

Microwave-initiated Catalytic Deconstruction of Plastic Waste into Hydrogen and High-Value Carbons

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20 **Abstract:**

21 The ubiquitous challenge of plastic waste has led to the modern descriptor
22 'plastisphere' to represent the human – made plastic environment and
23 ecosystem. Here we report a straightforward, rapid method for the
24 deconstruction of various plastic feedstocks into hydrogen and high-value
25 carbons. We use microwaves together with abundant and inexpensive iron-
26 based catalysts as microwave-susceptors to initiate the catalytic
27 deconstruction process. The one-step process typically takes some 30 – 90
28 seconds to transform a sample of mechanically - pulverised commercial
29 plastic into hydrogen and (predominantly) multi-walled carbon nanotubes. A
30 high hydrogen yield of $55.6 \text{ mmol} \cdot g_{\text{plastic}}^{-1}$ is achieved, with over 97 % of the
31 theoretical mass of hydrogen being extracted from the deconstructed plastic.
32 The approach is demonstrated on widely used, real-world plastic waste. This
33 proof-of-concept advance highlights the potential of plastics waste itself as
34 valuable energy feedstocks for the production of hydrogen and high-value
35 carbon materials.

36

37 **Introduction:**

38 Plastic materials are used extensively throughout the world, with their ever- rising
39 proliferation being particularly marked during the past half century. Currently, of the
40 4.9 billion tonnes of plastics ever produced, the vast majority are accumulated into
41 landfills or in the natural environment; this number is estimated to increase to around
42 12 billion tonnes by 2050^{1,2}.

43 Polymer polyolefins such as polyethylene (PE), polypropylene (PP) and
44 polystyrene (PS), are currently produced, used and discarded at the highest rate of
45 all plastics, thereby accounting for over half of all plastic waste^{2,3}. In order to
46 overcome the problem of such large quantities of plastic waste, researchers have
47 studied various ways to convert these waste polymers into value-added products
48 such as hydrocarbon fuels and carbon nanotubes (CNTs) etc.⁴⁻⁷.

49 Over the past decade there has been increasing interests and research into the
50 conversion of plastic waste into synthetic oil mixtures^{5,6,8,9} and great efforts have
51 been made to improve the energy efficiency and to exert precise control over the
52 resulting products⁹. Gasification of plastic waste^{7,10,11} is one such approach to
53 produce a stream of synthesis gas for energy or synthesis purposes^{2,7}. More recently,
54 researchers have focussed on producing hydrogen as the main product from plastic
55 waste as an alternative renewable process since plastic materials represent
56 hydrogen-rich energy feedstocks which contain between some 8 – 14 wt.% of
57 hydrogen¹²⁻¹⁷. Czernik *et al.*¹⁵ and others^{12-16,18-22} have proposed an important two-
58 step process to thermally decompose plastics to produce hydrogen - rich gases. In
59 this two-step process (idealised in Fig. 1a), plastic polymers are first decomposed
60 into a mixture of small hydrocarbons via pyrolysis at high temperature, followed by

61 catalytic steam reforming ($> 750\text{ }^{\circ}\text{C}$) of the pyrolysis gases and vapours for syngas
62 production ($\text{H}_2 + \text{CO}$)^{15,18}. This represents an important advance but there is,
63 inevitably, a significant energy input required for the two reaction steps and the
64 problem of large volumes of CO_2 which are also produced ($\sim 12\text{ kg CO}_2$ per 1 kg H_2
65 production)¹⁷. Moreover, the pyrolysis-reforming two-step process, by its very nature, of
66 course, is invariably complicated.

67 Here, we illustrate a new, simple and rapid one-step process for the deconstruction of
68 plastic waste (Fig. 1b). This involves the microwave-initiated, solid-solid reaction;
69 whereby a mixture of mechanically pulverised plastics ($1\text{ mm} - 5\text{ mm}$) are mixed with
70 an additive catalyst (microwave-susceptor) composite of iron oxide and aluminium
71 oxide and subjected to microwave treatment. A schematic experimental configuration
72 is given in Fig. 1c. Widely used plastic waste comprised milk containers (high density
73 polyethylene, HDPE), food wraps (polypropylene, PP) and plastic foam (polystyrene,
74 PS) used in this study were collected from commercial materials used by large
75 supermarket chains. Following the microwave initiation, a large volume of H_2 gas is
76 rapidly evolved arising from the deconstruction of mechanical mixture of plastics and
77 microwave – receptors (catalysts) (Fig. 1d and Movie 1). H_2 levels in the evolved gas
78 stream can reach nearly 90 vol.% with a H_2 yield of $55.6\text{ mmol}\cdot g_{\text{plastic}}^{-1}$ achieved
79 (theoretically, the maximum is $71.4\text{ mmol}\cdot g_{\text{plastic}}^{-1}$) - leaving only a residue of
80 carbonaceous materials, the bulk of which are identified as carbon nanotubes.

81

82 **Results:**

83 The nomenclature FeAlOx refers in this paper to the catalyst that was prepared by
84 a citric acid combustion method (see Methods for full details), with a molar ratio of

85 Fe:Al:citric acid = 1:1:1, unless otherwise noted. We define as “Selectivity”, the
86 measured volume % of the product composition in the evolved gases obtained from
87 GC analysis. The mass of each gas products was calculated according to the
88 measured volume of gases obtained and the composition analysis from GC. The
89 yield of gas, liquid and solid are therefore determined as their respective mass
90 fractions in relation to the total weight of plastic. We describe the H₂ yield as the
91 moles of H₂ obtained divided by the total weight of plastic. The “Hydrogen Efficiency”
92 is determined as the total mass of hydrogen contained in all gas products as
93 compared to the theoretical amount of hydrogen contained in the plastic (See Eq. 1-
94 5 in the Methods section).

95

96 **One-step microwave-initiated deconstruction of HDPE using FeAlO_x catalysts**

97 The data for a representative ‘time-on-stream’ experiment for the microwave-
98 initiated dehydrogenation of mechanically- pulverised HDPE (in this case, waste milk
99 containers) using the FeAlO_x catalyst is illustrated in Fig. 2. Following mechanical
100 pulverisation of the plastic, the individual pieces were physically mixed with FeAlO_x
101 catalyst particles in a weight ratio of 1:1. Upon exposure to microwaves, hydrogen
102 was rapidly evolved (a dehydrogenation of hydrogen-stripping process) and solid
103 carbon and other small fragments were formed over a period of ca. 90 seconds (Fig.
104 2a). The evolved hydrogen rapidly increased to ca. 80 vol.% of the evolved gases in
105 30 seconds from the onset of the microwave initiation process. And, as will be
106 evidenced in our ‘*in-situ*’ characterisation, the HDPE was almost decomposed or
107 deconstructed in ca. 20s.

108 Unlike conventional thermal heating processes in which *both* catalytic particles

and the feedstock (here plastic polyolefins) are necessarily heated, in this alternative approach, microwave electromagnetic energy is absorbed *directly and preferentially* at, and in, the microwave - absorbing points of the catalyst particle. Thus, heat is instead generated initially and rapidly *solely* at the microwave absorbing FeAlO_x catalyst particles, without (initially) heating the surrounding pieces of HDPE. In that sense, this approach is fundamentally different to conventional, thermally-initiated catalytic processes where the entire plastic “bath” must be heated externally and then - through diffusive heat transfer and thermal convection - the catalyst particle is ultimately heated and activated. Importantly, we find that this microwave approach significantly minimises the side reactions from the thermolysis of plastic and therefore achieves an excellent control and yield of hydrogen production.

