Rational design and solvent-free synthesis of iron-embedded 2D composite materials derived from biomass for efficient oxygen reduction reaction

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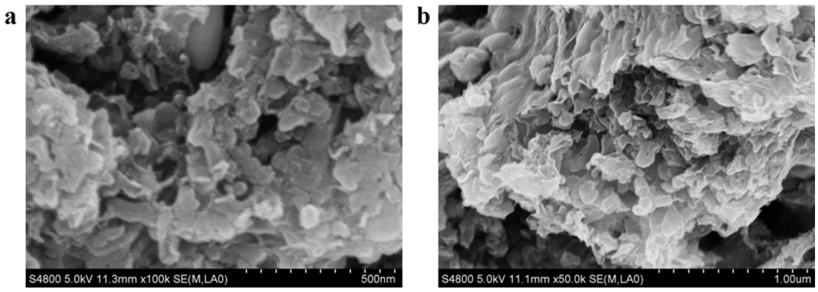

Fig. S1. Typical SEM (a and b) images of the as-synthesized CHC.

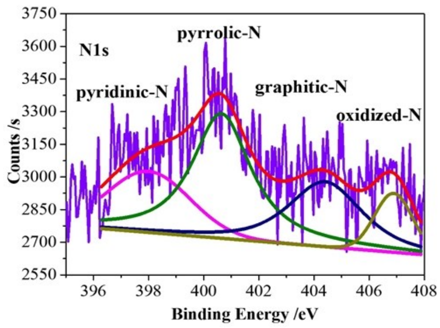

Fig. S2. The high-resolution N 1s (f) of the as-synthesized CHCFe.

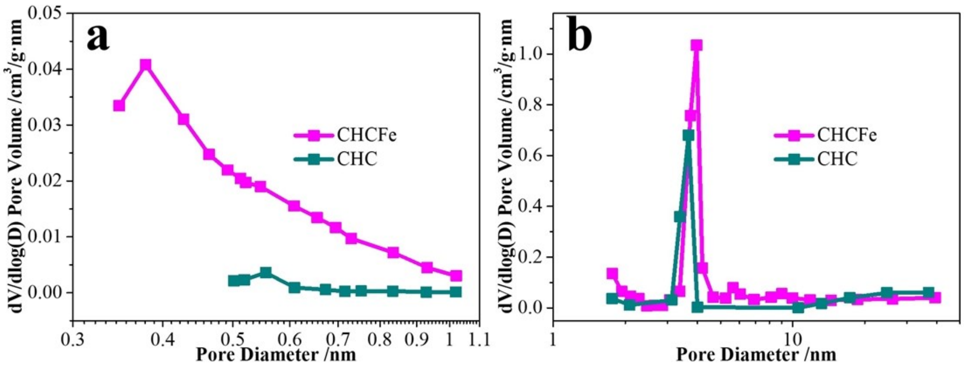

Fig. S3. The micropore (a) and mesopore (b) size distributions of the CHC and CHCFe.

