Less Defective Graphene Aerogel and Application in Microwave-Assisted Biomass Pyrolysis to Prepare H_2-rich Gas

Wenlu Liu[a, b†], Haibin Jiang[b†], Xiaohong Zhang[b], Yating Zhao[b], Shuqi Sun[b], Jinliang Qiao*[a, b]
Correspondence to: qiaojl.bjhy@sinopec.com

Materials and Equipment

The aqueous graphene oxide (GO) suspension was purchased from Nanjing JCNANO Technology Co., Ltd. Ascorbic acid was obtained from Sino-Pharm Chemical Reagent Co., LTD. Biomass were collected from the farmland in Hebei Province. The household microwave oven was made by Galanz Microwave Oven and Electric Appliances Manufacturing Co., Ltd. The microwave oven (MKX-R1C1B) was made by Makewave Research Institute. Alumina temperature measuring cuboid was purchased from JFCC Corporation of Japan.

Characterization

The morphology of LD-graphene aerogel was characterized by scanning electron microscopy (SEM), which was performed on HATICHI S4800. Transmission electron microscope (TEM) was conducted on a FEI Tecnai20. Raman spectroscopy was obtained with a Lab RAM HR800 Raman microscope using a 532 nm laser beam as the probing light source. The element compositions in samples were investigated by X-ray photoelectron spectroscopy (XPS, ESCA-LAB 250, Thermo Fisher, 2009). X-ray diffraction (XRD) was conducted by using a PAN analytical X-ray diffraction system with the source wavelength of 1.542 Å at room temperature. FTIR spectra were recorded on a Nicolet Nexus 470 spectrometer in the frequency range 4000-400 cm^{-1}. N_2 adsorption/desorption isothermal curves at 77 K were recorded using a volumetric gas analyzer Autosorb 1-MP by Quantachrome Instruments.

Preparation of LD-graphene aerogel

50 mg ascorbic acid was homogeneously dispersed into 100 mL GO aqueous suspension (5 mg/mL) by ultrasonication for 30 min. They were then transferred into a Teflon-lined autoclave and hydrothermally treated at 120 ℃ for 6 h to form a graphene gel. The hydrogel was frozen at -55 ℃ for 12 h and then freeze-dried into graphene aerogel. The synthesized graphene aerogel was placed in a nitrogen-filled quartz glass box and heated in a household microwave oven at 700 W for 2 min to form less defective graphene aerogel (LD-graphene aerogel).

Temperature measurement of LD-graphene aerogel

Alumina temperature measuring cuboid was used to measure the heating ability of LD-graphene aerogels under microwave irradiation. The mechanism for temperature measuring is that the volume of alumina cuboid will shrink linearly during the heating process. It is a temperature measuring tool with an error control of 2 ℃ and is usually used for temperature calibration of tube furnace. The alumina temperature measuring cuboid and LD-graphene aerogel were placed in the quartz container, and alumina temperature measuring cuboid was embedded in LD-graphene aerogel. In order to maintain an inert atmosphere during the experiments, N_2 with 80 mL/min flow rate was passed through the system for 20 min prior to the commencement of the experiment, and then the microwave oven was turned on. The microwave heating process lasted for 10 minutes and the microwave power was maintained at 900 W. The alumina temperature measuring cuboid was taken out 30 minutes later and measured its length. The temperature shown by alumina temperature measuring cuboid can be obtained by comparing the measurement result with standard data, which was expected to represent the average temperature of intermediate products quite accurately.

Microwave-assisted pyrolysis of biomass using LD-graphene aerogel as heating material

Rice husk, rice straw, poplar branch and cornstalk are the biomass used in the pyrolysis experiment. For the batch process, 10 g of biomass and 5 g of LD-graphene aerogel were mixed in the quartz container. In order to maintain an inert atmosphere during the experiments, N_2 with 80 mL/min flow rate was passed through the system for 20 min prior to the commencement of the experiment, and then the oven was turned on. The volatiles released from pyrolysis of biomass were passed through the condensing system which consists of two connected condenser pipes immersed in ice-water bath. Condensable volatiles (liquid product) were collected from the condensing system by dissolving it in methanol and then subjected to further evaporation to remove the solvent. The non-condensable gas was collected in 3 L gas collecting bags. Solid products and graphene aerogels were separated by simple mechanical sorting with tweezers. Solid and liquid yields were calculated from the direct weight of each fraction after the reaction was completed, while gas yields were calculated based on the mass balance.