As a preliminary comparison of the measured temperatures of HDPE and FeAlO_x particles separately under the influence of microwave irradiation, an average temperature difference of over 400 °C was observed (Fig. 2b). The temperature of the sample (FeAlO_x catalysts + HDPE) was measured by an optical pyrometer as ca. 300 °C during the microwave initiation; thus, heat then being provided for the necessary catalytic reactions, and leading to the deconstruction of HDPE. This plastic melts at about 120 -180 °C, so we clearly have a most complex heating process evolving in this heterogeneous mixture of rapidly heating solid FeAlO_x catalyst particles, (locally) melting HDPE plastic (in the immediate vicinity of the catalyst) and a surrounding “bath” of colder, solid plastic as one moves away from the catalyst particles into the bulk of the plastic ‘host’.

The measured microwave absorption of the sample (FeAlO_x + HDPE) surged in the initial time-on-stream of 10s to 20s and then dropped in the following 10 seconds (Fig. 2c); indicating, remarkably, that the catalytic chemical reactions occurred in this

short period where HDPE was almost completely decomposed. This has been confirmed by our x-ray diffraction (XRD) studies (Fig. 2d) and ATR-FTIR spectrum (Fig. 2e) where no HDPE peak appears visible after 30s. The diffraction peaks of HDPE at 21.6° and 23.9° , corresponding to the typical orthorhombic unit cell structure of (110) and (200) reflection planes of HDPE²⁴, were found dramatically decreased from 10s to 20s and subsequently disappeared after 30s. In the ATR-FTIR spectrum, the three sets of peaks ascribed to the C-H and C-C absorption of HDPE²³ also disappeared after 30s treatment with the microwaves.

XRD studies on FeAlO_x catalyst before and after the microwave treatment revealed that the initially -prepared FeAlO_x catalyst particles contain primarily Fe₃O₄²⁵. The absence of XRD peaks of Al₂O₃ is ascribed to the low calcination temperature (350 °C), which indicates the Al₂O₃ is amorphous under these conditions²⁶. Importantly, the presence of metallic iron and also iron carbide was detected as the microwave initiation process progressed (Fig. 2d). The peaks for elemental iron particles were observed at 2 Theta = 44.79° , and the diffraction peaks of Fe₃C at the angles (2θ) of 37.84° , 42.92° , 43.82° , 44.72° , 45.04° , 45.9° , and 49.18° were observed²⁷ some 20s from the microwave initiation, corresponding to the degradation of plastic to yield elemental carbon and hence Fe₃C. The intensity of Fe₃O₄ peaks decreased after reaction and a broad peak observed at about $2\theta = 26^\circ$, indicating the formation of MWCNTs.

Parametric studies of the microwave-initiated process

We have investigated different catalyst systems under microwave initiation using metals other than Fe (typically Ni and Co) and also experiments with FeAlO_x of

158 varying Fe content as well as Fe-based catalysts on different support materials. We
159 find that different metal catalysts exhibited a marked variability in performance under
160 their exposure to microwaves, with noticeably different product distributions and H₂
161 yields (Fig. 3a-b).

162 The FeAlO_x catalysts proved to be the most effective with a H₂ yield of over 55.6
163 mmol·g_{plastic}⁻¹ whilst other metals or metal oxides gave less than 35 mmol·g_{plastic}⁻¹.
164 The theoretical H₂ yield is ca. 71.4 mmol·g_{plastic}⁻¹ for complete dehydrogenation
165 (deconstruction) of the plastic if we consider that the HDPE is fully decomposed to
166 only H₂ and carbonaceous materials. Moreover, the hydrogen efficiency obtained
167 over FeAlO_x catalyst is about 97% which indicates over 97% of hydrogen contained
168 in plastic has been extracted as gases. In contrast to thermal catalytic processes, we
169 find negligible volatile (liquid) produced (Fig. 3c) using FeAlO_x. And the mass
170 balance, calculated on the sum of gas and solid carbon is close to 100%. In contrast,
171 Ni and Co catalysts are found less effective under microwave initiation and various
172 small hydrocarbons, and liquid and solid are produced (Supplementary Table 1).

173 Our investigation of Fe on different support materials and indeed carbon materials
174 themselves (activated carbons, MWCNTs, graphite etc.) demonstrated the varying
175 catalytic performance when different catalyst systems interact with microwaves in the
176 catalytic initiation process (Fig. 3b). All these Fe supported catalysts and carbons -
177 except MWCNTs- were able to drive the HDPE decomposition reactions upon
178 microwave irradiation, but with markedly different product distributions and very low
179 hydrogen yield and selectivity (Fig. 3b and Supplementary Table 2).

180 Although carbon materials have been widely acknowledged as excellent
181 microwave -susceptors²⁸, in our experiments, such carbon materials gave a very low

H₂ yield of less than 8.3 mmol·g_{plastic}⁻¹ and the hydrogen efficiency was typically below 40%. This again highlights the superior activity of FeAlO_x catalysts under microwave initiation for producing almost exclusively hydrogen and carbon nanotubes, as will be highlighted in our characterisation of carbonaceous products (Fig. 4).

In contrast, experiments using traditional thermal pyrolysis and catalytic cracking using the same FeAlO_x catalyst showed a very low H₂ yield of only 4.3 mmol·g_{plastic}⁻¹ and also produced oil products with a yield of 66% (Fig. 3c). We attribute this to the fundamental differences between conventional and microwave heating processes with the microwave electromagnetic energy being selectively, effectively and preferentially absorbed by FeAlO_x particles without (initially) heating the bulk of plastic. This leads to a significant narrowing of the products distribution and the preferential extraction of hydrogen from plastic polymers through the microwave-initiated catalytic scission of C-H chemical bonds.

We have also tested different starting weight ratios of HDPE and FeAlO_x catalyst particles, from 0.3 to 10 (Fig. 3d). The preferred mixing ratio is found to be 1 - 2 where the very high H₂ yield (over 50.3 mmol·g_{plastic}⁻¹) was obtained. Negligible amounts of liquid were produced when the mixing ratio is less than 2. At higher mixing ratios, both the oil and solid yields increased, and with the mixing ratio over 10 there was no visible reactions take place.

Importantly, at the optimal mixing ratio, the catalyst system can continue to function efficiently in the degradation of plastic for several catalytic cycles through successive additions of the plastic substrate.

Data for successive cycles of deconstruction of different kinds of plastic waste

(HDPE, PP and PS) are illustrated in Fig. 3e-f. Successive additions of plastic pieces were added, *importantly*, with no further FeAlO_x additions, between every test cycle. The highest H₂ yield obtained from the deconstruction of HDPE, PP and PS are 55.6, 51.4 and 26.9 mmol·g_{plastic}⁻¹, respectively (Fig. 3e). The H₂ yield of HDPE and PP are typically between 35 – 55.6 mmol·g_{plastic}⁻¹ (theoretically, the maximum is 71.4 mmol·g_{plastic}⁻¹) and was found gradually decreased throughout the cyclic tests; whilst the H₂ yield of PS remained constant at around 24 mmol·g_{plastic}⁻¹ (theoretically, the maximum is 38.4 mmol·g_{plastic}⁻¹). Moreover, over 80 - 97 % of the (theoretical) mass of hydrogen contained in these plastics was rapidly extracted through this process leaving only MWCNTs. This corresponds to a carbon yield of around 70, 60 and 80 wt.%/g-plastic from the HDPE, PP and PS, respectively.

