



Recycling and recovery of perovskite solar cells

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Over the past decade, lead halide perovskite materials have emerged as a promising candidate for third-generation solar cells and have progressed extremely rapidly. The tunable band gap, strong absorption, high power conversion efficiency, and low cost of perovskite solar cells makes them highly competitive compared to current commercialized silicon-based and thin film-based photovoltaic technologies. However, commercial products unavoidably result in large amounts of waste and end-of-life devices which can cause serious environmental impacts. To address this issue, recycle and recovery technologies of perovskite solar cells should be researched and developed proactively. In this review, the development of perovskite solar cells and their necessary materials are first introduced. Subsequently, the potential environmental impacts of perovskite solar cells are discussed, including their stability and lifetime, use of critical materials (i.e., indium, tin, and lead), and toxicity. Accordingly, the present recycle and recovery technologies are reviewed, providing information and recommendations of key strategies for recycling and recovering. Finally, future works and strategies for recycling and recovering perovskite solar cells are proposed.

Introduction

Perovskite solar cells (PSC) are considered as a highly promising candidate for third-generation solar cell owing to their near-perfect crystalline structure [1], tunable direct band gaps [2], large absorption coefficient [3], high ambipolar mobility [4,5], long carrier diffusion lengths [6], small exciton binding energy [7], high defect tolerance [8], solution processability [9,10], and low processing cost [11–17]. Recently, the efficiency of PSCs has reached 25.2% as reported by National Renewable Energy Laboratory (NREL) in the U.S. [18]. Notably, a PSC with an interfacially-engineered (FAPbI₃)_{0.95}(MAPbBr₃)_{0.05} perovskite absorber layer has been demonstrated to possess a 23.3% efficiency [19], surpassing polycrystalline silicon (Si)-based solar cells and copper indium gallium (di)selenide/(di)sulfide (CIGS)

based thin-film solar cells. Furthermore, PSCs with a 22.7% efficiency and lower cost than CIGS solar cells [20] have been manufactured on flexible substrates, further extending the applications of photovoltaic (PV) cells. Because of these outstanding results, PSCs stand as promising options for next-generation photovoltaic technology. However, PSCs still face many challenges for commercialization, such as stability, lifetime, toxicity, and detrimental environmental impacts [21,22]. Device stability is considered to be the largest challenge preventing commercialization of PSCs [23]. Both academia and industry have conducted intensive studies on PSCs, focusing primarily on power conversion efficiency (PCE) and stability. These studies have uncovered methods to enhance performance and stability towards commercialization but often concurrently led to higher toxicity and environmental issues. Lead (Pb) is an indispensable material for high PCE halide perovskite-based solar cells [24,25] and is well known as a hazardous and toxic material, which

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may induce heavy metal intoxication through gastrointestinal, respiratory, and dermal routes [26]. When PSC devices experience structural failure during usage or at their end of life (EoL), harmful compounds carrying heavy metals may leach into the environment [27]. In addition, although PSCs can be fabricated at a relatively lower cost than silicon-based and thin-film solar cells, valuable and expensive materials are still needed. For example, gold or silver are often used as an electrode and transparent conducting oxides (TCO) (like indium tin oxide (ITO) or fluorine tin oxide (FTO)) are often deposited on glass substrates to serve as a front electrode [25]. After the successful commercialization of PSCs, the usage of these valuable materials (e.g., Ag, Au, In, etc.) will increase dramatically, as will the amount of waste PSC products. Based on the consideration of toxicity, environmental impacts, and sustainable resource usage, the development of effective and efficient recycling technologies for PSCs is urgently needed.

Because the architectures and materials of PSCs are diverse and complex, developing a general and suitable process to recycle and recover the valuable materials of PSCs remains challenging. Nevertheless, some pioneering works have begun to grapple with this issue. An electrochemical method to recycle Pb from hybrid organic–inorganic PSCs using deep eutectic solvents was developed in 2015 [28]. Later, selective dissolution of halide perovskites was used as a step towards recycling PSCs [29]. In 2016, a rapid dismantling process to recover all major components of PSCs and fabricate new PSCs from the recycled substrates was demonstrated [30]. Recently, degraded perovskite films from PSCs were successfully recycled and were found to retain considerable order of crystal structure [31]. High performance all-inorganic CsPbIBr₂ PSCs were crafted by recycling FTO/TiO₂ substrates from the degraded PSCs [32]. Recycling technologies can be as diverse as the architectures and materials of PSCs. Hence, we organize the recycling technologies of PSC into four parts: transparent conductive oxides and electron transport layers, perovskite films and hole transport layers, mitigation of Pb, and reuse of most major components of PSCs. In this review, we summarize the important recycling technologies following the classification noted above and discuss the methods and concerns for future development of recycling and recovery technologies of PSCs.

This review is organized as follows: First, the development and materials of PSCs are introduced. Second, the environmental impacts of PSCs are critically examined. Third, recycling and recovery technologies of PSCs are outlined. Finally, a summary and proposed future works are presented.

Development and materials of perovskite solar cells

The first organic–inorganic lead halide PSC was demonstrated in 2009 [33]. It was assembled with a liquid electrode, possessed a PCE of 3.8%, was stable for only a few minutes, and had a small active area of only 0.24 cm². This initial finding inspired years of intensive study, and two milestone breakthroughs were achieved in 2012: (1) a solid-state PSC with a meso-structured architecture achieved the PCE of 10.9% [34] and (2) an all solid-state PSC with a PCE of 9% and excellent stability over 500 h was demonstrated

[35]. These remarkable studies suggested that PSCs held great promise as emerging third-generation solar cells. In the following years, the PCE of PSCs was continuously enhanced. In 2013, a reported PCE soared over 15%, as demonstrated by Kelly's and Snaith's groups respectively [1,36]. Few years later, a PCE greater than 20% was shown [37]. Recently, the highest PCE of PSCs has surged to over 25%, eclipsing the performance of multi-crystalline Si (22.3%) and thin-film CIGS (22.9%) [38]. As noted above, the PCE of PSCs has dramatically grown more than six times since 2009, promoting research into PSCs as a promising material for photovoltaic technologies. Therefore, to optimize the PCE and even stability, much research worldwide has centered on conducting various process and designing different structures of PSCs, leading to extremely diverse PSC architectures and materials.

Although there are various structures of PSCs, the most common architectures can be classified into four types: mesoporous, planar, inverted planar, and inverted mesoporous, as shown in Fig. 1 [25,39–41]. A typical PSC includes an electron transport layer (ETL), a perovskite absorber layer, and a hole transport layer (HTL), all of which are deposited and synthesized on a transparent conductive oxide (TCO)-coated glass substrate with a metal back electrode on the top of layers (the TCO is used as a front electrode). The layer deposition order and structure differentiate the four types of PSC architectures. The mesoporous type, as shown in Fig. 1a, is the initial PSC architecture [33] and has a perovskite absorber layer covering a porous ETL scaffold. An intermixed layer forms between the perovskite layer and ETL. The planar architecture is similar to the mesoporous but lacks porous structure in its ETL. Because of this, there are no intermixed layers formed in this architecture, as illustrated in Fig. 1b. Inverted planar and the inverted mesoporous architectures can be formed if the deposition order of the ETL and HTL is inverted, as shown in Fig. 1c and d. The inverted types of PSC have also displayed PCEs close to 20% [42].

