中国工程物理研究院
CHINA ACADEMY OF ENGINEERING PHYSICS

Shock wave synthesis of graphene materials from carbonate/dry ice

Hao Yin[a]* (PHD, Engineer)
Qiuhua Du[a], Pengwan Chen[b]

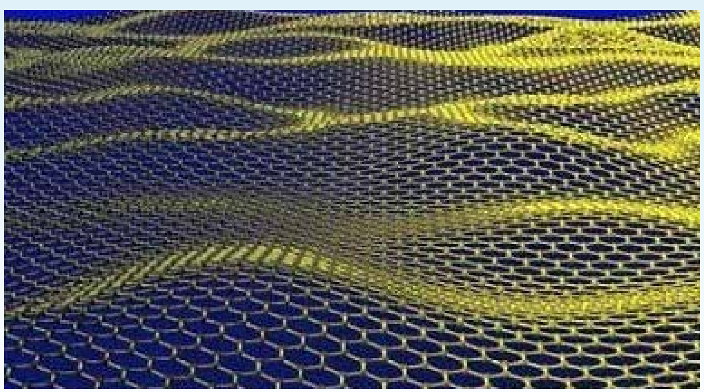
[a]Institute of Systems Engineering, China Academy of Engineering Physics, Mianyang 612900, Sichuan Province, China
[b]State Key Laboratory of Explosion Science and Technology, Beijing Institute of Technology, Beijing 100081, China
*E-mail:**412yinh@caep.cn**

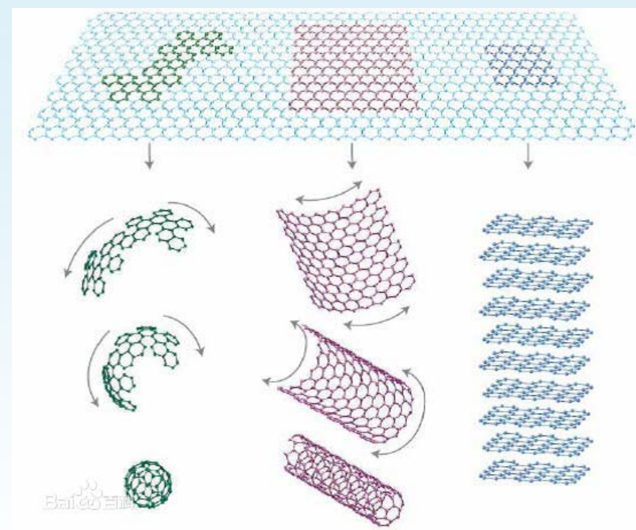
Outline

- Introduction
- Experiment
- Results and discussion
- Conclusions

Introduction-graphene

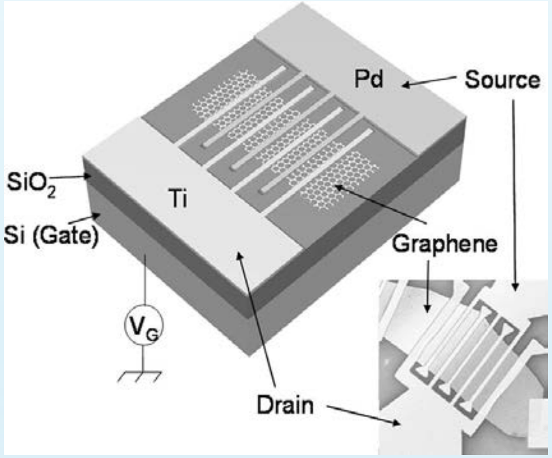
- Graphene is known as the thinnest materials: a two-dimensional structure of carbon atoms packed into a honeycomb lattice.
- It can be used as a basic building block to build other carbon materials: can be (1) folded into fullerenes, (2) rolled up into nanotubes, (3) stacked into graphite.
- Only one atom thick carbon material has attracted great interest due to its unique physical and chemical properties.





