Electronic Supplementary Information

Edge-Iodine/Sulfonic Acid-Functionalized Graphene Nanoplatelets as an Efficient Electrocatalyst for Oxygen Reduction Reaction

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Electrochemical Study: Electrochemical tests were performed using a computer-controlled potentiostat (1470E Cell Test System, Solartron Analytical, UK) with a standard three-electrode cell. Samples/glassy carbon electrodes were used as the working electrode, a platinum wire as the counter electrode, and an Ag/AgCl (saturated KCl) electrode as the reference electrode. Rotating disk electrode (RDE) experiments were carried out on a MSRX electrode rotator (Pine Instrument) and the 1470E potentiostat. For all CV and RDE measurements, an aqueous solution of KOH (0.1 M) was used as the electrolyte. N_2 or O_2 was used to purge the solution to achieve oxygen-free or oxygen-saturated electrolyte solution. Procedures for the pretreatment and modification of glassy carbon electrode are described as follows: the working electrode was polished with alumina slurry to obtain a clean surface and washed with deionized water and dried in air. Samples (2 mg) were dissolved in 1 mL solvent (N-methyl-2-pyrrolidone). The sample suspensions were pipetted as much as 10 μg on the glassy carbon electrode surface, followed by drying at room temperature and Nafion (0.05 wt%) stock solution (5 μL) in ethanol was coated on the surface of the catalyst layer to form a thin protective film. The detailed kinetic analysis was conducted according to Koutecky-Levich plots:

$$\frac{1}{j} = \frac{1}{j_k} + \frac{1}{B\omega^{0.5}} \qquad (1)$$

where j_k is the kinetic current and B is Levich slope which is given by:

$$B = 0.2nF(D_{O_2})^{2/3}v^{-1/6}C_{O_2} \quad (2)$$

Here n is the number of electron transfer in the reduction of one O_2 molecule. F is the Faraday constant (F = 96485C/mol of e), Do_2 is the diffusion coefficient of O_2 (Do_2 =1.9 x 10^{-5} cm^2 s^{-1}), v is the kinematics viscosity of KOH (v = 0.01cm^2s^{-1}) and Co_2 is the concentration of O_2 in the solution (Co_2 =1.2 x 10^{-6}mol cm^{-3}). The constant 0.2 is adopted when the rotation speed is expressed in rpm.

