Electronic Supplementary Material (ESI) for Energy & Environmental Science.

Electronic Supplementary Information

Future Paper based Printed Circuit Boards for Green Electronics: Fabrication and Life Cycle Assessment

Content

Mechanical property

Adequate mechanical strength of a substrate material is a basic requirement to maintain integrity and protect the electronic components. The printing paper with sticker on the back (Avery Dennison Co. America, FASSON series, AW5416) was chosen as a motif for this study. The tested samples were of 10 mm in width and 50 mm in length, and they were dried at 80 ^{o}C for 1h before being stretched on an electromechanical universal testing machine (SANS CMT 6104) with the crosshead moving speed of 2 mm/min. The test results are shown in Table S1 and Figure S1.

Table S1 the mechanical property of paper.

Sample	Tensile failure stress (MPa)	Tensile stress (MPa)	Tensile yield stress (MPa)
Single layer	4.57	4.59	4.43
Double layers	5.95	6.60	6.60
Three layers	5.21	5.97	5.97

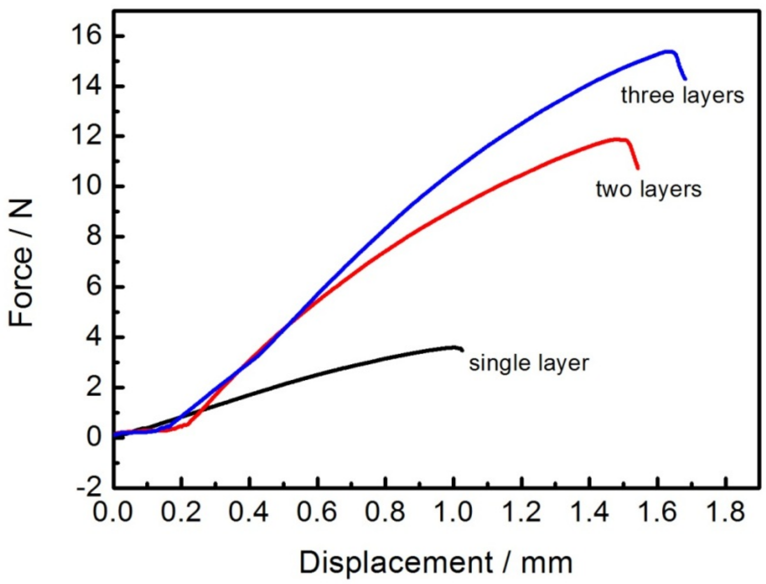

Figure S1 the tensile force versus displacement of single layer, two layers and three layers printing paper

Conductivity and stability of the printed circuits

The PU based ECA with 50 wt% of silver filler loading showed an electrical conductivity of ~1 × 10^{-5} Ohm·cm after being cured at 150°C, indicating a promising application for conductive circuits. Higher silver content would improve the electrical conductivity, yet it would also cause a higher viscosity of the paste which may not be suitable for screen printing. The electrical conductivity was tested with a four point probe method (LORESTA-GP MCP-T610).

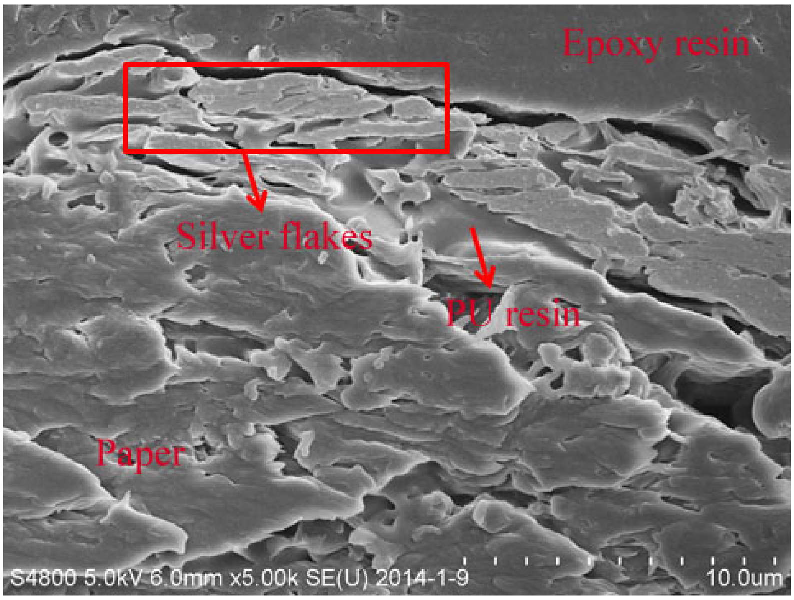

Figure S2 SEM image of cross section of printed ECA conductive line.