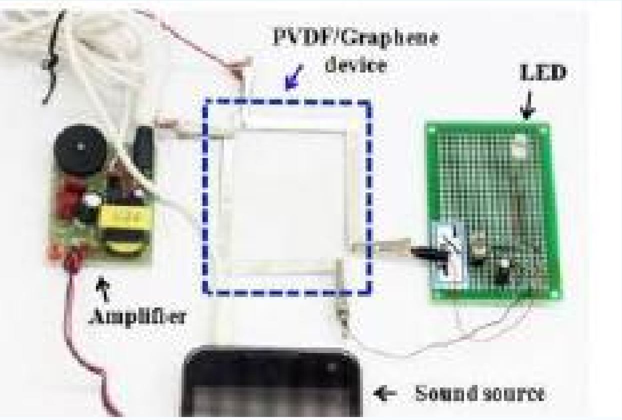
Introduction-graphene

Storage materials

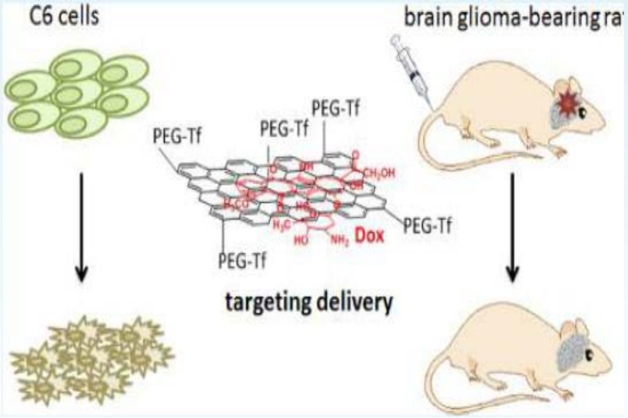


Sensor

Superhard materials

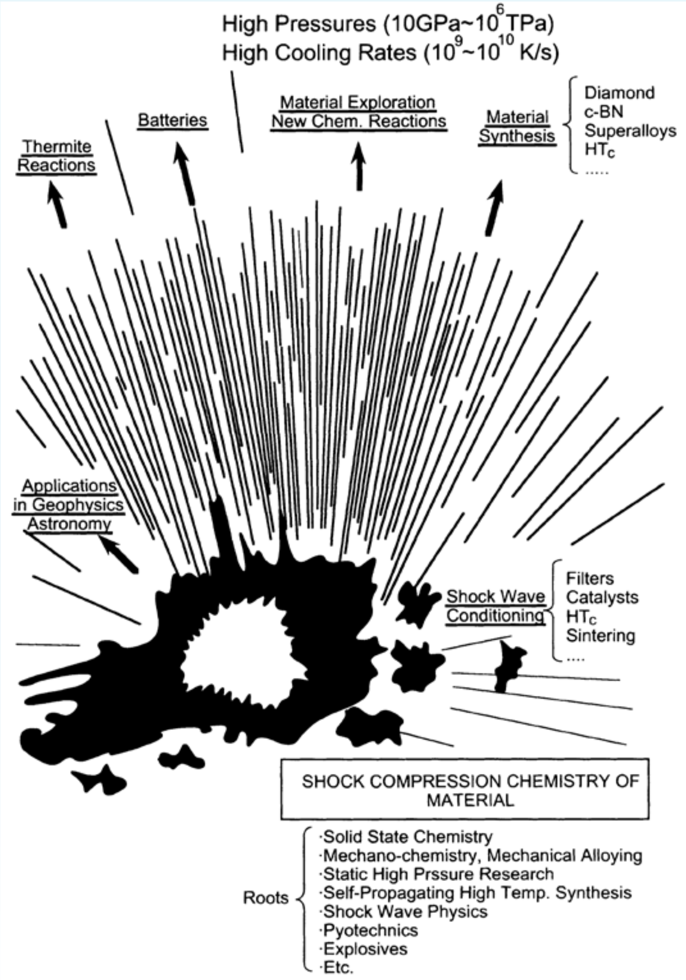


Electronic devices



Drug delivery

Introduction-shock wave



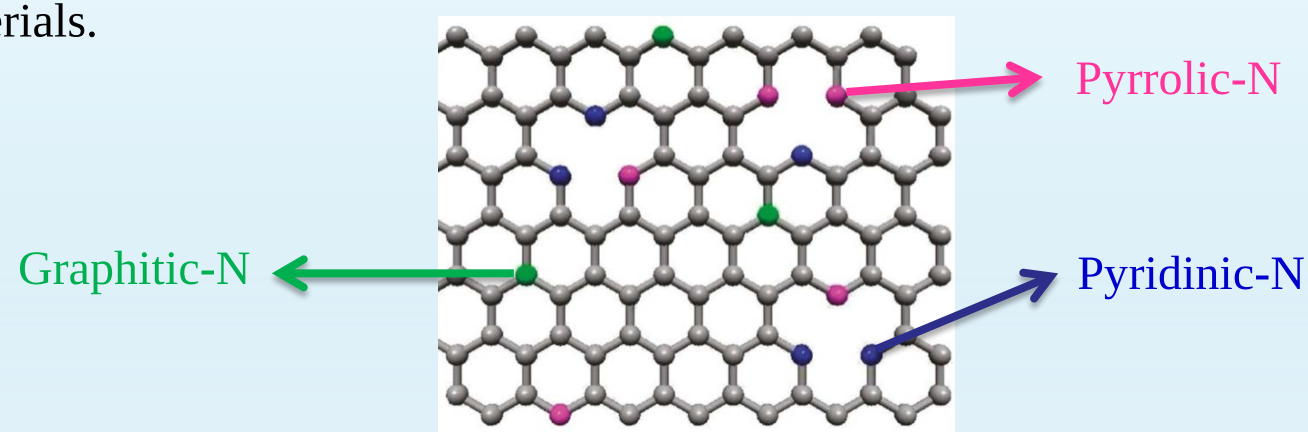
HP HT HCR

phase transition, synthesis and decomposition

uranology、geology、high pressure physics、mechanics

Introduction

- Nitrogen (N) has a comparable atomic size and five valence electrons for bonding with carbon atoms, and has been widely used for doping carbon materials.



- N-doped graphene (NG) exhibits a high metal-free electrocatalytic activity for the ORR in alkaline solution and better long-term operation stability than Pt-based electrodes(high cost, poor durability).

- Shock waves have been successfully used to produce various carbon-based materials. In this study, we present a new approach to synthesize graphene and NG using the shock wave method.

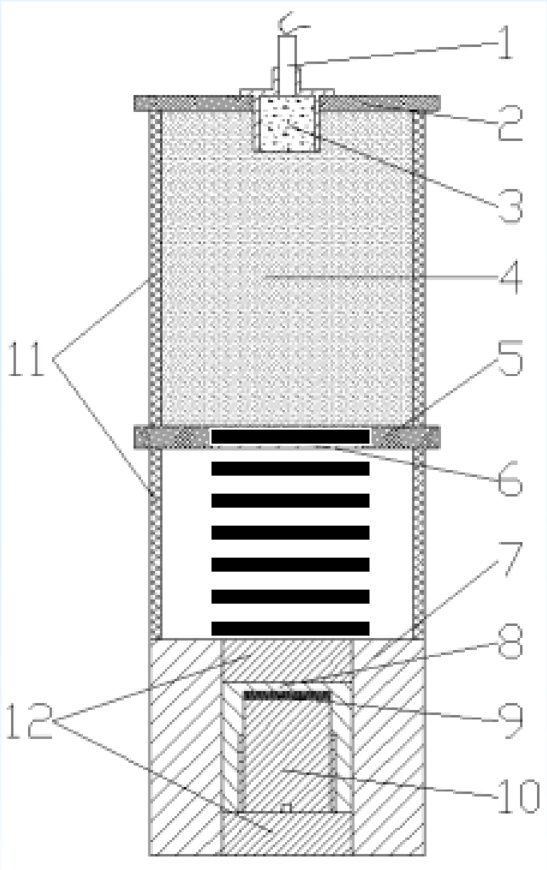
Experimental conditions

No	Carbon source	Reductant	Doping nitrogen resources
1[a]	carbonate ($CaCO_3$)	magnesium(Mg)	ammonium nitrate(NH_4NO_3)
2[b]	dry ice	calcium hydride (CaH_2)	

Shock loading experiments were carried out using the impact of detonation-driven of the main charge of nitromethane(NM)