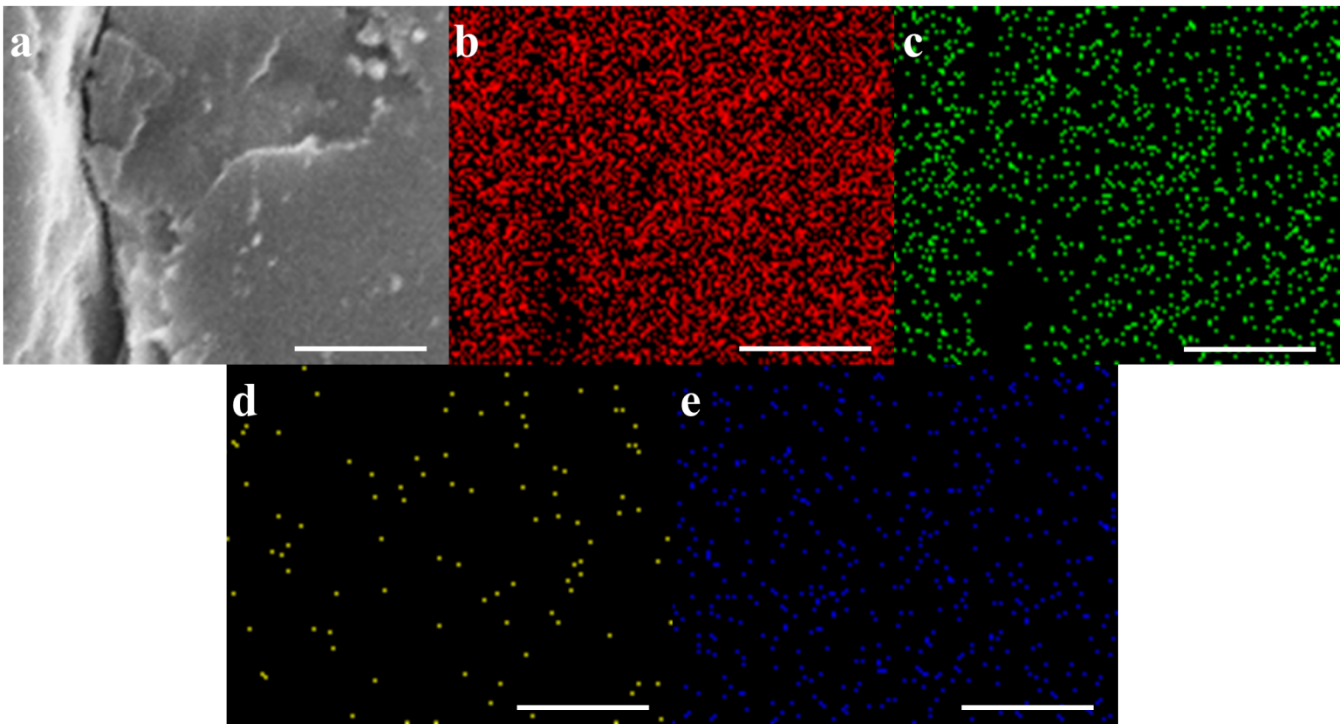

Figure S1. (a) FE-SEM image of ISGnP; (b) corresponding EDX element mappings: (b) carbon; (c) oxygen; (d) iodine; (c) sulphur. Scale bars are 250 nm.

