

Grave-to-cradle Dry Reforming of Plastics via Joule Heating



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REVIEWER COMMENTS

Reviewer #1 (Remarks to the Author):

This study converts plastic and CO₂ into syngas through Joule heating. FeCrAl heating wire acts as a catalyst and thermionic support as well as heating. This process is a sustainable process that can prevent greenhouse gas emissions and cope with fossil fuel depletion by using photovoltaic cells. This study deals with an interesting topic. However, there is lack of details of experimental setup and conditions. For example, how to control temperature in a constant way with suppressing temperature fluctuation during reaction - this is the most important point of Joule heating-based process. To publish in a flagship journal like Nature communications, such experimental details must be fully clarified and justified, given that this is a kind of new process. Other comments that need to be considered before publication are listed below.

- ① Introduction: In the introduction part, the author emphasizes that this study is a method that can reduce carbon dioxide at the same time as plastic. It is recommended to add a brief explanation of how carbon dioxide emitted from industry can be utilized in this research system.
- ② Page 4, line 86: The author stated that a deposit of 12 mg of carbon was obtained. A detailed explanation of how this quantitative value was measured must be provided.
- ③ Page 4, line 86: The author implied that only hydrogen was generated in addition to 12 mg of carbon. An explanation is needed as to whether no other types of gas products other than hydrogen were generated at this point.
- ④ Page 5, Fig 1(a): The author inserted a schematic diagram of the reactor. However, it is necessary to further specify this schematic diagram to provide detailed information on the feed loading method and reactor configuration.
- ⑤ Page 6, Fig 2: In Fig 2(d): There are research results that obtained better yields at lower temperatures than this study. It is recommended to explain why the author's study is better than these results.
- ⑥ Page 6, Fig 2: Fig 2(d) specifies the pyrolysis yield. It is necessary to provide specific information about exactly what the yield is for.
- ⑦ Page 8, Fig 3: It is necessary to consider whether the heating zone is excessively long compared to the amount of feed.
- ⑧ Page 9, line 160: The author mentioned that it is difficult to obtain good results with PET and PS. If so, it is recommended to mention the reason for choosing PE between PP and PE.
- ⑨ Page 9, line 173: In large scale experiments, the sum of weight percent of CO and H₂ is less than the amount of feed. That is, it may suspect the presence of other products. If products other than H₂ and CO are generated, it is necessary to indicate their phase and amount.
- ⑩ Page 9, line 173: In large-scale experiments, as the size of the reactor becomes relatively large, it should be noted whether there is a negative impact on performance compared to a small reactor due to heat loss, etc.
- ⑪ Discussion: It is recommended to mention any limitations of this reactor or process that require further development or research.
- ⑫ Supplementary: The author mentioned that author used the UTi-260B product to recode the temperature. It is necessary to confirm whether this product can accurately detect temperatures above 550 °C.

Reviewer #2 (Remarks to the Author):

This study presents a novel catalytic reforming process that converts plastics and carbon dioxide (CO₂) into value-added chemicals using an electrified FeCrAl heating wire. In this process, the heating wire can quickly reach temperatures above 800 °C, facilitating the decomposition of polyethylene into

gaseous hydrocarbons. This heating method has been widely used in plastic conversion, representing significant progress in this field. However, this research does not discuss the carbon material production, the energy consumption and associated costs of operating an electrified heating wire at such high temperatures. Although CO₂ was introduced to facilitate syngas production, this concept is not particularly novel, as it has already been extensively studied in traditional heating-assisted conversion processes. More comments are as follows.

Introduction: A more comprehensive review of the conversion of plastics and CO₂ is needed, as this topic is extensively covered in the literature. Additionally, the current explanation of the research gap is not convincing. You should clearly outline why you are focusing on the catalytic conversion of plastics and CO₂ using Joule heating, and explain why you chose this specific catalyst for your study.
Line 64: Please check the statement again.

Line 66-75: More research methodologies should be provided.

Figure 2d: What does "Pyrolysis yield" mean? It is a bit confusing.

Mass balance plays a crucial role in the conversion of plastics and CO₂, and it should be detailed in this study.

When using CO₂ as a reactant, how did you determine the yield of the CO₂ product (Figure 1-3)?

Electrifying chemical processes is known to benefit the environment, but the cost implications are significant. I suspect the energy consumption in this process could be extremely high. Would it still be economically feasible for large-scale production?

Line 275: Conclusion?

Reviewer #3 (Remarks to the Author):

In "Grave-to-cradle Dry Reforming of Plastics via Joule Heating" the authors present an approach for the concurrent recycling of plastic waste and CO₂ gas to produce CO and H₂. The key part of the presented methodology is the use of the electrified catalytic FeCrAl wire. In a rather empirical field, it is admittedly exciting to see a systematic study of the effects various factors have on the products (Joule heating vs. conventional heating, electrified wire vs. unelectrified heated one, the material of the wire, etc.) I believe that alone warrants the publication of the manuscript; however, several points must be addressed in the minor revision.

1) The title is somewhat misleading, implying that plastics themselves are subjected to Joule heating, as was, for example, the case during H₂ production from waste plastics (Advanced Materials 35 (48), 2306763, 2023). Here, the catalytic wire is subject to the Joule heating instead. Also, a metaphor "Grave-to-cradle" may be more suitable for a follow-up news item or editorial blurb than for an article in technical journal; I leave this choice to the Editor though...

2) Page 3, line 64 mentions "conversion of waste plastic and CO₂ into syngas under sunlight irradiation", while "sunlight irradiation" does not seem to play any role in the process and is never mentioned again.

3) Fig. 2d shows several processes that display comparable or even higher conversion achieved at lower temperatures which generally would mean lower energy costs. The authors should explain the benefit of the proposed method over those other methods.

4) I found the comparison of the various catalyst wire materials very interesting. In particular, the use of carbon fiber seems very promising due to its simplicity and affordability. Did the authors perform any further characterization/analysis of the process with the use of carbon fiber?

5) The solid byproduct of the process is not necessarily useless, as some similar processes were shown to produce graphene/graphite (as seen in, again, Advanced Materials 35 (48), 2306763). Was the solid product characterized? This knowledge can significantly affect how the current process is optimized.

6) The conclusion slightly overstates the usability of this process for other plastics. Fig. 2b clearly shows that no other plastic can match the performance in PE reforming. I think corresponding

sentences should be adjusted to reflect that.

Overall, with the proper revisions the paper can become suitable for Nat Comm.

Point-to-point reply to comments

Reviewer #1 (Remarks to the Author):

This study converts plastic and CO₂ into syngas through Joule heating. FeCrAl heating wire acts as a catalyst and thermionic support as well as heating. This process is a sustainable process that can prevent greenhouse gas emissions and cope with fossil fuel depletion by using photovoltaic cells. This study deals with an interesting topic. However, there is lack of details of experimental setup and conditions. For example, how to control temperature in a constant way with suppressing temperature fluctuation during reaction - this is the most important point of Joule heating-based process. To publish in a flagship journal like Nature communications, such experimental details must be fully clarified and justified, given that this is a kind of new process. Other comments that need to be considered before publication are listed below.

Comment 1: Introduction: In the introduction part, the author emphasizes that this study is a method that can reduce carbon dioxide at the same time as plastic. It is recommended to add a brief explanation of how carbon dioxide emitted from industry can be utilized in this research system.

Reply: A brief explanation of how to use the CO₂ from industry has been supplemented in the introduction as follow:

Combined with the mature post-combustion CO₂ capture technology, such as cyclic adsorption/desorption by using amine-based solvents, up to 90 % of CO₂ emission from industrial processes and power generation will be captured and used for reforming with plastic to produce syngas.

Comment 2: Page 4, line 86: The author stated that a deposit of 12 mg of carbon was obtained. A detailed explanation of how this quantitative value was measured must be provided.

Reply: A detailed description about quantifying the mass of residual solid has been supplemented in the experimental section in the Supporting information as follow:

Because the carbon residual mainly deposits on the boat, resistance wire and quartz tube, the mass of solid was determined by weighing the total mass of the three parts before and after reaction.

