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Recycling progress of organic-inorganic perovskite solar cells for eco-friendly fabrication

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Abstract: Perovskite solar cells (PSCs) has been regarded as a promising next-generation photovoltaic technology with an unprecedented development on power conversion efficiency (PCE) during a decade exploitation because of the intriguing optoelectronic natures of perovskite materials. Although the certificated PCE of PSCs has been enhanced up to 25.5% in a single-junction structure, the tender long-term stability is still a critical restraining factor for commercial application, because the frail stability of organic-inorganic perovskite materials inevitably induces the degradation of photoactive layer, reduction of devices' photovoltaic performance, increase of fabrication cost and impact of potential application. Moreover, the degradation of perovskite materials cannot flee the leakage of lead compounds, which will lead to healthy and ecological-environmental issues. Therefore, it is necessary to recycle PSCs components for industrial fabrication-application. In this review, we discuss the necessities of recycling and different recycling methods, including the recycling of transparent conductive oxide substrates without/with carrier transport materials, toxic lead compounds of perovskite, metal electrode and monolithic structure. Moreover, the recycling protocol has been discussed according to the various stacked architectures. Finally, the outlook of next-stage perovskite-photovoltaics recycling has also been suggested for promoting the eco-friendly large-scale fabrication and application.

Keywords: perovskite solar cells, recycling, eco-friendly fabrication, toxicity, stability

1. Introduction

Organic-inorganic solid-state perovskite solar cells (PSCs) was first developed in 2009 and sharply increased the power conversion efficiency (PCE) from 3.8% to 25.5% in single-junction architecture.[1–5] The derived perovskite photovoltaics also achieved an unprecedented development, including 29.1% of perovskite/silicon, 24.2% of perovskite/copper-indium-gallium-selenide and 24.8% of perovskite/perovskite monolithic tandem solar cells.[3,6] The unprecedented development of PSCs should be attributed to the intriguing natures of perovskite materials, including large light photon absorption,[7] high generated carriers mobility,[8,9] long-term diffusion of carriers,[10–12] tunable bandgap,[13–15] low exciton binding energy.[10,16] Although the highest efficiency (25.5%) of PSCs is approaching to the theoretical Shockley–Queisser limited efficiency (30.5%), the stability is still a fatal limitation factor for further development because of the apt degradation of perovskite materials undergoing the functions of internal-external conditions: including quality of perovskite crystal phase, perovskite film, ionic migration, ambient humidity, oxygen and thermal stress.

Although countless endeavor has been invested into improving the stability of PSCs, the highest stability of the encapsulated module PSCs could sustain one-year without significantly decreasing at ambient condition with 55 °C by using 2-dimensional (D)/3D $(HOOC(CH_2)_4NH_3)_2PbI_4/CH_3NH_3PbI_3$-perovskite as light harvester.[17] But the efficiencies of this work were only 14.6% and 11.6% on the small and module active area, which are much far from the requirement of commercial application. The RbI additive composition engineered PSCs just maintained 92% after 1000 h under 85°C/85% on 1 cm^2 active area with glass encapsulation.[18] Other endeavor has been invested into enhancing stability of PSCs, such as reduced or removed methylammonium (MA) composition,[19,20] 2D perovskite interface engineering,[21,22] molecule interfaces passivation[23,24] and perovskite precursor modification.[25,26] Although the precious endeavor has been invested, the stability still lags behind the satisfication and requirements of commercial application because the inevitable degradation of perovskite materials triggers the issues of toxic materials' dispose and rare materials consuming.

The mainstream PSCs have a toxic element of lead and other un-ecofriendly components, which would inevitably generate the toxic substances leakage, environment pollution and materials consuming, especially the long-term remaining inside living body and uncertained effects. Additionally, the expensive electrodes application of transparent conductive oxide (TCO) substrates (such as fluorine-doped tin oxide (FTO),[27] indium tin oxide (ITO)) and noble metal electrode (such as gold, Au) are about 15% and 20% of total cost of PSCs fabrication according to the previous calculation,[28] which seriously consumes the rare resources, especially the noble materials of Au and indium. The only one-time utilization of above materials tremendously increases the fabrication cost of PSCs to hinder the massive application. Therefore, it is necessary to recycle the critical components of PSCs to reduce the environmental pollution, scarce materials consuming and fabrication cost for industrial application.

Based on aforementioned issues, herein we reviewed the progress of PSCs' components recycling, including TCO substrates (FTO and ITO), TCO substrates with electron transport layer, lead compounds (such as lead iodide, PbI_2), metal electrode and monolithic structure substrate with carrier transport layers. We first reviewed the all possibilities of components to realize more eco-friendly and low-cost fabrication of PSCs because of their frail long-term stability. Finally, the summarization and recycling protocol, and outlook of the next-stage PSCs recycling have also been discussed for further low cost-ecofriendly fabrication, and potential industrial application.

2. Importance of recycling

2.1 Degradation process and encapsulation of PSCs

As we all known, the organic-inorganic perovskite solar cells (PSCs) are not so stable because of the organic composition of perovskite materials and sensitivity of internal-external factors, such as phase behavior,[29,30] crystallinity,[29] ionic migration (such as iodide and lithium ions),[2,31,32] interface properties,[31] electrical properties,[31] humidity,[33] oxygen,[34] ultraviolet (UV) light,[35] and temperature,[36,37] which are critical challenges and must be urgently addressed for improving stability, further development and industrial application of PSCs. Moreover, the degradation of moisture frequently happens and usually induces reversible and irreversible damages of perovskite films,[38,39] especially the irreversible degradation. For example, $MAPbI_3$-perovskite induces degradation after exploring in ambient condition without encapsulation. This degradation process will be finished within few hours and accelerated with additional functions of light illumination and thermal stress.[34,36]

The degradation process of $MAPbI_3$-perovskite usually divides into 4 stages, including the formation of methylammonium iodide (MAI) and PbI_2 (eq 1) at function of H_2O, subsequently decomposing the MAI into CH_3NH_2 and hydroiodic acid (HI) (eq 2),[40,41] HI continuous breaking into H_2 and I_2 with function of the light illumination and oxygen (eqs 3 and 4) [42]

$$CH_3NH_3PbI_3 \overset{H_2O}{\leftrightarrow} CH_3NH_3I\ (aq) + PbI_2 \qquad (1)$$

$$CH_3NH_3I\ (aq) \leftrightarrow CH_3NH_2\ (aq) + HI\ (aq) \qquad (2)$$

$$2HI\ (aq) \overset{hv}{\leftrightarrow} H_2\uparrow + I_2 \qquad (3)$$

$$4HI + O_2 \leftrightarrow 2I_2\ (s) + 2H_2O \qquad (4)$$

Along with degradation process of eq 1, the semiconductor characteristics of perovskite materials gradually deteriorates and reduces photovoltaic performance of PSCs, including PCE and working stability.

Additionally, the oxidation of carrier transport materials (CTMs) will affect the stability of PSCs because the most of CTMs use at least one of organic materials, small molecules and polymers, which are usually susceptible to oxide both in the excited and ground states.[43,44] The degradation of CTMs would accelerate the moisture and oxygen penetration and induce perovskite decompose.

How to improve operational stability of PSCs has become an interesting issue. Encapsulation seems an effective apparoch to improve solar cells operational stability and prevent the some external impacts, such as moisture, oxygen invasion, thermal stress, and mechanical disruptions. A series of encapsulation methods have been developed for various solar cells. This includes a structure of glass/ ethylene vinyl acetate (EVA)/ silicon photovoltaics module/EVA/backsheet,[45] a structure of glass/EVA or polyvinyl butyral/ copper-indium-gallium-selenide photovoltaics module/transparent conductive electrode stack,[46] a architecture of TCO/photoanode/ dye-sensitized solar cells electrolyte/photocathode/TCO with surlyn polymer.[47] Some of encapsulation approaches have also been developed for PSCs for enhancing the operational stability to isolate the external affects from ernvironment, such as glass moisture barrier,[18] a SiO_2 film and a UV-curable epoxy with an adesic-cant sheet,[48] polyisobutylene as moisture barrier with glass-glass,[49] an EVA and a paraffin encapsulants.[50,51] Although the encapsulation methods can prevent the PSCs to directly exposing in some external factors, such as thermal stress, oxygen invasion, and mechanical disruptions. The components of PSCs are still can not flee the degration with internal-external factors impacts, such as halide segregration,[52,53] ionic migration[54] and UV light.[55]

Therefore, the treatment after PSCs degradation has promoted to an urgent misgiving and wash-out the dazzling halo because of the inevasible degradation process of PSCs by using low stability of halide perovskite and organic-CTMs.