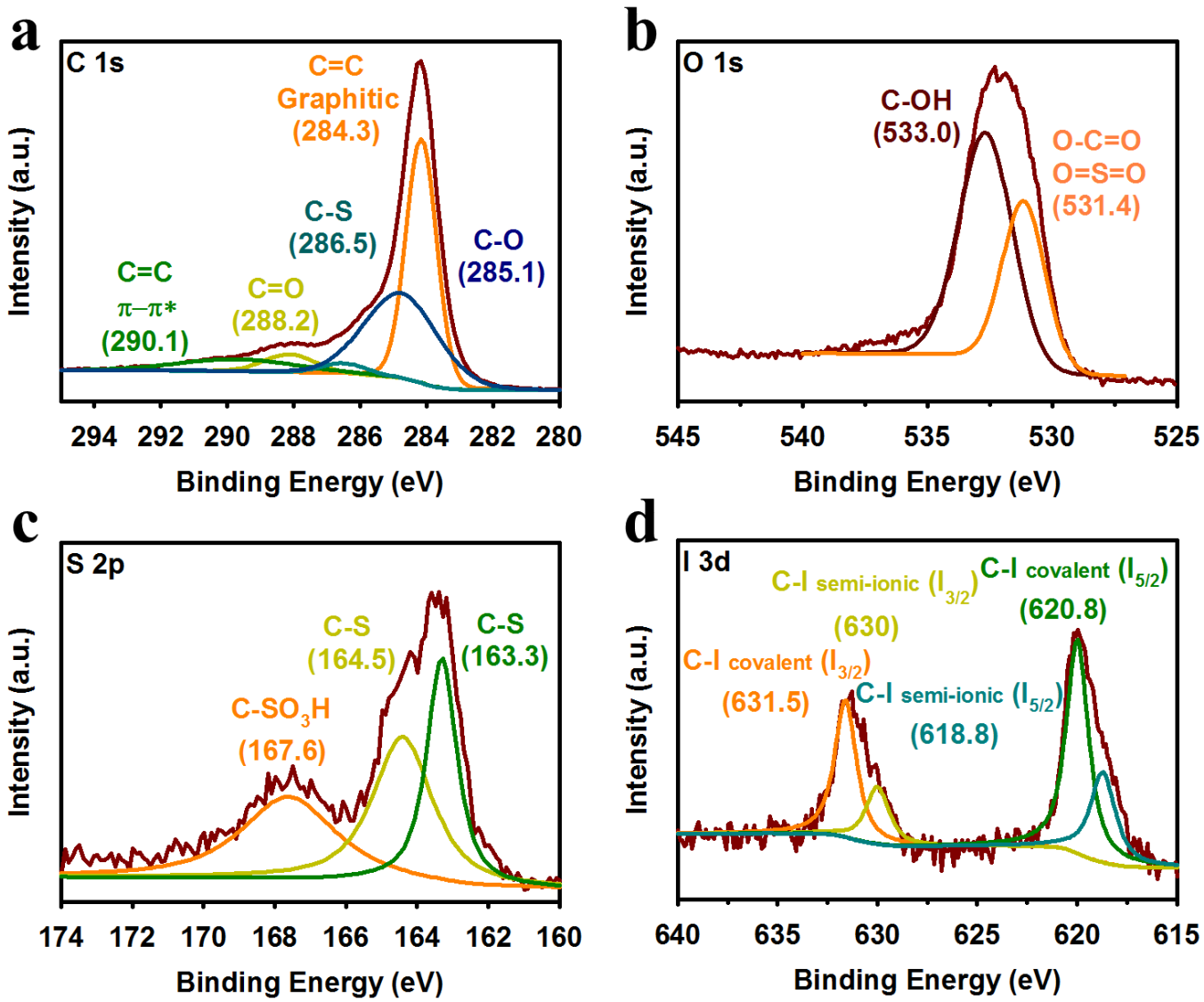

Figure S2. High-resolution XPS survey spectra of the ISGnP: (a) C 1s; (b) O 1s; (c) S 2p; (d) I 3d.

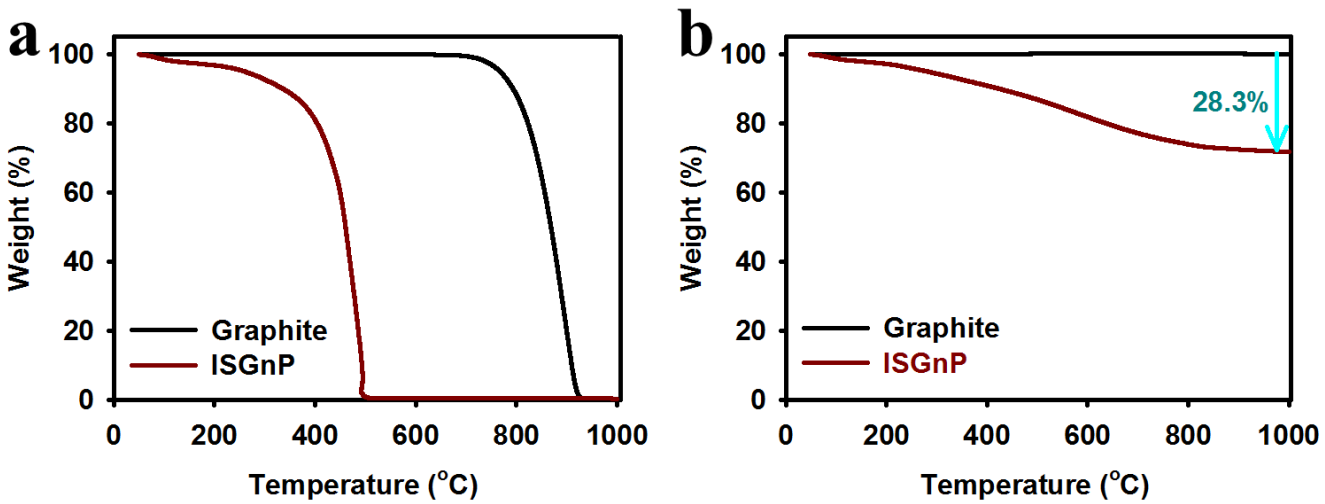

Figure S3. TGA thermograms obtained at the heating rate of 10 °C/min: (a) in air; (b) in nitrogen.

