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The research progress on recycling and resource utilization of waste crystalline silicon photovoltaic modules

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A B S T R A C T

The exponential growth in global photovoltaic installations has led to a continuous increase in photovoltaic (PV) waste. This review article focuses on the recycling of waste crystalline silicon PV modules. In terms of recycling management policies, it points out that China's management of waste PV modules started relatively late and lacks clear categorization. Despite the establishment of relevant standards and extended producer responsibility (EPR) systems, there is still a need for improvement in the recycling system. The review delves into recycling technologies such as pyrolysis, chemical treatment, and mechanical crushing for waste PV modules. It particularly emphasizes the high-pressure crushing recycling process, highlighting its effective dissociation and crushing based on environmental friendliness. Comparative environmental impact analysis shows that pyrolysis technology has the least environmental impact, followed by mechanical treatment, while chemical treatment, incineration, and landfilling have relatively larger environmental impacts. Therefore, the review advocates for pyrolysis treatment as the mainstream technology for the recycling of waste PV modules. Finally, the article discusses the challenges faced by PV module recycling in China and proposes recommendations for the formulation of reasonable subsidy policies and dynamic adjustment of standards. In conclusion, this review provides in-depth research and comprehensive analysis of the recycling and resource utilization of waste crystalline silicon photovoltaic modules, offering important references and guidance for future development.

1. Introduction

As a crucial component of renewable energy, photovoltaic (PV) power generation technology has rapidly emerged in the energy sector in recent years. In comparison to traditional fossil fuels, PV technology not only exhibits significant advantages in energy production [1] but also holds crucial significance for environmental conservation. However, with the exponential growth in global PV installations, the quantity of PV waste is steadily rising [2,3]. The typical lifespan of PV modules is approximately 25 years [4,5]. Predictions suggest that by 2050, the global market will generate an estimated 60 to 78 million tons of waste PV [6]. Concerningly, only about 10% of waste PV modules worldwide are currently recycled and reused, with the majority being abandoned or landfilled. This disposal method may lead to the infiltration of hazardous substances, such as lead and cadmium, into the ground, posing potential threats to ecosystems and human health [7]. Moreover, waste PV modules contain renewable resources like glass, plastic, copper, aluminum, silicon, and silver. Complete recovery of metal components from PV modules can generate approximately $72 in value for every 100 kg of modules [8]. Furthermore, reusing high-purity intact silicon wafers in battery manufacturing could potentially save manufacturers over 20% in production costs [9]. Therefore, the regulation of recycling and reuse for these materials serves a dual purpose by both alleviating environmental risks and fostering economic value creation [10].

With the rapid development of photovoltaic technology, its evolutionary journey primarily encompasses three generations of technology: the first generation being crystalline silicon cells, the second generation comprising thin-film cells, and the third generation presenting novel cell technologies. Currently, crystalline silicon PV cells dominate the market with a market share of approximately 95% [11]. Their significant advantages in terms of cost, lifespan, and relatively high efficiency have led to an increasing volume of discarded cells, emphasizing the urgent need for resourceful recycling management.

To effectively address the management challenges of waste PV modules, some countries have begun formulating and implementing relevant recycling management policies. For instance, the European Union (EU) took the lead in issuing waste electronic regulations specifically for the collection, recycling, and recovery of PV modules, known as the Waste Electrical and Electronic Equipment (WEEE)

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Nomenclature

Abbreviations and acronyms

PV	Photovoltaic
EPR	Extended Producer Responsibility
EU	European Union
WEEE	Waste Electrical and Electronic Equipment
EVA	Ethylene Vinyl Acetate
PVDF	Polyvinylidene Fluoride
PET	Polyethylene Terephthalate
TCLP	Toxic Characteristic Leaching Procedure
LCA	Life Cycle Assessment
EHF	Electro-Hydraulic Fragmentation

Symbols

Ag	Silver
Al	Aluminum
Cu	Copper
Si	Silicon
Pb	Lead
Cd	Cadmium
Sn	Tin
DMPU	$C_6H_{12}N_2O$
DBE	$C_{21}H_{36}O_{12}$
EGDA	$C_6H_8O_4$
HNO_3	Nitric Acid
NaOH	Sodium Hydroxide
H_2SO_4	Sulfuric Acid
CH_3COOH	Acetic Acid
NaCl	Sodium Chloride
H_2O_2	Hydrogen Peroxide
HF	Hydrofluoric Acid
KOH	Potassium Hydroxide
H_3PO_4	Phosphoric Acid

Directive [12,13]. This directive mandates that manufacturers or importers of PV modules, when supplying them to the EU market, bear the responsibility and cost of collecting and recycling waste PV modules, incorporating them into the category of WEEE management [14]. China also implemented the 'General technology requirements for photovoltaic module recycling and recovery' starting from February 1, 2022. This comprehensive regulation manages the whole life cycle of waste PV modules, covering collection, transportation, storage, disassembly, disposal, and recycling. It establishes standards for recycling rates and purity of recovered materials [15].

However, technical challenges persist in the process of addressing the recycling and disposal of waste crystalline silicon PV modules. Numerous scholars have conducted extensive research, exploring methods such as pyrolysis, chemical treatment, and mechanical processing for recycling. Comparing and analyzing these methods aids in determining the optimal green recycling path for PV modules. Furthermore, some studies emphasize exploring the environmental impact of the whole life cycle of waste PV modules, often assessing indicators such as human toxicity potential, terrestrial ecotoxicity potential, and carbon emissions. In summary, the primary technical obstacles faced in the recycling of waste PV modules [16] include the removal of fluoropolymer back sheets, the treatment of encapsulation material ethylene-vinyl acetate (EVA), the separation of glass and silicon wafer cells, and achieving high recovery rates of valuable materials with minimal chemical reagents. Simultaneously, efforts to reduce toxic gas and wastewater emissions for minimizing environmental impact [17] have become a crucial focus for optimizing current PV module recycling processes.

This review focuses on exploring the issue of recycling waste crystalline silicon PV modules, delving into its associated challenges. The first section will provide an in-depth overview of the characteristics and features of crystalline silicon PV modules. Following that, the second section elaborates on the formulation and implementation of policies governing the recycling of discarded PV modules. Subsequently, the third section thoroughly discusses the recycling technologies for waste crystalline silicon PV modules, while the fourth section concentrates on the analysis of the resource utilization of discarded PV modules. The subsequent fifth section compares and analyzes the environmental impact of the whole life cycle of waste crystalline silicon PV module recycling. Finally, the sixth section summarizes the entire article and anticipates future trends in the recycling of waste crystalline silicon PV modules. This review seeks to thoroughly investigate the challenges associated with recycling crystalline silicon PV modules, conducting a detailed exploration of relevant policies, technologies, and environmental implications. The objective is to offer essential insights and guidance for the future development of PV module recycling.

2. The composition and materials of crystalline silicon photovoltaic modules

The principle of crystalline silicon PV power generation is based on the photovoltaic effect at the semiconductor interface. The internal structure of crystalline silicon photovoltaic modules resembles a five-layer sandwich, consisting, from top to bottom, of tempered glass, EVA, solar cells, another layer of EVA, and the backsheet, forming an integrated structure known as a laminated assembly.

The top tempered glass typically highly possesses impact-resistant characteristics, designed to withstand adverse weather conditions such as hail. EVA, a copolymer of ethylene and vinyl acetate, serves as the most used encapsulation material in PV modules. It is employed to bond the glass, cells, and backsheet together. Its molecular formula is $(C_2H_4)_n{\cdot}(C_4H_6O_2)_m$, offering enhanced moisture resistance, insulation, and mechanical strength to protect solar cells from excessive stress, fractures, and environmental impacts [18].

