

Development of Nano-sized Graphene Flowers as Neutron Reflectors

-Structural Control of Nano-sized Graphene and Application as Neutron Reflectors -

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- Team Graphene Flower -

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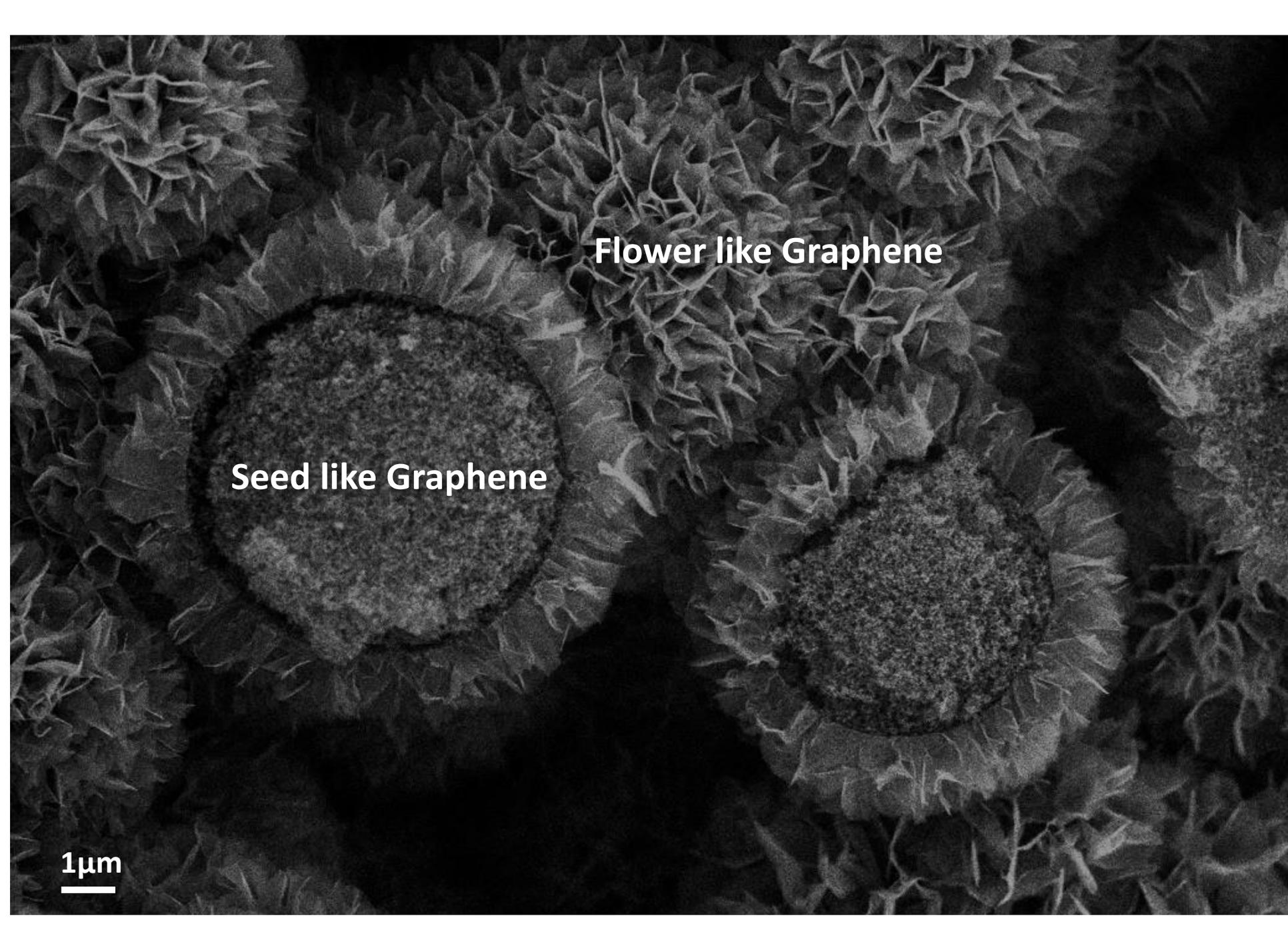
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Scanning electron micrograph showing two circular graphene structures. The structure on the left is a dense, dark, circular disk labeled 'Seed like Graphene'. The structure on the right is a similar disk with a highly textured, porous, and irregular outer edge, labeled 'Flower like Graphene'. The background is a dense network of interconnected, thin, needle-like or leaf-like structures.

Flower like Graphene

Seed like Graphene

1 μ m

A white horizontal line representing a scale bar of 1 micrometer.

The performance of the improved Graphene sample showed significant improvement as neutron reflectors and is almost the same as nano-diamond

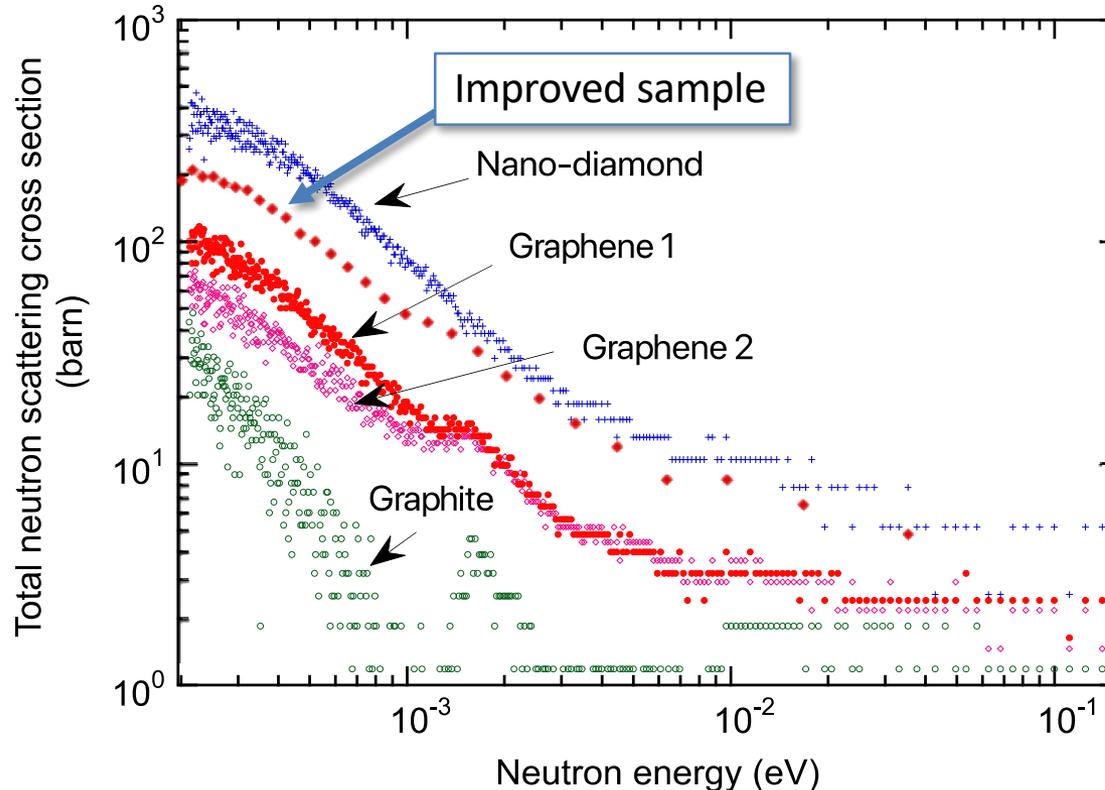


Fig. 1 Comparison of total neutron cross sections of various samples

○ M. Teshigawara, Y. Ikeda, M. Yan, K. Muramatsu, K. Sutani, M. Fukuzumi, Y. Noda, S. Koizumi, K. Saruta, Y. Otake, Development of Nano-sized graphene material for neutron intensity enhancement below cold neutrons, Journal of Neutron Research. 2024, № 2-3, p. 69-74. <https://doi.org/10.3233/jnr-240002>.