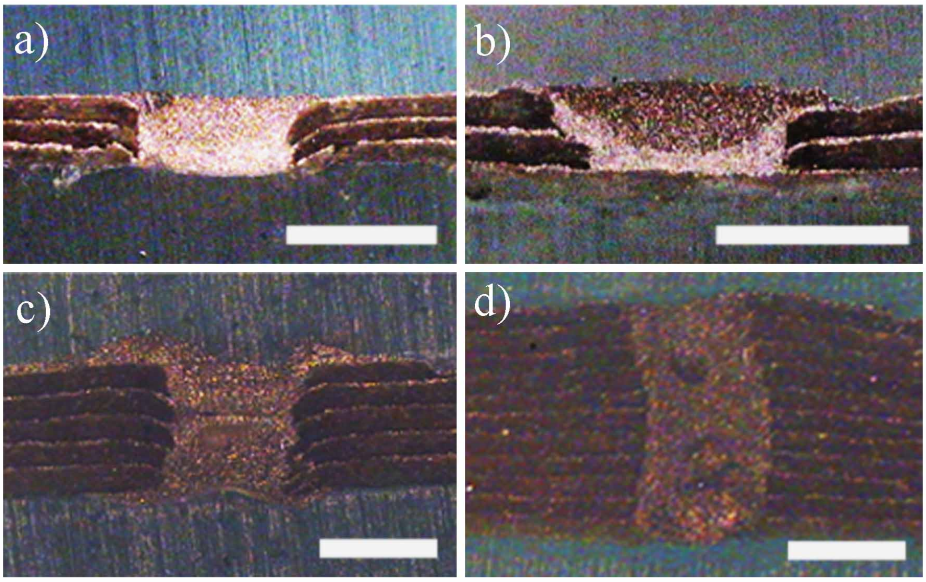

Figure S3 Optical images of the cross-sectional images showing the junctions of three-layered, five-layered and ten-layered P-PCB. a) A through-via of a three-layered P-PCB. b) A blind-via of a three-layered P-PCB. c) A through-via of a five-layered P-PCB. d) a through-via of a ten-layered P-PCB. The scale bars are 0.5 mm.

The screen printed conductive track was only 4~5μm thick (Figure S2), which is close to the electroplated copper layer for the O-PCB. It can be observed under SEM that the silver flakes arrange closely after being cured and this results in an improved electrical conductivity, which is related to the capillary property of the porous paper substrate. The SEM sample was prepared with a hot mounting press (STRUERS Labopress-3), after being sawed in half and the cross section was smoothed with a blade.

The situation of the inter-layer connections is one of the most important issues for a multi-layer PCB. We filled ECA in the vertical interconnect access (via) that were mechanically punched or drilled to connect different layers. The key factor for the connection is aligning the junction points on each layer; and thus we tailored a position-alignment setup to achieve this. The samples for optical microscope were prepared with a hot mounting press (STRUERS Labopress-3) and the cross-sectional images are shown in Figure S3. As can be seen, the ECA filled in the vias connects well with each layer and the silver flakes were dispersed uniformly. Attempts have been made to construct five to ten layers of printed circuits (Figure S3 c and d); the cross-sectional view shows good connection of different layers, which means it is possible to fabricate up to ten-layers of the PCB with paper, indicating more complicated circuits and broader applications of the paper based PCB.

In addition to the simple and feasible fabrication process, reliable functional performance is very important to paper based PCB in practical uses. We tested the paper based PCB referring to the standard of ICP-6013.

i. Adhesion test (ICP-6013-3.3.6)

We conducted the tape test in accordance with ICP-TM-650, method 2.4.1. From Figure S4 we can see that of the tested samples, the conductive pattern remains intact and unnoticeable ECA material could be removed by the tape. This can be ascribed to the excellent mechanical strength of the PU-based ECA and the excellent bonding towards the paper substrate.