Solar cells, the core components of PV modules, have gradually reduced in thickness to below 180 μm with technological advancements. These cells are typically doped with boron or phosphorus to form a PN junction, generating a potential difference to create a power source. To enhance light utilization efficiency, an anti-reflective coating is often applied to the silicon wafer to minimize surface reflections. The current is then extracted to external circuits through silver, aluminum, or copper electrodes. Crystalline silicon PV modules consist of multiple solar cells connected by photovoltaic ribbons. These ribbons are typically composed of a copper core and tin-lead solder. The backsheet is commonly made of various types of fluoropolymer materials, such as polyvinyl fluoride (Tedlar®, a product of DuPont), and polyvinylidene fluoride (PVDF). These backsheets often adopt a three-layer sandwich structure of Tedlar®/polyethylene terephthalate (PET)/Tedlar® (TPT film), effectively isolating the internal components from the external environment and providing electrical insulation, thus extending the outdoor lifespan of the PV modules. Beneath the laminated assembly, there is a junction box covered by an aluminum alloy frame. The primary function of the frame is to protect the laminated assembly and the bottom junction box for energy collection, conversion, storage, and transmission. The structure of crystalline silicon PV modules is illustrated in Fig. 1 [19]. This design enables efficient conversion of solar radiation into electricity and ensures stable operation in various environmental conditions. A comprehensive understanding of the

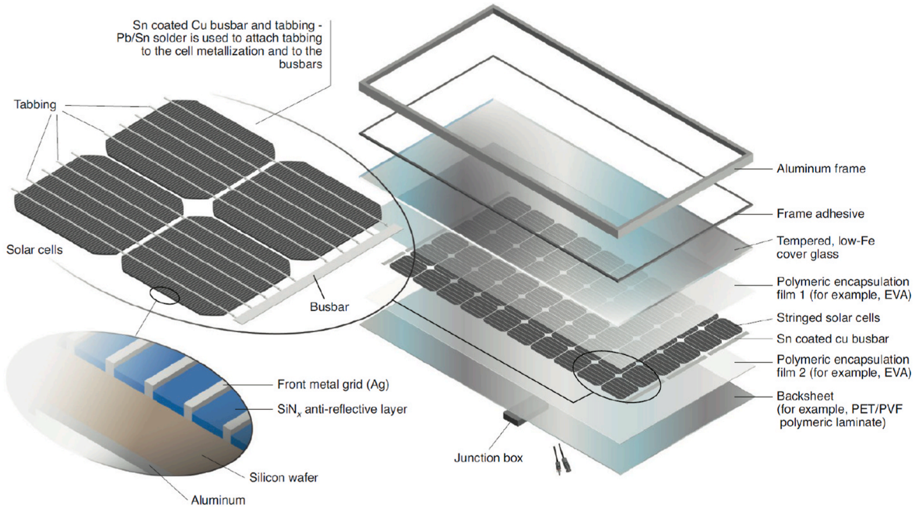

Fig. 1. Structure of crystalline silicon photovoltaic modules [20].

composition and materials of crystalline silicon PV modules facilitates more effective planning and implementation of recycling processes after their end-of-life.

3. Policies on the management of waste PV modules in different countries and regions

According to relevant studies, it is predicted that by 2030, the EU, China, and the United States are expected to generate approximately 710,000 tons, 265,000 tons, and 147,000 tons of waste photovoltaic modules, respectively [21]. Given their significant waste volume and dual attributes of high recovery value, countries and regions are actively researching management policies for waste PV modules [22] (see Table 1). Against this backdrop, the EU has formulated the WEEE Directive, categorizing waste PV modules as electronic waste and specifying clear recycling requirements [23]. These requirements encompass specific collection and reuse targets, the separate treatment of silicon-based and non-silicon-based photovoltaic panels, and decontamination requirements for metals such as cadmium, selenium, and lead during the disassembly process [15]. To achieve closed-loop management of waste photovoltaic modules, the EU photovoltaic industry has established non-profit organizations such as PV CYCLE, which provides tailored management solutions built upon the extended producer responsibility (EPR) system [24]."

Table 1
Management policies on the recycling of waste PV modules in different countries and regions.

Countries/ Regions	Policies	Related content
The EU	WEEE Directive	Waste PV modules are categorized as one of the types of WEEE, with clear requirements for collection and reuse. The recycling rates of key materials in discarded photovoltaic modules are explicitly specified."
The United States	Resource Conservation and Recovery Act	Waste PV modules are treated as solid waste, but if the waste contains high concentrations of heavy metals such as lead and cadmium and has not undergone the TCLP, these waste photovoltaic modules will be classified as hazardous waste. However, different states have different management schemes.
China	General Technology Requirements for Photovoltaic Module Recycling and Recovery	While there is no explicit categorization of specific waste types for waste PV modules, the recycling rates for key materials in these modules are explicitly specified.

The United States classifies waste PV modules as solid waste. However, if the waste contains high concentrations of heavy metals such as lead and cadmium and has not undergone the toxic characteristic leaching procedure (TCLP), these discarded photovoltaic modules will be categorized as hazardous waste, requiring compliance with the Resource Conservation and Recovery Act (RCRA) [25] to ensure safe recovery or disposal. To effectively manage waste PV modules, certain states have enacted relevant recycling management policies [26]. For instance, Washington state will implement the 'Photovoltaic Module Management and Recycling Program' starting July 1, 2025. This program mandates PV manufacturers to develop plans for the collection and recycling of waste photovoltaic modules, specifying legal recycling requirements for modules purchased after July 1, 2017. Additionally, the program sets a minimum recycling rate for waste PV modules, requiring it to be no less than 85% of the total weight of collected modules. Starting January 1, 2021, PV manufacturers can only sell modules in Washington state if they join the management program and receive approval. The program operates under the EPR system, requiring manufacturers to provide adequate funding for the recycling and disposal of waste PV modules [27]. Furthermore, in New York state, manufacturers selling solar components are required to implement collection and recycling programs for waste photovoltaic modules, with no cost passed on to consumers, and a landfill ban has been enacted [28]. In California, for ease of management, reduction of regulatory requirements, exemption from hazardous waste manifest, and reduced labeling, waste photovoltaic modules are managed as universal waste [29].

While China has not explicitly specified the specific categories of waste photovoltaic modules, it has formulated the ' General Technology Requirements for Photovoltaic Module Recycling and Recovery.' This standard, based on the principles of maximizing resource utilization and minimizing environmental pollution, provides guidelines for the disposal and treatment of waste photovoltaic modules. The standard explicitly specifies the recycling rates for key materials, with recycling rates for silicon materials, aluminum frames, and copper set at 70%, 80%, and 75%, respectively [15]. Additionally, China has issued the 'Guiding opinions on promoting the circulation and utilization of retired wind power and photovoltaic equipment,' offering a clearer direction for the improvement of the recycling system for waste PV modules [30].

The policies and standards in these countries and regions aim to promote the effective recycling and reuse of waste photovoltaic modules, reducing resource waste and environmental pollution. Simultaneously, they contribute to the sustainable development of the PV industry. The formulation and implementation of these policies and standards have positive implications for addressing global challenges in sustainable development. However, considering that the management of waste PV modules is still in an exploratory phase for most countries, extending and expanding producer responsibility is crucial [31].