Outline

1. Motivation

2. How to make Graphene “Nano-Gorogoro”

2.1 Vapor-grown graphite formed in pores

2.2 Vapor-grown graphene production using powder packing method

2.3 Mechanism of vapor-grown graphene production

2.4 Optimization of pre-baking and HIP processing temperatures

3. Structure of Vapor-Grown Graphene

3.1 Petal-like graphene structure formed on the surface of carbonized material

3.2 Seed-like graphene structures formed within carbon particles

3.3 Evaluation of repeating structures using small-angle neutron scattering (SANS)

3. Summary

1. Motivation

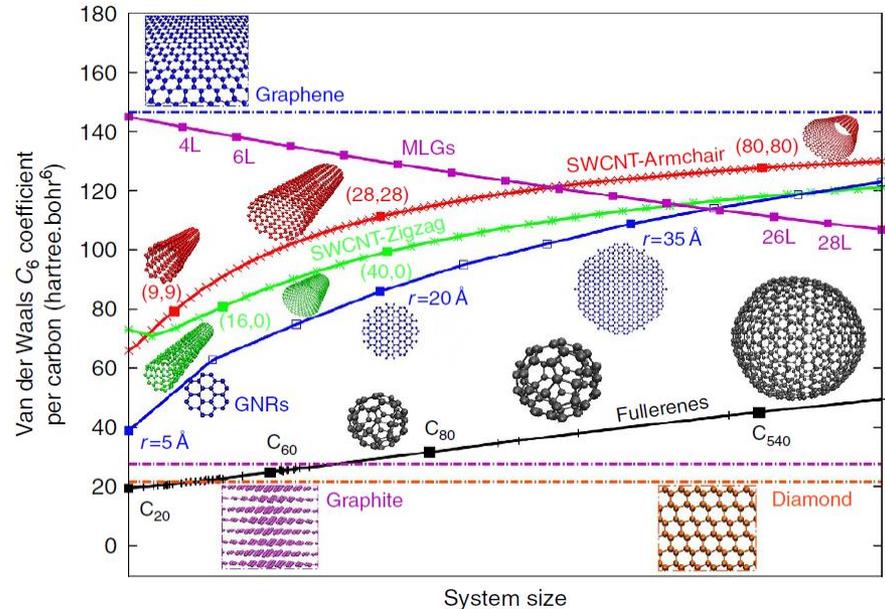
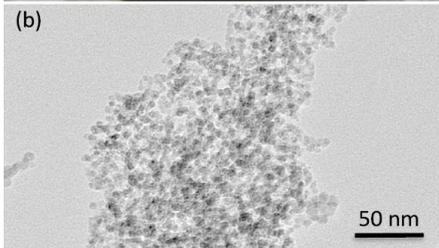
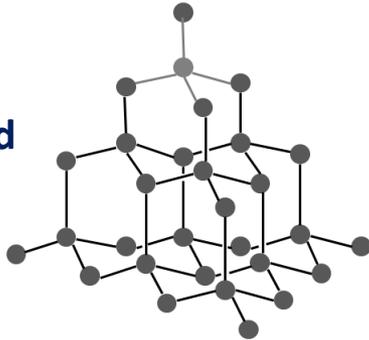
Form a self-supporting structure using “nano-gorogoro” of carbon (C).

(1) Van der Waals Force

Single-layer graphene has the greatest van der Waals force!

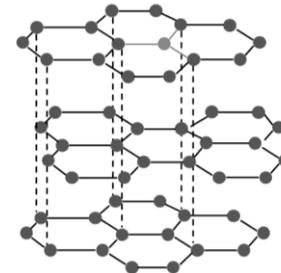
Nano-diamond

sp^3



VV Gobre et al. Nature Communications 4 (1), 2341

sp^2



Graphene

M. Teshigawara et al. Nucl. Instrum. Methods A 929 (2019) 113–120

(2) Purity and stability

Nanodiamond on market containing remarkable impurities and unstable typically.

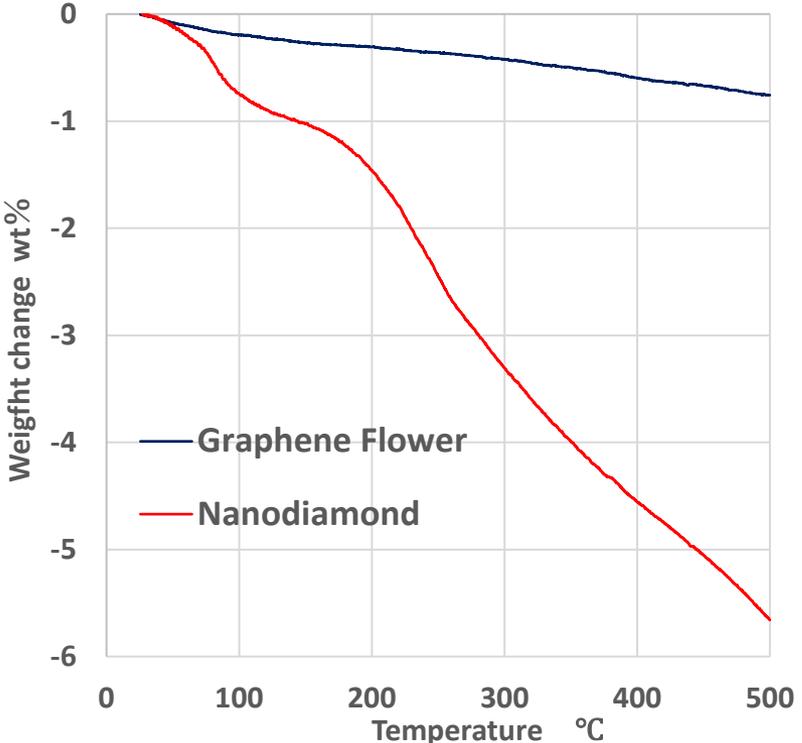


Fig. TG of Graphene and Nanodiamond

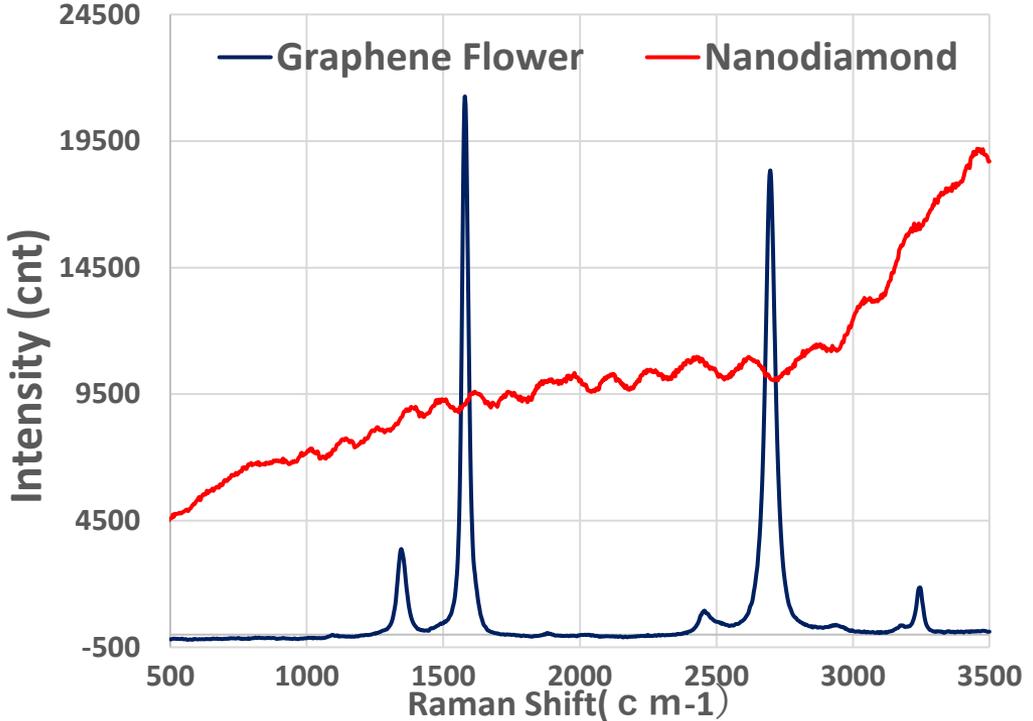


Fig. Comparison of Raman spectra of Graphene and Nanodiamond

Table Ash contents for Graphene and Nanodiamond

| Products | Ash [wt%] |
|-----------------|------------|
| Nanodiamond | < 6 wt% |
| Graphene Flower | < 0.10 wt% |