a: Carbon,2015,94:928-935
b: Submitted

Shock-loading apparatus



Scheme of shock-loading apparatus

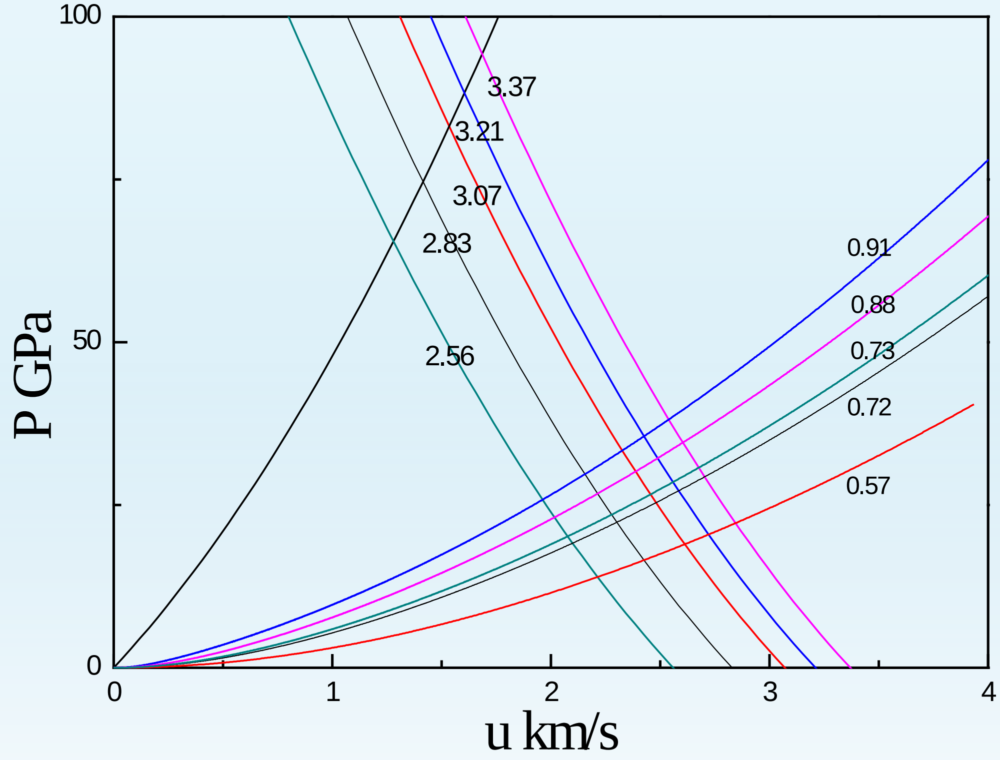
Experimental conditions

No	Samples[a]	Packing density	Porosity	Impact velocity (km/s)	Shock pressure (GPa)	Shock temperature (K)	Phase identified
1	A	1.72	0.72	2.83	22.3	2628	no carbon
2	A	1.35	0.57	3.37	22.1	5215	2-8graphene +nanotube+>10L
3	A	1.73	0.73	3.07	25.4	2968	2-8L graphene
4	A	2.10	0.88	3.21	32.0	1956	1-6L graphene
5	B	2.18	0.91	2.83	29.7	1438	1-4L NG

Sample A: $CaCO_3$(2g)+Mg(1g), Sample B:$CaCO_3$(2g)+Mg(1g)+NH_4NO_3(0.2g)

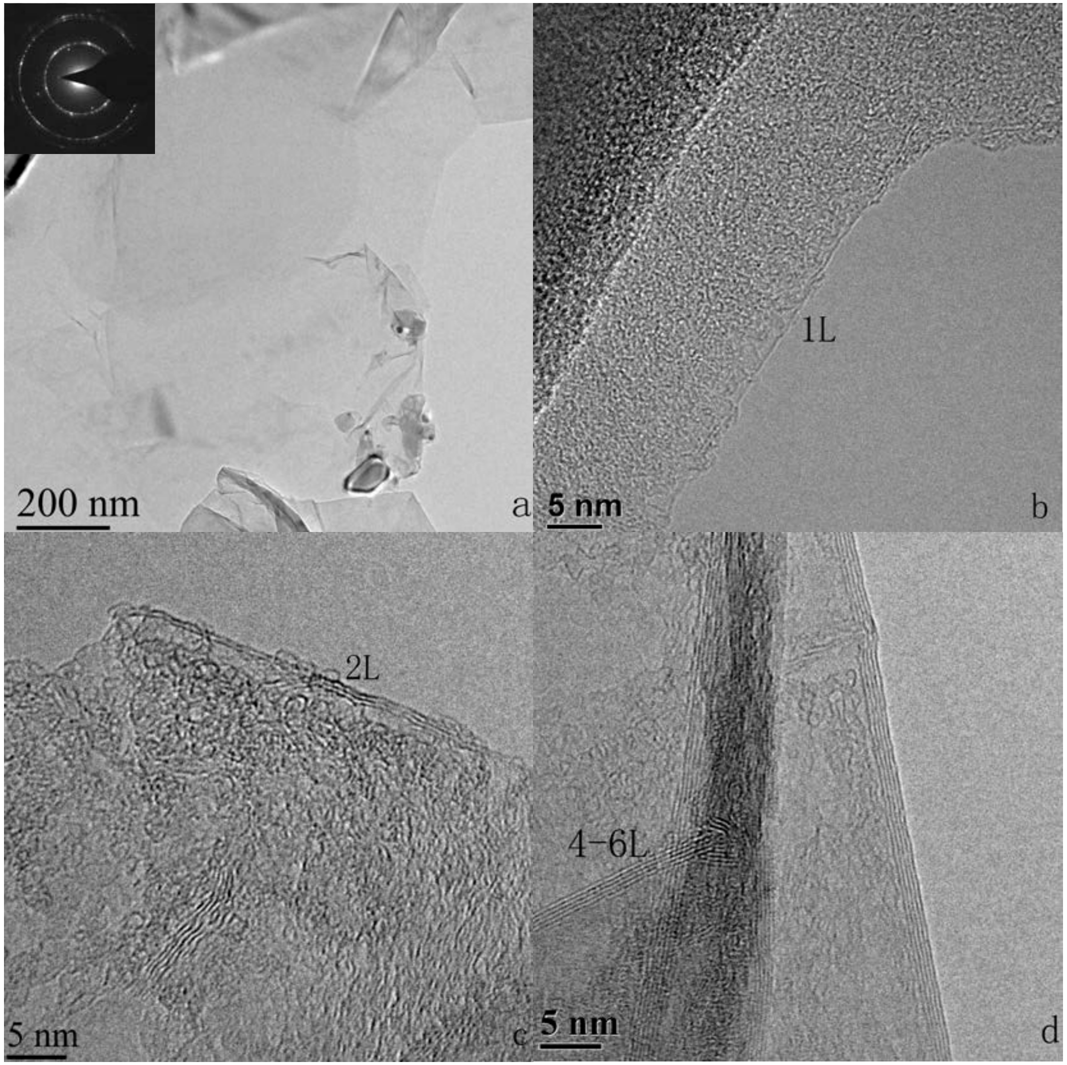
The carbon atoms are hard to be formed under the impact velocity of 2.83km/s due to too low pressure and temperature.