2.2 High cost induced by raw materials' consumption

The TCO substrates and metal electrodes are quite expensive, and contribute a high cost ratio of PSCs fabrication. Such as the calculation of fabrication cost on each piece PSC,[28] as shown in Table 1. The cost of gold (Au), hole transport materials (HTM) and fluorine-doped tin oxide (FTO), indium tin oxide (ITO) are about 25, 40, 100 and 2000 $ per square according to the previous reports.[27,28] Additionally, the only one-time utilization of the Au and indium will generate the noble materials consuming and rare resource wasting, inducing a weak competitiveness of PSCs in photovoltaics market. Therefore, the recycling approach of PSCs components will become a more valuable and interesting issue to solve the aforementioned challenges of the perovskite materials degradation, callow working stability, long-term energy payback and toxicity issue of perovskite-photovoltaics.

Table 1. Calculated fabrication costs of chemicals and raw materials used in each PSC by using evaporated and nanoporous Au films as electrodes, including one, six, and twelve iterations of recycling. The volume of nanoporous Au film is estimated as 20 × 20 × 95 nm. The currency exchange ratio is 105.4 between the US dollar and Japanese yen. Copyright 2020, Wiley-VCH.

Chemicals	Price (yen/g)	Company	1 piece cost (yen)	Evaporation device (yen)	Nanopsrous device (yen)
Au	5300	Tanaka Kikinzoku Kogyo	178.6	178.6	
Ag	60.37	Tanaka Kikinzoku Kogyo			
PbI_2	2200	TCI	223.1	223.1	223.1
$PbBr_2$	4600	TCI	67.5	67.5	67.5
CsI	500	TCI	1.3	1.3	1.3
FAI	6500	TCI	223.6	223.6	223.6
tBP	1660	TCI	16.5	16.5	16.5
Co-TFSI	780	Sigma-Aldrich	4.9	4.9	4.9
Li-TFSI	276	Wako	1.2	1.2	1.2
spiro-OMeTAD	7800	Merck	63.7	63.7	63.7
SnO_2	18	Alfa Aesar	1.9	1.9	1.9
ITO	135 (piece)	Geomatec	135	135	135
$Au_{35}Ag_{65}$ film			1.1		1.1
One time use				917.5 (8.71 $)	740.0 (7.03 $)
6 times use				5505 (52.27 $)	4433.4 (41.99 $)
12 times use				11010 (104.53 $)	8866.8 (83.61 $)

2.3 Toxicity of lead

As aforementioned degradation process, the leakage and treatment of lead contents has become an inevitable issue because of the toxic natures and ecological-environmental pollutions. The non-biodegradable property of lead is a critical and prime consideration of ecological-environmental pollutions, especially the living body. Fig. 1 shows the circulation of lead compounds of human body includes absorption, distribution and excretion.[56] As this summarization, the intakes of lead chemicals could be divided into three ways: gastrointestinal, respiratory and dermal uptake.[57,58] The lead compounds kinetics of metabolization could be divided into three compartment categories,[57,59,60] including blood transports (category one) throughout body to soft tissues (category two), finally to the skeleton with a total encumbrance of 90% for 20-30 years. Additionally, the toxicity of lead compounds generates a potential of incalculable human health effect because of a particularly insidious hazard, even the "hazard level" has not be precisely made a definite diagnosis after exploring to lead. Some of human body functions will be interfered with lead invade and impact the central nervous, hepatic, hematopoietic and serious disorder of rental system.[61] The chronic toxicity of lead is quite common and usually happen at blood lead with about 40-60 μg/dL level, which will really severe if not treat in time and accompany with symptoms of encephalopathy, persistent vomiting, delirium, lethargy, convulsions and coma.[62,63]

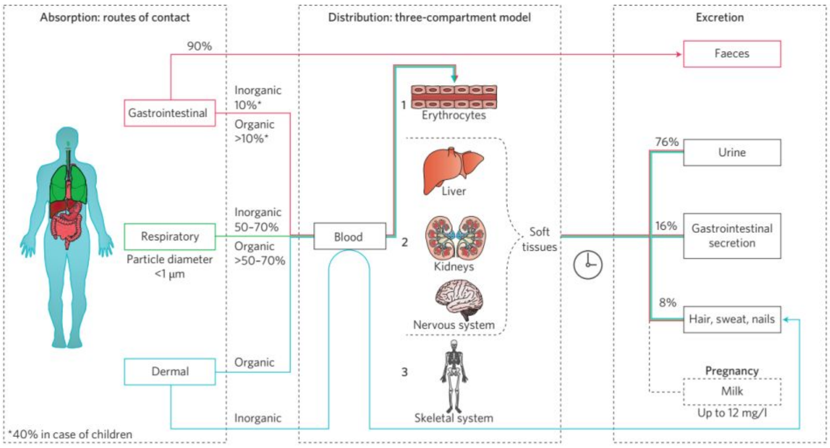


Fig. 1. Schematic summarization of the lead compounds inside human body includes absorption, distribution and excretion. For the absorption, the each intake route shows the amount of lead compounds could be absorbed. Lead could not be absorbed through gastrointestinal and leave the body by faces; Lead also could not be absorbed through respiratory and dermal leave body or lost contact as body movement, respectively. Lead remains inside body with threes compartments categories with some specific organs before excrete from human body. Copyright 2016, Springer Nature.

From the several critical factors of PSCs, it is necessary to discuss and develop an efficient approach of recycling to solve the confronted challenges: fragile stability and degradation of PSCs, toxicity of lead compounds and commercial interests, especially the low cost-ecofriendly fabrication and potential industrial application.

3. Recycling various components of PSCs

3.1 TCO recycling

The TCO substrates divide into two categories of fluorine-doped tin oxide (FTO) and indium tin oxide (ITO) glass according to the various composition. These TCO substrates are the most easy component of PSCs to realize the recycling process because of the oxide materials stability, and don’t need specially treatment only wash the perovskite materials and CTMs by various solvents after PSCs degradation. Therefore, the recycling of TCO substrates has been studied and realized in the earliest compared with other components. The recycling of FTO/glass substrate has been first realized by washing the other components from degraded PSCs devices with procedures of the dimethylformamide (DMF) immersing, ultrasonicating and solvents rinsing (chlorobenzene, deionized water, ethanol and acetone),[64] as shown in Fig. 2a. The re-collected FTO/glass substrate sustained almost same transmittance, composition and sheet resistance compared with fresh, as shown in Fig. 2b-d. The collected FTO/glass substrate was re-deposited the $CH_3NH_3PbI_{3x}Cl_x$-perovskite, 2,2’,7,7’-tetrakis[N,N-di(4-methoxyphenyl)amino]-9,9’-spirobifluorene (spiro-OMeTAD) hole transport layer (HTL) and silver electrode, which achieved 9.97% power conversion efficiency (PCE) comparable with that of the fresh FTO/glass PSCs (11.82%) on electron transport layer (ETL) free, as shown in Table 2. The main reduction of performance should attribute to the slightly increased series resistance and reduced shunt resistance of recycled PSCs. The increased series resistance of recycled PSCs is resulted from the slightly increased sheet resistance of substrate because other layers are same, as shown in Fig. 2d and Table 2.