* C 561 – 918(ASTM)

Table Residual H₂ for Graphene and Nanodiamond

| Products | Residual H ₂ ppm |
|-----------------|-----------------------------|
| Nanodiamond | 7400 |
| Graphene Flower | 670 |

* JIS H 1619

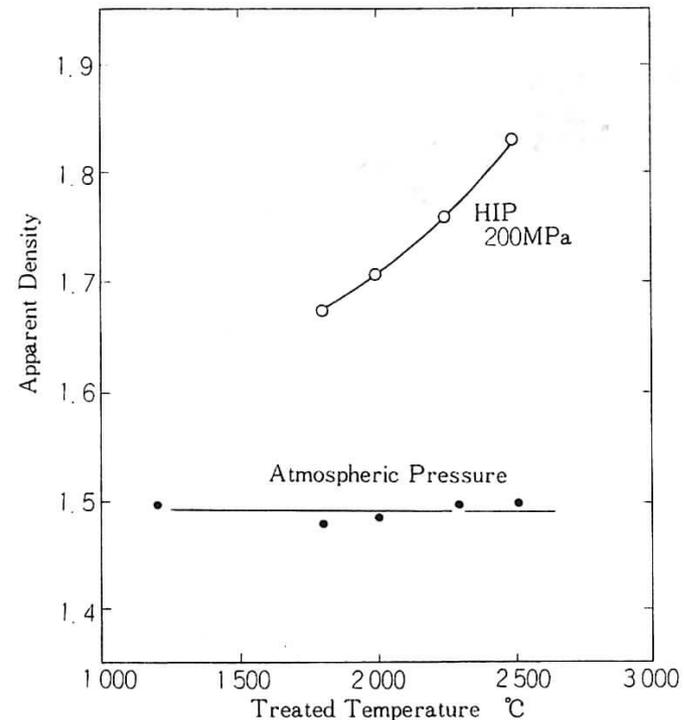
2. How to make Graphene “Nano-Gorogoro”

1) Ultra Densified Amorphous Carbon (UDAC)

- The pores (defects) in the material were removed by HIP treatment (2500°C) of glassy carbon, and the material was commercialized as HDD disks and wafers.



Fig. 2 Appearance of carbon disks



- K. Muramatsu , Y. Sakashita, N. Hara, Y. Onishi "Development of high-density amorphous carbon and its application to substrate materials" Kobe Steel Technical Report/Vol. 39 No. 4 (1989)

➔ The material defects in the carbon disk are converted into graphene

- We found out that, depending on the manufacturing conditions, minute amounts of vapor-grown carbon were formed in the pores, causing defects.
- The aim is to convert the defective vapor-grown carbon into graphene and produce it in large quantities.

a small amount of vapor-grown carbon is produced.

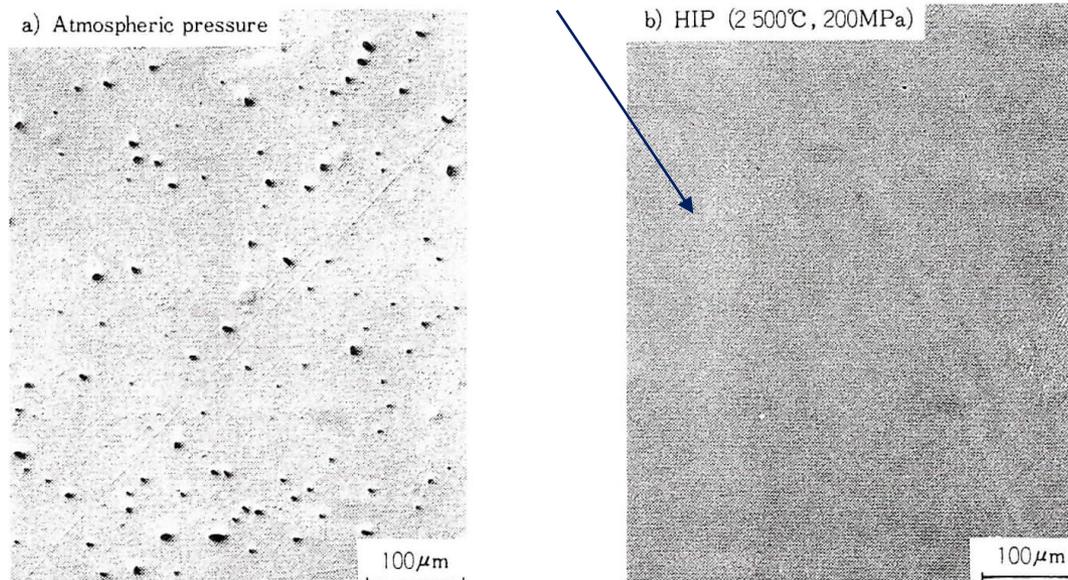
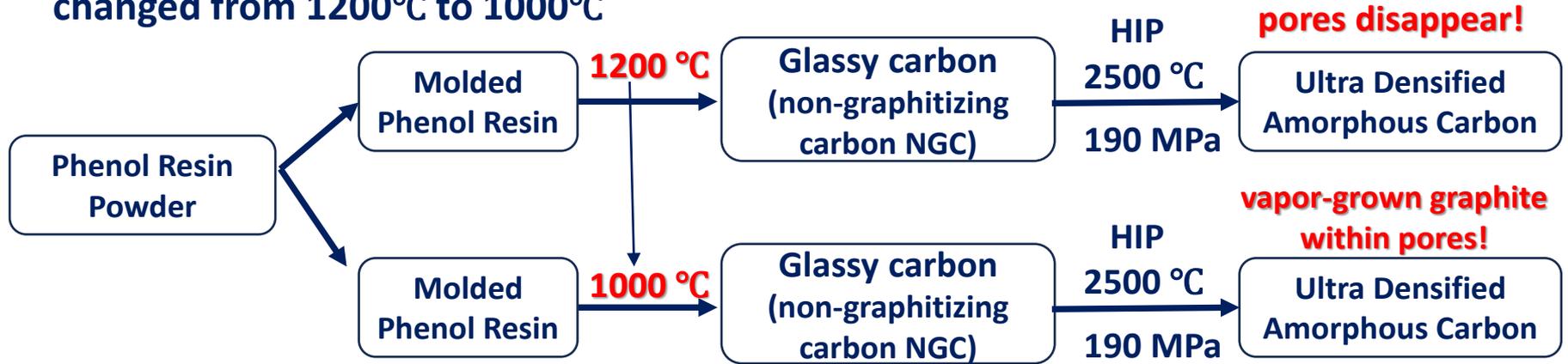


Fig. 4 SEM comparison of atmospheric pressure and HIP treatment at 2500°C

○ K . Muramatsu , Proc CARBON 88, held at Univ. Newcastle upon Tyne (1988)

2.1 Vapor-grown graphite formed in pores

- The pre-baking temperature for Ultra densified amorphous carbon (UCAD) was changed from 1200°C to 1000°C



- Carbon with a different morphology from the surrounding non-graphitizing carbon (NGC) is significantly generated within the pores

