Non-thermal plasma-assisted rapid hydrogenolysis of polystyrene to high yield ethylene

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The evergrowing plastic production and the caused concerns of plastic waste accumulation have stimulated the need for waste plastic chemical recycling/valorization. Current methods suffer from harsh reaction conditions and long reaction time. Herein we demonstrate a non-thermal plasma-assisted method for rapid hydrogenolysis of polystyrene (PS) at ambient temperature and atmospheric pressure, generating high yield (>40 wt%) of C₁–C₃ hydrocarbons and ethylene being the dominant gas product (Selectivity of ethylene, \( S_{C_2H_4} > 70\% \)) within ~10 min. The fast reaction kinetics is attributed to highly active hydrogen plasma, which can effectively break bonds in polymer and initiate hydrogenolysis under mild condition. Efficient hydrogenolysis of post-consumer PS materials using this method is also demonstrated, suggesting a promising approach for fast retrieval of small molecular hydrocarbon modules from plastic materials as well as a good capability to process waste plastics in complicated conditions.
or over a half century the fast development of plastic industry has been contributing greatly to the prosperity of human society. The global production of plastics has reached 400 million tons in 2018 and is still quickly growing, with the annual production being projected to double within two decades\(^1\). Accompanied by the big demand for plastic products, more and more plastic wastes (PWs) have been generated. It is reported that more than 300 million tons of PWs were generated in 2015\(^2\). As of date only less than 20% of these PWs can be recycled, with the rest ending up in landfills and incineration or being directly released to environment\(^3\).

Mechanical process, which incorporates shredding, heating, and remolding of plastics, remained as the primary recycle method\(^4\). Despite the attraction for “closed-loop cycles”, this method mainly produces “downgraded” plastics which have inferior properties\(^5,6\).

As a result, the number of reprocessing cycles is limited. Chemical processes including pyrolysis and gasification have been actively investigated for converting PWs to relatively low value-added synthesis gas and carbonaceous materials\(^7–8\). However, a high operating temperature (700–1300 K) is typically required to overcome the unfavorable thermodynamics and kinetics that makes these methods cost prohibitive. More recently, there have been a few studies on plastics hydrogenolysis. However, harsh reaction conditions of high temperature (600–700 K) and pressure (10–30 bar) and relatively long reaction time (>6 h) were still needed, suggesting low hydrogenolysis kinetics\(^9–11\).

Polystyrene (PS) has been widely used as food packages and foams and is among the top five most-produced plastic materials, other than polyethylene (PE), polypropylene (PP), polyethylene terephthalate (PET), and polyvinyl chloride (PVC), accounting for about 10% of global production\(^12\). Despite some active research efforts\(^13–15\), few successes have been achieved in recycling this plastic material. As a matter of fact, only 1% of PS waste was recovered in US in 2015\(^12\). This comes from complex situations for separation (blended products and abundant sources of contaminants) and sorting (diversified density range 0.02–1.1 g/cm\(^3\)) of PS wastes that restrain their collection and the inability to process wastes under aforementioned complicated conditions. To overcome these practical challenges and claim better energy advantage, a method with the versatility to effectively depolymerize PS material under mild reaction conditions is needed.

Herein, we report a non-thermal plasma-enabled method which allows efficient hydrogenolysis of pure and post-consumer PS under ambient temperature and atmospheric pressure condition. Non-thermal H\(_2\) plasma provides a unique medium for generating reactive hydrogen species, primarily in form of ions and radicals, which can effectively break the C–C bond in the polymeric structures and drive kinetically unfavorable reactions under mild reaction conditions\(^16,17\). In plastic pyrolysis, DBD plasma was also implemented to alter product selectivity\(^18–20\), but the process is still subject to high temperature (>773 K) together with extra power input which makes it less energetically attractive. This method achieves fast depolymerization of PS and generates C\(_1–C_5\) hydrocarbons as major gas products. Interestingly, ethylene, an important precursor in the polymer industry, can be produced at a yield as high as 38 wt%. Moreover, this non-thermal plasma-assisted hydrogenolysis method allows direct valorization of post-consumer PS products without a need for pretreatments and shows minimal influences by the contaminants and impurities. These findings reveal a great promise of this method for PWs valorization application.