The perovskite in the absorber layer has an ABX₃ unit cell, which manifests in the crystal as corner sharing three-dimensional octahedron. Both inorganic and organic cations such as cesium (Cs), methylammonium (MA), or formamidinium (FA) occupy the A site. Metal ions with +2 electric charge like lead (Pb), tin (Sn), or germanium (Ge) often occupy the B site. The X site is occupied by –1 charge halogens like chlorine (Cl), bromine (Br), or iodine (I). Both organic and inorganic materials are commonly used in the HTL. Organic HTL materials include spiro-OMeTAD (2,2',7,7'-Tetrakis [N,N-di(4-methoxyphenyl)amino]-9,9'-spirobifluorene) and various polymers like PTAA (poly(triaryl amine)), P3HT (Poly(3-hexylthiophene-2,5-diyll)) [23,43]. Commonly used inorganic HTL materials include carbon, carbon-based structures as graphene and single-wall carbon nanotubes (SWNT) [44], and metal oxides such as nickel oxide (NiOx), Copper(I) thiocyanate (CuSCN), chromium oxide (CrOx), copper oxide (CuOx), and copper chromium oxide (CuCrOx) [45]. Metal oxides are commonly used as ETL materials, such as titanium dioxide (TiO₂), tin dioxide (SnO₂), zinc oxide (ZnO), and ternary oxide zinc stannate (Zn₂SnO₄) [17,46]. A variety of carbon-based materials have also applied, like fullerene (C₆₀), SWNT, PCBM ([6,6]-phenyl-C61-butyric acid

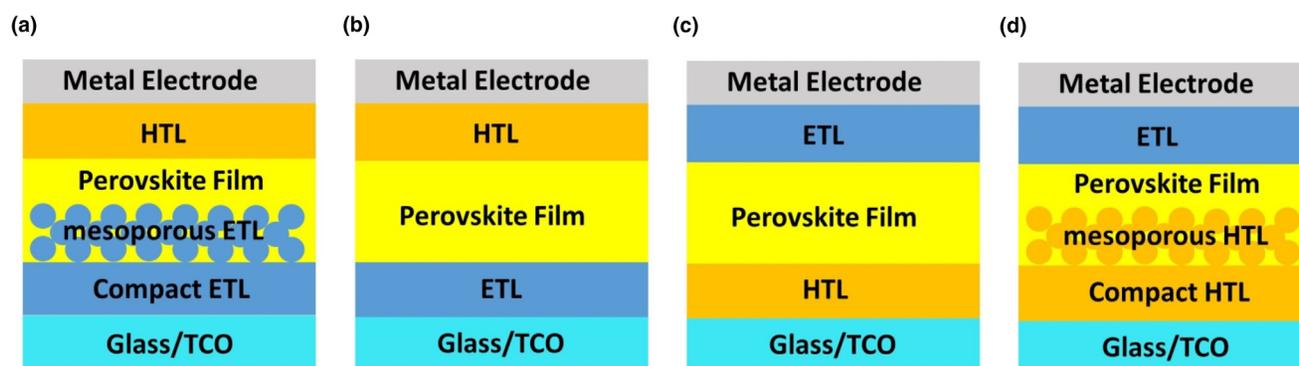


FIGURE 1

Schematic of most common layered structures in perovskite solar cells: (a) mesoporous; (b) planar; (c) inverted planar; (d) inverted mesoporous.

methyl ester), graphene, polymers, and small organic molecules [47]. Similar to thin-film solar cells, TCOs are widely employed in PSCs as front electrodes. Indium tin oxide (ITO) and fluorine tin oxide (FTO) are the most commonly utilized, but PSCs using indium zinc oxide (IZO) and aluminum-doped zinc Oxide (AZO) have also been developed [25]. The back electrode is most commonly composed of highly conductive metals such as gold (Au), silver (Ag), copper (Cu), aluminum (Al), and nickel (Ni) [48]. A selection of materials commonly used for PSC components are shown in Table 1.

Environmental impacts

To analyze the environmental impacts of devices like PSCs, Life Cycle Assessment (LCA) is a common methodology. LCA is regulated by the International Organization for Standardization (ISO) 14,040 family, which offers information on the environmental impacts of materials, products, or services [23]. According to standards in the ISO 14040 and 14044, LCA includes four distinct phases: scope definition, inventory analysis, impact assessment, and interpretation [49–51]. In short for conducting LCA, it is using software (e.g., SimaPro, EcoReport, DO IT Pro, and GaBi4) to analyze how materials, processing methods, and lifetime of products impact the environment through a variety of avenues, including global warming potential, acid potential, and human toxicity potential. LCAs of PSCs have attracted significant attention and have analyzed various parameters such as materials, architectures, and fabrication processes. According to published LCA studies, PSCs show relatively positive out-

comes for the environment [52]. However, the poor stabilities, short lifetimes, necessity for using Au, Ag, and ITO, and toxicity of PSCs bring evitable environmental impacts.

Stability and lifetime

Since the International Summits on Organic Photovoltaics Stability (ISOS) protocols have not yet applied as specific testing standards of stability and lifetime for PSCs [23,53,54], T_{80} , the time at which the performance of a solar cell has reached 80% of its original value in ambient conditions, has been used instead. In early studies of PSCs, poor crystallinity of the perovskite layer resulted in hysteresis and thus brought poor stability. To combat this, additives such as 1,8-diiodooctane (DIO) and N-cyclohexyl-2-pyrrolidone (CHP) were used in the solution processes and resulted in enhanced crystallinity and stability [55,56]. Interfacial engineering was also found to improve PSC stability. Metal oxide, organic, and carbon-based interfaces have all been used to improve charge transport and passivate defects in the HTL, ETL, and buffer layers of PSCs [15,16]. In a seminal work, PSCs with Al-doped ZnO ETLs were found to possess a T_{80} of 500 h in constant 1 Sun illumination [57]. Recently, interfacial engineering of 2D/3D interfaces has been demonstrated as a promising technique to boost PSC stability. Using aminovaleric acid iodide (AVAI) as the 2D/3D interface was recently found to yield an amazing T_{80} of 12000 h in storage [58]. Fig. 2 shows the historical trends of PCE and T_{80} in storage for various materials and architectures of PSCs [23]. These findings suggest that the structural stability of PSCs may not be the critical issue that hin-

TABLE 1

Commonly used materials for each component of PSCs.

Perovskite Layer	HTL	ETL	TCO	Back Electrode
ABX_3 A = Cs, MA, FA B = Pb, Sn, Ge X = Cl, Br, I	Organic: spiro-OMeTAD, PTAA, P3HT Carbon-based: carbon, graphene, SWNT Metal oxide: NiO_x , CrO_x , CuO_x , $CuCrO_x$, $CuSCN$	Metal oxide: TiO_2 , SnO_2 , ZnO, Zn_2SnO_4 Carbon-based: C60, SWNT, PCBM, graphene	ITO, FTO, IZO AZO	Au, Ag, Cu, Al, Ni

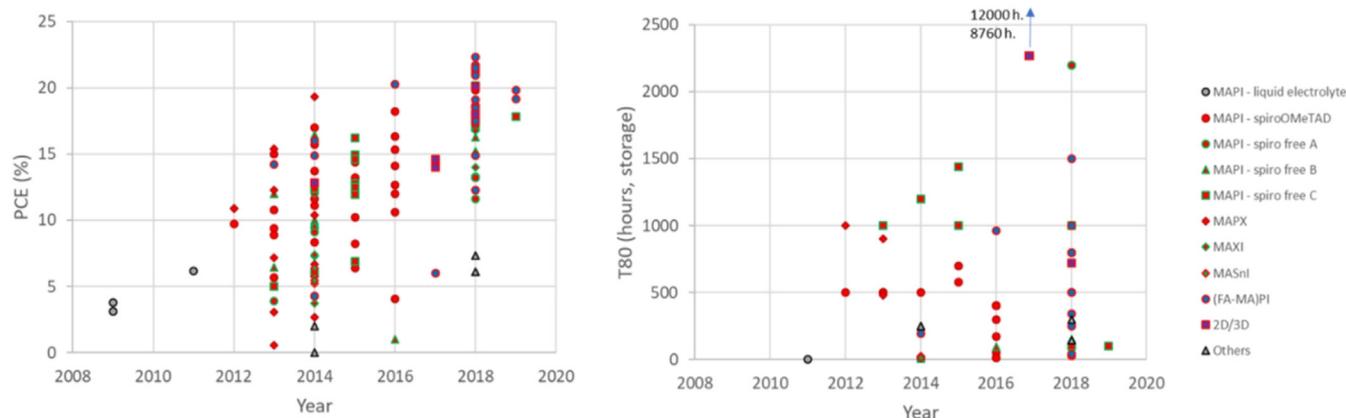


FIGURE 2

Historical trend for PCE and T_{80} in storage for all combinations of materials and architectures of perovskite solar cells [23] Copyright 2020, IOP Publishing.

ders mass commercialization. However, oxygen, moisture, and chemical degradation remain critical challenges for mass application of PSCs.

