Chemical Modification of Graphene Oxide

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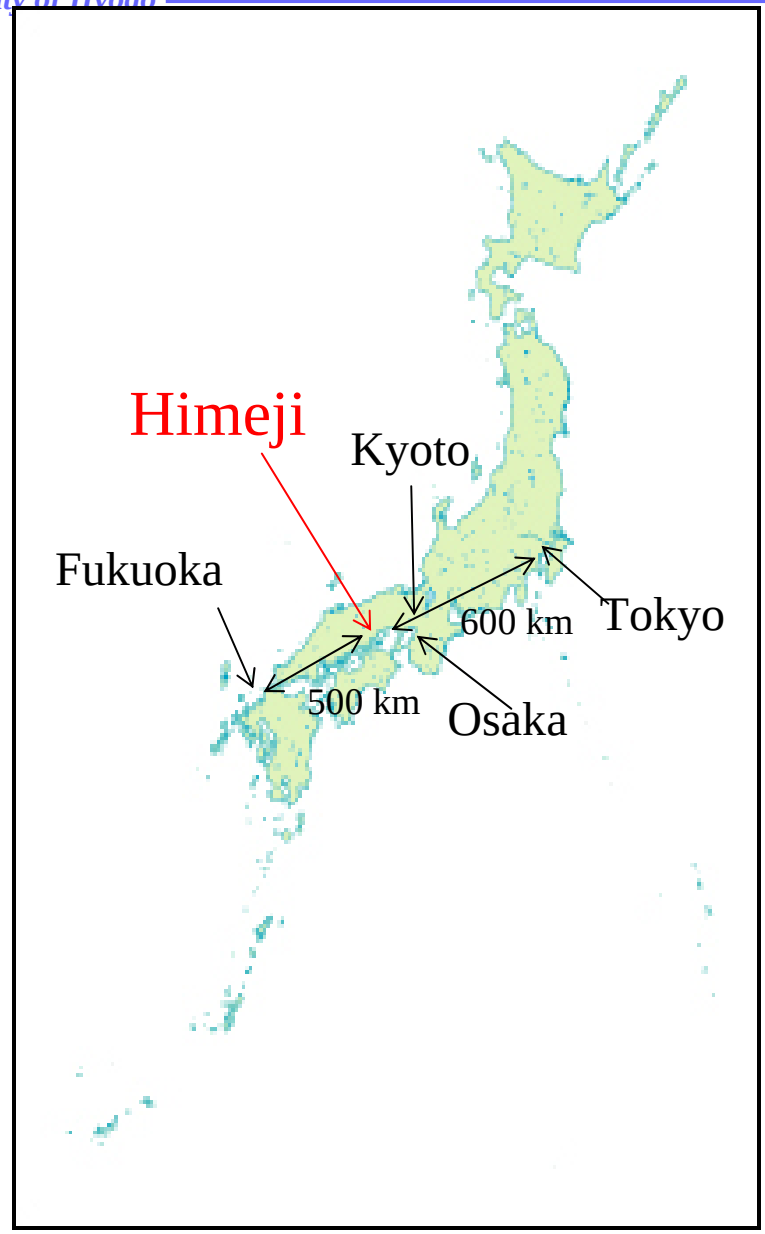

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Himeji Castle, one of the UNESCO World Heritage

Outline

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- ✓ Introduction
  - Graphene and graphene oxide (graphite oxide: GO)

- ✓ Checmail modification of GO
  (Preparation of intercalation compounds of GO)
  - Polymer
  - Cationic surfactant
  - Alkylamines
  - silylation of GO

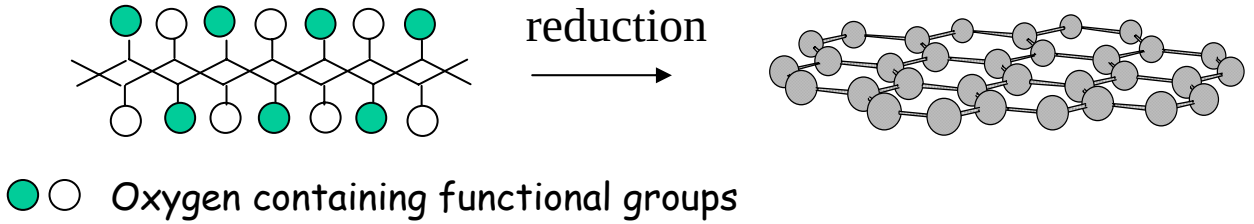
- ✓ Preparation and adsorption properties of pillared carbons

- ✓ Preparation of transparent and conducting carbon films

Graphene and graphite oxide

Preparation of graphene

- ✓Scotch Tape Method (Mechanical exfoliation of graphite)
- ✓Thermal decomposition of SiC
- ✓CVD
- ✓Reduction of graphite oxide nanosheet



About graphite oxide: GO

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- Preparation of GO

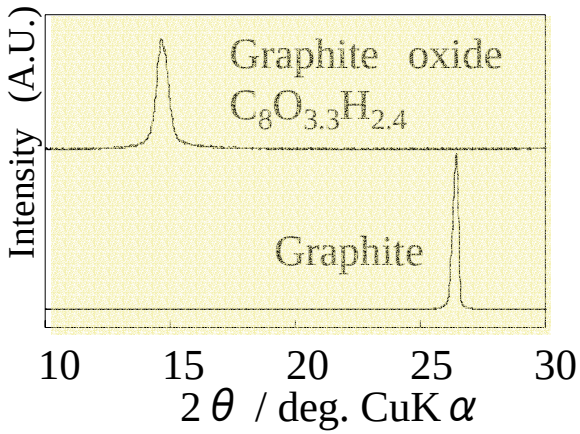
strong oxidizing reagents — excess water

$nC + HX \rightarrow C_n^+X^- \rightarrow$ "overoxidized" $C_n^+X^- \rightarrow$ GO

concentrated acid

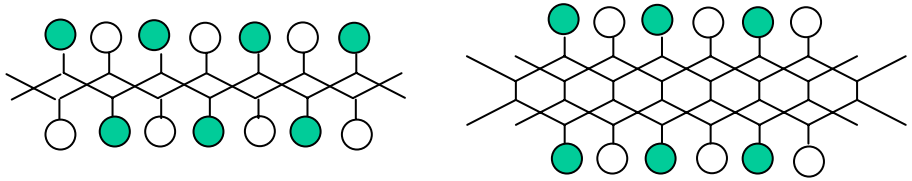
X^- : NO_3^-, ClO_4^-, HSO_4^-, etc

Oxidizing reagents: $KClO_3$, $KMnO_4$



- Functional groups: -COH (acidic, important for chemi modification of GO), C-O-C, -COOH (edge)

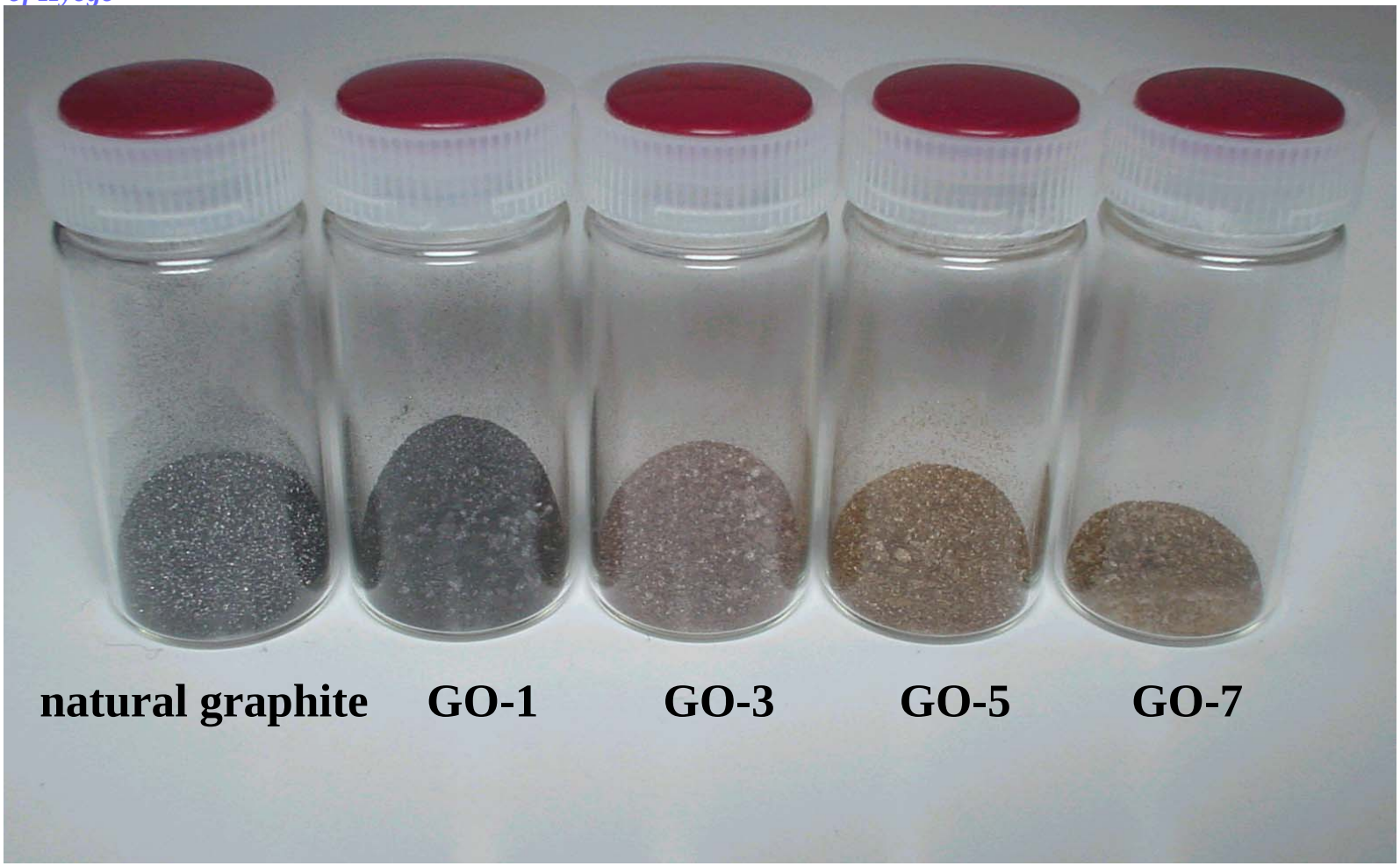
- C/O=2～3
- interlayer spacing: 0.6-1.1nm
- Structure models



Stage 1 type Stage 2 type

Nanosheet solution of GO

Color of various GO



The color changed from black to brown when graphite was oxidized by the modified Brodie's method repeatedly.