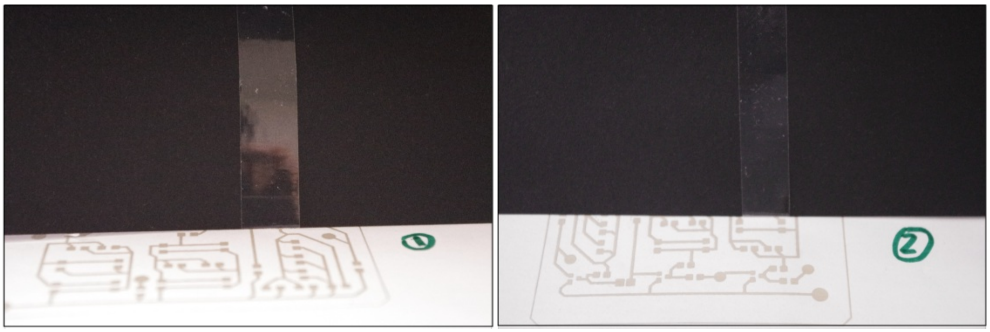

Figure S4 the adhesive test of P-PCB. The tests were conducted on two different samples, only some paper scrape was attached to the tape.

ii. Flexibility test (ICP-6013-3.6.2)

Paper based conductive circuits can be folded and still maintain high conductivity. We rolled the printed circuits at different curvature diameters for 1000 times respectively. Figure S5 shows the volume resistivity change versus rolling cycles. The resistance increased with rolling cycles, and when the diameter was smaller, the resistance increased more because of more severe deformation. The bulk resistivity of the tested samples still maintained at $2\sim3\times10^{-5}$ Ω·cm after 1000 cycles at the smallest folding diameter.

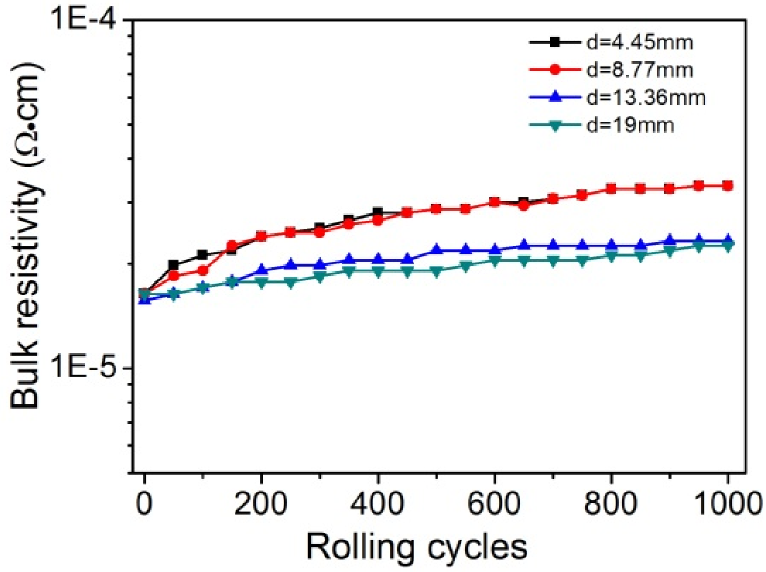

Figure S5 Variation of bulk resistivity versus rolling cycles. d refers to the curvature diameter.

iii. 85 ^{o}C /85RH reliability test

The tested conductive lines were of 0.5mm width and 20mm length. After being exposed in an 85 ^{o}C/85RH chamber for 1500 hours, the bulk resistivity still remained at 1.6×10^{-5} Ω·cm (Ag content in the ECA was 50wt%).

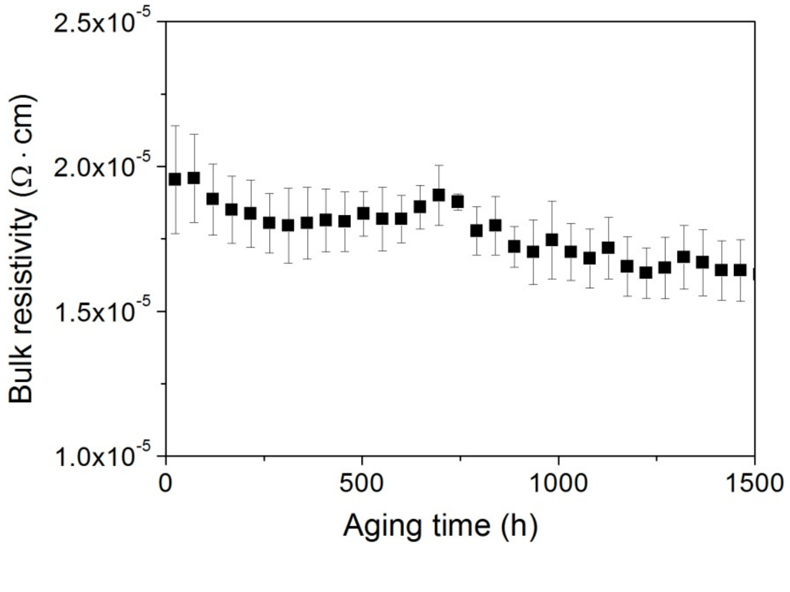

Figure S6 Variation of bulk resistivity versus aging time, the printed ECA samples (50wt% Ag content) were kept at 85 ^{o}C/85RH for more than 1500 hours.