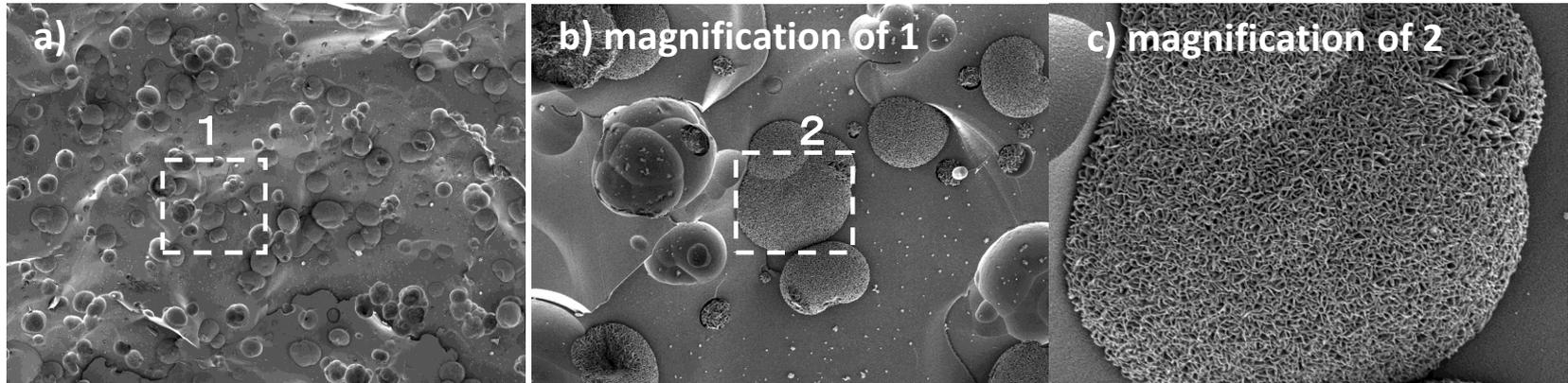


Fig. 5 FE-SEM of sample after HIP treatment

○ K. Muramatsu, M. Toyoda, CARBON MATERIAL AND METHOD FOR PRODUCING SAME, US PAT 8,883,112 B2

- The carbon generated in the pores was confirmed to be graphite from the G band of the Raman spectrum.
- Also, based on the morphology observed by FE-SEM, it was inferred that the product was grown in the vapor phase.
- It is believed that non-graphitizing carbon (NGC) does not graphitize in the solid phase, but graphite precipitates if it is grown in a vapor phase.

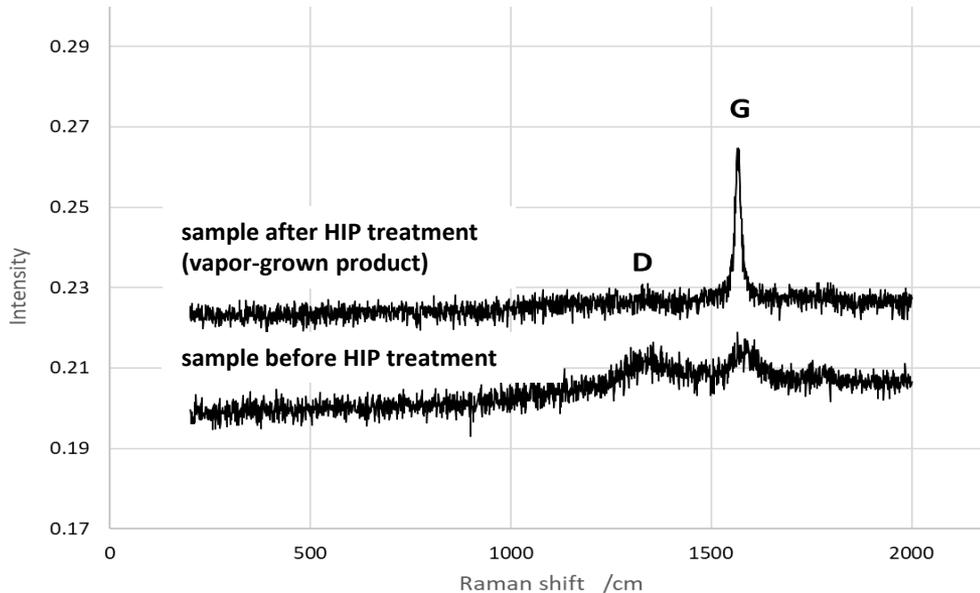


Fig. 6 Raman spectra of the sample before and after HIP treatment

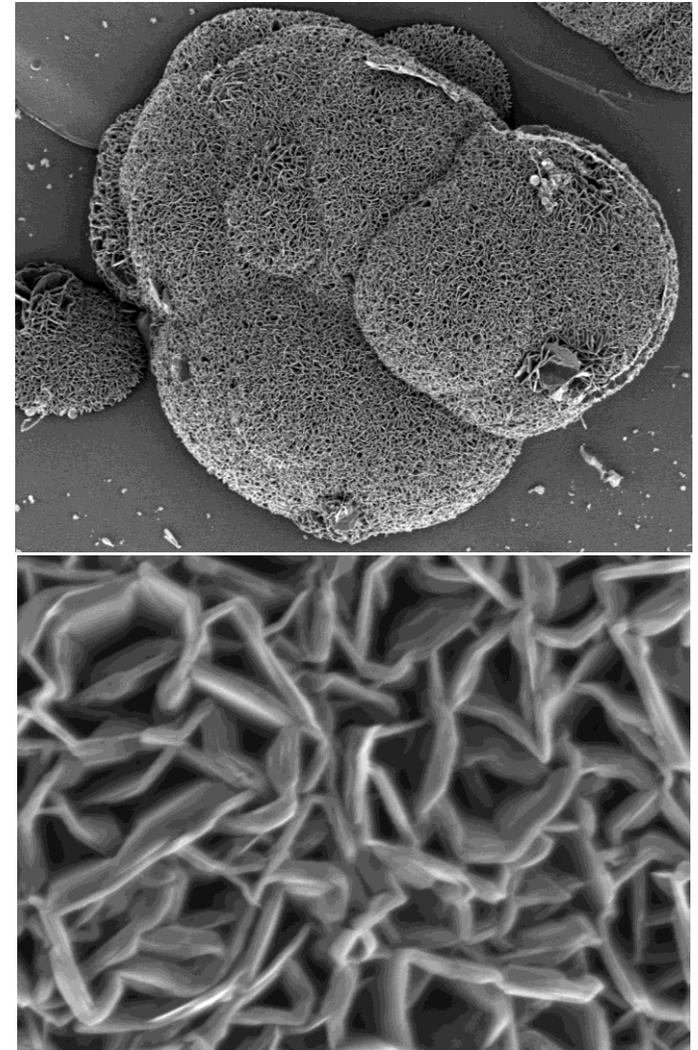


Fig. 7 FE-SEM of the sample before and after HIP treatment

2.2 Vapor-grown graphene produced by powder packing method

Vapor-grown graphite formed in pores

- resin is molded into a plate and carbonized
- the yield of vapor-grown graphite is low
- The material must be destroyed for extraction

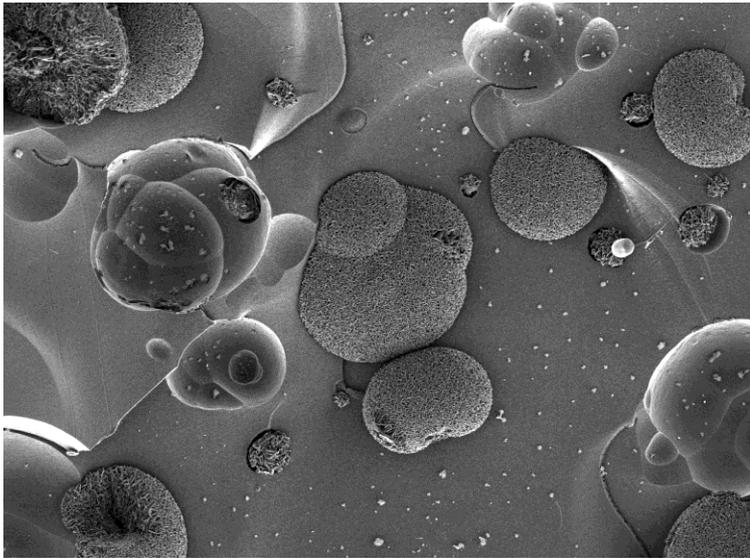


Fig. 8 Vapor-grown graphite formed in pores

Aiming for formation from the surface of carbonized materials

- resin is powdered, pre-heated and HIP-treated.
- formed from the particle surface, resulting in high yields
- powder packing method (container required)

