



化学剥離グラフェンの合成と評価

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グラフェンの化学的合成法
酸化グラフェン

合成法

表面形態, 構造モデル

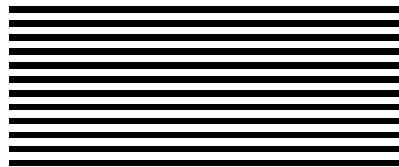
還元による導電性の回復

有機トランジスタ電極応用

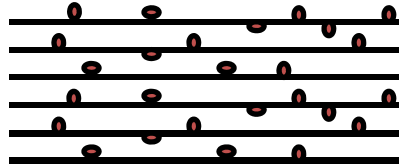
グラフェンの化学的合成法

トップダウンプロセス

バルク物質から



グラファイト



化学反応
官能基の付加

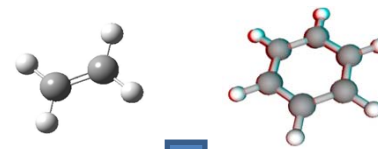
可溶化
不純物添加

化学剥離グラフェン

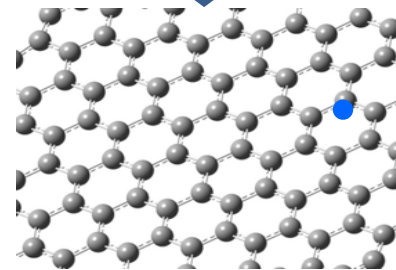
(Chemically exfoliated graphene)

ボトムアッププロセス

原子・分子から



炭化水素



縮重合

不純物添加



化学気相成長

CVD (Chemical vapor deposition)

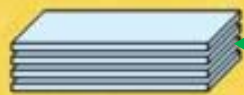
化学的合成法の特長

1. 迅速かつ大量合成
2. 不純物添加による物性の制御

グラフェンの化学的合成(バルクから)

機械的剥離

グラファイト



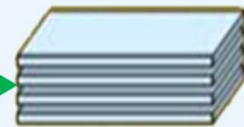
↓ スコッチ
テープ



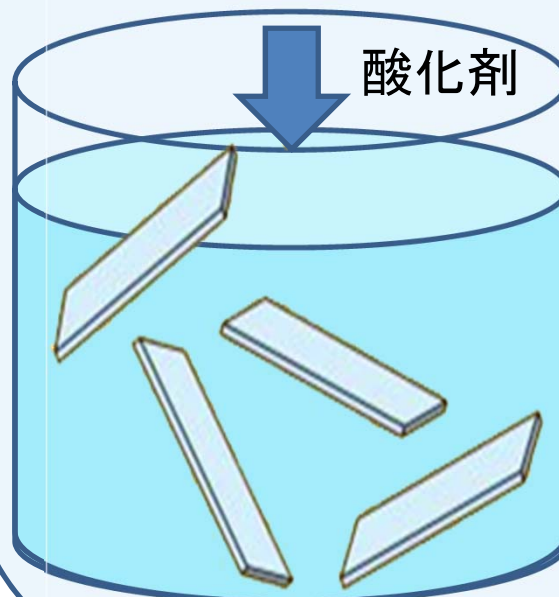
グラフェン

vdW
int.

グラファイト

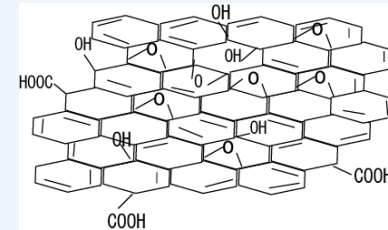


酸化剤



化学的剥離

酸化



官能基の付加



層間引力の弱化



溶媒中に1枚で分散

大量合成可能
ただし、
グラフェンに戻すには
還元が必要

酸化グラフェン(GO) 合成法

改良ハマーズ法

天然グラファイト粉末,
NaNO₃, H₂SO₄

氷浴中
撹拌

KMnO₄

撹拌 20 °C

5日間



高粘性液体
(濃紫)

撹拌
1時間

5 wt. %
H₂SO₄

濃茶色液体

撹拌
2日間

*

H₂O₂

*

撹拌
2時間

黄色液体

1000 rpm,
10 min.

沈殿 (黄色)

(15)

3000 rpm,
20 min.

3 wt. % H₂SO₄
0.5 wt. % H₂O₂

沈殿
(薄茶色)

H₂O

(2)

7000 rpm,
30 min.

**

※ rpm, min
for centrifugation
(N); number of
repetition

H₂O

**

1日間
静置

上澄み(茶色)

7000 rpm,
30 min.

沈殿 +
粘性液体

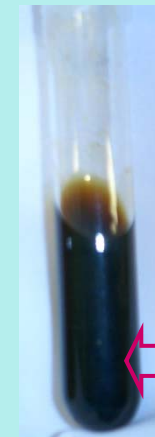
H₂O

(20)

7000 rpm,
60 min.

沈殿 (茶色)

粘性液体 (茶色)
(0.44 wt.%)₄



酸化グラフェン(GO) 合成法の原論文

March 20, 1958

PREPARATION OF GRAPHITIC OXIDE

1339

[CONTRIBUTION FROM THE BAROID DIVISION, NATIONAL LEAD COMPANY¹]

Preparation of Graphitic Oxide

By WILLIAM S. HUMMERS, JR., AND RICHARD E. OFFEMAN

RECEIVED SEPTEMBER 25, 1957

The preparation of graphitic oxide by methods described in the literature is time consuming and hazardous. A rapid, relatively safe method has been developed for preparing graphitic oxide from graphite in what is essentially an anhydrous mixture of sulfuric acid, sodium nitrate and potassium permanganate.

Introduction

Graphitic oxide, sometimes called graphitic acid, has been known for almost a century. It was first prepared by Brodie² in 1859 by repeated treatment of Ceylon graphite with an oxidation mixture consisting of potassium chlorate and fuming nitric acid. Since then, many other procedures have been devised for forming graphitic oxide, nearly all dependent upon strong oxidizing mixtures containing one or more concentrated acids and oxidizing materials.³⁻⁶

The methods most commonly used at the present time are the original Brodie synthesis and one described by Staudenmaier,⁹ in which the graphite is oxidized in concentrated sulfuric and nitric acids with potassium chlorate. Recent workers in the field such as Hofmann and Frenzel⁶ and Hamdi⁷ using the Staudenmaier method found the process time consuming and hazardous. The Staudenmaier-Hofmann-Hamdi method involved the addition of potassium chlorate to a mixture of concentrated sulfuric acid, concentrated (63%) nitric acid and graphite. The potassium chlorate was stirred slowly and carefully into the mixture over a period of one week with cooling. The chlorine dioxide evolved was removed with an inert gas such as carbon dioxide or nitrogen. The process required more than 10 g. of potassium chlorate for each gram of treated graphite and explosion was a constant hazard.

In the present method,⁸ the oxidation of graphite to graphitic oxide is accomplished by treating graphite with essentially a water-free mixture of concentrated sulfuric acid, sodium nitrate, and potassium permanganate. The entire process requires less than two hours for completion at temperatures below 45° and can be carried out safely providing reasonable care is maintained in observing the temperature limitations.

Experimental

The graphitic oxide was prepared by stirring 100 g. of powdered flake graphite (Dixon's #635, 325 mesh) and 50 g. of sodium nitrate into 2.3 liters of 66° Be technical sulfuric acid. The ingredients were mixed in a 15-liter battery jar that had been cooled to 0° in an ice-bath as a safety measure. While maintaining vigorous agitation, 800 g. of potassium permanganate was added to the suspension. The rate of

addition was controlled carefully to prevent the temperature of the suspension from exceeding 20°.