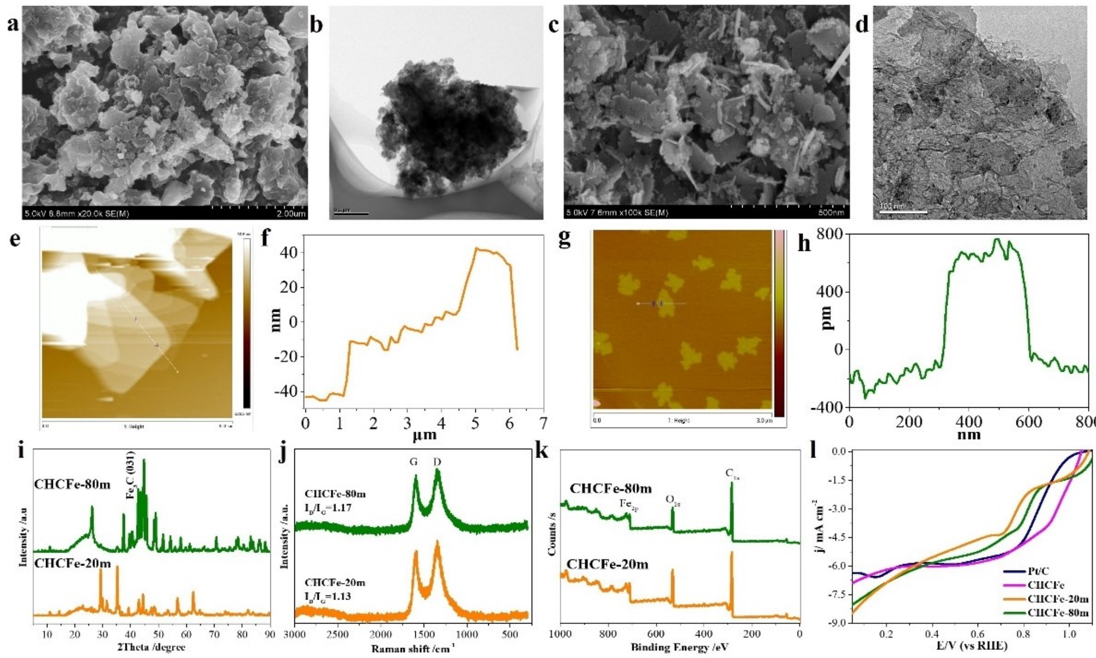

Fig. S4. Typical SEM (a and c) images, TEM (b and d) images, AFM (e and g) images with the corresponding height profiles (f and h), XRD spectra (i), Raman spectra (j), XPS spectra (k), and LSV polarization curves at a rotation rate of 2000 rpm in O_2-saturated 0.1 M KOH solutions (l) of the as-synthesized CHCFe-20 and CHCFe-80.

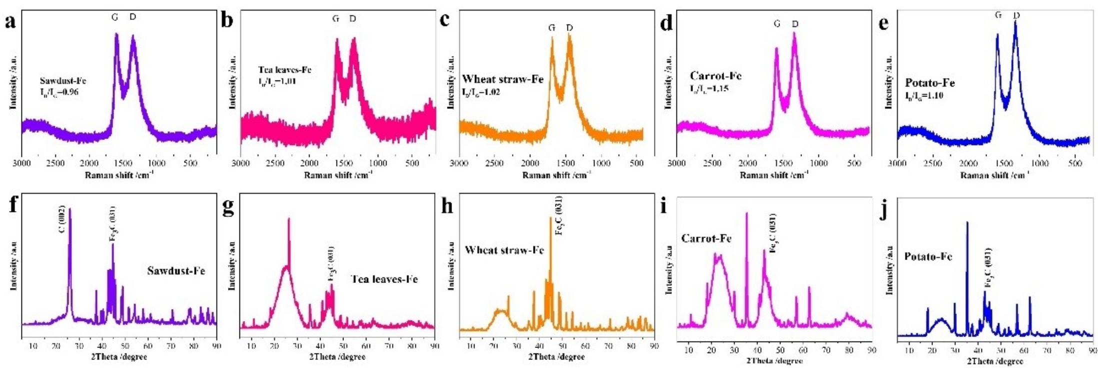

Fig. S5. Raman spectra (a–e) and XRD spectra (f–j) of the as-synthesized 2DFe/BC derived from sawdust, tea leaves, wheat straw, carrot, and potato, respectively.