4. Technology for separation and recycling of waste crystalline silicon PV modules

Komoto et al. [32] asserted that the recycling objectives for crystalline silicon photovoltaic modules involve the separation and recovery of glass, silicon cells, and other metals. Furthermore, they provided a comprehensive summary of the R&D processes for the recycling of crystalline silicon photovoltaic modules and present a detailed recycling process diagram in Fig. 2. It is evident from the diagram that pyrolysis, mechanical processing, chemical treatment, among others, are commonly utilized methods for recycling waste crystalline silicon photovoltaic modules. This study will also elucidate the current status of waste crystalline silicon photovoltaic module recycling through an exploration of these three methods.

4.1. Pyrolysis

Pyrolysis is a method for treating waste PV modules, involving high-temperature heating in an inert (oxygen-free) atmosphere. The process aims to decompose organic volatile substances, particularly the backsheet and EVA, converting them into gas or liquid forms. This process has minimal chemical oxidation impact on inorganic materials such as glass and metal [33]. The key to recycling discarded crystalline silicon PV modules lies in the removal of EVA [34]. Pyrolysis is a method that can effectively remove EVA and separate solar cells from glass during the recycling process [35,36]. Consequently, numerous researchers have conducted studies on the pyrolysis treatment of waste PV modules to explore optimal pyrolysis conditions.

Tao, Wang et al. [37,38] employed a two-stage pyrolysis technique to achieve complete decomposition of EVA in waste PV modules. Similarly, Fiandra et al. [39] utilized a two-step pyrolysis process, first removing the backsheet, followed by the removal of EVA. During the pyrolysis process, Dias et al. [40] pyrolyzed discarded photovoltaic modules at 500 °C for 30 min in a nitrogen gas environment at 1 L/min, successfully removing over 99% of polymers. Tammaro et al. [41] subjected waste crystalline silicon PV modules to heating at 600 °C, resulting in the complete degradation of EVA. However, this treatment process may release some harmful components. Zhang et al. [42] employed nitrogen pyrolysis for waste PV modules and found that at conditions of 773K, 30 min, and N_2 flow rate of 0.5 L/min, the conversion rate of organic components approached 100%. Farrell et al. [43] evaluated the pyrolysis behavior of EVA in crystalline silicon PV modules and confirmed its potential for energy recovery. Feng et al. [44] demonstrated that a temperature of 500 °C and a dwell time of 30 min are optimal pyrolysis conditions, ensuring both high dissociation efficiency and avoiding excessive fragmentation of glass particles and solar cells. A summary of pyrolysis treated EVA is shown in Table 2.

In summary, the main purpose of pyrolysis treatment is to decompose EVA and achieve mechanical separation between glass and solar cells [45]. From the perspective of recovering intact and undamaged solar cells, pyrolysis treatment is a feasible recycling method. However, it poses certain difficulties in practical implementation and is prone to causing damage to solar cells. Additionally, the pyrolysis process

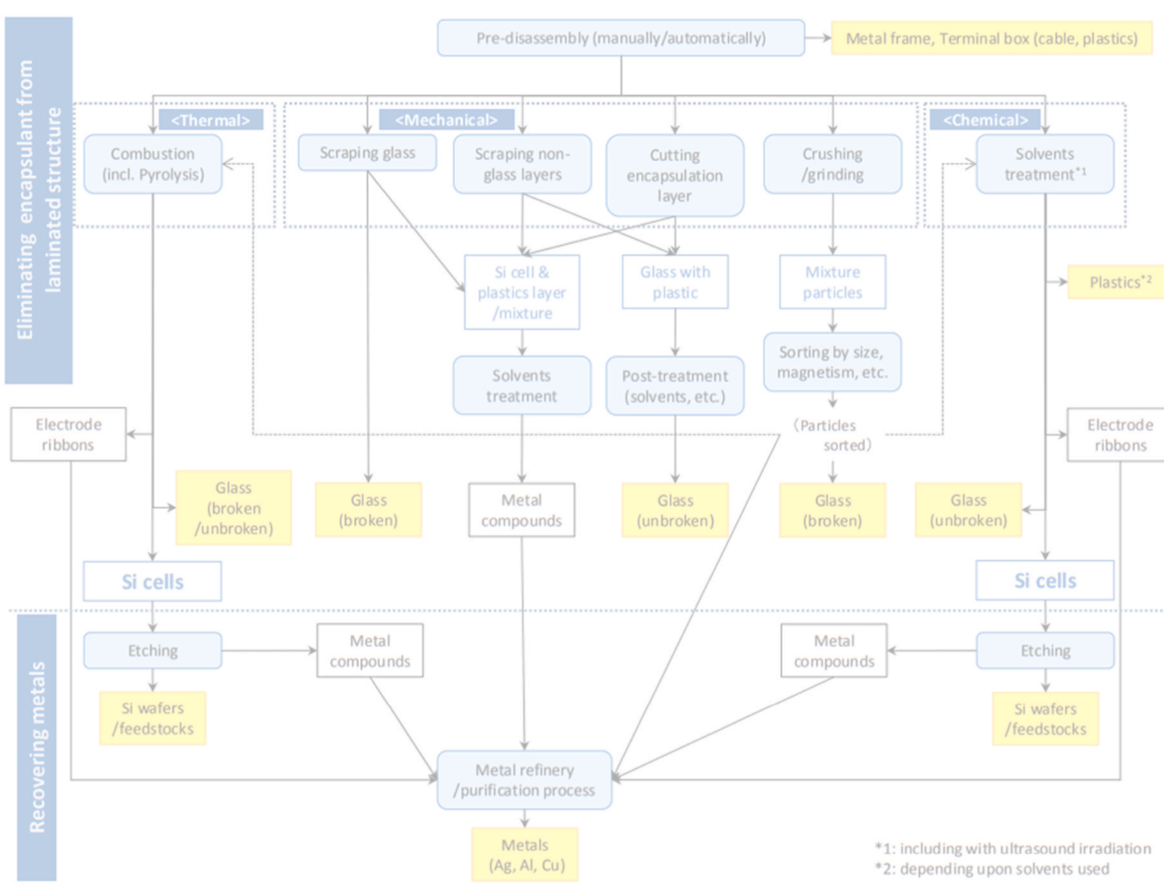

Fig. 2. Future recycling process route for crystalline silicon photovoltaic modules.

Table 2
Summary of pyrolysis process for crystalline silicon photovoltaic modules.

Conditions for processing	Processing time	Reference number
50 ml/min N_2, 600 °C (rates of 5, 10, 20 and 30 °C/min)	2h/1h/30min/20min	[36]
20 ml/min N_2, 500 °C	30min	[37]
24 L/h nitrogen/oxygen mixtures, 500 °C, 450 °C/h	1h	[38]
1L/min N_2, 500 °C	30min	[39]
1L/min air,600 °C, 12.8 °C/min	30min	[40]
0.5 L/min N_2, 773K, 30K/min	30min	[41]
50 mL/min, 550 °C, 15 °C/min	40min	[42]
200 ml/min N_2, 500 °C, 10 °C/min	30min	[43]

generates toxic and harmful gases, including hydrogen fluoride emissions [41,46], which need to be treated before being released into the atmosphere [19]. This increases the recycling cost and, to some extent, adds to the environmental impact throughout the life cycle of photovoltaic power generation. Pyrolysis, as a potentially significant method for recycling waste PV modules [47], contributes to the development of a circular economy. However, its implementation requires a comprehensive consideration of factors such as operational difficulty and environmental impact.