Calculation of shock pressure and temperature



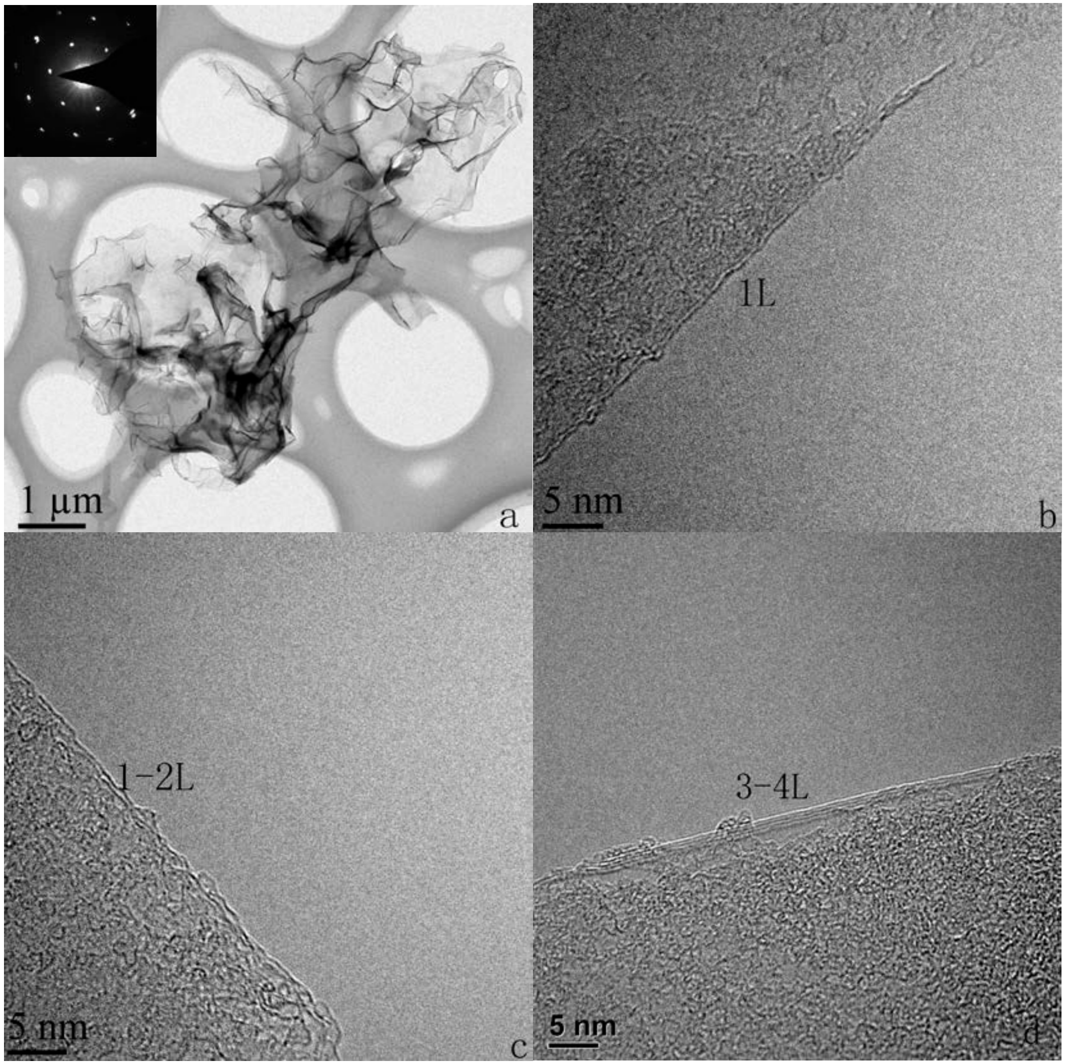
- Rankine-Hugoniot equations
- Mie-Gruneisen equation
- Impedance match method
- Weight averages

Results and discussion-TEM



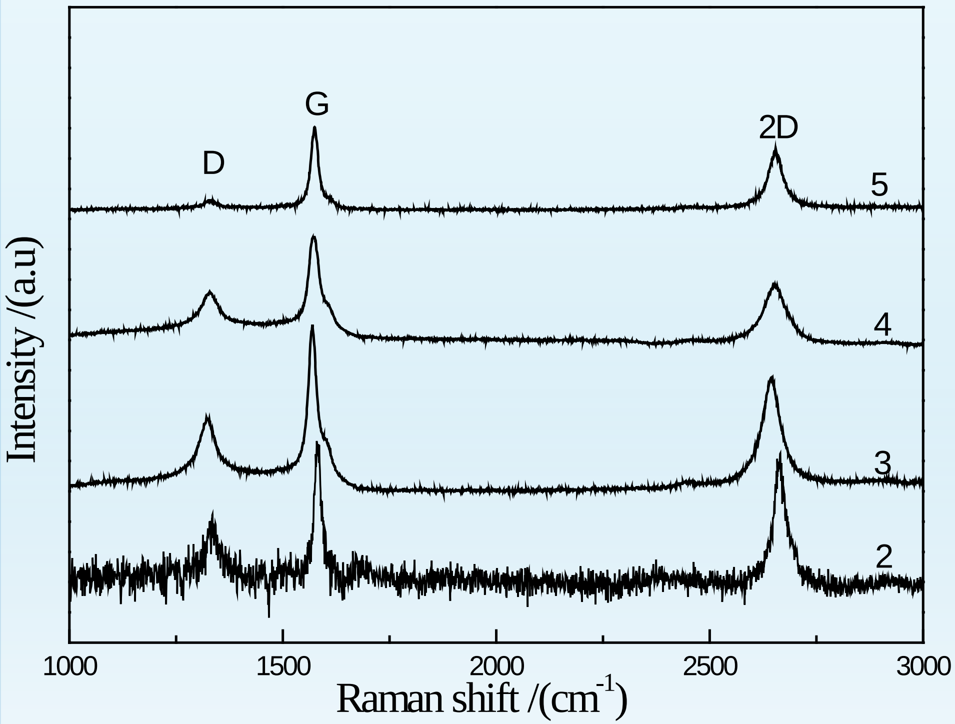
TEM images of the No. 4 samples. TEM images of (a) typical films. The insert of (a) shows SEAD pattern. HRTEM images of (b) monolayer, (c) double-layer, (d) 4-6 layers.

Results and discussion-TEM

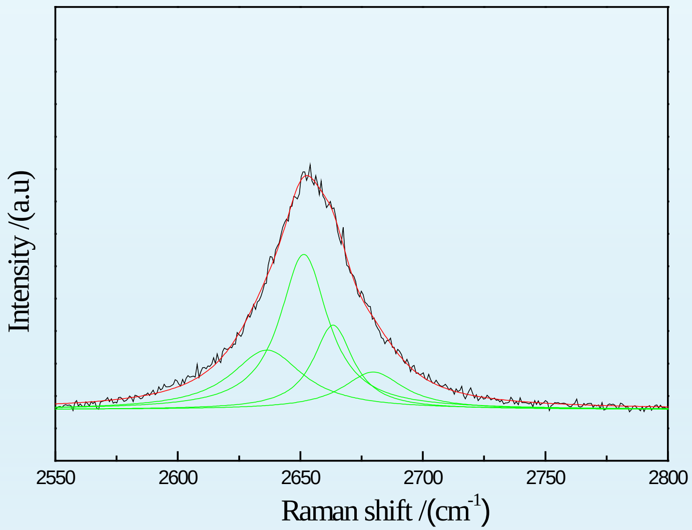


TEM images of the No. 5 samples. TEM images of (a) typical films. The insert of (a) shows SEAD pattern. HRTEM images of (b) monolayer graphene, (c) double-layer and (d) 3-4 layers.