Recent researches on GO

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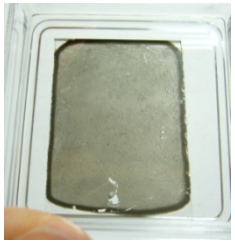
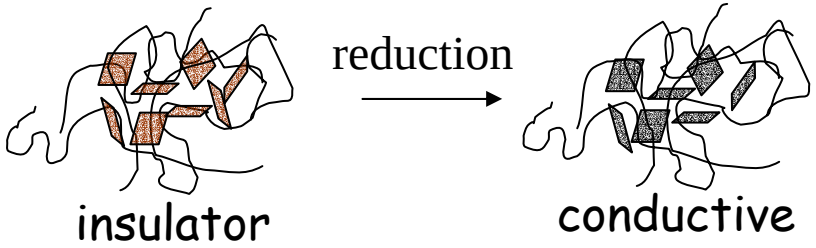
2005～
precursors of graphene

transparent and conductive carbon films ⟶



---Many papers!!

additive to polymers

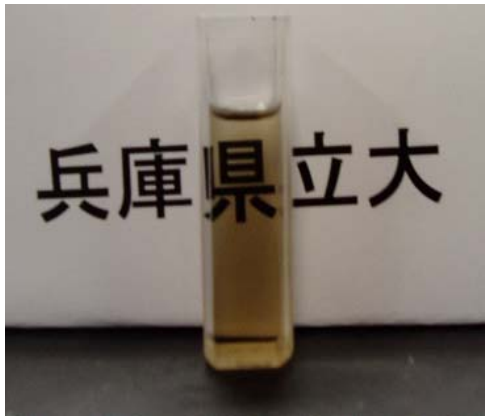


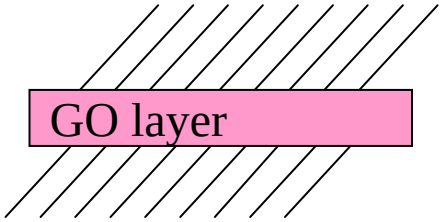
1995～

host of intercalation compounds

- Polymers (poly(ethylene oxide), polyvinylalcohol, polyaniline, etc)
- Cationic surfactants
- Alkylamine
- Dibutyltinoxide
- silylating reagents

} Hydrophobic and exfoliate in organic solvents





Nanosheet solution of hydrophobized GO

Type of chemical modifications

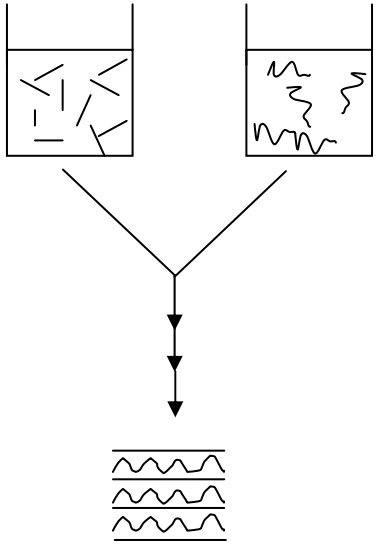
Type of interaction	Intercalated species	reaction
Hydrogen bonding	Polymer	C-OH + P → C-OH ··· P
Ionic bonding	cationic surfactant	$C\text{-}O^{-}H^{+} + X^{+} \rightarrow C\text{-}O^{-}\ X^{+} + H^{+}$ (ion exchange)
	alkylamines	$C\text{-}O^{-}H^{+} + XNH_2 \rightarrow C\text{-}O^{-}NH_3^{+}X$ (acid/base)
Covalent bonding	silylating reagents	$C\text{-}OH + XSiCl_3 \rightarrow C\text{-}O\text{-}X + 3HCl$
		$C\text{-}OH + XSi(OR)_3 \rightarrow C\text{-}O\text{-}X + 3ROH$
		C-OH + RNCO → C-OCONHR [1]
		$C\text{-}O\text{-}C + IL\text{-}NH_2 \rightarrow C\text{-}NH\text{-}IL$ *, [2]
		$C\text{-}O\text{-}C + NaN_3 + LiAlH_4 \rightarrow C\text{-}NH_2$ [3]

* IL: ionic liquid

1. Stankovich et al, Carbon, 44, 3342 (2006)
2. Yang et al, Chem. Commun., 3880 (2009)
3. R. Salvio, et al, Chem. Eur. J. 15, 8235 (2009)

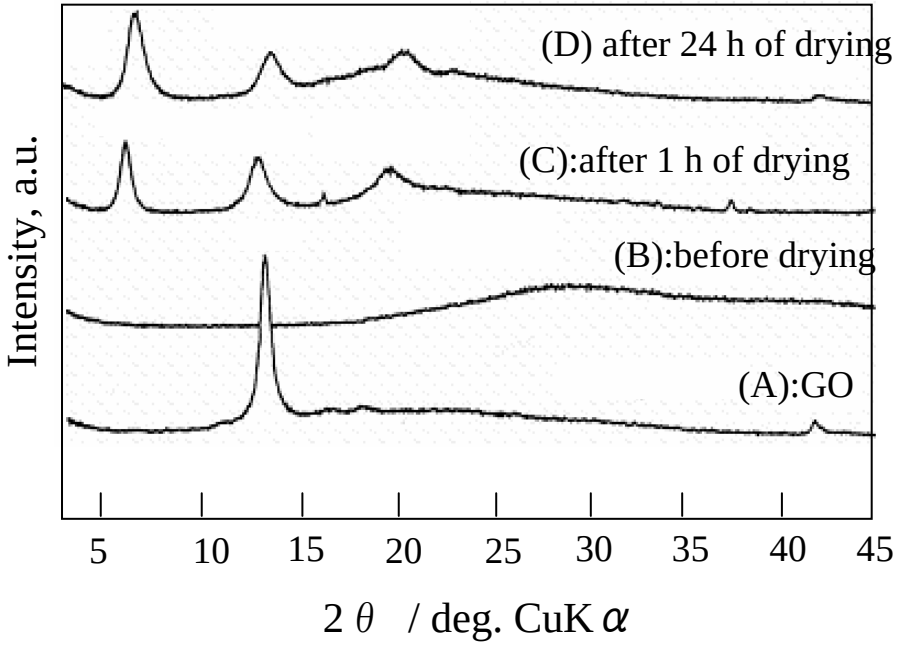
Preparation of polymer intercalated GO

Nanosheet solution of GO



Aqueous solution of polymer

Polymer-intercalated GO
Very stable



Preparation of surfactant intercalated GO

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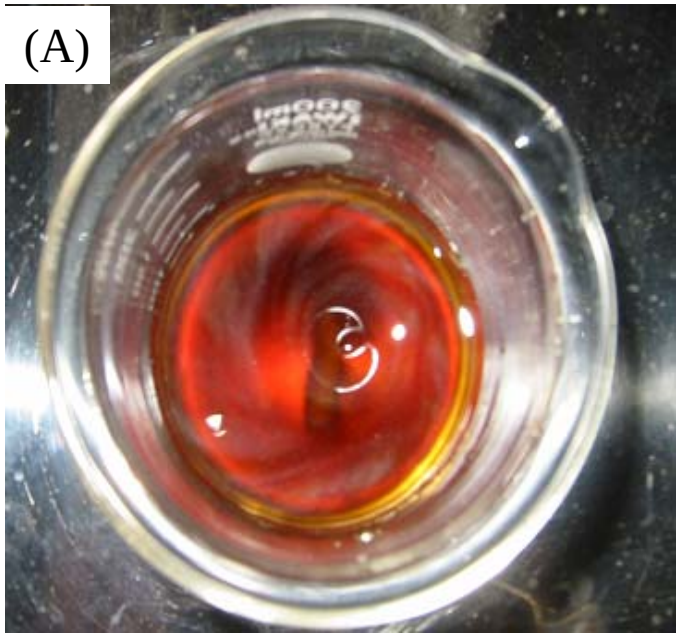
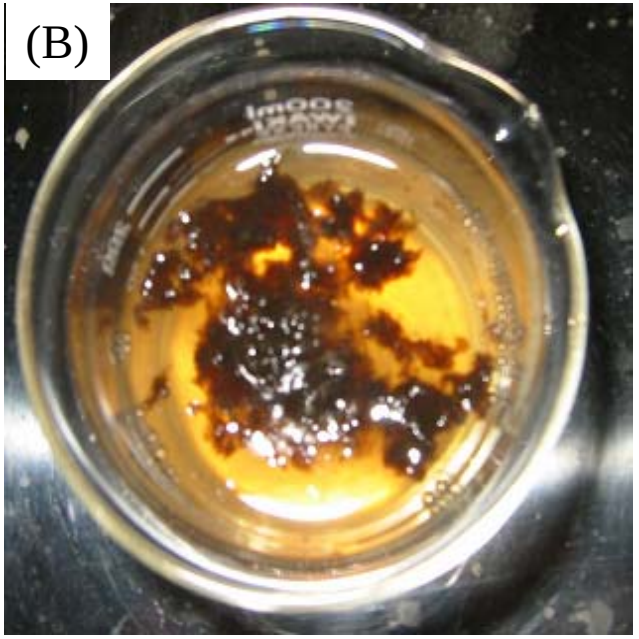
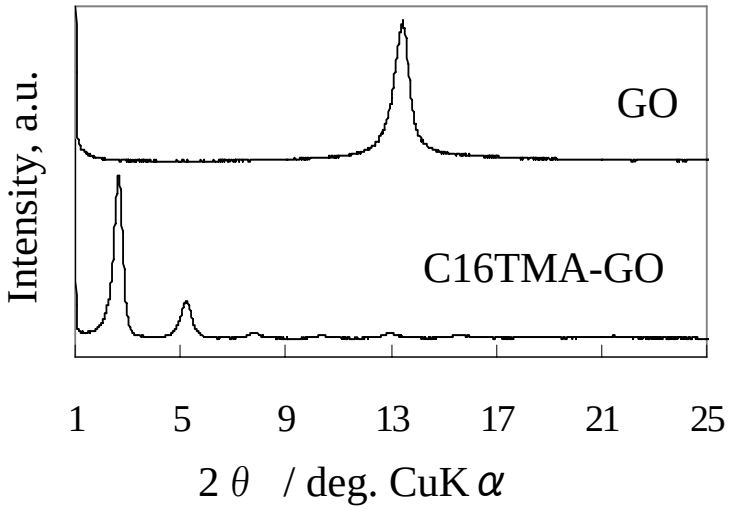


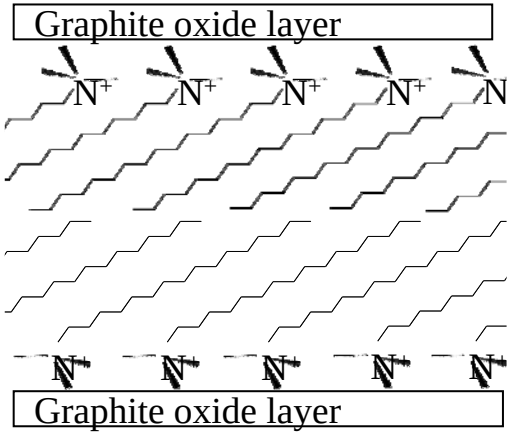
Aqueous solution of cationic surfactant

→

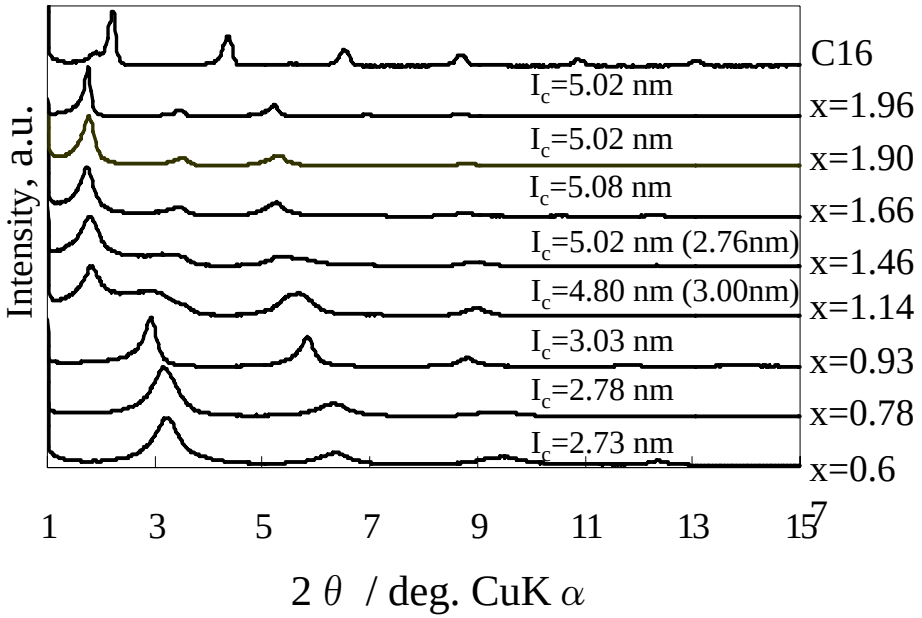
C16TMA
($C_{16}H_{33}N(CH_3)_3^+$)