The H₂ selectivity in the evolved gases remained steady at ca. 76 – 90 vol.% and interestingly the highest H₂ selectivity was achieved at the 2nd or 3rd cycle (Fig. 3f) due to the inevitable extraneous oxygen contained in the FeAlO_x that produced CO_x in the initial cycle of experiment. For all test cycles, the mass balance which is determined as the sum of gas and solid yield, ranged from 93.6 to 100.4 % (Supplementary Table 3-5). These values reflect the almost complete degradation of these plastics through this microwave-initiated solid-solid reaction to only gases and carbons. It is worth noting also that the process can be used to degrade mixtures of HDPE, PP and PS with different mixing ratio which showed similar results (Supplementary Table 6).

Since the polymeric molecules that constitute the plastics are of high Molecular Weight (typically 5,000 – 5,000,000 g/mol), in conventional pyrolysis or pyrolysis – catalysis processes, plastic polymers are invariably decomposed to a myriad of small

molecules via side reactions, and these can result in even thousands of products^{5,8,29}. The state-of-the-art catalysts and processes designed for plastic thermal pyrolysis are now primarily aimed, understandably, to narrow down the products in a desired diesel range⁹. For this reason, it is more difficult to selectively produce only H₂ and carbon by these routes. Thus, important previous work^{12-16,18-22} on hydrogen production from plastic always involves a two-step processes where plastics are first thermally decomposed to small molecules before the instigation of catalytic cracking or reforming reactions for ultimate hydrogen production.

The approach used in this work significantly simplifies the process; it achieves, selectively - in a one-step reaction - high purity hydrogen and high-value carbon materials (The results have been compared with literature in Supplementary Table 7).

The characterisation of carbonaceous products

Carbon nanotubes are almost the sole solid product from these processes. These product materials continue to attract attention due to their high commercial value and multiple applications^{13,14,19,30}, including the aerospace, automotive and civil engineering industries^{30,31}. Thus, this work illustrates a process making use of an inexpensive and abundant catalyst, iron, in an oxide form to produce hydrogen fuel whilst also producing multi-walled carbon nanotubes (MWCNTs) as a valuable by-product.

In Fig. 4a, we show a 10-cycle test on HDPE@ FeAlO_x. The plastic pieces were physically mixed with FeAlO_x catalyst particles in a weight ratio of 1:1, and the resulting residues at each cycle were additional mixed (only) with the same amount of fresh plastic pieces between every cycles of test. The H₂ yield was found to

gradually decrease throughout the successive degradation of added HDPE. We attribute this gradual diminution to the substantial amount of ever- growing carbon deposition. As demonstrated in our temperature programmed oxidation (TPO), x-ray photoelectron spectroscopy (XPS) and electron microscopy studies (Fig 4c -f) the produced carbon materials consisted primarily of MWCNTs.

The carbon yield at each cycle of test – except cycle 1 – was nearly constant ranging from 57.6 to 73.1 wt.% (Fig 4a); and the low carbon yield obtained in cycle 1 is ascribed to the formation of CO_x during the reactions. After 10 successive cycles of test, around 1.9 g of carbons were ultimately accumulated on the catalyst, thus the overall carbon (MWCNTs) yield in the process is ca. 620 mg · g⁻¹_{plastic}. As also shown in our thermogravimetric analysis (Fig. 4b), the spent sample after 7 cycles contained nearly 88.6 wt.% of MWCNTs and subsequently the resulting residue after 10 cycles is composed of ca. 92 wt.% of MWCNTs.

Scanning electron microscopy / Energy-dispersive x-ray spectroscopy (SEM / EDS) images of resulting carbon nano-materials confirmed the growth of a substantial amount of filamentous carbon (Fig. 4d). The MWCNTs observed in TEM images (Fig. 4e-f) showed outer diameters of ca. 10 - 20 nm, with inner diameters ca. 6 nm, and spacing values of the produced MWCNTs are ca. 0.32 – 0.34 nm.

The TPO analysis supported the proposal of the formation of MWCNTs on the FeAlO_x catalyst (Fig. 4c), whereby the spent samples in cycle 1 gave two peaks at around 450 °C and 560 °C, associated with amorphous carbons and CNTs, respectively^{20,32}. These peaks shifted to the higher temperatures throughout the successive cycles of reaction and in addition, the peak observed at lower temperature tended to merge into the peak at higher temperature. Consequently,

only one peak at about 610 °C was detected in the spent samples after 10 cycles of test, which indicates that high purity MWCNTs can indeed be manufactured from plastic waste via this process. Furthermore, the XPS spectrum (Supplementary Fig. 1) and Raman spectrum (Supplementary Fig. 2) of carbon also suggests the resulting carbon materials are primarily MWCNTs^{33,34}.

Proposed reaction scheme

Despite the acknowledged – and continually rising- interest in the application of microwaves in many areas of chemistry, there is still controversy about the fundamental nature of the interaction of microwaves with chemicals and materials. This is particular the case for microwave-initiated heterogeneous catalysis^{35,36}.

What we have in this present system is the initiation or activation of the heterogeneous catalysts by microwaves; the starting objects are obviously non-uniform, multi-phase systems that undergo catalysis under the action of the incident electromagnetic radiation.

Notwithstanding the controversy concerning the relative importance of thermal effects and non-thermal effects in microwave chemistry^{35,36}, we propose here a tentative mechanistic model of the microwave-initiated solid-solid reaction using Fe-based catalysts for hydrogen and carbon nanotubes production from plastic waste (Fig. 5).

The fundamental difference and advance of using microwaves is due to the fact that FeAlO_x catalyst particles play two roles simultaneously in this process; First, there is efficient energy transfer from the incoming microwave electromagnetic radiation to initiate the physical heating process (driving force) of the catalyst particle.

Secondly, the ensuing catalytic reaction at the particle surface occurs when the particle reaches the necessary temperature. When microwaves interact with FeAlO_x catalyst particles, heat is rapidly generated throughout the catalyst particles themselves (these particles have physical dimensions below the characteristic microwave skin depth at these operating frequencies). Moreover, since the microwave heating is itself a function of the electrodynamic properties of the catalyst (i.e. the charge dynamics associated with the susceptibility of the catalyst material), electromagnetic heating is closely connected to the material properties which dictates the heating rate – thereby influencing accompanying the catalytic processes.

In contrast, plastics are essentially fully transparent to incoming microwaves and the plastic substrate will initially remain cold (Fig. 5b). As have been shown in Fig. 2b that the temperature gap between the catalyst and substance can be over 400 °C.

Therefore, heat is generated selectively at the catalyst and subsequently transferred to the plastic (reactant). This is an important fundamental distinction in that the heat flux (flow) is obviously directed from the surface of the catalyst particle and mass transfer will obviously occur in the same direction. This will help facilitate the desorption of neutral hydrogen (either atoms or molecules) from the active sites on the catalyst surface. This is fundamentally different from a conventional heating catalytic process, usually limited by the mass transfer rate of molecular desorption.

We believe that this advantageous effect is fundamentally important for narrowing the possible chemical product distribution by avoiding the many side reactions from the (usual) self-decomposition of plastic polymers. Thus, we propose that the overriding catalytic mechanism here is the microwave-initiated catalytic scission of chemical C-H bonds.

Given that the plastic is surely melted in the vicinity of the (constantly) heating catalyst particle, the polymer molecules have large kinetic energy in order to create a high frequency of collisions on the catalyst active sites. That will clearly lead to an increase in the key factors in the Arrhenius reaction equation ($k = A \exp(-E_a / kT)$), most notably the pre-exponential factor, A , which represents the collision frequency between the (incoming) reactant (polymer) molecules and the active sites, while the exponential factor represents the quantity of species that can overcome the activation energy barrier.

In addition, important interfacial polarisation at the surface of the microwave – absorbing FeAlO_x catalyst particles causes a major, local increase in the electric field strength³⁷ and hence dramatic differences in heating rates³⁸ exist between the two constituents - the catalyst particles and the plastic pieces and at their interface.

