

Supplementary Information

Low-temperature Rapid Synthesis of High-quality Pristine or Boron-doped Graphene via Wurtz-type Reductive Coupling Reaction

Xujie Lü,^{a,b} Jianjun Wu,^{a,b} Tianquan Lin,^{a,b} Fuqiang Huang,^{*a} Xiaoming Xie^c and Mianheng Jiang^c

^a CAS Key Laboratory of Materials for Energy Conversion, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, P.R. China;

^b Graduate School of the Chinese Academy of Sciences, Beijing 100049, P.R. China;

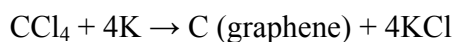
^c State Key Laboratory of Functional Materials for Informatics, Shanghai Institute of Microsystem and Information Technology, Chinese Academy of Sciences, Shanghai 200050, P.R. China

E-mail: huangfq@mail.sic.ac.cn

* To whom correspondence should be addressed. E-mail: huangfq@mail.sic.ac.cn Tel: +86-21-5241-1620,

Fax: +86-21-5241-6360

Estimate of Reaction Enthalpy. The reaction of graphene formation can be expressed as:



The molar enthalpy of reaction can be roughly estimated from the difference of molar enthalpy of formation between the products and reactants:

$$\Delta_r H_m = \Delta_f H_m(\text{C, graphene}) + 4\Delta_f H_m(\text{KCl}) - \Delta_f H_m(\text{CCl}_4, \text{gas}) - 4\Delta_f H_m(\text{K, liquid})$$

Whereas, the molar enthalpy of formation of graphene is still unknown. Herein, it was estimated to be 513 *kJ/mol* from the bond enthalpy of graphene.¹

Thus, using the thermodynamical data,² the molar enthalpy of reaction can be estimated as follows:

$$\Delta_r H_m = 513 + (-4 \times 436.7) - (-96.0) - 4 \times 2.3 = -1147 \text{ kJ/mol}$$

Therefore, the proposed reaction is a fiercely exothermic reaction. This contributes to the rapid preparation of graphene at low temperature in short time.

For the reaction of CCl_4 and Na, the molar enthalpy was calculated to be -1046 kJ/mol , lower (around 10%) than that of the reaction of CCl_4 and K.

Figures:

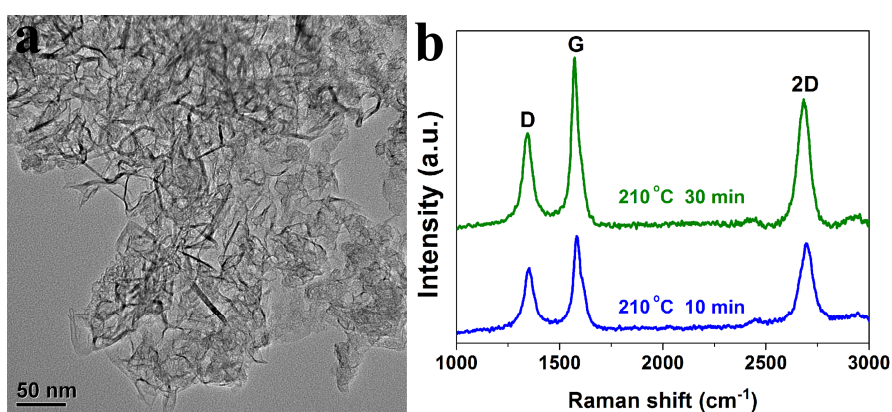


Fig. S1 (a) TEM image and (b) Raman spectrum of graphene nanosheets prepared in 10 min at 210 °C using near-stoichiometric CCl_4 (1.5 ml) and K (2.0 g), compared with the Raman spectrum of graphene prepared in 30 min as a reference.

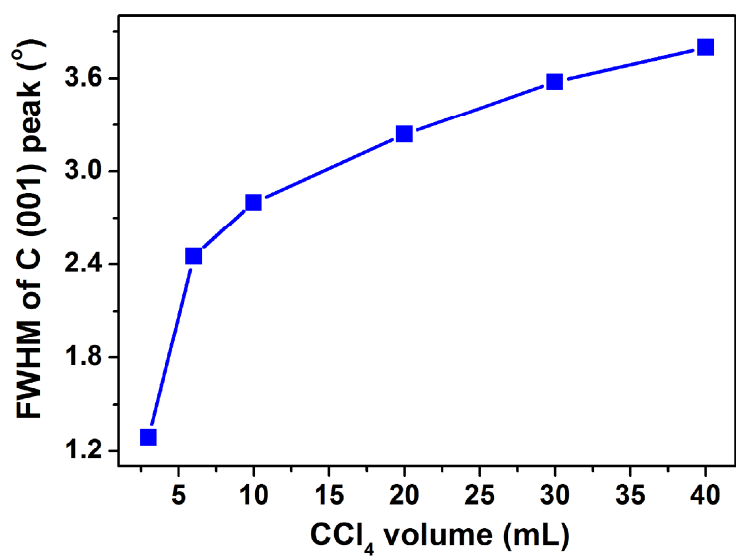


Fig. S2 The crystallinity (expressed as the FWHM of C (001) peak of XRD patterns) variation with the CCl₄ volume.

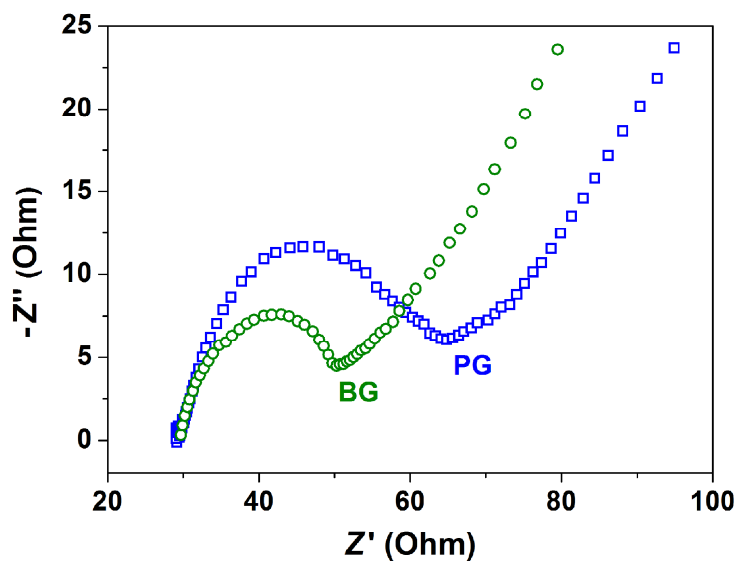


Fig. S3 The typical electrochemical Nyquist plots of pristine graphene (PG) and boron-doped graphene (BG) measured by electrochemical impedance spectra (EIS).

Table S1. Elemental abundances determined by XPS in PG and BG samples.

	C		BBr₃ volume (μL)	B		Cl Content (at. %)	O Content (at. %)
	Peak (eV)	Content (at. %)		Peak (eV)	Content (at. %)		
PG	284.7	89.92	/	/	/	2.60	7.18
BG	284.8	88.85	52	192.0	1.02	2.52	7.41
BG'	284.6	82.82	104	191.6	1.90	4.01	11.07
BG''	284.5	81.88	156	191.4	2.56	4.58	10.54

REFERENCES AND NOTES

1. Berry, Rice, Ross. Physical Chemistry, Part II. 1980; pp 564.
2. Barin I, Knacke O. Thermochemical Properties of Inorganic Substances. Berlin: Springer, 1973; Supplement, 1997.