quartz. 	<ul style="list-style-type: none"> • Aging processes under visible or UV-A illumination • Vortex or RAM configuration 	111 and 127
PMMA	<ul style="list-style-type: none"> • High transmittance in visible and UV-A (365 nm) • Cost-effective • Light weight and easy to fabricate for complex geometries • Allows <i>in situ</i> Raman or photoluminescence monitoring 	<ul style="list-style-type: none"> • Blocks UV-C • Solvent-sensitive • Prone to scratching • It emits its own Raman bands 	<ul style="list-style-type: none"> • <i>In situ</i> milling with Raman or photoluminescence monitoring 	23, 110 and 128



carbide) has high hardness and minimizes the risk of contamination, but this material is expensive and presents risks of damaging the jar.^{90,115,116} Agate or PTFE (Teflon) balls are low in contamination and ideal for delicate chemical synthesis, but they offer lower energy transfer.^{117,118} In general, depending on the synthesis to be performed, it is recommended to look for the optimal materials for both the jars and the balls used in the grinding process. (c) Continuous extrusion with integrated lighting. One of the most promising processes is twin-screw extrusion because it allows continuous feeding and control during the process (kneading, photoreaction, retting zones). Radiation sources can be adapted with different modules, such as windows where the outside is irradiated with LEDs (UV-Vis), internal reflectors to unify the photon flow, or optical fibers located along the channel. Furthermore, according to the literature, the twin-screw extruder presents excellent viability to take this process to large scales,^{24,25} where flow mechanochemistry tests (Resonant Acoustic Mixing) confirm the potential it presents as light-assisted mechanochemistry.¹⁵

However, a significant limitation within the photo-mechanochemical process is light penetration into dense, opaque solid mixtures. The main problem is that light absorption in the material is not uniform, being limited to the absorption of photons in a homogeneous way. To overcome this problem, it is crucial to consider that when the surface renewal rate (determined by shear and mixing efficiency) is lower than the local rate of photon absorption, the process is limited by the mixing, resulting in incomplete material activation. Conversely, uniform photoactivation can be achieved when the surface renewal rate increases.^{119,120} Consequently, the reactor design must ensure coupling between mechanical mixing and photon supply, either by designing and installing different zones in the process, each irradiated with internal reflectors, by integrating optical fibers, or by using segmented regions to achieve greater light distribution and uniform, homogeneous reactions.

When adequate control is achieved in the hybrid reactor process, the synergy between mechanical force, light, and the generated heat has given rise to a new process capable of operating under conditions outside of thermodynamic equilibrium. This reactor allows controlled access to the photo-tribothermal zone, where materials are synthesized. The formation of metastable phases increases atomic diffusion, and the reduction of kinetic barriers is also possible through coupled systems, such as the combination of mechanical impact, controlled photoexcitation, and heat generation management.^{15,115,121}

3.3.1. Key parameters and process control. Light-assisted mechanochemistry requires the control of different parameters because in this type of hybrid system, mechanical, photonic, and thermal energy act simultaneously, generating a synergy during the process. For this reason, it is of utmost importance to maintain a balance between these parameters to improve efficiency, selectivity, and stability. This multiphysics interaction has been studied in hybrid catalytic and photochemical systems, where the reaction reactivity and equilibrium are

associated with the energy inputs that interact with the material.^{121–123} This type of reactor requires control over stress distribution, photon flux, and the generated thermal energy. Critical parameters are photon flux and mechanical energy. Low illumination limits photoactivity, while high irradiation causes overheating or other undesirable effects. Having an optimal photon flux frequency improves the generation of electron–hole pairs.^{102,124}

Another parameter to consider is thermal control, as friction and the incidence of light can lead to temperatures that affect the system's reproducibility and stability. For this reason, it is important to plan various strategies to avoid this, such as pulsed illumination, active cooling, heat-dissipating or heat-conducting housings to help uniform heating and avoid hotspots.^{6,129} In the case of continuous processes such as twin-screw extrusion, simulation plays a crucial role in process optimization, allowing the modelling of radiation exposure and the stresses to which the material will be subjected.^{130,131} In general, these reactors must be monitored and automated with the help of sensors to facilitate the adjustment of optimal parameters within the system, such as the appropriate wavelength for irradiation, rotation speed, and the amount of operating time, among others, and thus make the process more efficient and intelligent.^{132,133} Control of these systems is essential for them to be operated at an industrial level. A multiphysical and integrated vision is required to control the different parameters (light, mechanical force, heat) and maintain conditions outside of thermodynamic equilibrium that are efficient, stable, and sustainable.

