

## Supporting Information

### **Bottom-up synthesis of nitrogen-doped nanocarbons by a combination of metal catalysis and solution plasma process**

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#### **General information**

ESR spectra were measured by JEOL JES-X310. XPS spectra were measured by JEOL JPS-9030 with pass energy 20 eV, survey and narrow respectively. We used the Gauss-Lorentz mixing ratio of 0.7, following the previous research to deconvolute the XPS N1s spectra. The morphology of carbon were measured by transmission electron microscopy (TEM) JEOL JEM-2100F, while the functional groups on the surface of prepared carbon were recorded by Fourier transform infrared spectrometer (FT-IR SHIMADZU IR Tracer 100), the sample for FT-IR were dried and mix with KBr, and then pressed up to 1.3 mm-diameter pellets. Raman spectra were measured by JAIMA NRS-3100. At first, the background was subtracted using a line connecting the first point (1100 cm<sup>-1</sup>) to the last point (1900 cm<sup>-1</sup>), and then ID/IG is calculated from the heights of D peak and G peak. BET was measured by BEL JAPAN - BELSORP mini II.

#### **Experimental method**

A Pekuris MPP04-A4-200 high-voltage bipolar pulse generator was used to apply a 2.8 kV bipolar high-voltage pulse to the tungsten electrode. Bipolar pulse power supply was connected to generate an SP with a pulse width of 1 μs and a pulse frequency of 26 kHz. 40 mL cyclohexane and 8 mL raw material were used as the precursors for the synthesis with Pd catalyst. In order to maintain the stability of the experimental conditions, we used cooling water so that the reaction solution can be kept at room temperature. The nanocarbon products were collected by filtration, washed with organic solvents and water three times respectively to remove soluble compounds. Finally, the nanocarbon product was obtained after drying under vacuum.

#### **Preparation of C1**

Tungsten electrodes wrapped with insulating ceramic tubes were inserted on both sides of the glass reactor, and the interval was set at 1 mm. Cyclohexane 40 mL and pyridine 8 mL were added to the vessel, and a bipolar pulse power supply was connected to

generate a plasma in the solution at a pulse width of 1  $\mu$ s and a pulse frequency of 26 kHz. After discharging for 5 min with stirring, the product was filtered off to obtain C1. Then, C1 was washed by 10 mL of benzene, cyclohexane, acetone, and water three times respectively to remove soluble compounds, and dried in vacuo at 60 °C for 15 h.

### **Preparation of C2**

Tungsten electrodes wrapped with insulating ceramic tubes were inserted on both sides of the glass reactor, and the interval was set at 1 mm. Cyclohexane 40 mL, pyridine 8 mL and Pd (acac)<sub>2</sub> 0.1 mmol were added to the vessel, and a bipolar pulse power supply was connected to generate a plasma in the solution at a pulse width of 1  $\mu$ s and a pulse frequency of 26 kHz. After discharging for 5 min with stirring, the product was filtered off to obtain C2. Then, C2 was washed by 10 mL of benzene, cyclohexane, acetone, and water three times respectively to remove soluble compounds, and dried in vacuo at 60 °C for 15 h.

### **Preparation of C3**

Tungsten electrodes wrapped with insulating ceramic tubes were inserted on both sides of the glass reactor, and the interval was set at 1 mm. Cyclohexane 40 mL, pyridine 8 mL and Pd (OAc)<sub>2</sub> 0.3 mmol were added to the vessel, and a bipolar pulse power supply was connected to generate a plasma in the solution at a pulse width of 1  $\mu$ s and a pulse frequency of 26 kHz. After discharging for 5 min with stirring, the product was filtered off to obtain C3. Then, C3 was washed by 10 mL of benzene, cyclohexane, acetone, and water three times respectively to remove soluble compounds, and dried in vacuo at 60 °C for 15 h.