Most significant, therefore, we believe that microwave electromagnetic radiation enhances the desorption of product H_2 molecules from the catalyst surface. This does raise also the fundamental issue of the comparison of traditional conditions (thermal heating) with this microwave-initiated regime. As noted elsewhere³⁹, direct comparison is not always possible because of the intrinsic difficulties relating to the true (“local”) process temperature at the catalyst in the latter case. If indeed, this “local” temperature is much higher than our pyrometer –measured temperatures, the kinetic energy of our gaseous product, H_2 will also assist rapid diffusion away from the catalyst.

In Fig. 5f we show a representative finite element simulation model mapping of the E-field strength and the heating rate at the interface of a spherical Fe particle with plastic, based upon a quasi-static solution of the electromagnetic fields³⁸ (see

Method for details). From these simulations, we find both the E-field strength and the heating rate at the interface increased significantly due to the interfacial polarisation. The E-field strength at the interface of catalyst and plastic is about 3 times larger than in the bulk plastic. Due to the fact that microwave electric fields will be screened from the deep interior of the Fe particle, localised high E-field and heating will occur at the particle surface³⁷. Recent advances in the field-assisted catalysis have shown electric fields can affect catalytic activity and selectivity with a focus on heterogeneous catalysts in much the same way as temperature and pressure⁴⁰. The computational and experimental studies by Che et al.^{41,42} for the methane steam reforming reaction (MSR) have shown an electric field can improve the efficiency of MSR processes and lower the overall temperature requirements.

In this microwave-initiated solid-solid reactions, typically, the microwave heating rate per unit volume $\langle P_E \rangle$ in Joules per second is given by $\langle P_E \rangle = \frac{1}{2} \omega \varepsilon_0 \varepsilon_2 E_0^2$, where ω is the angular frequency, ε_0 is the permittivity of free space, ε_2 is the local imaginary permittivity and E_0 is the applied microwave electric field strength. Since the heating rate is proportional to the square of the electric field strength, a three-fold local increase in field strength at the particle-plastic interface due to interfacial polarisation – typical for high permittivity materials of spherical shape - leads to a nine-fold increase in the interfacial heating rate. In addition, as the deposition of highly microwave absorbing carbon takes place, the microwave heating rate will increase still further³⁸. Importantly, the growth of high aspect ratio carbons will also increase this effect by orders of magnitude due to the high depolarisation factor of the growing carbon nanostructures. As shown in the simulations (Fig. 5f), the heating rate at the interface increased due to the polarisation field and with a 500nm layer of carbon that becomes deposited, the heating rate will be over three orders of magnitude

375 greater than in the bulk plastic.

376 Furthermore, the close contact/ proximity of catalyst particles and plastic pieces in
377 the interaction with the incoming microwave irradiation could potentially generate
378 non-equilibrium plasma in their interface and thus enhance the catalytic reactions. In
379 several studies⁴³⁻⁴⁵ the combination of plasma and catalysts has been found to have
380 synergistic effects. Combining plasma with a solid catalyst whose dielectric
381 properties and morphology are suitable, enhancement of the average electric field
382 strength can occur, resulting in an enhanced efficiency of the chemical reactions
383 taking place on the dual system. Surface adsorption within a plasma volume can
384 make a significant contribution to improved reaction performance. When reactant
385 molecules (here plastic polymers) are adsorbed onto the catalyst surface, the
386 retention time and concentration of those species in the plasma can be enhanced.
387 This could lead to an increased probability of reactive collisions with active species in
388 the plasma volume.

389 In summary, for the present process, we believe that the very nature of microwave
390 initiation of these catalytic chemical reactions significantly minimises the (potentially
391 numerous) chemical side reactions. Hence the catalytic process takes place only at
392 the interface between the hot (and almost certainly constantly heating) catalyst
393 particle and the (initially) cold plastic (substrate or “bath”) and the cleavage of C-H
394 bonds is dominant.

395 As the catalytic process must always be preceded by incoming reactant
396 adsorption⁴⁶, it suggest that the plastic polymer in the vicinity of the catalyst particle
397 may well be molten. The polymer is then absorbed on the catalyst particle with rapid
398 activation-decomposition occurring on the Fe catalyst surface (Fig. 5c). Thus, H₂ and

carbon are subsequently produced via a (proposed) consecutive reaction pathway as given in Fig. 5 (eqn. 1).

Our TGA analysis (Supplementary Fig. 3) has confirmed the presence of intermediate compounds (i.e. alkenes/aromatics) as several peaks other than plastic were detected in samples collected in the first 10s to 20s. This suggests plastic could initially be catalytically decomposed to small alkene/aromatics through a dehydrogenation step, and then these intermediates quickly and completely decomposed to produce further H_2 and MWCNTs. We note again that this interlude with the presence of intermediates is limited and importantly the $FeAlO_x$ catalyst can efficiently convert these species in a very high turnover rate under microwave irradiation.

Following carbon production, we propose that carbon species then diffuse into the Fe catalyst to form Fe_3C (Fig. 5d). Our XRD study (Fig 3c) showed that the diffraction peaks of Fe_3C were detected after 20s turned on the microwave. Previous work by Zhou et al.^{47,48} reported the mechanism models of catalytic methane decomposition (CMD) over Fe-Al catalyst, and they claimed the important role of Fe_3C in terms of CNTs formation. Thus, we assume the formation of Fe_3C to be vital for the subsequent –and selective - formation of MWCNTs.

With continuing carbon formation and precipitation, carbon then crystallizes in the form of a cylindrical network on the surface of the catalyst particle and finally grows into tubular structures (Fig. 5e). In addition, the surrounding “sink” of cold (not yet heated) plastic pieces may also produce thermal cooling of the “Hot spot” catalyst particle to the surrounding lattice or “bath” as well as the catalytic process itself. This is clearly an extremely unusual and complex heating / catalytic process and further

studies are underway to ascertain more details of the precise mechanisms at the heating surface.

Concluding Remarks:

We have described a simple one-step microwave-initiated process for rapidly deconstructing pulverized samples of common bulk plastics into hydrogen and high value carbon materials. The combination of the highly effective FeAlO_x catalyst / microwave-susceptor through its interaction with incident microwaves can rapidly extract almost 97% of the hydrogen from plastic waste in about 20 seconds. A high H₂ yield of 55.6 mmol·g_{plastic}⁻¹ was achieved with the H₂ concentration in the evolved gases reaching ca. 90 vol.%. Through the successive additions of plastics, the FeAlO_x catalyst produced 85.7 mmol-H₂ / g_{plastic} · g_{catalyst}, accompanying with a carbon production of 1560 mg-C / g_{plastic} · g_{catalyst} which the resulting sample is composed of > 92 wt.% MWCNTs.

Such a rapid and selective production of H₂ and carbon nanomaterials from the deconstruction of plastics reveals a potential new route for helping tackle the burgeoning issue of plastics waste. The applicability and sustainability credentials (including energy minimisation) of this approach for scale- up must obviously be the next steps for any practical utilisation. However, we feel that these findings are important in representing a new and attractive potential solution for plastic waste; thus, now and in the future, plastics waste can be utilised as a valuable, anthropogenically-sourced feedstock for producing clean H₂ fuel and value-added carbon products.

Methods

Preparation of FeAlO_x catalyst

The FeAlO_x particles were prepared using the so-called citric acid combustion method. Analytical grade iron nitrate (Fe(NO₃)₃·9H₂O, Iron (III) nitrate nonahydrate, Sigma-Aldrich), aluminum nitrate (Al(NO₃)₃·9H₂O, aluminum nitrate nonahydrate, Sigma-Aldrich) and citric acid (Sigma-Aldrich) were used as starting materials. Appropriate amount of Fe(NO₃)₃·9H₂O, Al(NO₃)₃·9H₂O and citric acid were mixed in a desirable molar ratio. A minimum amount of distilled water was then added into the mixture to produce a viscous orange gel. The gel was burnt and calcined in air at 350 °C for 3 hours. The gel burnt in a self-propagating combustion manner and formed a loose powder. Finally, the powders were ground into fine particles.