The ice-bath was then removed and the temperature of the suspension brought to 35 ± 3°, where it was maintained for 30 minutes. As the reaction progressed, the mixture gradually thickened with a diminishing in effervescence. At the end of 20 minutes, the mixture became pasty with evolution of only a small amount of gas. The paste was brownish grey in color.

At the end of 30 minutes, 4.6 liters of water was slowly stirred into the paste, causing violent effervescence and an increase in temperature to 98°. The diluted suspension, now brown in color, was maintained at this temperature for 15 minutes. The suspension was then further diluted to approximately 14 liters with warm water and treated with 3% hydrogen peroxide to reduce the residual permanganate and manganese dioxide to colorless soluble manganese sulfate. Upon treatment with the peroxide, the suspension turned bright yellow. The suspension was filtered resulting in a yellow-brown filter cake. The filtering was conducted while the suspension was still warm to avoid precipitation of the slightly soluble salt of mellitic acid⁹ formed as a side reaction.

After washing the yellowish-brown filter cake three times with a total of 14 liters of warm water, the graphitic oxide residue was dispersed in 32 liters of water to approximately 0.5% solids. The remaining salt impurities were removed by treating with resinous anion and cation exchangers. The dry form of graphitic oxide was obtained by centrifugation followed by dehydration at 40° over phosphorus pentoxide *in vacuo*.

Results

The effectiveness of the oxidation method can be judged by the proportion of graphitic oxide in the product or by its carbon to oxygen ratio. Well reacted samples of graphitic oxide will have a carbon to oxygen atomic ratio lying between 2.1 and 2.9. Also the color of the product when suspended in water may be used as criterion for the degree of oxidation of the graphite. The product richest in graphitic oxide will have a bright yellow color whereas poorer samples with higher carbon-to-oxygen ratios will have a green to black hue.

An analysis of the dried graphitic oxide prepared by the present method is compared in Table I with a sample made by the Staudenmaier procedure. The present synthesis resulted in approximately 188 g. of graphitic oxide containing 23% water and 2% ash. The carbon and hydrogen were determined by the combustion of graphitic oxide with cupric oxide.^{10,11}

TABLE I

Method	% by weight				Carbon-to-oxygen atomic ratio
	Carbon	Oxygen	Water	Ash	
Acid-permanganate-nitrate	47.06	27.97	22.99	1.98	2.25
Staudenmaier	52.11	23.99	22.22	1.90	2.89

HOUSTON, TEXAS

(9) E. Juettner, *This Journal*, **89**, 208 (1937).

(10) W. A. Selvig and W. C. Ratliff, *Trans. Amer. Electrochem. Soc.*, **37**, 121 (1920).

(11) H. Thiele, *Z. anorg. allgem. Chem.*, **190**, 145 (1930).

(1) This research conducted under National Lead Company Fellowship at the Mellon Institute of Industrial Research.

(2) B. Brodie, *Phil. Trans.*, **149**, 249 (1859).

(3) B. K. Brown and O. W. Storey, *Trans. Amer. Electrochem. Soc.*, **83**, 120 (1928).

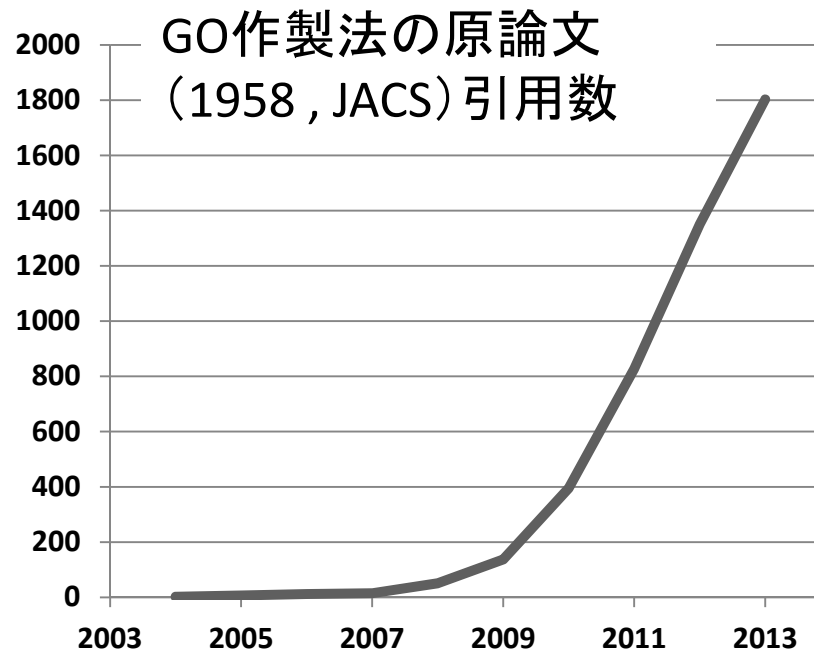
(4) G. Charpy, *Compt. rend.*, **148**, 920 (1909).

(5) U. Hofmann and A. Frenzel, *Ber.*, **63B**, 1248 (1930).

(6) L. Staudenmaier, *ibid.*, **31**, 1481 (1898); **33**, 1394 (1899); **35**, 2824 (1900).

(7) H. Hamdi, *Kolloid Beihfte*, **84**, 554 (1943).

(8) W. S. Hummers, U. S. Patent No. 2,798,878 (1957).



[Citation](#) (Web of knowledge)