Results and discussion-Raman



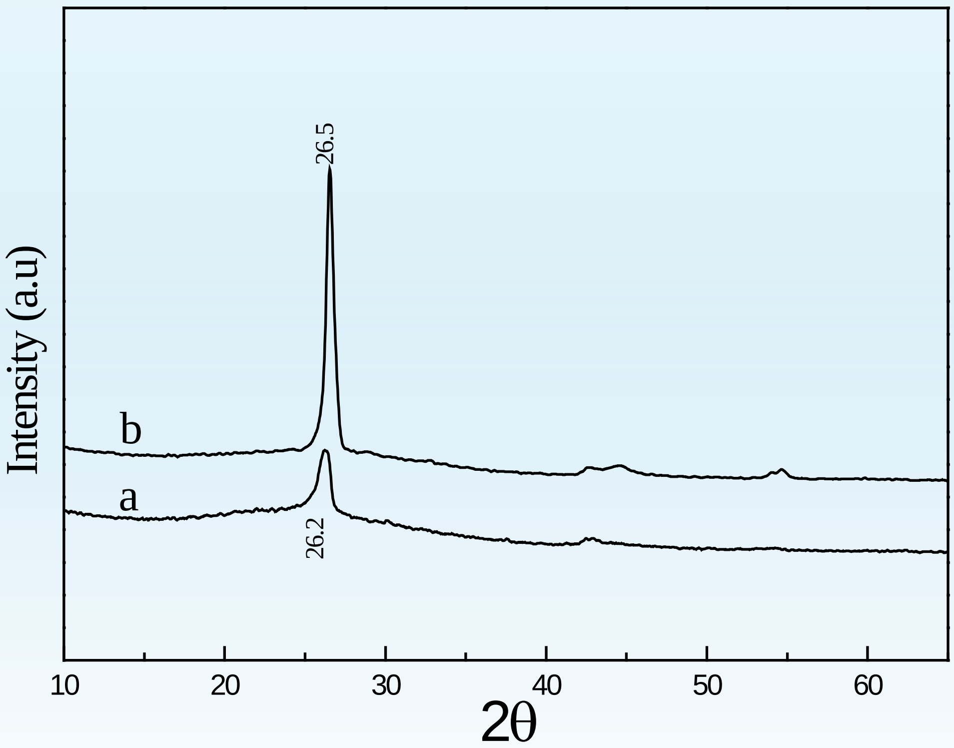
Raman spectra of shock-synthesized samples



The green lines show the four Lorentzian peaks used to fit the data, the red lines are the fitted results of No. 4 samples

No	I_D/I_G	I_{2D}/I_G	2D-FWHM(cm^{-1})
2	0.6	1.43	41
3	0.5	1.14	54
4	0.35	1.	51
5	0.16	1.39	45

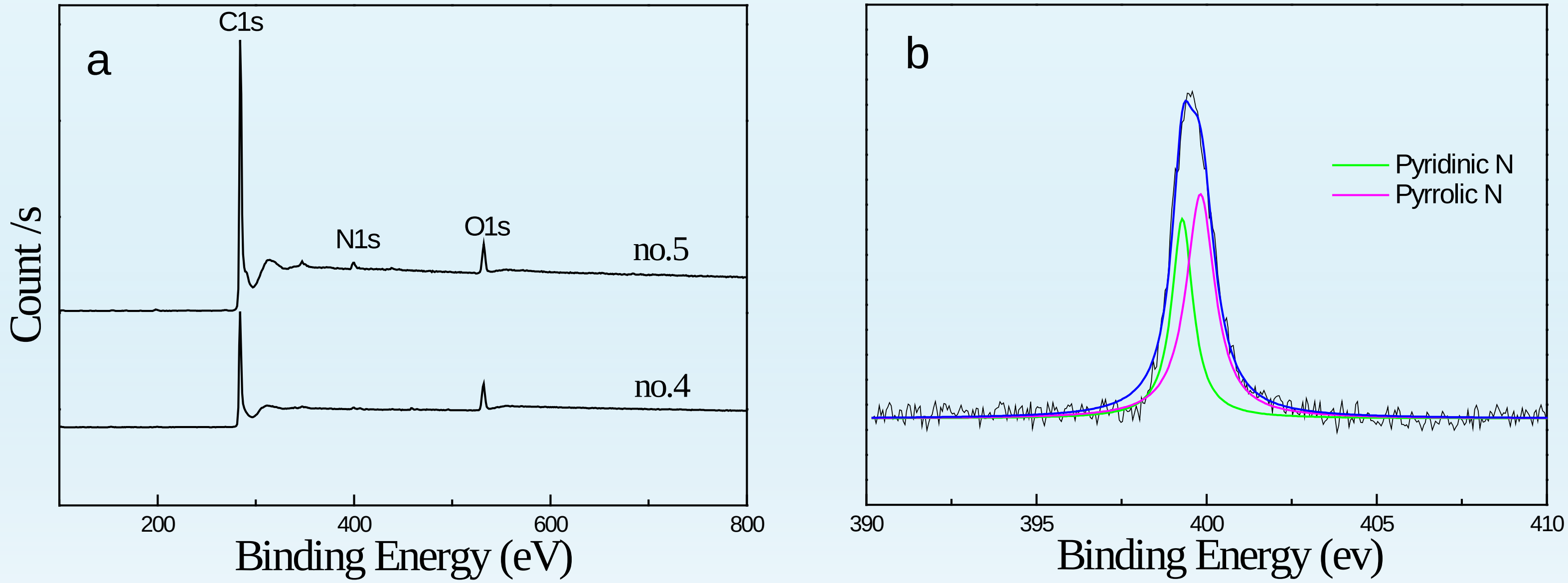
Results and discussion-XRD



XRD spectra of as-synthesized graphene and NG

The (002) peak in XRD is the typical character of synthesized graphene samples although the peak location may shift a little bit.