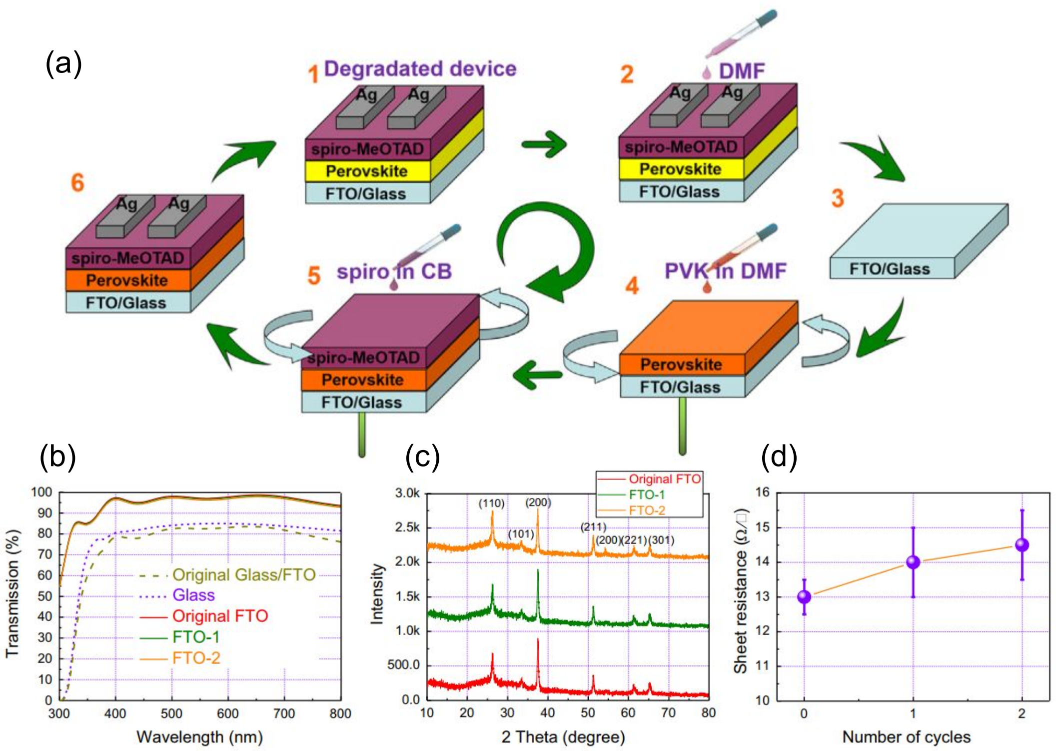


Fig. 2. (a) Schematic demonstration of process to fabricate PSCs with ETL-free via recycling the FTO/glass substrates. (b) Optical transmission spectra, (c) X-ray diffraction (XRD) patterns and (d) Sheet resistance of fresh, one-time (FTO-1) and two-times (FTO-2) recycled FTO/glass substrates. Copyright 2016, Elsevier Inc.

Table 2. Photovoltaic parameters of PSCs on fresh and recycling process with various recycling materials and times are listed in the table.

Structure	Recycling time	V_{OC} [V]	J_{SC} [mA/cm^2]	FF [%]	PCE [%]	R_s [Ω cm^2]	R_{sh} [Ω cm^2]	Ref
Ag/spiro-MeOTAD/Perovskite/FTO/Glass (Recycling of FTO/glass)	0	0.98	17.98	67.08	11.82	8.23	804.23	64
	1	0.95	17.29	65.11	10.81	10.05	598.80	
	2	0.94	16.75	63.32	9.97	13.16	650.34	
Au/spiro-OMeTAD/Perovskite/TiO_2/FTO/Glass (Recycling of FTO/glass)	0	1.03± 0.01	18.2± 1.2	69± 4	13.0± 1.1	-	-	27
	1	1.04± 0.01	17.9± 1.4	71± 2	13.4± 1.1	-	-	
	2	1.04± 0.01	17.4± 1.8	70± 3	12.8± 1.3	-	-	
	3	1.04± 0.01	18.5± 2.0	70± 3	13.5± 1.5	-	-	
Al/Ca/PC60BM/Perovskite/PEDOT:PSS/ITO/Glass (Recycling of ITO/glass)	0	-	-	-	8.15	-	-	65
	1	-	-	-	7.20	-	-	
Au/spiro-OMeTAD/Perovskite/TiO_2/FTO/Glass (Recycling of TiO_2/FTO/glass)	0	-	-	-	15%	-	-	66
	10	-	-	-	>15%	-	-	
Au/spiro-OMeTAD/Perovskite/TiO_2/FTO/Glass (Recycling of TiO_2/FTO/glass)	0	1.07	22.1	67	16.1	-	-	67
	1	1.06	19.7	73	16.0	-	-	
	2	1.07	21.5	67	15.0	-	-	
Ag/spiro-OMeTAD/Perovskite/TiO_2/FTO/Glass (Recycling of TiO_2/FTO/glass)	0 (a)	1.01	20.02	69.64	14.08	4.43	1030.93	68
	1	0.98	19.28	67.05	12.67	6.42	632.91	
	2	0.96	18.50	66.83	11.87	17.10	478.31	
	0 (b)	0.96	20.31	75.85	14.79	4.43	1030.93	
	1	0.96	19.82	66.20	12.60	6.42	632.91	
	2	0.93	18.04	65.77	11.03	17.10	478.31	
Au/spiro-OMeTAD/Perovskite/ZnO/AZO/Glass (Recycling of ZnO/AZO substrate)	0 (c)	0.96	19.6	72	13.5	-	-	69
	1	0.98	18.8	68	12.6	-	-	
	0 (d)	0.78	18.6	50	7.2	-	-	
	1	0.78	16.7	52	6.8	-	-	
n-Au/spiro-OMeTAD/Perovskite/ITO/Glass (Recycling of n-Au electrode)	0	0.96± 0.01	21.63± 0.04	78.9± 0.2	16.45± 0.08	-	-	28
	1	0.96± 0.00	21.62± 0.05	78.6± 0.3	16.40± 0.07	-	-	
	2	0.96± 0.00	21.64± 0.05	78.2± 0.2	16.30± 0.09	-	-	
	3	0.97± 0.00	21.14± 0.06	79.3± 0.2	16.23± 0.10	-	-	
	4	0.97± 0.00	21.37± 0.02	78.1± 0.1	16.29± 0.06	-	-	
	5	0.97± 0.00	21.13± .017	77.6± 0.3	15.97± .018	-	-	
	6	0.96± 0.00	21.10± 0.07	78.8± 0.3	16.04± 0.12	-	-	
	7	0.96± 0.00	21.04± 0.09	78.7± 0.0	15.97± 0.07	-	-	
	8	0.96± 0.00	21.09± 0.06	77.6± 0.2	15.71± 0.05	-	-	
	9	0.96± 0.01	21.32± 0.04	76.2± 0.5	15.60± 0.23	-	-	
	10	0.97± 0.00	20.91± 0.23	76.8± 0.1	15.49± 0.20	-	-	
	11	0.96± 0.01	20.70± 0.13	76.6± 0.4	15.16± 0.34	-	-	
	12	0.94± 0.01	20.79± 0.02	76.4± 0.3	14.89± 0.19	-	-	
m-NiO/Perovskite/m-Al_2O_3/TiO_2/FTO/Glass (Recycling of m-Ni, m-Al_2O_3, TiO_2, FTO/Glass)	0	0.953	19.1	75	13.6	-	-	79
	1	0.937	18.0	72	12.1	-	-	
n-Au:NiOx/Perovskite//m-Al_2O_3/TiO_2/FTO/Glass (Recycling of n-Au:NiOx, mAl_2O_3, TiO_2, FTO/Glass)	0	0.89	15.4	0.62	8.52	-	-	80
	1	0.83	15.0	0.66	8.17	-	-	
	2	0.80	14.4	0.67	7.72	-	-	

Note: 0 means fresh PSCs before recycling. (a) and (b) indicate mesoporous and planar structures. (c) and (d) represent rigid and flexible substrates.

The photovoltaic performance of PSCs with ETL-free still not enough after recycling the FTO/glass, especially the significant decrease of PCE after recycling. Therefore, A. Binek *et al*. also realized the recycling of FTO/glass substrate by using TiO_2 as ETL. The compact TiO_2 layer was prepared from sol-gel precursor solution, consisting of a 0.43 mM solution of titanium isopropoxide and a 27.2 mM solution of

HCl in 2-propanol. The components of $MAPbI_3$-perovskite, spiro-OMeTAD, Au and TiO_2 were washed or removed by using water, chlorobenzene, adhesive tape and DMF,[27] as shown in Fig. 3a. The recycled FTO/glass substrate was dried at 100 °C before re-loading the fresh TiO_2 ETL. The PSCs could keep almost same performance compared with fresh device even after 3rd time recycling, as shown in Fig. 3b-c.

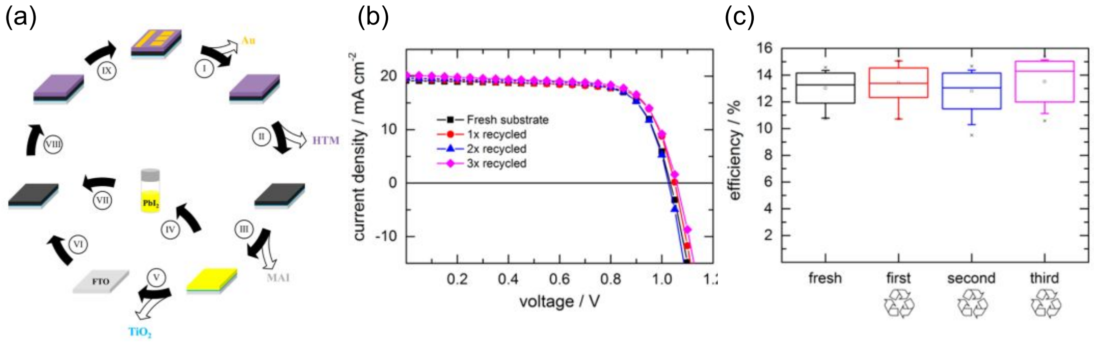


Fig. 3. (a) The illustration of recycling procedure for PSCs. (I) Removal of Au electrode by using adhesive tape. (II) Removal of the HTL by immersing in chlorobenzene. (III) Dissolution of the perovskite into MAI and PbI_2, and separation of MAI in water. (IV, V) Removal of PbI_2 and TiO_2 by employing DMF. (VI) Re-loading of a new TiO_2 film. (VII) Fabrication of the perovskite film on recycled FTO/glass from recycled PbI_2. (VIII) Deposition of the HTL layer. (IX) Evaporation of the Au top electrode. Photovoltaic performance of PSCs on the fresh and recycled FTO/glass. (b) *J*−*V* curves and (c) statistic distribution of PSCs. Copyright 2016, American Chemical Society.