Fig. 2 shows the schematic of the different light-assisted mechanochemistry processes, indicating the differences in control and scalability available in each. This figure shows the progression of reactor engineering, from manual grinding to ball mills or extruders. Manual grinding is the process with the most limitations, due to a lack of control over the grinding process, making it a very artisanal system, exclusively for laboratories. Mills (rod mills, planetary ball mills, and mixing ball mills) are presented as the transition from those systems that can be used both in the laboratory and are promising for industrial use. Ball mills offer greater advantages due to the control of process parameters and the reproducibility that can be achieved by allowing larger volumes to be processed. On the other hand, continuous extrusion is the most promising process since the volumes of material typically worked are larger than those in mills. Furthermore, parameter control is more precise, and this system can improve its efficiency in the photoactivation process by adapting different modules along the channel, better distributing light irradiation, or, if necessary, placing cooling systems or internal reflectors to improve the synergy between mechanical energy, irradiation, and generated heat, thus improving the process efficiency and making it more sustainable. The proposal to position extrusion as the most promising process to take this to an industrial level is based on recent reports that show that continuous line grinding processes offer greater control over torque, process time, specific mechanical energy (SME), among others, and greater



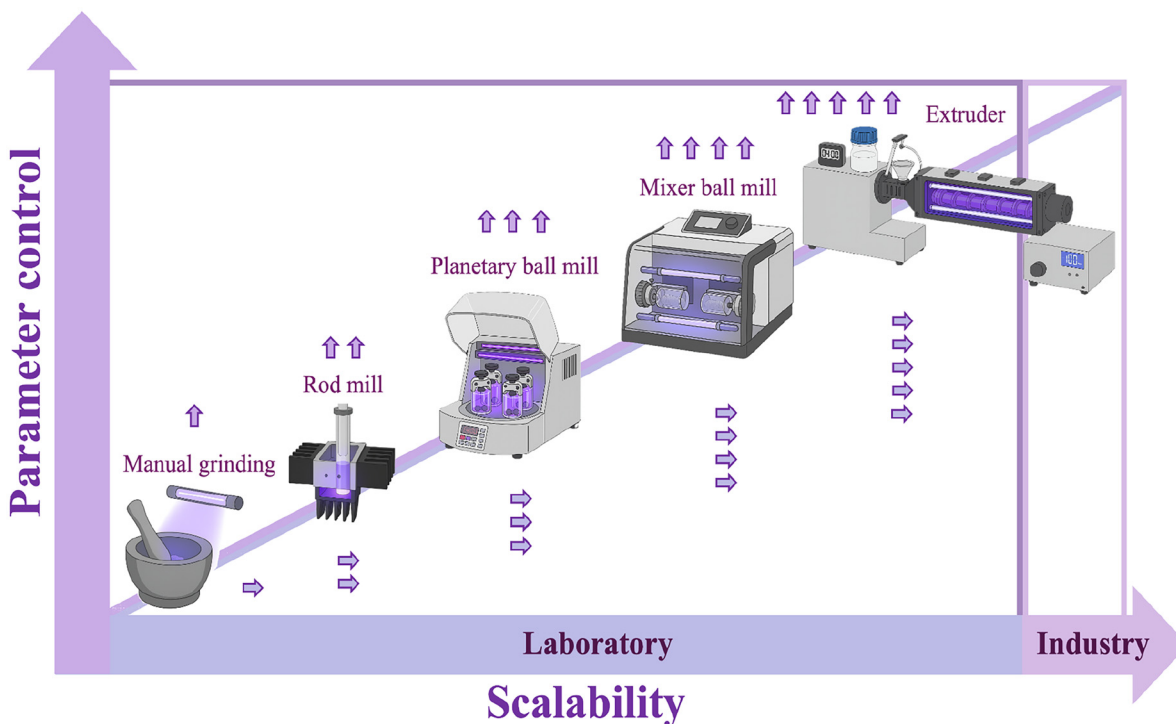


Fig. 2 Schematic of different light-assisted mechanochemical processes (can be any UV-Vis-NIR spectrum), illustrating the evolution and integration of mechanical, photonic, and thermal control from manual grinding to continuous extrusion, where extrusion is shown as the most promising process to reach industrial scales.

reproducibility.^{25,121} The transition from the laboratory-level to the industrial scale is well underway and growing significantly. These reactors hold great promise for materials synthesis and pose a significant engineering challenge. However, conceptually, what we consider scale-up should be associated with the required volume of the final product. Therefore, if small quantities of a component (*e.g.*, an active pharmaceutical ingredient) are sufficient for it to be considered a marketable product, batch-type systems such as ball mills can still be relevant at the industrial level.