Selective formation of graphene

- optimization of pre-baking temperature (amount of residual hydrogen)
- optimization of processing vessel
- optimization of HIP processing conditions

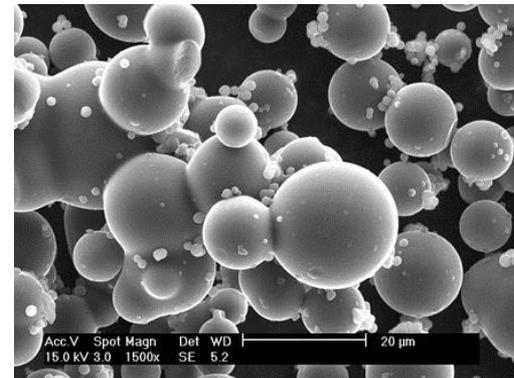


Fig. 9 Carbonized resin powder

- K. Muramatsu, K. Sutani, M. Toyoda, Preparation of vapor-phase grown graphene by HIP method and its formation mechanism, Carbon Reports Vol.4 No.1, DOI: 10.7209/carbon.040102

Hot Isostatic Pressing (HIP) Method and Powder Packing Method

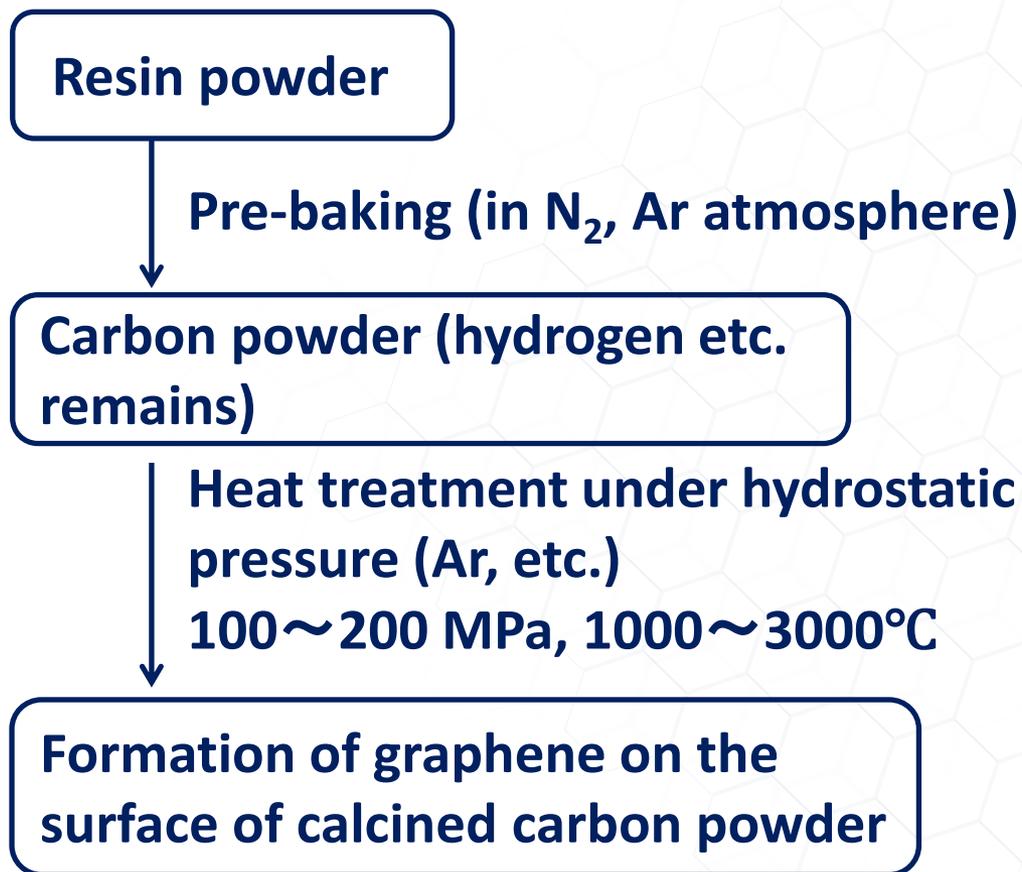


Fig. 10 Example of HIP equipment (manufactured by Kobe Steel)

○ K. Muramatsu, *Graphene Manufacturing and Processing Technology*, Tanso 2013(256) 60-66

2.3 Mechanism of vapor-grown graphene formation

- HIP (hydrostatic pressure) creates an atmosphere in which CVD occurs on the entire surface of the carbonized material.
- Thermal excitation of the generated gas causes CVD on the carbonized material surface, producing vapor-grown carbon.
- At the same time, nanostructures are formed inside the carbonized material by etching.

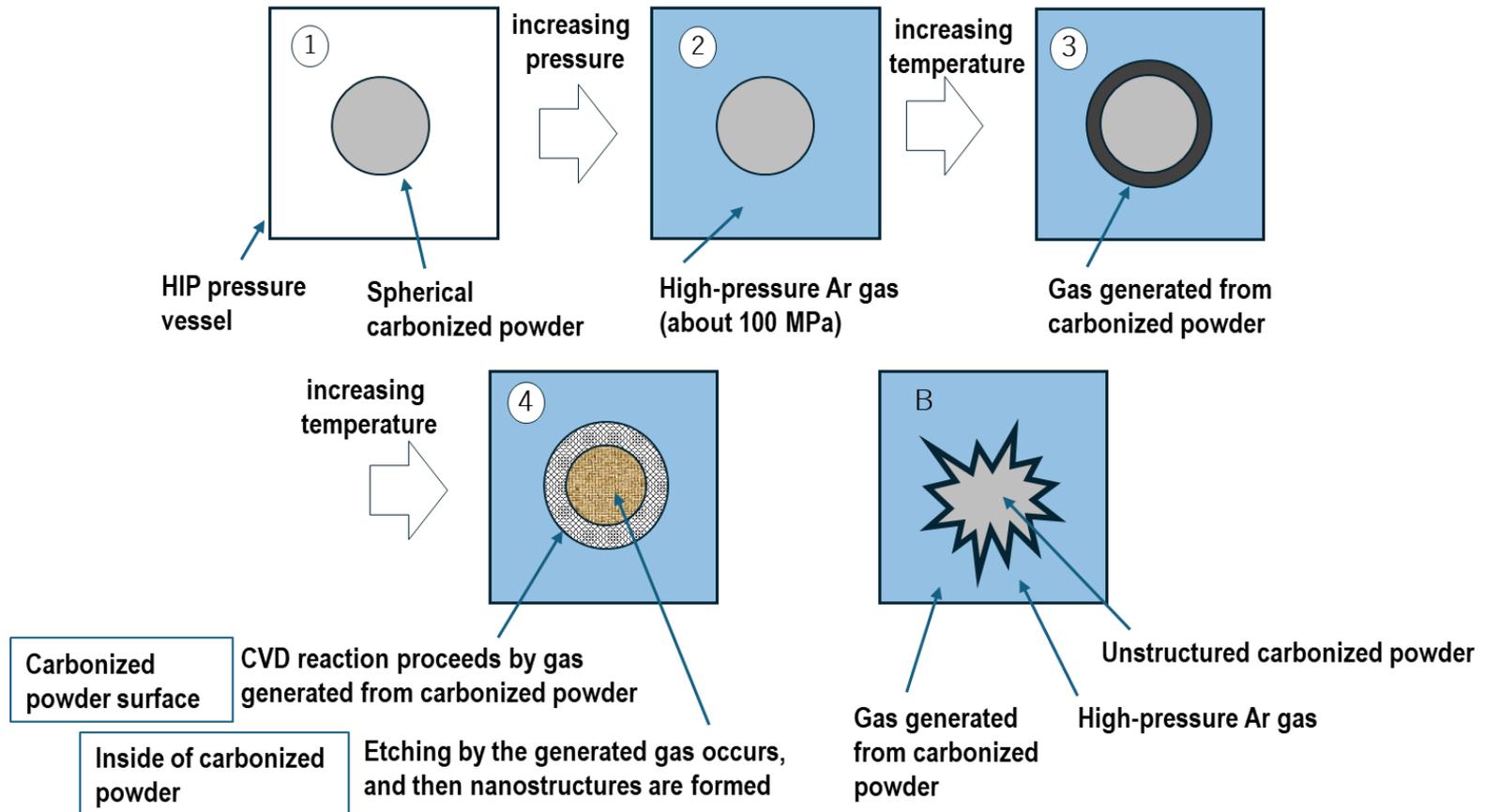


Fig. 11 Mechanism of vapor-phase carbon formation

2.4 Optimization of pre-baking and HIP processing temperatures

We optimized the pre-baking temperature and HIP processing temperature conditions to selectively produce vapor-grown graphene with several layers using the powder packing method in the steps shown in the figure below.