**Results**

**Time-dependent plasma-assisted PS hydrogenolysis.** The non-thermal plasma-assisted PS hydrogenolysis experiments were conducted in a continuous flow fixed-bed reactor equipped with a dielectric barrier discharge (DBD) plasma generator (“Methods”, Supplementary Fig. 1). The reaction results in the generation of gas, liquid, and solid products (Fig. 1a), which adds up to over 93 wt% of the total mass recovered (Supplementary Note 1 and Supplementary Tables 1, 2), with a few percent of mass loss during the collection of liquid and solid products. Time-dependent product distribution (denoted as PS-reaction time) shows a continuous increase in the gas products yield (Y\(_G\)) with reaction time, which reaches as high as 41.0 wt% after 12 min of reaction. Meanwhile, the solid phase keeps diminishing until to a minimal amount and the liquid products are obtained at a yield (Y\(_L\)) ranging from 50 wt% to 56 wt% throughout the experiment. More than 95% of PS is converted to gas and liquid products within 12 min of reaction (Fig. 1a), indicating a fast hydrogenolysis rate. Online GC-MS analyses of the gas effluent from the ESI results, C\(_1–C_3\) hydrocarbons as the major gas products (Fig. 1b). Except at the beginning of the reaction when methane is the dominant gas product with 53.2 wt% selectivity at \(t = 2\) min, ethylene is found as the primary gas product after a longer reaction time. The ethylene selectivity (S\(_{\text{C}_2\text{H}_4}\)) can reach as high as 70%, equivalent to 38 wt% yield among all products (PS-12min). This result confirms the efficient conversion of PS to gaseous hydrocarbons, especially the more valuable ethylene, via plasma-assisted hydrogenolysis.

The liquid products were collected using CHCl\(_3\) extractant from the resultant liquid–solid mixture after reaction. \(^1\)H NMR spectra of the obtained liquid products indicate the transformation of polystyrene to styrene-based monomers and oligomers which is evidenced by the emergence of sharp, dense peaks in response to aromatic rings (0–8 ppm), vinyl groups (–6–5 ppm) and H\(_S\) with respect to aromatic functional groups (3–2 ppm), suggesting the significant extent of depolymerization in the liquid components (Fig. 1c)\(^21\). The monomer and oligomer formation is further confirmed by \(^13\)C NMR spectroscopy (Supplementary Fig. 4)\(^22\). GPC was employed to characterize Mw of the liquid product components (Fig. 1d). The Mw profiles of all examined samples exhibit a multi-modal distribution (1–3 modes) owing to the feature of PS feedstock\(^23\). Two Mw modes, with one at 119,000 Da and the other at 1700 Da, were observed for pure PS (Table 1), amounting to ~35,000 Da average molecular weight. From PS-0min to PS-12min, the hydrogenolysis reaction reduces the high Mw mode by a factor of 10 and the weight percentage of the lower Mw mode also exhibits a significant decrease. Meanwhile, a mode with a much lower Mw of about 300 Da emerges intensively, indicating fast depolymerization of PS within a short reaction time. Characterizations of the solid residues using FT-IR and high-resolution solid-state \(^13\)C NMR suggest the remaining solids are primarily PS with no detection of other species (Supplementary Figs. 5, 6, Supplementary Table 3).

Detailed structural and compositional information of the liquid products was obtained with Matrix-assisted Laser Desorption/Ionization (MALDI-MS) and Electrospray Ionization (ESI-MS) techniques (“Methods”, Supplementary Note 2). The former one was used to characterize large polymer units (>800 Da), and the latter was used to characterize the low Mw range molecules (0–800 Da)\(^24\). MALDI-MS detects a series of styrene oligomers with 5–45 monomer units (500–5000 Da) consisting of cyclic (red) and linear (blue) structures with 16 Da Mw difference (Fig. 2a, b, Supplementary Fig. 7), depending on whether end groups (–CH\(_3\) on one end, –H on the other) were available. A sharp increase in the fraction of 5–15 monomer units was observed with a longer reaction time (Supplementary Fig. 8), suggesting an accelerated degree of depolymerization. Four types of compound structures were identified from the ESI results, including linear hydrocarbons, PS, hydro-PS, and dehydro-PS.
oligomers (Supplementary Figs. 9–14, Fig. 2c). Their relative amounts as a function of reaction time were analyzed based on the ESI signals intensity (Supplementary Fig. 15), with the trends pointing to possible interconversion among these compounds through hydrogenation. With these characterization results, carbon number and ring distribution of the liquid products are summarized in Fig. 2d and Supplementary Fig. 16–21. A longer reaction time leads to the production of lighter and more narrowly distributed liquid products, with more C6–C9 chemicals in form of linear alkanes and alkylbenzenes being eventually produced after 12 min of hydrogenolysis reaction (Supplementary Fig. 22). Besides the reaction time, other reaction parameters, including H2 flow rate (\(\nu_{H2}\)), partial pressure (\(P_{H2}\)), mass of PS (\(m_{PS}\)) and power input (\(P\)) were also examined and exhibited certain influences on the PS hydrogenolysis properties (Supplementary Note 3, Supplementary Figs. 23–27).