In addition, the description of the quantification for the PE dehydrogenation experiment was also improved as follow:

Under the conditions of 4 amperes current for 15 minutes, 0.998 mmol H₂ was achieved according to the quantify result of gas chromatograph except of the negligible hydrocarbons, CO and CO₂ (Supplementary Table 2). The trace amount of oxygen and positive deviation of mass or carbon balance may come from the FeCrAl heating wire because there are 2.06 wt % oxygen and 6.57 wt % carbon according to energy dispersive X-ray microanalysis of scanning electron microscope (SEM-EDS, Supplementary Fig. 2). The mass of the residual carbon was about 12 mg, indicating the successful dehydrogenation of PE (Fig. 1b).

Supplementary Table 1. The detailed weight analysis from one practical experiment¹

Conditions	Part	Weight (g) ²
Before reaction	LDPE	0.0140
	A (Porcelain boat + wire)	9.3547
	B (Quartz tube)	44.9872
After reaction	C (Porcelain boat + wire + quartz tube)	54.3544

1 Reaction conditions: 14 mg PE, Ar, 4 A (6 Ω) 15 min.

2 All involved mass was weighted by a balance, and the mass of carbon was calculated by the following formula:

Comment 3: Page 4, line 86: The author implied that only hydrogen was generated in addition to 12 mg of carbon. An explanation is needed as to whether no other types of gas products other than hydrogen were generated at this point.

Reply: Thanks a lot for this professional question. We checked the original data carefully and found that there were tiny amounts of CH₄, CO₂ and even CO on the spectrum of GC indeed except hydrogen. The quantified result is as follow:

Supplementary Table 2. The detailed products distribution, carbon balance and mass balance in the PE dehydrogenation.

Reaction time(min)	n _{H2} (mmol)	n _{CO} (mmol)	n _{CO2} (mmol)	n _{CH4} (mmol)	n _{C2+} (mmol)	n _{solid} (mmol)	Carbon balance (%)	Mass balance (%)
15	1.003	0.000468	0.000430	0.0137	0.000759	1.05	106.5	106.2

Based on this result, the description about this experiment in the manuscript was modified and improved as provided in the Reply to Comment 2.

Comment 4: Page 5, Fig 1(a): The author inserted a schematic diagram of the reactor. However, it is necessary to further specify this schematic diagram to provide detailed information on the feed loading method and reactor configuration.

Reply: A new schematic diagram of the reactor containing more details has been provided. Besides, the description about the reactor was also provided.

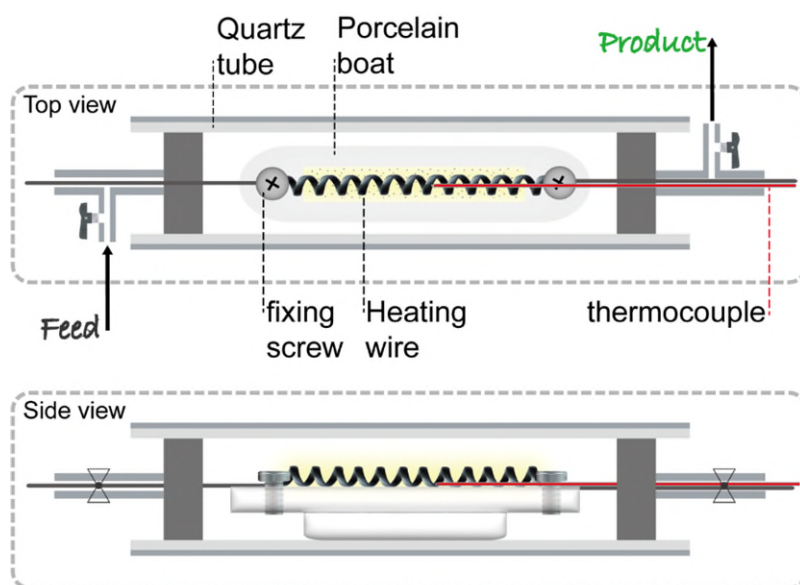


Fig. 1 | Reactor configuration and reaction conditions screening. a Schematic of an electrified reactor for CO₂ reforming of plastics;

In our study, a reactor being composed of one quartz tube (outer diameter: 25mm, inner diameter: 19 mm, length 100mm), a length of spring-like FeCrAl heating wire (diameter: 0.3 mm), a porcelain boat as sample holder, a pair of metal flange seals equipped with two ball valves and two copper wires was designed so that the heating wire can be electrified in and used as key component to promote the reaction involving plastics and CO₂ in a sealed environment. The actual temperature around the heating wire in the reactor can be measured by a thermocouple installed in the reactor (Fig. 1a and Supplementary Fig. 1). During our research, a piece of heating wire with a resistance value of 6 ohms was electrified by a direct current (DC) power generator (MAISHENG, MP3030D) in the reactor containing 14 mg of polyethylene (PE) powder and being full of argon gas. The gas products can be quantified by a gas chromatograph and the residual carbon can be determined by weighing the total mass of main parts of the reactor before and after reaction, including the quartz tube, porcelain boat and resistance wire.

Comment 5: Page 6, Fig 2: In Fig 2(d): There are research results that obtained better yields at lower temperatures than this study. It is recommended to explain why the author's study is better than these results.

Reply: We carefully re-examined the references included in Fig. 2d. The pyrolysis yield referred to the various gas products in the pyrolysis process, including CO, H₂, CH₄ and other gaseous hydrocarbons.

However, only molar yields of H₂ and CO were provided in the Fig.2d for our research. Therefore, the result of our study is not the best “pyrolysis yield” in comparison with the reported results. Actually, it is not reasonable to compare the “pyrolysis yield” in the context of research on how to achieve high-yield syngas. Consequently, the Fig. 2d was re-compiled and the “pyrolysis yield” is replaced by “syngas yield”.

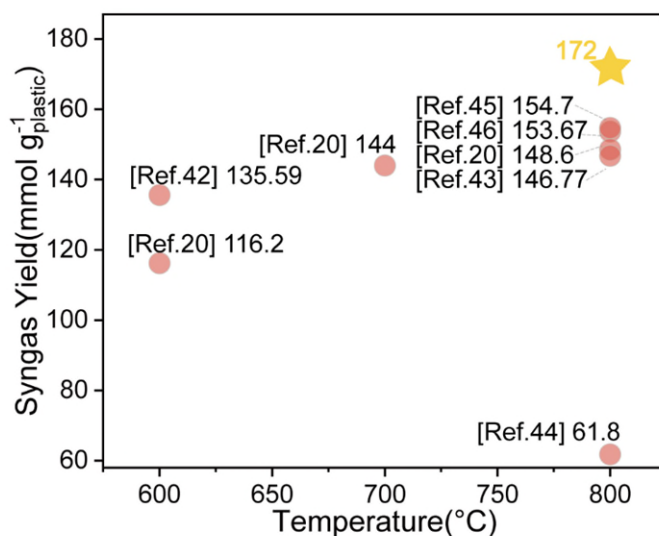


Fig. 2 | d the comparison of our result with ones from other reported catalytic system.

Comment 6: Page 6, Fig 2: Fig 2(d) specifies the pyrolysis yield. It is necessary to provide specific information about exactly what the yield is for.

Reply: The answer for this comment is the same as comment 5.

Comment 7: Page 8, Fig 3: It is necessary to consider whether the heating zone is excessively long compared to the amount of feed.

Reply: This comment is professional. To carry out the large-scale experiment, various reactors with different sizes and types were designed and evaluated for the efficiency of reforming processes. It was concluded that the heating zone should be as long as the reactor so that the gaseous hydrocarbons

cannot be condensed on the wall of the reactor, or the condensation of gaseous hydrocarbons will generate more carbon deposit. The corresponding discussion has also been supplemented in the revised manuscript as follow.

We conclude that the fast heat loss through the large-size quartz tube results to the condensation of hydrocarbons. These condensed hydrocarbons cannot reform with CO₂ on the surface of heating wire and subsequently be converted into carbon deposit on the reactor wall. Therefore, in the practical large-scale experiment, some important factors, such as the pressure in the reactor, the distribution of the heating zone and the insulation technology for minimizing the heat loss, should all be considered.