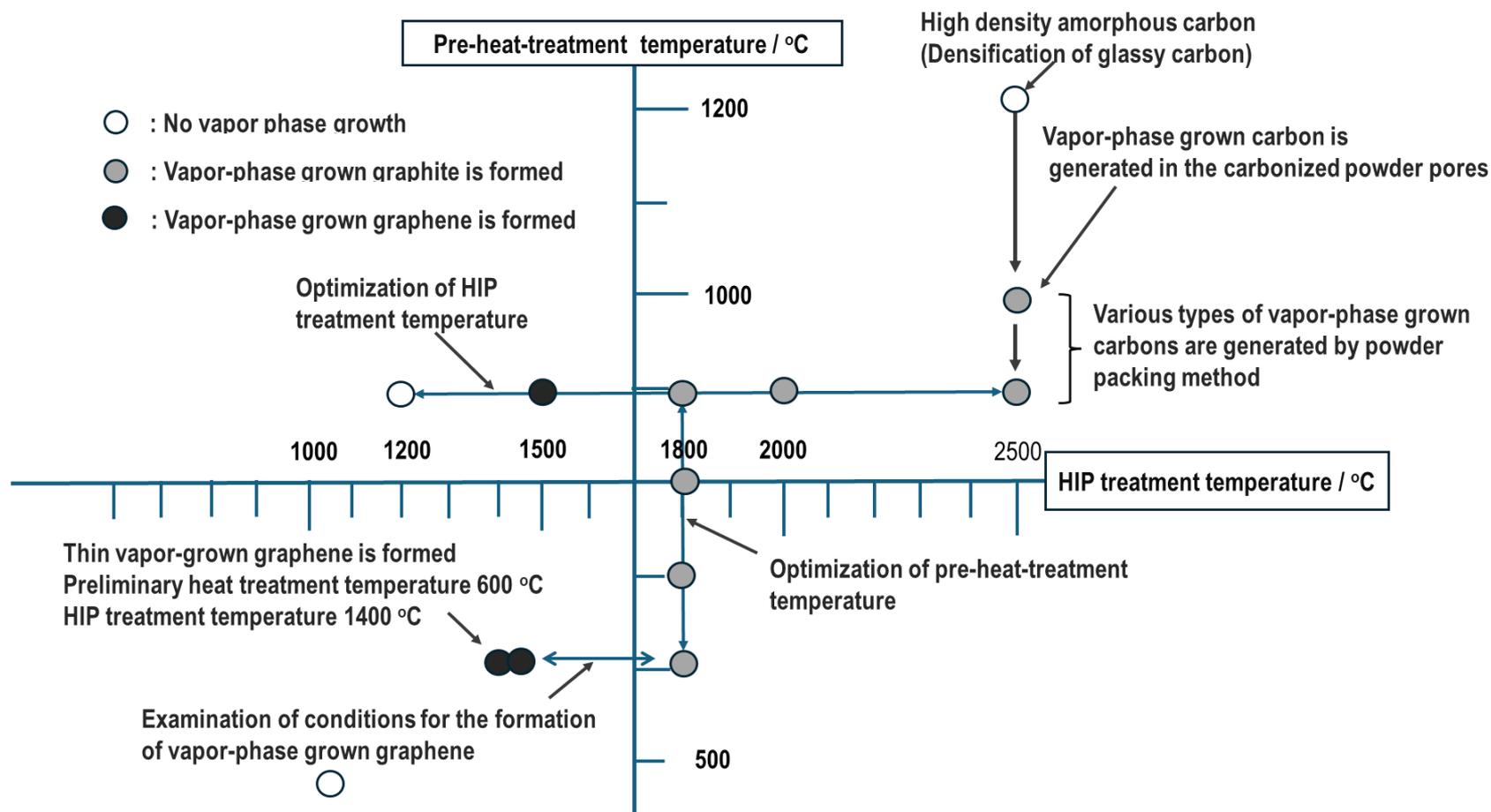


Fig. 12 Understanding the conditions for vapor-grown graphene production using the powder packing method

○ K. Muramatsu, K. Sutani, M. Toyoda, Preparation of vapor-phase grown graphene by HIP method and its formation mechanism, Carbon Reports Vol.4 No.1, DOI: 10.7209/carbon.040102

The morphology of the vapor-grown carbon was observed and evaluated using FE-SEM, and the conditions were optimized to achieve a thinner form!

There is a high probability that the carbon particles are cracked.

There are also clear voids within the particles and products inside the particles.