### **Preparation of C4**

Tungsten electrodes wrapped with insulating ceramic tubes were inserted on both sides of the glass reactor, and the interval was set at 1 mm. Cyclohexane 40 mL, pyridine 8 mL and Pd (OAc)<sub>2</sub> 0.5 mmol were added to the vessel, and a bipolar pulse power supply was connected to generate a plasma in the solution at a pulse width of 1  $\mu$ s and a pulse frequency of 26 kHz. After discharging for 5 min with stirring, the product was filtered off to obtain C4. Then, C4 was washed by 10 mL of benzene, cyclohexane, acetone, and water three times respectively to remove soluble compounds, and dried in vacuo at 60 °C for 15 h.

### **Typical procedure for Table 2**

Tungsten electrodes wrapped with insulating ceramic tubes were inserted on both sides of the glass reactor, and the interval was set at 1 mm. Cyclohexane 40 mL, benzene 8 mL and catalyst 0.5 mmol were added to the vessel, and a bipolar pulse power supply was connected to generate a plasma in the solution at a pulse width of 1  $\mu$ s and a pulse frequency of 26 kHz. After discharging for 5 min with stirring, the product was filtered off to obtain carbon. The obtained solution was transferred into a flask to remove the solvent by rotary evaporation. After dried in vacuo at 60 °C for 15 h, the product mass was calculated by subtracting the mass of the empty cake.

### **Preparation of the electrodes for the ORR tests**

All catalysts were prepared by mixing 2.2 mg of the catalyst in a solution containing 2.2 mL of IPA, 3.8 mL of H<sub>2</sub>O, and 20  $\mu$ L 5% Nafion solution, followed by ultrasonication for 1 h to form homogenous catalyst inks. Then 10  $\mu$ L of the catalyst was dropped to a glassy carbon rotating disk electrode. Linear sweep voltammetry at a rotation rate of 1600 rpm and a scan rate of 10 mV/s.

### **Catalytic reaction**

25 mL of screw-capped glass reactor was charged with catalyst (20 mg), iodobenzene (0.4 mmol), <sup>t</sup>BuOK (1.2 mmol) and benzene (4 mL). The reaction mixture was then stirred at 120 C for 24 h. After completion of the reaction, the mixture was cooled to room temperature and the catalyst was removed by filtration. To analyze the product yield by GC, 0.4 mmol of dodecane was added as an internal standard.

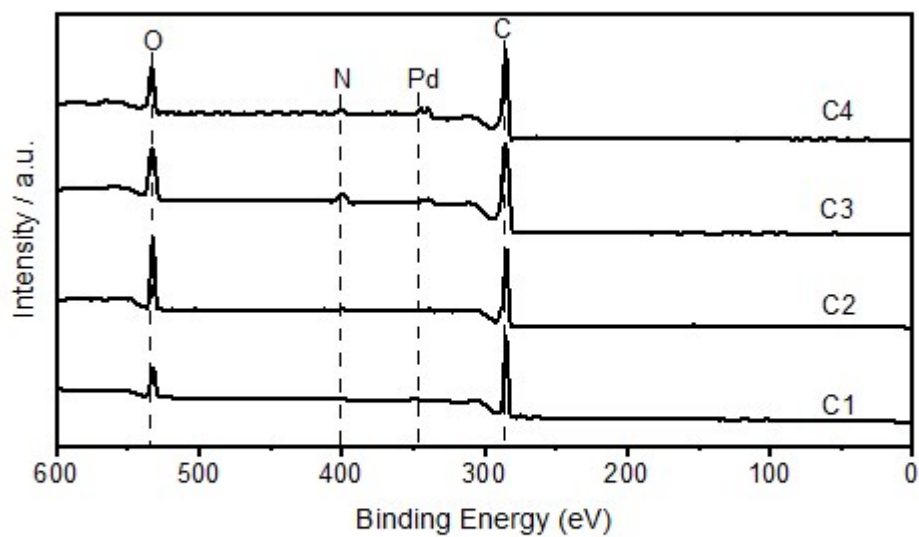
## Additional Figures and Tables.