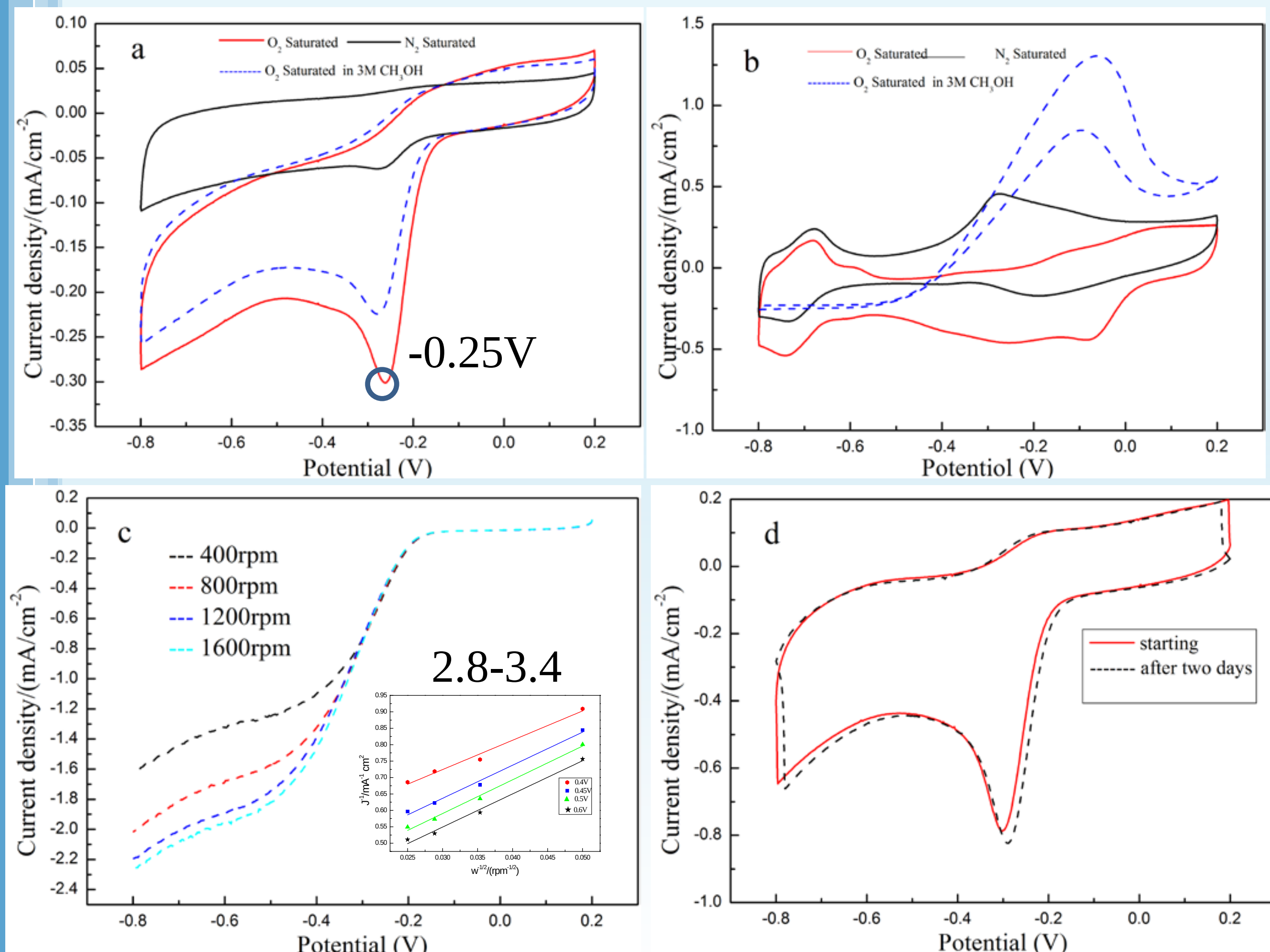
Results and discussion-XPS



XPS spectra of as-synthesized graphene and NG

The N 1s peak was observed in the NG, whereas the N 1s peak was absent in the no doping graphene. The high-resolution N 1s spectrum of NG shows the presence of both pyridinic-like (398.7 eV) and pyrrolic-like (400.4 eV) N atoms.

Electrochemical measurements



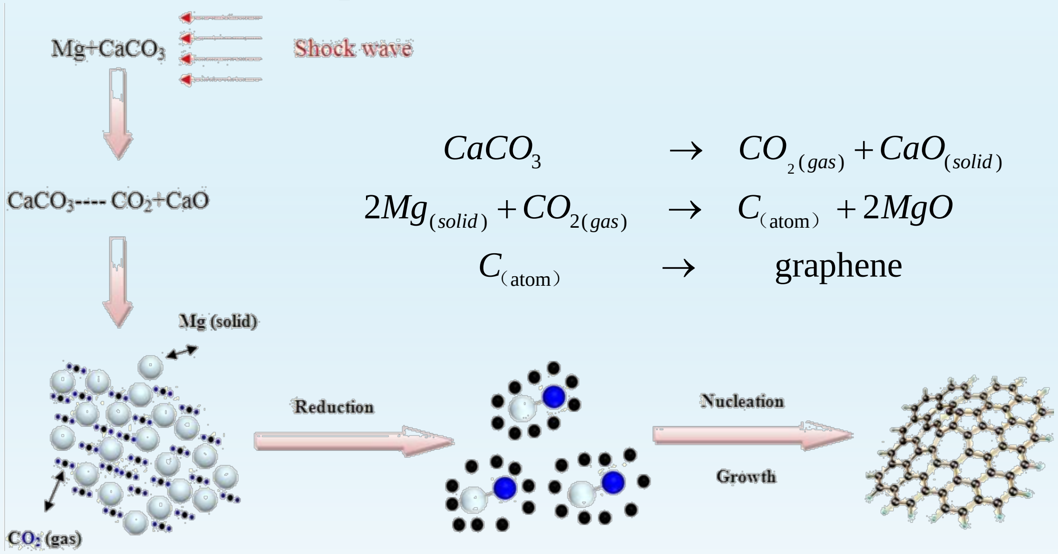
Electrochemical measurements were performed using a computer controlled potentiostat (CHI 660D) in a standard three-electrode cell.