D2 isotope labeling experiments and proposed reaction pathway. D2 isotope labeling experiments were conducted by replacing H2 with D2 to achieve insights into the plasma-assisted PS hydrogenolysis mechanism. It should be noted that the reaction pathway was proposed based on analyses of gas and liquid products, the potential influence of surface etching and irradiation and their impacts on PS decomposition was neglected due to fast kinetics of hydrogenolysis reaction. Figure 3a–d shows the time-evolved MS spectra collected under the reaction condition. HD
Signals are detected starting from about 40 s after the reaction is switched on (Fig. 3a). Considering only PS contains hydrogen, the generation of HD should be resultant of reaction between highly active deuterium plasma species and PS, which generates hydrocarbon fragments and hydrogen species that would further react with deuterium. Interestingly, the generation of various hydrocarbon gas products exhibits a different reaction time dependence. Methane and deuterium-exchanged methane products begin to be detected simultaneously with HD generation (Fig. 3b), with CH₃D and CD₄ being the major products. In comparison, there are about 10 more seconds of delay for C₂ products detection and about 20 more seconds of delay for C₃ products detection (Fig. 3c, d). These results suggest the formation of gas products following an order of CH₄ > C₂H₄ ≈ C₂H₆ >...
Post-consumer PS (PCPS) hydrogenolysis. Our study on post-consumer PS (PCPS) materials proves a good capability of this plasma-assisted hydrogenolysis method to effectively convert PS wastes into valuable chemicals. Commercially available yogurt containers (Supplementary Fig. 30), an important application for PS, were used as feedstock. Identical reaction conditions were applied for PCPS as for pure PS. An 85.2 wt% conversion is achieved after 12 min of reaction (Fig. 5a), which is about 10% lower than that for PS. The existence of unconvertable impurities, such as contaminants, dyes and reinforcement materials, etc., is likely responsible for the conversion reduction by increasing the weight percentage of solid and uncollected substances (Supplementary Tables 11, 12). As high as 41 wt% gas yield is obtained at PCPS-12min, with ethylene still being the dominant gaseous product (71 wt% selectivity and 34 wt% yield, Fig. 5b). The liquid products show a decrease in both yield and average molecular weight as a function of time (Fig. 5a, c, and d). Almost one order of magnitude reduction in the Mw is observed from PCPS-4min to PCPS-12min, based on which a high degree of PS depolymerization from the feedstock can be concluded. This was further confirmed by the MALDI-MS spectra (Fig. 5e). Like the experiments for pure PS, the ESI-MS results exhibit resemblance in the structures of components (Supplementary Figs. 31–34). The carbon number distribution also indicates an enrichment of C6–C9 chemicals, and a reduction of heavier components with reaction time (Supplementary Fig. 35). Furthermore, the capability of processing various substrates such as polyethylene (PE) and polypropylene (PP), as well as mixtures of the three substrates (3P) was demonstrated (Supplementary Fig. 36). Even higher gas yield was obtained by PE (51.7%), PP (68.5%), and 3P (50.55%) compared with PS, with a dominant gas product varying from plastic monomers. These results suggest the capability of this method in processing real-world plastic wastes which typically consist of mixtures of various polymers.
In summary, our study demonstrates a method for rapid polystyrene hydrogenolysis to light hydrocarbons. Enabled by H$_2$ non-thermal plasma, over 90 wt% PS can be swiftly depolymerized and converted to C$_1$–C$_3$ hydrocarbons and liquid products within 12 min of reaction. The valuable ethylene gas is the most dominating product, accounting for as high as 38 wt% of total yield. Enriched C$_6$–C$_9$ paraffins and alkylbenzenes that possess high commercial values are obtained in the liquid products. Furthermore, investigation on post-consumer PS materials exhibits similarly efficient gas production regardless of the existence of contaminants and additives. Our studied method for PS hydrogenolysis not only achieves fast and efficient transformation to valuable gas products, but also shows the capability of processing waste plastics with complicated forms and conditions, which is one of the most challenging issues for plastic valorization.