Comment 8: Page 9, line 160: The author mentioned that it is difficult to obtain good results with PET and PS. If so, it is recommended to mention the reason for choosing PE between PP and PE.

Reply: The corresponding discussion has been improved as follow:

With PP as reactant, the CO yield was slightly lower than with PE as reactant and more residual solid was left, which maybe resulted from the recombination of radicals generated during the reaction at high temperature. Furthermore, the residual solids amounts were higher for PS or PET than for PE or PP, demonstrating the difficulty of destroying the benzene ring in PS or PET. As a result, the components that are difficult to be destroyed tends to be transformed into coke. Consequently, PE was selected as a candidate to carried out the exhaustive study.

Comment 9: Page 9, line 173: In large scale experiments, the sum of weight percent of CO and H₂ is less than the amount of feed. That is, it may suspect the presence of other products. If products other than H₂ and CO are generated, it is necessary to indicate their phase and amount.

Reply: Indeed, there are other products such as methane, ethane and solid carbon. The generated various components after reaction are listed and presented in Supplementary Table 3. The corresponding discussion has also been improved in the revised manuscript.

Supplementary Table 4. The quantitative analysis of various products from the large-scale reaction¹.

Reaction time	n H ₂	n CO	n CO ₂	n CH ₄	n C ₂₊	m	Carbon
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(min)	(mmol)	(mmol)	(mmol)	(mmol)	(mmol)	solid (mg)	balance (%)
30	45.3	101.4	110	2.5	1.7	480	99

1 Reaction conditions: 1g LDPE, 3.3g CO₂, 18Ω, 30min.

Actually, some carbon deposit (480 mg) on inner wall of the quartz tube can be observed. In addition, the productions of methane and other hydrocarbons were not negligible and small amount of CO₂ (110 mg) was also left (Supplementary Table 4). We conclude that the fast heat loss through the large-size quartz tube results to the condensation of hydrocarbons. These condensed hydrocarbons cannot reform with CO₂ on the surface of heating wire and subsequently be converted into carbon deposit on the reactor wall. Therefore, in the practical large-scale experiment, some important factors, such as the pressure in the reactor, the distribution of the heating zone and the insulation technology for minimizing the heat loss, should all be considered.

Comment 10: Page 9, line 173: In large-scale experiments, as the size of the reactor becomes relatively large, it should be noted whether there is a negative impact on performance compared to a small reactor due to heat loss, etc.

Reply: This is a professional question. The discussion about the negative impact on performance has been provided in the revised manuscript.

We conclude that the fast heat loss through the large-size quartz tube results to the condensation of hydrocarbons. These condensed hydrocarbons cannot reform with CO₂ on the surface of heating wire and subsequently become into carbon deposit on the reactor wall. Thus, CO₂ was not reformed entirely in the large-scale reaction system. Therefore, in the actual large-scale experiment, some important factors, such as the pressure in the reactor, the distribution of the heating zone and the insulation technology for minimizing the heat loss, should all be considered.

Comment 11: Discussion: It is recommended to mention any limitations of this reactor or process that require further development or research.

Reply: The limitations and the corresponding suggestions of the reactor have been discussed in the part of discussion as follow:

However, some problems should be addressed if this kind of reforming reactor will be magnified and applied in the practical industry for the reforming of waste plastics and CO₂. Firstly, the reactor is a kind of batch reactor and the duration is crucial to comprehensively reform plastics with CO₂, which make it difficult to achieve the continuous feed of plastics and CO₂ to reactor. Even if the intermittent feeding is acceptable for the batch reactor, a feeding inlet should also be designed on the tube so that solid plastic can be fed around the heating wire. Secondly, in the large-scale reaction, considering the molar amount of CO₂ should be same with the molar amount of carbon in plastics in order to reform entirely, the volume of reactor should be large enough to accommodate the enough amount of CO₂. Consequently, the heating zone should be expanded to the whole reactor. In addition, insulation measures should be adopted to minimize the carbon deposit and ensure the reforming reaction entirely. More importantly, since the reforming reaction is a volume expansion process, safety for the experiment operator must be ensured. If a metal reactor is designed to improve the safety, the electric and thermal insulation must be taken into account to ensure normal electrification and resistance to heat loss. The corresponding investigations are currently being carried out in our laboratory.

Comment 12: Supplementary: The author mentioned that author used the UTi-260B product to recode the temperature. It is necessary to confirm whether this product can accurately detect temperatures above 550 °C.

Reply: The infrared thermal imager (UTi-260B, Uni-Trend Technology Co., Ltd.) was used in our research to detect the outer temperature of the reforming reactor. Due to the presence of a quartz tube, the exact temperature of the electrified heating wire cannot be determined. More importantly, the temperature measurement range of the thermal camera (UTi-260B) is -20 °C ~550 °C according to its operating instruction. However, during the actual operation, the record temperature can reach up to 680 °C. The inserted image in Fig. 1d was 609 °C, higher than the measurement range. The actual temperature around the heating wire was measured by a K-type thermocouple connecting to a digital multimeter (Fig. 1c and 1d). To avoid the confusion, the method to detect temperatures for the Supplementary Fig. 1 was supplemented in the caption of Fig. 1.