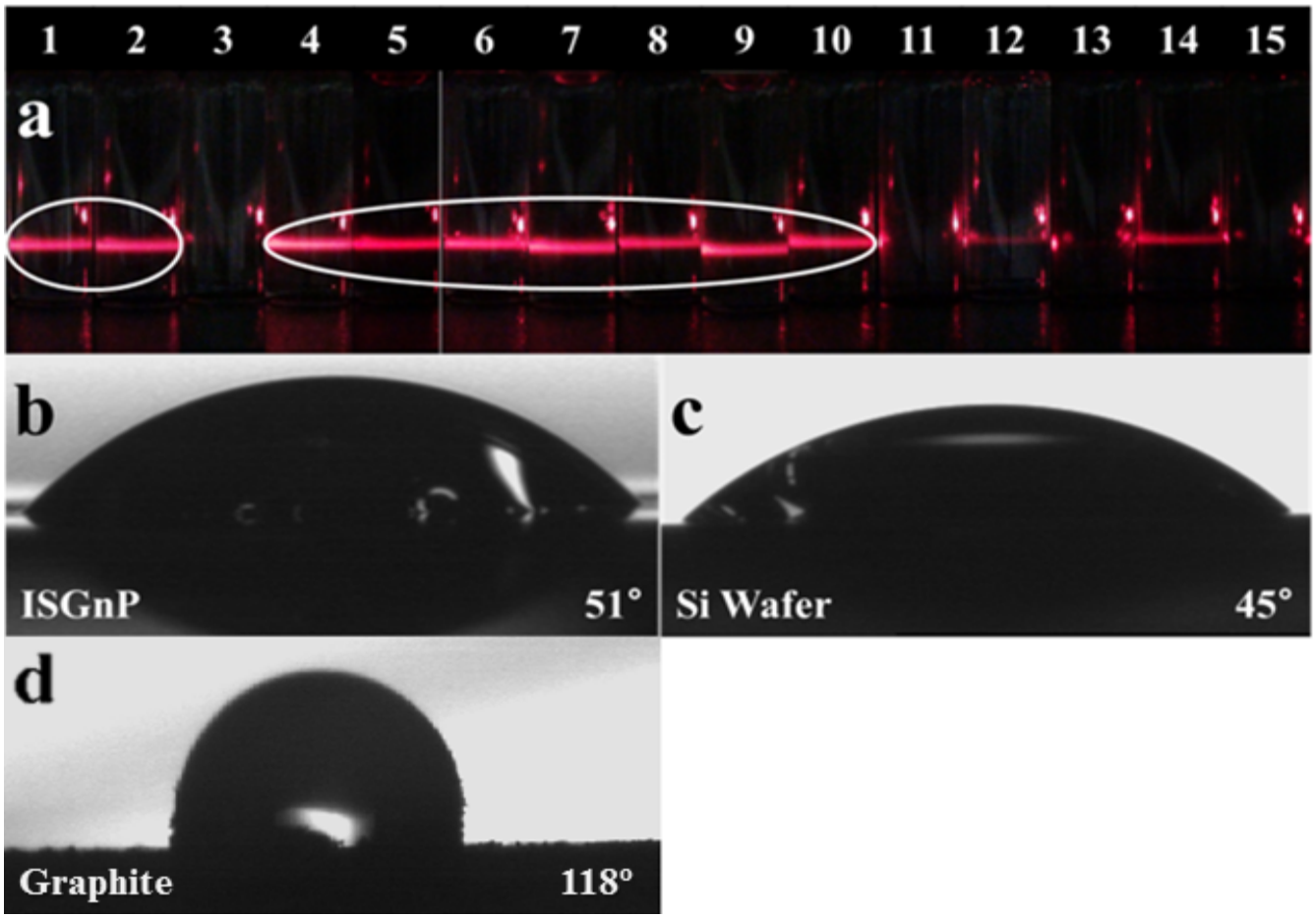

Figure S4. Photographs of ISGnP dispersed solutions in various solvents after one week standing on bench top in the normal laboratory condition: (a) (1) H2O; (2) 1M aq. NH4OH; (3) 1M aq. HCl; (4) MeOH; (5) EtOH; (6) ethyl acetate; (7) acetone; (8) DMAc; (9) DMF; (10) NMP; (11) toluene; (12) CH2Cl2; (13) hexane; (14) diethyl ether; (15) THF. Contact angles: (b) the surface of ISGnP coated on Si wafer; (c) the surface of Si wafer; (d) the surface of pristine graphite coated on Si wafer. The contact angle is an average value of ten measurements.

