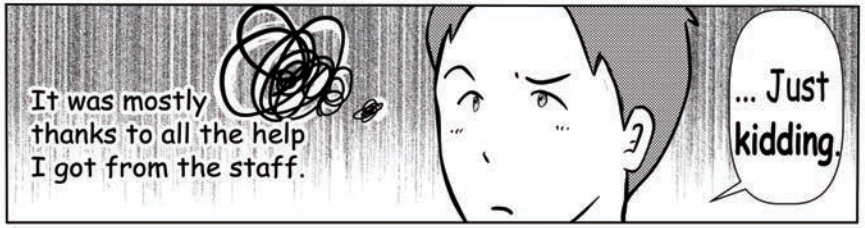
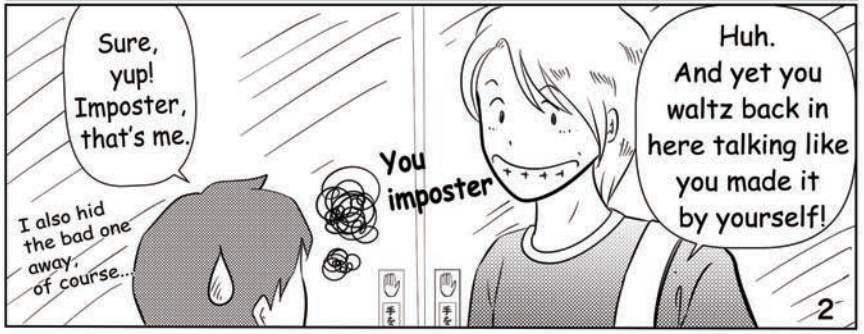
Chapter Four: 2.5-Dimensional Intercalation





令和3(2021)年度学術変革領域研究(A)
2.5次元物質科学：
社会変革に向けた物質科学のパラダイムシフト
2.5D Materials
NEWS LETTER

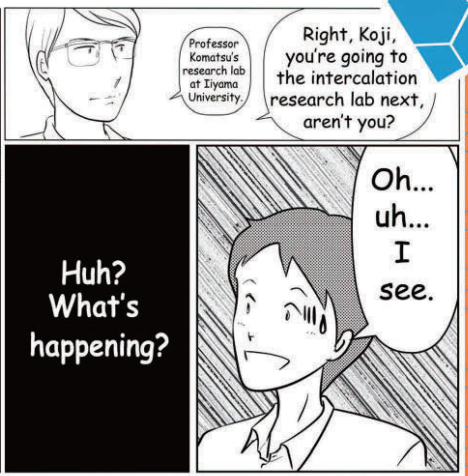
Welcome to the 2.5D Laboratory

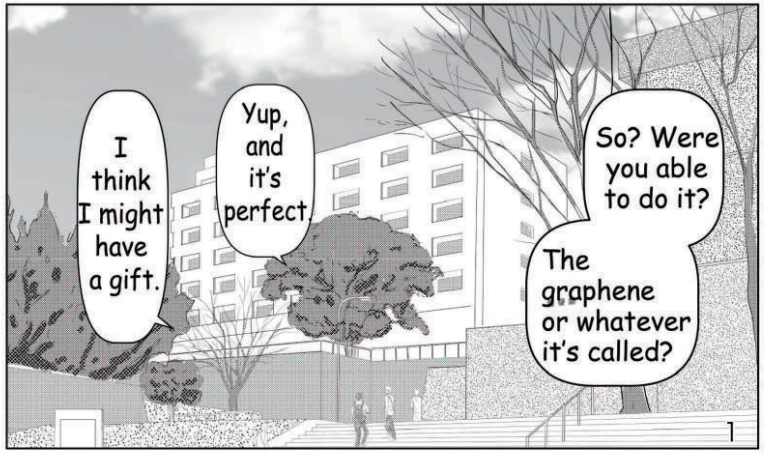
Previously in the series

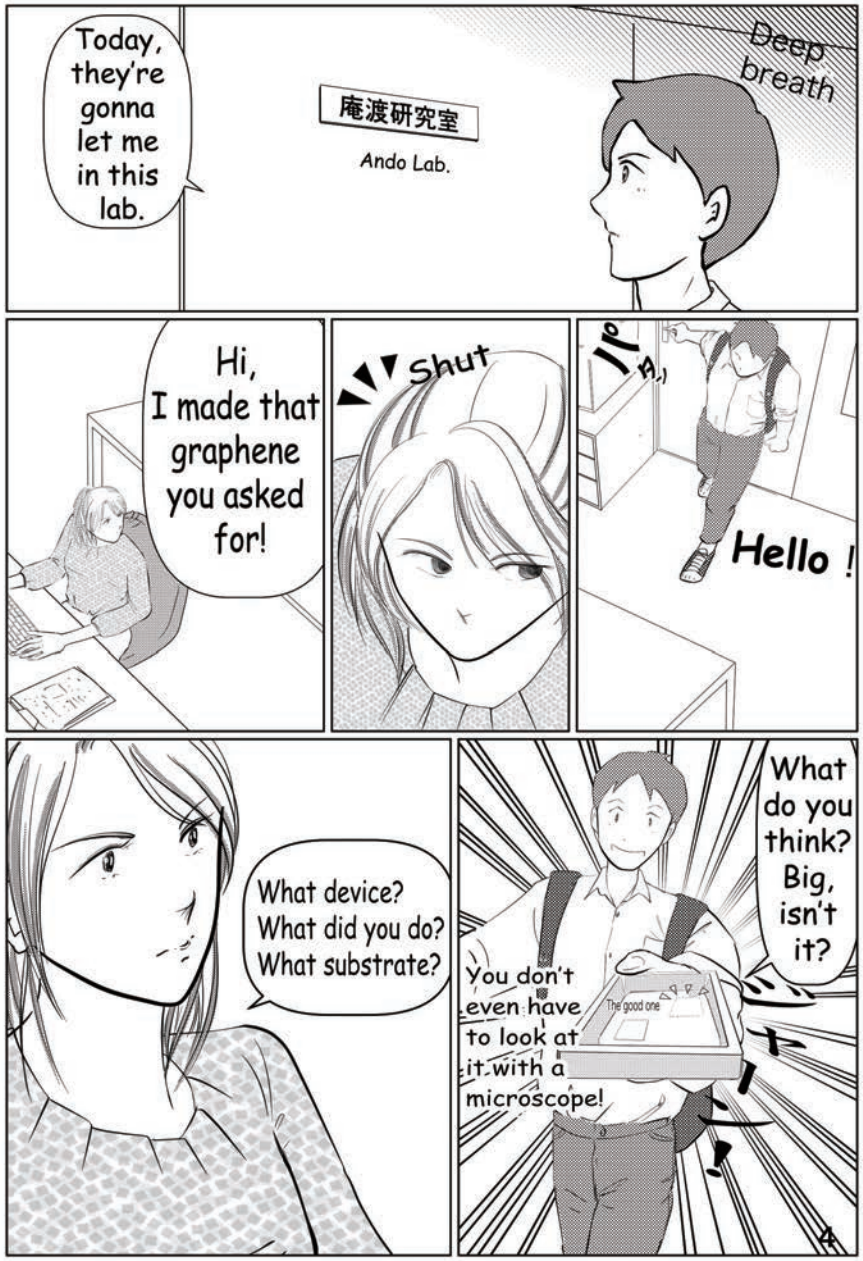
In his desperate attempt to gain entry into a cutting-edge science lab, Koji Ota, a senior in university, has tried to produce large-area graphene using the CVD method—going as far as to visit another university to do so.

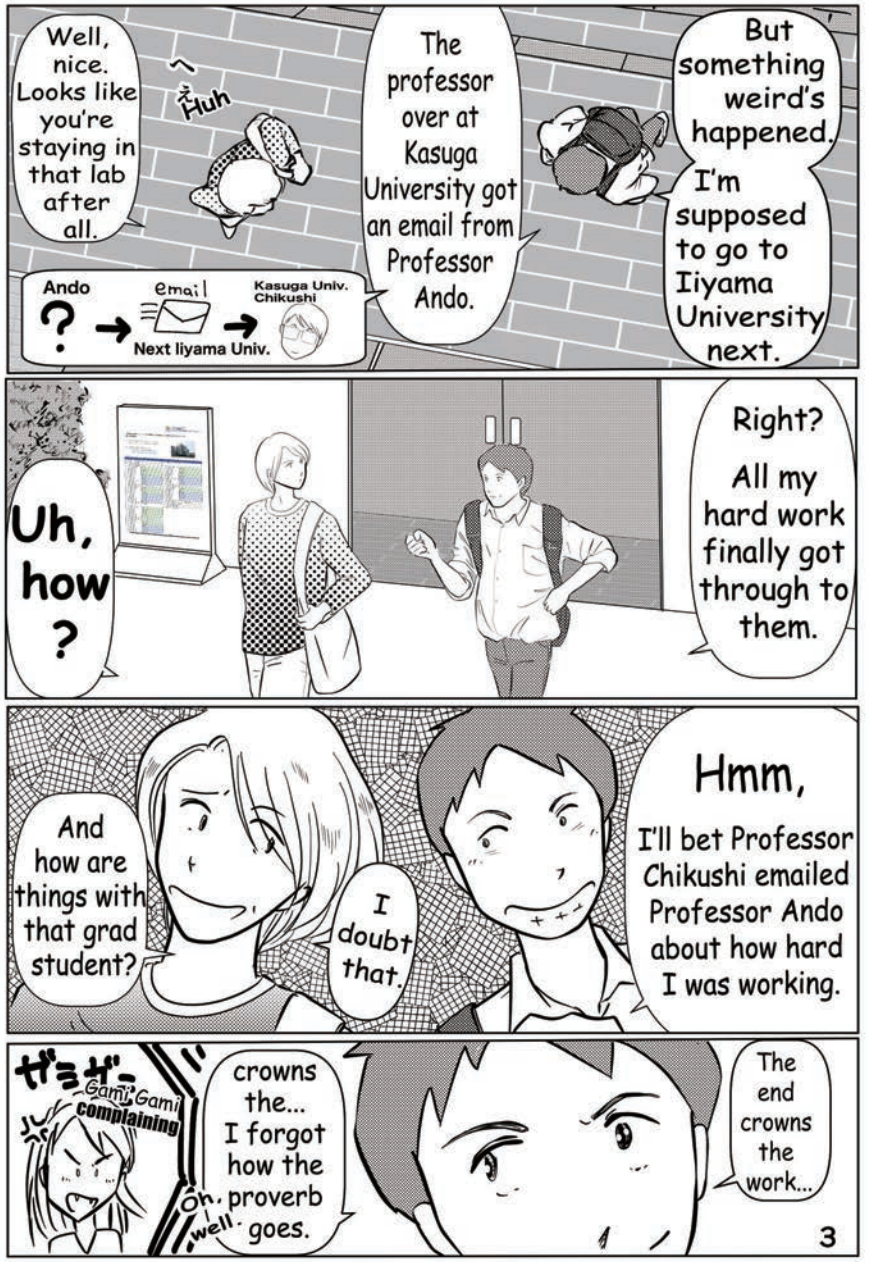
Koji finally makes some graphene, learns how to inspect it, and meets a doctoral student studying ways to apply the technology and solve social issues, and is very happy with his progress. That is, until he finds himself confused by even further instructions.