- ✓great catalytic ability of NG for ORR
- ✓the 2-4 electron pathway
- ✓a stable ORR without any electroactivity specific to methanol in the methanol-containing electrolyte
- ✓long-term stability

(a)CVs of NG and (b) commercial Pt/C on a glass carbon electrode in N2-saturated, O2-saturated 0.1M KOH, (c) RDE cures of the NG in O2-saturated 0.1M KOH with different speeds

The mechanism for graphene formation

- The formation mechanisms of graphene under shock conditions are difficult to investigate due to the extremely fast and nonequilibrium process.
- We speculate that the formation of graphane under shock loading experience a gas-phase condensation-like process.



$$CaCO_3 \rightarrow CO_{2(gas)} + CaO_{(solid)}$$

$$2Mg_{(solid)} + CO_{2(gas)} \rightarrow C_{(atom)} + 2MgO$$

$$C_{(atom)} \rightarrow \text{graphene}$$

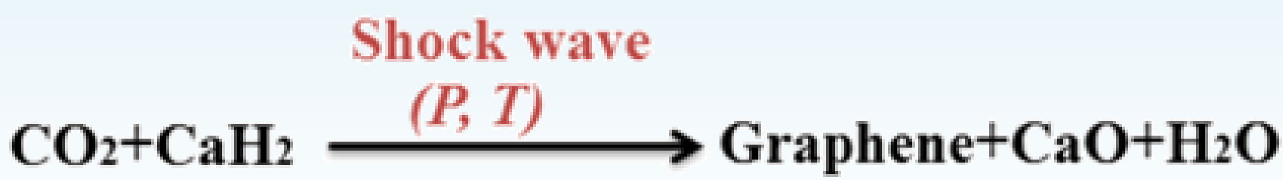
- With respect to the shock synthesis of **NG**, ammonium nitrate was broken to form active nitrogen atoms during the shock loading.
- During the formation of graphene, the nitrogen atoms **form a chemical bond** with the carbon atoms, and **nitrogen doping occurs**.

- The rapid increase in the level of carbon dioxide is a matter of great concern associated with global warming and climate change.
- Recent years have seen a significant growing international interest in both developing CO_2 capture/sequestration technologies and conversion of CO_2 into useful products to solve the global challenge.
- Hosmane have found that burning magnesium metal in dry ice could result in few-layer graphene nanosheets.
- We provide an innovative shock wave loading methodology that can instantaneously transform CO_2 into larger quantity of high crystalline few layer graphene.

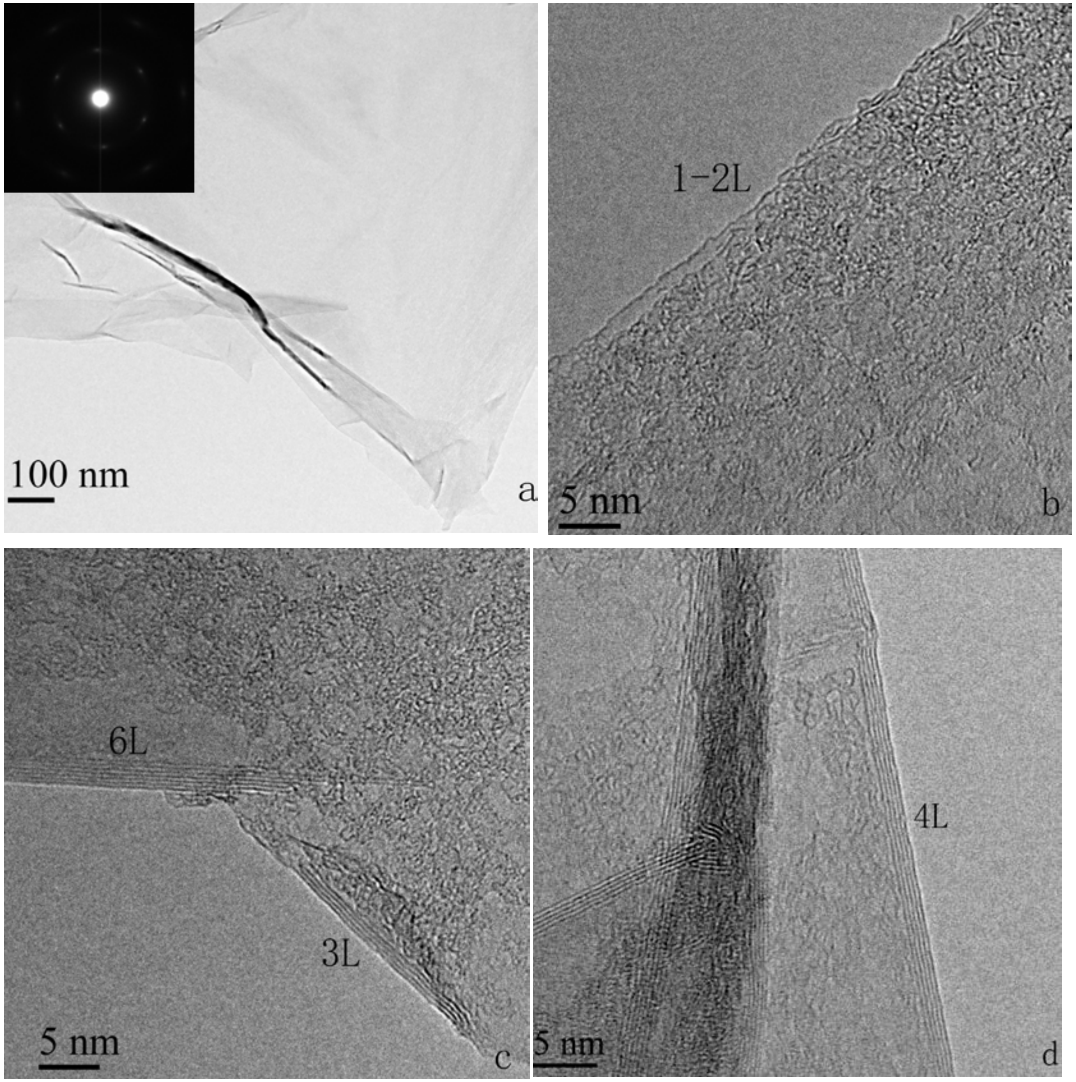
No	Samples[a]	Packing density	Porosity	Impact velocity (km/s)	Shock pressure(GPa)	Shock temperature(K)	Phase identified	carbon conversio n ratio [b]
1	A	1.27	0.80	1.50	5.60	1694	---	---
2	A	1.24	0.78	1.67	6.85	2047	graphite multi-layer graphene	0.40
3	A	1.30	0.82	1.75	7.92	1980	1-6L	0.25
4	A	1.42	0.88	1.90	12.3	1895	---	---