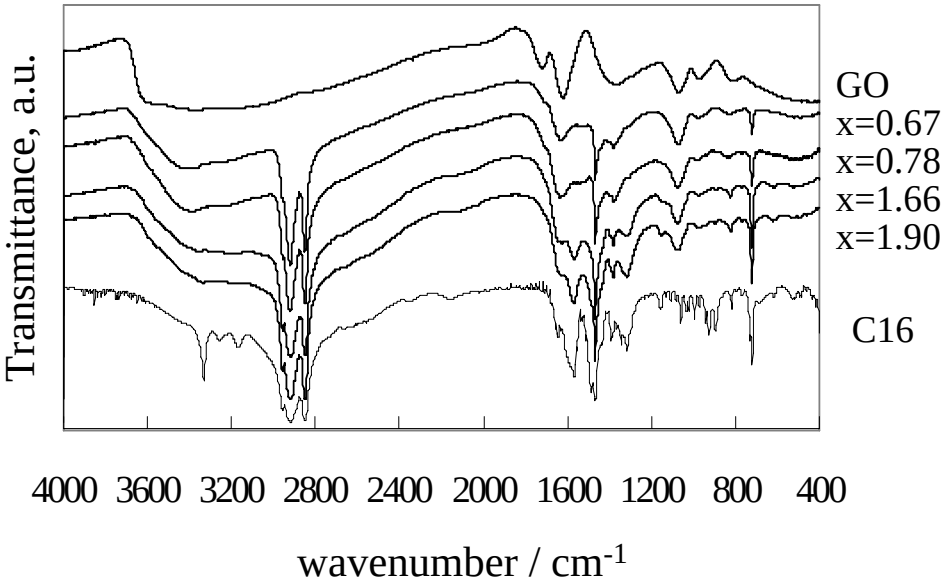






Intercalation of alkylamines

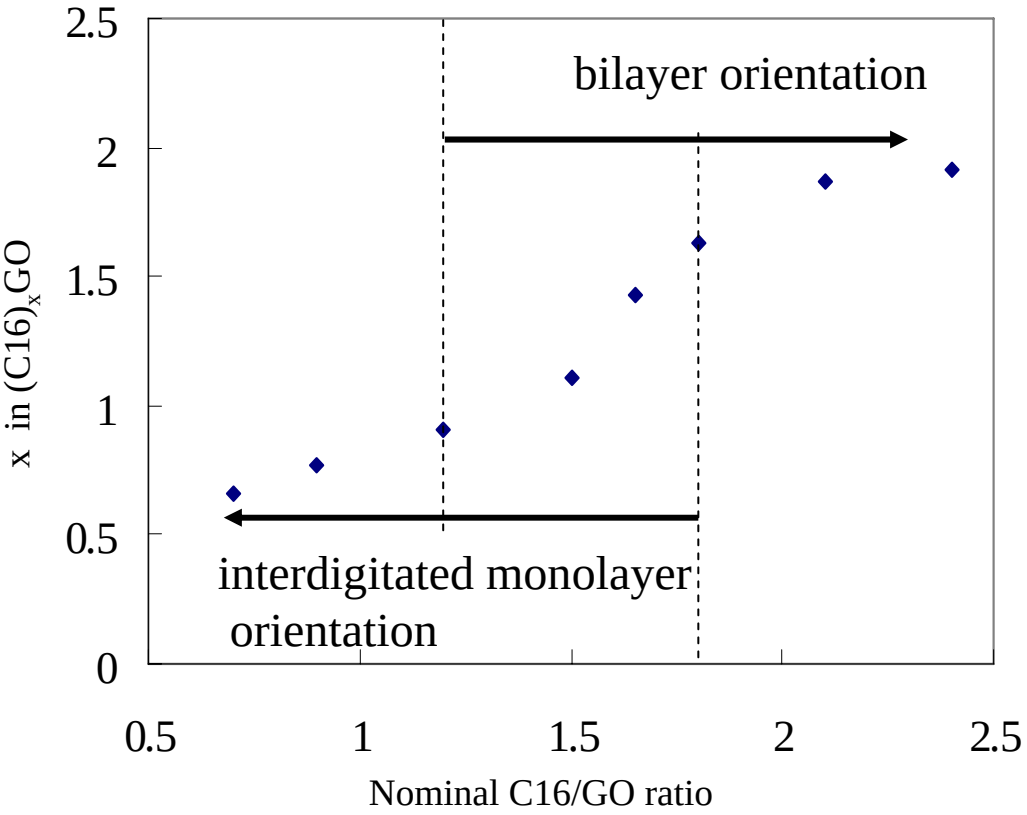


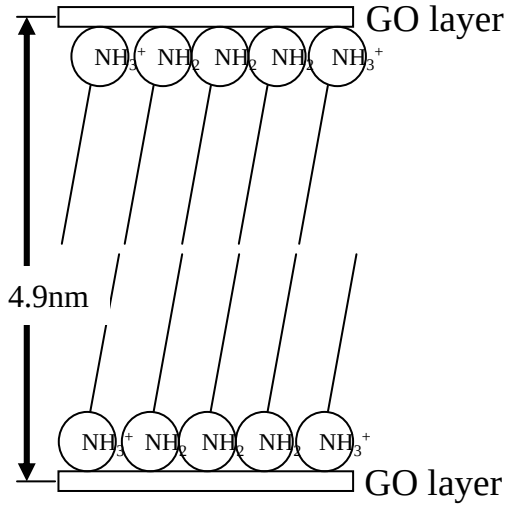


1525 cm^{-1} : NH_3^+ 1380 cm^{-1} : C-OH

1654, 1583 cm^{-1} : NH_2 1090 cm^{-1} : C-O-C

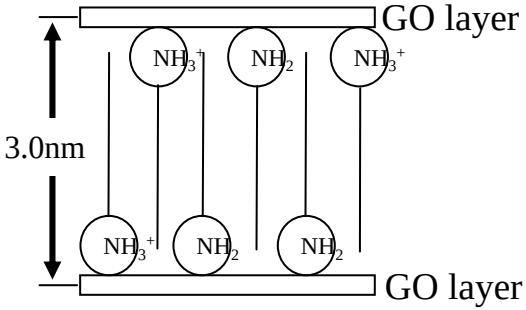
Composition and c-axis structure





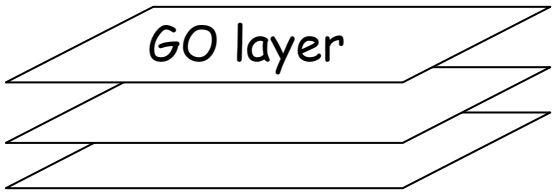
Paraffin type bilayer orientation of alkyl chains

The interlayer spacing was saturated by C16 at 1.9 moleules/GO unit



Interdigitated monolayer type orientation of alkyl chains

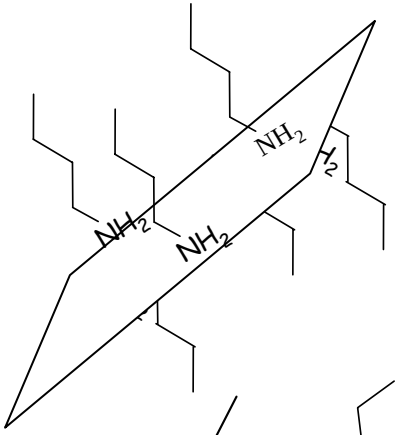
Silylation of GO by alkyltrichlorosilanes



GO

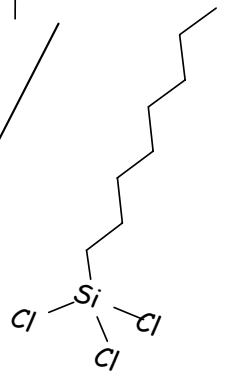
$C_4H_9NH_2$

exfoliation in toluene

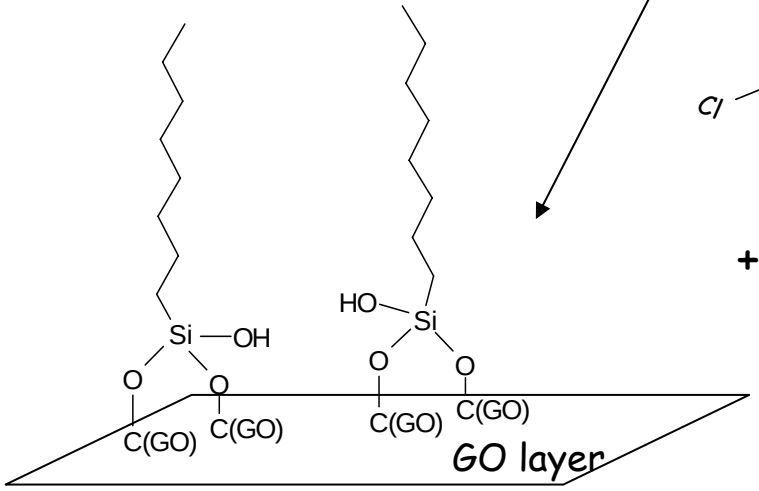


Exfoliated alkylamine-intercalated GO

After adding silylating reagent



+ H_2O



+ $C_4H_9NH_3Cl$

Reaction of GO with 3-aminopropyldiethoxymethysilane

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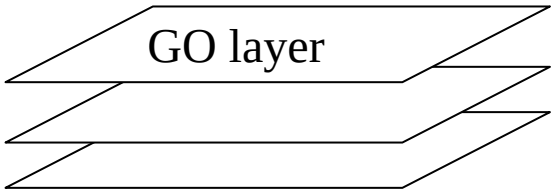
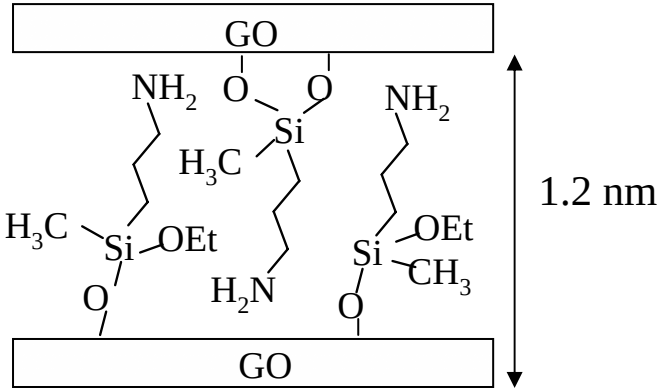


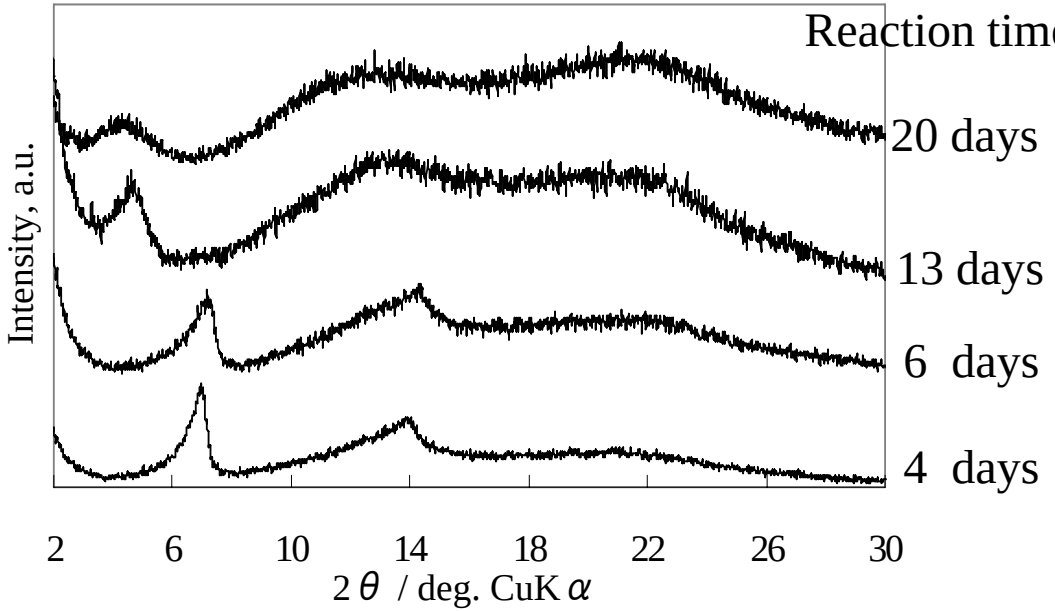
GO

$NH_2C_3H_6SiMe_x(OEt)_{3-x}$

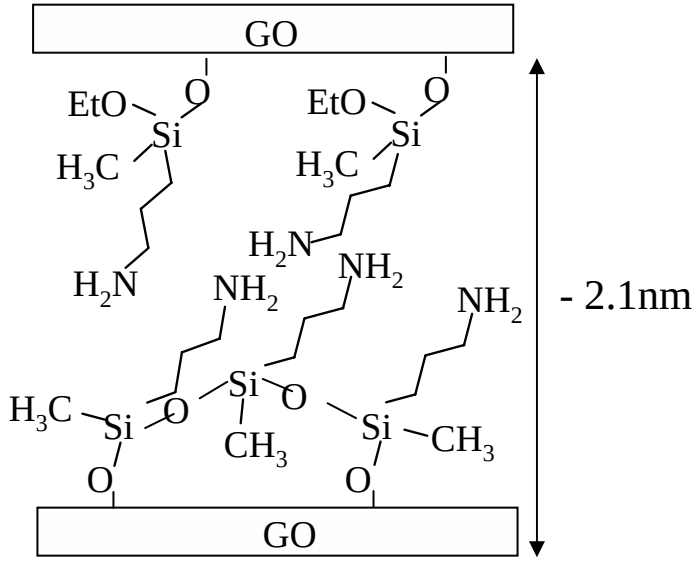
Organic solvent
exfoliation and silylation