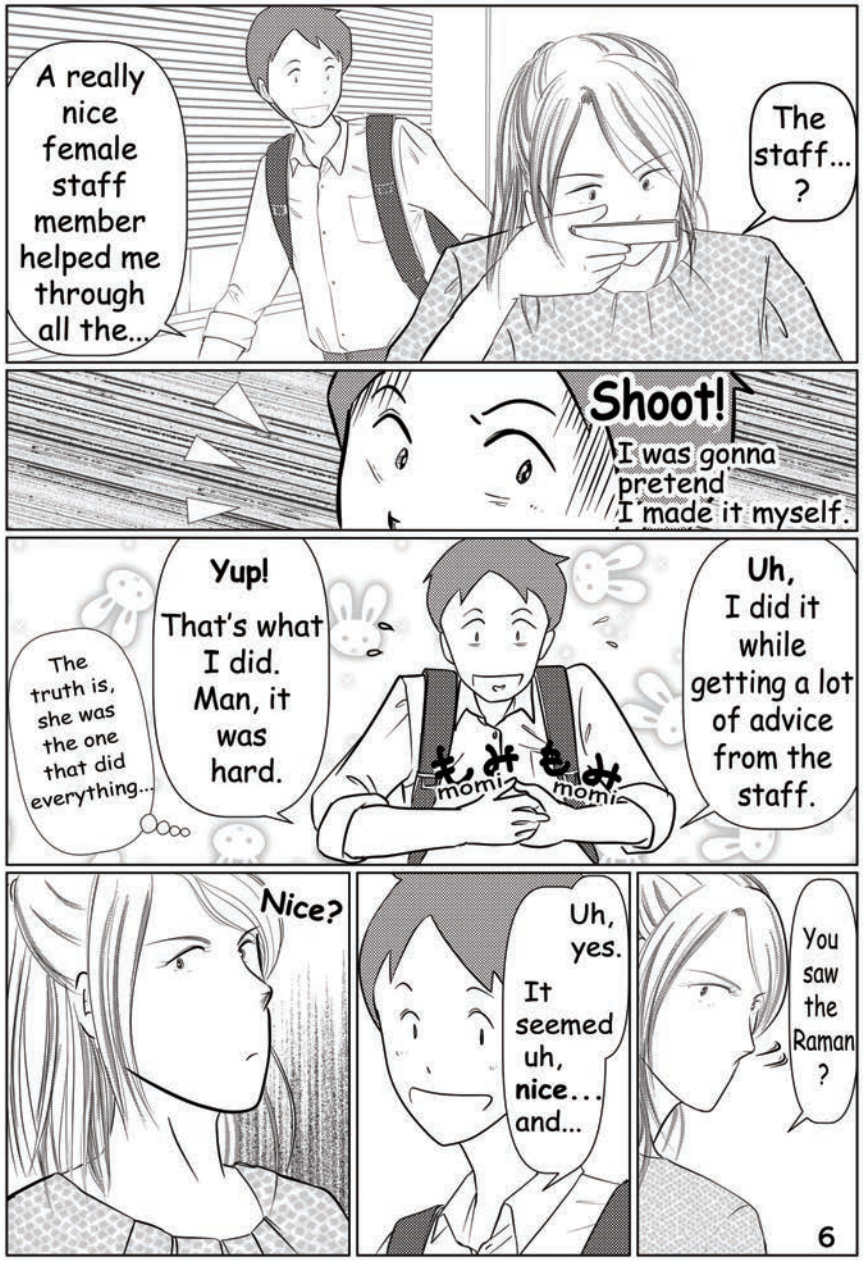
What will his next research topic be?