4.2. Chemical treatment

The key to chemical treatment lies in utilizing organic solvents to dissolve EVA, thereby achieving effective separation of waste PV modules. To expedite this process, methods such as microwave heating and ultrasonic radiation are often employed to enhance the dissolution rate of EVA and shorten the reaction time. The microwave-assisted swelling mechanism is primarily based on the differences in microwave absorption and thermal expansion among the layers of discarded photovoltaic modules, inducing deformation and stratification during the heating process. Under high-frequency vibrations, the stability of EVA decreases, its microstructure is disrupted, and organic solvents enter the fissures at the stratified interface, reducing the cross-linking density of EVA and rapidly and efficiently achieving the separation of different layers of PV panels.

Kang et al. [48] found that at room temperature, organic solvents can only partially dissolve EVA, requiring further heat treatment to achieve complete dissolution. They delved into the mechanism of EVA dissolution and expansion, as shown in Fig. 3. EVA resin is divided into cross-linked and non-cross-linked portions. The dissolution primarily targets the non-cross-linked resin, while the expansion mainly focuses on the cross-linked portion of the EVA resin, leading to an increase in resin volume. To shorten the reaction cycle, researchers use auxiliary processes such as ultrasonic irradiation and microwave heating to accelerate the rate of EVA dissolution. Studies indicate that Pang et al.

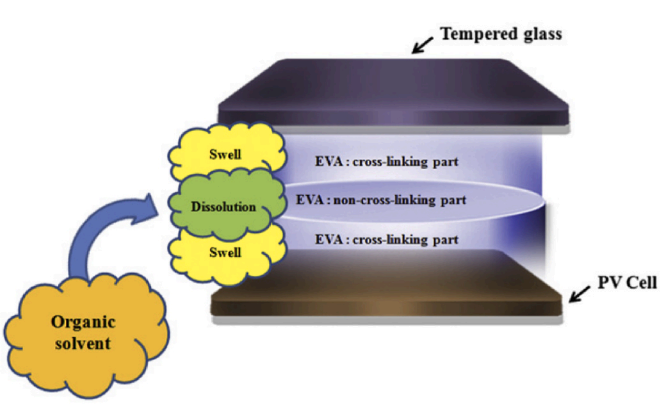

Fig. 3. Principle of dissolving/expanding EVA with organic solvents [47].

[49], using microwave-enhanced EVA swelling mechanisms, significantly increased the separation speed between layers of waste PV modules. They compared the efficiency of different swelling agents and found that trichloroethylene was the most effective. Under conditions of 4 mol/L trichloroethylene concentration, 70 °C reaction temperature, and a solid-liquid ratio of 50 g/L, effective separation of discarded photovoltaic modules was achieved in just 2 h. Azeumo et al. [50] optimized the recovery process of waste PV modules using ultrasound and determined the optimal conditions: 60 °C, reaction time less than 60 min, and 200W and 50 kHz ultrasound. They found that, compared to five other solvents, toluene could dissolve EVA more quickly, achieving maximum separation of module layers.

Considering the high toxicity of traditional chemical agents, Li et al. [51] utilized the green reagent DMPU ($C_6H_{12}N_2O$) to achieve the separation of waste PV modules while ensuring that the separated solar cells retained their initial size, facilitating effective resource recovery. Additionally, Li et al. [52] employed DBE ($C_{21}H_{36}O_{12}$) as a green reagent to control the swelling of EVA, ensuring that the solar cells did not undergo excessive rupture during the process. In another study, Min et al. [53] achieved layer separation of waste PV modules using EGDA ($C_6H_8O_4$). The summary of EVA dissolved in organic solvents is shown in Table 3.

In summary, traditional chemical processing involves long reaction cycles, large amounts of consumed reagents, and the subsequent handling of waste liquids and gases, adding to the difficulty of recycling waste PV modules. From an environmental perspective, green chemical processing emerges as a promising method for the recycling of discarded photovoltaic modules. The optimization of technical conditions remains a crucial aspect that requires further exploration in research and practice to achieve efficient, safe, and environmentally friendly recycling and resource utilization of waste PV modules.

4.3. Mechanical processes

For the treatment of waste PV modules, various mechanical processes such as room temperature traditional crushing, pyrolytic crushing, low-temperature crushing, high-pressure pulses, and sorting have demonstrated their importance in separating and recovering valuable materials.

In the field of room temperature traditional mechanical processing, numerous researchers have undertaken explorations. Fiandra et al. [54], considering the generation of hydrogen fluoride (HF) and fluoride by-products during the heat treatment due to the presence of the backsheet, opted for mechanical processing using a milling machine to completely strip off the backsheet. Azeumo et al. [50], after removing the aluminum frame from waste PV modules, used a knife grinder to crush it to below 0.4 cm and subjected it to heavy medium separation. In this process, the float mainly contained organic materials such as the backsheet and EVA, while the sink mainly consisted of glass and metals. Subsequent grinding and screening were employed to further process the sink, obtaining approximately 76% glass (with a grade of approximately 100%) and 100% metal (with a grade of 67%).

While room temperature crushing processes have to some extent achieved the separation of PV modules, they often fail to dissociate the

Table 3
Summary table of organic solvents dissolving EVA.

Conditions for processing	Processing time	Reference number
90 °C, toluene	2d	[48]
4 mol/L trichloroethylene, 70 °C, microwave field	2h	[49]
60 °C, ultrasound at 200W, toluene	1h	[50]
100 °C, ultrasonic power 600W, DMPU	50min	[51]
180 °C, ultrasonic power 900W, DBE	30min	[52]
160 °C, ultrasonic power 300W, EGDA	50min	[53]

EVA present in the modules, necessitating further research. Pagnanelli et al. [55] employed a triple-stage process of crushing, pyrolysis, and chemical treatment to recycle waste PV modules. This method not only reduces the amount of pyrolytic treatment but also effectively achieves material separation. To enhance the efficiency of mechanical processing of waste PV modules, Li et al. [34] utilized 1064 nm fiber pulse lasers to irradiate the EVA bonding interface, raising the temperature in that region and reducing the adhesion of EVA. This process enabled the mechanical detachment of solar cells while ensuring the integrity of the cells. Nevala et al. [56] compared electro-hydraulic fragmentation (EHF) with traditional crushing techniques for processing waste PV. They found that disassembling PV modules using EHF with the metal concentrated in clearly defined particle size fractions exhibited higher selectivity. This method allows for the direct recovery of metals from solar panels through simple means such as screening. The crushing achievable through EHF technology concentrates approximately 99% of the copper, 60% of the silver, and 80% of the lead, tin, and aluminum elements in the total weight of the photovoltaic panel only within the size range of >4 mm. Additionally, high purity (>99%) silicon can be found in portions between >0.50 mm and <2 mm. It is evident that processes such as pyrolysis, fiber pulse, and EHF provide better dissociation and crushing effects on PV modules.