Prototyping

Here we evaluate the feasibility of P-PCB in device applications:

i. Twinkling LED array

A complete circuit mounted with relevant electrical components is the most basic application of printed circuits. We fabricated a twinkling “THU” (Capital letters for “Tsinghua University”) LED array (Figure S7) by mounting LED chips, resistors, capacitors and transistors on the surface of a three-layered P-PCB. The conductive lines (width = 0.5 mm, thickness = 3 μm) were printed with PU based ECA (50 wt% Ag loading), and cured at 150 ^{o}C (30 min). The adhesive we used to bond the electrical components on the circuits was the epoxy based ECA, because epoxy based ECA can be cured at a low temperature (40^{o}C 15min). The names and types of the electrical components were labelled aside, which were ink printed previously. Paper based PCB is flexible and can be potentially pasted on surface of wall, bottles, boxes etc. for temporary decoration or integrated in protection suit, bandage or other short-term used wearable devices for reminding, sensing, warning etc.

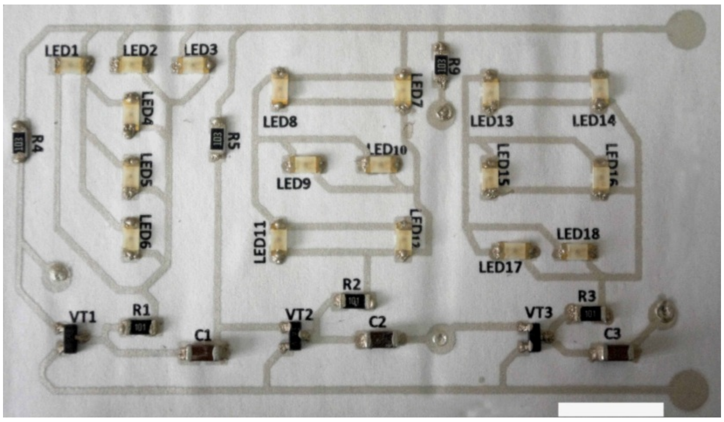

Figure S7 prototype of a three-layered P-PCB: the twinkle “THU”. The scale bar is 10 mm.

ii. Doorbell

The paper based PCB can also be applied in some simple and low cost household appliance. For example, we prototyped a doorbell with the paper based PCB. It is powered with a button cell and the buzzer rings when pressing the switch. The paper based PCB is thin and flexible. It can be pasted on many rigid substrate and still maintain functionality, e.g. curving walls or gatepost. The good processing property makes it facile to assembling and packaging, indicating a potential in low cost consumer electronics.

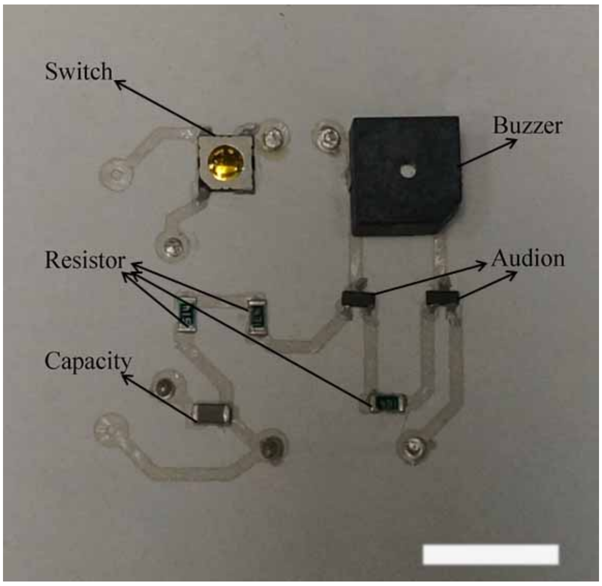

Figure S8 A prototype of doorbell assembled on a three-layered P-PCB. The scale bar is 10mm.

iii. Control panel

We replace the control panel of a temperature controller using the P-PCB. It can provide support for the ICs, switches, resistors, LEDs, capacitors, transistors, a buzzer and a LED digital display. It works just as well as the original epoxy based organic substrate that it replaces.