2013 1803

2012 1351

2011 827

2010 395

2009 137

2008 51

2007 15

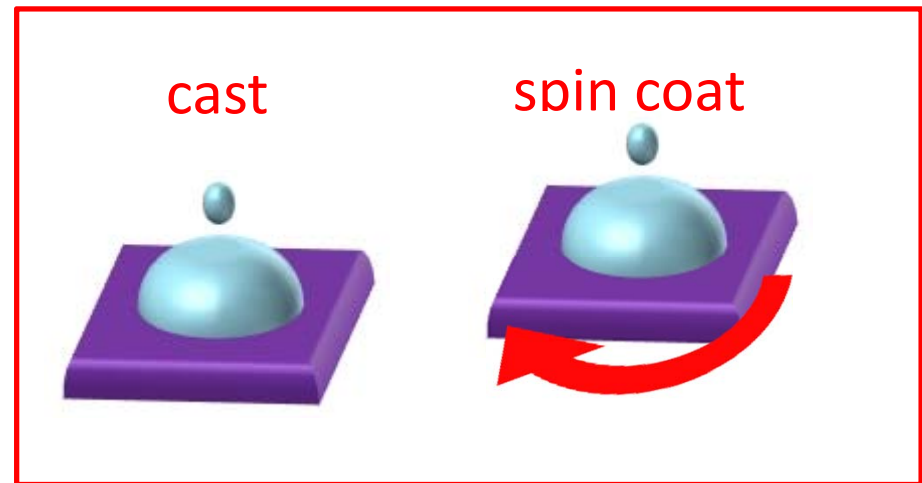
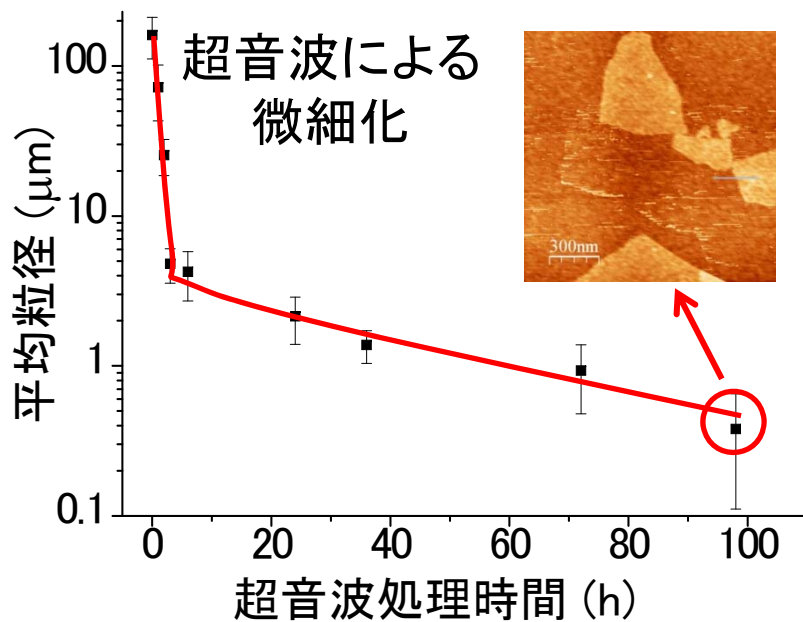
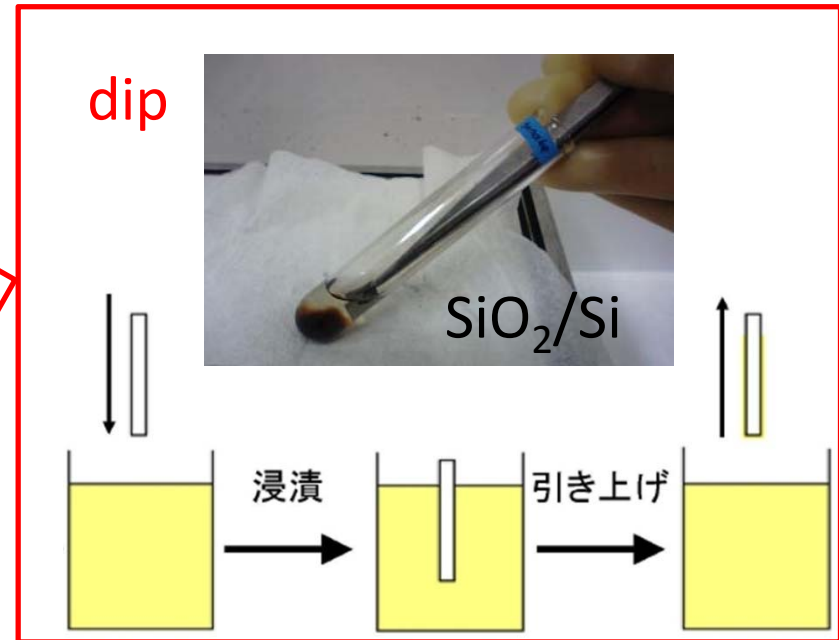
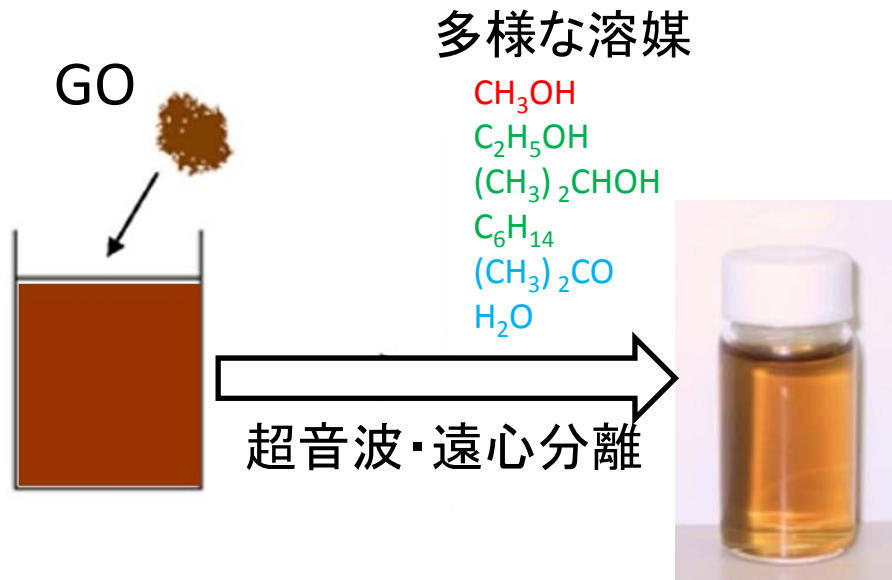
2006 12

2005 7

2004 0

-1958 103 (2.2回/年)

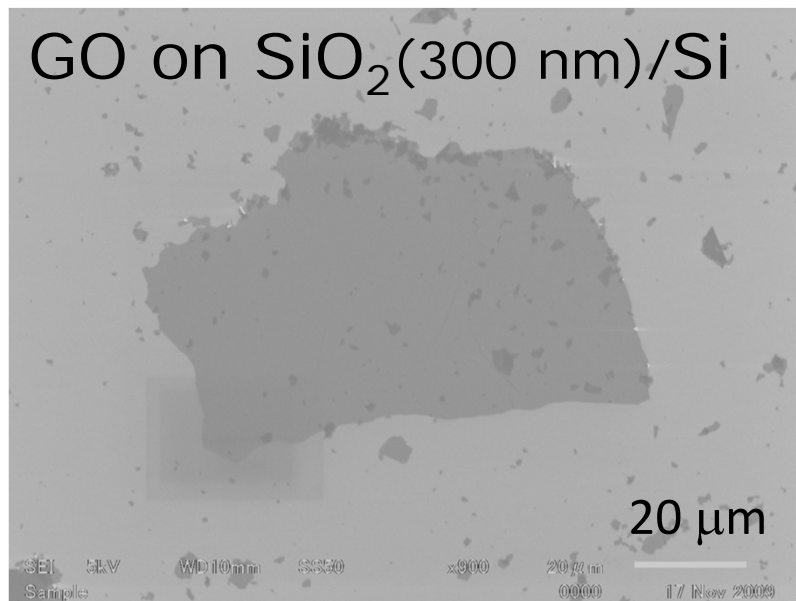
酸化グラフェン (GO) シートの成膜



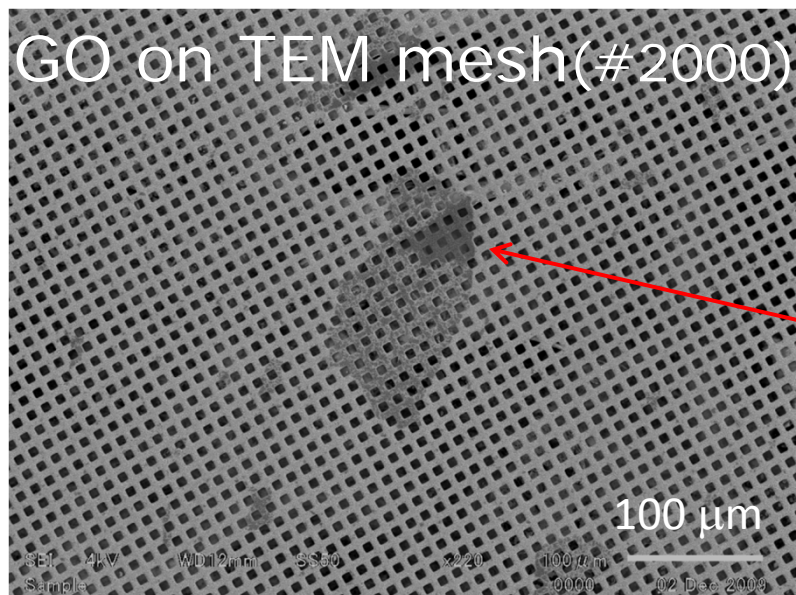
酸化グラフェン (GO) 顕微鏡観察

SEM(電子顕微鏡)