The high-voltage pulse crushing technology is widely used in the recycling of electronic waste circuit boards. To some extent, waste PV modules share common characteristics with electronic waste, prompting researchers to apply high-voltage pulse technology to the recovery of discarded photovoltaic modules [57]. This technology primarily utilizes high-voltage pulses propagating along the discharge channel to create high-temperature and high-pressure conditions in the interface layer of the modules, ultimately causing expansion and rupture of materials [58]. The process schematic is illustrated in Fig. 4. Song et al. [59] employed a novel environmentally friendly method of high-voltage pulse discharge in water for the selective recovery of waste PV modules. With parameters set at 160 kV, 300 pulses, and an energy consumption of 192.99 J/g, the PV panels were crushed into particles averaging 4.1 mm (13.7% of the initial size). The study indicated that after high-voltage pulse crushing, 95% of copper and 96% of silver were concentrated in particles with a diameter less than 1 mm, while 85% of aluminum, 85% of lead, and 87% of tin were concentrated in particles with a diameter less than 0.5 mm. Zhao et al. [60] found that during the high-voltage pulse crushing process, there were differences in the selectivity of different components. This is primarily due to the high-voltage pulse crushing, which preferentially fractures at interfaces of materials with large differences in dielectric constants, achieving material separation. The selectivity of materials, from largest to smallest, was Ag > Si > glass. High-value elements generally concentrated in fine particles, with the purity of crushed products in the range of 0.5–4 mm reaching above 98%. The crushed particles of waste PV modules under high-voltage pulses are shown in Fig. 5. It is evident that high-voltage pulse technology can effectively achieve the dissociation and enrichment of discarded photovoltaic modules, and this technology holds the potential for achieving harmless recycling processes, presenting certain development prospects."

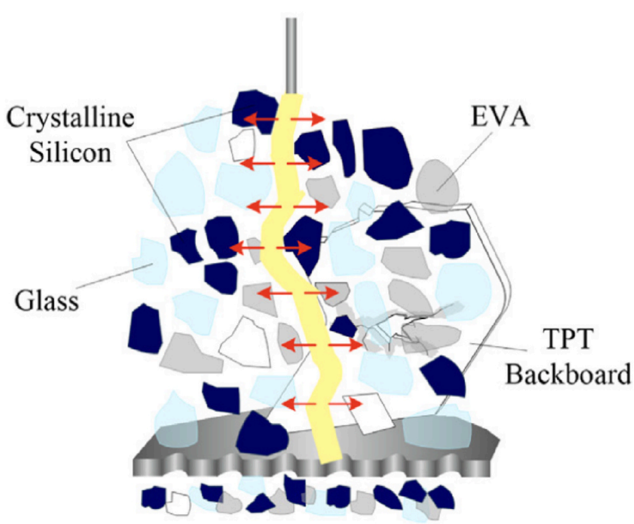

Fig. 4. Principle of high-voltage pulse crushing [58].

After the mechanical crushing of waste PV modules, effective separation of the crushed mixed particles is essential. The most direct method is to employ vibration screening based on different particle sizes. Sim et al. [61] achieved the separation of polymer and metal components by cutting and mechanically crushing waste PV modules, combined with screening technology. They observed that over 90% of polymers were distributed in two particle size ranges, 1–5 mm and >5 mm, while high-value Ag was primarily concentrated in particles <0.25 mm. Some researchers utilized electrostatic separation based on the differences in conductivity between materials. Li et al. [62] employed electrostatic separation and found that under conditions of particle size 0.30–0.45 mm, rotation speed 30 rpm, and voltage 15 kV, the separation effect was optimal, with a Si content of 91.0% and a Si recovery rate of 48.9%. Others used the shape and density differences of materials, employing gas-solid fluidized bed technology to achieve effective separation of glass and silicon wafers. Feng et al. [44], using materials obtained after pyrolysis, implemented separation using gas-solid fluidized bed technology. At an airflow velocity of 85 m^3/h, the recovery rates for solar cells with particle sizes >4 mm and 2–4 mm were 91.09% and 82.29%, respectively. Although separation improves the concentration of materials, there are still some shortcomings in the separation technologies. The purity of materials obtained from vibration screening needs improvement, and electrostatic separation and gas-solid fluidized bed technology have higher requirements for the particle size of mixed materials, making them less suitable for separating smaller particles and affecting separation efficiency.

These research findings indicate that mechanical processing holds significant potential for the recycling of waste PV modules, achieving effective separation and enrichment of materials to some extent. However, the mixed particle materials resulting from the mechanical crushing of PV modules are diverse, posing a technical challenge for further sorting of all materials. Moreover, there is room for improvement in the purity of separation products.

4.4. Industrial application of waste crystalline silicon PV module recycling

For the recycling of crystalline silicon photovoltaic modules, the processes of crushing and sorting have already been commercialized in Europe. Pyrolysis can effectively achieve the separation of glass and silicon wafers, making it a mainstream industrial recycling technology. Currently, in certain countries and regions globally, the industrialized recycling of photovoltaic modules is predominantly carried out through a combination of pyrolysis, mechanical, and chemical methods (refer to Table 4). Additionally, we conducted a research analysis on the processing capacity and techniques employed by some large-scale production enterprises (refer to Table 5). Given that China currently leads the world in photovoltaic installed capacity, and its annual installation capacity is expected to maintain a leading position, the volume of decommissioned photovoltaic modules is considerable. In recent years, the photovoltaic recycling industry has been in a developmental stage, and in the future, more institutions capable of large-scale production are expected to emerge.

5. Resource utilization of waste photovoltaic modules

The preliminary stages, including pyrolysis, chemical solvent dissolution, and mechanical processing, have achieved initial separation of

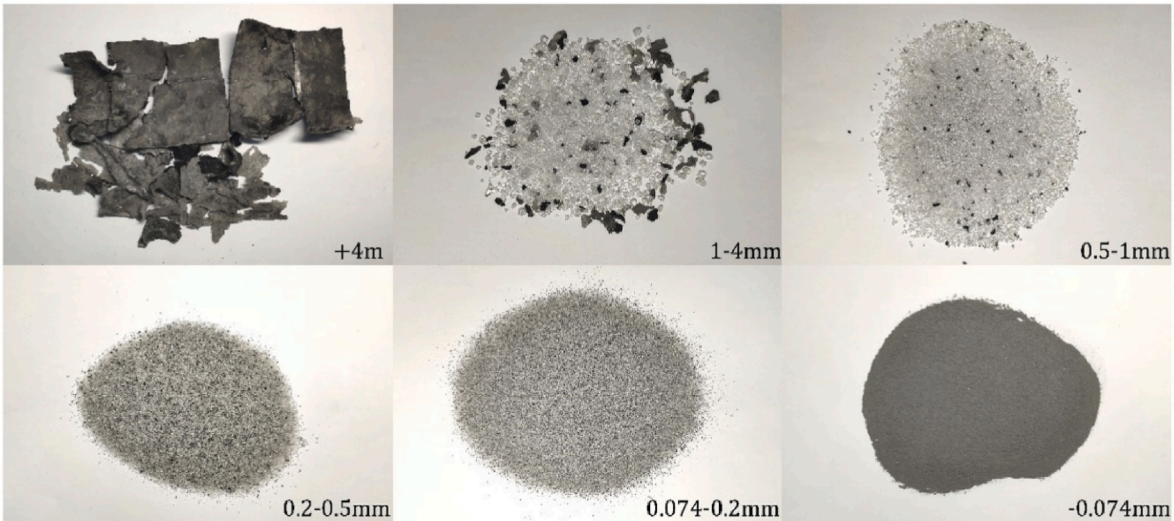

Fig. 5. Crushed particles at different particle sizes of waste PV modules under high-voltage pulses [59].

waste PV modules. However, these modules still contain valuable metals such as precious metals, which require further efficient extraction, impurity removal, and ultimately achieve resource reuse and environmental protection.