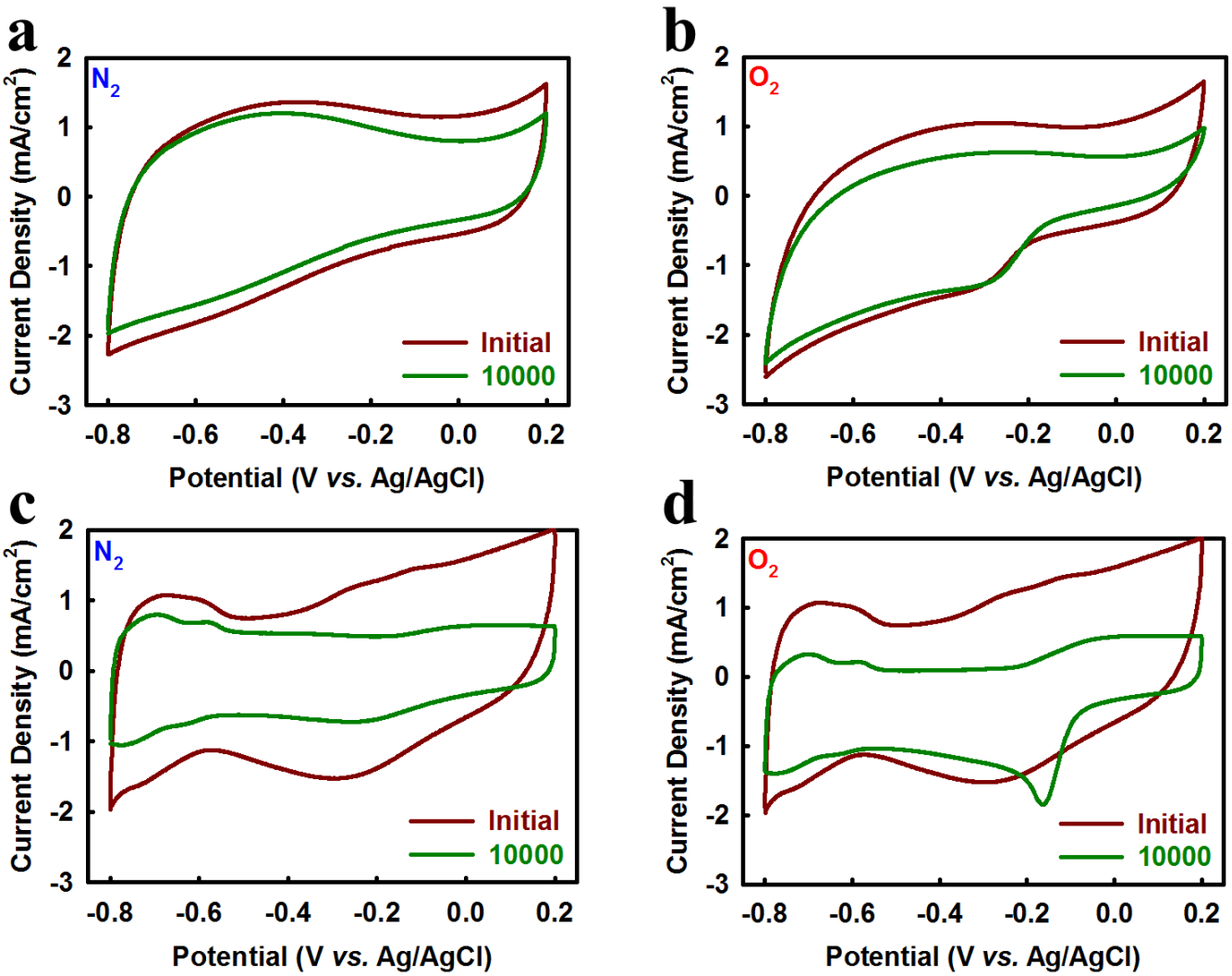

Figure S5. Comparison of cyclic voltammograms (CV) of samples on glassy carbon (GC) electrodes in 0.1 M aq. KOH solution with scan rate of 100 mV/s: (a) ISGnP in nitrogen-saturated condition; (b) ISGnP in oxygen-saturated condition; (c) Pt/C in nitrogen-saturated condition; (b) Pt/C in oxygen-saturated condition.

Table S1. TGA, EA, EDX, and XPS of the pristine graphite, IGnP and ISGnP

Sample	TGA char yield in N_2 (%)		Element	EA (wt.%)	EDX (at.%)	XPS (at.%)
	800 °C	1000 °C				
Graphite	99.7	99.1	C	99.64	98.80	98.35
			O	0.13	1.20	1.65
IGnP	75.8	74.6	C	75.79	92.79	88.30
			H	1.04	-	-
			O	10.52	6.31	11.08
			I	12.65*	0.89	0.62
ISGnP	73.4	71.7	C	74.52	81.69	83.55
			H	0.84	-	-
			O	17.37	16.20	13.17
			I	3.51*	0.51	0.16
			S	3.76	5.57	1.50

* Estimated values

Table S2. Zeta-potential of samples at different concentrations in NMP solution

Sample	Concentration (mg/mL)		
	0.4	0.5	0.6
IGnP	-38.7	-38.5	-34.8
ISGnP	-43.4	-45.4	-43.6

Table S3. The relationship between Zeta-potential and colloidal stability*

Zeta-potential (mV)	Stability behavior of the solid
From 0 to ±5	Rapid coagulation or flocculation