For comparison purpose, same method and procedure is used to prepare Ni and Co alumina catalyst. Nickel nitrate (Ni(NO₃)₂·6H₂O, Nickel (II) nitrate hexahydrate, Sigma-Aldrich) and cobalt nitrate (Co(NO₃)₂·6H₂O, Cobalt (II) nitrate hexahydrate, Sigma-Aldrich) are used as precursors.

For studies on the effect of different support materials, the catalyst was prepared using incipient wetness impregnation method. Iron nitrate, Fe(NO₃)₃·9H₂O (Iron (III) nitrate nonahydrate, Sigma-Aldrich) was used as iron precursor. We synthesised a series of Fe catalysts supported by SiC (silicon carbide, Fisher Scientific), AC (activated carbon, Sigma-Aldrich), Al₂O₃ (aluminium oxide, Sigma-Aldrich) and ZSM-5 (Sigma-Aldrich) with Fe loading of 20 wt.%. The details of catalyst preparation have been described elsewhere⁴⁹.

All the carbon materials were used as purchased without further purification. Activated carbon (AC), carbon nanoplatelets (GNPs), Graphite and carbon nanotubes (multi-walled) were purchased from Sigama Aldrich.

Experimental setup and microwave reactor

The microwave reactor setup is given in Fig. 1d. The system consists of a microwave generator, a purpose-built microwave cavity and a controller^{50,51}.

The microwave heating system chain prior to the applicator consisted of a power generator, microwave head, microwave circulator, dummy load, microwave power meters and tuneable waveguide sections (Sairem Ltd.). The system was computer controlled using Labview software. The applicator section was fabricated in the Inorganic Chemistry Laboratory at the University of Oxford. The operating frequency was 2450 MHz (± 25 MHz) from 10% to 100% of nominal power. The maximum output power was 2000 W with 1% stability from 10% to 100% of maximum power after thirty minutes on. The microwave source is a magnetron with a ripple rate of $< 1\%$ RMS from 10% to 100%. The power rise time is about 100 μ s. The power generator is a resonant switching converter with frequencies of 30 kHz up to 80 kHz and an efficiency of 93% at nominal power. The power supply and microwave head are both water and air cooled. The microwave output is via WR 340 waveguides. The generator is controlled remotely via an RS232 MODBUS gateway using Labview software. The reflected power R , was measured by a crystal detector mounted onto the isolator load, from which we determine the power absorbed by the sample, P . If the power transmitted to the applicator is W , then $P = W - R - X$, where X is the microwave power lost in the cavity walls and through minor applicator leakages. The

applicator used was a TM₀₁₀ resonant cavity to enable a well-characterized field distribution and high nominal field strength. Thus, in this work we investigate electric field driven processes, with a high electric energy density in the sample region^{50,51}.

The sample temperature was measured using an infrared (IR) pyrometer, which was also used to control the power to the generator. The pyrometer was positioned horizontally to face a side hole in the microwave cavity. The IR thermometer can only measure the external surface temperature of the sample. During the microwave experiment a temperature (T) versus time (t) of reaction profile was recorded^{50,51}.

Experimental procedure

The real-world plastic waste of milk containers (high density polyethylene, HDPE), food wraps (polypropylene, PP) and plastic foam (polystyrene, PS) used in this study were collected from waste materials used by large supermarket chains. The plastics were pre-treated by crushing/pulverising into small pieces (< 5mm) using a household blender. These pieces of plastic were then physically mixed with catalyst particles in a typical weight ratio of 1:1 unless otherwise noted. Typically, 0.3-0.4g of plastic is used for single cycle of test.

The sample of mixture (catalyst + plastic) was placed in a quartz tube (inner diameter 6mm, outer diameter 9mm), with typically volumes of about 1.13 cm³ and the height of about 3.5-4cm. This is to ensure the sample is fully exposed to the axially polarised (TM₀₁₀) uniform electric fields (4 cm long). Then, the filled tube was placed axially in the centre of the TM₀₁₀ microwave cavity in order to minimise depolarisation effects under microwave radiation. Before starting microwave irradiation, the samples were purged with an Ar flow at a rate of 100 mL/min for a

period of 15 minutes. Then, the sample was irradiated under 1000 W microwave power (unless stated otherwise) for 3-5 min. The generated gases are collected and analysed by Gas Chromatography (GC) using a Perkin-Elmer, Clarus 580 GC. A “Cold trap” was set up for collecting liquid products.

For comparison purpose, the conventional thermal experiments on deconstruction of HDPE using same FeAlO_x catalysts were carried out in an electric furnace. The experimental setup is shown in Supplementary Fig. 4. The temperature set for the thermal cracking of plastic in the electric furnace is 550 °C with the heating rate of 20 °C/min. The thermal experiments follows the same procedure as microwave experiments which has been described above.

We define the volume % of the product composition in the evolved gases from GC analysis as selectivity. And the mass of each gas products was calculated according to the volume of gases obtained and the composition analysis from GC. We therefore describe the H_2 yield as the mole of H_2 obtained divided by the total weight of plastic (Eq. 1). The Hydrogen Efficiency is determined as the total mass of hydrogen contained in all gas products divided by the theoretical mass of H contained in the plastic (Eq. 2). The gas yield is calculated by the mass obtained in relation to the total weight of plastic which is given by Eq. 3. The solid (carbon) yield was then determined as the mass difference between fresh and spent sample in relation to the total weight of feedstock (Eq. 4). The mass balance is obtained based on the sum of gas and solid yields because a negligible amount of volatile (liquid) is produced in these processes and undetectable. But for comparison purpose, we estimated the oil yield (liquid yield) as, 100% - gas yield – carbon yield (Eq. 5).

$$H_2 \text{ yield} = \frac{\text{Mole of } H_2 \text{ produced}}{\text{Mass of plastic}} (\text{mmol} \cdot g_{\text{plastic}}^{-1}) \quad \text{Eq. 1}$$

543

$$\text{Hydrogen Efficiency} = \frac{\text{Total mass of H contained in all gas products (g)}}{\text{Theoretical mass of H in plastic (g)}} (\%) \quad \text{Eq. 2}$$

545

$$\text{Gas yield} = \frac{\text{Mass of Gas}}{\text{Mass of Plastic}} \times 100\% (\text{wt. } \%) \quad \text{Eq. 3}$$

547

$$\text{Solid yield (Carbon yield)} = \frac{\text{Mass of spent catalyst} - \text{Mass of fresh catalyst}}{\text{Mass of Plastic}} \times 100\% (\text{wt. } \%) \quad \text{Eq. 4}$$

549

$$\text{Oil yield (Liquid yield)} = 100\% - \text{Gas yield} - \text{Solid yield} \quad \text{Eq. 5}$$

551

552 **Characterisation and analysis of samples**

553 The samples were carefully characterised before and after experiments by powder
 554 X-ray diffraction (XRD, BRUKER D8 ADVANCE), Thermogravimetric analysis (TGA,
 555 TA Instrument, SDT Q-600), X-ray photoelectron spectroscopy (XPS, ESCALAB
 556 250XI), ATR-FTIR analysis, Laser-Raman spectroscopy (PerkinElmer
 557 RamanStationTM 400F spectrometer), Scanning electron microscope and Energy-
 558 dispersive X-ray spectroscopy (SEM-EDS, ZEISS EVO).