For the continuous pyrolysis process, 15g powdered poplar wood was mixed with 30g palm oil (feedstock PWPO), and PWPO was continuously pumped into microwave cavity through a quartz tube at the feed rate of 0.5 g/min and pyrolyzed to gas with 900W microwave and 5g LD-graphene aerogel.

Analysis of gas products

The gas products were analyzed according to ASTM D1945-14 method using a Refinery Gas Analyzer (HP Agilent 7890 A, configured with three channels, including one FID and two TCD (thermal conductivity detector)). Hydrocarbons were analyzed on the FID channel. One TCD with nitrogen carrier was employed to determine hydrogen because of the small difference in the conductivity of hydrogen and helium carrier. The other TCD with helium as carrier gas was used

to detect CO and CO_2. For quantitative analysis, the response factor was determined by using an RGA (Refinery Gas Analysis) calibration gas standard.

Analysis of liquid products and solid products

The compositions of the liquid products were identified using an Agilent 7890A–5975C gas chromatography/mass spectrometer with an HP-5 MS capillary column. Helium was used as the carrier gas at the flow rate of 1.2 mL/min. The temperature of oven was programmed from 35 °C to 250°C at the heating rate of 10°C /min. The injection size was 1 μL with a split ratio of 1:10. The National Institute of Standards and Technology (NIST) mass spectral data library was used to compare their mass spectra with those from identified compounds. In order to identify the elements present on solid products, XPS analysis was performed by X-ray photoelectron spectroscopy. The morphology of solid products was characterized by SEM, which was performed on HATICHI S4800.

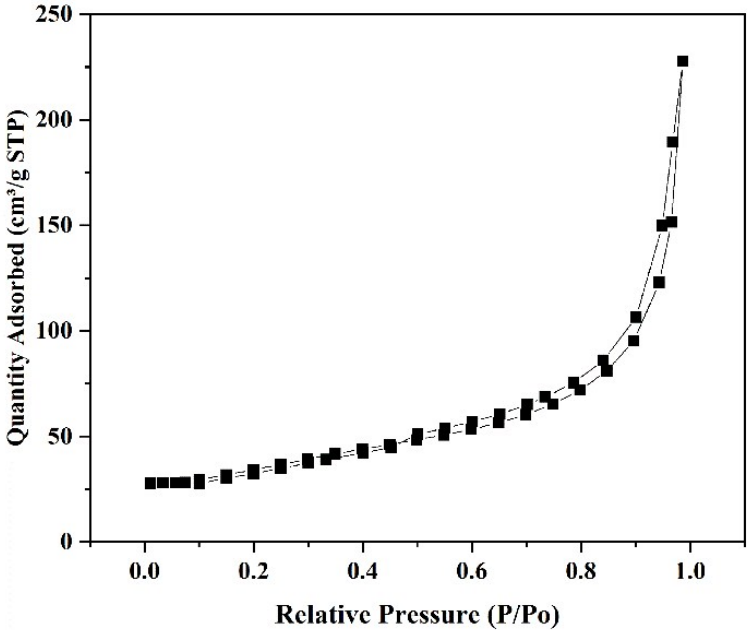

Fig. S1 Nitrogen adsorption–desorption isotherms of LD-graphene aerogel.