To be protect PSCs from oxygen, moisture, and weathering, photovoltaic modules are commonly encapsulated. Studies of PSC encapsulation have attracted much attention and have been found to greatly enhance device stability and lifetime [59–63]. PSC encapsulation technologies can be classified into three methods: thin-film, polymer, and glass-glass encapsulation (hereby referred to as TFE, PE, and GGE, respectively). A variety of methods have been used to create thin-film based barrier layers on PSC devices for TFE, including chemical vapor deposition (CVD), plasma-enhanced chemical vapor deposition (PECVD), atomic layer deposition (ALD), plasma-enhanced atomic layer deposition (PEALD), and physical vapor deposition (PVD) [64]. For PE, polymer (e.g., PMMA and Teflon) barrier layers are coated on PSC devices by solution-processed, roll-to-roll, or lamination methods [59,65]. GGE is a typical method for many types of PV-product encapsulation. In GGE, the PSC device is first sandwiched between two glass sheets and then covered with an encapsulant adhesive and a sealant such as ethylene–vinyl acetate (EVA) and butyl rubber [66]. A selection of materials commonly used for PSC encapsulation are summarized in Table 2. In addition, there are mature encapsulation technologies from other commercial photovoltaic products that can be applied to PSCs. The stability and lifetime of PSCs are being continuously enhanced by various strategies, which will enable commercializa-

tion in the coming future. Once PSC modules have a PCE of 18% and a lifetime of 20 years, they will be competitive in the market of photovoltaic products [67]. The increase in demand for critical materials and widespread application of toxic substances from the eventual commercialization of PSCs will present a new challenge.

Critical materials for PSCs

Critical materials, as described by Critical Materials Institute of the U.S. Department of Energy (DOE), are substances used in technology that have supply risks, and for which there are scarce substitutes. Every governmental organization has its own definition and category of critical materials. For example, the DOE classifies rare earths like dysprosium, terbium, europium, neodymium, yttrium, lithium, and tellurium as critical materials [68] while European Commission even includes natural graphite and rubber [69].

For PSCs, the indium (In) used in TCOs is official recognized as a critical material worldwide. Because In is expensive and scarce, FTO has been used to replace ITO because of its good performance, simple processing, and no obvious stability reduction [70]. It is notable that tin (Sn) used in FTO is regarded as a strategic material in the EU due to its low substitution potential and limited production countries [71,72]. Nearly all metals used in the back electrode of PSCs (Au, Ag, Cu, Al, and Ni) are expensive and are extensively used in industry. Therefore, the metal supply chain should be considered if PSCs are rapidly commercialized. Iodine (I), as a necessary non-metallic element in PSCs, is a naturally scarce material due to its relatively low abundance on earth [52,73,74]. Hence, although I is not a widely recognized critical material, the prices of I are volatile and the large amount needed for PSC production may cause significant price fluctuations. Another important element in perovskite structures is Pb, which is regarded as a critical material by both the Canadian and the Dutch governments [68]. Though Sn-based PSCs have been developed to avoid the controversial toxicity of Pb-based PSCs, Sn-based PSCs have been shown to possess inferior PCE and stability to those based on Pb [75]. Since Pb plays an important role in the PSC development, the potential issue of toxicity should be seriously discussed and considered.

TABLE 2

Commonly used materials for PSC encapsulations.

Thin Film Encapsulation	Polymer Encapsulation	Glass–Glass Encapsulation
Al_2O_3 , SiN_x , SiO_x , Organosilicon	Teflon, PMMA, PET, PTFE, PC, ORMOSIL aero-gel, Cyclized perfluoropolymer, Fluoropolymer, Adamantane, Ethylene vinyl alcohol	EVA, butyl rubber, UV curable epoxy, PIB blanket, Surlyn ionomer, Hermetic glass frit

Toxicity

Pb is usually considered to be the major source of toxicity in PSCs, which has promoted many LCA studies. However, Sn, as a critical material in TCOs and Pb alternative in perovskite layers, has also been found to potentially induce detrimental environmental and health effects [26,76,77]. The upper limit for safe levels of lead in blood is 10 µg/dl for adults and 5 µg/dl for children [78]; and the normal range for tin levels in blood is from 2 to 9 µg/L [79]. For commercialization and industrialization of PSCs, the toxicity of both Pb and Sn should be understood and considered. Pb has been observed to enter human body through gastrointestinal, respiratory, and dermal routes, inducing impaired functionality of enzymes and receptors and causing heavy metal intoxication in breastfed infants [26]. Chronic exposure to Sn has been found to result in effects similar to Pb poisoning, also seriously harming the human body [77,80].

Since the toxicity of PSCs is a serious and evitable concern, many LCA studies have been done to evaluate exact environmental impacts. Leaching of Pb from PSC panels during their lifetime is the major concern for the toxicity of PSCs. Pb from the leachate of a broken PSC panel was found to result in a low level of contamination compared to background values of Pb in urban areas, which is undesirable to the environment yet not catastrophic [81]. If PSCs were used to supply the USA's demand for electricity, the total amount of Pb used in PSCs would still be much lower than that from car and aviation emissions per year [82]. Recently, as indicated by Baxter's group, the toxicity potential of PSCs over a 20-year operational lifetime was determined to be approximately 20 times lower than that of grid electricity [83]. Most studies have concluded that the toxicity during PSC lifetime is not a serious concern compared to other Pb-containing products. Nonetheless, large amounts of PSCs at their end of life will still be a critical issue when commercial PSC products are implemented extensively, so recycling and recovery technologies of PSCs should be intensively developed.

Recycling and recovery technologies of PSCs

Recovering valuable materials and recycling toxic metals from PSC products is urgent and necessary for both technical and environmental demands and international regulations. In 2012, the European Union established Directive 2012/19/EU to manage and regulate waste electrical and electronic equipment (WEEE) [84]. The regulation requires that producers take responsibility for collecting, recycling, and recovering waste products. In addition, China, as one of the largest markets in the world, has similar regulations [85,86]. Accordingly, the commercialization of PSCs will be regulated by these directives which promote the importance of recycling and recovery technologies of PSCs. Although recycling and recovery technologies of photovoltaic products are progressing quickly [87], such technologies for PSCs are currently under developed. Several groups have tried to conquer this challenge with their proposed studies. In this section, the proposed technologies are classified by which PSC component they effect: (i) TCO (FTO/ITO) and ETL, (ii) perovskite layer and HTL, (iii) Pb, and (iv) recycle and reuse most major components (three or more from TCO/ ETL, HTL, Pb, and back elec-

trodes). Table 3 illustrates the recycling and recovery technologies introduced in this review.