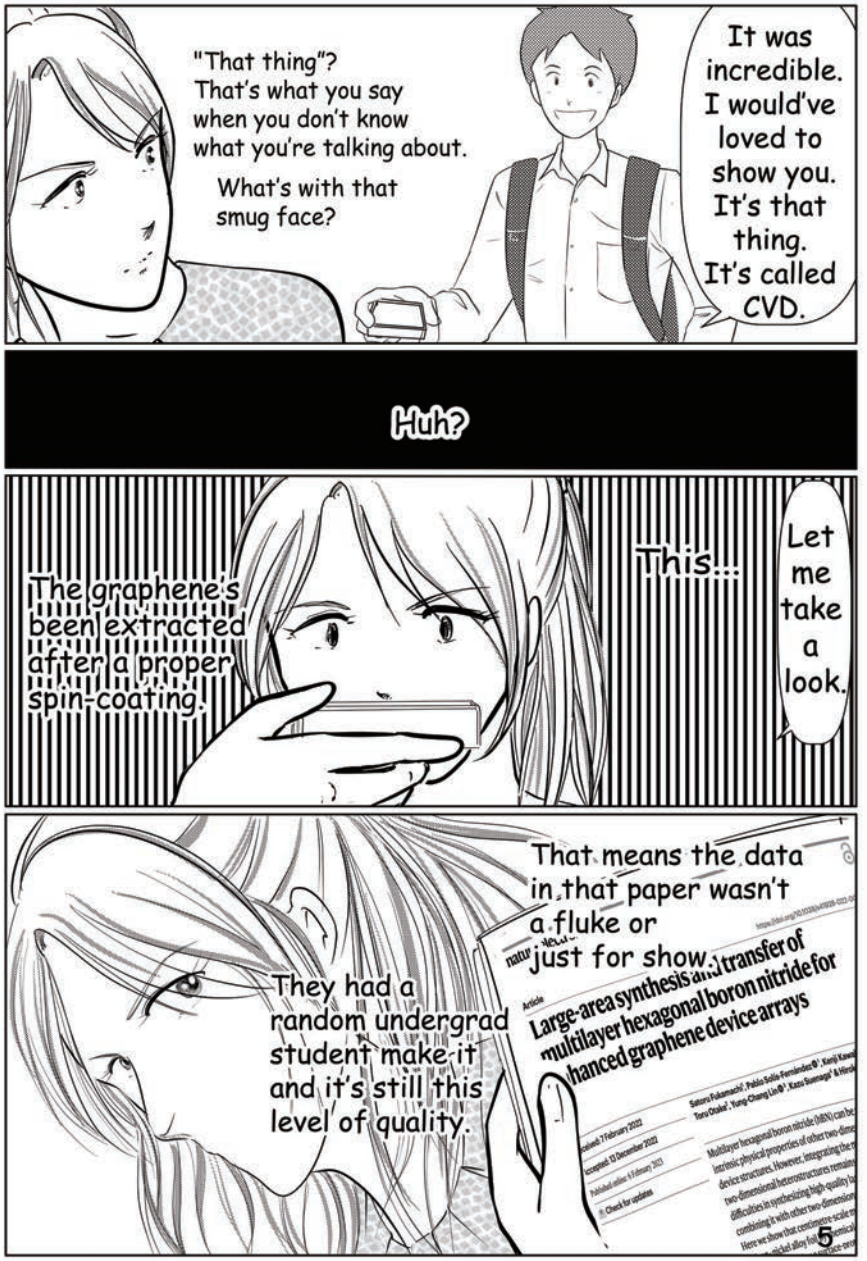




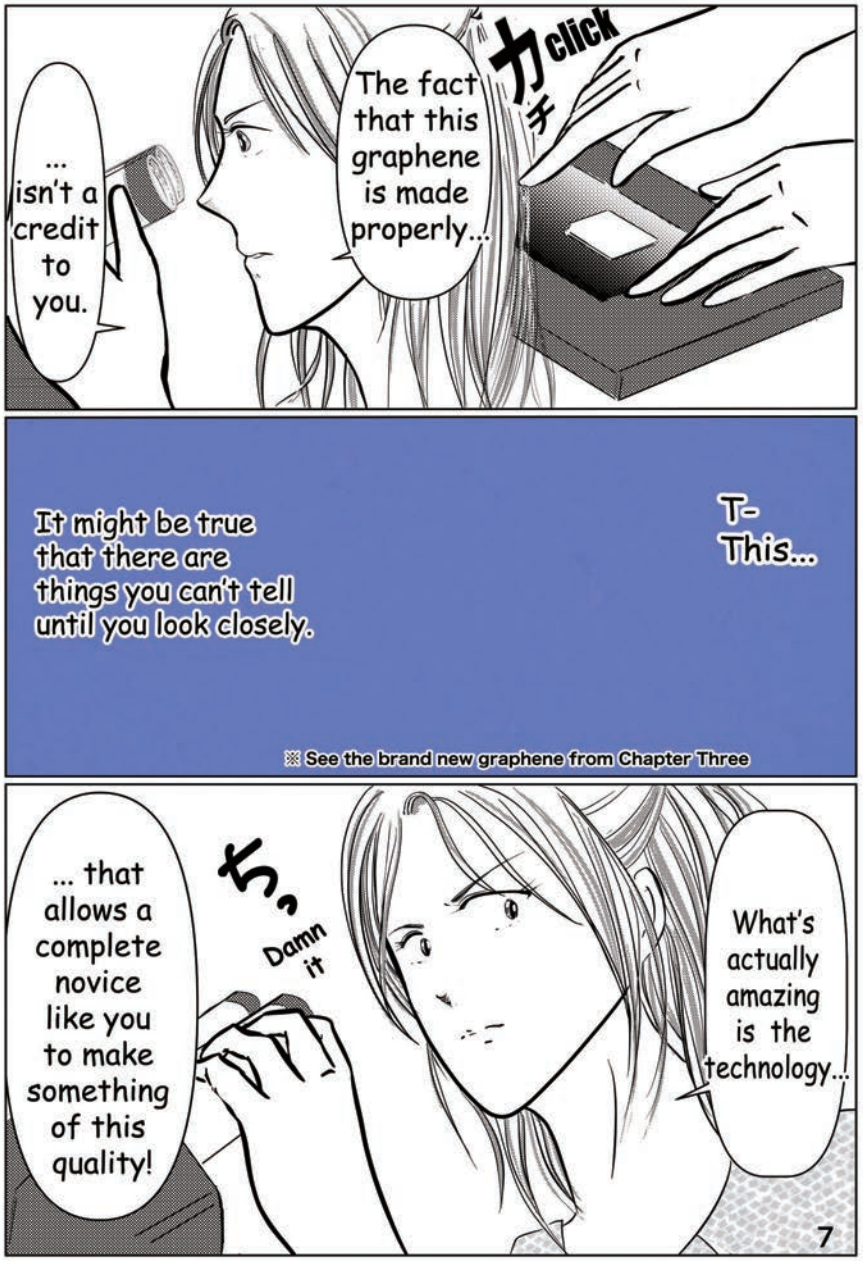

Today, they're gonna let me in this lab.
Deep breath
庵渡研究室
Ando Lab.
Hi, I made that graphene you asked for!
Shut
Hello !
What device? What did you do? What substrate?
What do you think? Big, isn't it?
You don't even have to look at it with a microscope!
The good one
4


Well, nice. Looks like you're staying in that lab after all.
Huh
The professor over at Kasuga University got an email from Professor Ando.
But something weird's happened. I'm supposed to go to Iiyama University next.
Ando
email
Kasuga Univ. Chikushi
Next Iiyama Univ.
Uh, how ?
Right? All my hard work finally got through to them.
And how are things with that grad student?
I doubt that.
Hmm, I'll bet Professor Chikushi emailed Professor Ando about how hard I was working.
ゼミゼミ
Gami Gami complaining
Oh well.
crowns the... I forgot how the proverb goes.
The end crowns the work...
3

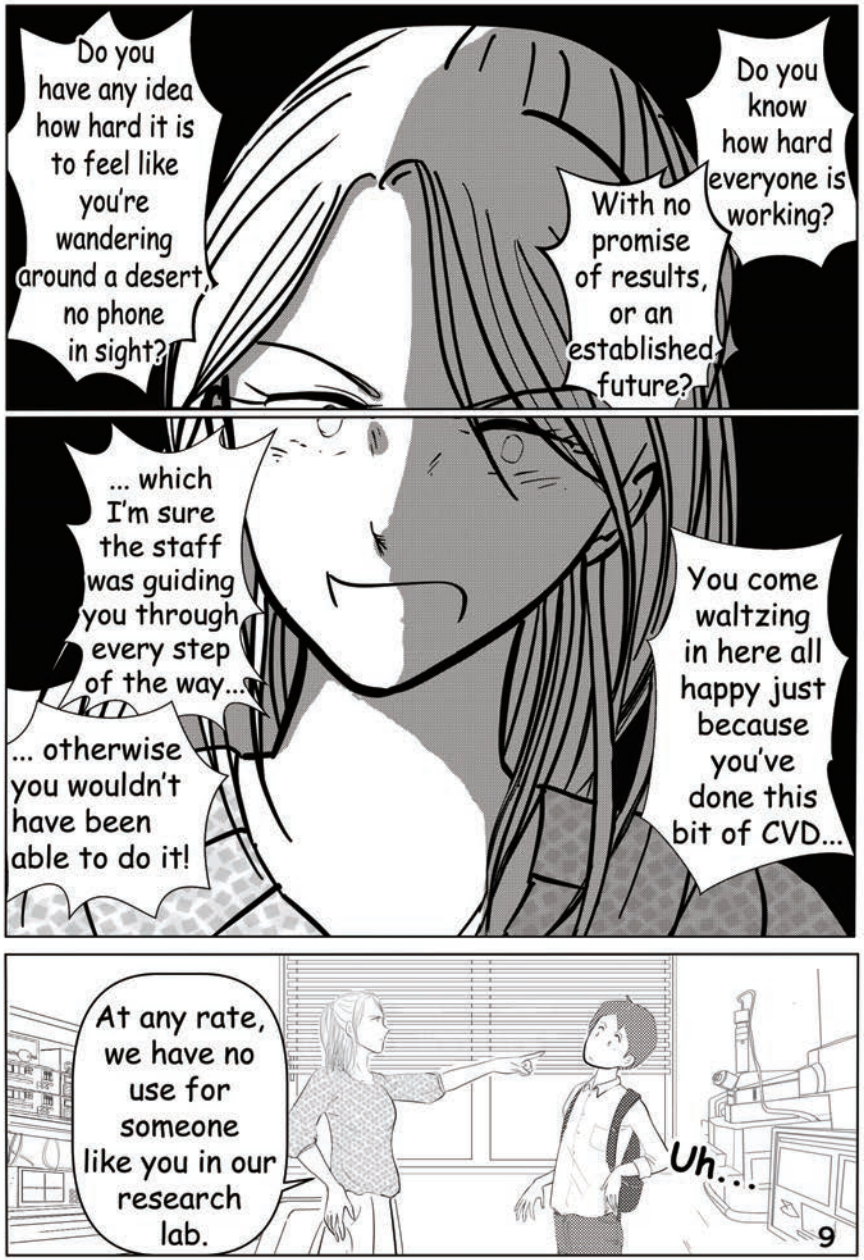

A really nice female staff member helped me through all the...
The staff...?
Shoot!
I was gonna pretend I made it myself.
Yup!
That's what I did. Man, it was hard.
The truth is, she was the one that did everything...
Uh, I did it while getting a lot of advice from the staff.
momi
momi
Nice?
Uh, yes.
It seemed uh, nice... and...
You saw the Raman?
6

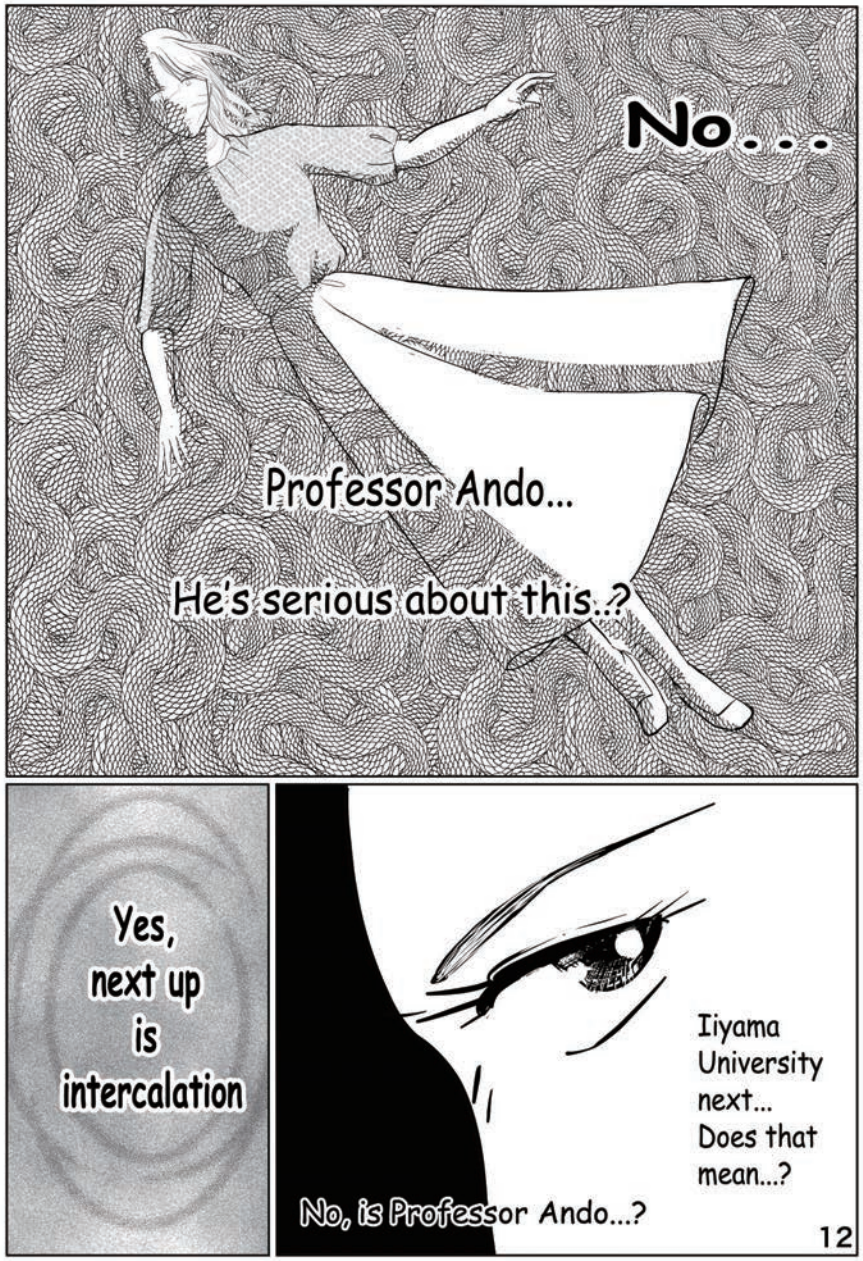

"That thing"? That's what you say when you don't know what you're talking about.
What's with that smug face?
It was incredible. I would've loved to show you. It's that thing. It's called CVD.
Huh?
The graphene's been extracted after a proper spin-coating.
This...
Let me take a look.
They had a random undergrad student make it and it's still this level of quality.
That means the data in that paper wasn't a fluke or just for show.
Large-area synthesis and transfer of multilayer hexagonal boron nitride for enhanced graphene device arrays
5


.. just because you've made a big thing of graphene.
Besides, don't think you've done something incredible...
What!?
.. if you're gonna come here to "play research,"
I suggest you go elsewhere
I've been saying this the whole time, but...
はぁ
elsewhere
You have no idea what real research is like.