Monolayer type（shorter reaction time）





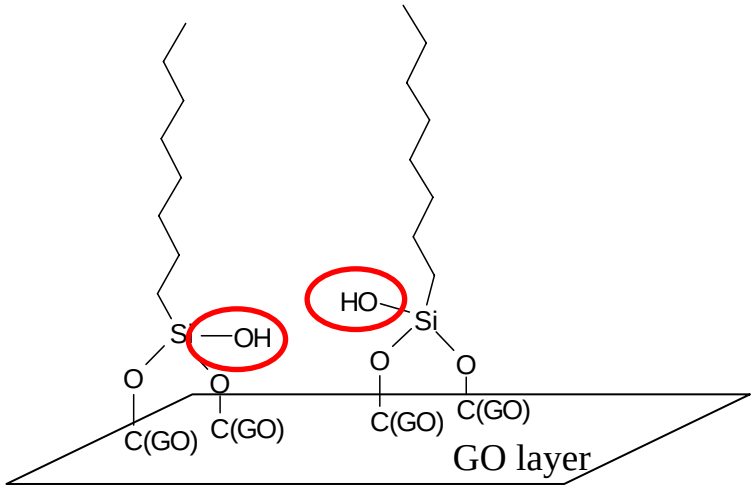
Bilayer type（longer reaction time）

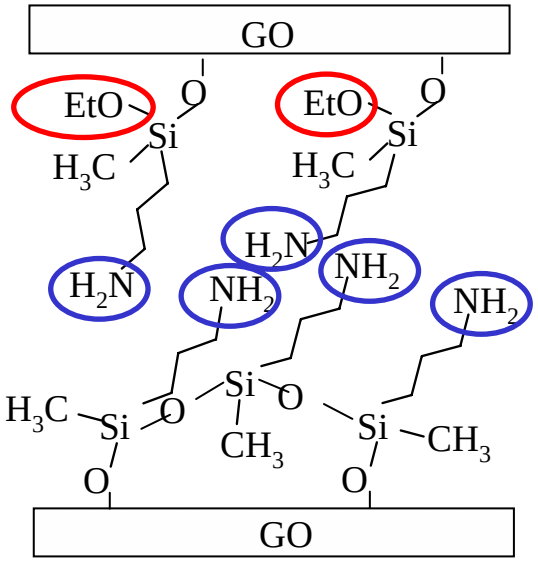


Further chemical modification of silylated GO

- ✓Reaction with aldehydes
- ✓Silylation of silylated GO

Expected reactions of silylated GO





silylated GO

$Si\text{-}OH + RSiCl_3 \rightarrow Si\text{-}O\text{-}SiR(OH)_2$

$Si\text{-}OH + RSi(OEt)_3 \rightarrow Si\text{-}O\text{-}SiR(OEt)_2$

Further silylation by various silylating reagents

$R_1NH_2 + R_2CHO \rightarrow R_1NH{=}CHR_2$

Reaction with aldehydes

↓

Adsorption of formaldehyde

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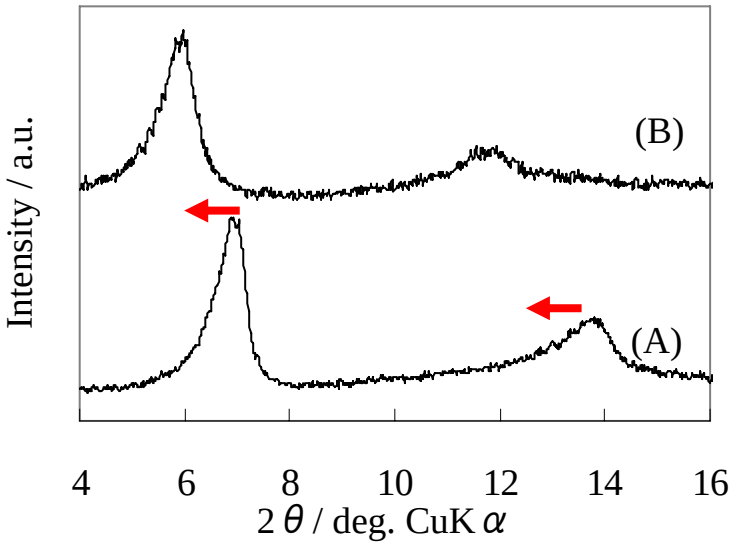
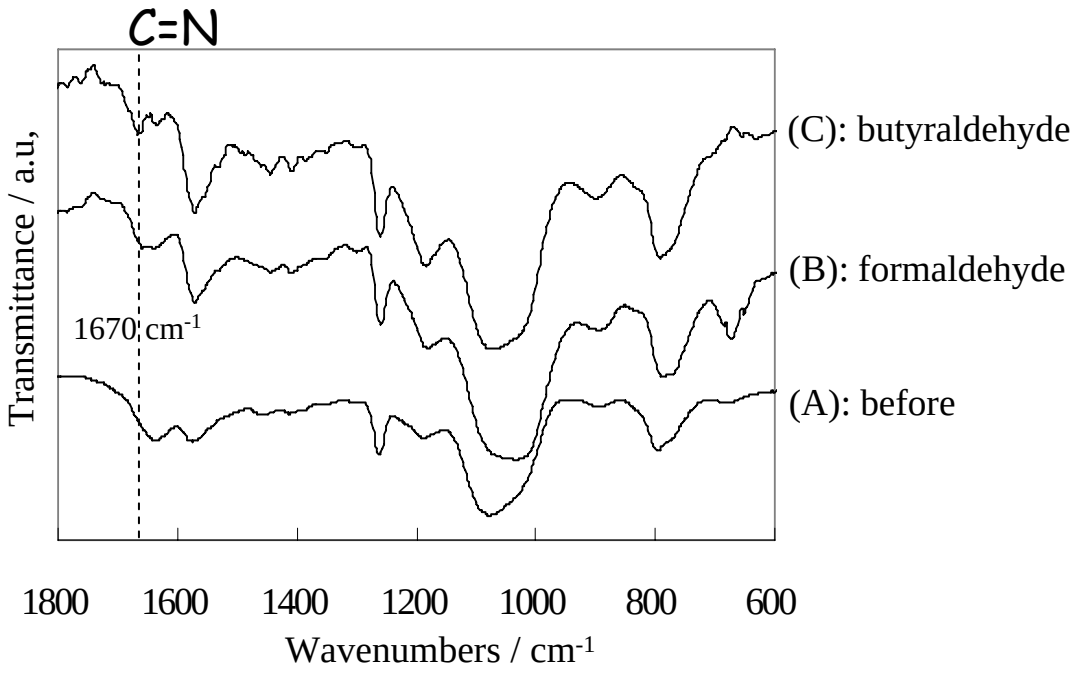
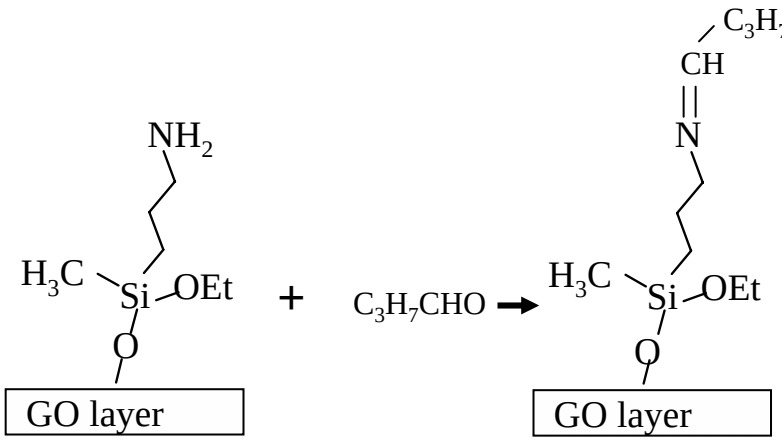
Reaction of silylated GO with aldehydes







Butyraldehyde molecules are successfully intercalated between the layers of silylated GO

The amount of chemically adsorbed aldehyde

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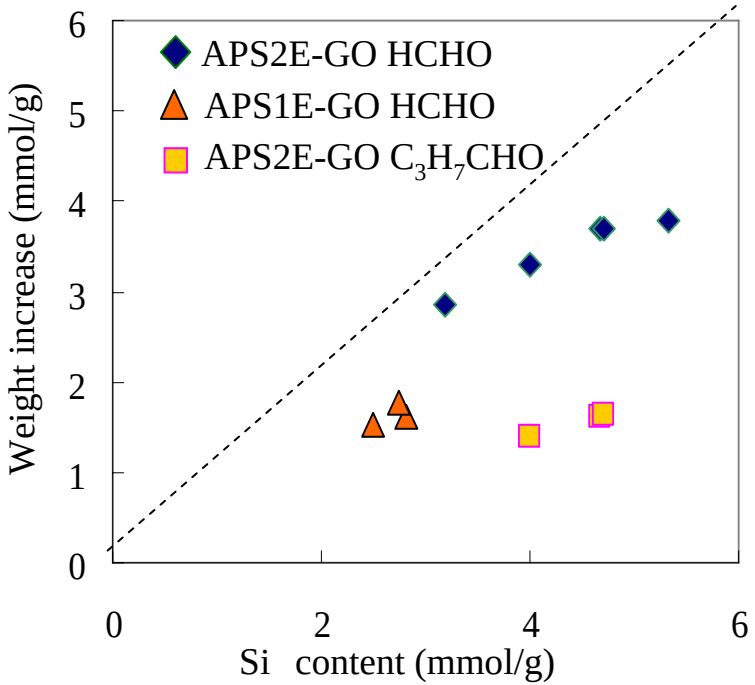

Fig. Weight increase after adsorption of formaldehyde and butyraldehyde.

The amount of adsorbed aldehydes increased with the increase of Si contents, accordingly NH_2 contents.
The utility of amino groups was 70-90% for formaldehyde and 25% for butyraldehyde.