3.3.2. Scale-up pathways. The transition from all laboratory processes to the industrial scale is usually gradual, and light-assisted mechanochemistry is no exception. Semi-continuous ball mills can be used as a starting point; however, this process presents some limitations regarding the volume required at the industrial level, as well as the thermal control and photonic distribution needed. As aforementioned, extruders are positioned as an alternative to carry out this process on a large scale due to their advantages, such as continuous feeding, management of the operating time, and cooling modules if necessary.^{24,25} Despite the advantages that extruders provide in a hybrid system where light irradiation plays a fundamental role, this presents an important challenge: materials with high optical transparency are sought for constructing the reactor. On the other hand, the high volumes required in many industrial applications can lead to light scattering and absorption limitations. To solve this problem, it is

proposed to section the reactor with different irradiation zones using windows made of materials such as quartz or sapphire that present high UV-Vis transmittance. In addition, it can be adapted to place optical fiber and internal reflectors to improve the lighting inside the channel, maintaining uniformity throughout the process.^{112,121} In continuous photoreactors, especially photocatalytic flow systems, the reactor performance is determined by the interaction between the flow rate, irradiation time, and light penetration into the reaction medium.¹³⁴ Unlike purely thermal flow systems, where heat transfer is typically more uniform and governed by temperature gradients, photon transport is inherently spatially heterogeneous and strongly influenced by the medium's optical properties, including absorption and scattering.^{135,136} As a result, the effective irradiation experienced by the catalyst is determined not only by the residence time, but also by the local photon flux distribution and light penetration depth.^{68,137} These factors directly affect the rate of photon absorption, which plays a key role in determining the reaction kinetics, selectivity, and efficiency.⁴⁴ Therefore, optimizing photocatalytic flow systems requires an integrated understanding of hydrodynamics and radiative transfer phenomena, rather than treating residence time as an isolated parameter.^{135–137}

One of the most significant aspects of interest to the industry is energy efficiency. For this reason, these types of reactors, which combine mechanical energy with light energy, facilitate the heating process, thus avoiding the need for an external



source to generate heat. Heating is generated by the friction of the material, which is enhanced by continuous light irradiation.^{15,138} The potential scalability of this light-assisted mechanochemistry process will depend on integrating automation to control all parameters, creating predictive digital models, and conducting on-site monitoring. If this is achieved, hybrid reactors could become continuous, modular systems with high energy efficiency, excellent for the sustainable production of polymers, catalysts, and functional materials.¹⁷

The procedure is, strictly speaking, complex. As deduced from the previous comments, the scale-up of the light-assisted mechanochemistry process cannot be approached as a simple superposition of mechanochemistry, photochemistry, and classical reactor engineering. Instead, it must be framed as a fundamentally coupled multiphysical problem in which mechanical energy input, photon transport, and reaction kinetics are intrinsically interdependent. This conceptual shift is essential for developing a rigorous and predictive framework suitable for industrial translation. Fig. 3 schematically illustrates how this phenomenon could be addressed, taking into account the knowledge of mechanochemical and photochemical processes separately. Although we return to the idea of extrusion-based schemes as conceptually more scalable, the approach is in fact transferable to the scale-up of other in-bath photo-mechanochemical systems that may be developed in ball mills with different configurations.

In the mechanochemical domain (described in Fig. 3 as “Mechanochemical energy input and mixing dynamics”), the reacting medium is best described as a dense, dynamically evolving granular phase subjected to controlled shear, com-

pression, and mixing. Unlike static or well-mixed fluid systems, the material experiences spatially heterogeneous stress fields and a distribution of residence times rather than a single characteristic value. Classical scale-up parameters, including specific mechanical energy, torque, screw speed, and fill ratio, remain relevant but require reinterpretation in a mechanochemical context.¹³⁹ Specifically, the role of specific mechanical energy extends beyond thermal effects to include direct activation of chemical transformations *via* localized stress events. Consequently, the relevant scaling criterion is not solely the preservation of macroscopic parameters, but rather the maintenance of the statistical distribution of effective mechanochemical events, such as interparticle collisions and shear-induced contact formation, which ultimately govern reactivity.