TCO (FTO/ITO) and ETL

Because TCOs are quite expensive components of PSCs, developing strategies to recycle and reuse TCOs from waste PSCs is the priority for economic viability of PSCs. In 2016, a pioneering study first demonstrated that efficient ETL-free PSCs would be fabricated via recycling FTO/glass substrates from degraded devices [88]. N, N-Dimethylformamide (DMF) was used to dissolve the perovskite layers and HTLs from glass/FTO/CH₃NH₃-Pb_{3-x}Cl_x/spiro-MeOTAD/Ag samples but maintain the FTO/glass substrates. Then, the FTO/glass substrates were reused to fabricate new PSC devices, as shown in Fig. 3a. The UV-vis optical transmission, crystal structure, sheet resistance, surface morphology, elemental composition, and static contact angle measurement of the recycled FTO/glass substrates demonstrated almost no difference compared to the original substrates. The refabricated ETL-free PSC devices showed PCEs of about 10%, which were comparable to the original devices. A similar study examined the ability to recycle not only FTO but also the TiO₂ ETL from PSCs with a glass/FTO/compact or mesoporous TiO₂ (c-TiO₂ or m-TiO₂)/spiro-MeOTAD/Ag architecture [89], as shown in Fig. 3b. The recycled FTO/TiO₂ substrates were used to craft new planar and mesoporous PSCs with peak efficiencies of 11.87% and 11.03%, respectively, which were slightly poorer than that of the devices based on the virgin substrates. ITO/glass substrates from inverted planar glass/ITO/PEDOT:PSS/MAPbI₃/PC60BM/Ca/Al PSCs have also been recovered using a potassium hydroxide (KOH) solution treatment, as depicted in Fig. 3c [90]. The recovered ITO substrates possessed transmittance and electrical uniformity similar to that of the original. Additionally, the KOH solution treatment increased the wettability of ITO surfaces, which has been shown to improve the contact area between the component layers and enhance the PCE. Recently, as illustrated in Fig. 3d, DMF was employed to recycle FTO/TiO₂ substrates from carbon-based, all-inorganic PSCs with a glass/FTO/TiO₂/CsPbI₃Br₂/carbon architecture (which have the most balanced stability and band gap features among typical inorganic halide PSCs) [32]. The recycled FTO/TiO₂ substrates maintained comparable optical and electrical properties, and the residual CsPbI₃Br₂-derived species on the recycled FTO/TiO₂ substrates was found to suppress halide phase separation and reduce defects of the upper CsPbI₃Br₂ film, which yielded a ~25% improvement in average PCE, from 6.51 ± 0.62 to 8.14 ± 0.63%, and the champion cell produced a high PCE of 9.12% [32].

These studies suggest that TCO/TiO₂ substrates can be effectively recycled, recovered, and reused from PSCs with various architectures, structures, and materials. Moreover, in some cases, the residuals on recycled substrates were even observed to enhance the performance of PSC devices. Note that KOH may not be a suitable solution for recycling perovskite layers of PSCs because K⁺ ions can interfere with separation or recovery process of the mixed solution [91]. Since the fabrication of TCO/ETL substrates from raw materials brings high costs and many environmental impacts [27], recycling and reusing TCO/ETL substrates stands as a remarkable method for economical and sustainable

TABLE 3

Present recycle and recovery technologies of PSCs.

Components or Materials	Architectures	Key Methods	Recycled/Recovered Materials	Refs.
TCO and ETL	glass/FTO/CH ₃ NH ₃ Pb _{3-x} Cl _x /spiro-MeOTAD/Ag	Dissolution by DMF	glass/FTO	[88]
	glass/FTO/c-TiO ₂ or (c-TiO ₂ /m-TiO ₂)/spiro-MeOTAD/Ag	Dissolution by DMF	glass/FTO/TiO ₂	[89]
	glass/ITO/PEDOT:PSS/MAPbI ₃ /PC60BM/Ca/Al	Dissolution by KOH	glass/ITO	[90]
	glass/FTO/TiO ₂ /CsPbI ₂ Br ₂ /carbon	Dissolution by DMF	glass/FTO/TiO ₂	[32]
Perovskite Film and HTL	glass/FTO/TiO ₂ /MAPbI ₃ /spiro-OMeTAD/Au	Dissolution by chlorobenzene, reuse of undegraded perovskite films	MAPbI ₃	[93]
	glass/FTO/TiO ₂ /MAPbI ₃	Recovery from PbI ₂ using MAI	MAPbI ₃	[31]
	glass/FTO/c-TiO ₂ /m-TiO ₂ /MAPbI ₃ /spiro-OMeTAD/Ag	Dissolution by chlorobenzene, thermal decomposition	MAPbI ₃	[94]
Pb	glass/FTO/TiO ₂ /MAPbI ₃ , FAPbI ₃ , or MAPb _{3-x} I _x	Dissolution by eutectic solvent, electrodeposition	Pb	[28]
	glass/FTO/TiO ₂ /MAPbI ₃ /spiro-OMeTAD/Au	Extraction by water, dissolution by DMF, reuse of PbI ₂	PbI ₂	[98]
	glass/FTO/c-TiO ₂ /m-TiO ₂ /MAPbI ₃ /carbon	NH ₃ -H ₂ O treatment, HI treatment	PbI ₂	[99]
All Major Components	glass/FTO/c-TiO ₂ /m-TiO ₂ /MAPbI ₃ or (FAPbI ₃) _{0.85} (MAPbBr ₃) _{0.15} /spiro-OMeTAD/Au	Dissolution by DMF, extraction by ether, ion-exchange by hydroxyapatite	glass/FTO/TiO ₂ , Pb, Au	[29]
	glass/FTO/c-TiO ₂ /m-TiO ₂ /MAPbI ₃ /spiro-OMeTAD/Au	Dissolution by chlorobenzene, ethanol treatment, dissolution by DMF	glass/FTO/TiO ₂ , Pb, Au	[30]
	glass/FTO/c-TiO ₂ /m-TiO ₂ /MAPbI ₃ /mp-Al ₂ O ₃ /np-Au:NiO _x	Special design for reusing most components but perovskite layer.	glass/FTO/c-TiO ₂ /m-TiO ₂ /mp-Al ₂ O ₃ /np-Au:NiO _x	[104]

purposes. Currently, reusing highly pure glass substrates from silicon-based PV waste panels is challenging because the silicon absorber layers are difficult to remove [92]. Conversely, perovskite absorber layers can be easily removed by dissolution in DMF, which is promising for industrializing recycling and reuse of TCO/ETL substrates from PSCs.

Challenges with recycling perovskite film and HTL

The absorber perovskite films play a key role in PSC devices, but their instability and toxicity of Pb are issues for the waste management of PSCs. One suitable approach is to recycle and recover perovskite films from waste PSC devices. In 2018, it was reported that the thermal performance degradation of planar PSCs with glass/FTO/TiO₂/MAPbI₃/spiro-OMeTAD/Au architecture might be involved with the deformation of spiro-OMeTAD HTLs at high temperature [93]. Thus, the unaffected perovskite films were worthy to be reused. The thermal deformed spiro-OMeTAD HTL was removed using chlorobenzene, but the perovskite film remained on the FTO/TiO₂ substrate from a thermal performance degraded PSC device, and then a new spiro-OMeTAD layer was coated on the recycled device. To assess the structural differences before and after heating the perovskite films, X-ray diffraction (XRD) and scanning electron microscopy (SEM) were conducted. The results showed that the perovskite films possessed similar structures before and after heating. The cell performance of refabricated devices was found to be slightly lower than the initial values because the modified perovskite/spiro-OMeTAD interface enhanced the recombination after recycling [93]. Additionally, new perovskite films could be recovered from residual lead iodide

(PbI₂) left on degraded MAPbI₃ PSC devices by spin coating methylammonium iodide (MAI) in isopropyl alcohol (IPA) solution and then annealing. In another study, recycled perovskite films formed via single-step chloride, single-step acetate, and sequential deposition routes were compared, as illustrated in Fig. 4a. Photoluminescence (PL) efficiency and crystal structure analysis (i.e., SEM, XRD) revealed the single-step acetate route created perovskite films were more efficiently recycled and recovered [31]. These results demonstrate that recycled perovskite films can retain both considerable PL efficiency and crystal structure. The XRD patterns of the recycled films are shown in Fig. 4a_{ii} and a_{iv}. Note that recycled PbI₂ was not be used to fabricate a new device for the further PCE analysis. Recycled PSC devices with an enhanced PCE of 14.84% (compared to the pristine PSC with a PCE of 14.35%) were fabricated through a thermal process that transformed degraded MAPbI₃ perovskite films left on glass/FTO/c-TiO₂/m-TiO₂ substrates, as shown in Fig. 4b_i [94]. SEM and XRD (Fig. 4b_{ii}) were used to examine the structure of the recycled perovskite film. The PCE enhancement was attributed to the formation of mesoporous PbI₂ scaffolds that facilitated perovskite crystallization after the thermal process.