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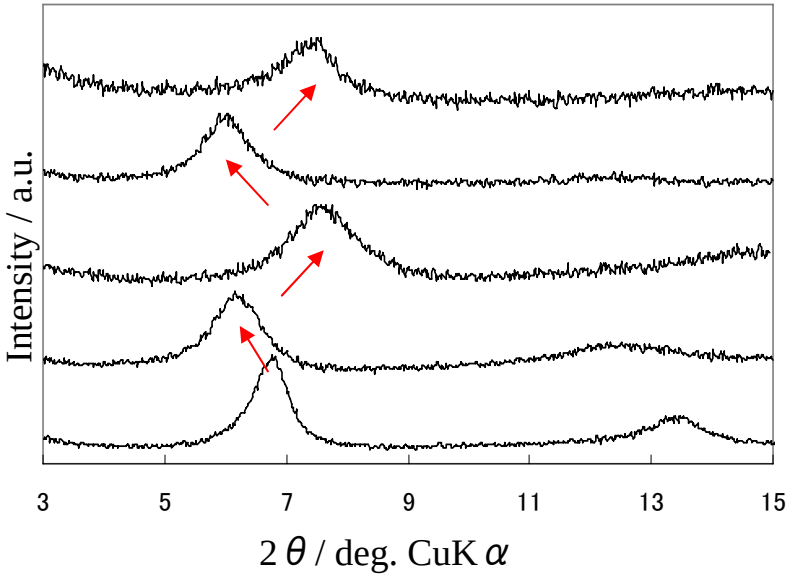
Adsorption and desorption of aldehydes



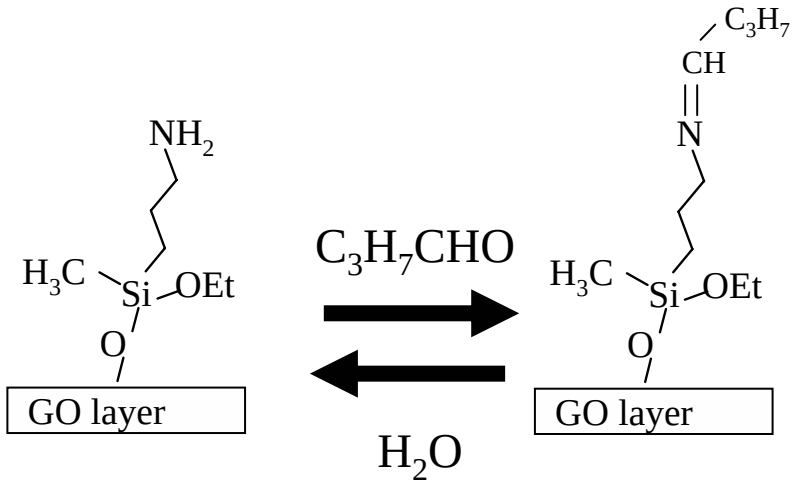
hydrolyzed

adsorbed

hydrolyzed

adsorbed

pristine



Hydolysis of aldehyde-adsorbed silylated GO
acetic acid : ethanol : H_2O = 1 : 1 : 1 (vol) at 60℃ for 3 days

The interlayer spacing of silylated GO changed almost reversibly during adsorption and desorption cycles.

Silylated GO containing amino groups is promising for the adsorbent of aldehydes !

Adsorption of formaldehyde onto silylated GO from gas phase

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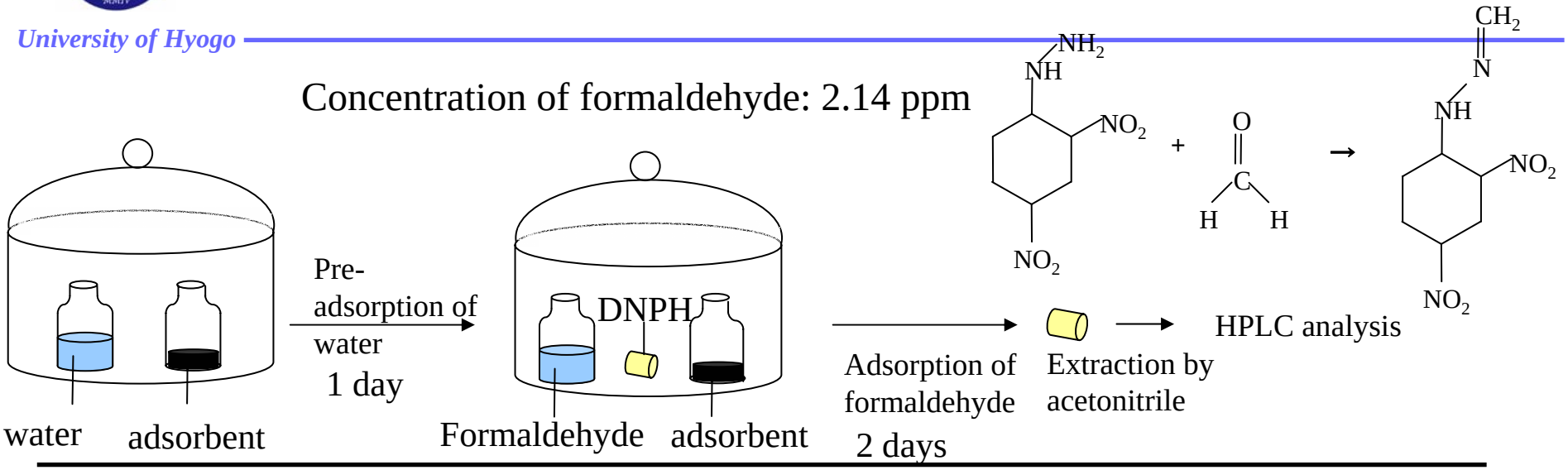
Concentration of formaldehyde: 2.14 ppm



	reaction time / days	pre-adsorption of water	Formaldehyde concentration after 48 h / ppm	Adsorbed formaldehyde / mg/g (mmol/g)
Active carbon	-	yes	1.98	15.1 (0.5)
Active carbon	-	no	1.82	30.4 (1.0)
GO	-	yes	2.10	3.8 (0.1)
Silylated GO	4	yes	1.34	76.0 (2.5)
Silylated GO	6	yes	1.76	36.1 (1.2)
Silylated GO	6	no	1.13	96.0 (3.2)
Silylated GO	8	yes	1.18	91.2 (3.0)
Silylated GO	13	yes	1.44	66.5 (2.2)

Silylated GO adsorbed considerable amounts of formaldehyde from gas phase.

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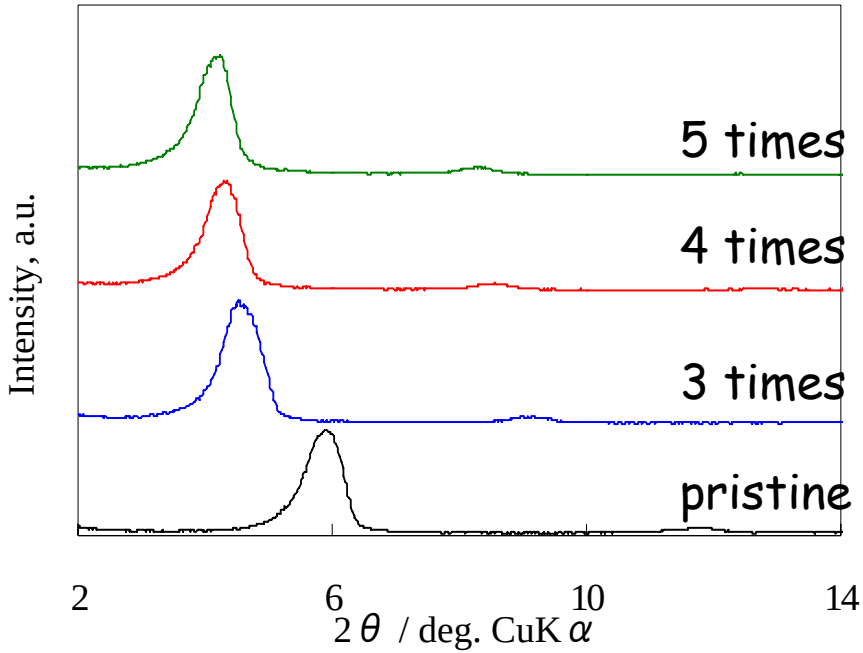
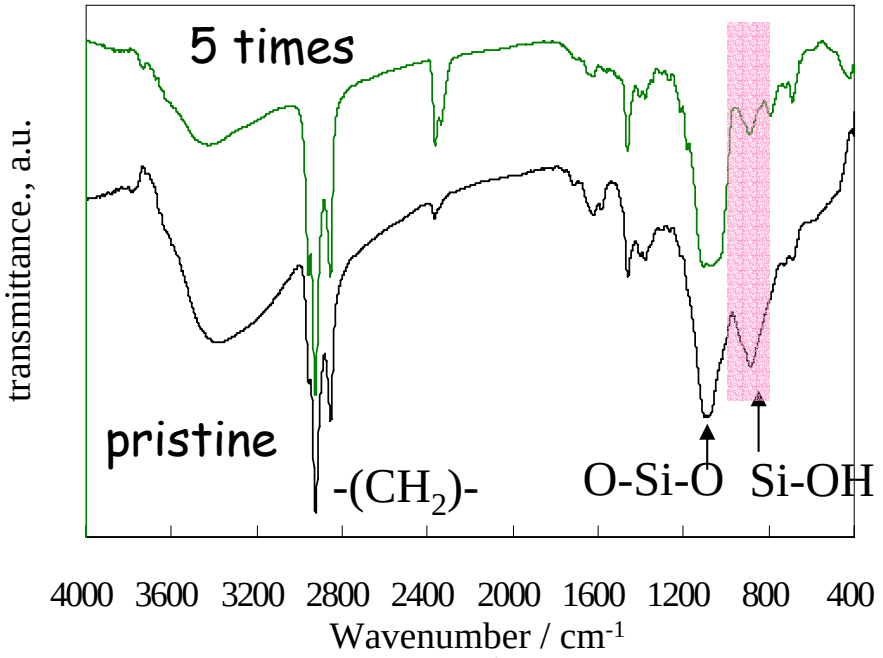
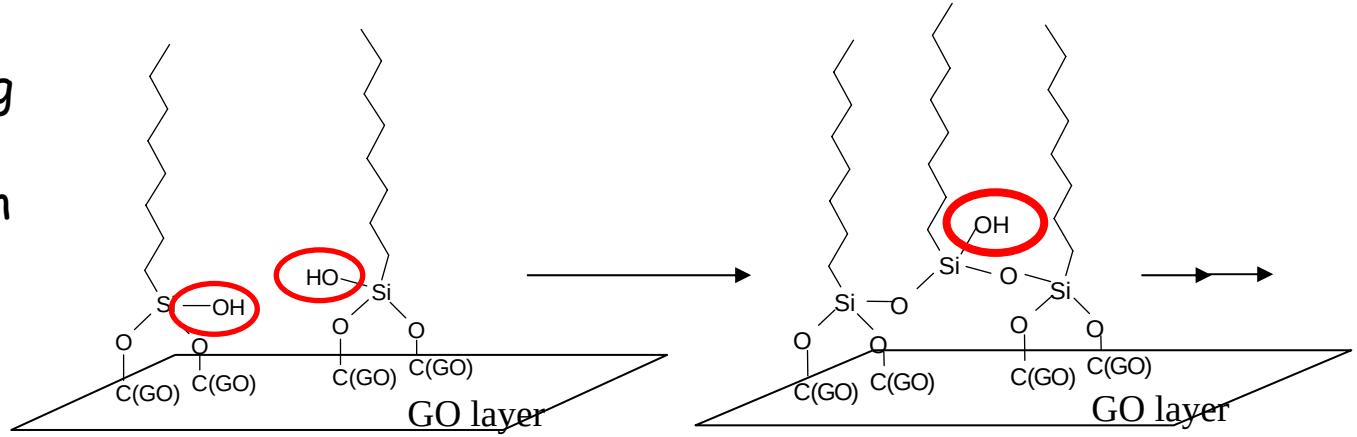
Reaction of silylated GO with alkyltrichlorosilane





The interlayer spacing increased from nm to nm and the absorption due to Si-OH group considerably decreased.