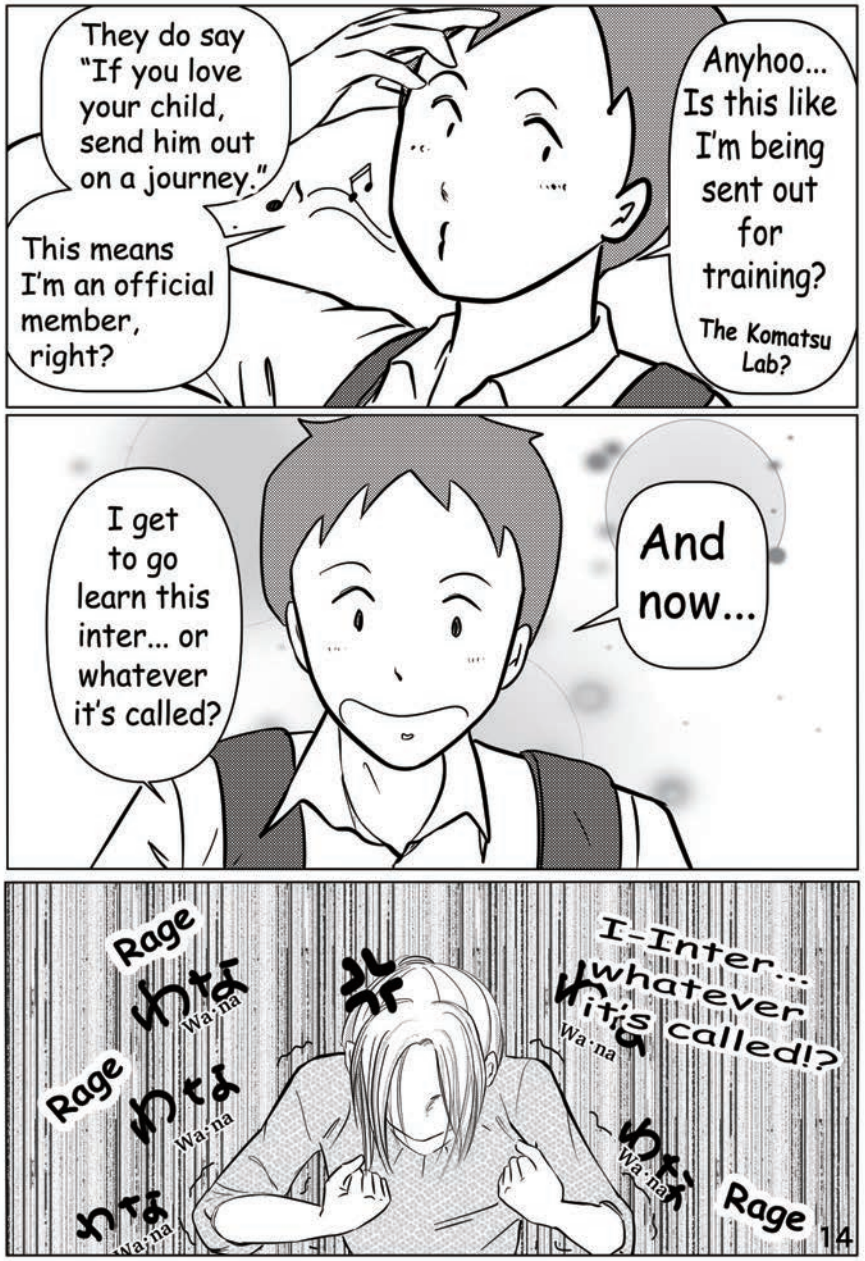

... isn't a credit to you.
The fact that this graphene is made properly...
カチ click
It might be true that there are things you can't tell until you look closely.
T- This...
※ See the brand new graphene from Chapter Three
... that allows a complete novice like you to make something of this quality!
ちっ Damn it
What's actually amazing is the technology...


Professor Ando told me which research lab to go to next, and...
But I...
It's insane that you would think...
Let's have him work with us...
Hey
... that Professor Ando would let someone like you...
P!
P!
P!

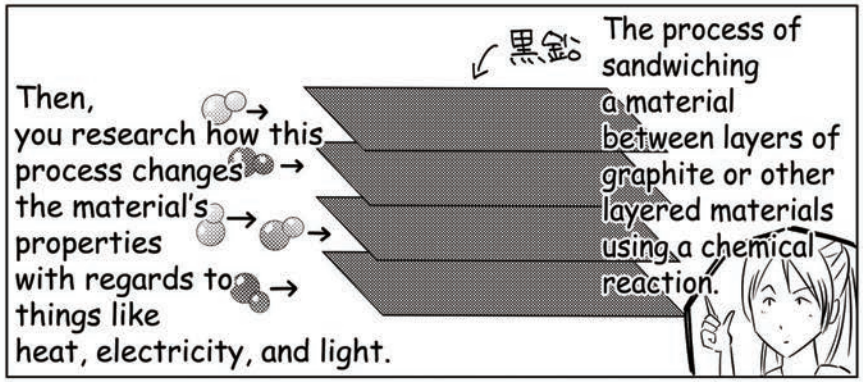

Do you have any idea how hard it is to feel like you're wandering around a desert, no phone in sight?
With no promise of results, or an established future?
Do you know how hard everyone is working?
... which I'm sure the staff was guiding you through every step of the way...
... otherwise you wouldn't have been able to do it!
You come waltzing in here all happy just because you've done this bit of CVD...
At any rate, we have no use for someone like you in our research lab.
Uh...

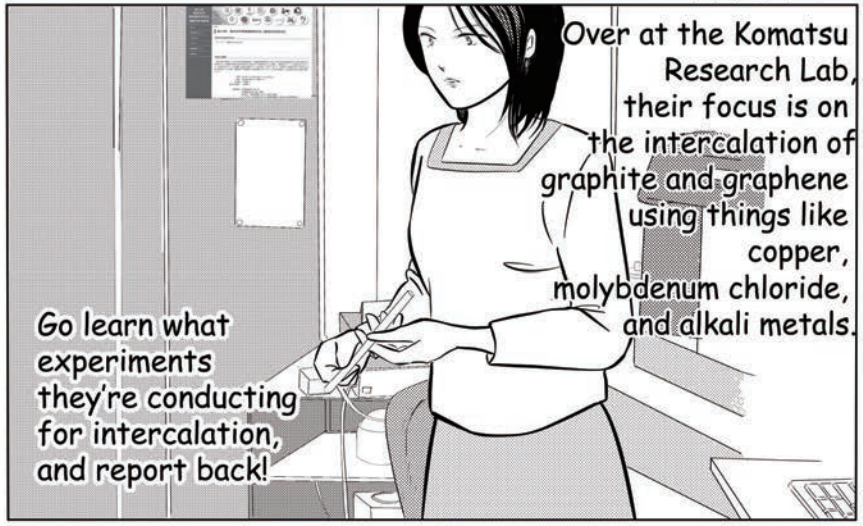

No...
Professor Ando...
He's serious about this..?
Yes, next up is intercalation
No, is Professor Ando...?
Iiyama University next... Does that mean...?
12


Lift
...into this lab!
...on our mission.
Ni
Grin
"Dear Koji,
I've forwarded you an email from Professor Ando.
Professor Chikushi, Kasuga University
Dear Professor Chikushi,
Please tell Koji, who is currently visiting your lab, to visit Professor Komatsu's lab at Iiyama University after this.
I apologize for the convenience, and thank you in advance."
Ando
Bam!
11

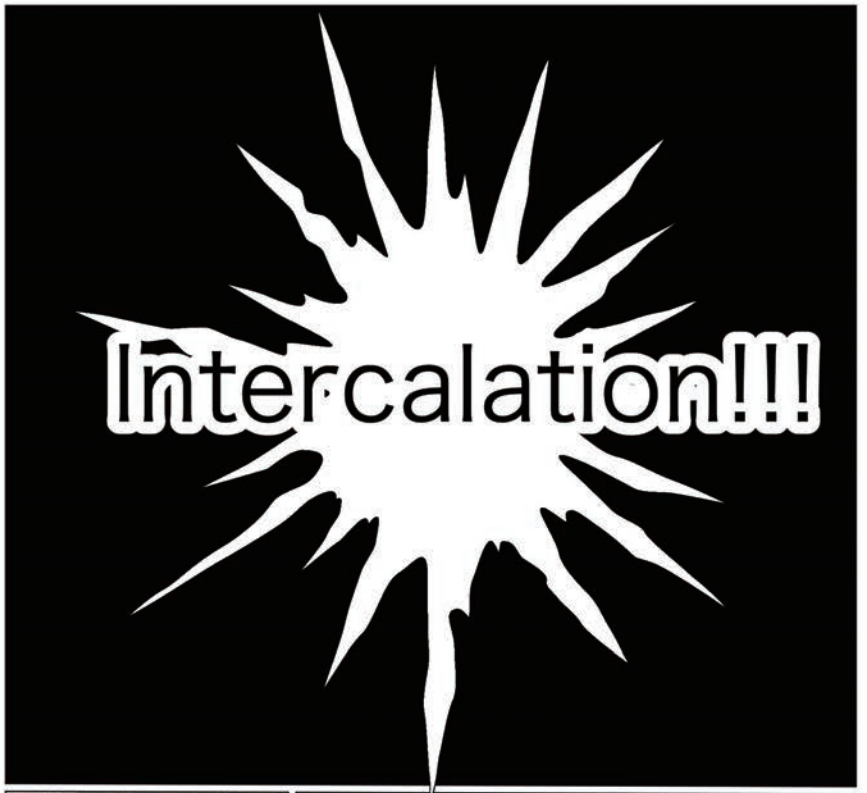

They do say "If you love your child, send him out on a journey."
This means I'm an official member, right?
Anyhoo... Is this like I'm being sent out for training?
The Komatsu Lab?
I get to go learn this inter... or whatever it's called?
And now...
Rage
わな
Wa·na
I-Inter... whatever it's called!?