From ±10 to ±30	Incipient instability
From ±30 to ±40	Moderate stability
From ±40 to ±60	Good stability
More than ±61	Excellent stability

* http://en.wikipedia.org/wiki/Zeta_potential.

Table S4. The specific capacitance (F/g) obtained from average value of 100 cycles

Sample	Capacitance (F/g)	
	N_2	O_2
Pristine graphite	3.5	11.0
HGnP	6.69	34.7
ISGnP	108.8	153.5
Pt/C	90.1	104.2

Table S5. BET surface areas of samples

Sample	Surface area (m^2/g)	Pore volume (mL/g)	Pore size (nm)
Pristine graphite	2.78	0.0016	22.7
HGnP*	437	0.3909	35.8
ISGnP	6.03	0.0205	13.58

* Adapted from Jeon, et al., *J. Am. Chem. Soc.*, 2013, **135**, 1386-1393.

Table S6. The cycle retention after 10000 cycles in oxygen- and nitrogen-saturated 0.1M aq. KOH electrolyte at the scan rate of 100 mV/s

Sample	Retention after 10000 cycles (%)	
	N_2	O_2
Graphite	99.0	91.8
ISGnP	77.1	66.4
Pt/C	57.7	53.4

Table S7. The average number of electrons (n) transferred for oxygen reduction reaction at different potential for sample electrodes in oxygen-saturated 0.1M aq. KOH electrolyte

Sample	Potential (V)		
	-0.4	-0.5	-0.6
Graphite	1.7	1.7	2.0
ISGnP	2.8	3.3	4.0
Pt/C	3.9	4.0	4.0