To realize the ITO recycling from degraded PSCs, the single solvent of potassium hydroxide (KOH) solution has been employed by B. Augustine *et al*. to dissolve aluminium electrode, calcium buffer layer, phenyl-C61-butyric acid methyl ester (PCBM), $MAPbI_3$-perovskite and poly-3,4-ethylenedioxythiophene (PEDOTS:PSS, PH500),[65] realizing the recycling of patterned ITO/glass substrate. The synchronized thermography has been employed to characterize the electrical uniformity of samples' surface, as shown in Fig. 4a. The ITO substrate exhibited an uniform electrical properties with various concentration of KOH treatment compared with the reference ITO. The electrical uniformity significantly changed on recycled ITO substrate with a low concentration KOH solution except for the 1.5 M, which should be inefficiently washed and remain some chemicals on ITO surface. The photovoltaic performance of PSCs decreased from 8.15% to 7.20% after reusing ITO with a 1.5 M concentration of the KOH. The FF and J_{SC} were the reasons of performance reduction because of the sheet resistance increase after recycling, as shown in Table 2 and Fig.4b. Interesting that the performance of PSCs using 1.5 M KOH pre-treated ITO was higher than without treatment because the KOH could improve the wettability of component layers.

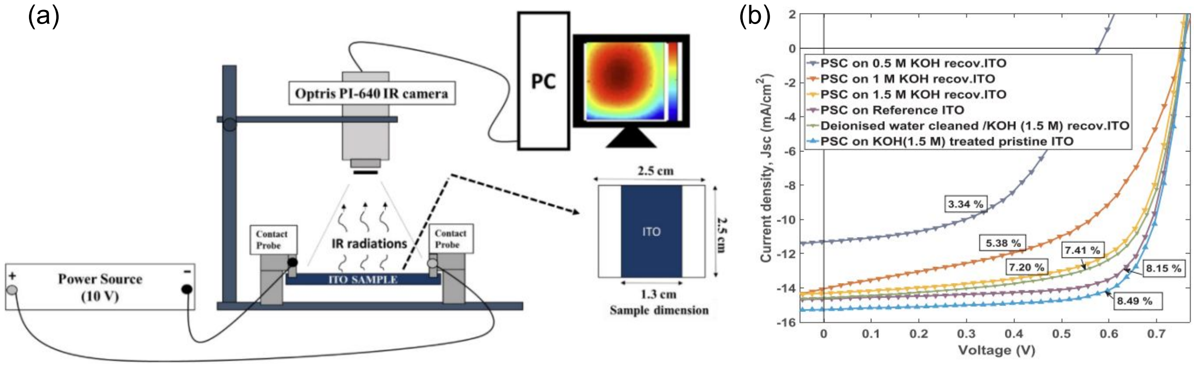


Fig. 4. Schematic the set-up of synchronized thermography for sample surface electrical uniformity by corresponding IR distribution (a). *J* *V* curves (reverse scan) of PSCs before and after recycling the ITO/glass substrate of the best working devices (b). Copyright 2019, Elsevier Inc.

Although the PSCs could sustain almost comparable photovoltaic performance with the fresh TCO/glass substrates, the performance still not enough for reducing the fabrication cost and environmental pollution, especially the wasted of ETL materials and metal electrodes.

3.2 ETL layer recycling

To improve recycling performance of PSCs and increase the recycling times, the TCO substrate with ETL layers has been exploited. A polar aprotic solvent, such as

DMF, γ-butyrolactone (GBL) or dimethyl sulfoxide (DMSO), has been introduced by B. J. Kim *et al*. to remove the $MAPbI_3$-perovskite layer and spiro-OMeTAD HTL, realizing the recycling process of the mesoporous TiO_2 (mp-TiO_2) coated transparent layer with FTO/glass substrate after 1 hour 500 °C annealing.[66] As shown in Fig. 6, the PSCs could sustain a high photovoltaic performance after ten-times recycling, except for the slight decrease of fill factor (FF) and open-circuit voltage (V_{OC}) because of the surface morphology change of TiO_2 after recycling according to the Fig. 5a-d. The authors also demonstrated the reproducibility of this recycling process of mp-TiO_2/FTO/glass substrates and shown the statistic distribution of results in Fig. 5e-h, which the PSCs sustained almost constant performance even after ten-times recycling compared with the fresh. It is the first time for realizing ten-times recycling process about one component of PSCs.

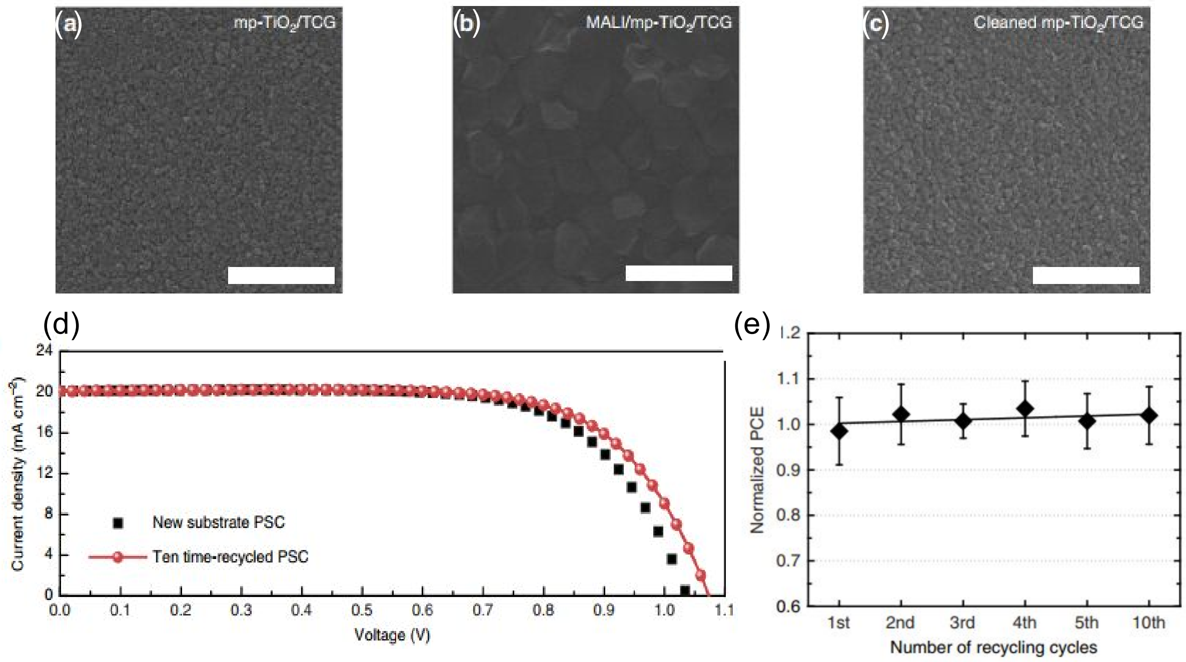


Fig. 5. SEM images of fresh mp-TiO_2 film on FTO/glass (a), $MAPbI_3$-perovskite on the top of TiO_2 (b), and recycled TiO_2 film after using DMF as dissolving solvent (c). The scale bar is 1 μm. TCG:

transparent conducting glass. *J* *V* curves of PSCs on fresh and after ten-times recycled mp-TiO_2/FTO/glass substrates (d). Normalized the PCE of PSCs on fresh and ten-times recycled mp-TiO_2/FTO/glass substrates (e). Copyright 2016, Springer Nature.

At the same time, J. M. Kadro *et al.* realized a much higher PCE after recycling the TiO_2/FTO/glass substrate by employing a rapid dismantling process of Au electrode and dissolving the other components by using chlorobenzene, ethanol and DMF solvents.[67] The achieved TiO_2/FTO/glass substrate was re-deposited the $MAPbI_3$-perovskite, spiro-OMeTAD and Au electrode, achieving almost constant photovoltaic performance after second-times recycling compared with the PSCs on fresh TiO_2/FTO/glass substrate (16.1% PCE), as shown in Fig. 6. The main reduction of photovoltaic parameters of PSCs by using recycled TiO_2/FTO/glass substrate was J_{SC}, which should be the impact of perovskite crystallization from the residual solvents during washing because the recycled substrate was consequently re-fabricated perovskite without additional treatment.