Despite these advantages features revealing a good potential of this method for real application that helps to realize recycling of currently untouched plastic waste materials, some issues need to be considered before taking on a larger scale. The most challenging problem, not only for the plastic processing but for any other better developed NTP-assisted reactions such as CO$_2$ conversion, VOC removal, and N$_2$ fixation is the energy efficiency$^{28,29}$. The mismatch between the power input and output (represented by the amount of product) restrains further application of this technique. The time-dependent energy efficiency ($\eta$, g/kWh) of gas production is calculated and shown in Supplementary Fig. 3. Methane and ethylene demonstrated the highest energy efficiency between 6 and 7 g/kWh within 4 min of the reaction, and gradually decreases with a longer reaction time. Comparing with other well-established DBD plasma-assisted reactions such as CO$_2$ conversion, VOC abatement and N$_2$ fixation (Supplementary Fig. 3b), the optimal energy efficiency values obtained from gas products only in the plastic hydrogenolysis exhibit comparable or even superior energy efficiency$^{30,31}$. Considering the unaccounted liquid products, the energy efficiency can be even higher. For future perspective, we propose there are three strategies that can be applied to further improve the energy efficiency. First, elegantly designing DBD plasma generator, reactor, as well as plastic packing methods could help mitigate the power lost to non-plasma zone and unavoidable heat. Second, screening appropriate catalyst, which has been proved in our previous study$^{16}$. Third, as the time-dependent energy efficiency shown in Supplementary Fig. 3a suggests the highest energy efficiency was achieved within the first 2–4 min, which then gradually decreased with a longer reaction time. It is suggested that pulsed or segmental instead of continuous plasma to be applied so that the reaction could remain high EE.

Fig. 5 Plasma-assisted post-consumer PS (PCPS) hydrogenolysis properties as a function of reaction time. a Product yield and conversion properties. b Gas products selectivity and ethylene yield properties. c, d GPC spectra and molecular weight evolution as a function of reaction time. e MALDI-MS spectra of liquid components obtained from PCPS-4min, PCPS-8min and PCPS-12min, respectively. Cyclic and linear polystyrenes were represented in red and blue, respectively.

Discussion

In summary, our study demonstrates a method for rapid polystyrene hydrogenolysis to light hydrocarbons. Enabled by H$_2$ non-thermal plasma, over 90 wt% PS can be swiftly depolymerized and converted to C$_1$–C$_3$ hydrocarbons and liquid products within 12 min of reaction. The valuable ethylene gas is the most dominating product, accounting for as high as 38 wt% of total yield. Enriched C$_6$–C$_9$ paraffins and alkylbenzenes that possess high commercial values are obtained in the liquid products. Furthermore, investigation on post-consumer PS materials exhibits similarly efficient gas production regardless of the existence of contaminants and additives. Our studied method for PS hydrogenolysis not only achieves fast and efficient transformation to valuable gas products, but also shows the capability of processing waste plastics with complicated forms and conditions, which is one of the most challenging issues for plastic valorization.

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An ideal industrial plastic chemical recycling/upcycling method should be able to process waste plastics swiftly, efficiently, and continuously. Currently, the rapidly growing research efforts in plastic hydrogenolysis mainly focus on depolymerizing various plastics in batch reactors, with pressurized H$_2$ atmosphere (20–60 bar), high temperature (200–300 °C) and long reaction time (1–40 h) being applied (Supplementary Table 13). Our presented method outperforms the state-of-art studies in the promise for scaling up with fast, selective, and continuous gas production.