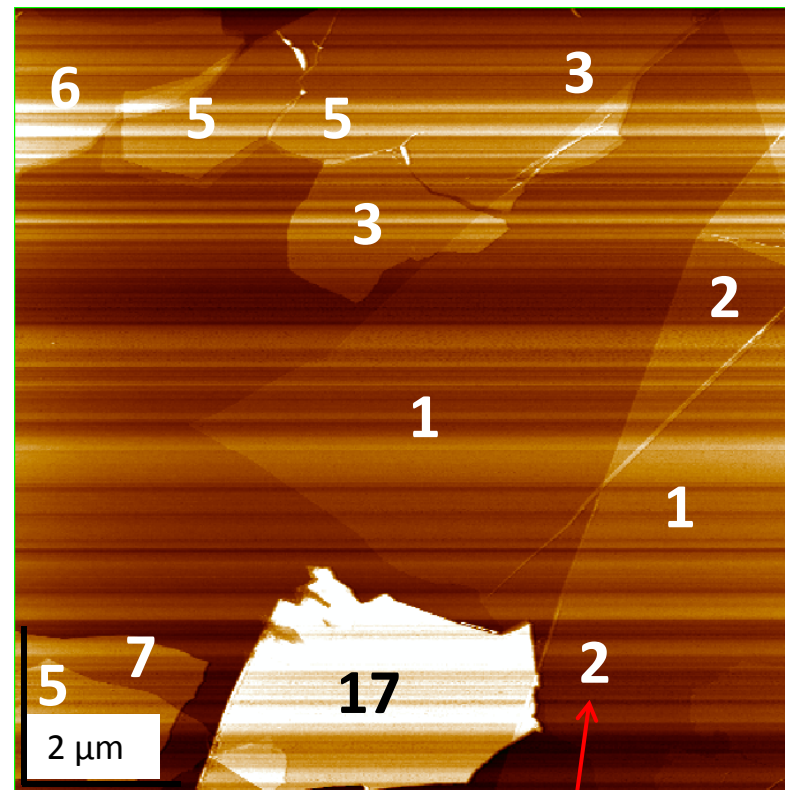
GO on SiO₂(300 nm)/Si



GO on TEM mesh(#2000)



AFM (原子間力顕微鏡)