Silicon is one of the valuable materials in waste PV modules, and numerous researchers have conducted a series of studies to obtain silicon. Yi et al. [63] proposed a method that involves leaching Ag, Al, and other metal ions using HNO_3/NaOH solution, obtaining 99% silicon. To improve the purity of Si, they employed a CaO–CaF_2–SiO_2 pyrometallurgical process at 1520 °C to eliminate other metal impurities, ultimately achieving 99.98% Si purity. Sim et al. [64] found that using HNO_3 and KOH can separate the metals in silicon cells but cannot remove the antireflection coating. However, utilizing phosphoric acid not only separates Ag and Al but also removes the antireflection layer, resulting in a silicon recovery rate of 98.9% and a purity of 99.2%. While recycling intact silicon wafers for the production of regenerated batteries presents operational challenges, processed silicon fragments, after etching and cleaning processes, can also be used as an anode for lithium-ion batteries, achieving recycling.

According to relevant studies, it is indicated that to meet the demand for silver in crystalline silicon photovoltaic modules, a substantial portion of current production and at least 30% of known reserves are required [65]. Perelman et al. [66] argue that the challenge in producing crystalline silicon PV modules lies in the scarcity of Ag and its price volatility (see Fig. 6). They also conducted a statistical analysis of the cumulative demand for various materials in photovoltaic modules (see Fig. 7). Li et al. [67], through methods such as Hubbert's theory, Weibull distribution, and demand intensity, studied the supply of Ag from mining, recovery supply, and manufacturing demand. They found that a shortage in Ag supply for manufacturing demand is likely to occur after 2023. The crystalline silicon PV industry may compete with other industries for Ag, exacerbating the Ag supply shortage. However, the research also reveals that the recycling of waste crystalline silicon PV modules can help alleviate the demand for silver from PV manufacturers. In the future, primary silver mining may face various constraints. With increasing demand for deep-earth resources, future silver deposits may be located in more complex geological conditions, such as deep layers or regions with intricate geological structures, thereby increasing the difficulty of exploration and extraction. As the demand for silver continues to rise, the challenges of mining high-quality silver ore may escalate. New deposits may become scarcer, and the output from existing deposits may gradually decrease, making mining more challenging. Extracting silver from deep-seated deposits and low-grade ores typically requires more advanced technologies, potentially leading to higher costs. However, secondary extraction (recovery) can effectively address these challenges, making the recovery of silver from discarded photovoltaic components essential. Dias et al. [68] conducted research on the extraction of Ag from waste PV modules and found that pyrolysis alone does not improve the recovery rate of Ag. Through grinding, sieving, and leaching in a solution containing 99% sodium chloride and 64% nitric acid for particles smaller than 0.5 mm, they successfully achieved a high silver concentration recovery rate of up to 94%. Yashas et al. [69] first used pyrolysis to separate solar cells and glass, and then selectively leached Ag using an H_2SO_4–H_2O_2 system. This method, combined with 1.0 M H_2SO_4 and 1.0% H_2O_2 at 70 °C, achieved a 96.75% Ag leaching rate within 24 h. Activated carbon (Pt/AC) was used in conjunction with hydrogen and air for selective recovery and concentration of $Ag+$ in the filtrate from PV cell leaching. Finally, traditional electrolysis extraction processes were employed to obtain pure metallic silver (Ag $>$ 99.0%). Deng et al. [70] used a reverse electroplating method to oxidize Ag on waste photovoltaic modules and recovered 99.90% pure metallic silver within a few minutes.

Waste PV modules not only contain Ag but also include metals such as lead and aluminum. Various researchers have contributed to the recovery of other metals. Lim et al. [71] achieved the recovery of 86% silver, 95% lead, and 97% aluminum from waste PV modules through three main steps: module delamination, acid etching, and sequential electrodeposition. Anna et al. [5] adopted an acidic and alkaline etching method for the recovery of waste PV modules. With 3 M HNO_3 at 50 °C and 3 h of etching, the silver recovery rate reached 99.99%. A 1 M NaOH solution removed the aluminum layer from the back of the solar cell after a 30-min etching process at 50 °C. Yousef et al. [72] used dimethyl sulfoxide solvent with ultrasound assistance to decompose the aluminum layer on waste solar cell wafers, achieving an aluminum recovery rate of $>$98%. Subsequently, nitric acid and other environmentally friendly agents (sodium chloride, ammonia solution, and glucose syrup) were used for leaching, assisted by ultrasound to dissolve Ag with a yield of $>$92%. Finally, a slurry containing H_3PO_4 was used for etching to remove the anti-reflective coating and purify the silicon substrate, resulting in a silicon recovery rate of $>$99%. Klugmann-Radziemska et al. [73] used 40% HNO_3 at a temperature of 40 °C to dissolve the silver coating, and silver was recovered by electrolysis from the waste acid. Subsequently, a 30% KOH aqueous solution at 80 °C removed the Al layer from the surface of the removed cell. Finally, using a mixture of 83.33 ml HNO_3 (65%) + 50 ml HF (40%) + 50 ml CH_3COOH (99.5%) + 1 ml Br_2 successfully removed the anti-reflective coating and the n-p junction.

Metal materials are typically subjected to chemical leaching,

Table 4
Recycling methods used by waste crystalline silicon PV module recycling companies in some countries and regions [32].

Year	Country/region	Implementing organization	Pyrolysis	Mechanical treatment	Chemical treatment
2018	Japan	Mitsubishi Materials Corporation		✓	
2016	Japan	Toho Kasei Co., Ltd.		✓	✓
2018	Japan	Hamada Corporation, NPC Incorporated		✓	✓
2017	Japan	Shinryo Corporation	✓		
2009	Korea	Korea Research Institute of Chemical Technology, Kangwon National University			✓
2013	Korea	Symphony Energy Co., Chonnam National University, Renew Energy Co.	✓		✓
2016	Korea	DSM Co., JSPV Co., Korea Interfacial Science and Engineering Institute, Korea Electronics Technology Institute	✓		✓
2015	Korea	Korea Institute of Energy Research, Chungnam National University, Pukyong National University	✓		✓
2019	Korea	Pretech Co., Korea Institute of Energy Research, Pukyong National Univeristy, Hapdong Hightechglass Co., Chungbuk Technopark	✓		✓
2015	China	Chinese Research Academy of Environmental Sciences, Institute of Electrical Engineering	✓		✓
2015	China	YingLi Solar, Institute of Electrical Engineering		✓	
2024	China	Shanghai Jinghuan Jiayuan Energy Technology Co., Ltd.	✓	✓	✓
2024	China	Changzhou Ruisai Environmental Protection Technology Co., Ltd.	✓	✓	✓
2017	Europe	Eco recycling (Italy), High-Tech Recycling Centre (Italy), Eco Power, Green Engineering	✓	✓	✓
2017	Europe	Sasil, S.p.A. (Italy), Stazione Sperimentale del Vetro (Italy), PV CYCLE (Belgium)	✓	✓	✓
2016	Europe	La Mia Energia (Italy), University of Florence, Department of Industrial Engineering (Italy), Leitat Technological Centre (Spain), PV CYCLE (Belgium)		✓	

followed by effective recovery through processes such as precipitation and electrolysis. This not only provides a technological pathway for the resource utilization of waste PV modules but also offers new ideas for sustainable development. By extracting and recovering valuable materials from them, we can reduce resource waste, decrease reliance on natural resources, and further advance the development of clean energy technologies, promoting environmental sustainability.

6. The environmental impact of the whole life cycle of waste crystalline silicon PV recycling

6.1. Life cycle assessment

The rapid development of PV technology underscores the crucial importance of planning for the recycling facilities of waste PV modules. To optimize recycling schemes and minimize environmental impacts to the greatest extent, evaluating the environmental performance of waste photovoltaic panels has become particularly necessary [20]. Life Cycle Assessment (LCA) is a comprehensive methodology used to assess the environmental impacts and energy usage of a product throughout its whole life cycle, from raw material extraction to the end of product life [74–76].