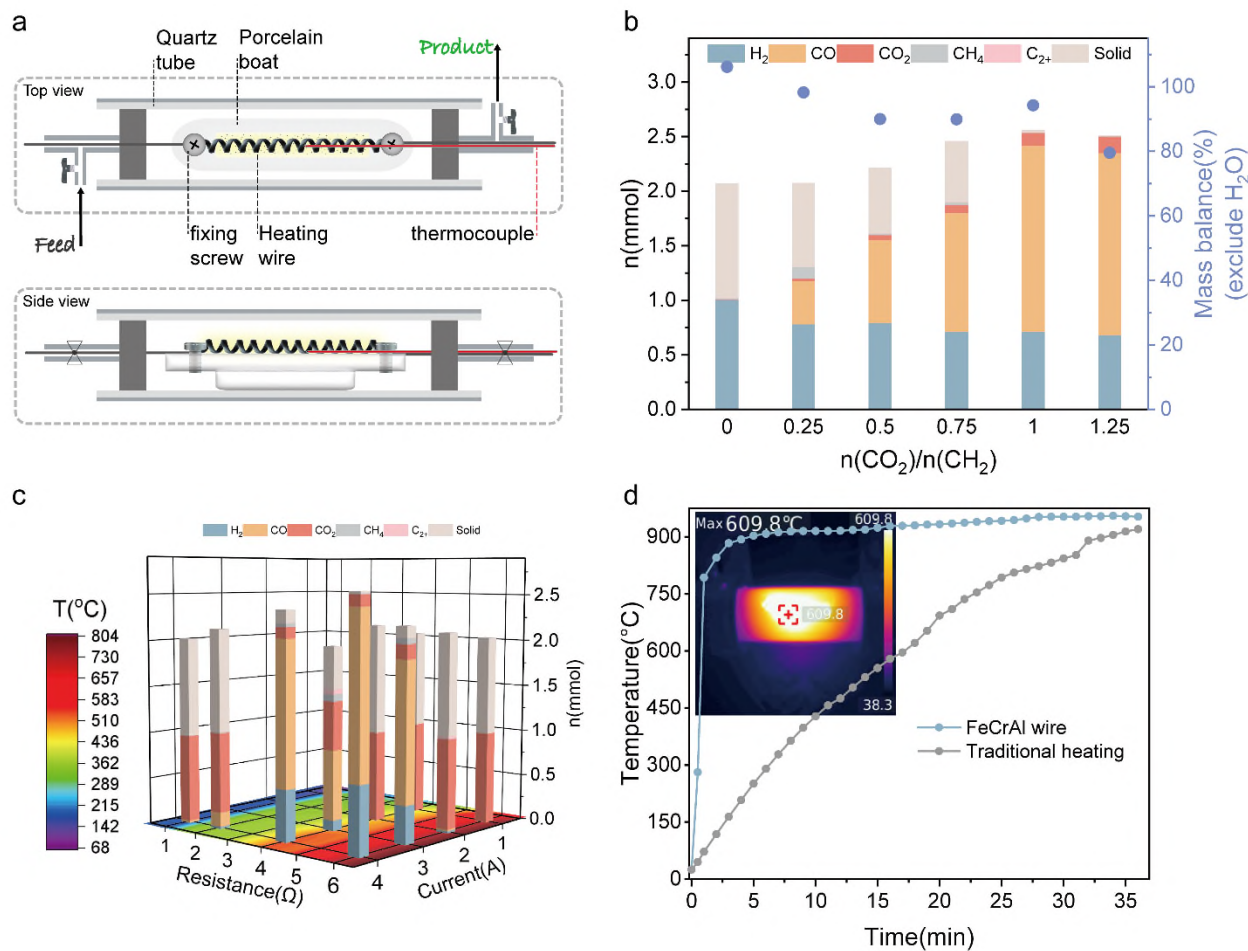


Fig. 1 Reactor configuration and reaction conditions screening. **a** Schematic of an electrified reactor for CO₂ reforming of plastics; **b** products distribution with different mole ratio of CO₂ to n (moles of CH₂ in PE), Reaction conditions: PE=14 mg, FeCrAl heating wire 6 Ω, current 4 A, T= 800 °C, 15 min; **c** the product distribution over temperature profile under different current and resistance values; Reaction conditions: PE=14 mg, n(CO₂)/n(CH₂)= 1, FeCrAl heating wire, 15 min. the temperatures were measured by a thermocouple; **d** the heating rates of electrified FeCrAl heating wire (power = 96 W) and traditional tube furnace (power = 1000 W), the temperatures for the profiles were measured by a thermocouple, the inserted thermal image was recorded by a thermal camera (UTi-260B).

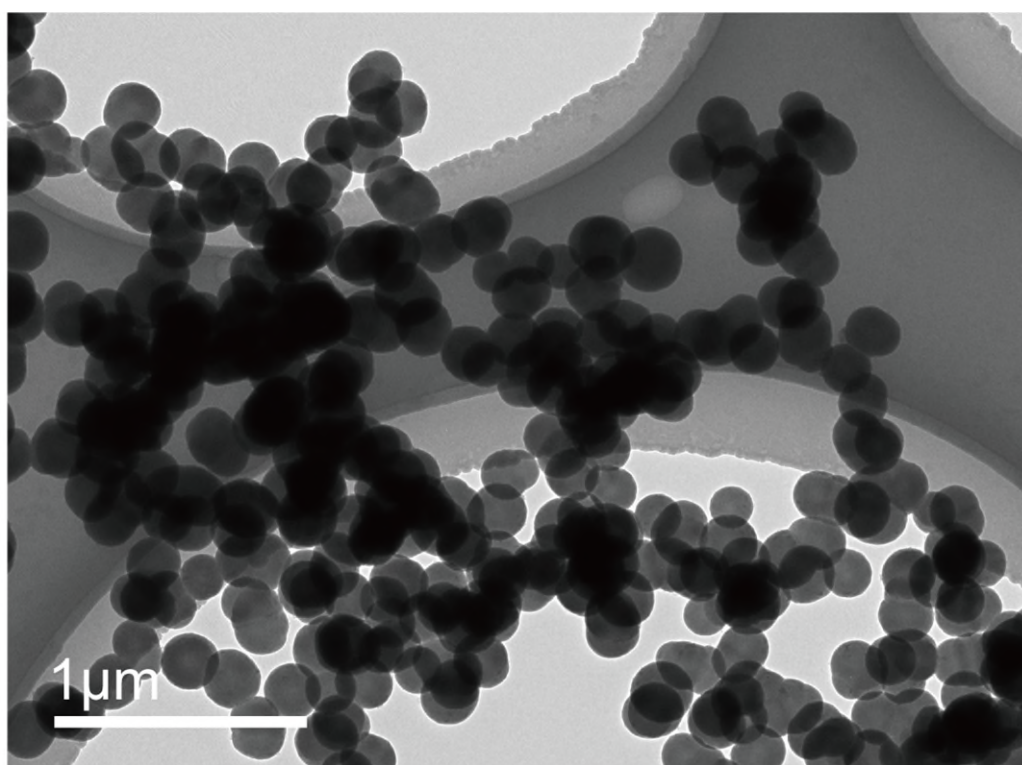
Reviewer #2 (Remarks to the Author):

General comment: This study presents a novel catalytic reforming process that converts plastics and carbon dioxide (CO₂) into value-added chemicals using an electrified FeCrAl heating wire. In this process, the heating wire can quickly reach temperatures above 800 °C, facilitating the decomposition of polyethylene into gaseous hydrocarbons. This heating method has been widely used in plastic conversion, representing significant progress in this field. However, this research does not discuss the carbon material production, the energy consumption and associated costs of operating an electrified heating wire at such high temperatures. Although CO₂ was introduced to facilitate syngas production, this concept is not particularly novel, as it has already been extensively studied in traditional heating-assisted conversion processes. More comments are as follows.

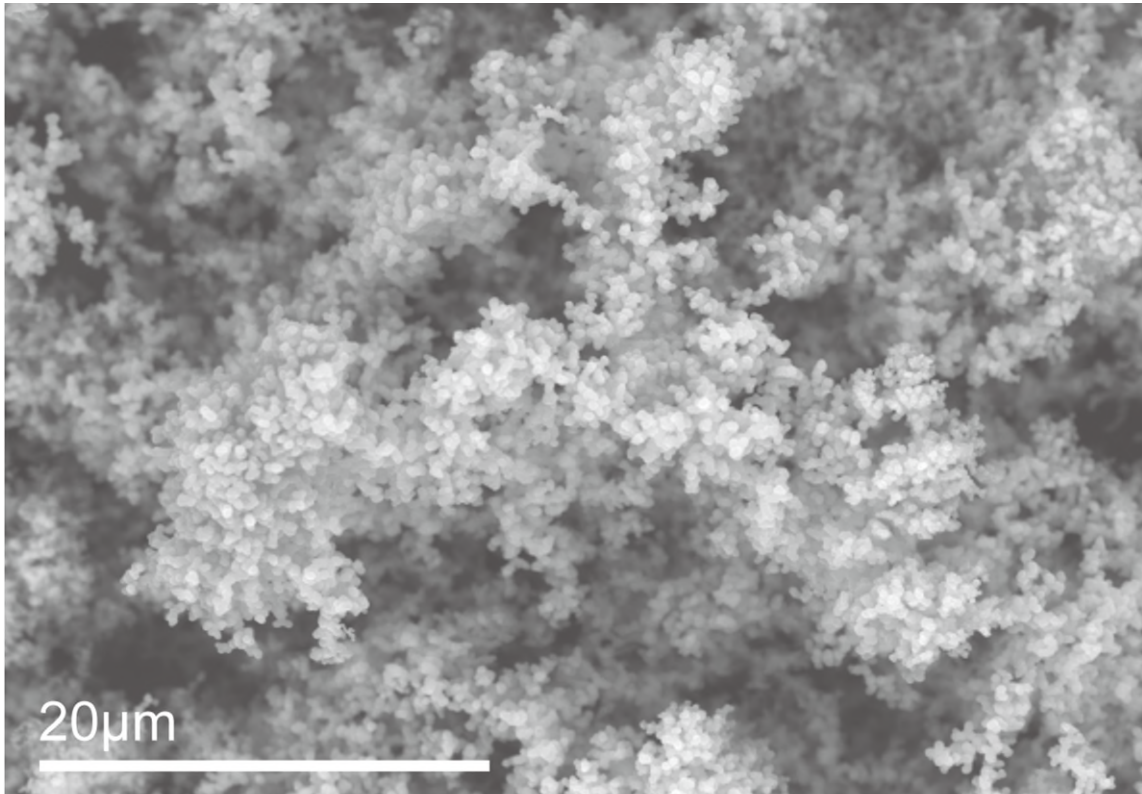
Reply: Thanks a lot for the constructive comment. The discussion about the carbon material production, the energy consumption and associated costs of operating an electrified heating wire at such high temperatures were all supplemented in the part of discussion in the revised manuscript.