ほら、Show
Dammit...
Show
うるさい
Shut up!!!
勝った
Grin
I win!


黒鉛
The process of sandwiching a material between layers of graphite or other layered materials using a chemical reaction.
Then, you research how this process changes the material's properties with regards to things like heat, electricity, and light.


Over at the Komatsu Research Lab, their focus is on the intercalation of graphite and graphene using things like copper, molybdenum chloride, and alkali metals.
Go learn what experiments they're conducting for intercalation, and report back!

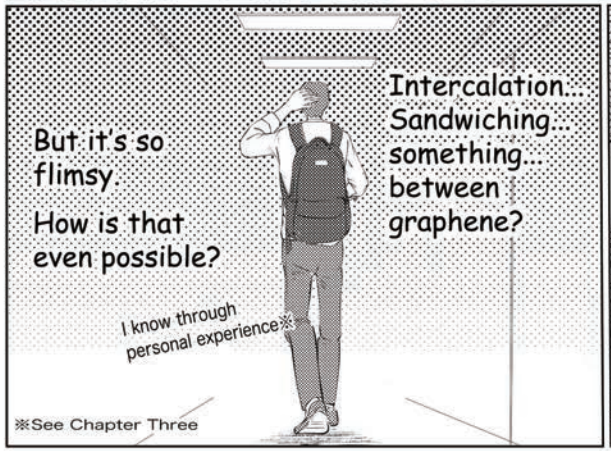

I see! Is that all?
あ、はい!! Uh, of course!


Intercalation!!!

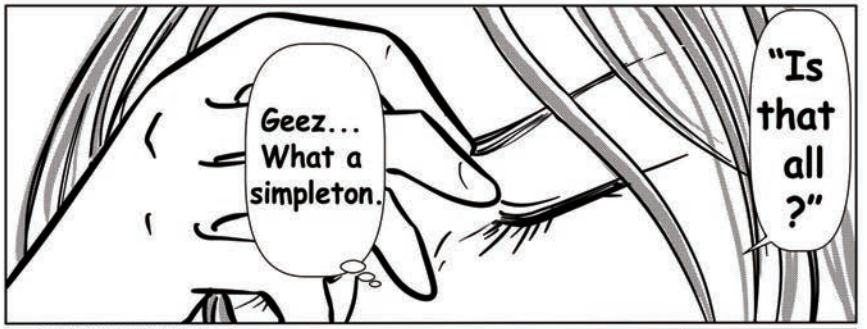

Ooh. What is it?
Squeeze
もみ momi
もみ momi


I'll have you know, intercalation is...
おっ... Oops


Yeeesss!!!
My dream, it's coming true!!!


But it's so flimsy.
How is that even possible?
Intercalation... Sandwiching... something... between graphene?
I know through personal experience※
※See Chapter Three


あへっ…
Uh…
Wait, wait

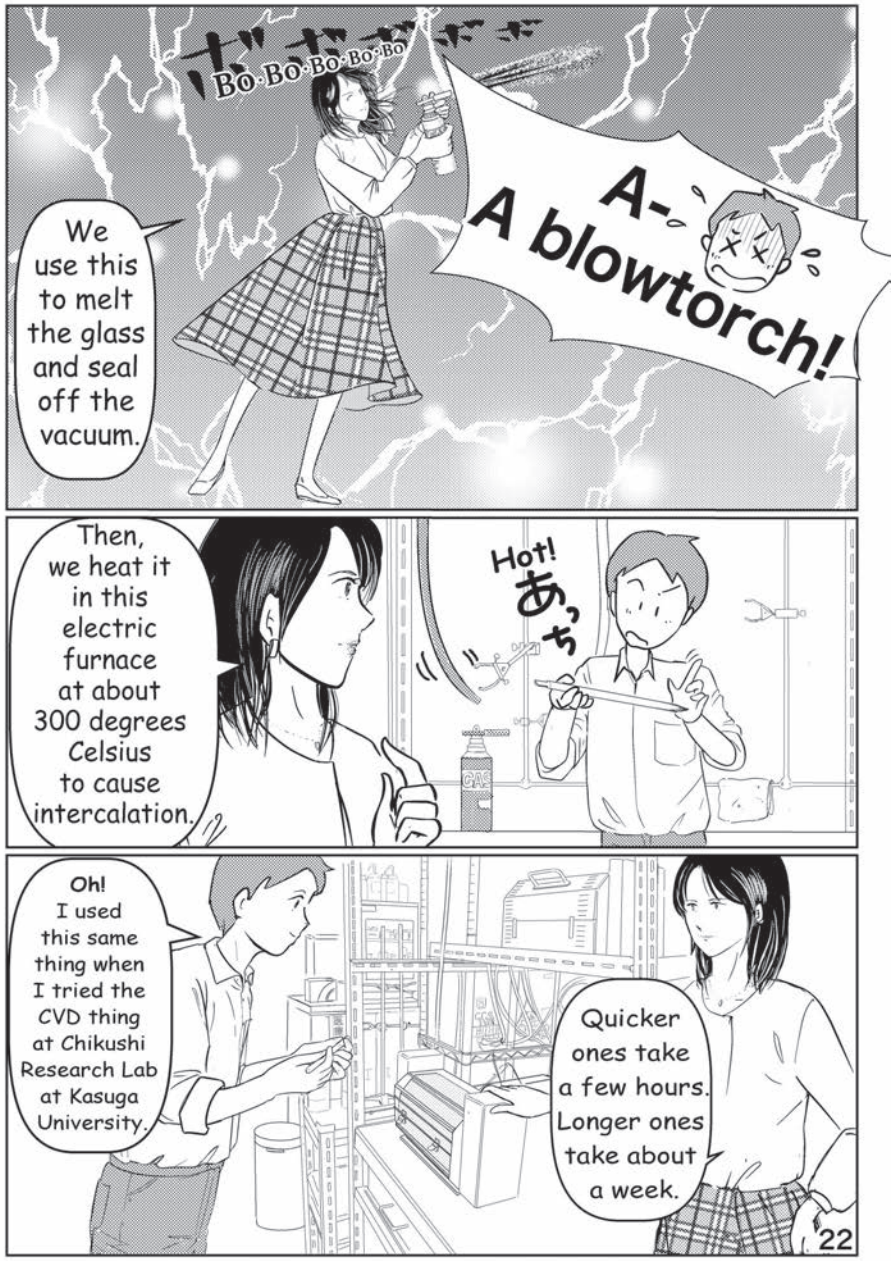

Geez… What a simpleton.
"Is that all?"


Um… of course.
And make sure to drop by before you head there.
Make sure to at least read the Komatsu Research Lab website before your visit next week.

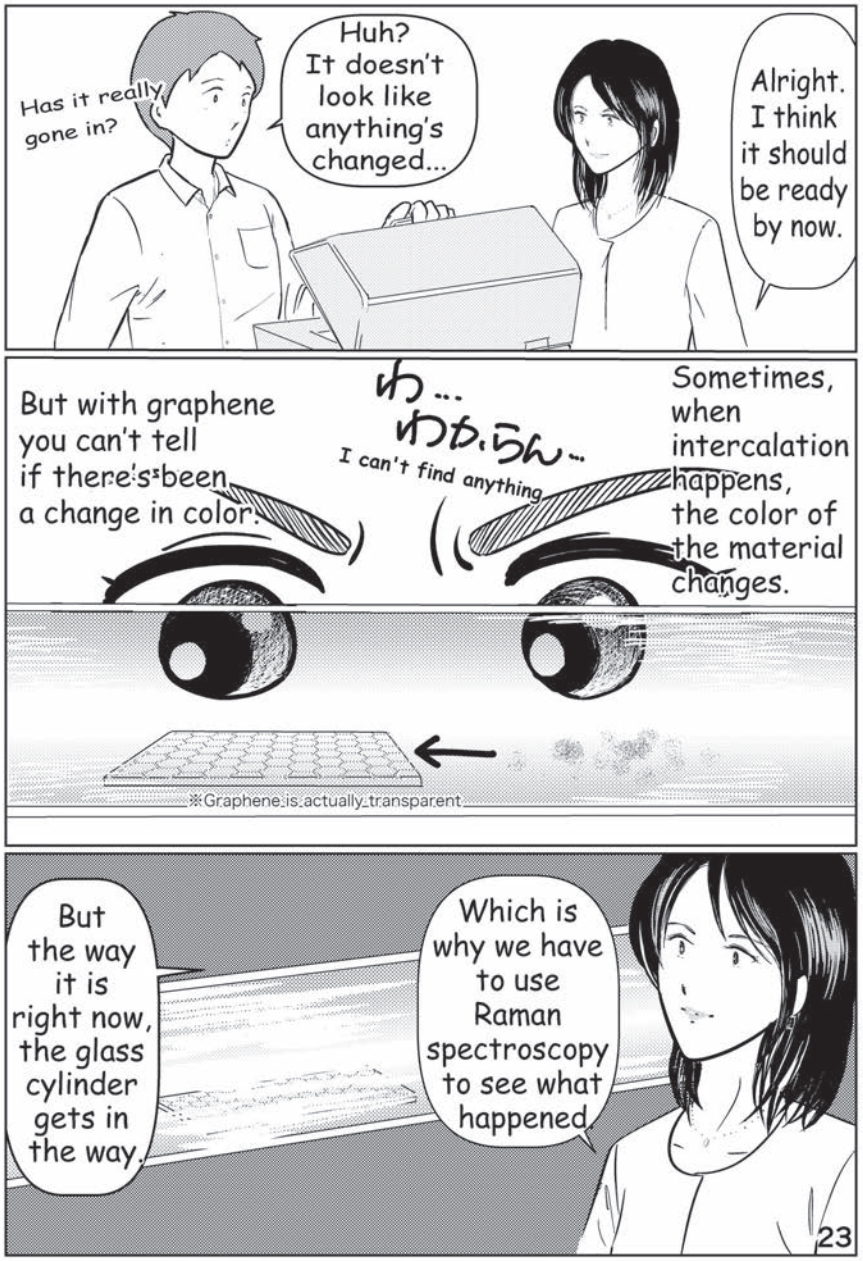

Doki Doki!!
ふっ
Uh
Thump Thump
パタン！
Shut
海波研究室


海波研究室
Alright then. I'll be back!