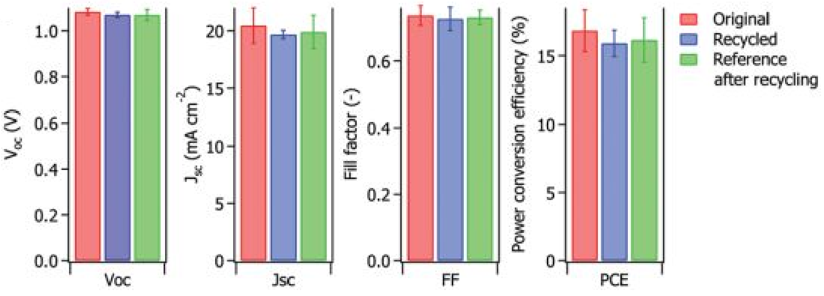


Fig. 6. Photovoltaic parameters summarization of PSCs on fresh, first- and second-times recycled mp-TiO_2/FTO/glass substrates. Copyright 2016, The Royal Society of Chemistry.

L. Huang *et al.* employed a procedure of DMF immersing, DMF and chlorobenzene ultrasonicating, deionized water, ethanol and acetone rinsing, and UV light treatment to recycle the TiO_2/FTO/glass substrates of planar and mesoporous structures, which prevented the lead content leakage, solid wastes and environmental pollution.[68] As shown in Table 2, the photovoltaic performance significantly decreased from 14.08% and 14.79% to 11.87% and 11.03% of the reused planar and mesoporous TiO_2/FTO/glass substrates, respectively. The serious reduction of performance on recycled substrates should be attributed to the increase of series resistance and reduction of shunt resistance in Table 2, which come from the surface morphology changes of perovskite films after twice re-loading. Moreover, the slightly increased series resistance of reused substrates results from augmented sheet resistance and impacts the performance of PSCs, as other layers are same.

All aforementioned explorations are concentrating on the high temperature and complicated process of TiO_2/FTO/glass substrates, which also require additional cost and energy investment. Therefore, X. Zhao *et al.* employed the chemical bath deposition (CBD) approach to synthesize superaligned ZnO nanorods as ETL on the rigid and flexible aluminum-doped zinc oxide (AZO) transparent conducting electrodes.[69] These ZnO/AZO substrates could be recycled by washing the $MAPbI_3$-perovskite by using DMF solvent and re-deposited the perovskite layer, HTL and Au electrode for new PSCs, as shown in Fig. 7a. The recycled ZnO/AZO PSCs could achieve slight lower PCEs of 12.6% and 6.8% on rigid and flexible substrates compared with those of the fresh ZnO/AZO substrates (13.5% and 7.2%), respectively. Authors also demonstrated the reproducibility of this process on rigid substrate, indicating that the narrow distribution performance on recycling, as shown in Fig. 7b. The main reduction of PSCs' performance on J_{SC} and FF should be attributed to the residual solvents on ZnO and impacted the crystallization of perovskite. The high bending durability of flexible PSCs also has been demonstrated and sustained about 90% after 1000 cycles with a bending radius of 4 mm. This outstanding performance indicates a more useful application and recycling of PSCs.

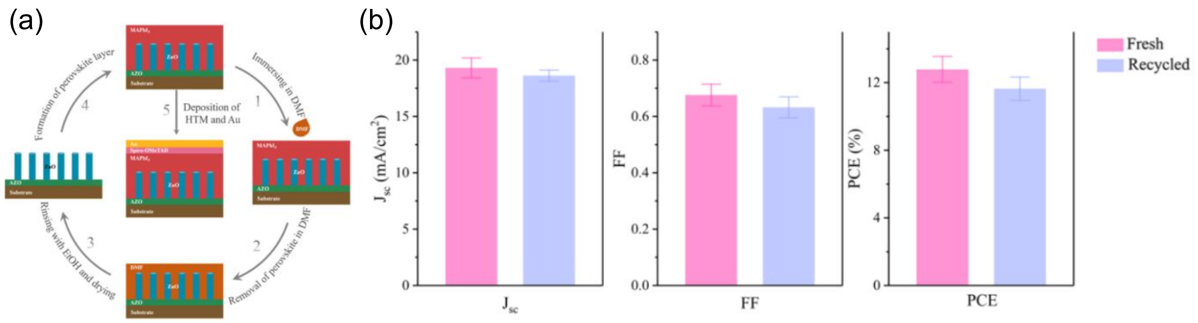


Fig. 7. Schematic of recycling process of ZnO/AZO substrates (a), V_{OC}, J_{SC}, FF and PCE of six PSCs devices before and after recycling. Copyright 2018, Wiley-VCH.

3.3 Toxic lead-content recycling

Apart from the ETL/TCO/glass substrates recycling, the most important component of lead compounds (such as PbI_2) is a critical issue of Pb-PSCs because the Pb content raises the concerns about the potential toxicity of perovskite materials and their impacts on biological system and environment.[70–72] Moreover, the Pb content is the most difficult component to separate and recycle because of the solubility and purification issues. Therefore, the recycling of Pb content is a valuable and challenge topic.

Authors employed the non-polar solvents, such as chlorobenzene, toluene, to remove the Au/HTL layers.[66] Then, they utilized the different dissolution kinetics of polar protic and aprotic solvents with various dipoles to realize the Pb component recycling, including 2-propanol, ethanol, methanol, water, and acetone, DMF, DMSO, acetonitrile, γ-butyrolactone, respectively. They found the ^{13}C nuclear magnetic resonance as (NMR) peaks of PbI_2–DMF shifted downwards compared with those of the DMF solution. Indicating that the polar aprotic solvent DMF could form metal halide-DMF bonds, generating in a PbI_2–DMF structure via the Pb–O bond after PbI_2 bond contacting with the DMF molecule. Because the partially negative oxygen atom in DMF can bond with partially positive atoms, such as Pb^{2+} cations, according to the resonance of DMF. This bonding can dissociate the PbI_6 octahedral frame to form the organic–inorganic perovskite material skeleton, resulting in a high solubility of the perovskite materials in polar aprotic solvents. Therefore, they took advantage of this merits of DMF to realize the heavy metal Pb components. The separation and re-collection of lead component has also been realized by using methanol, ethanol, 2-propanol, ethyl acetate and deionized water to dissolve the MAI for PbI_2 recycling.[67] They found the methanol could fastest change $MAPbI_3$ into PbI_2, following by deionized water, ethanol, 2-propanol, ethyl acetate. The ethanol would be the best choice because of the lower toxicity to human and environment. However, the deionized water would be preferable election for PbI_2 recycling because remained Pb content 0.03% after purification, which were much lower than ethanol, methanol and 2-propanol. In addition, the DMF could detected about 99.8% lead content and good for recycling. But the PbI_2 of this work could not be directly reused for perovskite fabrication without purification.

The non-volatile property of PbI_2 compared with the organic component of perovskite materials intrigued the recycling possibility of lead compounds,[42] as shown in Fig. 8. The PbI_2 component remained on TiO_2/FTO/glass substrates after $MAPbI_3$-perovskite degradation and released the volatile MAI. Then, the organic component of MAI was re-spin coated on aforementioned substrate with PbI_2, which the perovskite film could sustain almost same optical properties, as shown in Fig. 9. The absorption shoulder peaks blue-shifts from around 750 nm to approximately 500 nm for the characteristic peaks of PbI_2 after MAI evaporated compared with the fresh perovskite films, as shown in Fig. 9a-c**.** Meantime, the absorption peaks could recover back to about 750 nm after depositing fresh MAI to form perovskite film with comparable density in Fig. 8c, e and g. While, the PL intensity of single-step chloride perovskite film was almost like to degraded film, and single-step acetate approach reached maximum compared with that of the single-chloride and sequential deposition routes, even higher than the fresh perovskite film in Fig. 8d, f and g. Indicating that the single-step acetate approach of lead source was more easily realized recycling via microscopies technique.