a: CO_2 to CaH_2 molar ratios of 1:1

b: Carbon conversion ratio is recovery carbon mass/ the initial carbon mass

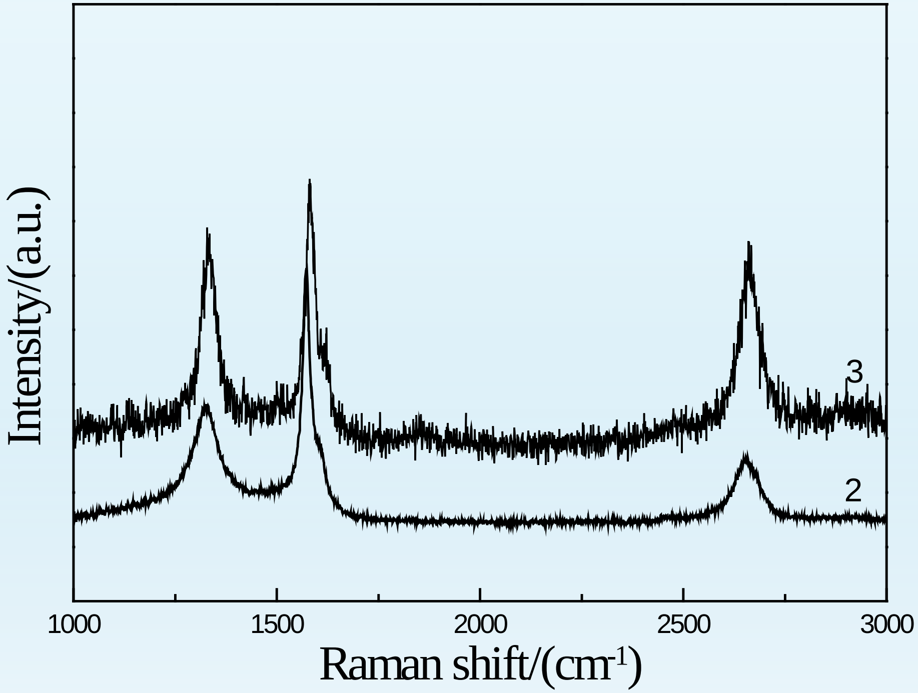


Results and discussion-TEM



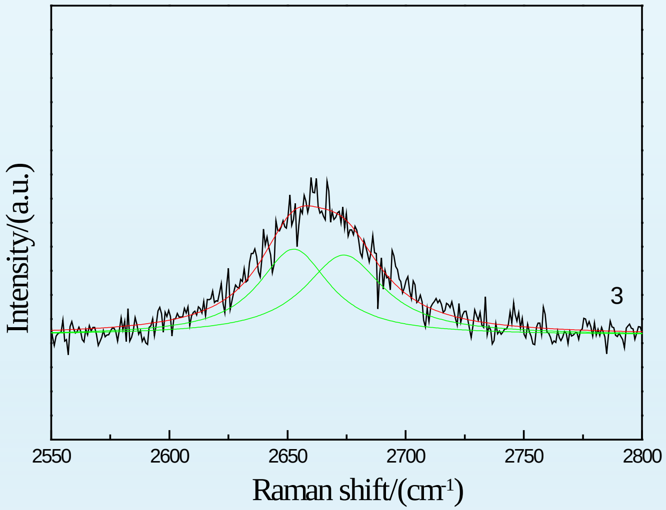
TEM images of the No. 3 samples. TEM images of (a) typical films. The insert of (a) shows SEAD pattern. HRTEM images of (b) monolayer, double layers, (c) 3,6 layers and (d) 4 layers.

Results and discussion-Raman



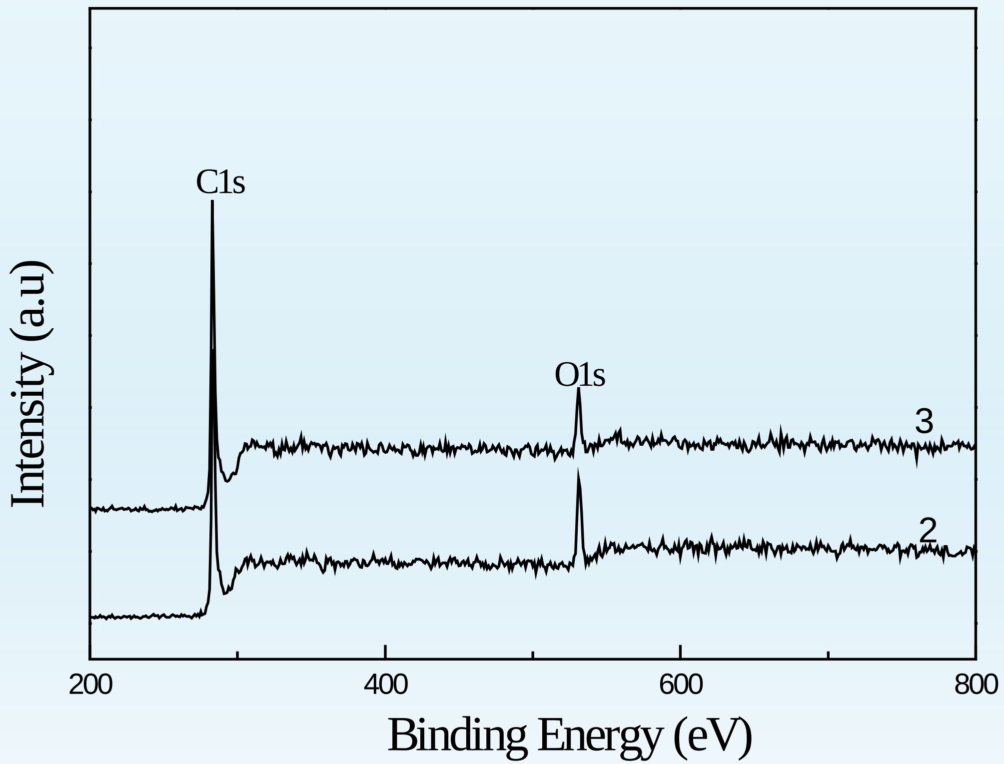
Raman spectra of shock-synthesized samples

No	I_D/I_G	I_{2D}/I_G	2D-FWHM(cm^{-1})
2	1.59	0.58	70
3	1.16	1.32	55



The 2D band of No.3 samples can be decomposed into two peaks (3L), providing strong evidence in favor of multilayer graphene as the major product.

Results and discussion-XPS



XPS spectra of shock-synthesized samples

The XPS spectra contain a sharp graphitic C 1s peak at 284 eV, along with a O 1s peak at ca.532.2 eV. The O/C atomic ratio of the shock-sythesized samples are calculated to be 8.6% and 5.4%, respectively.

Conclusion

- In this work, shock wave technique provides a simple and novel route to transform carbonate/carbon dioxide into useful graphene materials.

- The pressure and temperature are two important factors affecting the synthesis of graphene materials.

- When the shock pressure and temperature are too low, the shock waves cannot generate sufficient energy to induce the corresponding reaction.

- Shock synthesis of graphene requires a balance between the growth rate of graphene and the formation rate of carbon.

- The appropriate high pressure and low temperature can inhibit the formation rate of carbon, which is beneficial to form fewer graphene rather than graphite.

- The as-synthesized NG was demonstrated to act as a metal-free electrode with an electrocatalytic activity, long-term operation stability for oxygen reduction reaction in alkaline fuel cells.

Thank you for your attention!