559 The powder X-ray diffraction (XRD) used a Cu K α X-ray source (45 kV, 40 mA) on
 560 a BRUKER D8 ADVANCE diffractometer. The scanning range (in 2 θ) in this study
 561 was 10° to 90°. Thermogravimetric analysis (TGA) was used to characterise the

resulting carbons in spent samples. A temperature-programmed oxidation (TPO) was carried out to determine the thermal stability of the produced carbons. The sample was heated from room temperature to 1000 °C at a heating rate of 10 °C/min under an air atmosphere with a flow rate of 100 ml/min. The resulting carbon was also investigated via Laser-Raman spectroscopy, with laser excitation at 785nm. The scanning electron microscope (SEM, ZEISS EVO) was used to characterise the surface morphology of the samples before and after microwave initiation. The surface elemental was analysed by Energy-dispersive X-ray spectroscopy (EDS, ZEISS EVO).

The morphologies of produced multi-walled carbon nanotubes (MWCNTs) were also examined by transmission electron microscopy (TEM) using JEM-3000F microscope (300 kV). The sample powder was dispersed in ethanol in an ultra-sonic bath for 15 min. The solution was then drop cast onto a 300-mesh copper TEM holey carbon grid on a filter paper and allowed to evaporate. Scale bars of all the TEM images were calibrated using an oriented gold crystal grid.

Modelling of the electromagnetic fields and heating rates

Finite element modelling of microwave receptors and plastic was carried out using COMSOL v4.4 software. A representative, spherical particle of radius 2µm was used to provide a baseline for field distributions around particles. Changes in aspect ratio can lead to an increased depolarisation factor and a dramatic increase in the field strength at the extremities of the structure.

In the simulation model, a representative spherical catalyst particle is embedded in the surface of the plastic. In the quasi-static regime, we apply a uniform quasi-microwave E -field and solve for the field strengths with frequency appropriate complex permittivities assigned to the model domains. The microwave heating rate per unit volume $\langle \square_{\square} \rangle$ in Joules per second is then calculated by $\langle P_E \rangle = \frac{1}{2} \omega \epsilon_0 \epsilon_2 E_0^2$, where ω is the angular frequency, ϵ_0 is the permittivity of free space, ϵ_2 is the local imaginary permittivity and E_0 is the applied microwave electric field strength. The complex permittivity used for plastic in this work is $\epsilon = 2.35 - j2 \times 10^{-4}$ ⁵² and for the representative receptor particle, we use conducting, metallic Fe, with permittivity approximated by $\epsilon \approx 1 - j1 \times 10^7$. The carbon is modelled as a 500nm thick continuous layer, with permittivity $\epsilon \approx 25 - j15$ ⁵³.

- The quasi-static model and applied electric fields

The heating mechanism in this work is via the microwave-electric field at a frequency of 2.45GHz, thus the model is in the long-wavelength regime and uniform fields may be applied in a quasi-static analysis. In addition, the skin depth of iron at 2.45GHz is hundreds of microns, accounting for its increased permeability, and does not affect our simulation. The applied field strength used in the simulation is 10 kV/m, which corresponds to around 30W of absorbed power in our cavity under normal operation:

The peak field strength in a cavity at resonance is given by

$$\langle U \rangle = 2 \langle U_e \rangle = 2 \cdot \int_{\text{vol.}} \frac{1}{4} \epsilon_0 E^2 dV = \frac{1}{2} \epsilon_0 \int_{\text{vol.}} E^2 dV$$

606 where $\langle U \rangle$ is the time averaged, stored electromagnetic energy, $\langle U_e \rangle$ is the time
 607 averaged, stored electric energy and E is the peak electric field strength.

608 For TM_{010} fields in a cylindrical resonant cavity of radius 4.6cm and height 4cm, we
 609 have,

$$610 \quad \langle U \rangle = \frac{1}{2} \epsilon_0 \int_{\text{vol.}} E^2 dV = \frac{1}{2} \epsilon_0 E_0^2 (0.266) V_{\text{cav}}$$

611 Where V_{cav} is the volume of the cavity, giving,

$$612 \quad \langle U \rangle = \frac{Q_U \langle P_{\text{in}} \rangle}{\omega_0} \rightarrow E_0 \approx \sqrt{\frac{2Q_U \langle P_{\text{in}} \rangle}{\epsilon_0 \omega_0 (0.266) V_{\text{cav}}}}, \text{ i.e. } E_0 \propto \sqrt{Q_U P_{\text{in}}}$$

613 Q_U is the unloaded quality factor of the resonant cavity and $\langle P_{\text{in}} \rangle$ is the input power.

614 For a cavity of the dimensions used in this work, with $Q_U = 400$ and $P_{\text{in}} = 30\text{W}$, we
 615 have an applied peak electric field strength of

$$E_0 \approx \sqrt{\frac{2 \times 400 \times 30}{8.854 \times 10^{-12} \times 2\pi \times 2.45 \times 10^9 \times 0.266 \times 0.0002659044}} = 49.9 \text{ kV/m}$$

616 An applied peak electric field of at least 49kV/m is expected, though 10kV/m is used
 617 in this model.

618

619 **References:**

620 1 Geyer, R., Jambeck, J. R. & Law, K. L. Production, use, and fate of all plastics
 621 ever made. *Science advances* **3**, e1700782 (2017).

- 622 2 Lopez, G., Artetxe, M., Amutio, M., Bilbao, J. & Olazar, M. Thermochemical
623 routes for the valorization of waste polyolefinic plastics to produce fuels and
624 chemicals. A review. *Renewable and Sustainable Energy Reviews* **73**, 346-
625 368 (2017).
- 626 3 Achilias, D., Roupakias, C., Megalokonomos, P., Lappas, A. & Antonakou, E.
627 Chemical recycling of plastic wastes made from polyethylene (LDPE and
628 HDPE) and polypropylene (PP). *Journal of Hazardous Materials* **149**, 536-542
629 (2007).
- 630 4 Bazargan, A. & McKay, G. A review – Synthesis of carbon nanotubes from
631 plastic wastes. *Chemical Engineering Journal* **195-196**, 377-391 (2012).
- 632 5 Wong, S., Ngadi, N., Abdullah, T. & Inuwa, I. Current state and future
633 prospects of plastic waste as source of fuel: A review. *Renewable and*
634 *sustainable energy reviews* **50**, 1167-1180 (2015).
- 635 6 Ludlow-Palafox, C. & Chase, H. A. Microwave-induced pyrolysis of plastic
636 wastes. *Industrial & engineering chemistry research* **40**, 4749-4756 (2001).
- 637 7 Lopez, G. *et al.* Recent advances in the gasification of waste plastics. A
638 critical overview. *Renewable and Sustainable Energy Reviews* **82**, 576-596
639 (2018).
- 640 8 Kunwar, B., Cheng, H., Chandrashekar, S. R. & Sharma, B. K. Plastics to
641 fuel: a review. *Renewable and Sustainable Energy Reviews* **54**, 421-428
642 (2016).
- 643 9 Jia, X., Qin, C., Friedberger, T., Guan, Z. & Huang, Z. Efficient and selective
644 degradation of polyethylenes into liquid fuels and waxes under mild
645 conditions. *Science advances* **2**, e1501591 (2016).