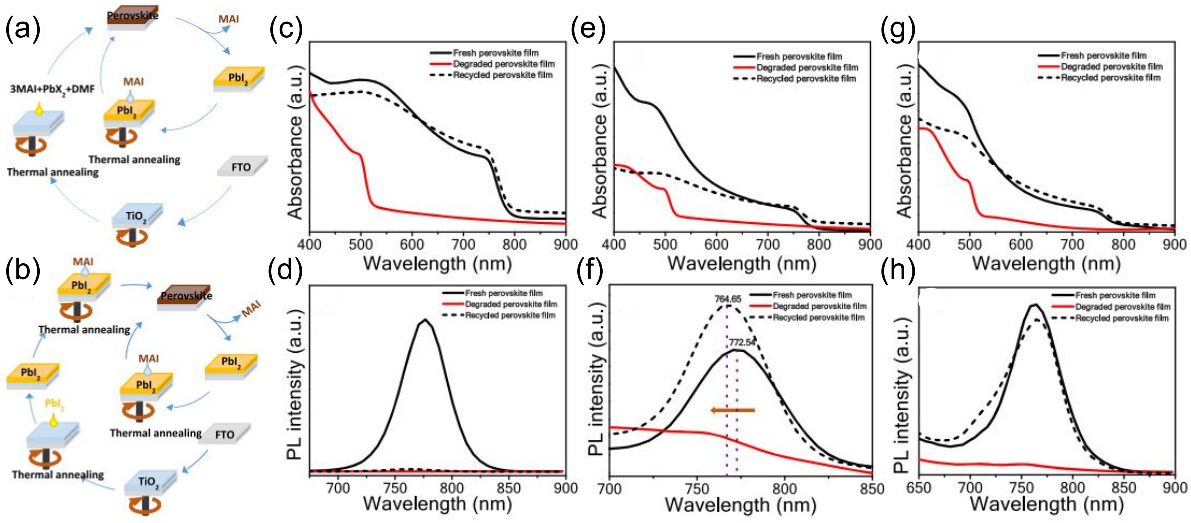
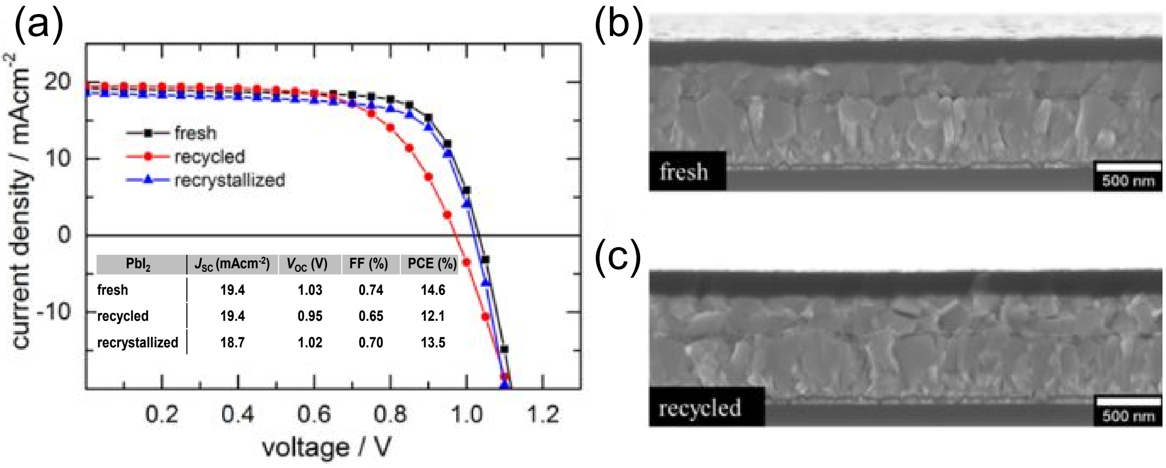


Fig. 8. Schematic of the recycling process for MAPbI$_3$-perovskite film deposited by (a) single-step chloride and acetate route and (b) sequential deposition route. Optical properties of MAPbI$_3$-perovskite film on fresh, degraded and recycled substrates. (c) single-step chloride, (e) single-step acetate, and (g) sequential deposition route of perovskite films UV−vis spectra. (d) single-step chloride, (f) single-step acetate, and (h) sequential deposition routes of the fresh, degraded film containing PbI$_2$, and the recycled perovskite films photoluminescence (PL) spectra. Copyright 2019, American Chemical Society.

The lead compounds direct recycling on PSCs still not realized because the challenges of segregation and purification from degraded MAPbI$_3$-perovskite. A. Binek *et al*. found the specially bonding between DMF-PbI$_2$ after washing the MAPbI$_3$-perovskite by using DMF solvent and realized the re-application of PbI$_2$ after recycling.[27] The collected PbI$_2$ was re-dissolved into DMF and deposited on the fresh TiO$_2$ film surface for new PSCs. As shown in Fig. 9a, the photovoltaic performance of

PSCs significantly decreased from 14.6% to 12.1% after first-time recycling of PbI_2, especially FF and V_{OC}. But the perovskite film exhibited almost same cross-sectional morphologies before and after PbI_2 recycling, as shown in Fig. 9b. The reduction of photovoltaic performance of PSCs should attribute to the lower purity of re-collected PbI_2 compared with that of fresh, and become much better after recrystallizing of the PbI_2, as shown in Fig. 9a.



PbI_2	J_{SC} (mAcm^{-2})	V_{OC} (V)	FF (%)	PCE (%)
fresh	19.4	1.03	0.74	14.6
recycled	19.4	0.95	0.65	12.1
recrystallized	18.7	1.02	0.70	13.5

Fig. 9. (a) J V curves of PSCs fabricated from fresh, recycled and recrystallized PbI_2 after recycling. (b) and (c) SEM cross-sectional images of PSCs on fresh and recycled PbI_2. Copyright 2016, American Chemical Society.

As aforementioned the direct recycling of lead compounds is quite difficult because of the high purity requirements for the satisfied photovoltaic performance of PSCs, inducing an inevitable process of lead leakage and treatment. Therefore, the encapsulation of PSCs during working seems a critical mean. Generally, the glass has been employed a typical material for the encapsulation but the lead leakage still too high according to the observation under various conditions by Y. Jiang *et al.*.[73] At same time, they found the epoxy resin based polymers could significantly reduce the lead compounds leakage rate from 30 to 0.08 mgh^{-1}m^{-2} under simulated weather conditions compared with that of the glass material, which realized the reduction of environmental and ecological system pollutions. The more safety encapsulation approach and material exploitation would be an another interesting issue for preventing lead compounds leakage.

3.4 Metal electrode recycling

Metal materials are typical used as contact electrode for high photovoltaic performance PSCs,[2,74–77] especially the Au electrode. The Au electrode has contributed 20% cost of PSCs because of the expensive of noble Au materials.[27,28] Therefore, the recycling of Au electrode is a critical issue for reducing noble materials consuming, fabrication cost and environmental pollution.The polar aprotic solvent, such as DMF, GBL or DMSO, could also recycle the Au electrode after removing the perovskite layer and HTL (spiro-OMeTAD),[66] as shown in Fig. 10. However, the recycled Au electrode could not be directly redeposited by using thermal evaporation under vacuum condition without any refining because of the light weight, small pieces and impossible direct transfer. The same challenge has happened on other work when authors recycled the Au electrode and could not directly re-utilize because of the low mass, and not withstand the suction produced during pumping.[67] Some of organic HTM still could be found in Au electrode film and need to be washed by using HCl.

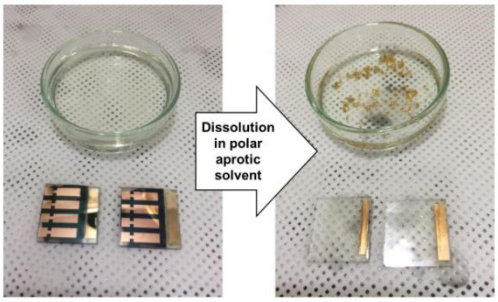


Fig. 10. Optical images of PSCs before and after selectively dissolution. The yellow color metal is Au electrode. Copyright 2016, Springer Nature.

Hence, it is necessary to develop a novel approach of Au electrode loading on PSCs to replace the typical procedure of thermal-high vacuum deposition and realize recycling. A mechanically dried transfer process has been developed by F. Yang *et al*. to load nanoporous Au (nano-Au) film on supported membrane film as contact electrode of PSCs by utilizing the high specific surface area of nano-Au film,[28] as shown in Fig. 11. This nano-Au electrode enabled the PSCs to achieve a high PCE of 19.0% on reversed scan, which could compared with the highest PCE of carbon based PSCs by using complicated multisteps preparation processes.[78] This nano-Au film was recycled and reused on fresh PSCs after dissolving the HTL and perovskite films with acetone, and drying on fresh membrane film at room temperature in ambient condition, as shown in Fig. 11a. The recycled nano-Au film PSCs could realize the almost same performance compared with the first-time utilization (*av*.16.45%) and much better than evaporated Au (evap-Au) film, as shown in Fig. 11b-c. Finally, the nano-Au film recycled PSCs sustained about *av*.14.89% PCE after twelfth-time reutilization, which was the highest photovoltaic performance of PSCs recycling and recycled-times compared with those of other reports, as shown in Fig. 11d-e and Table 2. The main reduction of recycled nano-Au PSCs come from the decreased of J_{SC} and FF, which should be attributed to the active area loss of nano-Au film and residual of chemicals in nanoporous holes of Au film from the characterization of the energy dispersive X-ray spectroscopy. This nano-Au film could be employed on flexible substrate to enhance the bending durability. This novel mechanically transfer of approach nano-Au film could reduce the energy source and noble metals consuming according to the calculation of the whole device cost, reducing the environmental pollution, as shown in Table 1 and Fig. 11f. Moreover, this process could solve the challenges of typical high temperature and vacuum deposition process and possibly applied in flexible PSCs.