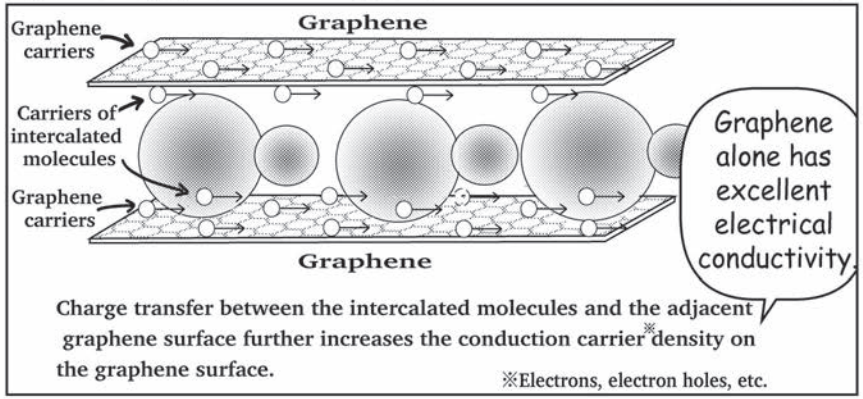

Day of visit
Morning !
I'll be heading over now. Was there anything you needed?
Nothing... You studied up?
Geez...
Go on.
Um, well... sort of
Alright then
Boon
Bzzz
Sneak
もぞ mo·zo
もぞ mo·zo
I'll be on my way!
ぴと Pi·to
Stick
Iiyama University
Hello!
It's nice to meet you. It's an honor to have a student of Professor Ando's come visit us.
Thank you for agreeing to meet me.
Intercalation is so uh, mysterious.
It's crazy how the molecules you want to have go in, end up going in the way you want them to, and...
You're right.
It's like they just slip in.
Oh, you can put your things there.
Ah, okay.
But come on, seeing is believing. Let's go on ahead and do an intercalation experiment.
19
20

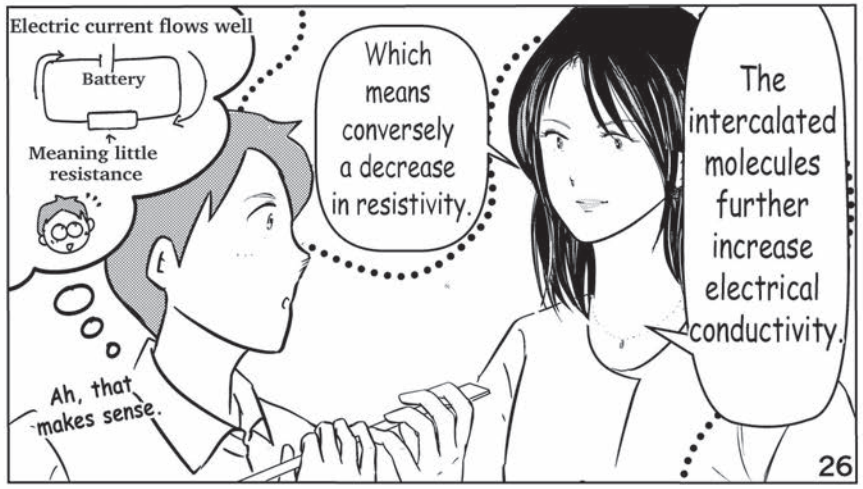

In this lab, we use this kind of glass tube.
First, you want to heat the thing you want to sandwich together with the graphite.
Bilayer Graphene
MoCl5
Substrate
Inside the glass tube
We'll set this tube up to make the vacuum.
We can't have anything enter, even air, so we've gotta create a vacuum.
Yup, which is why we have this.
Wait, but...
Air will get into the vacuum as soon as you take the tube off.
ぐいっ Push
21
We use this to melt the glass and seal off the vacuum.
A- A blowtorch!
Bo-Bo-Bo-Bo-Bo-Bo
Then, we heat it in this electric furnace at about 300 degrees Celsius to cause intercalation.
Hot! あっち
Oh! I used this same thing when I tried the CVD thing at Chikushi Research Lab at Kasuga University.
Quicker ones take a few hours. Longer ones take about a week.
22

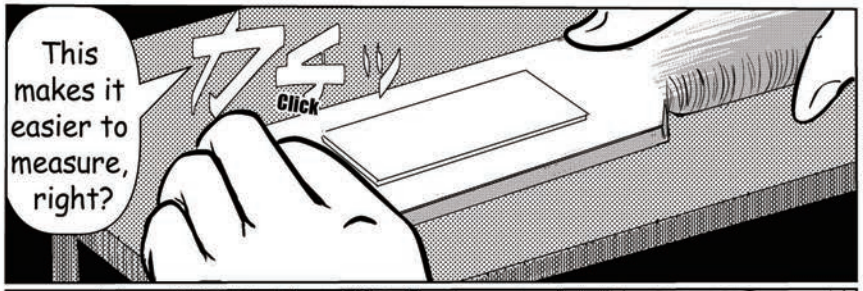

Do this, and...
Tilt
So we move what we've just made to this flat part here.
whiz
※Actually, graphene is transparent
Whoa! It slides right in!
Amazing!
おおお


Has it really gone in?
Huh? It doesn't look like anything's changed...
Alright. I think it should be ready by now.
But with graphene you can't tell if there's been a change in color.
わ... わからん...
I can't find anything
Sometimes, when intercalation happens, the color of the material changes.
※Graphene is actually transparent
But the way it is right now, the glass cylinder gets in the way.
Which is why we have to use Raman spectroscopy to see what happened.

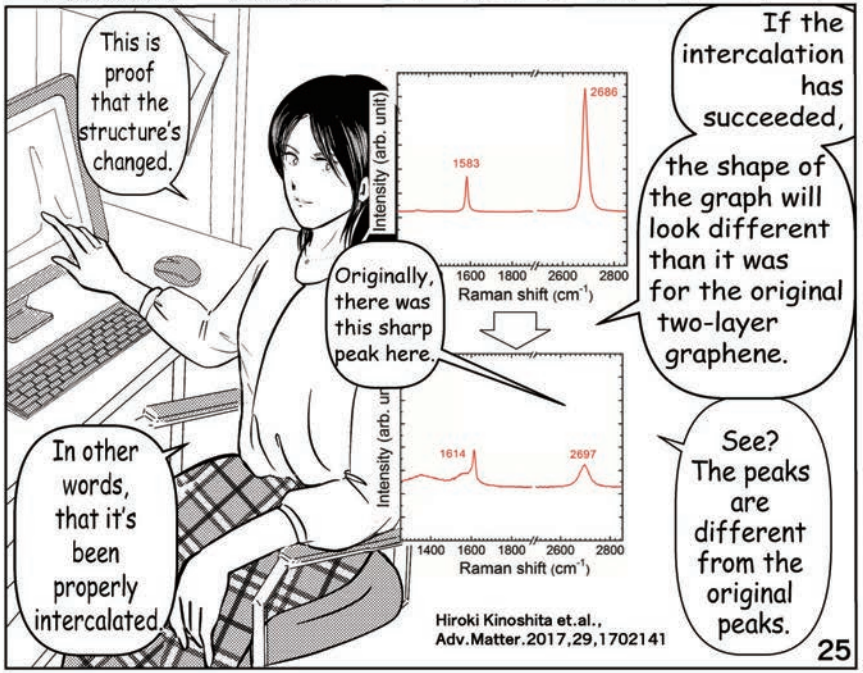

There are a bunch of things we have to check, but first up is electrical conductivity.
And what happens now?


Graphene
Graphene carriers
Carriers of intercalated molecules
Graphene carriers
Graphene
Graphene alone has excellent electrical conductivity.
Charge transfer between the intercalated molecules and the adjacent graphene surface further increases the conduction carrier※ density on the graphene surface.
※Electrons, electron holes, etc.