Indeed, Flash Joule Heating (FJH) technology has been used to convert plastics to one or two-dimension carbon nanomaterials in the presence of metal chloride as catalyst or carbon black as conductive additives. The achieved carbon nanotube must contain the metal nanoparticles and the conductive additive such as carbon black would impact the purity of the achieved graphene. Compared to the two FJH strategies, our reforming system with electrified heating wire as key component avoid the introduction of conductive additives or catalyst. In the absence of CO₂, PE can also be dehydrogenated to carbon nanospheres (Supplementary Fig. 8 and Fig. 9) and hydrogen quantificationally. The carbon nanospheres mainly deposit on the heating wire and the inner wall of reactor, which make the separation from reactor easier than other reaction system.

Although the electrification for heating wire is the main energy consumption during the entire reaction according to the LCA result, it is an energy saving process because the internal heating strategy avoid the heat conduction and heat exchange in the traditional heating measures. The chemical energy of plastics is fully converted into the products syngas according to the calculated energy recovery efficiency. To facilitate the observation of the experimental phenomena, the main part of the reactor is designed as quartz tube without a heat insulator. By reducing the heat loss during the reaction, the energy consumption will be reduced.



Supplementary Fig. 8 TEM image of residual carbon from LDPE dehydrogenation. Reaction conditions: 14 mg PE, Ar, 4 A (6 Ω), 15 min.



Supplementary Fig. 9 SEM image of residual carbon from LDPE dehydrogenation. Reaction conditions: 14 mg PE, Ar, 4 A (6 Ω), 15 min.

Comment 1: Introduction: A more comprehensive review of the conversion of plastics and CO₂ is needed, as this topic is extensively covered in the literature. Additionally, the current explanation of the research gap is not convincing. You should clearly outline why you are focusing on the catalytic conversion of plastics and CO₂ using Joule heating, and explain why you chose this specific catalyst for your study.

Reply: The discussion about the disposal of waste plastic and the corresponding explanation involving why we are focusing on the catalytic conversion of plastics and CO₂ using Joule heating have been supplemented in the part of Introduction.

Only a small proportion of plastic waste was recycled to produce low-quality plastic products or burned to recover chemical energy. Although incineration is an efficient strategy to dispose of solid plastic waste and generate heat for power generation, huge CO₂ emissions are unavoidable. In addition, due to the incomplete combustion or presence of the nitrogen or sulfur-containing additives in plastics,

some gaseous pollutants such as polycyclic aromatic hydrocarbons, NO_x and SO_x are generated. From an environmental protection perspective, there is an urgent need to develop a green and sustainable strategy to dispose of plastic waste accumulated in the environment. Moreover, with the rapid development of the society and the rapid improvement of the level of industrialization,

..... Along with the increase of availability and accessibility of green and sustainable electricity from sun and wind, using electricity energy to heat chemical reactor is a promising way to achieve the decarbonization of chemical process. The microwave heating, induction heating and Joule heating are the three ways to achieve the electricity-to-heat process, which have their special advantages and limitation due to the different power-to-heat principles. Among the three electricity-to-heat ways, the Joule heating has a theoretical energy efficiency of 100% because it directly transforms electricity to heat by driving charge carriers to flow through conductor to generate high temperature. By electrifying the catalyst, or support for active phase, or reactor wall, the higher reaction temperature required for reactions can be achieved instantly, avoiding heat transfer as in the conventional heating process and the transformation of electrical energy into electromagnetic energy as in microwave heating and induction heating. The fast heating rate and uniform heat distribution contribute to higher reaction efficiency, which translates into lower CO₂ emission.

Comment 2: Line 64: Please check the statement again.

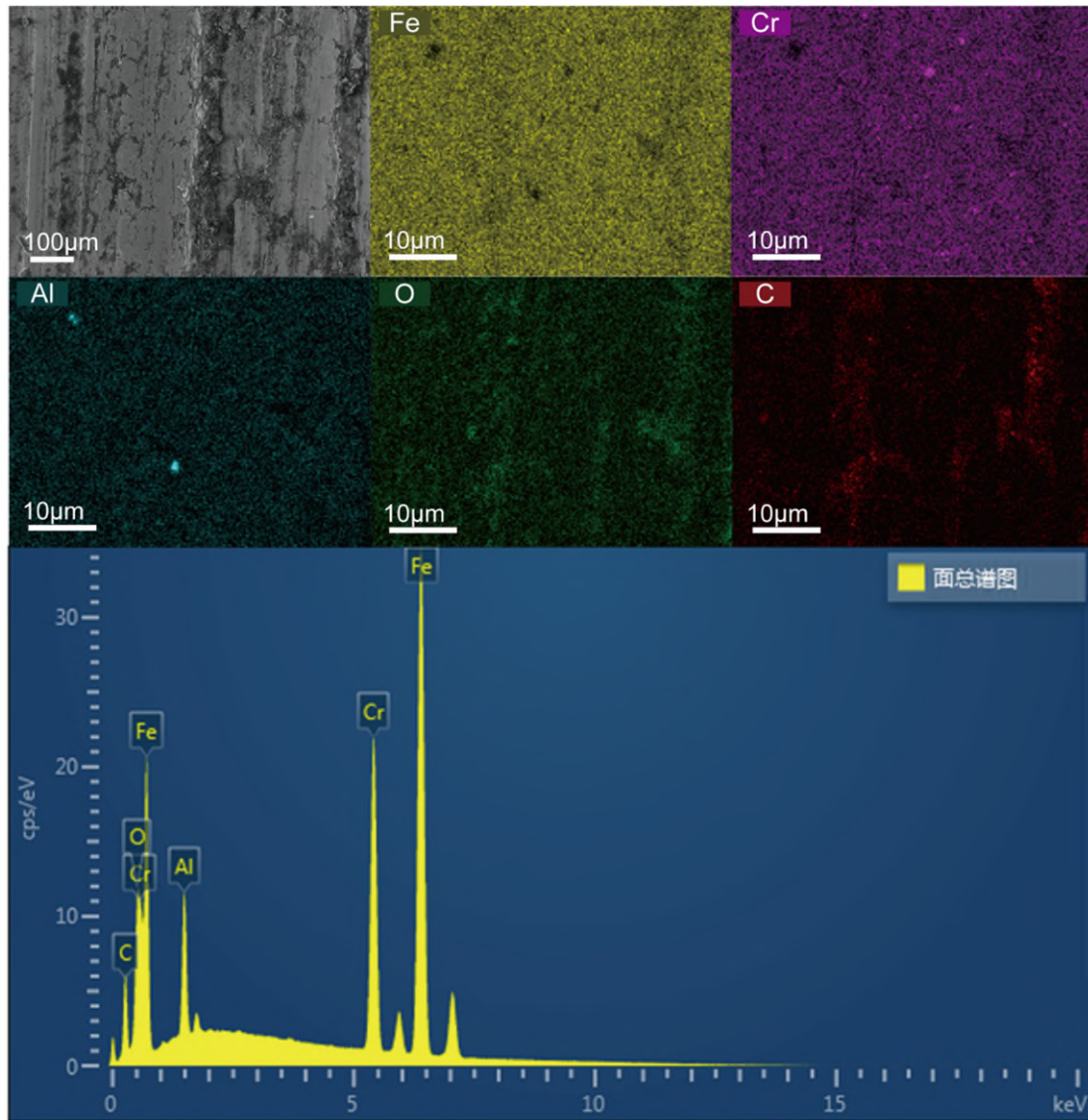
Reply: Although we present a demo experimental instrument through which the reforming of PE with CO₂ to syngas was achieved under solar irradiation, the main experiments were carried out by using the electricity from power grid in our laboratory. Therefore, the statement has been improved to avoid confusion.