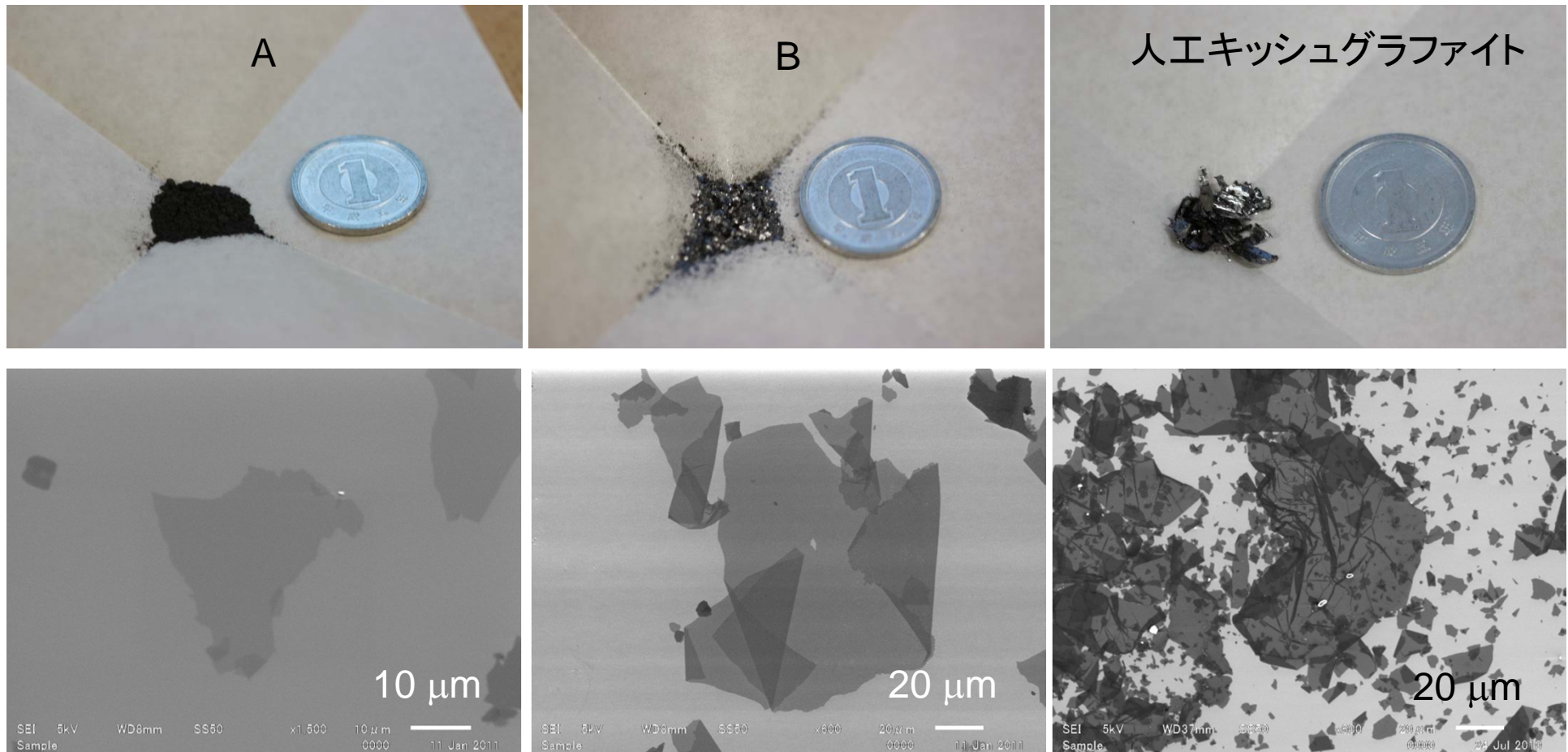


重なり

数字は層数

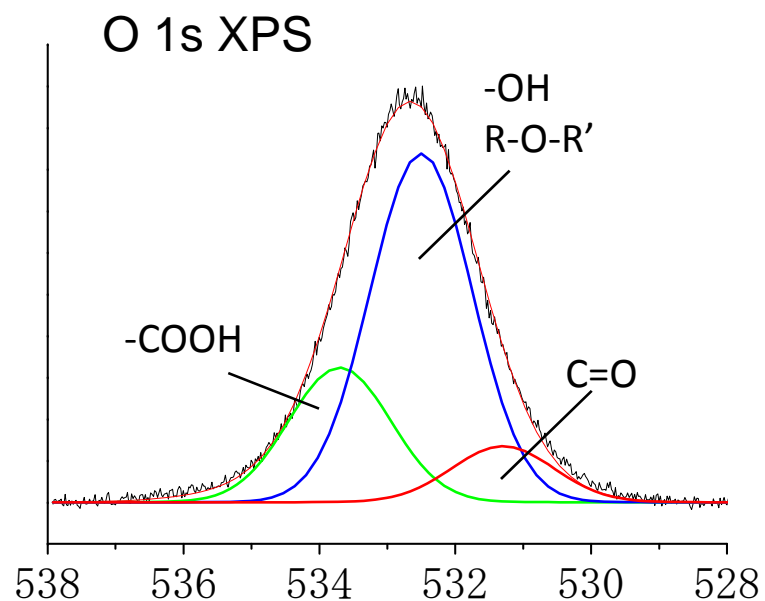
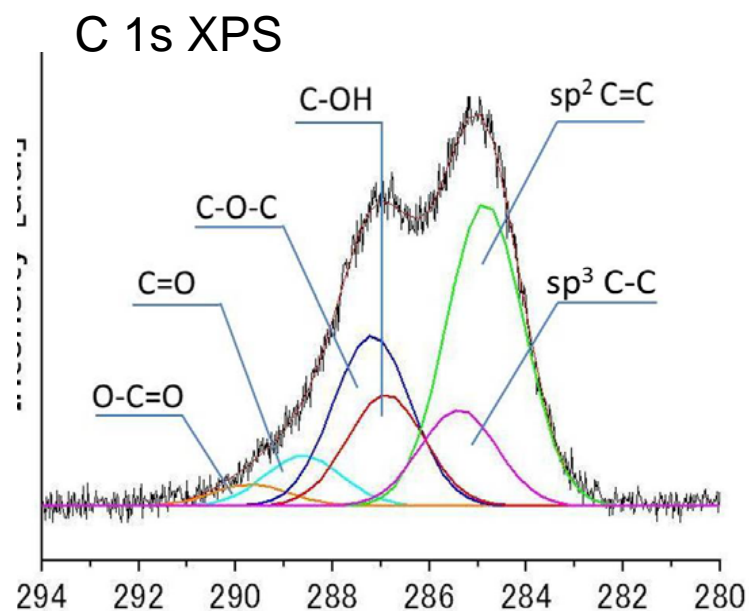
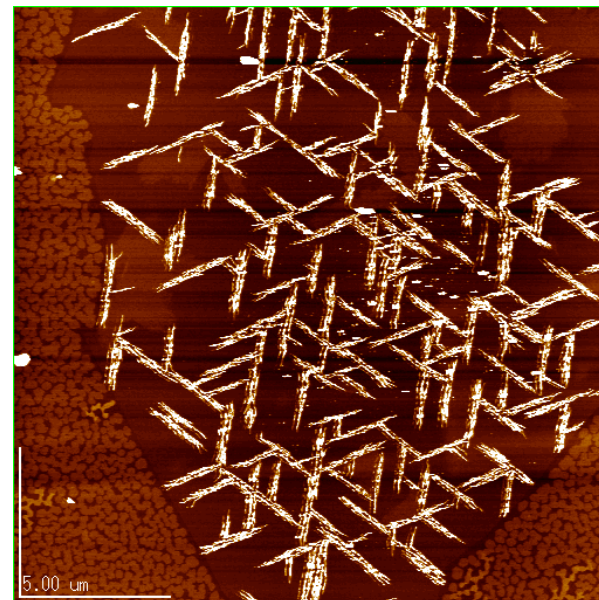
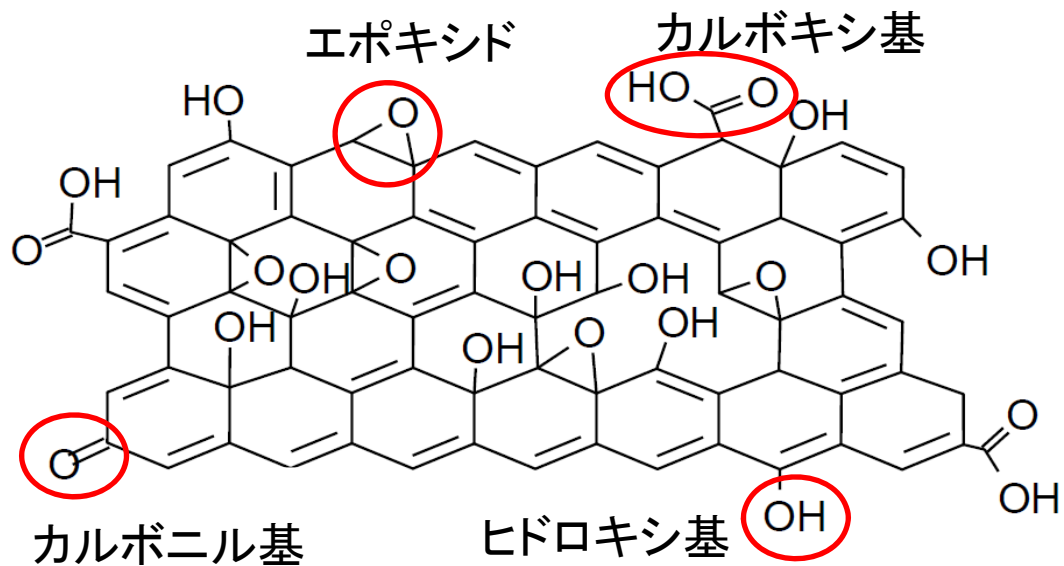
報告されている酸化グラフェンでは最大

黒鉛原料による酸化グラフェン (GO) のサイズ変化

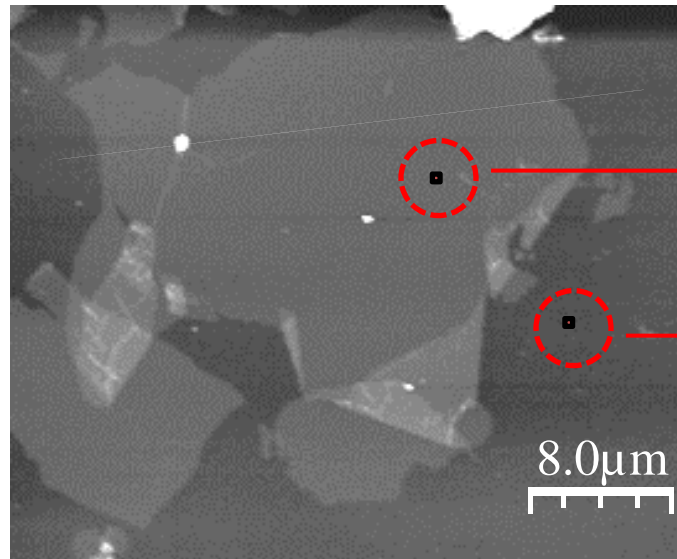


出発原料	A	B	人工キッシュ グラファイト
原料粒径 / μm	~30	several hundred	several thousand
GOのサイズ/ μm	10~30	40~100	40~100