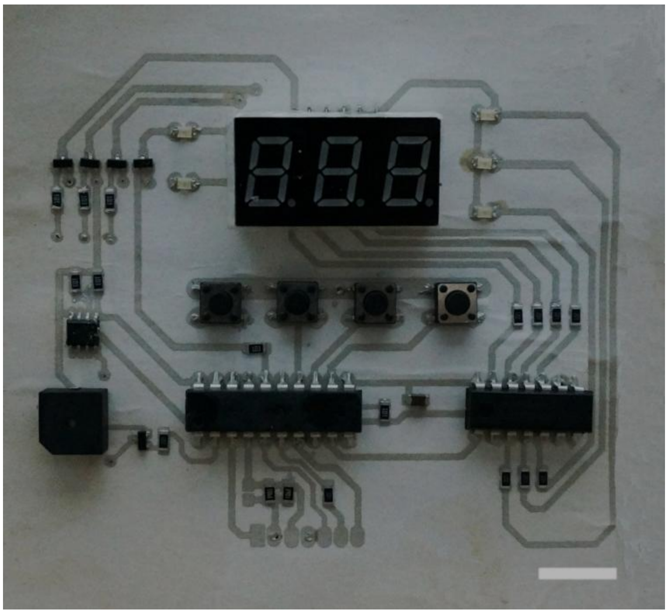

Figure S9 The control panel of a temperature controller. The scale bar is 10mm.

Life cycle assessment

i. P-PCB

The inventory data and data source of P-PCB are listed in Table S2. The paper we use is of 80 g/m^2. The mass of the ECA is calculated with the following equation: M=area×height×density, of which area=20000 m^2 (half of the 4-layered P-PCB), height=5μm and density=2.06×10^3 kg/m^3 (measured with water displacement method).

Table S2 material inventory of inputs and outputs of 4-layered paper based PCB (10000 m^2)

Inputs of 10000m^2 Paper based PCB(raw materials and energy)							
	Primary materials	**Consumption**	**Secondary materials**	**Consumption**	**Third grade materials**	**Consumption**	**Data source**
Paper	**Paper**	3200kg					Lab
ECA	**Resin （polyester）**	103kg					Lab
	Silver flakes	103kg	**$AgNO_3$**	162kg	**Ag**	103kg	Shenzhen Hangsheng Electronics Co., Ltd.
					HNO_3（50 %）	120kg	
			Ethanol	103kg			
			water	1030kg			
			NaOH50%	38.1kg			
			Formaldehyde	14.3kg			
Glue	**Glue**	240kg					Lab
Power	**Electricity**	2670kwh	824kwh for silver flake production， 1336.73kwh for screen printing397kwh for drilling and curing,111.7kwh for waste treatment.				Lab and reference
Outputs / 10000m^2 paper based PCB							
4-layered paper based PCB/3640kg			= 3200kg paper + 206kgECA + 240kg glue				
Wastes			waste paper				
Treatment of waste P-PCB							
Components	**Treatment**		**Remarks**				
Paper	50% incineration		Calorific value is 15MJ/kg，electricity generating efficiency is 24%				
	30% recycle		Paper pulp				
	20% landfill		Waste disposal				
Silver	98% recycle						
Resin	100% incineration						

Table S3 Ecoinvent inputs inventory of P-PCB g/m^2 (resources)

Nonrenewable energy resources			
Crude oil	6.03E+01	**Lignite**	6.33E+01
Hard coal	6.89E+01	**Uranium**	1.95E-03
Renewable energy resources			
Primary forest	6.24E-03	**Wood, forest, standing**	2.01E-01
Wood, hard, standing	1.79E+02	**Wood, soft, standing**	7.48E-04
Nonrenewable elements			
Aluminium	2.65E-01	**Lithium**	4.61E-06
Chromium	1.41E-01	**Magnesium**	2.35E-05
Copper	3.01E-01	**Manganese**	1.71E-02
Fluorine	3.68E-02	**Molybdenum**	2.25E-02
Gallium	6.52E-10	**Nickel**	3.49E-01
Gold	7.37E-06	**Palladium**	3.93E-07
Indium	1.95E-06	**Phosphorus**	8.92E-01
Iodine	2.35E-04	**Silver**	2.06E-01
Iron	4.32E+00	**Sulphur**	1.45E-02
Lead	5.38E-03	**Tantalum**	7.18E-06
Non-renewable resources			
Barium sulphate	2.21E-01	**Fluorspar**	4.78E-01
Borax	2.58E-06	**Limestone**	5.22E+01
Clay	5.19E+00		
Renewable resources			
Water	3.76E+04	**Carbon dioxide**	7.21E+02

ii. O-PCB

The inventory data of epoxy based PCB is mainly obtained from Shennan circuits Co., Ltd.