In this report, we develop a novel and sustainable catalytic system for the efficient and selective conversion of waste plastic and CO₂ into syngas. In order to ensure an environmentally friendly and sustainable process, a photovoltaic power system was used to supply energy. Consequently, the reforming of plastics with CO₂ to syngas can be carried out under sunlight irradiation.

Comment 3: Line 66-75: More research methodologies should be provided.

Reply: We have provided detailed description in the first part of Results: Plastics reforming with CO₂. Besides, the Fig. 1a presenting the experimental reactor was also updated, which exhibited more details. Accompanied with the following description, readers can knowledge the experimental methodologies.

In our study, a reactor being composed of one quartz tube (outer diameter: 25mm, inner diameter: 19 mm, length 100mm), a length of spring-like FeCrAl heating wire (diameter: 0.3 mm), a porcelain boat as sample holder, a pair of metal flange seals equipped with two ball valves and two copper wires was designed so that the heating wire can be electrified in and used as key component to promote the reaction involving plastics and CO₂ in a sealed environment. The actual temperature around the heating wire in the reactor can be measured by a thermocouple installed in the reactor (Fig. 1a and Supplementary Fig. 1). During our research, a piece of heating wire with a resistance value of 6 ohms was electrified by a direct current (DC) power generator (MAISHENG, MP3030D) in the reactor containing 14 mg of polyethylene (PE) powder and being full of argon gas. The gas products can be quantified by a gas chromatograph and the residual carbon can be determined by weighing the total mass of main parts of the reactor before and after reaction, including the quartz tube, porcelain boat and resistance wire (Supplementary Table 1). Under the conditions of 4 amperes current for 15 minutes, 0.998 mmol H₂ was achieved according to the quantify result of gas chromatograph except of the negligible hydrocarbons, CO and CO₂ (Supplementary Table 2). The trace amount of oxygen and positive deviation of mass or carbon balance may come from the FeCrAl heating wire because there are 2.06 wt % oxygen and 6.57 wt % carbon according to energy dispersive X-ray microanalysis of scanning electron microscope (SEM-EDS, Supplementary Fig. 2). The mass of the residual carbon was about 12 mg, indicating the successful dehydrogenation of PE (Fig. 1b).



element	wt%
C	6.57
O	2.06
Al	3.07
Cr	22.97
Fe	65.32
Total:	100.00

Supplementary Fig. 2 SEM and Energy-dispersive X-ray spectroscopy (EDS) mapping images of fresh FeCrAl heating wire.

Supplementary Table 1. The detailed weight analysis from one practical experiment¹

Conditions	Part	Weight (g) ²
Before reaction	LDPE	0.0140
	A (Porcelain boat + wire)	9.3547
	B (Quartz tube)	44.9872
After reaction	C (Porcelain boat + wire + quartz tube)	54.3544

1 Reaction conditions: 14 mg PE, Ar, 4 A (6 Ω) 15 min.

2 All involved mass was weighted by a balance, and the mass of carbon was calculated by the following formula:

Comment 4: Fig. 2d: What does “Pyrolysis yield” mean? It is a bit confusing.

Reply: We carefully re-examined the references included in Fig. 2d. The pyrolysis yield referred to the various gas products in the pyrolysis process, including CO, H₂, CH₄ and other gaseous hydrocarbons. However, only molar yields of H₂ and CO were provided in the Fig.2d for our research. Therefore, the result of our study is not the best “pyrolysis yield” in comparison with the reported results. Actually, it is not reasonable to compare the “pyrolysis yield” in the context of research on how to achieve high-yield syngas. Consequently, the Fig. 2d was re-compiled and the “pyrolysis yield” is replaced by “syngas yield”.

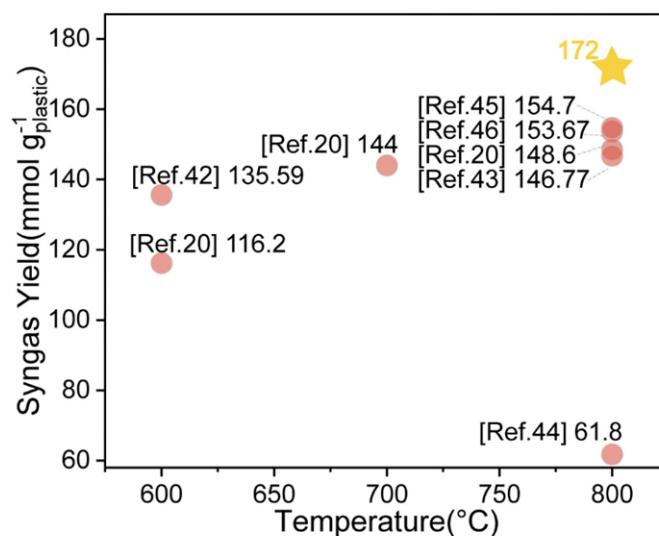


Fig. 2 | d the comparison of our result with ones from other reported catalytic system.

Comment 5: Mass balance plays a crucial role in the conversion of plastics and CO₂, and it should be detailed in this study.

Reply: Indeed, mass balance is important in this study, which can reflect the accuracy of the reaction. In particular, if the dehydrogenation of plastics has not yet been completed or residual carbon contains elements other than carbon, the calculation of the left moles of residual carbon is incorrect. Therefore, the mass balance values have been supplemented in the Fig.1-3. However, one question should be pointed out: some water may be produced during the reaction due to the presence of CO₂ and H₂ generated, which cannot be quantified by GC. Thus, the mass balances in this study are mainly concentrated around 85~95%.

Comment 6: When using CO₂ as a reactant, how did you determine the yield of the CO₂ product (Fig. 1-3)?

Reply: The ordinates of Fig. 1b, c, Fig. 2a, b and the horizontal ordinate of Fig. 3a represent millimole number of various products, such as CO, H₂ and CH₄. Because CO₂ is a reactant, the millimole number

of CO₂ represent the molar number left in the system. It is not suitable to exhibit the result as yield of various components.

Comment 7: Electrifying chemical processes is known to benefit the environment, but the cost implications are significant. I suspect the energy consumption in this process could be extremely high.

Reply: The higher heating values (HHV) of various products and the chemical energy of LDPE are listed in the Supplementary Table 7. Thus, the energy recovery efficiency of an electrified reforming reaction can be calculated as shown in the Supplementary Table 8. The power consumption for an optimal reaction was measured by a coulombmeter. According to the coulombmeter, 0.032 KWh of electricity was consumed in an optimal reaction, which corresponds to the energy of 115.2 kJ. The 0.071 mmol of H₂, 1.7 mmol of CO and small amounts of hydrocarbons can be achieved in an optimal reaction, corresponding to energy of 0.6912 kJ according to the HHVs of products. That is, the output energy is about 0.6912 kJ. The input energy includes the chemical energy of LDPE and the consumed electric energy, corresponding to 116.27 kJ. Therefore, the energy recovery efficiency is only about 0.60 %. It can be clearly observed that high electricity consumption causes the low energy recovery efficiency. To improve the sustainability of the electrified reforming system, a demo configuration powered by a photovoltaic power system using solar irradiation was developed. Thus, the electricity input from conventional grids was seen as zero and the energy recovery efficiency reached to 107.5%. Therefore, this solar-energy-driven reforming system can be seen as a strategy to store solar energy into plastic-derived syngas. The corresponding discussion was also provided in the part of **Life cycle assessment**.

Because the energy consumption of the reforming system mainly focused on the electricity, the energy recovery efficiency is only 0.60 % according to the corresponding calculations (Supplementary Table 8 and 9). This procedure is just like to transform electric energy to chemical energy. To improve the sustainability and energy recovery efficiency of the electrified system for converting waste carbon sources (such as waste plastics and CO₂) into syngas, the electrified FeCrAl heating wire can be

powered by a photovoltaic power system (PV) utilizing solar irradiation. As illustrated in Fig. 5b, the CO₂ reforming of PE can be smoothly carried out under natural solar irradiation in the solar-powered electrified system. This approach reduces PFE depletion and GHG emissions by 94.9 % and 95.7 %, respectively. More importantly, the energy recovery efficiency increases to 107.5%, showing a practical and potential strategy to store solar energy. Therefore, this environmentally friendly strategy for upvaluing waste plastics and carbon dioxide is both sustainable and efficient, with the potential for application in a low-carbon future.