- 646 10 Kim, J.-W., Mun, T.-Y., Kim, J.-O. & Kim, J.-S. Air gasification of mixed plastic
647 wastes using a two-stage gasifier for the production of producer gas with low
648 tar and a high caloric value. *Fuel* **90**, 2266-2272 (2011).
- 649 11 Arena, U. & Di Gregorio, F. Energy generation by air gasification of two
650 industrial plastic wastes in a pilot scale fluidized bed reactor. *Energy* **68**, 735-
651 743 (2014).
- 652 12 Erkiaga, A. *et al.* HDPE pyrolysis-steam reforming in a tandem spouted bed-
653 fixed bed reactor for H₂ production. *Journal of analytical and applied pyrolysis*
654 **116**, 34-41 (2015).
- 655 13 Wu, C., Nahil, M. A., Miskolczi, N., Huang, J. & Williams, P. T. Processing
656 real-world waste plastics by pyrolysis-reforming for hydrogen and high-value
657 carbon nanotubes. *Environmental science & technology* **48**, 819-826 (2013).
- 658 14 Yao, D., Zhang, Y., Williams, P. T., Yang, H. & Chen, H. Co-production of
659 hydrogen and carbon nanotubes from real-world waste plastics: Influence of
660 catalyst composition and operational parameters. *Applied Catalysis B:*
661 *Environmental* **221**, 584-597 (2018).
- 662 15 Czernik, S. & French, R. J. Production of hydrogen from plastics by pyrolysis
663 and catalytic steam reform. *Energy & fuels* **20**, 754-758 (2006).
- 664 16 Barbarias, I. *et al.* A sequential process for hydrogen production based on
665 continuous HDPE fast pyrolysis and in-line steam reforming. *Chemical*
666 *Engineering Journal* **296**, 191-198 (2016).
- 667 17 Uekert, T., Kuehnel, M. F., Wakerley, D. W. & Reisner, E. Plastic waste as a
668 feedstock for solar-driven H₂ generation. *Energy & Environmental Science*
669 **11**, 2853-2857 (2018).

- 670 18 Wu, C. & Williams, P. T. Pyrolysis–gasification of plastics, mixed plastics and
671 real-world plastic waste with and without Ni–Mg–Al catalyst. *Fuel* **89**, 3022-
672 3032 (2010).
- 673 19 Nahil, M. A., Wu, C. & Williams, P. T. Influence of metal addition to Ni-based
674 catalysts for the co-production of carbon nanotubes and hydrogen from the
675 thermal processing of waste polypropylene. *Fuel processing technology* **130**,
676 46-53 (2015).
- 677 20 Acomb, J. C., Wu, C. & Williams, P. T. The use of different metal catalysts for
678 the simultaneous production of carbon nanotubes and hydrogen from
679 pyrolysis of plastic feedstocks. *Applied Catalysis B: Environmental* **180**, 497-
680 510 (2016).
- 681 21 Dou, B. *et al.* Fluidized-bed gasification combined continuous sorption-
682 enhanced steam reforming system to continuous hydrogen production from
683 waste plastic. *International Journal of Hydrogen Energy* **41**, 3803-3810
684 (2016).
- 685 22 Yang, R.-X., Chuang, K.-H. & Wey, M.-Y. Carbon nanotube and hydrogen
686 production from waste plastic gasification over Ni/Al–SBA-15 catalysts: effect
687 of aluminum content. *RSC Advances* **6**, 40731-40740 (2016).
- 688 23 Gulmine, J. V., Janissek, P. R., Heise, H. M. & Akcelrud, L. Polyethylene
689 characterization by FTIR. *Polymer Testing* **21**, 557-563 (2002).
- 690 24 Chouit, F. *et al.* Synthesis and characterization of HDPE/N-MWNT
691 nanocomposite films. *Nanoscale research letters* **9**, 288 (2014).
- 692 25 Radpour, M., Masoudpanah, S. M. & Alamolhoda, S. Microwave-assisted
693 solution combustion synthesis of Fe₃O₄ powders. *Ceramics International* **43**,
694 14756-14762 (2017).

- 695 26 Zhou, L. *et al.* Catalytic Methane Decomposition over Fe $\square$ Al₂O₃.
696 *ChemSusChem* **9**, 1243-1248 (2016).
- 697 27 Fu, L.-S., Jiang, J.-T., Xu, C.-Y. & Zhen, L. Synthesis of hexagonal Fe
698 microflakes with excellent microwave absorption performance.
699 *CrystEngComm* **14**, 6827-6832, doi:10.1039/c2ce25836f (2012).
- 700 28 Domínguez, A., Fidalgo, B., Fernández, Y., Pis, J. & Menéndez, J.
701 Microwave-assisted catalytic decomposition of methane over activated carbon
702 for CO₂-free hydrogen production. *International Journal of Hydrogen Energy*
703 **32**, 4792-4799 (2007).
- 704 29 Aguado, J., Serrano, D. & Escola, J. Fuels from waste plastics by thermal and
705 catalytic processes: a review. *Industrial & Engineering Chemistry Research*
706 **47**, 7982-7992 (2008).
- 707 30 Wu, C., Nahil, M. A., Huang, J. & Williams, P. T. Production and application of
708 carbon nanotubes, as a co-product of hydrogen from the pyrolysis-catalytic
709 reforming of waste plastic. *Process Safety and Environmental Protection* **103**,
710 107-114 (2016).
- 711 31 Ansari, R., Hasrati, E., Shojaei, M. F., Gholami, R. & Shahabodini, A. Forced
712 vibration analysis of functionally graded carbon nanotube-reinforced
713 composite plates using a numerical strategy. *Physica E: Low-dimensional*
714 *Systems and Nanostructures* **69**, 294-305 (2015).
- 715 32 Shi, Z. *et al.* Large scale synthesis of single-wall carbon nanotubes by arc-
716 discharge method. *Journal of Physics and Chemistry of Solids* **61**, 1031-1036
717 (2000).

- 718 33 Zhang, Y. *et al.* Kinetics and interfacial thermodynamics of the pH-related
719 sorption of tetrabromobisphenol A onto multiwalled carbon nanotubes. *ACS*
720 *applied materials & interfaces* **6**, 20968-20977 (2014).
- 721 34 Munaiah, Y., Suresh, S., Dheenadayalan, S., Pillai, V. K. & Ragupathy, P.
722 Comparative Electrocatalytic performance of single-walled and multiwalled
723 carbon nanotubes for zinc bromine redox flow batteries. *The Journal of*
724 *Physical Chemistry C* **118**, 14795-14804 (2014).
- 725 35 Díaz-Ortiz, Á., Prieto, P. & de la Hoz, A. A critical overview on the effect of
726 microwave irradiation in organic synthesis. *The Chemical Record* **19**, 85-97
727 (2019).
- 728 36 Palma, V. *et al.* Microwaves and Heterogeneous Catalysis: A Review on
729 Selected Catalytic Processes. *Catalysts* **10**, 246 (2020).
- 730 37 Porch, A., Slocombe, D. & Edwards, P. P. Microwave absorption in powders
731 of small conducting particles for heating applications. *Phys. Chem. Chem.*
732 *Phys.* **15**, 2757-2763, doi:10.1039/c2cp43310a (2013).
- 733 38 Liu, B. *et al.* Microwaves effectively examine the extent and type of coking
734 over acid zeolite catalysts. *Nature communications* **8**, 514 (2017).
- 735 39 Horikoshi, S. e. & Serpone, N. e. *Microwaves in Catalysis : Methodology and*
736 *Applications*.
- 737 40 Che, F. *et al.* Elucidating the roles of electric fields in catalysis: A perspective.
738 *ACS Catalysis* **8**, 5153-5174 (2018).
- 739 41 Che, F., Gray, J. T., Ha, S. & McEwen, J.-S. Improving Ni catalysts using
740 electric fields: a DFT and experimental study of the methane steam reforming
741 reaction. *ACS Catalysis* **7**, 551-562 (2016).