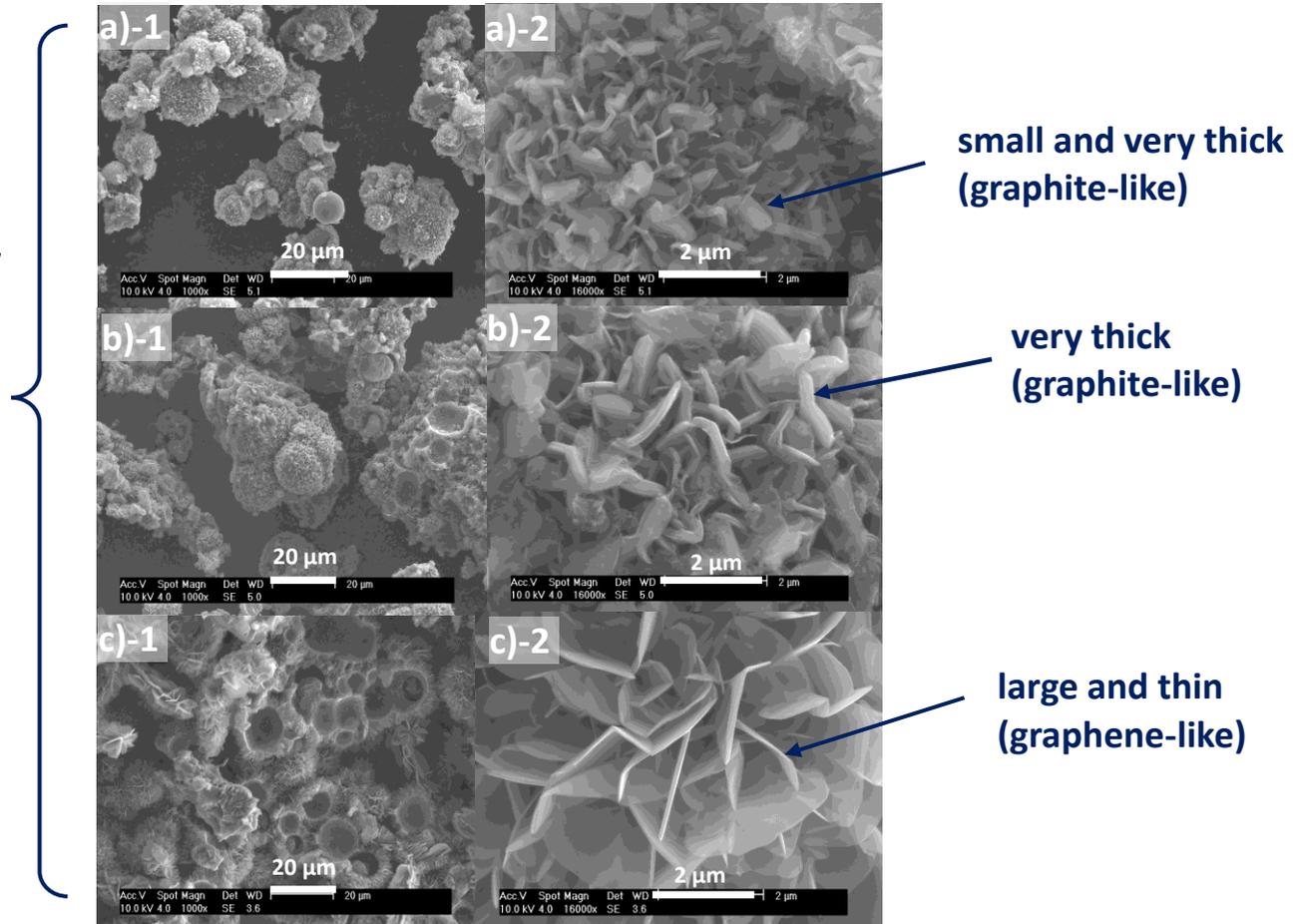


Fig. 13 FE-SEM of HIP-treated vapor-grown carbon products. a) No. 9, pre-baked at 800°C, HIP at 1800°C, b) No. 10, pre-baked at 700°C, HIP at 1800°C, c) No. 11, pre-baked at 600°C, HIP at 1800°C.

Through further optimization, they were able to obtain extremely thin, large, petal-like vapor-grown graphene!

The probability that the carbon particles are cracked is low.

The voids within the particles and the products inside the particles are unclear.

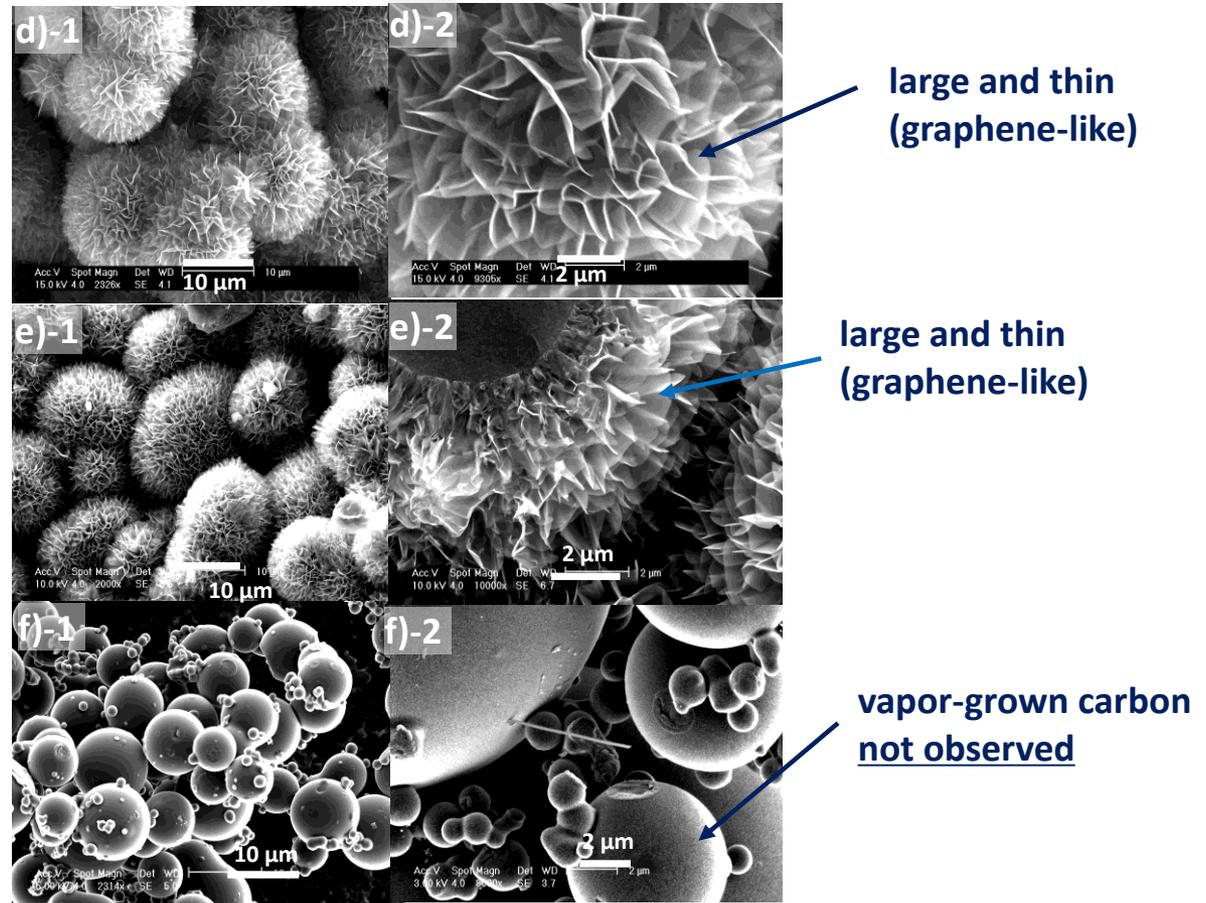


Fig. 14 FE-SEM of HIP-treated vapor-grown carbon products. d) No. 12, pre-fired at 600 °C, HIP at 1450 °C, e) No. 13, pre-fired at 600 °C, HIP at 1400 °C, f) No. 14, pre-fired at 500 °C, HIP at 1000 °C.

Graf et al. reported that the integrated intensity ratio of G/2D (referred to as D' in the paper) in the Raman spectroscopy spectrum is less than 0.8 when the number of layers is 6 or less.

No. 13, which was pre-baked at 600°C and HIP-treated at 1400°C, has an integrated intensity ratio of G/2D of less than 0.8, suggesting that vapor-grown few layers graphene was obtained.

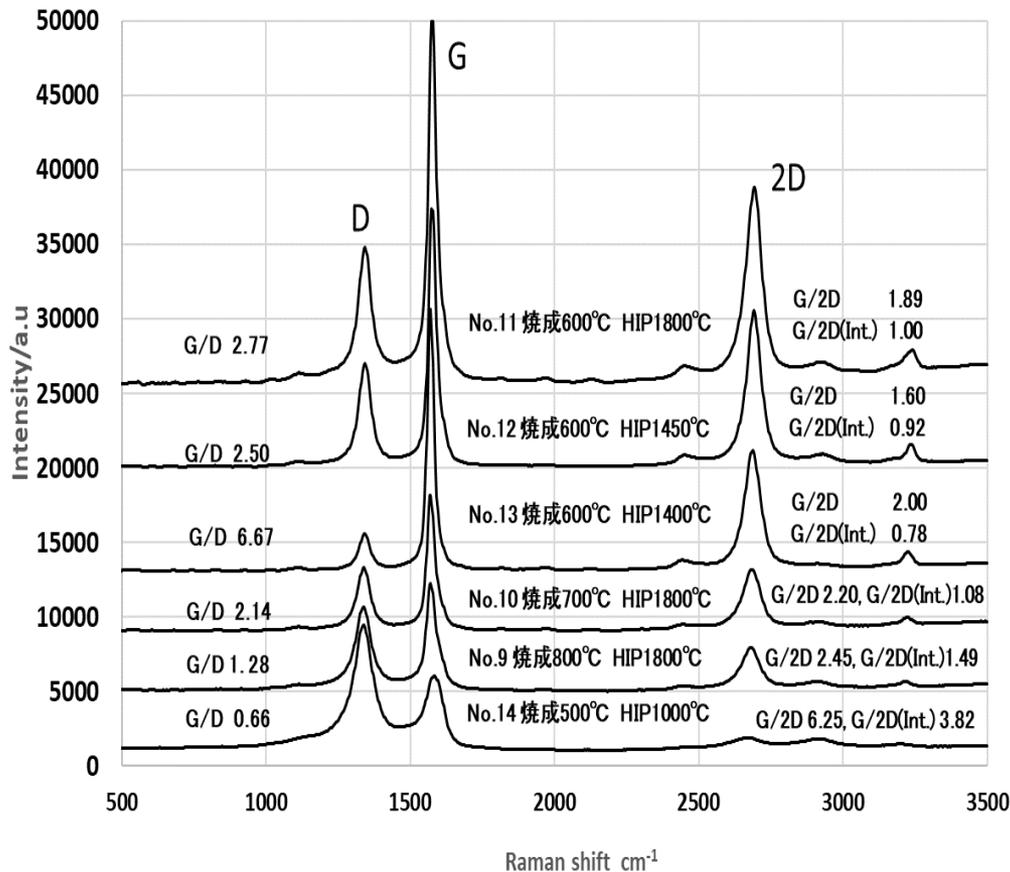
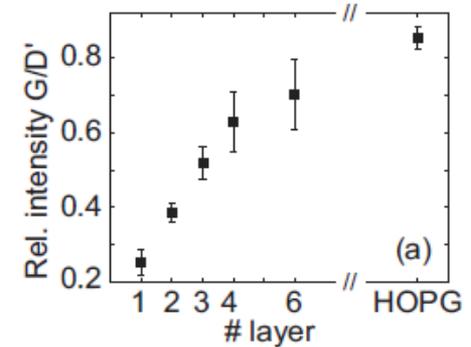