Supplementary Table 7. The higher heating values (HHV) of gaseous products and chemical energy of LDPE.

Chemicals	HHV ¹ (KJ/mol)	Chemical Energy (MJ/kg)
H ₂	286	
CO	283	
CH ₄	889	
C ₂ H ₄	1418	
C ₂ H ₆	1560	
C ₃ H ₆	2220	
LDPE	--	45.9 ²

Supplementary Table 8. The energy recovery efficiency of the reforming system powered by a photovoltaic power system (PV) utilizing solar irradiation or Chinese electricity grids.

Chemicals/electricity	n (mmol)	Chemical energy (KJ)	Output energy (KJ)	Input energy (KJ)	Energy recovery efficiency ³ (%)

					Electricity grids	Solar PV system
H ₂	0.71	0.2031	0.6912	-	0.60	107.5
CO	1.70	0.4811		-		
CH ₄	0.00672	0.0060		-		
C ₂ H ₄	0.0004487	0.00064		-		
C ₂ H ₆	9.868E-05	0.00015		-		
C ₃ H ₆	7.74884E-05	0.00017		-		
LDPE	1 (14 mg)	0.00017		0.6426		
Electricity	-	-		115.2		

The chemical energy of gaseous products was calculated according to the moles and the HHV or chemical energy listed in Supplementary Table 7. For example, the chemical energy of H₂ achieved in the optimal reaction can be achieved as follow:

The output energy is the sum of the chemical energy of all products.

The input energy in the optimal reaction powered by electricity grids includes the chemical energy of LDPE and the electricity consumption that was measured by a coulombmeter. According to the coulombmeter, 0.032 KWh of electricity was consumed in an optimal reaction, which corresponds to the energy of 115.2 kJ.

The energy recovery efficiency in an optimal reaction powered by electricity grids was calculated according to the following formula:

$$\text{Energy recovery efficiency} = \text{output energy} / (\text{LDPE chemical energy} + \text{electricity energy}) \times 100 \%$$

However, the energy recovery efficiency of a reaction powered PV system under solar irradiation was calculated according to the following formula:

$$\text{Energy recovery efficiency} = \text{output energy} / (\text{LDPE chemical energy}) \times 100 \%$$

1. https://www.liquisearch.com/heat_of_combustion/heat_of_combustion_tables.
2. Splitstone PL, Johnson WH. The enthalpies of combustion and formation of linear polyethylene. *Journal of Research of the National Bureau of Standards Section A, Physics and Chemistry* **78**,

611 (1974).

3. Luo J, *et al.* Leveraging CO₂ to directionally control the H₂/CO ratio in continuous microwave pyrolysis/gasification of waste plastics: Quantitative analysis of CO₂ and density functional theory calculations of regulation mechanism. *Chem Eng J* **435**, (2022).

Comment 8: Would it still be economically feasible for large-scale production?

Reply: In our large-scale experiment, the resistance value is 18 ohms and the electrified time is 0.5 h. The power consumption is about 1344 KWh, corresponding to the energy of 4840000KJ. However, the higher heating values (HHV) of H₂ and CO achieved in the reaction is only 41.65 KJ. According to these data, it is not economically feasible in large-scale production. The heat loss through the walls of reactor results a long heating process to an ideal high temperature. The heat insulator should be introduced in the large-scale production. The corresponding discussion has been supplemented in the part of Discussion.

Although the electrification for heating wire is the main energy consumption during the entire reaction according to the LCA result, it is an energy saving process because the internal heating strategy avoid the heat conduction and heat exchange in the traditional heating measures. The chemical energy of plastics is fully converted into the products syngas according to the calculated energy recovery efficiency. To facilitate the observation of the experimental phenomena, the main part of the reactor is designed as quartz tube without a heat insulator. By reducing the heat loss during the reaction, the energy consumption will be reduced.....

However, some problems should be addressed if this kind of reforming reactor is magnified and applied in the actual industry to reforming the waste plastics and CO₂. Firstly, the reactor is a kind of batch reactor and the duration is crucial to comprehensively reform plastics with CO₂, which make the continuous feed of plastics and CO₂ to reactor difficult. Even if the intermittent feeding is acceptable

for the batch reactor, a feeding inlet should also be designed on the tube so that solid plastic can be fed around the heating wire. Secondly, in the large-scale reaction, because the molar amount of CO₂ should be same to the molar amount of carbon in plastics in order to reform entirely, the volume of reactor should be enough large to accommodate the enough amount of CO₂. Consequently, the heating zone should be expanded to the whole reactor. Some insulation measures should be adopted to minimize the carbon deposit and ensure the reforming reaction entirely. More importantly, since the reforming reaction is a volume expansion process, safety for the experiment operator must be ensured. If a metal reactor is designed to improve the safety, the electric and thermal insulation must be taken into account to ensure normal electrification and resistance to heat loss. The corresponding investigations are currently being carried out in our laboratory.

Comment 9: Line 275: Conclusion?

Reply: According to the articles published in Nature Communications, the last part of an article is Discussion. So, we also named the last part Discussion and some conclusions were listed here. Moreover, some discussions about the notification and limitation of the electrified reactor have been provided in this part.

Reviewer #3 (Remarks to the Author):

In “Grave-to-cradle Dry Reforming of Plastics via Joule Heating” the authors present an approach for the concurrent recycling of plastic waste and CO₂ gas to produce CO and H₂. The key part of the presented methodology is the use of the electrified catalytic FeCrAl wire. In a rather empirical field, it is admittedly exciting to see a systematic study of the effects various factors have on the products (Joule heating vs. conventional heating, electrified wire vs. unelectrified heated one, the material of the wire, etc.) I believe that alone warrants the publication of the manuscript; however, several points

must be addressed in the minor revision.

Comment 1: The title is somewhat misleading, implying that plastics themselves are subjected to Joule heating, as was, for example, the case during H₂ production from waste plastics (Advanced Materials 35 (48), 2306763, 2023). Here, the catalytic wire is subject to the Joule heating instead. Also, a metaphor “Grave-to-cradle” may be more suitable for a follow-up news item or editorial blurb than for an article in technical journal; I leave this choice to the Editor though...

Reply: The waste plastics and CO₂ are seen as waste carbon, and are at the end the life cycle. Converting the waste carbon sources to syngas that can be used as raw materials to produce hydrocarbons or oils just likes the Grave-to-cradle transformation. Actually, there are several research paper titled as “Grave-to-cradle ...” .

1) “Grave-to-cradle upcycling of Ni from electroplating wastewater to photothermal CO₂ catalysis”, Nat Commun. 13, 5305 (2022).

2) “Grave-to-cradle photothermal upcycling of waste polyesters over spent LiCoO₂”, Nat Commun. 15, 2730 (2024).

3) “Grave-to-cradle upcycling of harmful algal biomass into atomically dispersed iron catalyst for efficient ammonia electrosynthesis from nitrate” Appl. Catal. B: Environ., 332, 122778, (2023).
2023,

Comment 2: Page 3, line 64 mentions “conversion of waste plastic and CO₂ into syngas under sunlight irradiation”, while “sunlight irradiation” does not seem to play any role in the process and is never mentioned again.

Reply: We have modified this description. Actually, Fig. 5b shows a demonstration of solar-powered reforming of plastic with CO₂ to syngas. Under solar irradiation, the photovoltaic power system powers the direct current (DC) power generator that electrifies the heating wire in the reactor. 14 mg of PE

can reform with 1 mmol CO₂ to produce syngas smoothly. By using this demo instrument, no other fossil fuel was consumed and two kinds of waste carbon source were converted to value-added syngas.

Comment 3: Fig. 2d shows several processes that display comparable or even higher conversion achieved at lower temperatures which generally would mean lower energy costs. The authors should explain the benefit of the proposed method over those other methods.