**Table S1.** Comparison of nanocarbon production methods.

Nanocarbon production method		Controllability	Productivity
Top-down	Ball milling	Poor	Good
	LPE	Poor	Good
Bottom-up	Organic synthesis	Perfect	Low
	CVD	Fair	Fair
	SP	Poor	Good
	<i>This method (MCSP)</i>	<i>Good</i>	<i>Good</i>

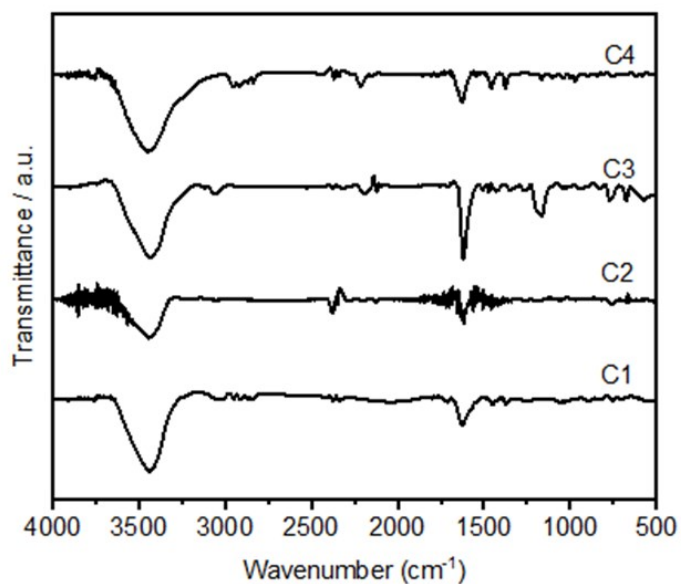
## Additional structure analysis

### a. XPS for C1-C4



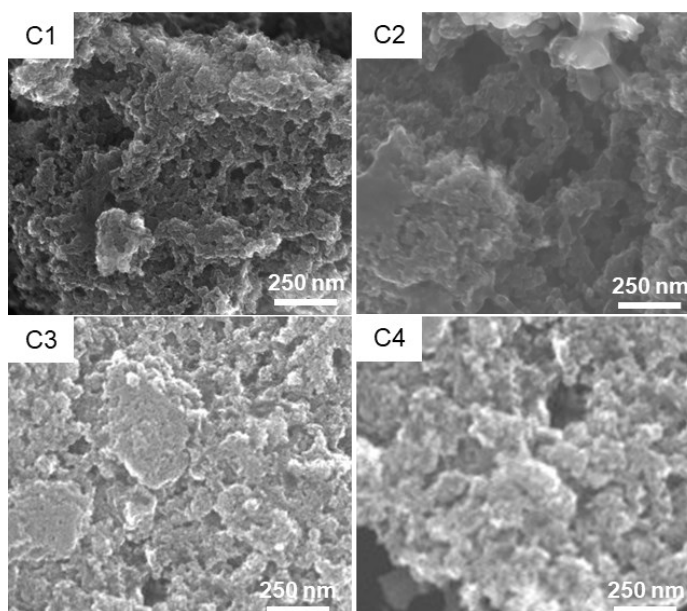
**Figure S1.** XPS survey analysis of C1-C4.

### b. FT-IR



**Figure S2.** IR analysis of C1-C4. Due to the blackness of the samples, FT-IR analyses did not provide any evidence for the present functional groups.

### c. SEM



**Figure S3.** SEM images of C1-C4.

#### d. BET

Table S2. BET surface area values.

entry	BET SA	Micropore volume	Pore diameter
C1	32.7 m <sup>2</sup> /g	0.33 cm <sup>3</sup> /g	40.5 nm
C4	8.7 m <sup>2</sup> /g	0.05 cm <sup>3</sup> /g	20.9 nm
C4-500	196 m <sup>2</sup> /g	0.82 cm <sup>3</sup> /g	16.7 nm