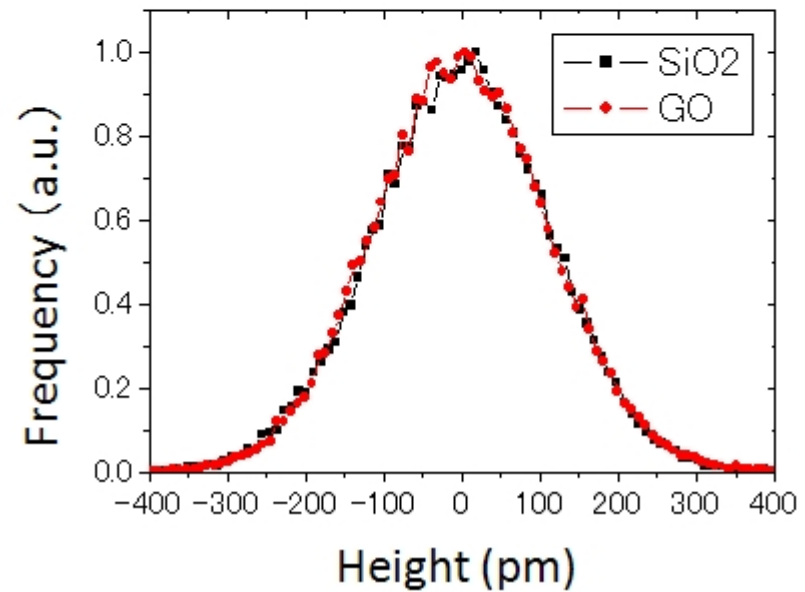
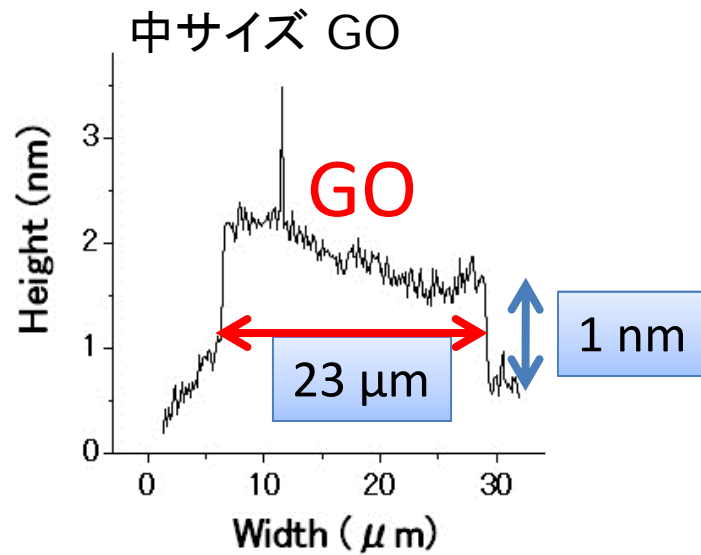
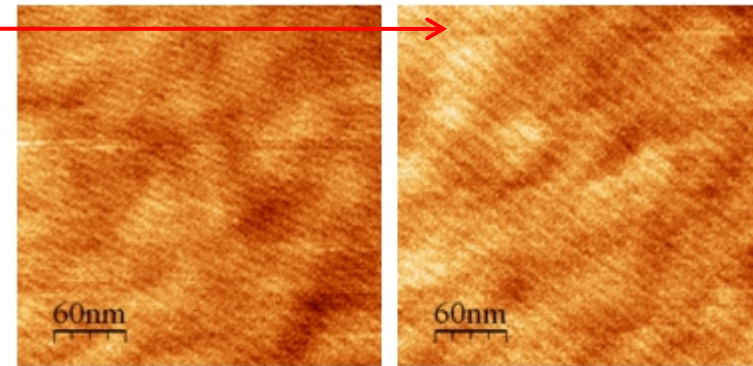
酸化グラフェン(GO) 構造モデル



酸化グラフェン(GO) 表面の平坦さ



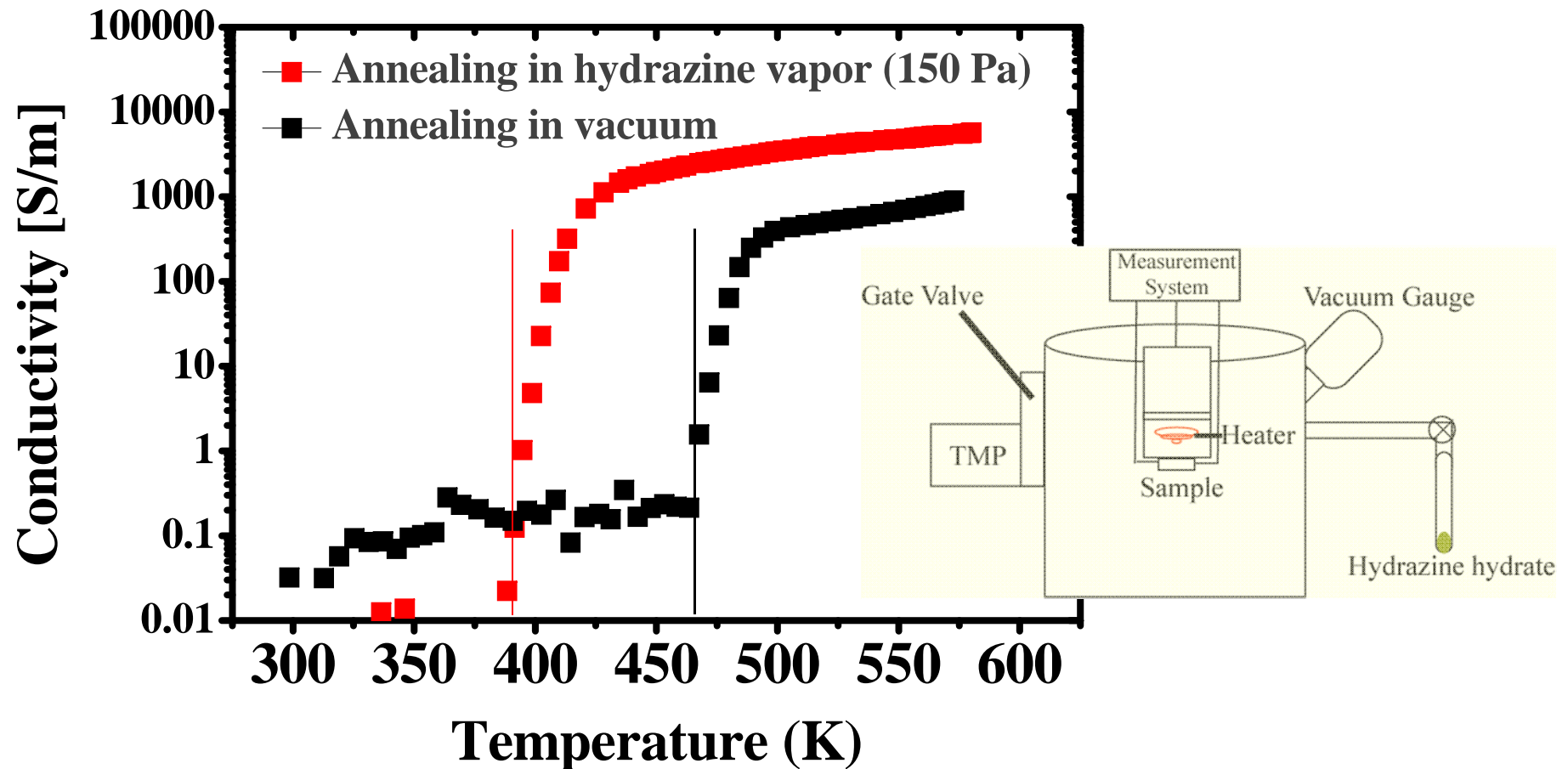
表面粗さ
300 nm □ (Si) 300 nm □ (GO)