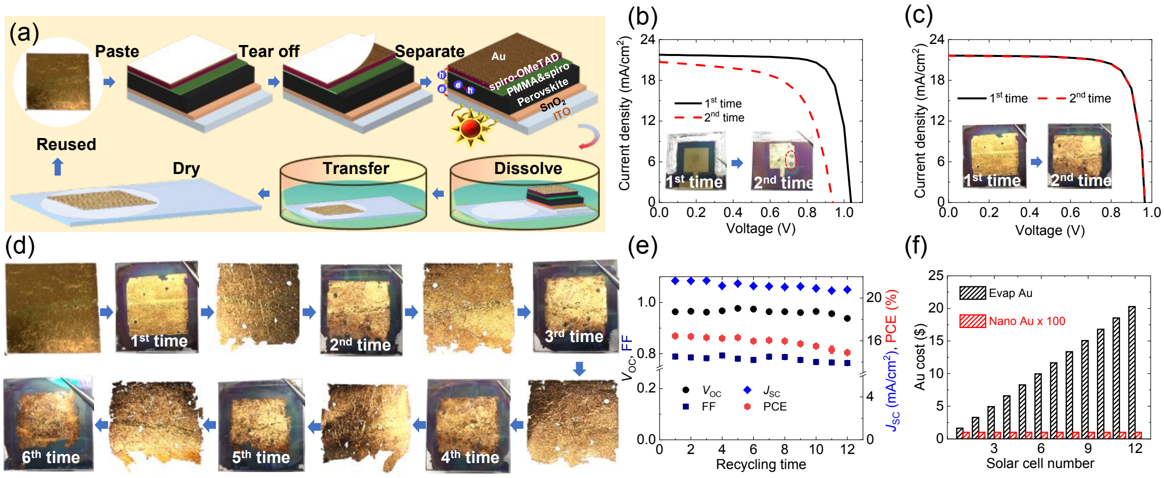


Fig. 11. (a) Schematic illustration of nano-Au film transferring and recycling on PSCs. (b, c) *J*–*V* curves of evap- and nano-Au PSCs; the evap- and nano-Au electrodes were reused (twice utilization process, where the red dotted lines refer to recycled photovoltaic performance). The photographs of the first- and second-time used evap- and nano-Au films in PSCs were inserted in the *J*–*V* curves. (d) Photographs of nano-Au film in the PSCs with sixth-time reutilization. The size of the PSC substrate is 25 × 25 mm^2. (e) Changes in photovoltaic parameters in the nano-Au PSCs during twelfth-time reusing. (f) Noble Au consumption of evap- and nano-Au films as the number of iterations of recycled utilization increased. Copyright 2020, Wiley-VCH.

3.5 Recycling of monolithic structure

To simplify the recycling process of PSCs, the re-fabricated monolithic structure has become preferable selection includes contact electrode, HTL, ETL and TCO/glass substrate. The 2 μm thick of mesoporous NiO has been deposited as back electrode using printing approach on TiO_2 ETL surface after printing 1 μm thick of Al_2O_3 spacer layer, forming a monolithic mesoporous structure before perovskite loading.[79] Then, the perovskite was deposited on the m-NiO/Al_2O_3/m-TiO_2/c-TiO_2/FTO/glass substrate to fabricate PSCs devices. As for recycling, the perovskite was re-loaded on above substrate after dissolving the degraded perovskite by using DMF, ethanol and drying on a hot plate at 100 °C for 10 min, as show in Fig. 12a. The performance of PSCs decreased from 13.6% of fresh to 12.1% on PCE of recycled monolithic substrate, especially the reduction of J_{SC} and FF, as shown in Table 2. This recycled approach has a high reproducibility on testing different 10 devices, as shown in Fig. 12b. The authors mentioned the reduction of photovoltaic performance after recycling should be attributed to some damages of m-NiO film the during rinsing process.

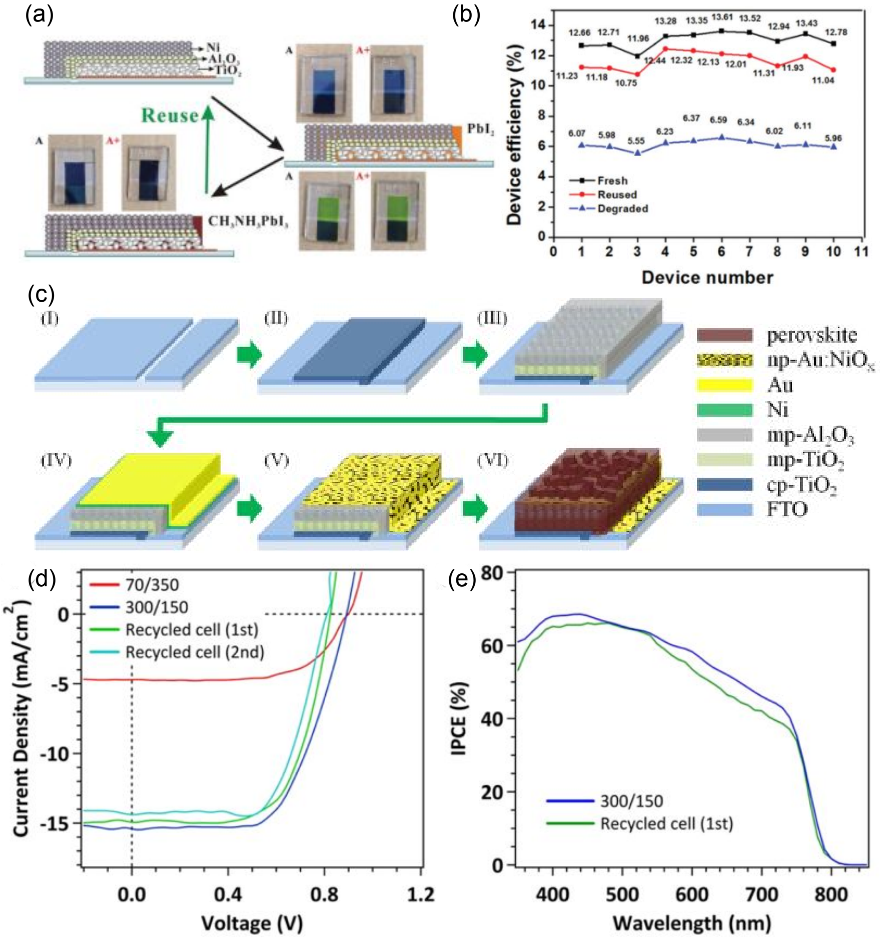


Fig. 12. Schematic of recycling process of m-NiO electrode PSCs (a), PCE distribution of PSCs with 10 devices under various condition: fresh, reused and degraded (b). Copyright 2015, The Royal Society of Chemistry. Illustration of the monolithic structure PSCs fabrication process. (I) Etching FTO substrate; (II) compact TiO_2 (cp-TiO_2) spray loading; (III) mp-TiO_2 spin coating; (IV) thermal deposition of Ni/Au

bilayer; (V) annealing of the Ni/Au bilayer to form nanoporous electrode; (VI) loading of perovskite light harvester (c). (d) *J–V* curves of PSCs with a monolithic structure of np-Au:NiO/mp-Al_2O_3/mp-TiO_2/cp-TiO_2/FTO/glass substrate. 70 nm/350 nm (namely 70/350) and 300 nm/150 nm (namely 300/150) of various configuration of mp-Al_2O_3/mp-TiO_2. A recycled device for mp-TiO_2/mp-Al_2O_3 of 300 nm/150 nm once (namely recycled cell (1st)) and twice (namely recycled cell (2nd)) were also presented. (e) IPCE response of pristine 300/150 cell and recycled cell (1st). Copyright 2017, American Chemical Society.