Fig. 15 Qualitative evaluation of the number of graphene layers in vapor-grown graphene (Raman spectroscopy)



D. Graf et al, Spatially Resolved Raman Spectroscopy of Single- and Few-Layer Graphene, Nano Lett. 7 (2007) 238-242,

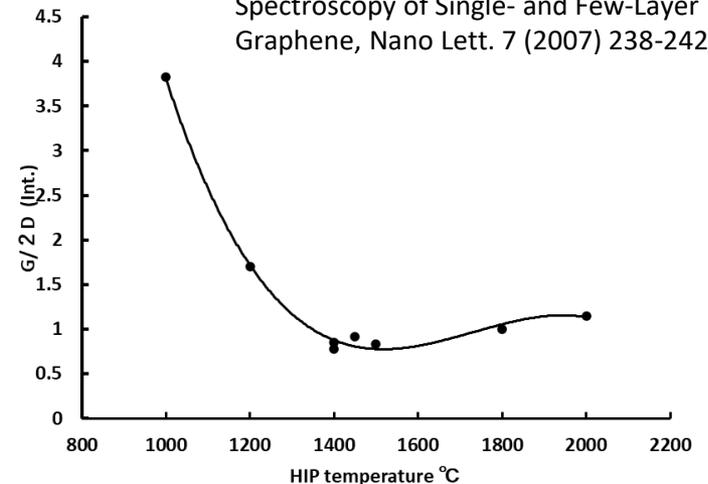


Fig. 16 Correlation between HIP temperature and G/2D integrated intensity ratio

FE-SEM of No. 13 (pre-baked at 600°C and HIP-treated at 1400°C), and No. 1 (pre-baked at 1000°C and HIP-treated at 2500°C). The starting materials are the same, but vapor-grown graphite is selectively produced in No. 1, and vapor-grown graphene is selectively produced in No. 13.

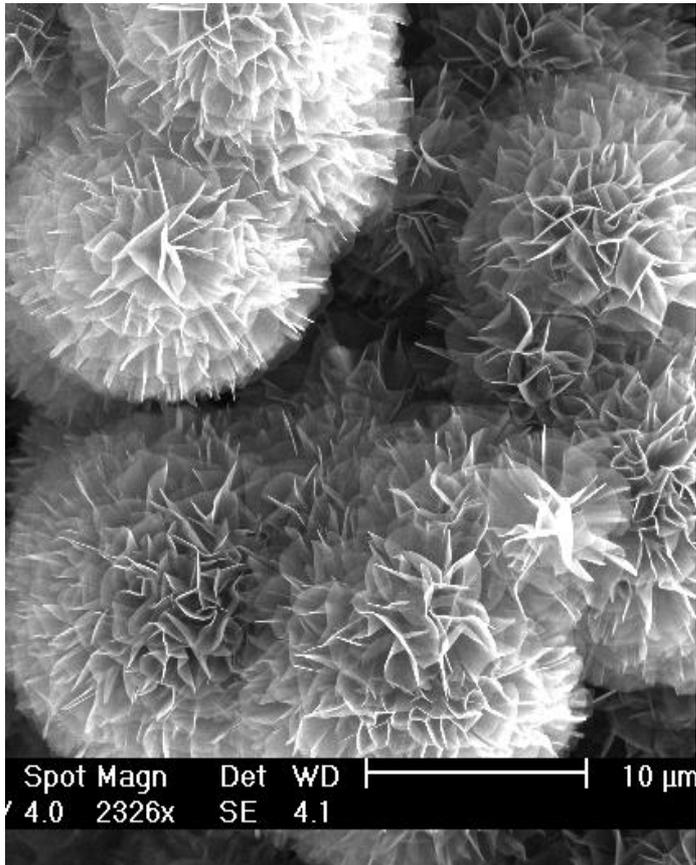


Fig. 17 FE-SEM of vapor-grown graphene No. 13

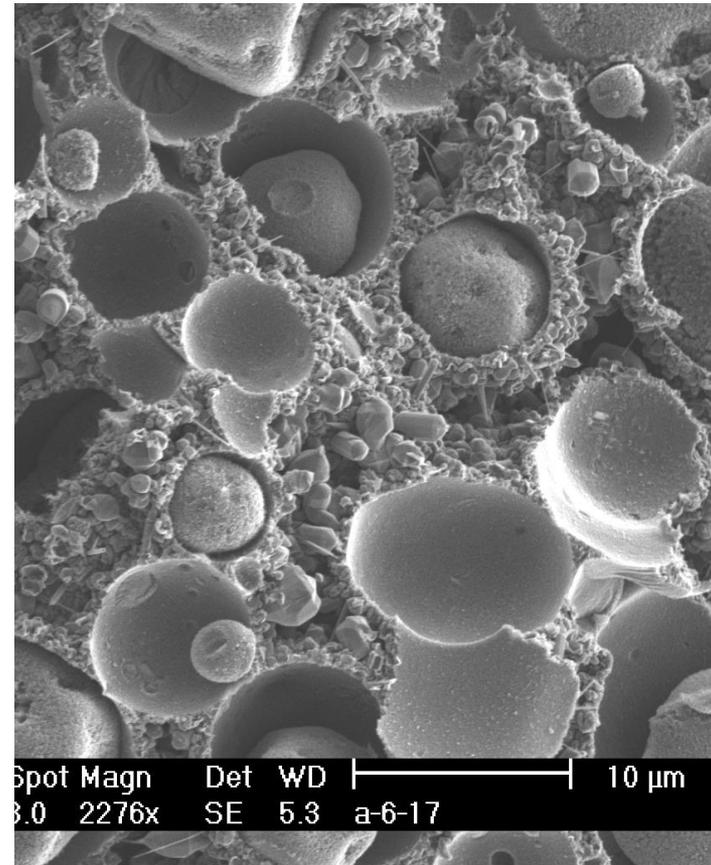


Fig. 18 FE-SEM of vapor-grown graphite No. 1

4. Summary

1. By optimizing the pre-baking conditions and HIP processing temperature of the HIP method, it has become possible to selectively produce vapor-grown graphene.
2. Petal-like graphene grew from the surface of the carbonized material, and a three-dimensional graphene structure was obtained in which seed-like graphene was formed within the carbonized material particles.
3. We observed coherent scattering of cold neutrons by a three-dimensional graphene structure, and found the possibility of using it as a neutron reflector. (Measurement results at RIKEN RANS)
4. Small-angle neutron scattering (SANS) analysis revealed that the repeat distance d of the graphene three-dimensional structure is about 5 nm, which roughly matches the shape of the seed-like structure observed by FE-TEM. (Measurement results at iMATERIA at J-PARC)
5. We are working hard to improve and prototype our graphene's neutron reflectivity, aiming to surpass that of nano-diamonds.

Thank you for listening

Team Graphene Flower

Japan Atomic Energy Agency



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RIKEN



理研小型中性子源 RANS

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