単層GO が 20 μm 以上広がる

GO の平坦さは SiO₂ と同程度

酸化グラフェン (GO) 還元による伝導度変化

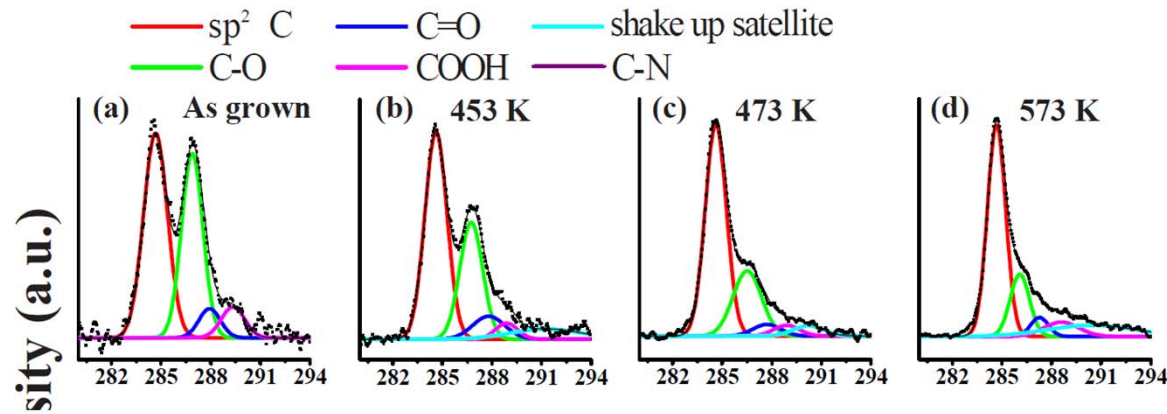




Threshold temperature; T_c

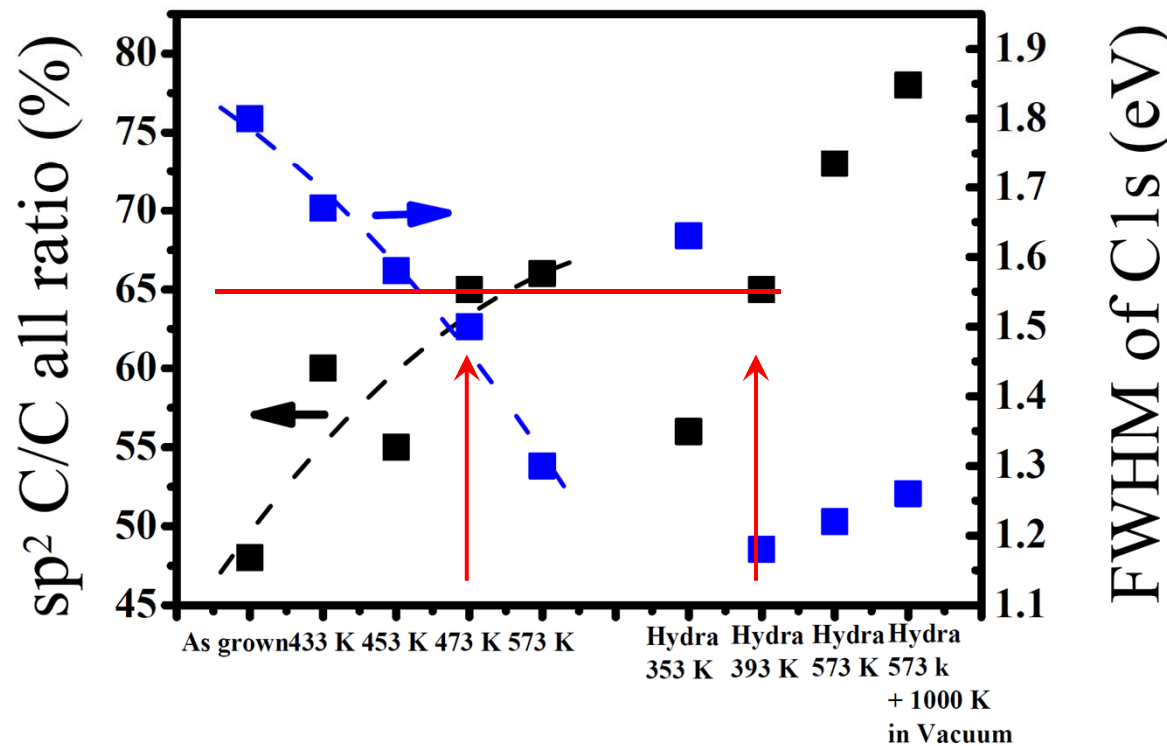
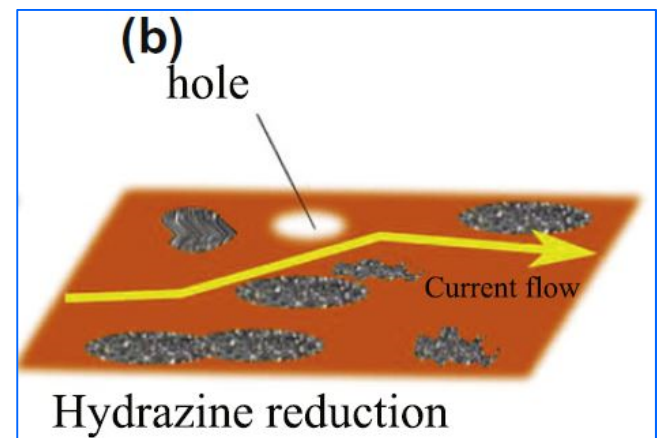
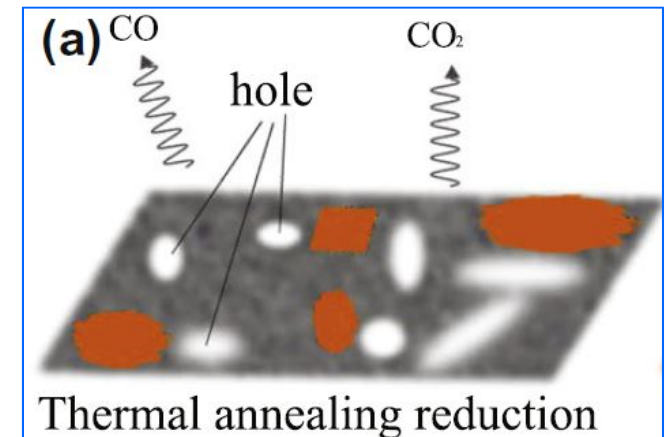
465 K (thermal annealing in vacuum)

390 K (annealing in hydrazine vapor)

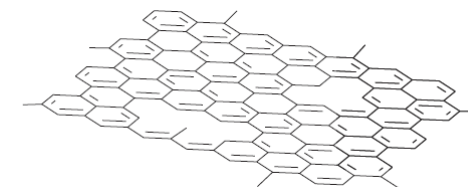
酸化グラフェン (GO) 還元による伝導度回復



 Disorder area
 Honeycomb structure

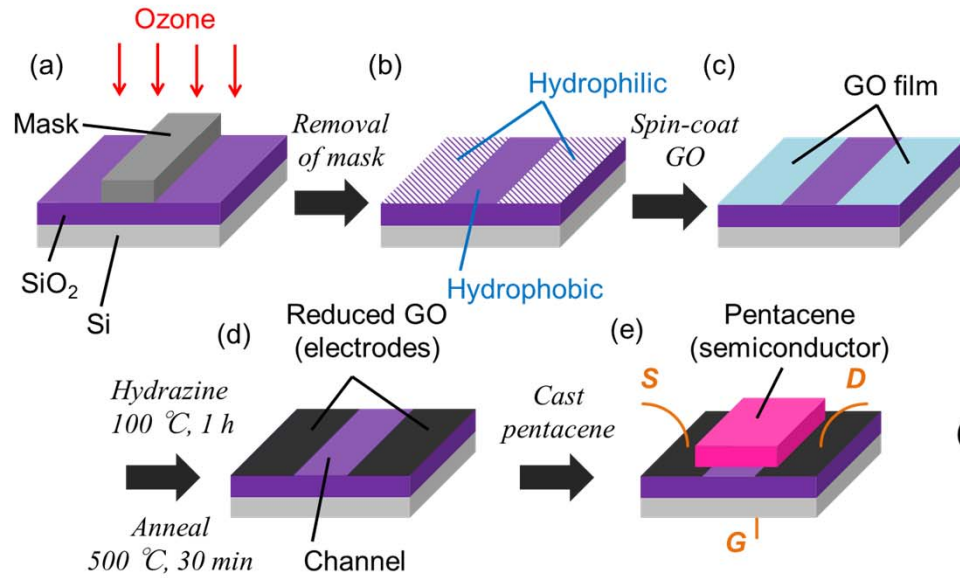


65 % sp² 2次元の伝導経路形成 (パーコレーション)