Reaction of silylated GO with alkyltrichlorosilane

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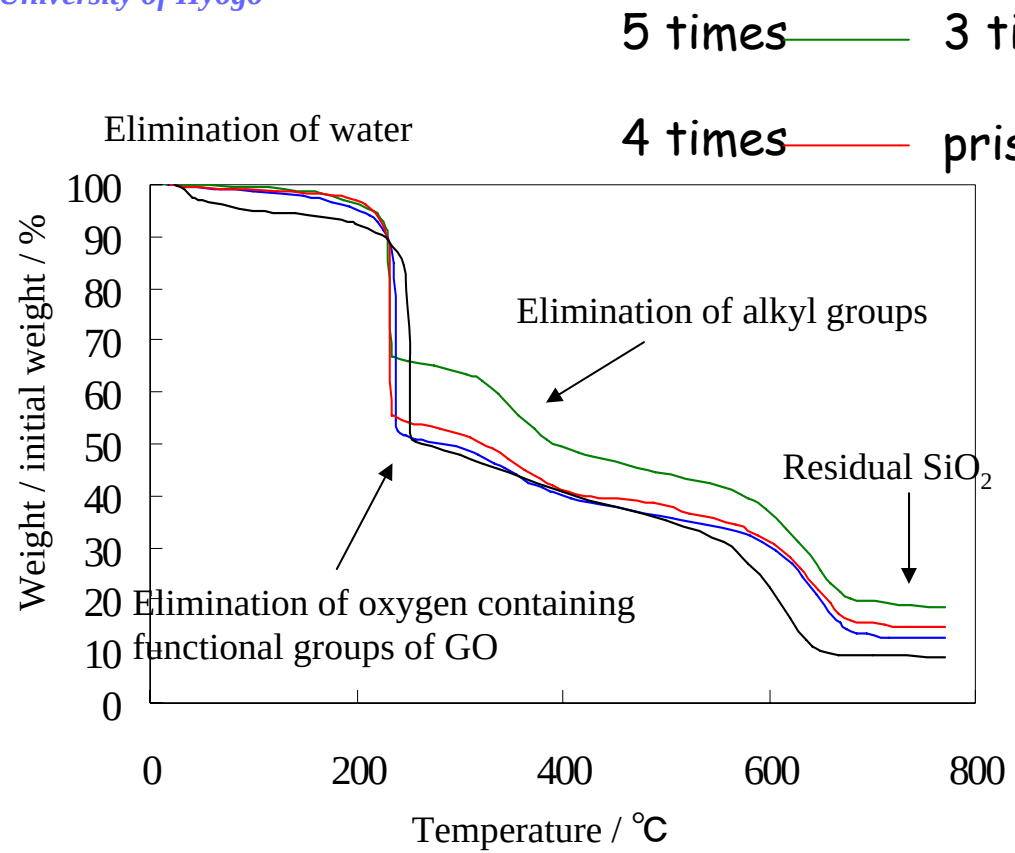

sample	Si content/ %	Si/GO ratio
pristine	1.87	0.16
2	5.96	0.68
3	6.83	0.83
5	8.90	1.35

✓The samples are hydrophobized because of the increase of the content of alkyl groups.

✓The silicon content increased when silylated GO was silylated repeatedly.

Reaction of silylated GO with 3-aminopropyltriethoxysilane

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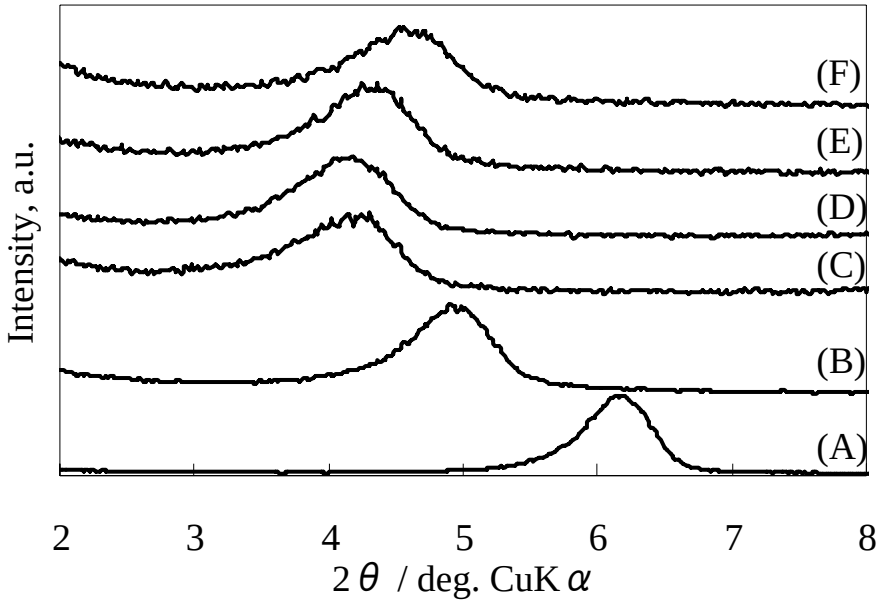


Fig.1 X-ray diffraction patterns of $(C8Si)_{0.39}GO$ (A): before and after silylation by AP3ES with the AP3ES/GO unit ratios of (B): 0.2, (C): 4.7, (D): 22, (E): 44 and (F): 67.

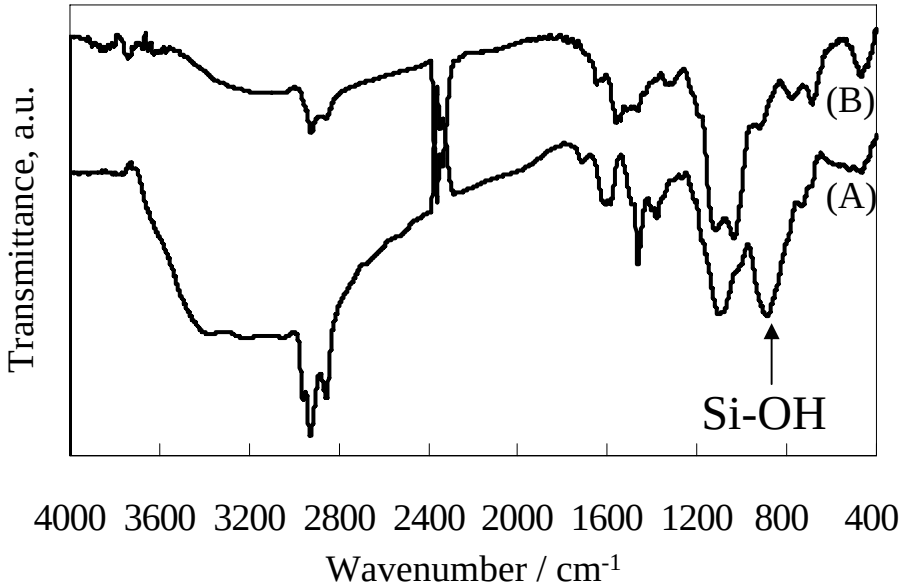
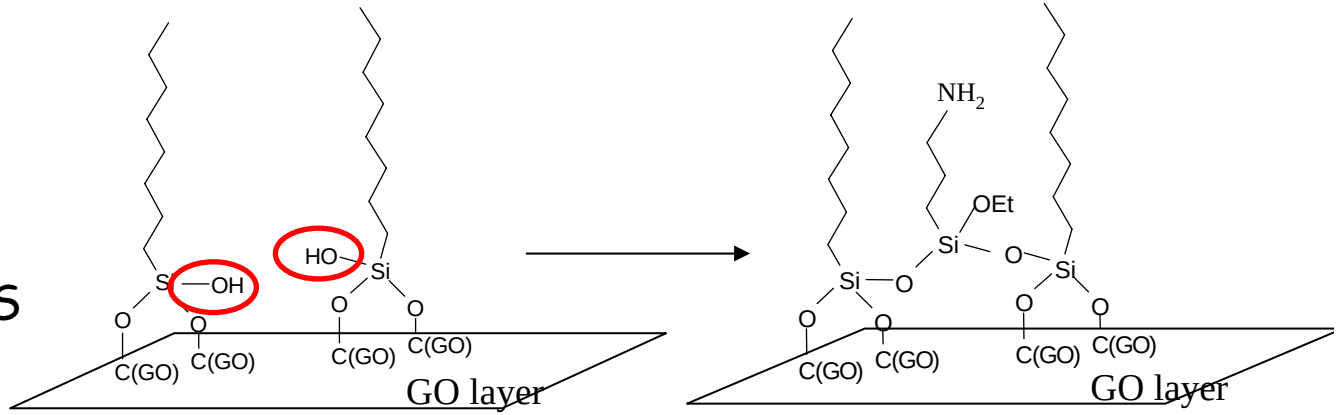


Fig.2 IR spectra of $(C8Si)_{0.39}GO$ (A): before and (B): after silylated by AP3ES with the AP3ES/GO ratio of 4.7.

Silylated GO was further silylated by silylating reagent with ethoxy groups.
Addition of excess AP3ES resulted in the decrease of interlayer spacing.



Summary of the reaction of silylated GO

Amino groups in silyalted GO are available for the adsorption of aldehydes.

Both silylating reagents with Si-Cl and Si-OEt groups react with Si-OH groups of silylated GO, forming Si-O-Si bonding.

The content of organic component in silylated GO increased as the result of silylation.
→ Good precursor of pillared carbons

Preparation of pillared carbons

Previous attempts to obtain "pillared carbons"

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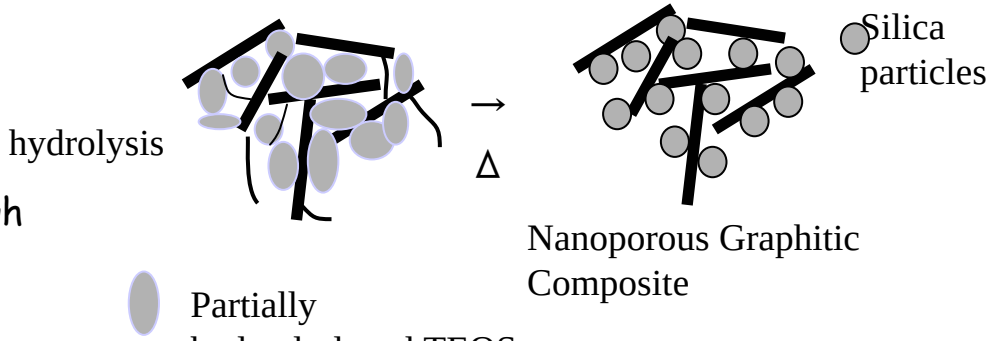
Wang,et al (Chem. Commun 2002, Chem. Mater. 2003, etc)

Surfactant-intercalated GO was used as an intermediate.

Surfactant-intercalated GO + TEOS ($Si(OC_2H_5)_4$) →



The order of carbon layers was almost lost, though the obtained carbon was porous.

Morishige et al (Langmuir 2005)

Iron trinuclear complex-intercalated GO was used as a precursor.

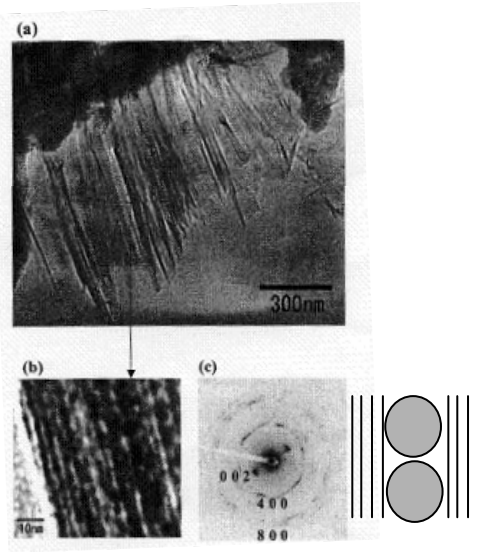
Ion exchange

$GO + [Fe_3(OCOCH_3)_7OH \cdot 2H_2O]NO_3 \rightarrow GO\ [Fe_3(OCOCH_3)_7OH \cdot 2H_2O]$

→ "iron oxide-pillared carbon"

Δ

However, no apparent peak due to "pillared carbon" was observed in X-ray diffraction pattern and some of the iron oxide particles are observed outside the interlayer space of carbons.