Methods

Materials and gases. Polystyrene (PS, Sigma Aldrich, average Mw 35000, Stock No. 331651). Chloroform-D (99.8%, Cambridge Isotope Laboratories, Inc. Lot# DLM-7-PK), CHCl$_3$ (>99.8%, Sigma Aldrich, Lot# 132950), H$_2$ (99.999%), D$_2$ (99.999%) and Ar (99.999%) gases were purchased from Praxair. Calibration gas for 1% methane (CH$_4$, 135N-1%), acetylene (C$_2$H$_2$, 17L-m24-1%-CGD), ethylene (C$_2$H$_4$, 17L-62a-1%), ethane (C$_2$H$_6$, 17L-m23-1%), propane (C$_3$H$_8$, 17L-175-1) and propylene (C$_3$H$_6$, 17L-292N-1) and propane (C$_3$H$_6$, 17L-175-1) were purchased from CAL GAS DIRECTTM.

Plasma-assisted PS hydrogenolysis reaction. Non-thermal plasma-assisted PS hydrogenolysis experiments were conducted in a quartz tube reactor equipped with a dielectric barrier discharge (DBD) plasma generator, with cold hydrogen plasma being generated at the plasma generation zone (Supplementary Fig. 1). The volume of the plasma zone ($V_{\text{plasma}}$) is approximately 6.28 cm$^3$. In a typical run, 200 mg PS pellets (sieved to the size of 125–250 µm) were packed in the DBD reactor. The standard reaction condition was 100 ml/min H$_2$ flow rate, 101 kPa H$_2$ partial pressure and 90 W plasma power unless being stated otherwise. Influences of
various reaction parameters, including reaction time (2–12 min), \( H_2 \) flow rate (20–100 ml/min), \( H_2 \) partial pressure (0–101 kPa), mass of reactant (100–600 mg) were examined.

The mass of the gas, liquid, and solid products were mainly measured via weight reduction method. The gas product was quantified by measuring the weight loss of the packed reactor before and after the reaction. The liquid product was obtained from the extractant of CHCl₃ from the liquid-solid mixture in the reactor, while the insoluble residues were the solid residues (PS + quartz wool). The weight of the solid product was calculated by the difference between quartz wool and solid residues, and liquid product was calculated by the total weight of CHCl₃ solution minus the weight of solvent. In Supplementary Table 1 a rigorous mass balance calculation is shown where all the reactants and products are accounted for.

\[
\text{Conversion (X)} = \frac{m_{\text{PS}} - m_{\text{null}}}{m_{\text{PS}}} \times 100 \%
\]

\[
\text{Yield (Y)} = \frac{m_{\text{gas/mass}} - m_{\text{solid}}}{m_{\text{PS}}} \times 100 \%
\]

**Product analysis and characterization.** Online gas product analysis. The gas effluent products, including \( C_2H_6, C_2H_4, C_3H_6, \) and \( C_2H_2 \) were analyzed with an online Agilent 6890 GC-MS equipped with the automatic gas injector. The gases were quantified separately by externally feeding standard calibration gas. Calibration curves at 0–5%/v were obtained for each gas. Selectivity was calculated by the respective gas production rate divided by the overall production rate (g/min).

**13C NMR spectroscopy.** Liquid products after plasma-assisted hydrogenolysis reaction were analyzed by \(^1\)H-NMR and \(^13\)C-NMR, respectively. \(^1\)H-NMR experiments were conducted with a Varian Mercury 300 MHz spectrometer. \(^13\)C-NMR spectra were recorded with Varian NMR 500 MHz spectrometer. Chemical shifts were calibrated against residual proton signals of the solvent and referenced to tetramethylsilane (TMS). Matrix-assisted laser desorption/ionization mass spectroscopy (MALDI-MS). MALDI-MS analyses were conducted with a Bruker UltrafleXtreme MALDI-ToF/ToF instrument. A sandwich method for matrix and sample application was applied. First layer: 20 mg/ml matrix (2:4-ter-butyl-2-methylpentane:malononitrile (DCTB) matrix and 10 mg/ml silver trifluoroacetate (AgTFA) salt (10:1). Second layer: tested sample at a given concentration. Third layer: 20 mg/ml DCTB matrix and 10 mg/ml AgTFA salt (10:1). The analyses were performed in reflection and a linear mode. Detection range between 500 and 10,000 Da. Laser intensity was 40%.