Table S4 Material inventory of inputs of epoxy based PCB

Inputs/10000m^2 Epoxy PCB			
Materials	**Quantity**	**Materials**	**Quantity**
Copper foil	12500kg	**$CuCl_2$**	260kg
Silica sand	2500kg	**Kraft paper**	10000m^2
Glass fiber	7500kg	**Al plate**	10000m2
Epoxy resin	5500kg	**$KMnO_4$**	200kg
Dry film	40000m^2	**Copper**	4500kg
Abrasive(Al_2O_3)	1000kg	**NaOH**	500kg
$NaCo_3$	3000kg	**NH_4HSO_4**	100kg
$NaHSO_4$	100kg	**Tin**	300kg
$KAu(CN)_4$	2kg	**DI water**	100000kg
Power	200000kwh	**Tap water**	11000000kg

Table S5 Material inventory of outputs of epoxy based PCB

Outputs of fabricating 10000m² epoxy based PCB				
PCB/10000m²	**Components and proportion**			
26.75t	=15t epoxy board + 10.75t Cu + 0.5t ink + 0.5t other metals			
Wastes emission in fabricating 10000m² epoxy based PCB				**Remarks**
Wastes	**Resources**	**Proportion**	**Treatment**	The Cu in the etching effluent is about 7t and was recovered from the waste in the treatment process.
Waste liquid	Cleaning effluent	90%/9900t	50% for reuse and the rest is discharged after treatment	
	Etching effluent	5%/550t	discharged after treatment	
	Electroplating effluent	0.01%	discharged after treatment	
	Others	5%/550t	discharged after treatment	
Waste residue	Fabrication process	5t	Treat as industrial waste	
Waste gas	Ignored			

Table S6 Ecoinvent inputs inventory of epoxy based PCB g/m²(resources)

Nonrenewable energy resources			
Crude oil	2.56E+03	**Lignite**	4.05E+03
Hard coal	8.04E+03	**Uranium**	1.87E-01
Renewable energy resources			
Primary forest	1.09E+00	**Wood, forest, standing**	1.30E+00
Wood, hard, standing	1.18E+02	**Wood, soft, standing**	1.12E-02
Nonrenewable elements			
Aluminium	8.68E+02	**Lead**	2.03E+01
Chromium	1.34E+01	**Manganese**	8.58E+00
Copper	4.07E+02	**Molybdenum**	5.38E+00
Fluorine	1.96E-01	**Nickel**	3.23E+01
Gallium	5.41E-08	**Silver**	2.45E+00
Gold	1.29E-03	**Sulphur**	1.58E+01
Indium	2.74E-05	**Tin**	1.24E+02
Iodine	2.74E-04	**Zinc**	1.37E+01
Iron	2.56E+02		
Nonrenewable resources			
Barium sulphate	1.17E+01	**Colemanite ore**	3.47E+02
Basalt	1.50E+01	**Dolomite**	2.57E+00
Carbon, in organic matter, in Soil	3.38E-01	**Fluorspar**	9.32E+00
Clay	1.76E+03		
Renewable resources			
Water	2.24E+06	**Carbon dioxide**	4.67E+03

Table S7 Contents of the discharged waste water after treatment (550kg/m^2)

Residues	Content mg/L	residues	Content mg/L
Pb	1	**Anilines**	1
Ag	0.5	**P**	0.1
Cu	0.5	**Cl**	0.5
Phosphate	0.5	**HF**	10
Sulfide	1	**COD**	60
Ammonia nitrogen	15	**SS**	20
Cyanide	0.5	**BOD5**	20

Table S8 Treatment of the waste epoxy based PCB

Waste treatment	Proportion	Recovery rate(Cu)	
Machenical method	70%	95%	The nonmetal parts can be used as raw materials for other products or just for landfill but we leave out the value of this part.
Incineration	25%	95%	Calorific value is 7.5mj/kg, electricity generating rate is 24%
Landfill	5%	0	

iii. Environmental profiles for the life cycle of P-PCB

Table S9 The contribution to the environmental impact categories of different raw materials in P-PCB fabrication