Research by Ewa et al. [77] compared the environmental impact of using recycled silicon wafers for solar cell production versus producing cells without recycled silicon. The results showed that recycling silicon wafers can reduce raw material consumption, production costs, and decrease greenhouse gas emissions by 42%. Artaş et al. [78] conducted a comparative analysis of carbon dioxide emissions and economic costs between solar modules produced from recycled materials and those produced without recycling. Recycling waste PV modules helps reduce environmental pollution and facilitates the secondary utilization of rare materials, creating economic value. Lim et al. [71], applying a life cycle assessment approach, compared the optimal waste PV module recycling process explored on a laboratory scale with landfill disposal. They found that recycling significantly reduces global warming potential by approximately 393% and decreases the impact of toxic substances on the environment.

The importance of standardized recycling for waste PV modules in terms of environmental benefits is evident from the above research. However, different recycling methods have significantly different environmental impacts, necessitating comparative studies of various recycling processes. Latunussa et al. [79], using LCA method, found that environmental impacts during the recycling process mainly involve transportation, incineration of encapsulation layers, screening, acid leaching, and electrolysis. Among these, the incineration process causes the most significant environmental impact, followed by the recycling processes of metal silicon, silver, copper, and aluminum. Corcelli et al. [36] conducted LCA of the environmental impacts of recycling waste

Table 5
Industrial demonstration lines of some typical large-scale photovoltaic recycling companies around the world.

Year	Country/ region	Company	Processing capacity	Industrial demonstration line
2016	Japan	Toho Kasei Co., Ltd.	200 MW/ year	Use a combination of mechanical and chemical methods to remove EVA and separate glass and silicon wafers.
2017	Japan	Shinryo Corporation	200 MW/ year	Pyrolysis to achieve EVA removal.
2018	Japan	Mitsubishi Materials Corporation	200 MW/ year	A demonstration line for the recycling of crystalline silicon photovoltaic modules that focuses on mechanical processing, enabling the removal of aluminum frames and junction boxes, and the separation of glass, silver, etc.
2018	Japan	Hamada Corporation, NPC Incorporated	200 MW/ year	The hot knife method separates glass and EVA, and the chemical method separates metals.
2017	Europe	Eco recycling (Italy), High-Tech Recycling Centre (Italy), Eco Power, Green Engineering	200 tons/ year	Recycling of glass and metal is achieved through mechanical crushing and hydrometallurgy.
2017	Europe	Sasil, S.p.A. (Italy), Stazione Sperimentale del Vetro (Italy), PV CYCLE (Belgium)	1 ton/hour	Using infrared light, lasers and knives to heat and separate glass, and chemical processing to recover metals.
2023	China	Yingli Group	12 MW/ year	A demonstration line for the production of complete equipment for the recycling and processing of crystalline silicon photovoltaic modules based on physical treatment methods. The comprehensive recovery rate of the product reaches 93%, of which the recovery rates of silicon, silver and copper are 96%, 93% and 97% respectively.
2023	China	Jinko Solar	12 MW/ year	A photovoltaic module recycling demonstration line built by combining pyrolysis and chemical treatment. The recovery rates of silicon, silver and copper are 95%, 95% and 98% respectively.
2023	China	Changzhou Ruisai Environmental Protection Technology Co., Ltd.	2000 tons/ year	Build a complete set of intelligent dismantling equipment and a fully automatic material sorting demonstration line, with a material recovery rate of 99% and a material recyclability rate of 97%.

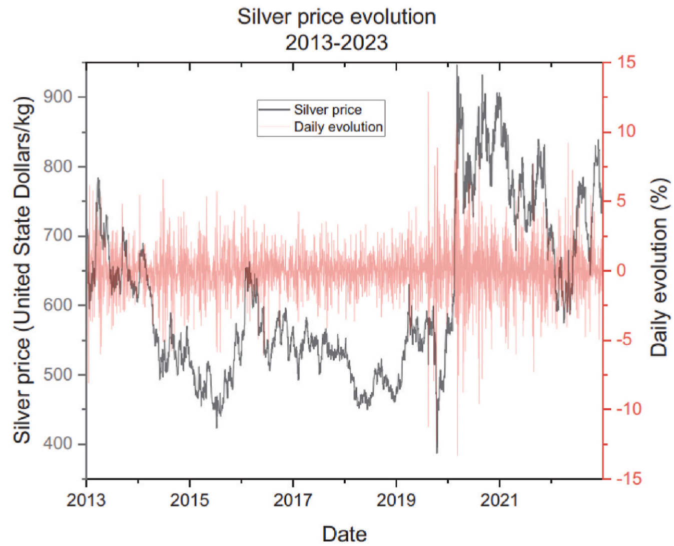

Fig. 6. Ag price changes from 2013 to 2023 [66].

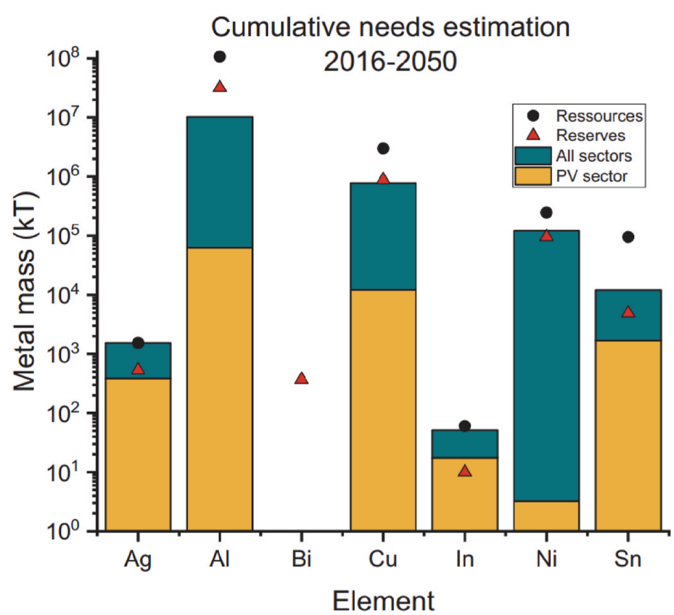

Fig. 7. Cumulative demand for various materials of photovoltaic modules [66].

crystalline silicon PV modules. The most noticeable environmental benefits were observed in the recycling of aluminum and silicon, leading to reduced extraction, and refining of raw materials and lower manufacturing costs. Ravikumar et al. [80] discovered that the environmental impact of thermal treatment for separation is superior to existing mechanical processes, with a 23% reduction in climate change effects. Additionally, the use of organic solvents poses a greater burden on the environment. Pero et al. [81], based on original data collected from recycling equipment for waste PV modules, conducted a life cycle assessment of the recycling process, including the construction and operation of recycling devices and the separation and incineration of different waste materials. They found that the energy consumption during grinding and sorting processes is primarily due to operations. Throughout the whloe recycling process, the pre-processing stage has the greatest environmental impact, followed by the separation of glass and silicon, and finally the separation of copper and polymers. Lunardi et al. [82] performed an environmental impact assessment of landfilling, incineration, reuse, and recycling (mechanical, thermal, and chemical) of waste crystalline silicon PV modules. They found that while recycling waste photovoltaic modules reduces environmental impact to some extent, attention should be paid to factors such as the use of toxic substances in chemical recycling and the transportation distance during recycling. Li et al. [83], based on LCA, compared the costs and benefits of mechanical recycling, chemical recycling, and thermal recovery. They proposed improvements in technology, scaling up recycling operations, reducing transportation distances, and government subsidies, all of which can promote the recycling of waste PV modules and achieve higher environmental and economic benefits.