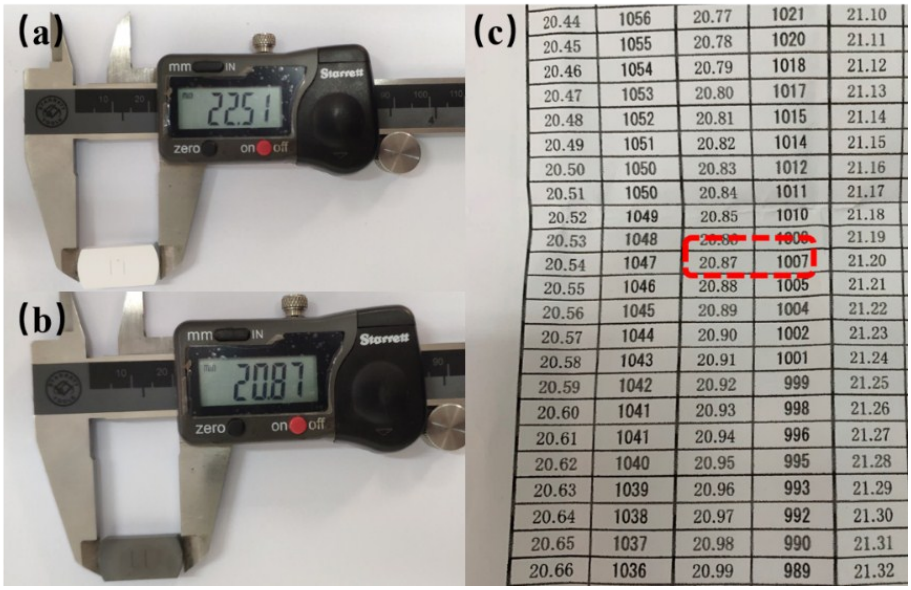

Fig. S2 (a) Original length of alumina temperature measuring cuboid; (b) length of alumina temperature measuring cuboid after the heating process is finished; (c) standard data table for the alumina temperature measuring cuboid.

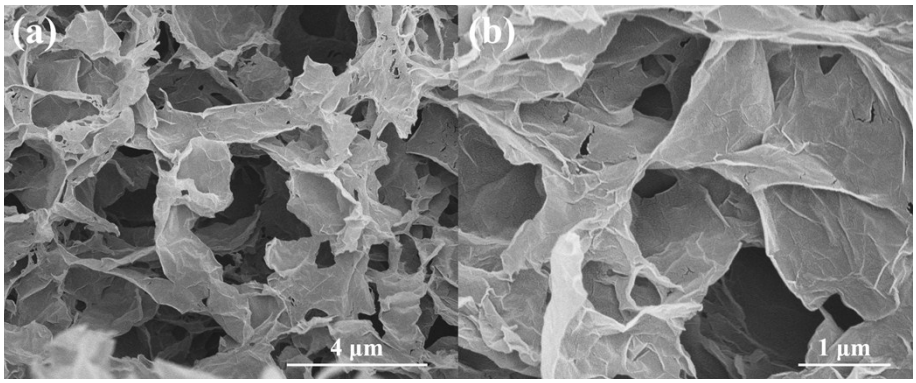

Fig. S3 SEM images of LD-graphene aerogel after several times of microwave-assisted pyrolysis reactions.

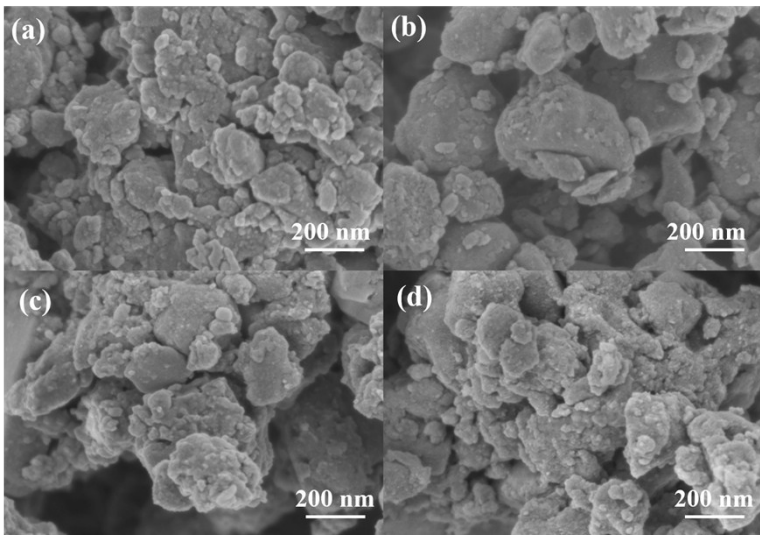

Fig. S4 SEM images for solid product from biomass pyrolysis: (a) rice husk; (b) rice straw; (c) cornstalk and (d) poplar wood.