	ADP	AP	EP	FAETP	GWP	HTP	ODP	POCP	TETP
Paper	51.14%	38.86%	45.11%	30.20%	47.91%	11.66%	67.30%	52.88%	40.68%
Water	0.01%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%
Electricity mix	10.22%	27.96%	4.41%	4.87%	18.09%	2.65%	1.61%	14.67%	2.73%
Ethanol	0.83%	1.70%	2.68%	0.89%	1.11%	0.28%	1.29%	1.17%	1.85%
Methyl Acrylate	21.81%	3.84%	3.03%	2.39%	13.38%	1.55%	12.10%	9.50%	4.02%
Silver	0.72%	18.97%	36.62%	57.94%	0.75%	78.79%	0.90%	9.78%	41.32%
Formaldehyde	0.69%	0.10%	0.09%	0.10%	0.29%	0.05%	0.79%	0.20%	0.14%
Methyl Acrylate	4.75%	2.29%	0.44%	0.18%	3.52%	0.15%	0.02%	3.19%	0.69%
HNO_3,50%	1.72%	2.86%	2.88%	0.57%	6.88%	0.65%	3.50%	1.33%	2.44%
Polyester resin	7.19%	2.86%	3.97%	2.07%	7.33%	3.92%	11.78%	6.89%	4.49%
NaOH,50%	0.92%	0.56%	0.76%	0.79%	0.75%	0.30%	0.72%	0.40%	1.63%

iv. Environmental profiles for the life cycle of O-PCB

We can see from Table S10 and Figure S10 that the environmental burdens of P-PCB mainly come from raw materials of copper, epoxy resin, glass fiber, water and energy consumption. This is mainly due to the energy intensive and high-emission production processes of copper-clad plate system as well as the large amount of water and electricity consumed in the O-PCB fabrication.

To be specific, life cycle of copper foil contributes the most to AP (45.15%), EP (63.56%), FAETP (89.52%), HTP (84.02%), TETP (85.09%), POCP (38.06%) for the energy consumption and emissions (gas emissions such as CO_2, SO_2, NO_2 and waste water emission) in the mining and refining processes of copper;[1] and the electroplating in the O-PCB fabrication consumes large sum of electricity which is responsible for ADP (31.33%), AP (31.39%), GWP (47.51%) and POCP (26.03%). In addition, the epoxy and glass fiber in the substrate of O-PCB have more burdens on environment: the SO_2, CO_2, NO_x and halohydrocarbon discharged in the epoxy production contribute to ADP, GWP and POCP, and thermal treatment processes in the glass fiber production account for ODP, GWP and ADP due to the CO_2 NO_x, and SO_2 emission and fuel consumption.[2]

Figure S11 shows the picture of a news report which represents the common phenomenon in Guiyu of China that people disassemble the e-wastes manually without any protection. Which is not only harmful to people but also hazardous to the environment.

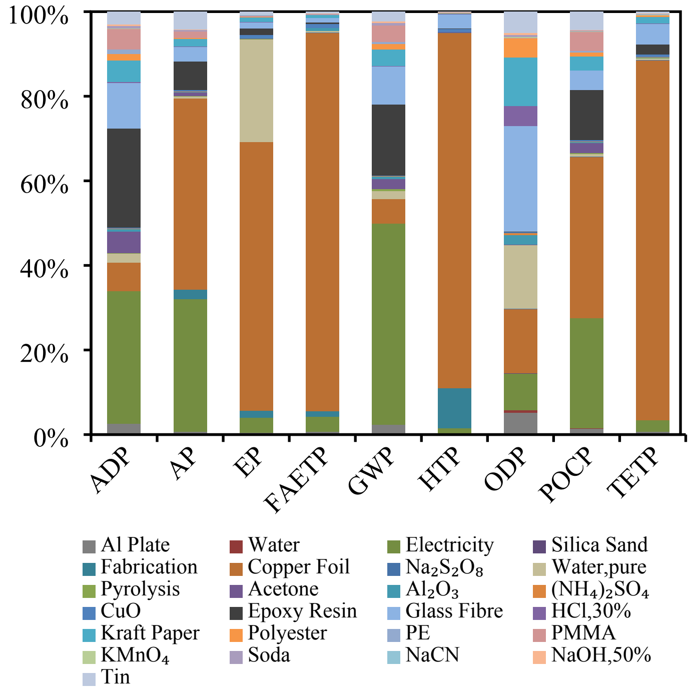

Figure S10 Environmental profile of O-PCB. The main raw materials and consumptions in the manufacture of epoxy based PCB are listed.

Table S10 The contribution to the environmental impacts categories of different raw materials of epoxy based PCB