- 742 42 Che, F., Ha, S. & McEwen, J. S. Catalytic Reaction Rates Controlled by Metal
743 Oxidation State: C–H Bond Cleavage in Methane over Nickel□Based
744 Catalysts. *Angewandte Chemie* **129**, 3611-3615 (2017).
- 745 43 Huelsey, M., Lim, C. W. & Yan, N. Promoting heterogeneous catalysis beyond
746 catalyst design. *Chemical Science* (2020).
- 747 44 Neyts, E. C., Ostrikov, K., Sunkara, M. K. & Bogaerts, A. Plasma catalysis:
748 synergistic effects at the nanoscale. *Chemical reviews* **115**, 13408-13446
749 (2015).
- 750 45 Chen, H. L., Lee, H. M., Chen, S. H., Chao, Y. & Chang, M. B. Review of
751 plasma catalysis on hydrocarbon reforming for hydrogen production—
752 interaction, integration, and prospects. *Applied Catalysis B: Environmental* **85**,
753 1-9 (2008).
- 754 46 Thomas, J. M. & Thomas, W. J. *Principles and practice of heterogeneous*
755 *catalysis*. (John Wiley & Sons, 2014).
- 756 47 Zhou, L. *et al.* Fe catalysts for methane decomposition to produce hydrogen
757 and carbon nano materials. *Applied Catalysis B: Environmental* **208**, 44-59
758 (2017).
- 759 48 Reddy Enakonda, L. *et al.* Methane□induced Activation Mechanism of Fused
760 Ferric Oxide–Alumina Catalysts during Methane Decomposition.
761 *ChemSusChem* **9**, 1911-1915 (2016).
- 762 49 Jie, X. *et al.* On the performance optimisation of Fe catalysts in the microwave
763 - assisted H₂ production by the dehydrogenation of hexadecane. *Catalysis*
764 *Today* **317**, 29-35 (2018).

- 765 50 Jie, X. *et al.* The decarbonisation of petroleum and other fossil hydrocarbon
766 fuels for the facile production and safe storage of hydrogen. *Energy &*
767 *Environmental Science* **12**, 238-249 (2019).
- 768 51 Jie, X. *et al.* Rapid Production of High-Purity Hydrogen Fuel through
769 Microwave-Promoted Deep Catalytic Dehydrogenation of Liquid Alkanes with
770 Abundant Metals. *Angewandte Chemie International Edition* **56**, 10170-10173
771 (2017).
- 772 52 Riddle, B., Baker-Jarvis, J. & Krupka, J. Complex permittivity measurements
773 of common plastics over variable temperatures. *IEEE Transactions on*
774 *Microwave theory and techniques* **51**, 727-733 (2003).
- 775 53 Hotta, M., Hayashi, M., Lanagan, M. T., Agrawal, D. K. & Nagata, K. Complex
776 permittivity of graphite, carbon black and coal powders in the ranges of X-
777 band frequencies (8.2 to 12.4 GHz) and between 1 and 10 GHz. *ISIJ*
778 *international* **51**, 1766-1772 (2011).

779

780 Figure legends

781 **Fig. 1: Schematic diagram** of (a) The two-step pyrolysis and gasification process
782 and, (b) The present one-step microwave-initiated catalytic process for
783 deconstruction of plastic waste to produce hydrogen and carbon multiwalled
784 nanotubes. (c) Experimental setup and reaction system configuration. (c1) The
785 purpose built TM010 mode aluminium cavity. 1) The central hole where samples are
786 inserted along the axis of the microwave electric field. 2) The viewing port for
787 temperature measurement by IR pyrometer. (d) A typical configuration of gas
788 collection for determining volumes of H₂ evolved when the microwave is switched on.
789 0.3g of HDPE and 0.3 g FeAlO_x catalysts were physically mixed before exposure to

microwaves. The H₂ is rapidly evolved and was collected over water (as indicated by the red arrows with the produced bubbles were circled in blue) and a movie illustrating the system in action can be found in the supplementary movie 1.

Fig. 2. Representative single cycle experiment of the microwave-initiated decomposition of 0.4g HDPE using 0.4g of FeAlO_x catalysts. **(a)** “Time on stream” analysis showing gas evolution as a function of time. **(b)** Bed temperature and **(c)** microwave absorbed power of FeAlO_x catalyst particles (red), HDPE (black) and a mixed sample of FeAlO_x catalysts and HDPE (blue). **(d)** and **(e)**: Mimicking an ‘*in-situ*’ characterisation of HDPE@ FeAlO_x under microwaves. Samples were exposed to microwave irradiation for different time of 10s, 15s, 18s, 20s, 30s, 60s and 90s, respectively. **(d)** XRD patterns, illustrating the evolved changes of HDPE and FeAlO_x catalyst; **(e)** ATR-FTIR spectrum. The strong bands appeared at 2916 and 2849 cm⁻¹ are assigned to CH₂ asymmetric stretching. Absorption band observed at 1474 and 1464 cm⁻¹ indicates the bending deformation of the CH₂ groups in the molecules. Another set of peaks at 719 and 729 are due to the rocking deformation²³.

Fig. 3: Microwave-initiated decomposition of HDPE. **(a)** Investigation on different metal catalysts and **(b)** various supported Fe catalysts and carbons. **(c)** Comparison of microwave and conventional thermal processes. The temperature used for thermal experiments were 550 °C and the highest temperature recorded under microwave was ca. 350 °C. **(d)** Experiments with a different starting weight ratio of HDPE and FeAlO_x catalysts. **(e)** and **(f)** Successive cycles of the deconstruction of HDPE, PP and PS on FeAlO_x catalysts. The resulting residues were additional mixed

(only) with fresh plastic pieces with a weight ratio of 1:1 between every cycles of test. The mixture was exposed to 1000W microwave irradiation for 5 min, and the generated gases were collected and analysed by GC. **(e)** H₂ yield and solid (carbon) yield. **(f)** Hydrogen efficiency and Evolved gas composition (vol.%).

Fig. 4: 10 cycles of successive deconstruction of HDPE over FeAlO_x catalysts under microwave irradiation. (a) H₂ yield and solid (carbon) yield; cumulative carbon production as a function of cycles. **(b)** Yield of carbon quantified by thermogravimetric analysis (TGA); **(c)** Derivative plots of temperature programmed oxidation (TPO) of representative spent samples throughout the successive tests; **(d)** Scanning electron microscope (SEM) images, showing the production of primarily carbon nanotubes. **(e)** Transmission electron microscopy (TEM) image of produced carbon nanotubes, inset (1) illustrates the enlarged tube wall with the spacing value ca. 0.34 nm. **(f)** Lattice fringe images of the tube wall. The distance between adjacent graphene layers is ca. 0.32 nm.

Fig. 5: Suggested mechanism of microwave-initiated decomposition of plastic over a FeAlO_x catalyst.

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837 **Author Contributions**

838 P. P. Edwards, T. Xiao and J. M. Thomas supervised the project. P. P. Edwards, T.
839 Xiao, H. AlMegren and S. Alshihri contributed to the funding acquisition. X. Jie, T.
840 Xiao and P. P. Edwards, conceived and then designed the project. X. Jie designed
841 and developed the experiments and evaluated and analysed the performance data.
842 X. Jie and W. Li designed and carried out the EM measurements, and analysis of
843 the data. D. R. Slocombe and X. Jie designed and carried out the modelling and
844 analysis of the data. X. Jie drafted the original manuscript. All authors, including J.
845 R. Dilworth, Y. Gao, I. Banerjee, S. Gonzalez-Cortes and B. Yao contributed to the
846 analysis, interpretation and discussion of results and the writing and revisions of
847 the manuscript.

848

849 **Conflicts of interest**

850 The authors declare no conflict of interest.

851