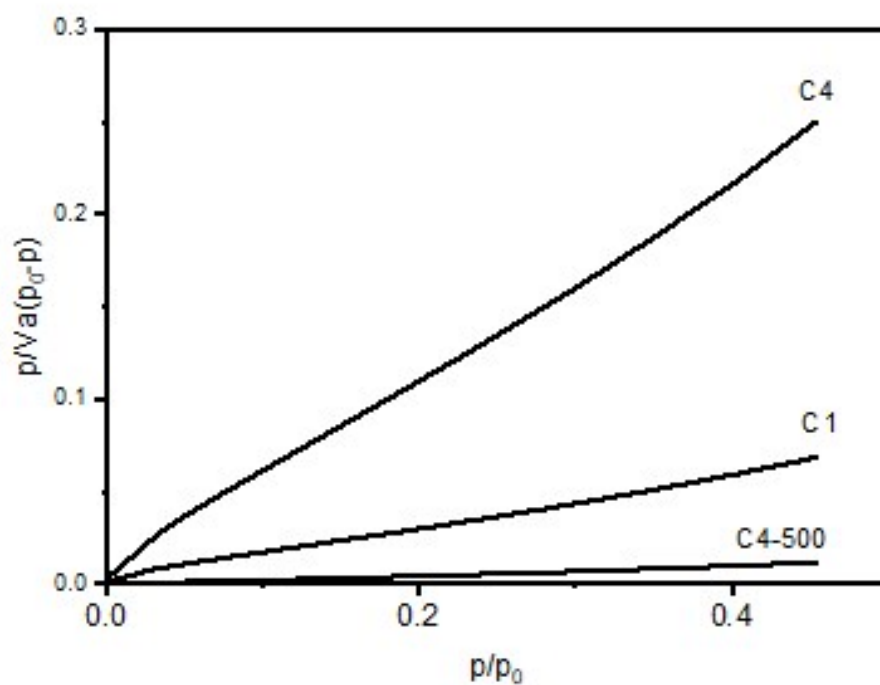
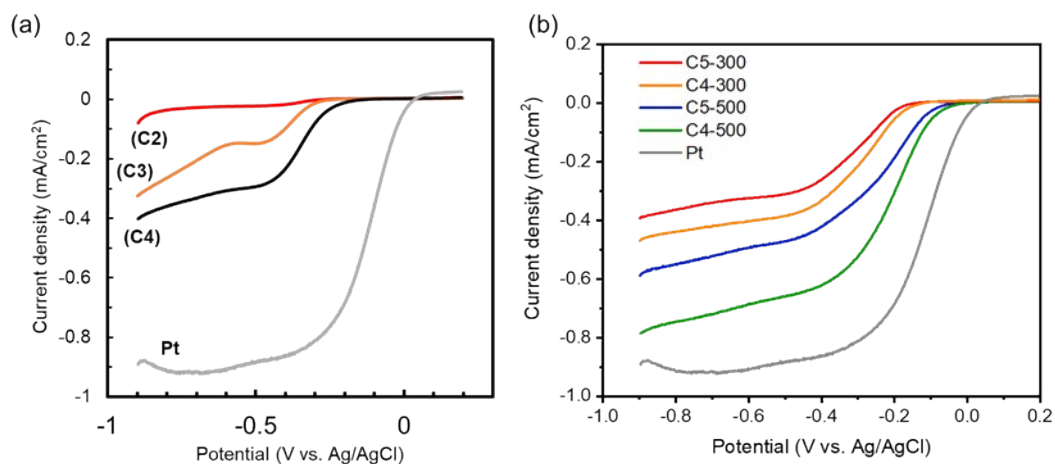


Figure S4. BET-Plot analysis.