	ADP	AP	EP	FAETP	GWP	HTP	ODP	POCP	TETP
Copper Foil	6.66%	45.15%	63.56%	89.52%	5.75%	84.02%	15.18%	38.16%	85.09%
Electricity	31.33%	31.39%	3.59%	3.53%	47.51%	1.35%	8.69%	26.03%	2.68%
Epoxy Resin	23.47%	6.65%	1.62%	0.30%	16.84%	0.14%	0.10%	11.88%	2.33%
Glass Fibre	10.76%	3.53%	1.38%	1.10%	8.99%	3.34%	25.00%	4.54%	4.89%
Water,pure	2.19%	0.49%	24.28%	0.44%	1.84%	0.10%	15.03%	0.68%	0.46%
Water	0.06%	0.01%	0.01%	0.01%	0.04%	0.00%	0.57%	0.02%	0.02%
Silica Sand	0.03%	0.00%	0.00%	0.00%	0.02%	0.00%	0.11%	0.01%	0.00%
Fabrication	0.00%	2.22%	1.62%	1.30%	0.00%	9.54%	0.00%	0.00%	0.00%
Al Plate	2.55%	0.66%	0.41%	0.67%	2.34%	0.14%	5.15%	1.47%	0.71%
$Na_2S_2O_8$	0.08%	0.05%	0.01%	0.01%	0.06%	0.00%	0.16%	0.05%	0.03%
Pyrolysis	0.00%	0.15%	0.05%	0.00%	0.46%	0.00%	0.00%	0.14%	0.00%
Acetone	5.15%	0.76%	0.12%	0.01%	2.43%	0.01%	0.02%	2.35%	0.12%
Al_2O_3	0.62%	0.18%	0.10%	0.64%	0.56%	0.07%	2.24%	0.30%	0.06%
$(NH_4)_2SO_4$	0.14%	0.03%	0.01%	0.01%	0.12%	0.01%	0.47%	0.05%	0.05%
CuO	0.12%	0.42%	0.69%	0.97%	0.11%	0.69%	0.28%	0.37%	0.70%
HCl,30%	0.20%	0.05%	0.04%	0.04%	0.14%	0.01%	4.65%	0.06%	0.11%
Kraft Paper	5.08%	1.77%	1.06%	0.61%	3.85%	0.22%	11.58%	3.33%	1.54%
Polyester	1.55%	0.23%	0.23%	0.11%	1.36%	0.14%	4.50%	0.86%	0.31%
PE	1.01%	0.10%	0.01%	0.00%	0.38%	0.00%	0.00%	0.47%	0.00%
PMMA	4.94%	1.46%	0.18%	0.03%	3.89%	0.02%	0.05%	4.50%	0.07%
$KMnO_4$	0.14%	0.03%	0.03%	0.02%	0.11%	0.01%	0.25%	0.04%	0.04%
Soda	0.53%	0.37%	0.15%	0.11%	0.60%	0.05%	0.47%	0.29%	0.22%
NaCN	0.01%	0.00%	0.00%	0.00%	0.01%	0.00%	0.00%	0.00%	0.00%
NaOH,50%	0.35%	0.08%	0.08%	0.07%	0.25%	0.02%	0.49%	0.09%	0.20%
Tin	3.03%	4.22%	0.75%	0.47%	2.34%	0.10%	5.00%	4.31%	0.36%

Figure S11 A Chinese woman manually heated up a computer main board to remove chips. 2010, Guiyu, China. (Copyright: Jeffrey Lau/IPS)

v. Cost estimation of the paper based PCB.

The production cost of the paper based PCB is roughly calculated as following.

Table S11 Paper based PCB(4 layers&10000m^2) production cost estimation.

Items	Details	Material consumption	Price/USD	Cost for 10000 m^2 P-PCB/USD
Raw Materials[a]	Paper base(with adhesive on the back)	4000m^2	1.9/m^2	7600
	PU resin	103kg	40/kg	4120
	Silver flakes	103kg	560/kg	57680
Energy[b]	For processing	2670kWh	0.144/kWh	384.48
Others[c]	-		0.1/m^2	1000
Total	-		-	70784.48

a. We take the 4-layer P-PCB as example for the estimation and set the costs by reference to the material price on Alibaba (www.1688.com).
b. The detail information of energy consumption is shown in table S2.
c. This item includes costs of labour, workshop machine wear and comsumable items in the fabrication process.

The costs estimated in table S is based on the information we take into consideration in the LCA study, and we just roughly caculated the costs of raw materials and consumptions in the fabrication process. The result shows that the costs for 4-layer P-PCB is about 7 USD/m^2. However, this result can't represent all of the costs of the P-PCB, such as costs of designation, patent fee or other necessary costs in a mass production scenario. So we estimate the costs of the P-PCB as 15-30 USD/m^2 to make it reasonable.

Reference:

1. R. U. Ayres, L. Ayres and I. Råde, *The life cycle of copper, its co-products and by-products*, Springer, 2011.
2. T. Corbière-Nicollier, B. Gfeller Laban, L. Lundquist, Y. Leterrier, J.-A. Månson and O. Jolliet, *Resources, Conservation and Recycling*, 2001, **33**, 267-287.