The introduction of light (defined in Fig. 3 as Photonic activation and light-matter interaction) into such systems represents a major conceptual and practical bottleneck. In conventional photocatalysis, photon transport can often be approximated using simplified radiative transfer models under steady-state conditions, with relatively well-defined optical paths and absorption profiles.^{68,74,119,136} In contrast, as schematically described in Fig. 3, photo-mechanochemical systems involve highly scattering, opaque, and continuously evolving media, where particle motion, aggregation, and the presence of macroscopic elements such as milling media or screw components disrupt any static description of the radiation field. As a result, the notion of a fixed spatial absorption profile becomes inadequate. Instead, photon transport could be treated as a time-dependent, stochastic process, where the rele-

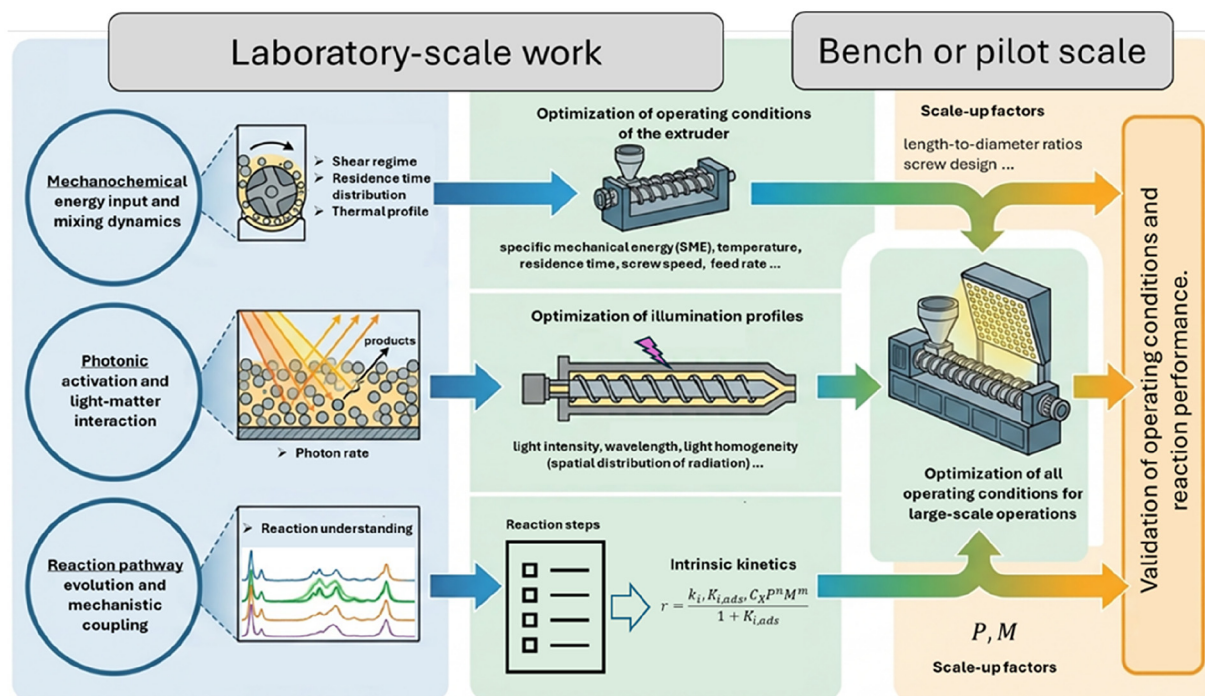


Fig. 3 Schematic representation of the proposed scale-up strategy for photo-mechanochemical reactors.



vant quantity is not the instantaneous local intensity, but the statistical distribution of photon exposure experienced by individual particles over their residence time within the reactor.