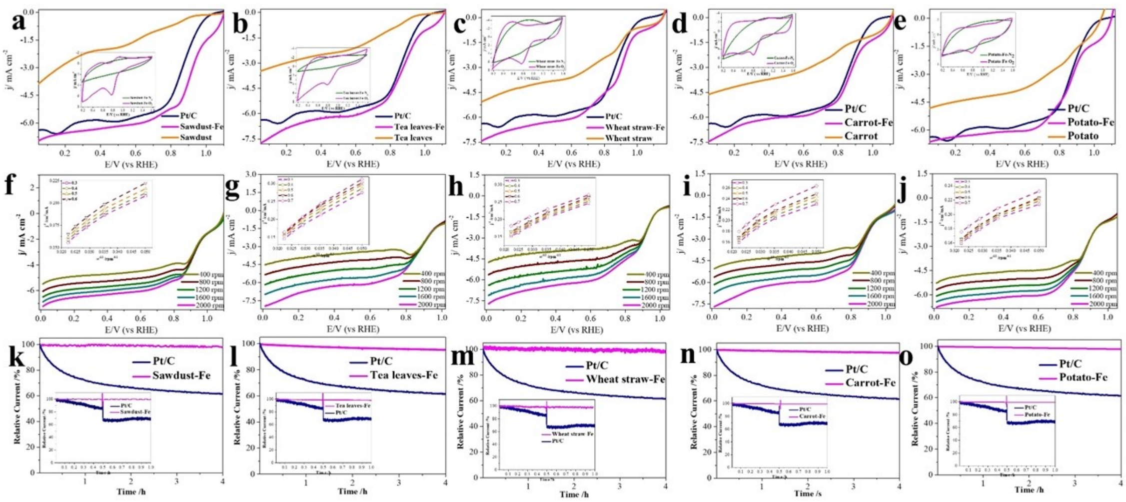

Fig. S6 (a–e) Comparisons of the LSV polarization curves, (f–j) LSV polarization curves with different rotation speeds, and (k–o) chronoamperometric responses at a rotation rate of 2000 rpm in O_2-saturated 0.1 M KOH solutions, with the insets showing the CV curves, the K-L plots, and the methanol crossover effect of the as-synthesized sawdust-, tea leaf- wheat straw-, carrot-, or potato-derived 2DFe/BCs, respectively.

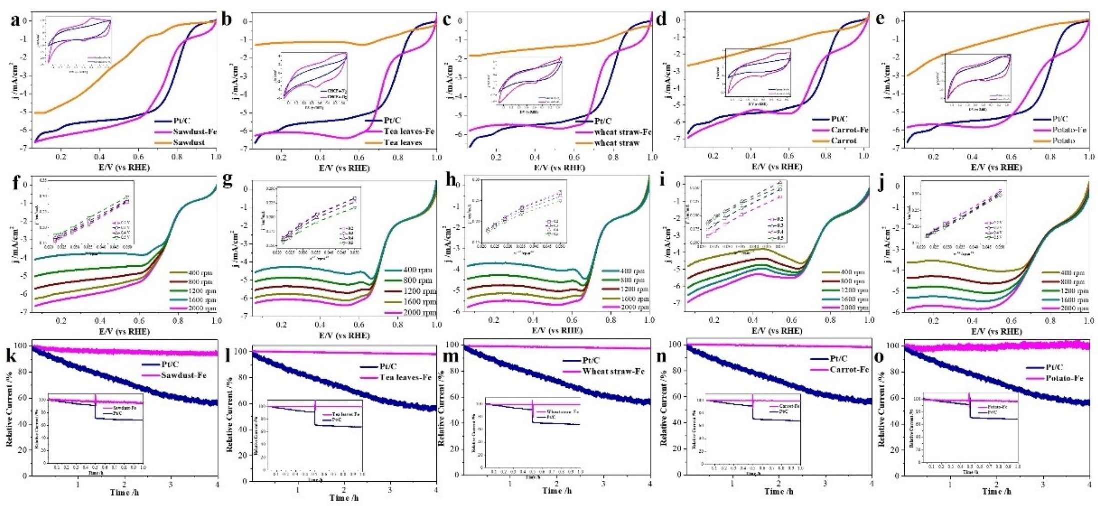

Fig. S7: (a–e) Comparisons of the LSV polarization curves, (f–j) LSV polarization curves with different rotation speeds, and (k–o) chronoamperometric responses at a rotation rate of 2000 rpm in O_2-saturated 0.5 M H_2SO_4 solutions, with the insets showing the CV curves, the K-L plots, and the methanol crossover effect of the as-synthesized sawdust-, tea leaf-, wheat straw-, carrot-, or potato-derived 2DFe/BC, respectively.

Table S1. Properties of the as-synthesized 2DFe/BCs

CHCFe	C	N	O	Fe
surface composition	78.25	1.57	14.64	5.54
bulk composition	72.12	2.27	16.42	7.81

Table S2. The ORR catalytic activities of the as-synthesized biomass derived 2DFe/BC in O_2-saturated 0.5 M H_2SO_4 solutions

	coconut husk	sawdust	tea leaves	wheat straw	carrot	potato	Pt/C
E_{onset}	0.99	0.99	0.99	0.99	1.02	1.00	0.95
I_{LCD}	5.90	5.93	6.40	5.67	5.49	5.83	5.49
n	3.83-3.85	3.78-3.81	3.74-3.91	3.89-3.96	3.71-3.85	3.90-3.93	