From Langmuir, 21, 6277 (2005)

The precursors of the pillar tend to aggregate before the transformation of GO to carbon.

Our method to obtain "pillared carbons"

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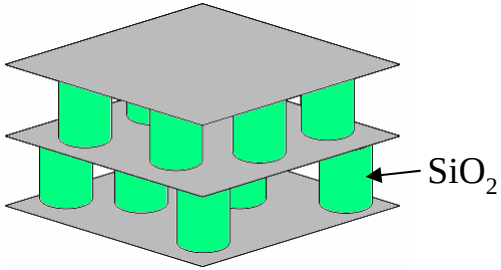
Precursors of the pillar should be strongly attached to GO layers!!

→ We chose silylated GO as a precursor.



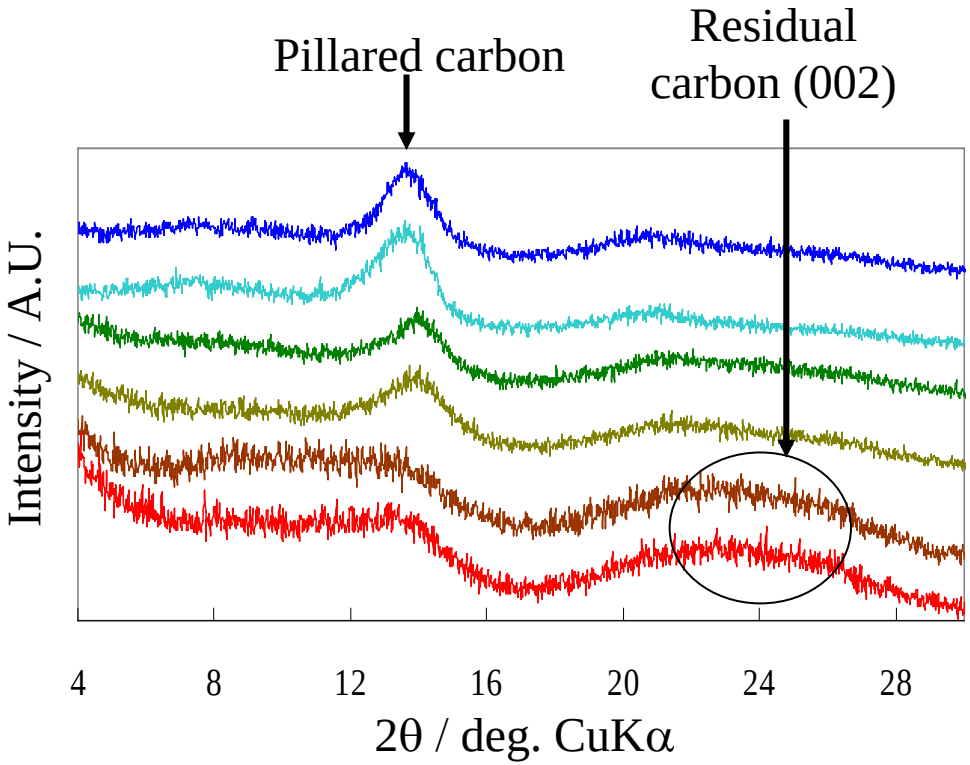


Fig. XRD patterns of silylated GO various silicon contents after pyrolysis at 500℃.

Reaction time	Si contents Before	After
20 days	15.8 →	21.6 %
13 days	15.1 →	20.5 %
6 days	13.3 →	17.6 %
4 days	12.6 →	16.8 %
3 days	10.7 →	14.6 %
1 day	9.3 →	12.7 %

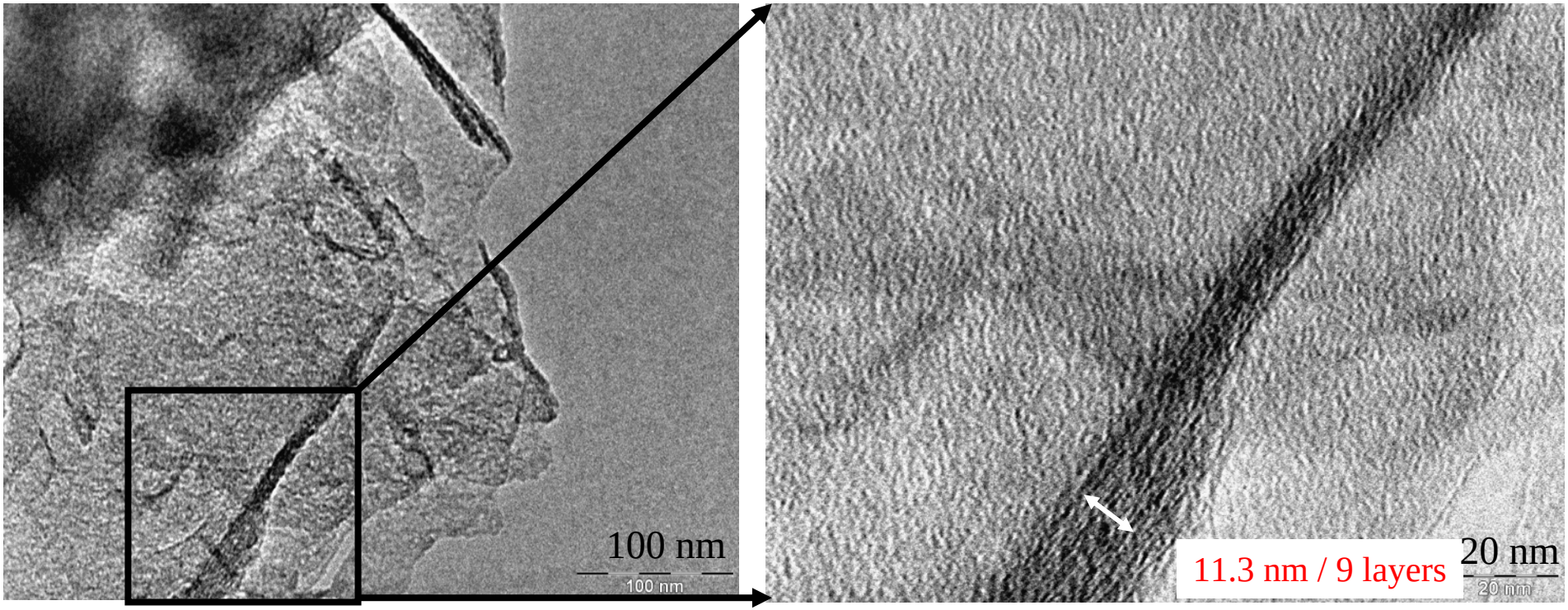
Pillared carbons

Pillared carbons were obtained from silylated GO with higher silicon contents

TEM observation of pillared carbon

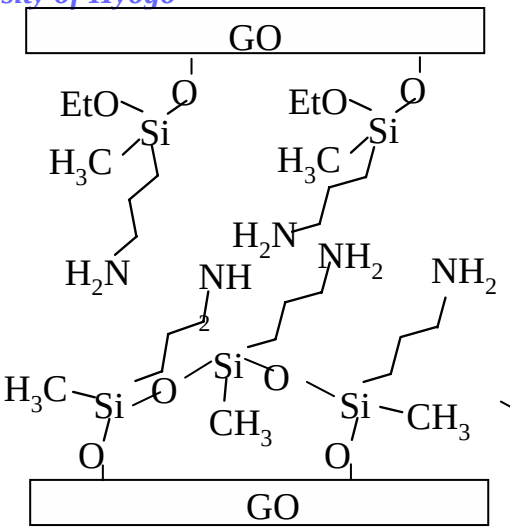
University of Hyogo

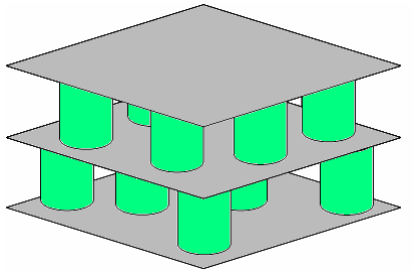
Pillared carbon obtained from pyrolysis of bilayer type AP2ES-GO



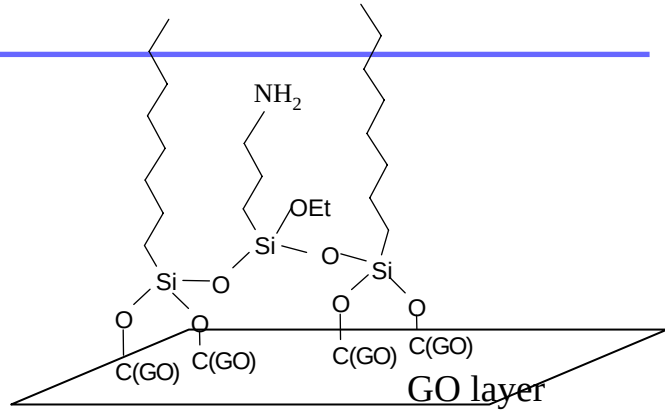
The lattice images of the layered structure were clearly observed and the distance between the adjacent layers was calculated to be 1.26 nm, which was almost the same as that obtained from X-ray diffraction data (1.29 nm).