Table S1. Elemental composition of GO, graphene aerogel and LD-graphene aerogel

Elements (At %)	C	O	C/O
GO	72.74	27.26	2.70
graphene aerogel	84.7	15.3	5.53
LD- graphene aerogel	93.01	6.99	13.3

Table S2. The distributions of the components produced by biomass pyrolysis

	Rice husk	Rice straw	Cornstalk	Poplar wood
Solid (wt.%)	25.17	21.38	22.34	19.73
Liquid (wt.%)	8.49	7.59	16.90	11.16
Gas (wt.%) a	66.34	71.03	60.76	69.11

[a] Gas yield was obtained by normalization of all products to 100% and subtraction of solid and liquid yield.

Table S3. The distributions and average value of the solid products and liquid products

	Solid product (wt.%)			Average value	Liquid product (wt.%)			Average value
Rice husk	25.17	25.16	25.18	25.17	8.47	8.47	8.53	8.49
Rice straw	21.32	21.40	21.42	21.38	7.63	7.60	7.54	7.59
Cornstalk	22.32	22.36	22.34	22.34	16.87	16.92	16.91	16.90
Poplar wood	19.73	19.71	19.75	19.73	11.11	11.21	11.17	11.16

Table S4. HHV of gas product from microwave pyrolysis of different biomass

	Rice husk	Rice straw	Cornstalk	Poplar wood
HHV (MJ/m^3)	14.80	14.45	13.23	14.55

Table S5. Products of different feedstocks with the continuous pyrolysis process

Products		Palm oil	Mixture of poplar wood powder and palm oil
Solid (wt.%)		20.62	19.73
Liquid (wt.%)		9.42	9.02
Gas (wt.%)		69.96	71.25
Gas Phase Composition (vol.%)	Hydrogen	42.70	48.21
	carbon monoxide	11.35	14.53
	methane	9.59	11.06
	carbon dioxide	10.64	5.70
	ethylene	18.60	16.5
	propylene	5.57	3.3
	Others (containing ethane, ethyne, 1-butylene etc.)	1.55	0.70

Table S6. Main organic compounds in liquid products for different biomass

RT	Peak name	Formula	Rice husk [a]	Rice straw	Corn stalk	Poplar wood
9.1823	Phenol	C_6H_6O	+	+	+	+
10.4549	Phenol, 2-methyl-	C_7H_8O	+	+	+	-
10.7854	Phenol, 4-methyl-	C_7H_8O	+	+	-	+
12.2342	Phenol, 4-ethyl-	$C_8H_{10}O$	+	+	+	-
13.0054	Benzofuran, 2,3-dihydro-	C_8H_8O	+	+	-	+
14.279	Phenol, 2-methoxy-	$C_7H_8O_2$	+	+	+	+
17.352	Phenol, 2-methoxy-4-methyl-	$C_8H_{10}O_2$	+	+	-	-
21.881	Benzene methanol, 3-hydroxy-5-methoxy	$C_8H_{10}O_3$	-	-	+	+
24,289	Phenol, 2-methoxy-5-(1-propenyl)-, (E)-	$C_{10}H_{12}O_2$	-	-	-	+

[a] "+" means included and "-" means not detected.

Table S7. Elemental analysis of solid products from biomass pyrolysis

Elemental composition (wt.%)	C	O	Si	K	Others
Rice husk	57.30	20.30	19.09	0.92	2.39
Rice straw	55.61	22.44	7.37	6.45	8.13
Cornstalk	79.30	15.29	1.07	3.11	1.23
Poplar wood	85.50	12.35	0.28	0.21	1.66