Table S3. Comparison of the synthesis catalytic activity of different catalysts

Starting materials	Synthesis process	Catalyst	Characteristics	Electrolyte		Reference
				0.1M KOH	Acidic media	
Biomass, biowaste	solvent-free shear mixed with $FeCl_3 \cdot 6H_2O$, 900 ^oC for 2 h in N_2	Fe-embedded graphene-like 2D composite materials	**universal, scalable, solvent-free**	comparable with Pt/C	close activities to Pt/C	**This work**
Reed stalk	cut into small pieces, washed with DI water, dried in oven at 80 °C for 2 days, pre-carbonized at 800 °C for 1 h under Ar flow, mixed with KOH (weight ratio of materials/KOH is 1:2, 1:6 and 1:10), heated in a homemade copper boat under Ar flow at 700 °C for 1 h, after KOH corrosion served as the carbon host for loading Fe and N in the next step preparation of Si-Fe/N/C catalysts…	Si-contained Fe/N/C catalyst	KOH activation and carbonization, long treatment times, water-consuming steps	comparable with Pt/C	unknown	*Applied Catal. B: Environ.* 2018, 237, 85-93.

coconut shell	mixed with $ZnCl_2$ in ferric trichloride ($FeCl_3$) solution, stirred at 80 °C for 2 h and dried at 100 °C , annealing in N_2 atmosphere 900 °C for 1 h, treated in 2 M hydrochloric acid thoroughly and dried at 60 °C for 12 h	porous graphene-like nanosheets	toxic $ZnCl_2$ activation and carbonization	-	-	*J. Mater. Chem. A* 2013,1, 6462-6470
taro stems	cut, washed by ethanol and water, dried out overnight, mixed with potassium hydroxide (mass ratio = 1:4), heated to 800 °C in Ar for 2 h, immersed in 2 M HCl for 12 h, repeatedly washed by distilled water until pH = 7, freeze-dried, grinded with melamine (mass ratio = 1:5), pyrolyzed at 800 °C with a flow of argon for 1 h	biomass-derived 3D nitrogen-doped porous carbon	KOH activation and carbonization, long treatment times, water-consuming steps	comparable with Pt/C	unknown	*Appl. Surf. Sci.* 2019, 465, 303-312.

water lettuces	washed with DI-water and freeze drying for 24 h, initial carbonization of WLs under N_2 atmosphere at a relatively low temperature of 500 °C, then annealing in NH_3 atmosphere at different temperatures (700, 800, and 900 °C), followed by washing with an aqueous solution of 2.0 M HCl.	N-doped porous carbon nanosheets with three dimensional hierarchical porous structures	pre-carbonized, annealing in NH_3 atmosphere	comparable with Pt/C	close activities to Pt/C	*Nano Energy* 2018, 49, 393-402.
Medulla stachyuri	cut, immersed into ammonium ferric citrate solution (ethanol/water = 4/5, v/v), dried for 12 h, pyrolyzed at 800-1000 °C for 2 h under N_2 flow, preleached with 0.5 M H_2SO_4 at 80 °C for 24 h, washing to neutral and drying, heat-treated under the same conditions for 1 h for a second time	iron and nitrogen co-doped 2D porous carbon-flakes	long treatment times, water-consuming steps	comparable with Pt/C	unknown	*Int. J.Hydrogen Energ.*2019, 44, 21726-21737.

Biomass, biowaste	Glucose, $[ZnCO_3]_2 \cdot [Zn(OH)_2]_3$ and urea were mixed in mortar and ground, heated at 900 °C for 2 h in N_2 flow, immersed in 2 mol L^{-1} HCl solution for 18 h, washed by high purity water repeatedly until pH = 7, dried at 40 °C for 24 h.	hierarchically porous carbon materials with homogeneous fluffy morphology	universal approach, basic zinc carbonate as solo porogen with two pore-creating mechanisms	comparable with Pt/C	unknown	*Nano Energy* 2019, 62, 628-637.
Biomass, biowaste	Glucose, urea, $Mg_5(OH)_2(CO_3)_4$ and $ZnCl_2$ are mixed and ground, pyrolyzed at 900 °C for 2 h under N_2 atmosphere, immersed in 2.0 M HCl solution for 18 h, washed with water several times and dried at 40 °C overnight.	biomass-derived hierarchically porous heteroatom-doped carbon materials	toxic $ZnCl_2$ activation and carbonization, dual-templating strategy	comparable with Pt/C	unknown	*Energy Environ. Sci.* 2019, 12, 648-655.
Guanine	pre-carbonized at 550 °C for 2 h, mixing with $ZnCl_2$, activation at 600 °C for 2 h and further carbonization at 1000 °C for 4 h in N_2 atmosphere	pyridinic-N dominated porous carbon nanosheets	pre-carbonized, toxic $ZnCl_2$ activation and carbonization	comparable with Pt/C	close activities to Pt/C	*Carbon* 2020, 156, 179-186.