These two studies highlight both the difficulty of reusing HTLs and the possibility of recycling perovskite films from EoL PSCs. Maintaining the performance of organic spiro-OMeTAD HTLs in recycled cells was found to be difficult because spiro-OMeTAD could deform and degrade easily due to crystallization, photo-oxidation, and Au diffusion [95–97]. Unlike Spiro-OMeTAD HTLs, degraded MAPbI₃ perovskite films can be recov-

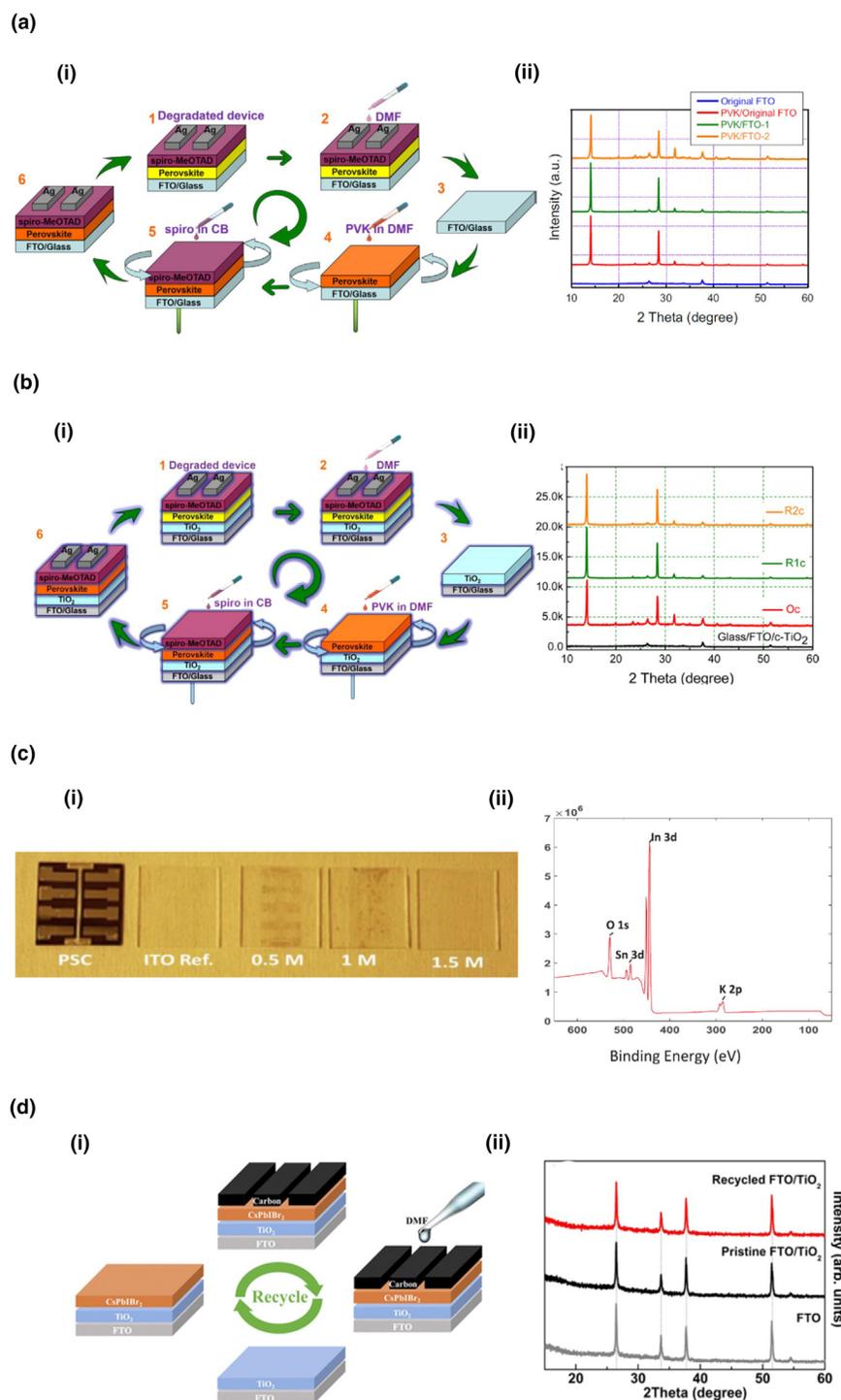


FIGURE 3

(a): (i) Schematic illustration of the process of fabricating efficient ETL-free PSCs using the recycled FTO/glass substrates from the degraded devices and (ii) XRD patterns of the original, once-recycled (FTO-1), and twice-recycled (FTO-2) FTO/glass substrates [88] Copyright 2016, Elsevier. (b): (i) Schematic illustration of the process to fabricate efficient PSCs by recycling the glass/FTO/TiO₂ substrates from the degraded devices and (ii) the XRD patterns of perovskite films deposited on the original and recycled glass/FTO/c-TiO₂ substrates [89] Copyright 2017, American Chemical Society. (c): (i) Effect of various KOH concentration in recovery of intact patterned ITO substrate from an inverted PSC and (ii) the XPS analysis of sample recovered from PSC with 1.5 M KOH [90] Copyright 2019, Elsevier. (d): (i) Schematic illustration of the steps to recycle FTO/TiO₂ substrate from a degraded carbon-based, all-inorganic PSC for fabricating a new device and (ii) the XRD patterns of recycled and pristine FTO/TiO₂ [32] Copyright 2020, American Chemical Society.

ered, which is promising for further recycling technology. Perovskite-recovery studies need to be conducted with a special attention paid to scaling to large areas. If perovskite films can

be recovered and reused on large-area substrates, PSCs may bring less environmental impacts than present PV products. Moreover, because current recycling technologies of perovskite films and