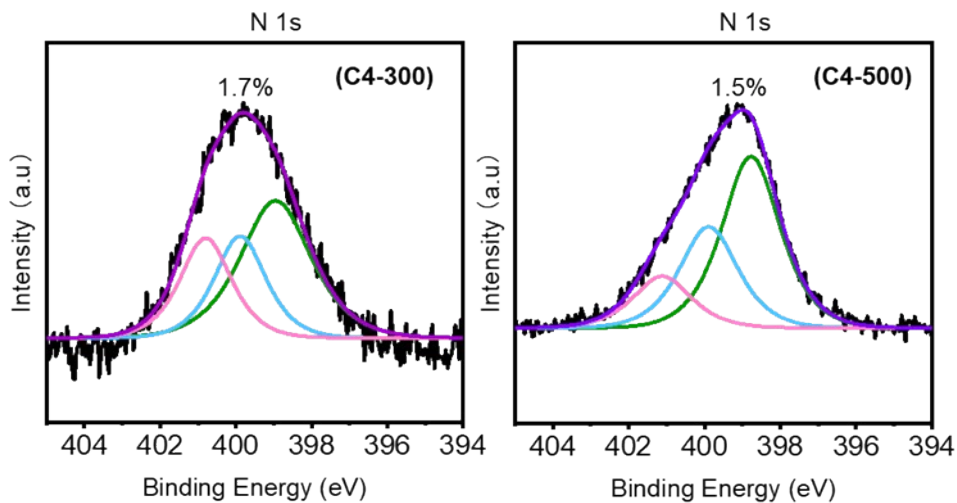
## ORR application of C4



**Figure S5.** ORR polarization curves of (a) as-prepared and (b) heat-treated catalysts in 0.1 M KOH, linear sweep voltammetry at a rotation rate of 1600 rpm, and a scan rate of 10 mV s<sup>-1</sup>.

## Effect of thermal treatment of C4

### a. XPS before and after thermal treatment



**Figure S6.** XPS N1s spectra of C4-500.

**Table S3.** XPS deconvolution analysis of C4-500.

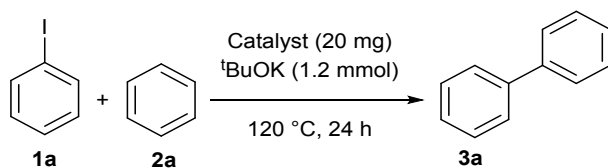
Nanocarbon	Chemical state of nitrogen (at%) <sup>a</sup>		
	Pyridinic (i)	Pyrrolic (ii)	Graphitic (iii)
<b>C4-300</b>	39.8	32.3	27.9
<b>C4-500</b>	52.8	31.2	16.0

### C-H activation application of C4

We have discovered carbon can catalyze organic reactions<sup>1</sup>.

To investigate the function of C4, we performed catalytic C-C bond formation. As a result, C4 showed better performance than conventional graphene derivatives, such as GO and rGO.

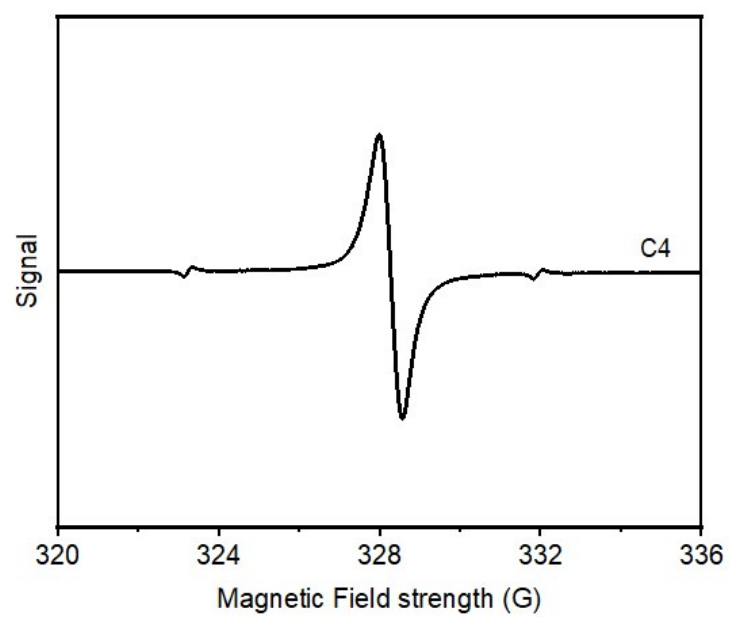
**Table S4.** Coupling reaction results<sup>[a]</sup>.



Entry	Catalyst	Yield % <sup>[b]</sup>
<b>1</b>	None	9
<b>2</b>	GO	35
<b>3</b>	rGO	44
<b>5</b>	C4	67

<sup>a</sup>) Reaction conditions: **1a** (0.4 mmol), **2a** (4 mL), catalyst (20 mg), <sup>t</sup>BuOK (1.2 mmol) 120 °C, 24 hours.; <sup>b</sup>) Yields were determined by GC using dodecane as an internal standard.;





**Figure S7.** ESR spectra C4.

#### Reference

- 1 M. Sohail Ahmad, H. Suzuki, C. Wang, M. Zhao and Y. Nishina, *J. Catal.*, 2018, **365**, 344–350.