This photonic environment would be describing the probability distribution of photon rate, which inherently incorporates the effects of mixing, motion and light scattering. Such a framework naturally couples with the residence time distribution and the dynamics of the granular flow. Experimentally, direct measurement of these quantities is challenging, but indirect strategies, such as photoresponsive probe species embedded within the reacting mixture, may provide access to effective photon exposure metrics.^{140,141} From a modelling standpoint, the integration of discrete element methods with radiative transfer simulations, for example *via* Monte Carlo approaches,^{142,143} offers a promising route to capture the interplay between particle dynamics and photon transport in these complex environments.

The definition and determination of intrinsic kinetics in photo-mechanochemical systems represent an equally critical challenge. In classical heterogeneous catalysis, intrinsic kinetics are defined under conditions free of mass and heat transfer limitations, typically relying on well-defined active sites and steady-state conditions.⁴⁴ However, in mechanochemical environments, reactive sites are continuously generated, modified, and annihilated through mechanical action, and local conditions such as temperature and pressure may fluctuate significantly at the microscale. Furthermore, the activation energy of a given transformation may include contributions from mechanical stress and photon absorption, rendering it inherently state-dependent. As such, intrinsic kinetics in this context must be redefined as a function not only of chemical composition and temperature, but also of the mechanical state of the material, including mechanochemical and optical related parameters. This must be accompanied by a rigorous analysis of the reaction mechanism (described in Fig. 3 as: reaction pathway evolution and mechanistic coupling). In this regard, several studies have developed relevant *in situ* analyses to carry out this task.^{17,23,40,125,128} Experimentally accessing such intrinsic kinetics requires the development of simplified model systems in which individual contributions can be decoupled. By systematically varying the mechanical energy-related parameter (defined in Fig. 3 as M) and the photon absorption-related parameter (defined in Fig. 3 as P), it becomes possible to construct effective kinetic models that incorporate these additional degrees of freedom. Importantly, the concept of diffusion limitation must also be reconsidered.

Building on these considerations, a generalized framework for scale-up can be proposed in which the overall reaction rate is expressed as a function of mechanical energy input, residence time distribution, photon exposure statistics, and intrinsic kinetics defined under mechanochemically relevant conditions. In practical terms, as described in the scheme of Fig. 3, scale-up would involve, first, the preservation of key mechanical parameters in the extrusion process to ensure comparable granular dynamics; second, the design of illumination systems capable of reproducing equivalent photon

exposure distributions at larger scales; and third, the validation of reactor performance through metrics that account for both mechanical and photonic energy inputs. Such an approach moves beyond traditional reactor design strategies and emphasizes the need for integrated optimization across multiple physical domains. Of course, all this work must provide an economically feasible design alternative, and final validation tasks must be carried out to ensure proper operation under the selected operating conditions and the desired reaction performance.

3.3.3. Case studies and applications. Over the years, different prototypes of hybrid reactors (photochemistry and mechanochemistry) have been reported. One of the first studies to report the use of mechanical energy alongside light irradiation is by Gracin *et al.* in 2014, who observed structural changes during the milling process through *in situ* characterization by X-ray diffraction (XRD) using PMMA milling jars.¹²⁸ A few years later, in 2016, Obst and König developed a method for solvent-free photocatalytic conversion using a rod mill with external irradiation from LEDs at a wavelength of 455 nm, where blue light served the dual function of heating the mixture and exciting the photocatalyst.⁸⁷ In 2017, Hernández *et al.* achieved photonic activation during the mechanochemical process by using a ball mixer mill with PMMA milling jars illuminated by a strip of blue and green LEDs, which was rolled onto the milling jars. This arrangement contributed to the experimental temperature increase, facilitating the formation of molten reaction mixtures.¹³⁸ In 2023, Baier *et al.* used a ball mixer mill with a quartz milling jar and polytetrafluoroethylene (PTFE) lids irradiated with UV-C LEDs (272 nm) placed around the mill covered with a reflective aluminum chamber, with this they demonstrated UV photoactivation synthesis of nanographene by a solid and sustainable route with yields greater than 90%;¹² this work corroborated the efficiency of light-assisted mechanochemistry. In 2024 and 2025, Millward *et al.* performed light-assisted mechanochemistry in ball mixer mills using PMMA or polypropylene milling jars and a blue LED radiation source (456 nm), obtaining photocatalytic and metallo-photoredox reactions.^{10,144} Also in 2025, Zgrablić *et al.* designed a system for *in situ* monitoring by Raman spectroscopy inside a ball mixer mill and sapphire-windowed aluminum milling jars using stainless steel balls. This work provides a breakthrough in the monitoring and control of the mechanochemical process.¹²⁶ It is worth noting that most of these reported systems rely on molecular photocatalysts, while the implementation of semiconductor-based photocatalysts in such setups remains comparatively less explored. In any case, these investigations consolidate the positive impact of these types of processes, laying the groundwork for the industrial transition to light-assisted mechanochemistry.