M. H. Li *et al*. also employed monolithic structure substrate to realize the recycling process by sequentially depositing the Ni and Au on the top of mesoscopic layer (mp-TiO_2 and mp-Al_2O_3, ETL) under a working pressure $<6 \times 10^{-6}$ Torr and realizing the fabrication of nanoporous NiO/Au electrode (HTL/contact electrode) after ambient atmosphere annealing with a high temperature of 500 °C with 45 mins,[80] as shown in Fig. 12c. Then the perovskite light harvester was deposited on the monolithic structure to form whole PSCs device. As for recycling process, the perovskite was re-deposited on monolithic structure after washing the $MAPbI_3$-perovskite material by DMF. The photovoltaic performance of PSCs slightly decreased after recycling the monolithic structure, especially the V_{OC} and J_{SC}, as shown in Fig. 12d and Table 2. The incident-photon-to-current-efficiency (IPCE) also caused relative obvious reduction, as shown in Fig. 12e. The main reduction of PSCs performance after recycled monolithic structure should be attributed to the decrease of specific surface area of nanoporous-mesoporous films after rising perovskite, and increase of the resistance because of the residual perovskite compounds. Moreover, the recombination loss of reused monolithic mesoporous substrate also would be increased because some PbI_2 did not convert into perovskite.

Although the monolithic structure could simplify the recycling process and saving the materials' consuming by using inorganic materials as HTL, the monolithic porous structure reduces the capacity of perovskite light harvester loading and ability of photon utilization. Moreover, the too thick of porous structure limits the carrier transport-diffusion and increases recombination loss, resulting in the relative unsatisfied photovoltaic performance compared with the mainstream development of PSCs, especially the J_{SC} and V_{OC}. Therefore, it is necessary to explore a more highly efficient approach for realizing the recycling of PSCs.

4. Recycling protocol

As aforementioned, although the recycling study just started recently, the eye-catching achievements of recycling has witnessed and accelerated the development of PSCs, as shown in Fig. 13. The recycling process has been studied and realized on several approach for specific componnents. And, the highest performance of recycled PSCs could sustain over 90% after twelfth-time recycling, demonstrating the feasibility of recycling, eco-friendly fabrication and harmless application. Additionally, the low-cost fabrication approaches of PSCs should be invested more endeavor to reduce consuming at initial step, such as using novel ETMs and cheap electrode contact.[78,81–83] However, the recycled cycles should be further enhanced because of the neat stability of PSCs for shortening energy-payback-time. Moreover, it is necessary to develop more eco-friendly solvents and techniques to realize the recycling of PSCs.

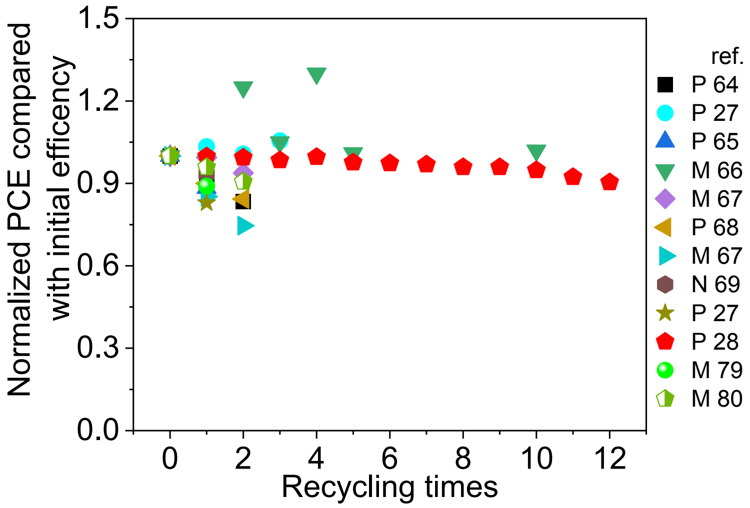


Fig. 13. Summarization the normalized PCE of PSCs compared with initial efficiency after recycling process with various approaches. P: planar, M: mesoporous and N: nanorods.

Additionally, the employed solvents for recycling were usually decided by the natures of components and main goals, as shown in Table 3. The architecture of PSCs also decided the solvents' selection. As for n-i-p structure, the DMSO and DMF could be used for only TCO recycling because of the strong polar nature and solubility. But for the layer-by-layer exfoliation or recycling, the tape, chlorobenzene (such as spiro-OMeTAD) and DMF should be employed to realize the removing of metal electrode, HTM, lead compounds and ETM (such as TiO_2). On the contrary architecture of p-i-n, the DMSO, DMF and KOH could be used for only TCO recycling because of high solubility. The recycling process could use tape, chlorobenzene, DMF and acetone to realize the layer-by-layer exfoliation of PSCs with bathocuproine (BCP) buffer layer by utilizing the various natures of recycling layers. But the recycling process would become more complicated by replacing the BCP with a atomic-layer-deposited SnO_2. In addition, the utilization of green solvents for PSCs recycling is also a critical issue, such as, ethanol, GBL and *N,N*-diethylformamide,[84] because the DMF, DMSO and chlorobenzene still have harmful effects for the biological-environmental system. Therefore, it is necessary to select the corresponding solvents for materials dissolving and PSCs components recycling with eco-friendly approach. Some challenges of recycling technology still need further investigation to realize a high performance of PSCs after recycling and accumulate scientific research findings for commercial application, such as structure dependent recycling routes, solvents exploitation-selection, devices' performance reduction mechanism.

Table 3. The selected solvents for PSCs recycling, CB: chlorobenzene.

Components	Reference / Solvents	27	41	42	43	44	56	28	65	66
Al			KOH							
PEDOT:PSS			KOH							
Spiro-OMeTAD	DMF	CB	KOH	DMF, DMSO, GBL	CB	DMF	DMF	Acetone	DMF	DMF
Perovskite	DMF	Water	KOH	DMF, DMSO, GBL	Ethanol, DMF	DMF	DMF	Acetone	DMF	DMF
TiO_2		DMF								
PCBM			KOH							

5. Outlook

Although perovskite-photovoltaics have achieved high PCE of 25.5% of single-junction and 29.1% of perovskite/silicon tandem architectures, the frail stability of perovskite-materials still hinders the further development and industrial application because of long-term-energy-payback. And, the lead compounds of perovskite-materials fabrication and degradation usually raises the concerns of environmental issues because of potential leakage of lead. Moreover, the noble metallic materials application significantly increases the fabrication cost and noble materials consuming for single-time utilization. Therefore, the recycling process of PSCs components has become a more interesting research topic for eco-friendly fabrication and application. Although some of precious endeavor has been invested into recycling process, the achievements of recycled PSCs still not enough because of the low photovoltaic performance for more high recycling cycles and re-application of some materials.

Hence, it is necessary to invest more endeavor into recycling research even the long-term stability of perovskite-photovoltaics would been solved in the future.

The mechanically transfer process of PSCs components seems a feasible and possible approach to further enhancing PCE by fabricating the carrier transport layer/TCO/glass substrate, perovskite light harvester and carrier transport layer/contact electrode. For instance, the HTL/contact electrode of copper film could be fabricated into nanoporous morphology, and fabricate one side of copper film into oxide component as HTL. This copper oxide film transfers onto perovskite/ETL/TCO/glass substrate to fabricate normal structure PSCs and realize mechanically transfer process according to the nanoporous Au film, which would possibly improve the photovoltaic performance of PSCs during recycling and approaching to the typical fabrication process. The individual layers recycling would become more easy and save the material consuming. Moreover, it is possible to employ the individual layers recycling to fabricate the large-scale module perovskite-photovoltaics and tandem solar cells because of the much higher PCE compared with single-junction, realizing the industrial production and accelerating the commercial application. Additionally, exploring and employing a more low-cost recycling material, such as carbon based material, is an another approach to reduce the fabrication cost, metal materials consuming, and replace the current expensive noble materials.

Conflict of Interest

The authors declare no conflict of interest.

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Recycling progress of organic-inorganic perovskite solar cells for eco-friendly fabrication

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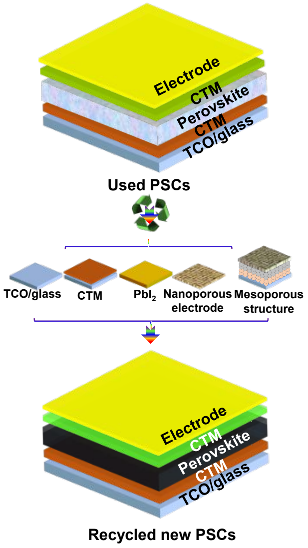
The reviewed paper has systematically summarized and proposed guidance of recycling research for organic-inorganic perovskite solar cells with ecofriendly fabrication.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CTM
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TCO/glass
Used PSCs
TCO/glass
CTM
PbI_2
Nanoporous electrode
Mesoporous structure
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Recycled new PSCs