Guanine, fructose, sodium oleate, P123	dispersed in water, kept at 180 °C for 8 h, collected by filtration, washed several times and dried at 60 °C under vacuum for 8 h, further carbonization at 1000 °C for 2 h in a N_2 atmosphere	2D morphology of crystalline carbons	long treatment times, water-consuming steps	comparable with Pt/C	lower than Pt/C	*J. Mater. Chem. A* 2017, 5, 23481-23488.
Guanine, ferric nitrate nonahydrate	guanine and ferric nitrate nonahydrate dispersed into deionized water and stirred to dry at room temperature, and pyrolyzed at 1000 °C under continuous N_2 flow	nitrogen-doped carbon nanosheets containing highly dispersed single iron atoms	stirred to dry at room and pyrolyzed at 1000 °C	comparable with Pt/C	unknown	*J. Power Source* 2019, 412, 125-133.
ginkgo leaves	heated at 60 °C, ground into uniform powde, annealed in a tube furnace at 1100 °C for 5 h under Ar flow, washed in 3 M HCl, distilled water, and ethanol, and then warmed at 60 °C,	nitrogen-doped porous carbon nanosheets	annealed under Ar flow, and then thermally treated under flowing NH_3	comparable with Pt/C	unknown	*J. Power Sources* 2014, 272, 8-15.

	further thermally treated under flowing NH_3 (80 sccm) at 1000 °C for 1 h					
Typha orientalis	hydrothermal 180 °C for 12 h, immersed into distilled water several times, freeze drying for 24 h, annealed in NH_3 atmosphere at 800 °C for 2 h	N-doped carbon nanosheets	hydrothermal 12 h and annealed in NH_3	comparable with Pt/C	lower than Pt/C	*Energy Environ. Sci*. 2014,7, 4095-4103.
Guanine	Guanine was mixed with aqueous SiO_2 nanoparticles, sonication and continuing stirring until completely drying, carbonization at 1000 °C for 4 h in N_2 atmosphere, etched by 10% HF solution twice, drying overnight at 100 °C	graphene-like carbon framework composed of three-dimensionally interconnected nanosheets	sonication and stirring until completely drying, etched by 10% HF solution twice	comparable with Pt/C	lower than Pt/C	*ChemNanoMat* 2019, 5, 682-689.
Prussian blue	750-1050 ^{o}C for 2 h, HCl washed for overnight followed by washing with Millipore water/ethanol several times and dried at 80 0C	Fe/Fe_3C nanoparticle encapsulated N-doped graphitic	long treatment times, water-consuming steps	comparable with Pt/C	unknown	*Green Chem*. 2016, 18, 427-432.

carbon nanotube, graphene	modified Hummers' method, 900 °C annealed in 2 torr of 10% NH_3/argon at for 30 min…	carbon nanotube–graphene complexes	long treatment times, water-consuming steps	comparable with Pt/C	comparable with Pt/C	*Nature Nanotech*. 2012, 7, 394-400.
$La(NO_3)_3\cdot 6H_2O$, $Sr(NO_3)_2$, $Co(NO_3)_2\cdot 6H_2O$ and $Fe(NO_3)_3\cdot 9H_2O$ in H_2O, C_2H_5OH and DMF, PVP, graphene oxide	Synthesis of $La_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_3$ catalyst, Synthesis of N-doped reduced graphene oxide	$La_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_3$ combined with N-doped reduced graphene oxide	long treatment times, water-consuming steps	comparable with Pt/C	unknown	*Nano Energy* 2014, 10, 192–200