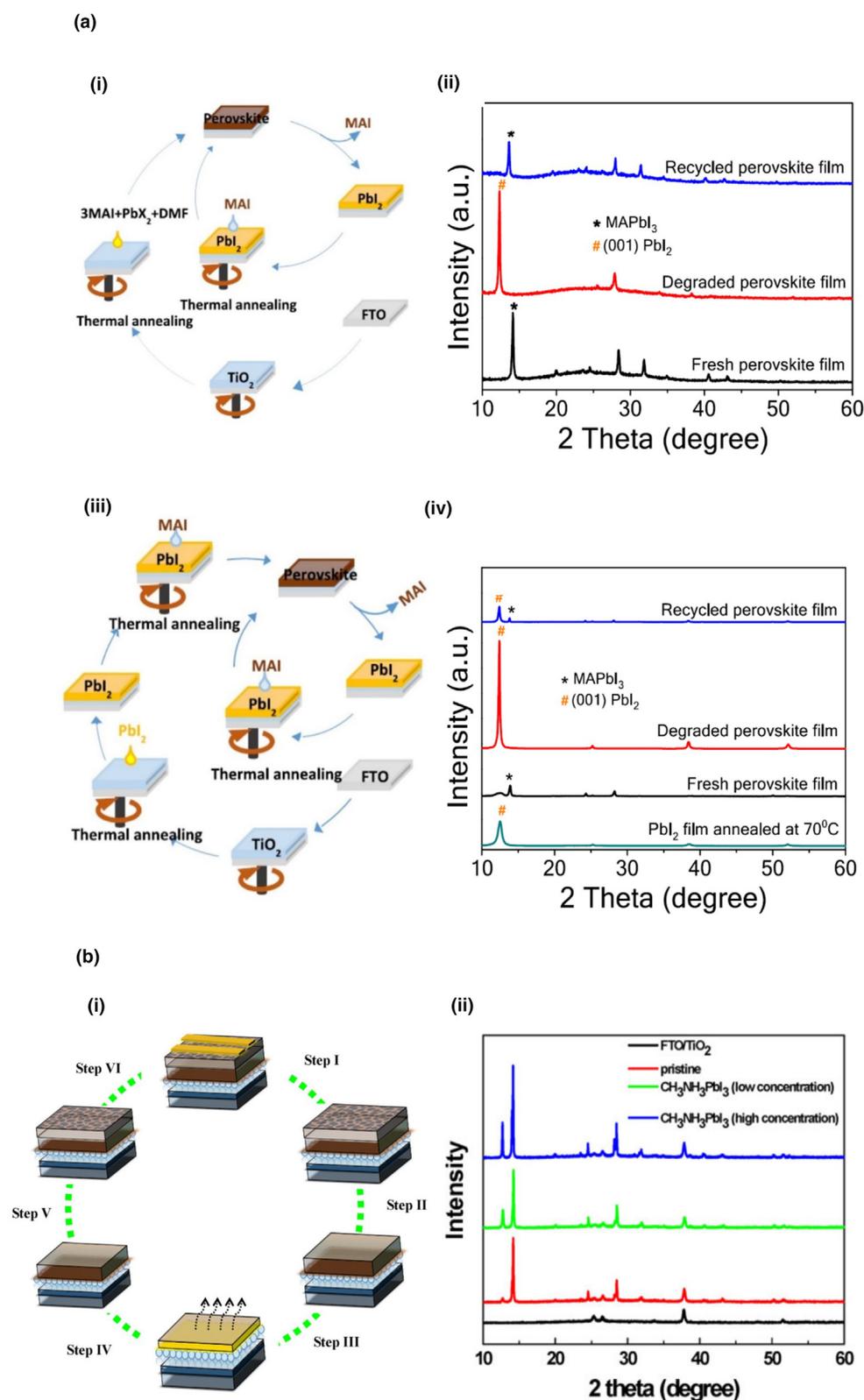


FIGURE 4

(a) Schematic illustration of the recycling process for MAPbI₃ films deposited by (i) single-step chloride and single-step acetate route and (iii) sequential deposition route. XRD patterns of freshly deposited perovskite film, degraded perovskite film left with PbI₂, and the recycled perovskite film for (ii) single-step acetate and (iv) sequential deposition routes [31] Copyright 2019, American Chemical Society. (b) (i) Schematic illustration of in situ recycling PbI₂ from PSCs and the sequential fabrication of new PSC devices. *Step I*: Removing Ag electrode using adhesive tape. *Step II*: Removing the HTM by immersing in chlorobenzene solvent. *Step III*: Thermal decomposition of the perovskite films into solid PbI₂ residues and emitted organic gases. *Step IV*: Developing new perovskite films by spin coating a CH₃NH₃I solution. *Step V*: Preparing spiro-OMeTAD layer. (VI) Evaporating Ag electrode. (ii) XRD patterns of the pristine PbI₂ and recycled PbI₂ heated for 30 min [94] Copyright 2017, Wiley.

HTLs only focus on the MAPbI₃/spiro-OMeTAD PSCs, recycling and recovery technologies for other perovskite films and HTLs should be investigated and developed.

Pb

Although Pb is not a highly valuable metal that needs to be recovered from waste PSCs for economic reasons, the notorious toxicity of Pb makes recycling Pb from EoL PSC devices a priority for environmental reasons. In 2016, an electrochemical method to recycle Pb was first used on PSCs [28]. A deep eutectic solvent (DES) comprised of choline chloride (ChCl) and ethylene glycol (EG) was used to dissolve the perovskite layers of PSCs with glass/FTO/TiO₂/MAPbI₃, FAPbI₃, or MAPb_{3-x}I_x architecture. Then, Pb was deposited and stripped on a Pb working electrode via electrodeposition in the perovskite-containing solution, as shown in Fig. 5a. This study demonstrated an excellent recovery rate of up to 99.8% Pb removal from the solution. Furthermore, an approach to recycle Pb and reuse FTO from PSCs with a glass/FTO/TiO₂/MAPbI₃/spiro-OMeTAD/Au architecture was developed [98]. This strategy worked by breaking down PSCs layer by layer, avoiding impurities to the target materials for recycling, as shown in Fig. 5b. After removing the Au electrode and HTL, the perovskite layer on the PSC was transformed into MAI and PbI₂ in water, and then the MAI was extracted by water. Accordingly, the PbI₂ was dissolved and recycled by DMF, and the recycled PbI₂ and FTO substrate were then used in the fabrication of new PSCs. PSCs fabricated from the materials recovered by this layer-by-layer technology demonstrated a PCE of 13.5%, which was slightly lower than that of PSCs (14.6%) prepared from highly pure PbI₂ (99%+, Sigma-Aldrich). This lower PCE most likely originated from a very small amount of impurities in the recycled PbI₂. In a later study, cyclic utilization of Pb in carbon-based PSCs was demonstrated [99]. The carbon-based PSCs with a glass/FTO/c-TiO₂/m-TiO₂/MAPbI₃/carbon architecture were simply treated with NH₃·H₂O, to obtain Pb(OH)₂ from Pb in the PSCs. After hydroiodic acid (HI) treatment, PbI₂ was obtained with a Pb recovery rate of 96.7%. The cyclic utilization process is shown in Fig. 5ci. The PCE of the refabricated carbon-based PSC using recycled PbI₂ was 11.36%, while the carbon-based PSC using commercial PbI₂ demonstrated a PCE of 12.17%. Since the perovskite films fabricated with commercial and recycled PbI₂ had similar structures (as shown in Fig. 5cii), the lower PCE of refabricated PSC could be ascribed to impurities in the recycled PbI₂.

These approaches have begun to address the Pb issue of PSCs. Although the Pb recovery rates of these studies were decent, the PCEs of the PSCs made using recycled PbI₂ were slightly lower than those using new PbI₂. Impurities in recycled PbI₂ have been identified as a potential source of the reduced efficiency. Raw materials used for electrical industries are often requested to be highly pure to meet fabrication standards or regulations. Therefore, purification strategies for recycled materials and recycling and recovery processes should be optimized to prepare for large amounts of EOL PSC devices. In addition, since more complicated structures of PSCs display better PCEs and stabilities (such as Cs_{0.05}(MA_{0.17}FA_{0.83})_{0.95}Pb(I_{0.83}Br_{0.17})₃ [100]), recovering and separating highly pure Pb-containing raw materials from PSCs will remain challenging. The lead acid battery industry has devel-

oped some very mature Pb recycling and technologies, such as electrodeposition and precipitation [101–103]. Therefore, Pb recycling and recovery from PSCs may have a relatively higher potential for industrial applications than other PSC components.

Recycling most components

Out of laboratories and facing the real situation, a practical technology cannot recycle highly valuable materials from waste products but disposal other components with less valuable materials. Thus, a general strategy should be considered to design the process to recycle and recover target materials in major components from waste devices. Two main strategies for PSC recycling and recovery have been proposed. The first is a one-step method using DMF as a polar aprotic solvent to separate most major components of PSCs (i.e., TCO, ETL, Pb from perovskite layer, back electrode) simultaneously, as shown in Fig. 6a [29]. When used on glass/FTO/c-TiO₂/m-TiO₂/MAPbI₃ or (FAPbI₃)_{0.85}(MAPbBr₃)_{0.15}/spiro-OMeTAD/Au architectures, the perovskite layer and HTL were selectively dissolved by DMF becoming a mixed solution, and the glass/TCO/ETL substrate and back electrodes were left. 99.99% of the Pb content in the mixed solution was removed by solvent extraction using ether and the ion-exchange. The Au electrodes were found to contain 0.41% Pb impurities, which suggested the need for a refining process; the glass/FTO/c-TiO₂/m-TiO₂ substrate was reused to fabricate a new PSC with comparable PCE.