Table 2 and Fig. 4 complement the engineering progress and developments in light-assisted mechanochemistry reported in the literature over the past decade. Table 2 compares different reactors with different light sources, reactions, and applications. Fig. 4 shows the chronological progression



Table 2 Experimentally demonstrated photo-mechanochemical systems

Equipment used for mechanochemistry	Light source, λ (nm)	Material synthesis or main reaction	Application or purpose	Ref.
Rod mill	Blue LEDs ~450 nm	Oxidation of benzyl alcohols with riboflavin tetraacetate	Solvent-free organic photo-oxidation	110
Ball mixing mill	Blue LEDs ~460 to 465 nm	Oxidation of diphenylacetylene	Benzyl production <i>via</i> mechanochemically assisted solid-state photocatalysis	77
Ball mixing mill	Visible lamp (green ~520 nm)	Borylation of aryldiazonium salts with eosin Y	Solid-catalyzed photoborylation	138
Ball mixing mill	UV-C LEDs ~272 nm with an Al reflective chamber	Synthesis of nanographene by UV photoactivation	Solid and sustainable formation of nanocarbons >90%	12
Modified ball mixer mill	Visible LEDs ~450 to 530 nm	Chlorosulfonylation, pinacol, [2 + 2] chalcone cyclization	Solvent-free mechanophotocatalysis	144
Vibrating mill with NIR dye-doped resin jar	NIR diode ~850 nm	Diels-Alder and the Sydona rearrangement	Controlled photothermal heating in mechanoreactions	145
Resodyn LabRAM II Acoustic Mixer	Blue LEDs ~450 to 470 nm	Solid-state photocatalytic C-X couplings	Sustainable photo-mechanochemical reactions	15
Modified ball mixer mill	Blue LEDs ~450 nm and green LEDs ~520 nm	Ni/photocatalytic C(sp ²)-C(sp ³) aminations and couplings	Solvent-free mechanophotocatalysis	10
Ball mill mixer with <i>in situ</i> Raman monitoring	UV-Vis LEDs ~348 to 440 nm and a Raman laser	Photoisomerization of azobenzenes and photolysis of diazirines	Development of a reactor with <i>in situ</i> photomechanochemical monitoring	146

of these reactors, with a clear trend toward more complex equipment for better control, scalability, and reproducibility. According to the research (cited in Fig. 4 and Table 2), the first reactors shown were mills with adaptations of various light sources (visible LEDs or UV), innovating with a new synthesis route. Although initially some experiments lacked much control over the process, over time, the systems evolved toward configurations that allow for greater mechanical, optical, and thermal control using materials with specific characteristics (PMMA, quartz, sapphire, *etc.*) and different equipment arrangements such as refractive modules that allow for uniform irradiation and *in situ* monitoring of some characterization techniques such as Raman spectroscopy. This progress shows that it is not only about photoactivation in the material *via* light irradiation, but also about functional engineering, where the goal is to modulate the photon and phonon fluxes in addition to controlling stress gradients. In summary, Table 2 and Fig. 4 reaffirm the progress of these reactors at the laboratory level, with the aspiration for an industrial transition, and offer promising prospects given the reactor designs already reported, which operate with high energy efficiency, a low environmental footprint, and good synthesis results. However, the major challenge remains transferring these laboratory prototypes into automated systems, where, with the help of simulation and continuous research-driven improvements, greater efficiency and reproducibility can be ensured to reach industrial levels.

As mentioned in previous sections, the evolution toward continuous processes presents greater potential for scaling up light-assisted mechanochemistry to an industrial scale. In 2024, Gugin *et al.* performed *in situ* energy-dispersive X-ray diffraction monitoring inside an extruder.¹⁷ This research is very innovative and opens the possibility of developing automated light-assisted mechanochemical processes to have

control over all parameters. Unlike mill processes, extruders are the most viable option for making the transition from laboratory to industrial scales.^{147,148} They offer a uniform stress distribution, and with the background, a uniform and controlled photonic flow is possible. In addition, operating times can be reduced without neglecting reproducibility and sustainability for the synthesis of different materials.