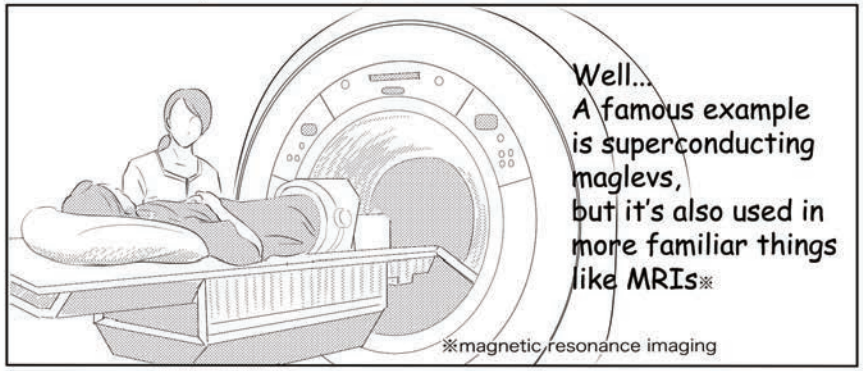

Electric current flows well
Battery
Meaning little resistance
Ah, that makes sense.
Which means conversely a decrease in resistivity.
The intercalated molecules further increase electrical conductivity.
26

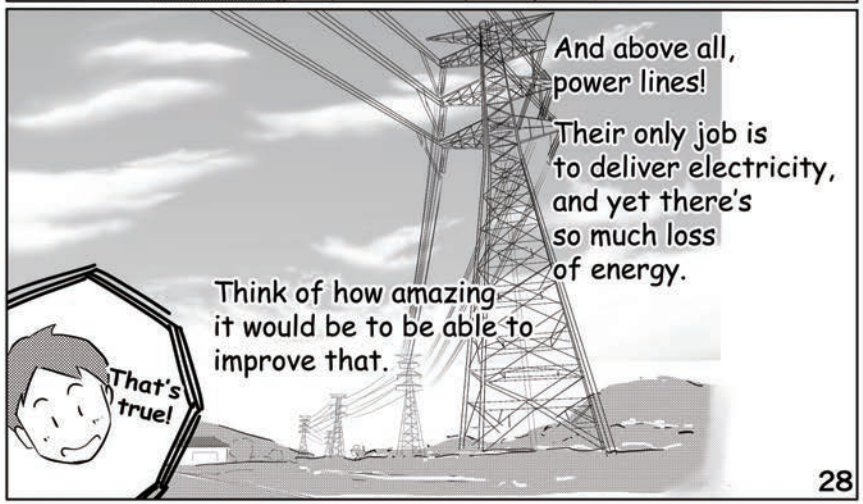

This makes it easier to measure, right?
Click

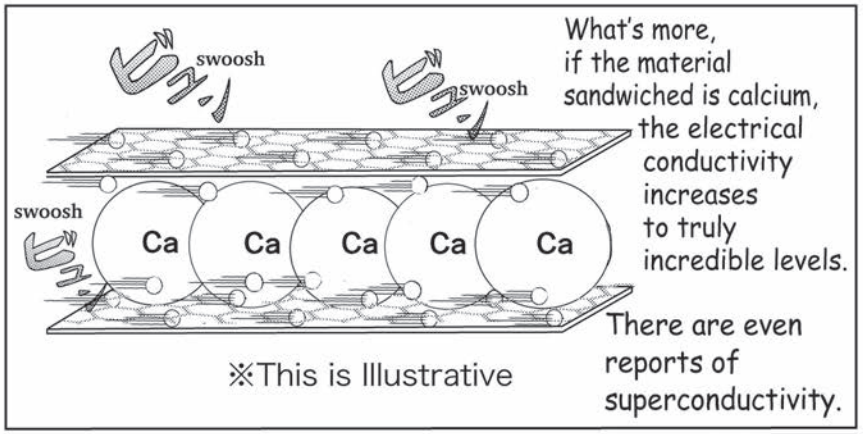

The perfect trick for a clumsy dude like me...
Geez, wow
Whee
We have craftsmen custom-make these glass tubes for us.

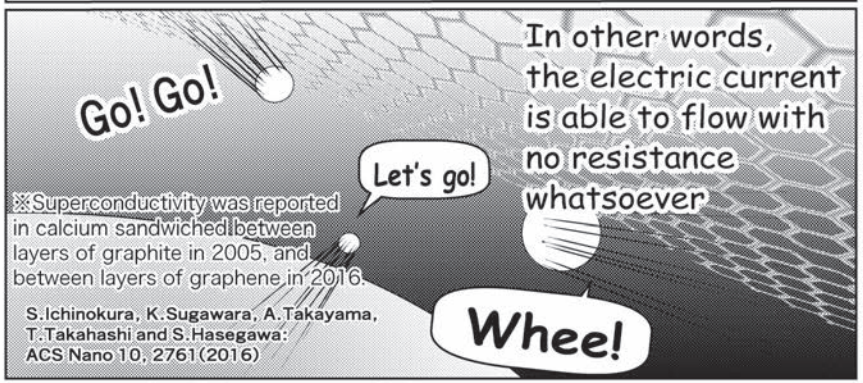

This is proof that the structure's changed.
If the intercalation has succeeded, the shape of the graph will look different than it was for the original two-layer graphene.
Intensity (arb. unit)
2686
1583
1600 1800 2600 2800
Raman shift (cm-1)
Originally, there was this sharp peak here.
Intensity (arb. unit)
1614
2697
1400 1600 1800 2600 2800
Raman shift (cm-1)
In other words, that it's been properly intercalated.
See? The peaks are different from the original peaks.
Hiroki Kinoshita et.al., Adv.Matter.2017,29,1702141
25

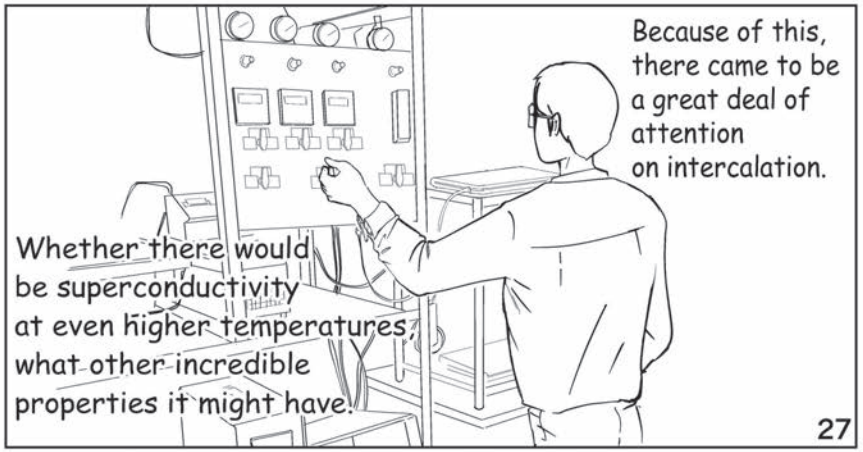

I can't at all imagine...
Superconductivity on its own does sound like a dream come true,
but what is it actually used for?


Well...
A famous example is superconducting maglevs,
but it's also used in more familiar things like MRIs※
※magnetic resonance imaging


And above all, power lines!
Their only job is to deliver electricity, and yet there's so much loss of energy.
Think of how amazing it would be to be able to improve that.
That's true!


swoosh
swoosh
swoosh
Ca
Ca
Ca
Ca
Ca
What's more, if the material sandwiched is calcium, the electrical conductivity increases to truly incredible levels.
※This is Illustrative
There are even reports of superconductivity.

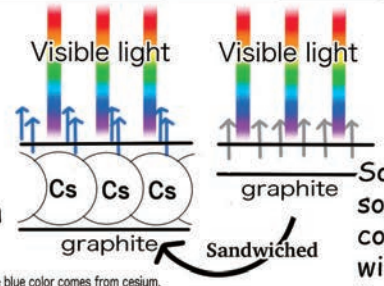

Go! Go!
Let's go!
Whee!
In other words, the electric current is able to flow with no resistance whatsoever
※Superconductivity was reported in calcium sandwiched between layers of graphite in 2005, and between layers of graphene in 2016.
S.Ichinokura, K.Sugawara, A.Takayama, T.Takahashi and S.Hasegawa: ACS Nano 10, 2761(2016)


Because of this, there came to be a great deal of attention on intercalation.
Whether there would be superconductivity at even higher temperatures, what other incredible properties it might have.

Ah,where did I put it?

There's a sample from an experiment we did a while back...

10 years ago, we sandwiched cesium in some graphite. The blue color from back then still hasn't changed.



It turns out, color is a reflection of a material's structure.

So what will happen sometimes is that the color of the material will change when it is intercalated.

What? Professor, you still have a material from all the way back then in storage?

That means its properties haven't changed in 10 years.

I wanna see!

An intercalated material from 10 years ago?

Graphite intercalation compounds are supposed to be unstable under atmospheric conditions.

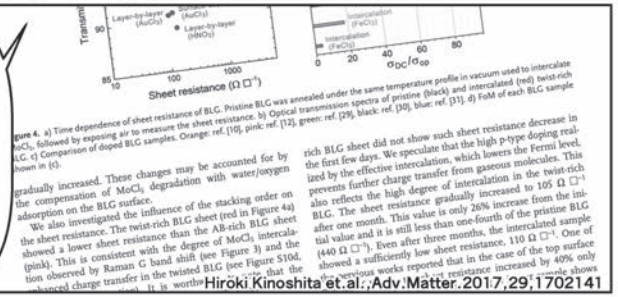
Intercalation materials are not very resilient under atmospheric conditions.

Depending on what it is, it can burn up immediately.

Exactly

I guess the big concern then is durability.

We've confirmed that the material we made in the experiment today, molybdenum chloride in graphene...



gure 4. a) Time dependence of sheet resistance of BLG. Pristine BLG was annealed under the same temperature profile in vacuum used to intercalate $MoCl_5$, followed by exposing air to measure the sheet resistance. b) Optical transmission spectra of pristine (black) and intercalated (red) twist-rich BLG. c) Comparison of doped BLG samples. Orange: ref. [10], pink: ref. [12], green: ref. [29], black: ref. [30], blue: ref. [31]. d) FoM of each BLG sample shown in (c).

gradually increased. These changes may be accounted for by the compensation of $MoCl_5$ degradation with water/oxygen adsorption on the BLG surface.