The other strategy for PSC recycling and recovery involves a layer by layer dismantling and recovery of most major components. As shown in Fig. 6b, a PSC with glass/FTO/c-TiO₂/m-TiO₂/MAPbI₃/spiro-OMeTAD/Au architecture was first treated with chlorobenzene to dissolve the HTL and recycle the Au electrodes. Then, ethanol was employed to remove MAI and leave PbI₂ from the MAPbI₃ layer. Finally, the PbI₂ on the glass/FTO/c-TiO₂/m-TiO₂ substrate was recycled by DMF [30]. To recover Pb in the mixed DMF solution, Payne's electrodeposition method was recommended [28]; the recycled glass/FTO/c-TiO₂/m-TiO₂ substrates were then reused to fabricate PSCs with a PCE of 15–16%.

Note that neither of these attempts to recycle and recover materials from PSCs was able to actually recover or reuse all major components. For example, HTLs and perovskites were removed but not reused or recovered as raw materials or other pure compounds. Nevertheless, these two studies did propose two fundamentally different strategies and concepts to design a mature process for recycling and recovering PSC devices. Each strategy had some inherent drawbacks. The one-step method displayed a fast and feasible process but dissolved some components in a same solution, complicating further separation. Layer by layer recycling of PSC components necessitates the use of many solvents, all of which were found to contain Pb impurities, which stand as an impediment to recovering highly pure raw materials. Since PSC technologies are still in the research and development stage, it is hard to decide which is the most suitable strategy from these two studies. However, these strategies can be helpful in the design of PSC products to facilitate recycling and recovering EOL devices. For example, a special PSC design with a glass/FTO/c-TiO₂/m-TiO₂/MAPbI₃/mp-Al₂O₃/np-Au:NiOx architecture that could be reused repeatedly was proposed, by replacing the

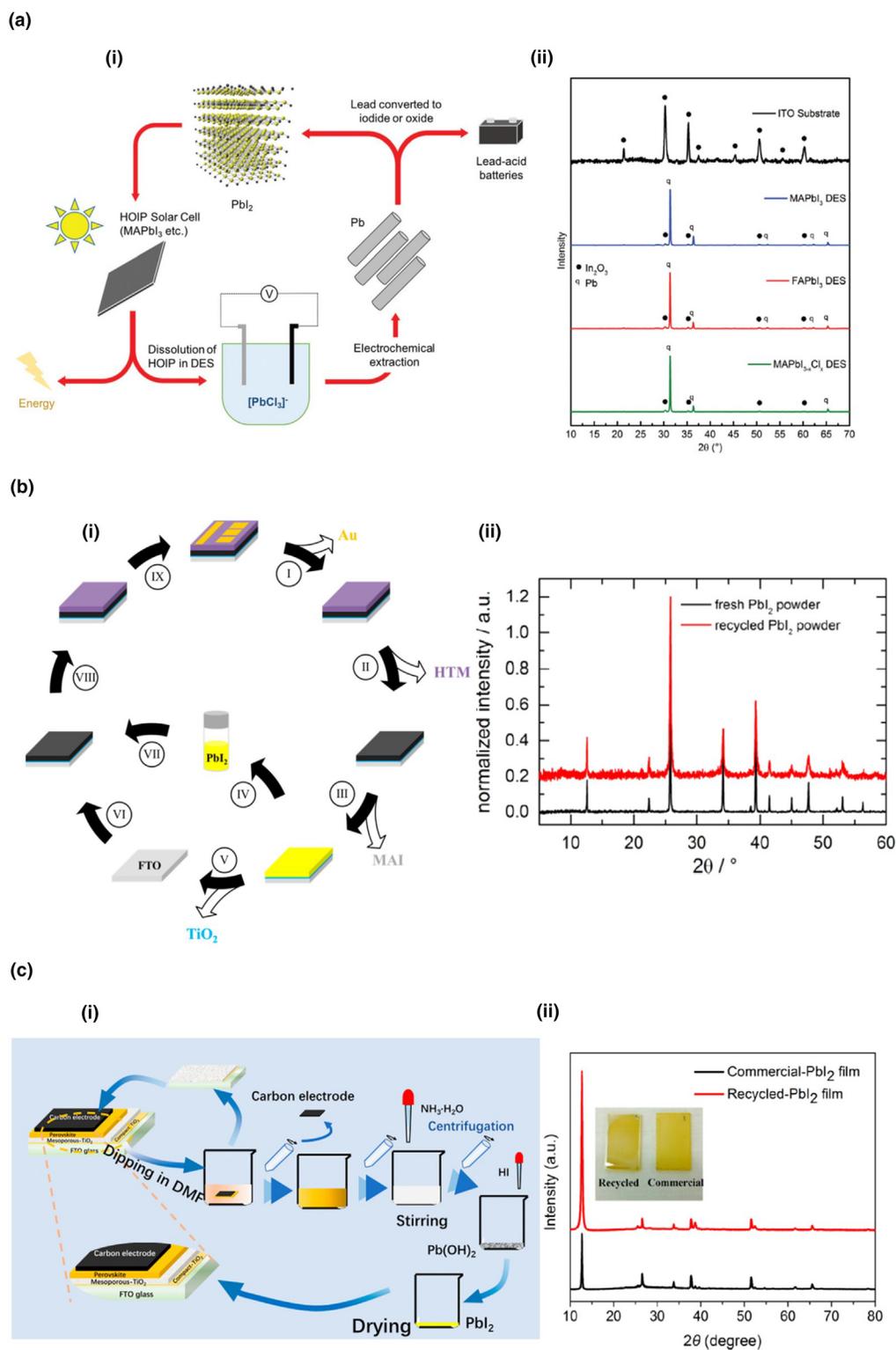
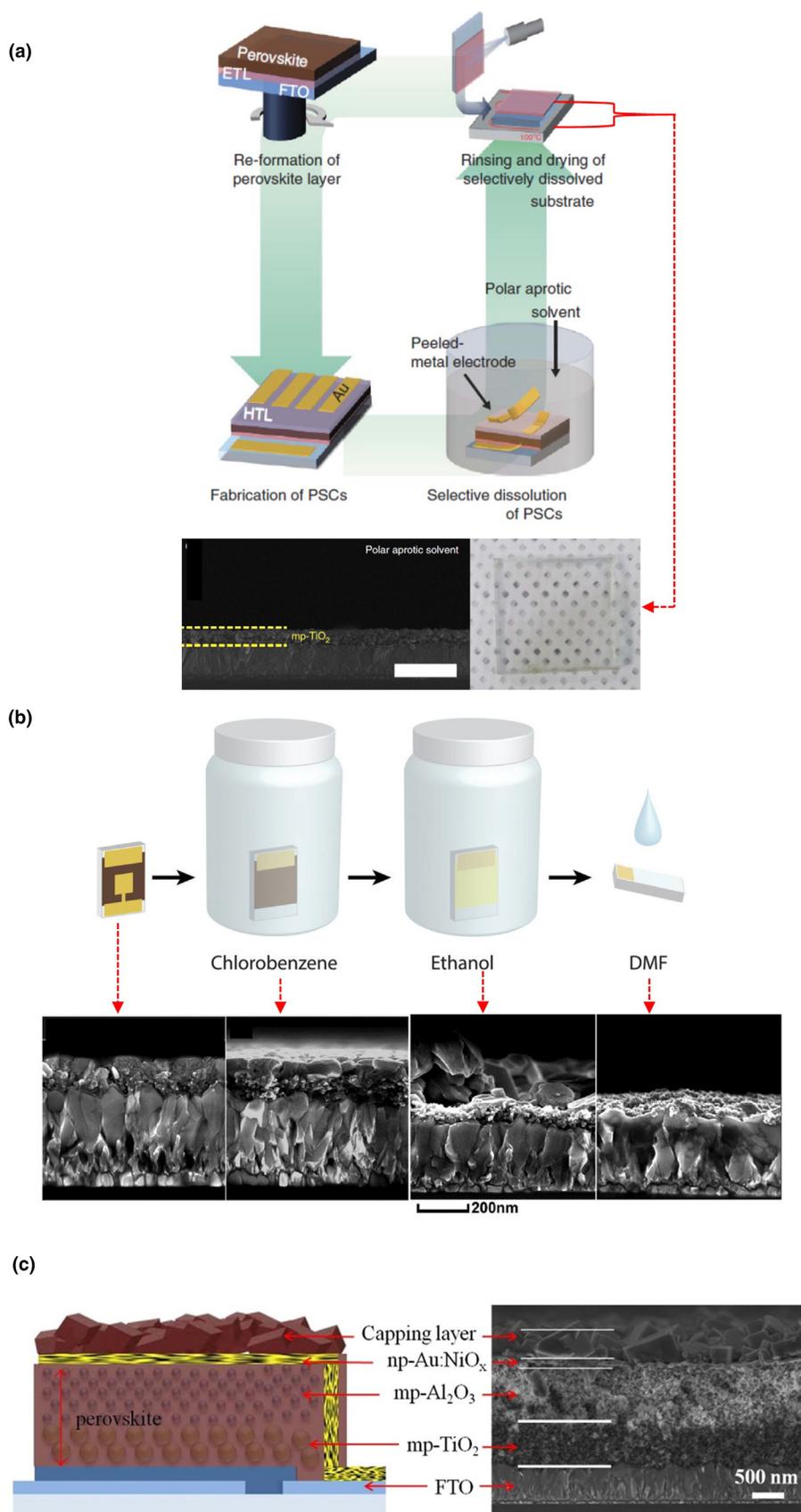