3.4. Sustainability considerations

From a sustainability perspective, photo-mechanochemical processes can leverage established green chemistry metrics, such as the *E*-factor, Process Mass Intensity (PMI), and energy intensity. In conventional photocatalytic processes, the *E*-factor is typically dominated by solvent use and post-purification steps, thereby significantly increasing waste generation.^{115,149,150} On the other hand, mechanochemical processes inherently reduce solvent use, thereby lowering the *E*-factor, especially under dry milling conditions or with minimal liquid assistance.^{5,115,151} However, this advantage requires further study and analysis due to the energy consumption associated with mechanical milling and light irradiation where the total energy intensity (kWh kg⁻¹) in photo-mechanochemical systems can be expressed as the sum of mechanical energy input (milling or extrusion power and residence time) and photonic energy input (light source power and irradiation time). Consequently, the use of high-energy grinding or inefficient light sources may offset the environmental benefits of solvent reduction.^{115,149}

Furthermore, another factor to consider is contamination that can be generated in the waste due to wear and tear on the containers, balls, or screws used in the mechanochemical process. Therefore, additional purification is required depending on the material to be obtained and the intended application. For this reason, although the use of solvents is effec-



throughout the entire process by minimizing solvent use while simultaneously optimizing the energy efficiency.^{115,149,150}

Importantly, advancing the sustainability assessment of photo-mechanochemical systems will require the development of more intrinsic efficiency descriptors. In photocatalysis, the quantum efficiency provides a fundamental metric by relating the rate of product formation to the rate of photon absorption,⁶⁸ the latter being strongly dependent on the illumination efficiency and reactor configuration.^{153,154} An analogous framework is needed for photo-mechanochemical processes, where both photon absorption and mechanical energy input are coupled.

Future efforts should therefore focus on defining metrics that relate product formation rates to the combined energy inputs, enabling a more rigorous evaluation of how efficiently the light intensity and mechanical energy are translated into chemical transformation. This would allow identification of optimal operating windows and avoid scenarios where increasing light intensity or mechanical energy input leads to diminishing returns in process efficiency. The development and adoption of such “green metrics” for mechanochemical and photo-mechanochemical processes¹¹⁵ will be essential to properly position these technologies in terms of sustainability. Ultimately, while photo-mechanochemistry holds strong potential for low-waste synthesis and reduced energy consumption, achieving true sustainability will depend on balancing solvent minimization with optimized energy efficiency and reactor performance.

4. Outlook and future directions

The transition from empirical mechanochemical activation toward engineered light-assisted systems will depend critically on the development of robust multiphysics models capable of describing the coupled mechanical, optical, and thermal phenomena that occur during milling and extrusion. In conventional mechanochemistry, energy input is dominated by impact and shear events, which generate localized temperature spikes and high-pressure zones at the contact interfaces. When illumination is introduced, additional photon-driven excitation pathways emerge, leading to local electronic transitions, photothermal effects, and, in certain cases, photocatalytic charge transfer at dynamically formed interfaces. Capturing the synergy between these effects requires a unified modelling framework that treats mechanical, thermal, and photonic energy transport on comparable spatial and temporal scales.

A critical aspect of photo-mechanochemical systems is the matching of timescales, between photophysical and mechanically promoted processes. Typically, photogenerated excited states and reactive intermediates exhibit short lifetimes, which must be considered when it comes to mechanochemical environments, including millers or extruders, where heat and mass transfer dynamics could significantly influence the overall reaction outcome.

A key step toward this goal involves the numerical solution of the Radiative Transfer Equation (RTE) within the dynamically evolving geometry of a milling or extrusion chamber.^{14,22,74} Coupling Computational Fluid Dynamics (CFD),^{155–157} or Discrete Element Method (DEM) models¹⁵⁸ with ray-tracing or Monte Carlo solutions of the RTE will allow accurate estimation of local photon flux distributions and Local Rate of Photon Absorption (LSRPA) profiles.^{74,159–162} These profiles can then be correlated with the frictional heating patterns obtained from DEM–CFD simulations, providing a spatially resolved picture of how photon absorption and mechanically induced thermal gradients co-exist or overlap. In any case, these efforts have not yet been developed within a comprehensive framework that integrates light–matter interaction modelling with the full set (DEM, CFD, *etc.*) of physico-chemical processes occurring under mechanochemical conditions.