Various precursors of pillared carbons

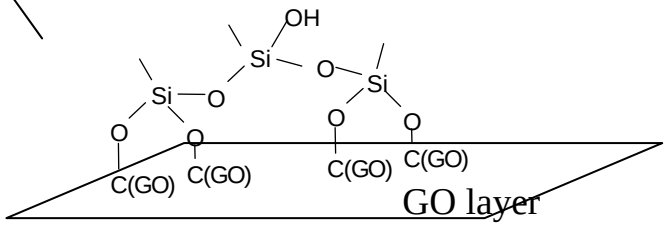




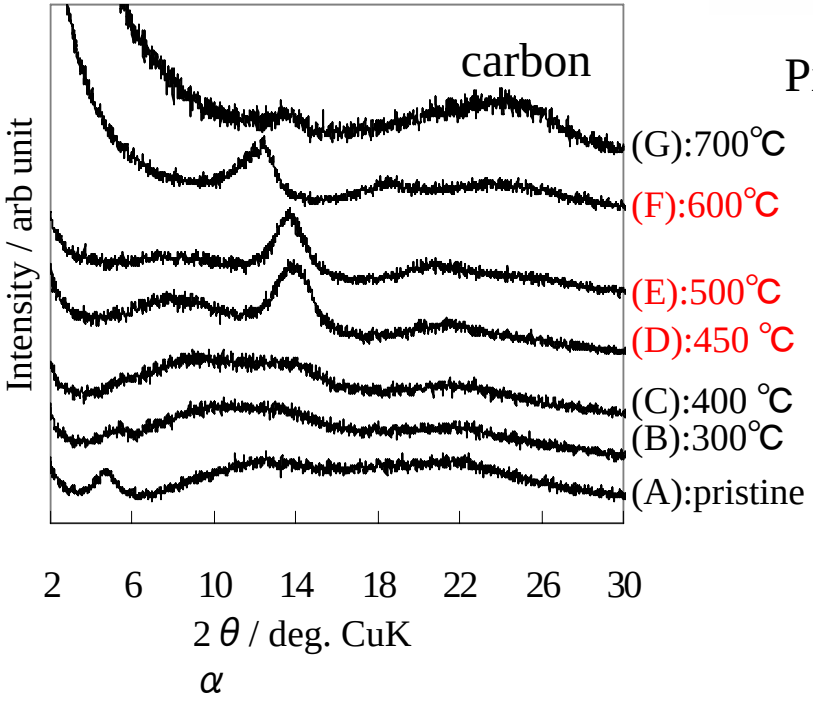
Pillared carbon



AP3ES-CnSi-GO



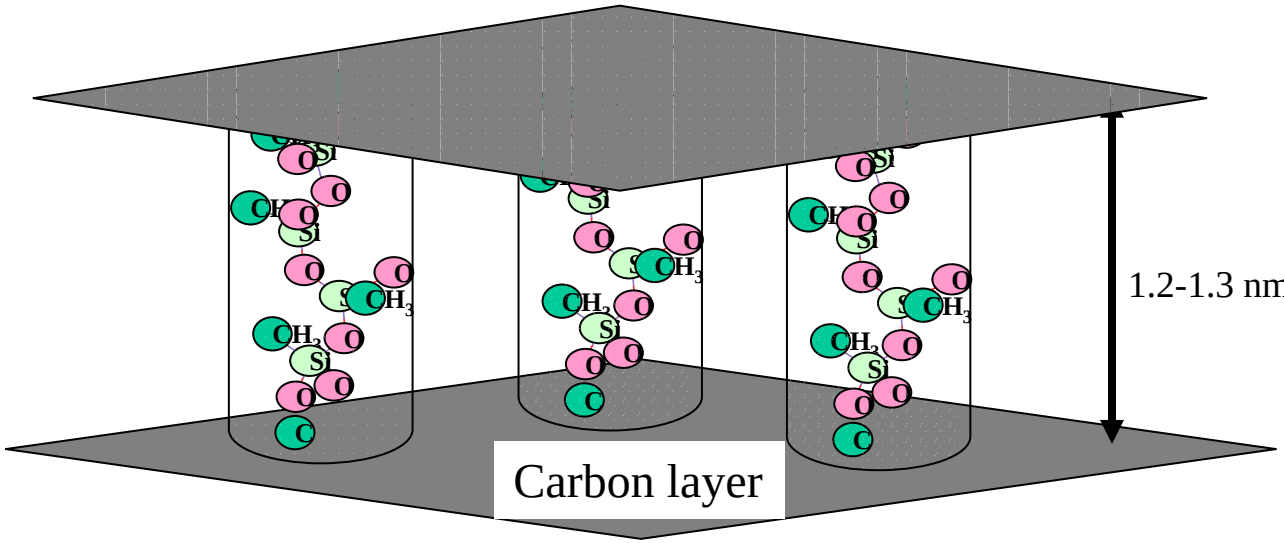
C1Si-GO



Pillared carbons are obtained by the pyrolysis of silylated GO with high silicon contents under vacuum between 450 and 600℃.

A structure model of pillared carbon

sample	H / %	C / %	N / %	O / %	Si / %	H/Si	N/Si	O/Si	C/Si
90-3	2.56	57.56	1.27	21.42	17.10	4.1	0.15	2.2	7.9
90-6	2.05	61.95	1.38	21.63	16.56	3.5	0.17	1.9	8.7
90-14	2.69	52.82	0.86	19.03	20.70	3.6	0.08	1.9	5.6
105-4	2.60	60.49	1.85	18.26	16.8	4.3	0.22	1.9	8.4
105-6	2.22	57.49	1.53	21.63	17.6	3.5	0.17	2.2	7.6
105-13	2.58	52.25	2.06	22.61	20.5	2.8	0.09	1.9	5.9
105-20	1.83	48.22	1.30	22.25	21.6	3.4	0.16	1.8	5.6



Composition

$C_{18\text{-}30}(Si_4O_7(OH)_2(CH_3)_4)$

Theoretical surface area

~ 3500m²/g

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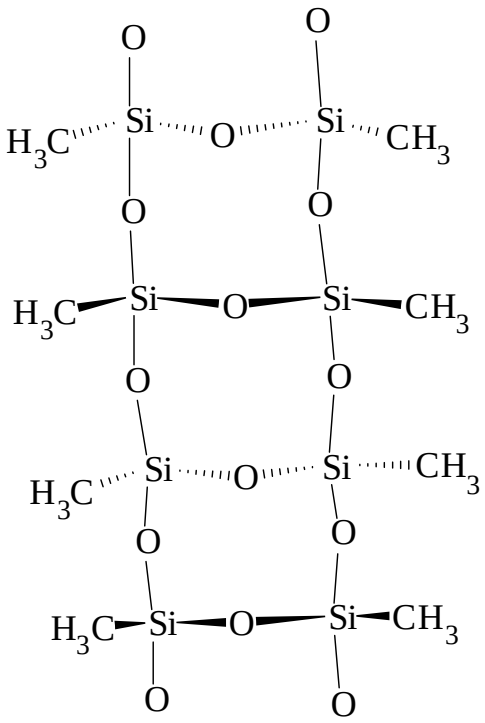
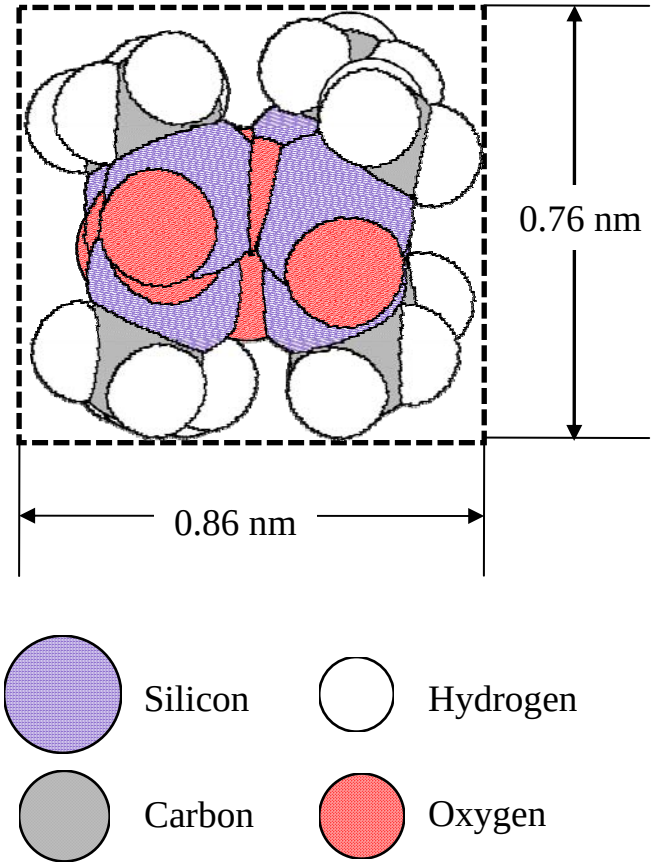
A structure model of pillars in pillared carbon obtained from C_1SiGO





When pillared carbon was prepared from C1SiGO with more stable Si-CH_3 groups, the ladder type silsesquioxane structure was proposed.

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Summary of the preparation of pillared carbons

Pillared carbons were prepared by the pyrolysis of silylated GO with high silicon contents around 500 ℃.

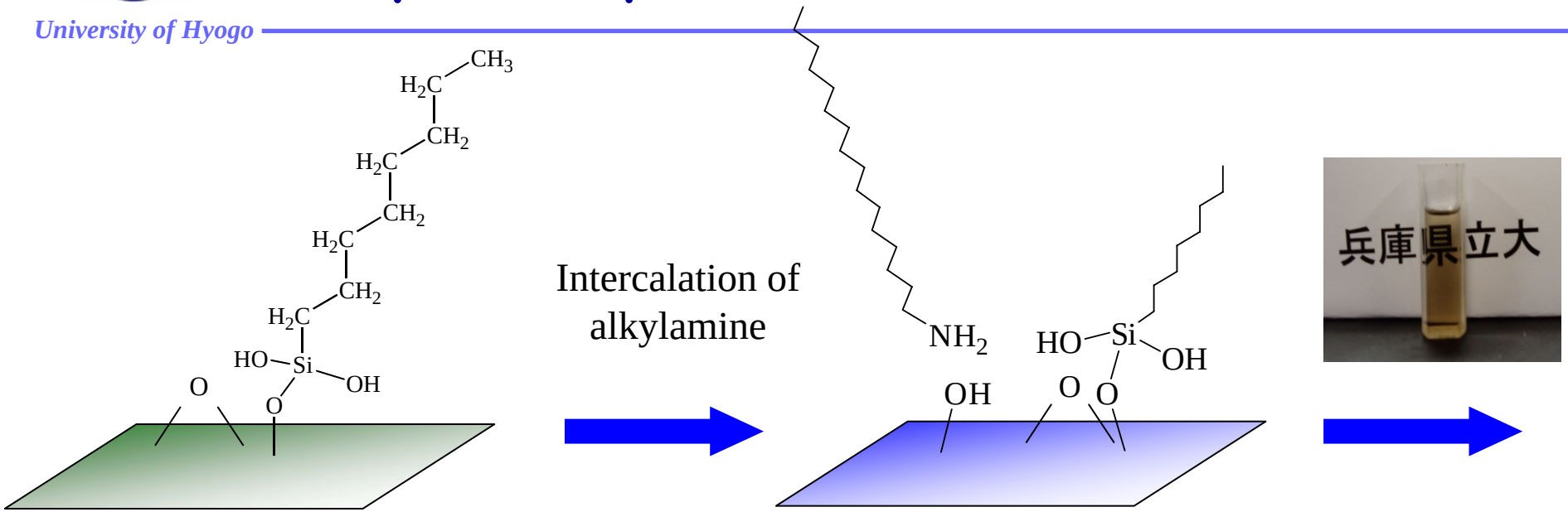
Microporous pillared carbons were obtained from the pyrolysis of silylated GO silylated by APS. The pore size was very small, less than 1 nm.

The surface nature of the pillared carbons were between those of silica and carbon black.

Preparation of transparent and conducting thin film electrode from silylated GO

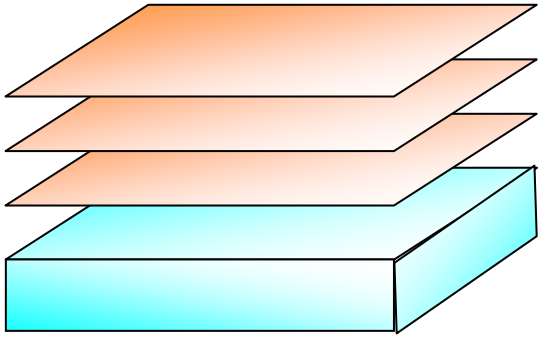
University of Hyogo

Preparation procedure

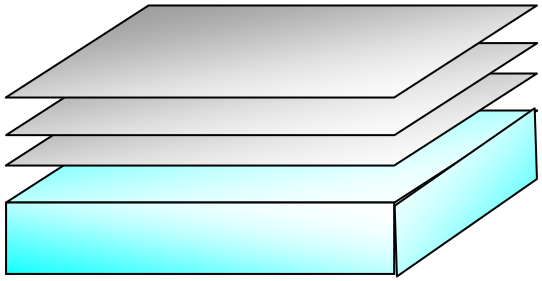


Cast

Removal of alkylamine



Pyrolysis



Carbon film

Summary of the preparation of transparent and conducting carbon film from silylated GO

✓Uniform thin films of silylated GO were obtained from the nanosheet solution of n-hexadecylamine intercalated silylated GO.

✓The carbon films from silylated GO well adhered to the glass or quartz substrate.

✓The sheet resistance of the carbon from silylated GO reached a small value of 700Ω/sq. with the transmittance of 80 % at 400 nm.

Acknowledgements

Prof. Y. Sugie (Univ. Hyogo)
Dr. T. Fukutuska (Kyoto Univ.)

Prof. T. Yazawa (Univ. Hyogo)	N_2 adsorption
Prof. Z. Ogumi (Kyoto Univ.)	TEM
Dr. A. Mineshige (Univ. Hyogo)	Raman, Ellipsometry
Prof. M. Kawaguchi (Osaka Electro-Commun Univ.)	XPS
Dr. H. Usami (Shinshu Univ.)	Conductivity

Students
Intercalation of surfactants: Mr. T. Niwa, K. Hatase
Polymer intercalated GO: Mr. K. Tahara, Mr. Y. Takahara, Dr. S. Higashika
Intercalation of alkylamine: Mr. N. Tokura, Mr. K. Watanabe
Silylation: Mr. T. Fukunaga, Mr. T. Tabata, Ms. Orita, Mr. Y. Nishino
Pillared carbon: Ms. Y. Matsumoto, Mr. Y. Sakai, Mr. T. Komiya,
Mr. M. Arimura, Mr. S. Ueda, Mr. K. Konishi
Transparent and conducting film: Mr. Iwasa, Mr. Mimura

Thank you for your attention !