FIGURE 5

(a): (i) Schematic illustration of the deep eutectic solvent based electrochemical recycling process, demonstrating a route of regenerating HOIP material, or getting metallic lead back into the supply chain. (ii) XRD patterns of Pb electrochemically deposited on ITO from each HOIP-DES (a blank ITO substrate is used as control) [28] Copyright 2016, Royal Society of Chemistry. (b): (i) Schematic illustration of the recycling process for PSCs, including (I) Removing Au electrode with adhesive tape, (II) Removing the HTM by immersing in chlorobenzene, (III) Transformation of the perovskite film into MAI and PbI₂ and extracting MAI in water, (IV, V) Removing PbI₂ and TiO₂ by DMF, (VI) Fabricating a new TiO₂ film, (VII) Formation of the perovskite film on the recycled FTO substrate from recycled PbI₂, (VIII) Preparing the HTM layer, and (IX) Evaporating the Au top electrode. (ii) XRD patterns of recycled and fresh PbI₂ [98] Copyright 2016, American Chemical Society. (c): (i) Schematic illustration of cyclic utilization process of lead from carbon-based PSCs [99]. (ii) XRD patterns of the recycled PbI₂ film and commercial PbI₂ film. Copyright 2018, American Chemical Society.

**FIGURE 6**

(a) The detailed process of recycling PSCs via selective dissolution and cross-sectional FESEM and digital images of dissolved PSCs obtained after treatment with polar aprotic solvents [29]. Copyright 2016, Springer Nature. (b) The process outline and the corresponding cross-sectional SEM images of PSCs in each process: PSC devices were immersed into chlorobenzene, after completed dissolution of the HTL and removal of the cathode, ethanol was used to dissolve MAI, and small amounts of PbI₂ was completely removed using small amounts of DMF [30]. Copyright 2016, Royal Society of Chemistry. (c) The device configuration of the nanoporous electrode-based PSCs [104]. Copyright 2017, American Chemical Society.

degraded perovskite layer but keeping other components, as illustrated in Fig. 6c [104].

Conclusions and outlook

PSCs are an emerging and rapidly evolving photovoltaic technology that have a chance to dominate the photovoltaic market due to their low cost and high PCEs. Following their commercial success, large amounts of end-of-life PSC products will bring dramatic environmental impacts. This review summarizes the present recycling and recovery technologies of PSCs and provides considerations for establishing a complete PSC-recycling process. The most expensive components of PSCs, the glass/TCO substrates (and even with TiO₂ ETLs), can be reused for new PSCs with descent performances, which alleviates the demand for critical materials (e.g., In, Sn). Unfortunately, the current studies provide limited information for practical recovery or reuse because commercial perovskite films and HTLs may contain many elements whose recyclability have not yet been studied. The recycling and recovery methods of Pb should be modified and refined due to the increasingly complicated compositions of perovskite layers in PSCs. PSCs can be recycled either via layer-by-layer or one-step methods, and while both processes have been initially demonstrated, further optimization and investigation is needed.

Considering the summary notes above from the present technologies, a future blueprint to recycle and recover PSCs can be outlined. Except glass/TCO substrates may be reused as components, every major PSC component should be recovered to raw materials. The industrial standards and specifications (e.g., materials, proportion of ingredients, and product design) of electronic products are often adjusted for the highly competitive market, and EOL products may have significantly different components than new generation ones. Because of the ever evolving nature of electronic devices, the reuse of most components (e.g., ETL, perovskite layer, HTL, and back electrode) of waste PSCs is not practical. A better strategy to address the challenge of end-of-life PSC products is developing technologies to recycle and recover waste PSC devices to raw materials with high stability and purity, which can then be used not only for PSCs but also in other industrial manufacturing processes.

There are mature industrial technologies that may be applied in recycling and recovering EoL PSCs into raw materials. Electrolysis, active carbon, ion-exchange resins, chemical reduction, and solvent extraction can be used to recover back electrodes (i.e., Au or Ag) [105–108]. In addition to reuse for PSC fabrication, glass substrates may also be used in the rubber industry after being ground into powders, to increase hardness and wear resistance of products [109,110]. The halogens in perovskite layers can be separated via distillation [111]. Encapsulation materials can be recycled by pyrolysis and chemical decomposition [112], which are often used in the plastic-recycling industry. Additionally, pyrometallurgy and hydrometallurgy, often used in lead-acid batteries recycling, may be applied to recover Pb in PSCs [113]. However, developing and integrating the above technologies to a general recycling and recovery process for PSCs requires significant research effort. Both academia and industry are needed to integrate recycling and manufacturing into a circular process,

which may promote PSCs as relatively green and eco-friendly commercial products. In addition, an integrated circular process may potentially cause secondary pollution and waste (e.g., using strong acids, high thermal budget, and waste solutions), so Life Cycle Assessment is necessary to evaluate and avoid possible environmental impacts.

Previous experience from older generation waste PV management (i.e., silicon, thin film) suggests that incentive policies and effective infrastructures are necessary to develop and implement recycling and recovery of PSCs. Governments will play important roles in organizing policies and regulations to encourage and enforce environmentally friendly commercialization and recycling protocols of PSCs. For example, all PV modules sold to EU member states are regulated by the Waste Electrical and Electronic Equipment (WEEE) Directive, which compels manufacturers to design products that can be easily recycled and recovered, take responsibility for recycling EOL PV products, and build recycling infrastructure. As a huge market of PV products, the U. S. should keep up the pace to make direct policies and legal responsibilities for manufacturers related to PV recycling. A business model including PSC manufacturing and recycling needs to be established at the commercialization stage. Based on the model, governments can then build policies and regulations to facilitate the PSC commercialization and recycling.

In summary, with suitable policies, regulation, and integrated technologies, PSCs can be potentially sustainable PV products by reusing or producing raw materials recovered from waste PSC modules.

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.

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