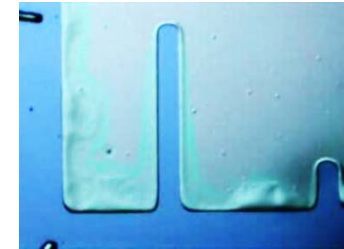
酸化グラフェン (GO) デバイス応用

GO electrodes for organic FET

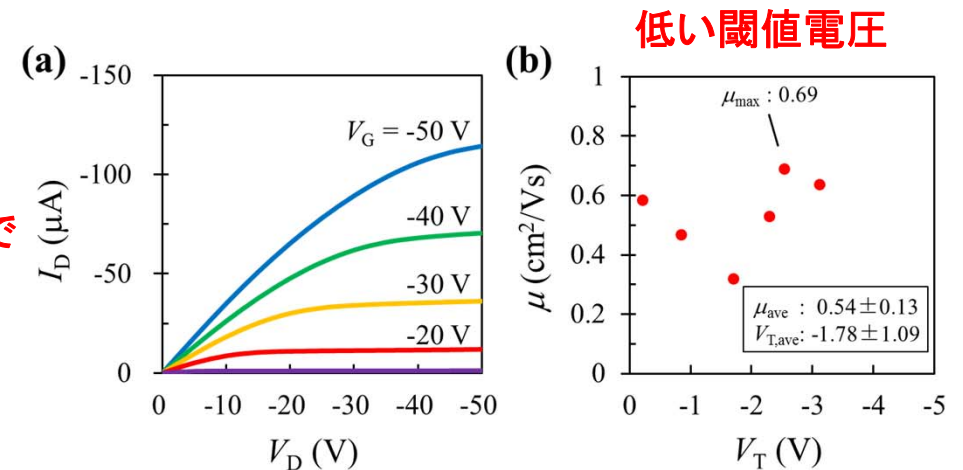
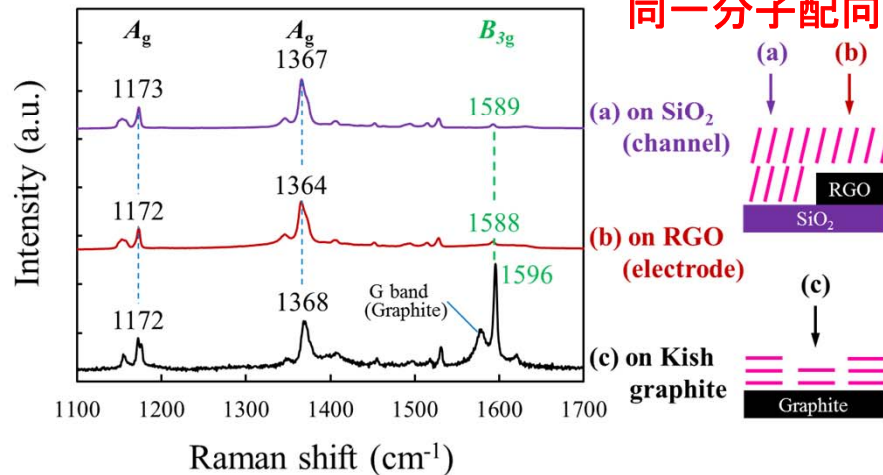


GO liq. cast

partially dried



チャンネル上, 電極上で
同一分子配向

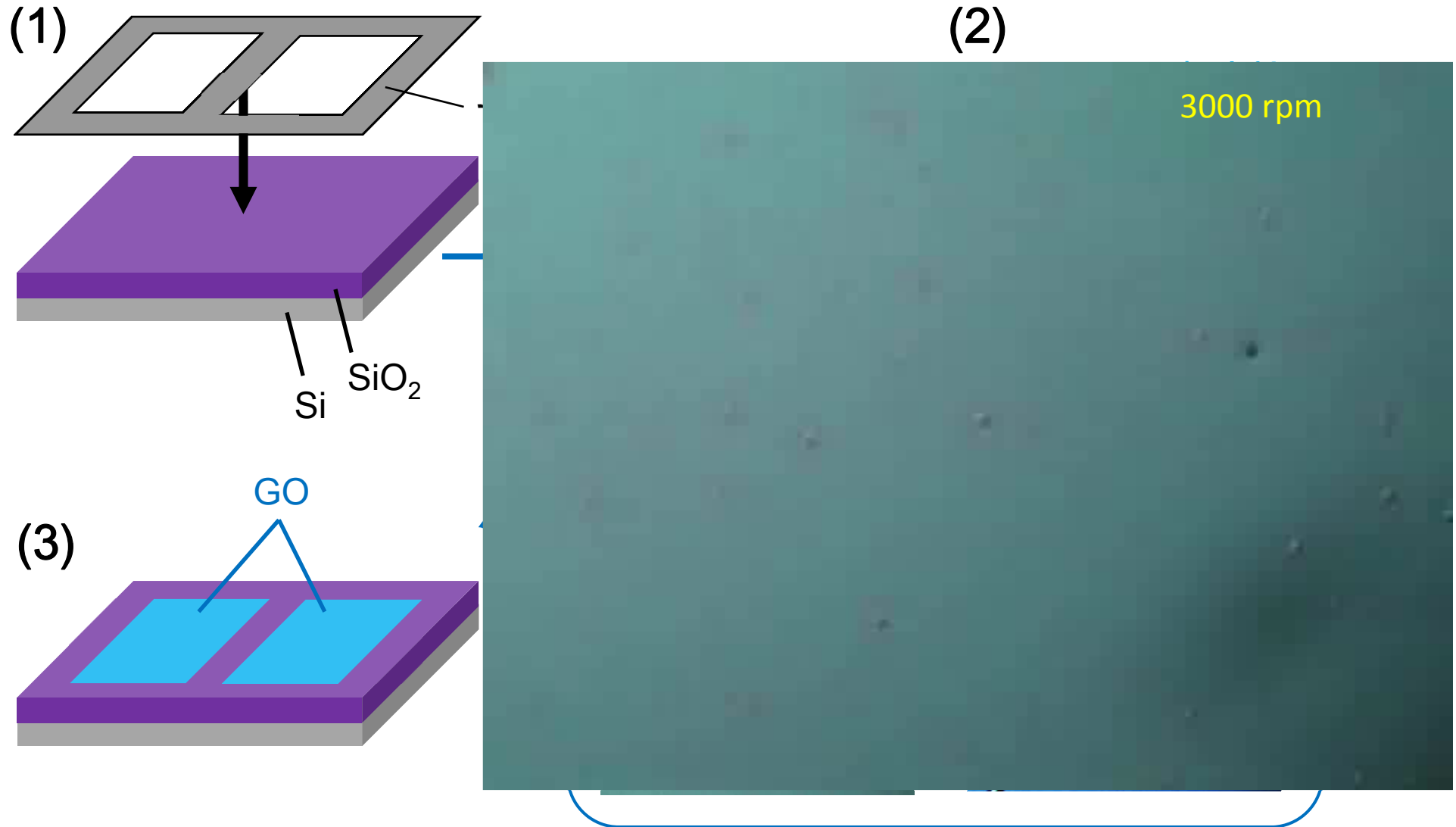


溶液プロセスによる
有機トランジスタ電極に最適

submitted

酸化グラフェン (GO) デバイス応用

スピコート動画



酸化グラフェン (GO) 応用研究例

特徴

大量合成	可
コスト	低
環境負荷	低
可溶	親水性, 疎水性

応用研究例

- energy storage materials
- paper like materials
- polymer composites
- liquid crystal devices
- mechanical resonators
- electrode for Li ion battery
- transparent electrode for solar cell
- supercapacitor
- electrochemical sensor