The superposition of both fields defines a new operational regime, photo-(thermo-mechanochemical), where light and friction act as co-drivers of chemical transformation. Such integrated models will enable exploration of analogies with autothermal or thermo-photocatalytic processes,⁷³ where exothermic surface reactions sustain local temperature fields that feed back into reaction kinetics. In the context of light-assisted mechanochemistry, impact-induced hotspots could play a similar role,^{163,164} creating transient thermal gradients that modulate light absorption and scattering within the reacting medium. Conversely, photo-induced heating and carrier excitation may influence the viscoelastic behaviour and tribochemical response of the material, closing a feedback loop between optical, mechanical, and thermal domains.¹⁶⁵ Mapping these interactions in space and time could clarify how mechanical stress and illumination jointly define non-equilibrium conditions conducive to new reaction pathways or metastable phase formation.

The implementation of digital twins for light-assisted mechanochemical reactors could provide a powerful platform to achieve this objective, as already demonstrated for other systems such as catalytic reforming processes.¹⁶⁶ By integrating experimental diagnostics (*e.g.*, *in situ* pyrometry, optical sensors, acoustic monitoring) with predictive CFD/DEM/RTE simulations, it will be possible to continuously update virtual replicas that mirror the real reactor state. These digital environments would allow the testing of illumination geometries, mechanical frequencies, and reactor materials prior to physical implementation, accelerating optimization cycles and improving the process reproducibility.

Furthermore, AI-driven optimization frameworks can be employed to explore the multidimensional parameter space inherent to coupled mechanical/photonic systems. By correlating operating variables (rotation speed, ball-to-powder ratio, light wavelength, pulse modulation, feed rate, torque) with measurable outcomes (conversion, crystallinity, selectivity, morphology), machine learning models could identify optimal regions where mechanical and optical energy inputs are synergistically balanced. Such frameworks have shown promising



results in mechanochemical systems and photocatalytic processes.^{35,167–169}

As described in this contribution, continuous light-assisted extrusion could unlock new strategies for producing sustainable catalysts or developing a wide range of reactions, with minimized solvent use and reduced energy footprints.^{14,36} From a circular economy perspective, integrating these hybrid reactors into plastic-to-catalyst or waste-to-energy valorization schemes could bring us closer to near-zero-waste manufacturing chains.^{170–172} To ensure responsible deployment, Life Cycle Assessment (LCA) and exergy analysis should accompany future developments, quantifying the environmental and energetic gains relative to conventional synthesis routes.^{173–175}

In summary, the next generation of light-assisted mechanochemical reactors will emerge from the fusion of modelling, data-driven control, and scalable reactor design. By resolving the complex interplay between light–matter interactions and friction-induced effects, researchers should be able to advance from empirical optimization toward a predictive, physics-based understanding of photo-mechanochemical reaction mechanisms.

5. Conclusions

The photo-mechanochemical processes emerge from a highly complex interplay between light–matter interactions, force-driven bond activation, and friction-induced physical effects. Despite recent progress, a predictive understanding remains limited, and advancing the field will require deeper mechanistic insight supported by modelling approaches capable of capturing the coupled optical, mechanical, and thermal phenomena involved. In this regard, *in situ* and operando methodologies should play a central role, enabling direct observation of transient states and reaction pathways that are otherwise inaccessible.

From an applications perspective, many questions remain open; however, the growing number of publications in recent years clearly indicates both the scientific potential and the possibility that certain reaction mechanisms may only emerge under the combined action of mechanical forces and light. Pathways toward scalable implementations will likely diverge depending on the targeted application: continuous extrusion-based systems may be required for high-volume production, whereas irradiated milling platforms could remain highly valuable for synthesizing small quantities of high-value materials, *e.g.* active pharmaceutical ingredients. Coupling these processes with sunlight remains challenging, and current evidence suggests that selective and energy-efficient irradiation sources, such as LEDs or lasers, will be more viable for controlled photo-mechanochemical processing.

Conflicts of interest

The authors declare no conflict of interest.

Data availability

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

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