Reply: We carefully re-examined the references included in Fig. 2d. The pyrolysis yield referred to the various gas products in the pyrolysis process, including CO, H₂, CH₄ and other gaseous hydrocarbons. However, only molar yields of H₂ and CO were provided in the Fig.2d for our research. Therefore, the result of our study is not the best “pyrolysis yield” in comparison with the reported results. Actually, it is not reasonable to compare the “pyrolysis yield” in the context of research on how to achieve high-yield syngas. Consequently, the Fig. 2d was re-compiled and the “pyrolysis yield” is replaced by “syngas yield”.

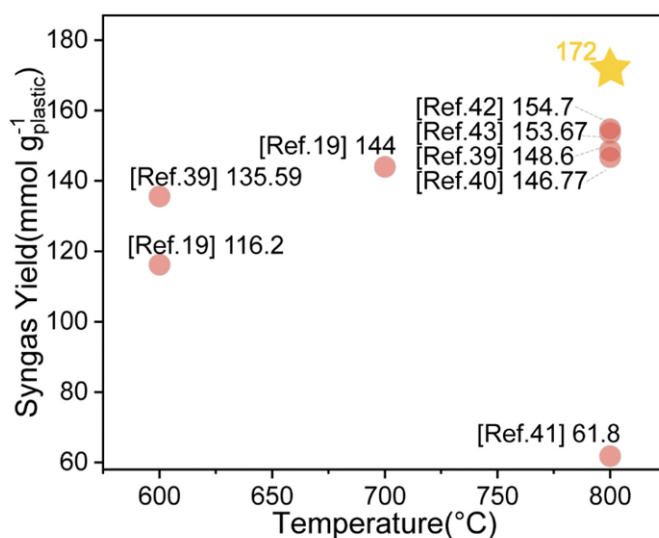


Fig. 2 | d the comparison of our result with ones from other reported catalytic system.

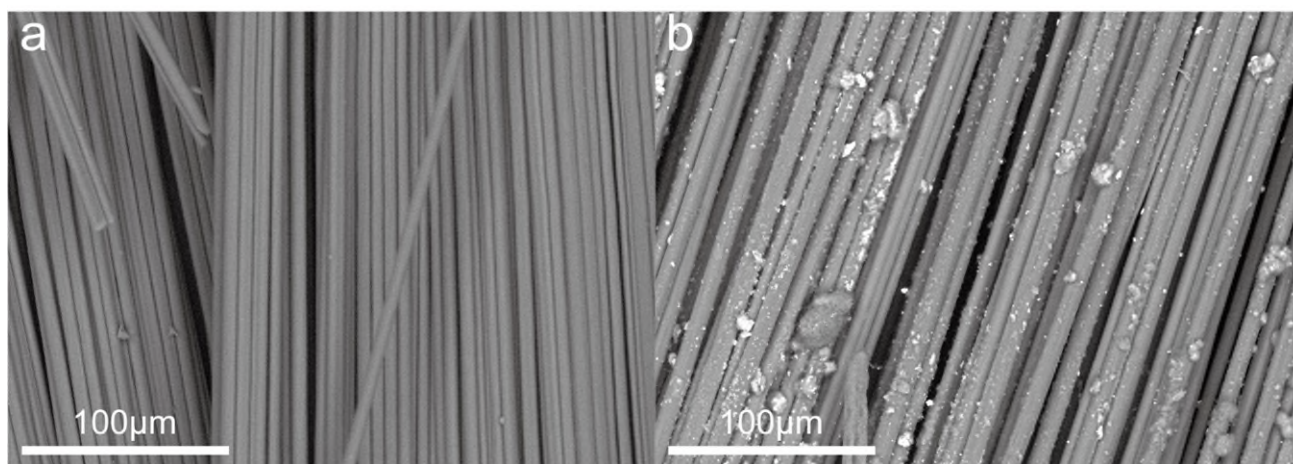
Comment 4: I found the comparison of the various catalyst wire materials very interesting. In particular, the use of carbon fiber seems very promising due to its simplicity and affordability. Did the authors perform any further characterization/analysis of the process with the use of carbon fiber?

Reply: The detailed productions of various products in the reforming experiment with carbon fiber as heating element were presented in the following table. Besides, the SEM characterization for the carbon fibers before (a) and after (b) reaction was also carried out. It can be clearly observed that many residual dusts adhered on the surface of carbon fiber.

Using a carbon fiber as a heating element, CO₂ reforming of PE was also observed, with a slightly higher H₂ yield of 57.3 % and a lower CO yield of 59.1 %, but more residual solid of 14.5 %. (the detailed products distribution of carbon fiber and SEM images are showed in Supplementary Table 3 and Supplementary Fig. 3).

Supplementary Table 3. The detailed products distribution with carbon fiber as heating element in dry reforming of LDPE.

Reaction time(min)	n H ₂ (mmol)	n CO (mmol)	n CO ₂ (mmol)	n CH ₄ (mmol)	N C ₂₊ (mmol)	n solid (mmol)	Carbon balance of reaction (%)
15	0.57	1.18	0.26	0.018	0.003	0.29	87



Supplementary Fig. 3 SEM images of carbon fibers a) before and b) after reaction. Experimental conditions: 14 mg PE, 44 mg CO₂, 15 min.

According to the reforming performance of carbon fiber, it needs an exhaustive study to explore the application and performance of carbon fiber in the upcycling of plastics. We will conduct the corresponding researches in our laboratory in the next stage. Thanks a lot for this valuable suggestion.

Comment 5: The solid byproduct of the process is not necessarily useless, as some similar processes were shown to produce graphene/graphite (as seen in, again, *Advanced Materials* 35 (48), 2306763). Was the solid product characterized? This knowledge can significantly affect how the current process is optimized.

Reply: Thanks for this constructive comment.

Indeed, Flash Joule Heating (FJH) technology has been used to convert plastics to one or two-dimension carbon nanomaterials in the presence of metal chloride (*Adv. Mater.* 2023, 35, 2209621) as catalyst or carbon black as conductive additives (*Adv. Mater.* 2023, 35, 2306763). The corresponding discussion has been supplemented in the revised manuscript.

In the absence of CO₂, PE can also be dehydrogenated to solid carbon in our reforming system. According to the TEM (Supplementary Fig. 8) and SEM (Supplementary Fig. 9) characterization, the solid carbon is composed of carbon nanospheres. Because we are using this carbon nanosphere as carbocatalyst to promote some reaction now, the TEM and SEM images were not provided in the manuscript and supplementary information. Now that the constructive comment concerns this problem, the characterizations of solid carbon are provided in the revised supplementary information.

Comment 6: The conclusion slightly overstates the usability of this process for other plastics. Fig. 2b clearly shows that no other plastic can match the performance in PE reforming. I think corresponding sentences should be adjusted to reflect that.

Reply: Indeed, the reforming performance of polyolefins is better than PS and PET according to the Fig. 2b because of the formation of more residual carbon. However, a visual misleading should be here at a glance of Fig.2b because the short columns of H₂ for PS and PET in comparison with PE or PP. Actually, the hydrogen contents in PS and PET are smaller than in polyolefins. In our experiments, the dosages of plastics were determined by 1 mmol carbon atoms in various plastics. Thus, the total hydrogen content in the experiments with PS or PET as raw reactant is smaller than with PP and PE. So, we think the reforming system is also effective to the PS and PET. However, to avoid confusion, the statement was improved as follow:

Significantly, polyolefin plastics, such as PE and PP, can be effectively reformed with CO₂ to produce CO and H₂ with high yields and carbon balance. The plastics containing phenyl groups, such as PS and PET, can also be reformed with CO₂ to produce syngas, although relatively more residual carbon remained. However, prolonging the reaction time, the remained carbon will be less. Actually, the residual carbon derived from plastics with special nanostructure and without impurity may have other potential application.

Comment 7: Overall, with the proper revisions the paper can become suitable for Nat Comm.

Reply: Thanks for this positive support.

REVIEWERS' COMMENTS

Reviewer #1 (Remarks to the Author):

All comments are addressed well.