In summary, standardized recycling of waste PV modules is crucial for reducing environmental impact and achieving sustainable development. Among the various recycling methods, thermal treatment results in the least environmental impact, followed by mechanical processing. Additionally, chemical treatment exhibits lower environmental impact compared to landfilling and incineration. Exploring the optimal selection of recycling methods and refining the recycling processes to minimize the environmental burden of waste photovoltaic modules is a key area for future research. This contribution aims to support the sustainable development of clean energy technoloies.

6.2. Sustainability indicators and policies

The management of waste PV modules poses a series of challenges, and researchers are actively exploring solutions in various aspects to address these challenges. While analyzing the problems at hand, they are proposing sustainable metrics and policies, aiming to improve the current state of PV module recycling.

Predictive studies on waste quantity can provide a more accurate estimate of the future quantity and distribution of discarded PV modules, laying the foundation for effective waste management strategies. Wang et al. [84] estimated the distribution of PV waste in China from 2020 to 2050, finding that the cumulative PV waste could reach a maximum of 88 million tons by 2050, mainly concentrated in the northern or northwestern regions, with crystalline silicon PV waste accounting for over 50% of the total waste. Clear spatial assessments of waste PV modules, understanding information such as the quantity, location, and types of decommissioned modules, help different provinces in China formulate tailored management strategies under the concept of a circular economy. Before formulating management policies, it is essential to address the challenges faced by the recycling of waste PV modules. Wang et al. [85] highlighted challenges including the difficulty of long-term bulk recovery, high initial investment costs, lack of incentive measures, and a small market scale. They proposed improvements to the current state of PV recycling from four aspects: recycling standards, incentive policies, technological development, and the construction of demonstration sites. Marcuzzo et al. [86] utilized a system dynamics simulation method to estimate the potential market size of PV deployment in China, Germany, Japan, the United States, and India, and they assessed the quantity of waste PV modules. They studied the policy formulation of national governments for managing waste PV module recycling and determined the responsibilities of relevant stakeholders. Zhang et al. [87] also used this model to explore the impact of subsidy systems on the overall economic feasibility of waste PV module recycling. They found that subsidizing discarded PV module recycling in China under current circumstances can rapidly achieve the recycling rate target. However, with the expansion of recycling scale and changes in recycling technology costs, reasonable subsidy standards should be adopted at different stages, and timely implementation of subsidy reduction mechanisms is necessary.

Policy optimization is another key area, and governments can guide the industry towards more sustainable practices by improving recycling standards and implementing incentive policies. The cost and profit of recycling are critical factors influencing the recycling of waste PV modules. Some studies have explored government subsidies to ensure the development of the PV recycling industry. Li et al. [88] developed a complex network model to simulate three recycling modes and three policy scenarios for discarded PV modules. They found that, under current recycling technologies, recycling profits are insufficient to cover the costs of recycling transportation and dismantling. Government subsidies help offset the negative impacts of mandatory recycling and safeguard the stability of the PV market. In the context of waste PV module recycling, Zhang et al. [89] explored investment and pricing decisions from a supply chain perspective using game theory. They suggested that, for a low-cost investment PV recycling system, subsidies are superior to fines, effectively increasing recycling rates and profits. Under high-cost investments, both subsidies and fines can promote the formal recycling of discarded PV modules.

For more suitable policies for waste PV module management, it is necessary to research waste recycling costs, recycling technology development, and reverse logistics [90]. Cui et al. [91] simulated the costs of different waste PV module recycling methods, including operating costs, material income, etc., and found that improving material purity and tapping into high-value markets are effective ways to reduce recycling costs. Sahajwalla et al. [92] proposed the product-centric approach, emphasizing the recyclability of PV modules. They believe that modular design and the development of alternative materials can significantly enhance the reusability of waste PV modules. Komoto et al. [93] conducted a comparative study on the current status of waste photovoltaic module recycling in different countries. They propose that to effectively manage the recycling of waste photovoltaic modules, it is essential to integrate regulatory and technological approaches efficiently. Additionally, these potential choices should be adjusted based on the specific circumstances of each country or region. Due to factors such as limited available recycling technologies and logistical challenges during transportation, the recycling of photovoltaic modules generally faces a situation of high costs and low returns. Therefore, further improvements are needed in the processes of waste PV module recycling.

The integration of predictive waste quantity studies, policy optimization, and technological innovation forms a comprehensive solution for sustainable management and reuse of waste PV modules. These efforts not only contribute to environmental protection and waste reduction but also provide substantial support and guidance for the sustainable development of the clean energy industry. Continuing to deepen research and practice in these areas in the future will have positive and far-reaching effects on promoting the green development of the clean energy industry.

7. Summary and outlook

In the future, the global volume of waste PV modules is expected to increase significantly, necessitating prompt adoption of effective management measures and feasible recycling technologies. This study analyzes the management policies for waste PV modules in different countries and regions, evaluates the effectiveness of various recycling technologies, and compares the environmental benefits of different recycling methods. Through exploration, the following conclusions are drawn:

(1) Compared to the EU and the United States, China started managing waste PV modules relatively late. Different countries have different categories for discarded modules, and China has not yet provided clear categories. However, China has specified relevant standards, defined the recycling rates of key materials in waste PV modules, and based on the EPR system, improved the construction of a formal recycling system for waste PV modules.

(2) Pyrolysis treatment, chemical processing, mechanical crushing, and other processes have indeed achieved the separation of waste PV modules. From an economic perspective, pyrolysis treatment is one of the widely applied technologies in the industry. Chemical processing has a long cycle, requires large and expensive amounts of chemicals, and involves a complex process for

treating subsequent waste liquids. Therefore, this technology is not suitable for industrial development. Mechanical crushing is a simple technique that can effectively separate glass but cannot efficiently remove EVA and the backsheet, leading to the inability to obtain clean solar cells that require further separation.

(3) High-pressure crushing and recovery processes in mechanical processing are expected to become one of the technological routes applied in the industry. Since the environmentally harmless whole process, it achieves the effective disintegration and crushing of PV modules. Chemical leaching, precipitation, electrolysis, and other methods are used to extract metals, but improving the efficiency of separating valuable materials in mixed particles is one of the key points for future research.

(4) Different recycling technologies for waste PV modules result in different environmental impacts. Pyrolysis treatment has the smallest environmental impact, followed by mechanical processing, then chemical processing, and finally incineration and landfilling. From an environmental impact perspective, promoting pyrolysis as the mainstream technology for waste PV module recycling is advisable.

(5) Considering the limited photovoltaic recycling technologies and logistical challenges during transportation faced by various countries globally, it is essential to tailor appropriate measures based on specific circumstances. China faces challenges in waste PV module recycling, including large quantities, uneven geographical distribution, difficulties in recycling, high costs, and a small market size. To promote the sustainable development of the PV recycling industry, it is necessary to formulate rational subsidy policies based on recycling scale and cost changes and dynamically adjust subsidy standards. Additionally, if PV manufacturers adopt green modular design, it can significantly reduce the difficulty of recycling waste PV modules.

CRediT authorship contribution statement

Jie Wang: Writing – original draft, Formal analysis. **Yi Feng:** Writing – review & editing. **Yaqun He:** Writing – review & editing, Funding acquisition.

Declaration of competing interest

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

Data availability

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

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