Electrospray ionization mass spectroscopy (ESI-MS). The experiments were conducted using Waters Synapt G1 ESi-Q Time-of-flight (ToF) MS instrument. The desolvation temperature was 250 °C, the source temperature was 120 °C, the capillary voltage was 3.00 kV and the flow rate was 10 μl/min. Samples were diluted to 10 μl in μl of methanol.

**Gel permeation chromatography (GPC).** Analyses were performed on a Waters GPC system comprised of a Waters 1515 isocratic HPLC pump, using two 7.8 × 300 mm Styragel HR 4E THF (waters WAT044240), with a Waters 2414 refractive index detector. The system was calibrated using 14 polystyrene standards ranging 201–410 kDa. The injection volume was 100 μl with a flow rate of 1.0 ml/min. Samples were diluted in THF in concentrations 1–10 mg/ml. Data were processed using the Waters Breeze V3.30 software.

**FT-IR spectroscopy.** Solid residues (mixture of quartz wool and reacted polystyrene solids) obtained after reaction were characterized by ex situ Fourier-transform IR spectroscopy with Nicolet 6700 IR spectrometer in diffuse reflectance IR Fourier-transform spectroscopy (DRIFTS) mode under ambient condition. The spectra were recorded by collecting 32 scans with a resolution of 2 cm⁻¹. No specific correction was applied.

\(^1\)C Solid-state NMR spectroscopy. \(^1\)C solid-state NMR experiments on pure and reacted PS samples were conducted by a Bruker Avance Ultraspect 300 NMR apparatus equipped with a 4 mm double resonance VT CP/MAS probe. The \(^1\)H and \(^13\)C carrier frequencies were 75.6 and 300.1 MHz, respectively. Samples were packed in a 4 mm Zirconia MAS rotor with a Kel-F drive cap and were measured with a MAS speed of 13000 ± 5 Hz at 25 °C. \(^1\)H and \(^13\)C rf field strength was adjusted to 55.6 and 75 kHz, respectively. \(^1\)H T1PM decoupling was used during acquisition. Cross polarization and recycle delay were set to 2 ms and 3 s, respectively. \(^13\)C chemical shift was externally referenced as the CH carbon of adamantane as 29.46 ppm.

**Post-consumer PS hydrogenolysis.** Post-consumer polystyrene plasma-assisted hydrogenolysis reaction was conducted using commercially available yogurt packages that are made of polystyrene blended with dyes and reinforcement materials. The post-consumer material was cut, shredded, and packed in the DBD reactor with a similar configuration to that of pure PS powder. The methods applied for reaction evaluation (i.e. yield calculation, product analysis, and reaction parameters) were identical to those conducted for pure PS material.

**Data availability**

The main data supporting the findings in this study are provided in the paper and Supplementary information. Additional data are available from the corresponding authors upon reasonable request.

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25. Benson, S. W. et al. Additivity rules for the estimation of thermochemical properties. Chem. Rev. 69, 279–324 (1969).
26. Rodrigues, F., Pascoa, J. & Trancossi, M. Heat generation mechanisms of DBD plasma actuators. Exp. Therm. Fluid Sci. 90, 55–65 (2018).
27. Wang, J. et al. One-step plasma-enabled catalytic carbon dioxide hydrogenation to higher hydrocarbons: significance of catalyst-bed configuration. Green. Chem. 23, 1642–1647 (2021).
28. Van Laer, K. & Bogaerts, A. Improving the conversion and energy efficiency of carbon dioxide splitting in a zirconia-packed dielectric barrier discharge reactor. Energy Technol. 3, 1038–1044 (2015).
29. Wang, L., Yi, Y., Guo, H. & Tu, X. Atmospheric pressure and room temperature synthesis of methanol through plasma-catalytic hydrogenation of CO₂. ACS Catal. 8, 90–100 (2018).
30. Winter, L. R. & Chen, J. G. N₂ Fixation by Plasma-activated Processes (Joule, 2020).
31. Wu, Z. et al. Enhanced energy efficiency and reduced nanoparticle emission on plasma catalytic oxidation of toluene using Au/γ-Al₂O₃ nanocatalyst. Chem. Eng. J. 427, 130983 (2022).

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Author contributions
L.Y., Z.P., S.C. and T.M. conceived the project and designed experiments; L.Y., J.K., D.W., J.M., J.L. and R.X. performed all the experiments; L.Y. wrote the manuscript with edits from all authors.

Competing interests
The authors declare no competing interests.

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