We also investigated the influence of the stacking order on the sheet resistance. The twist-rich BLG sheet (red in Figure 4a) showed a lower sheet resistance than the AB-rich BLG sheet (pink). This is consistent with the degree of $MoCl_5$ intercalation observed by Raman G band shift (see Figure 3) and the enhanced charge transfer in the twisted BLG (see Figure S10d, ...ote that the ...rthe...

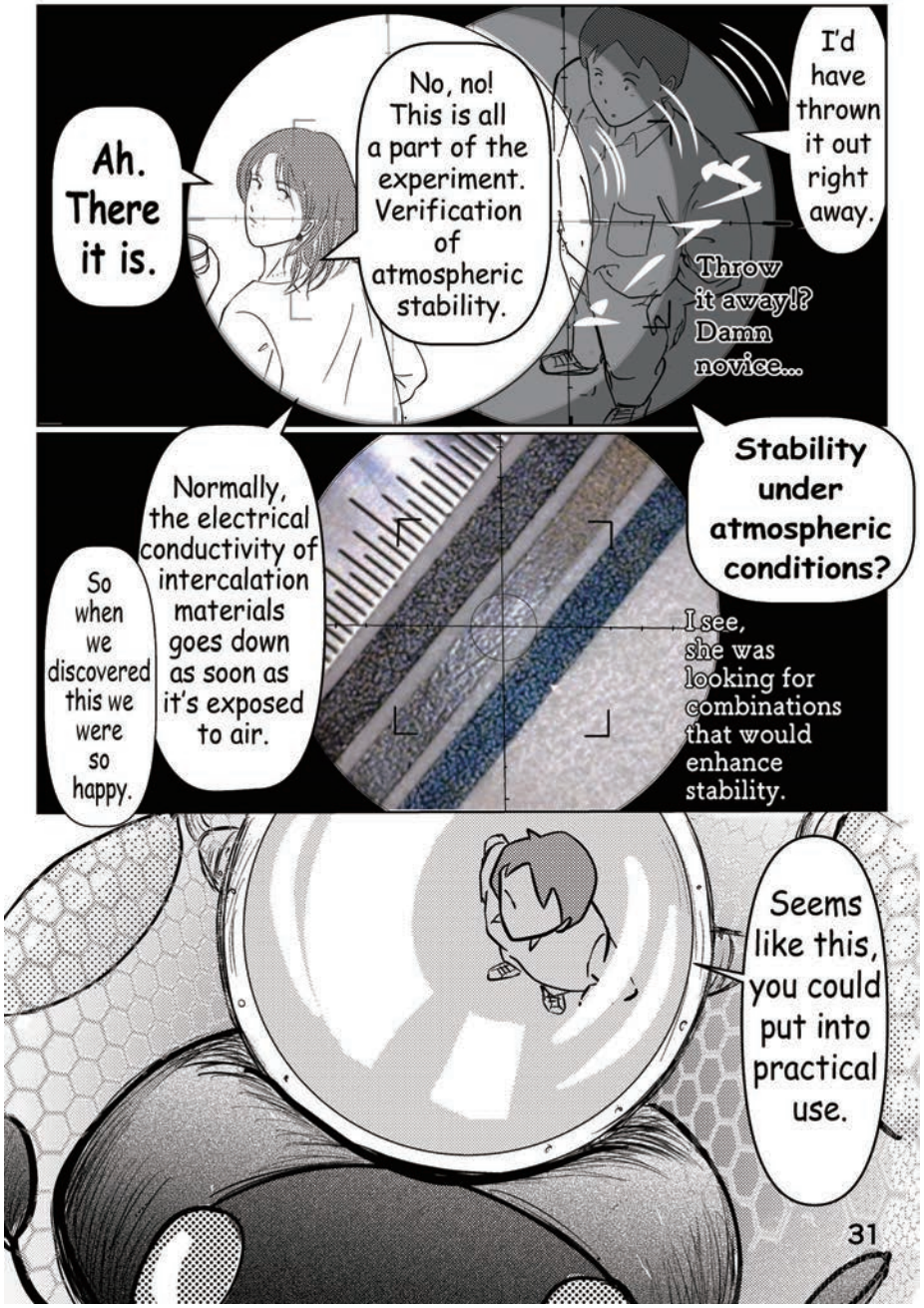
rich BLG sheet did not show such sheet resistance decrease in the first few days. We speculate that the high p-type doping realized by the effective intercalation, which lowers the Fermi level, prevents further charge transfer from gaseous molecules. This also reflects the high degree of intercalation in the twist-rich BLG. The sheet resistance gradually increased to 105 Ω $□^{-1}$ after one month. This value is only 26% increase from the initial value and it is still less than one-fourth of the pristine BLG sheet resistance. Even after three months, the intercalated sample showed a sufficiently low sheet resistance, 110 Ω $□^{-1}$. One of previous works reported that in the case of the top surface ...e resistance increased by 40% only ...e shows

Hiroki Kinoshita et.al.; Adv.Matter.2017,29,1702141

Oh, here, I have something to show you.

... lasts for at least three months, but...


Yes. I take good care of my things, but I also take good care of my research.
You have this decade-old intercalation material...
You've been doing this research for a long time?
Loyal, I guess you could say...
Huh? I feel like I've heard that before
※See Chapter Three
I've been studying intercalation all the way since grad school.
.. but every time, there was some interesting discovery or another, which would make me wanna go out and experiment too.
There were times when I thought about quitting ...
Uh
GA·BA!
Whoa! Maybe this will work!
32


Ah. There it is.
No, no! This is all a part of the experiment. Verification of atmospheric stability.
I'd have thrown it out right away.
Throw it away!? Damn novice...
So when we discovered this we were so happy.
Normally, the electrical conductivity of intercalation materials goes down as soon as it's exposed to air.
Stability under atmospheric conditions?
I see, she was looking for combinations that would enhance stability.
Seems like this, you could put into practical use.
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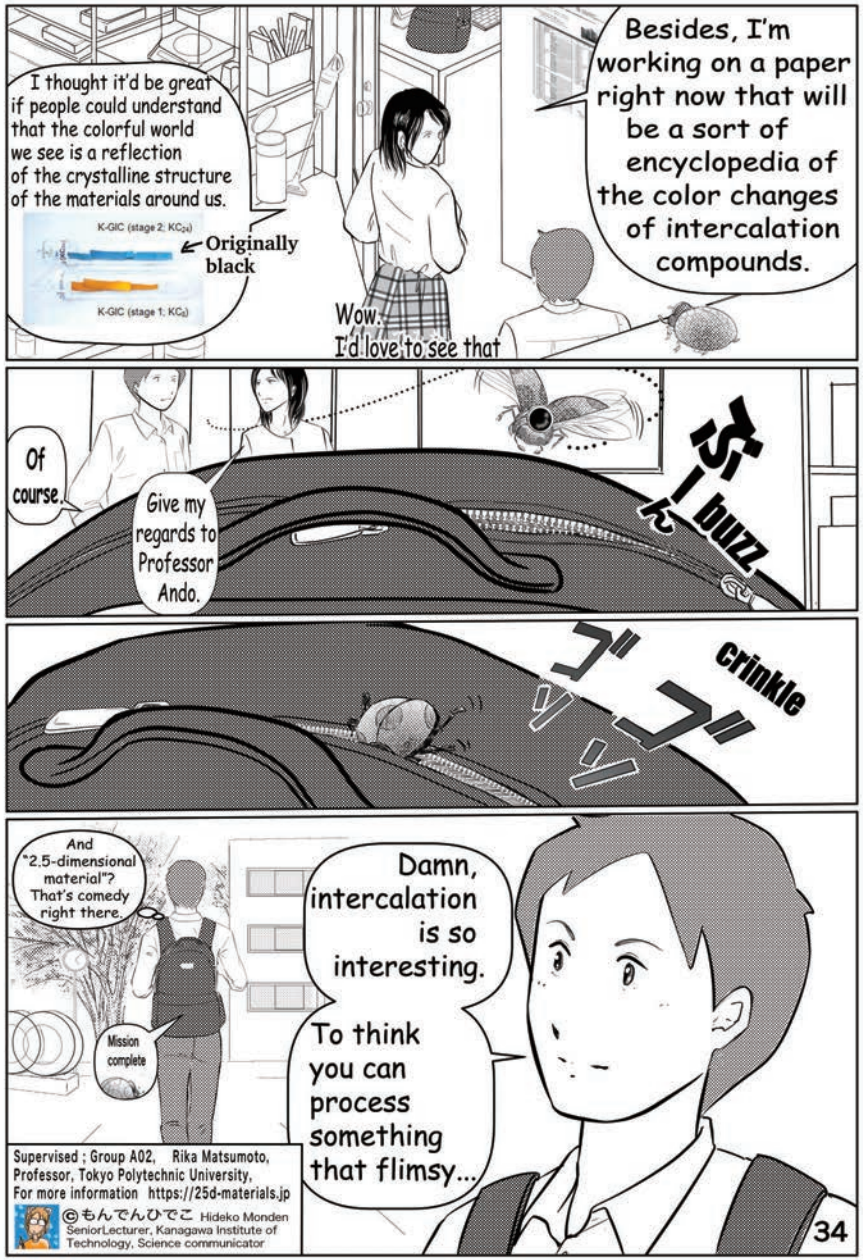
I thought it'd be great if people could understand that the colorful world we see is a reflection of the crystalline structure of the materials around us.
K-GIC (stage 2; KC_{24})
Originally black
K-GIC (stage 1; KC_8)
Wow. I'd love to see that
Besides, I'm working on a paper right now that will be a sort of encyclopedia of the color changes of intercalation compounds.
Of course.
Give my regards to Professor Ando.
ぶーん buzz
グゾグゾ crinkle
And "2.5-dimensional material"? That's comedy right there.
Mission complete
Damn, intercalation is so interesting.
To think you can process something that flimsy...
Supervised ; Group A02, Rika Matsumoto, Professor, Tokyo Polytechnic University,
For more information https://25d-materials.jp
©もんでんひでこ Hideko Monden SeniorLecturer, Kanagawa Institute of Technology, Science communicator
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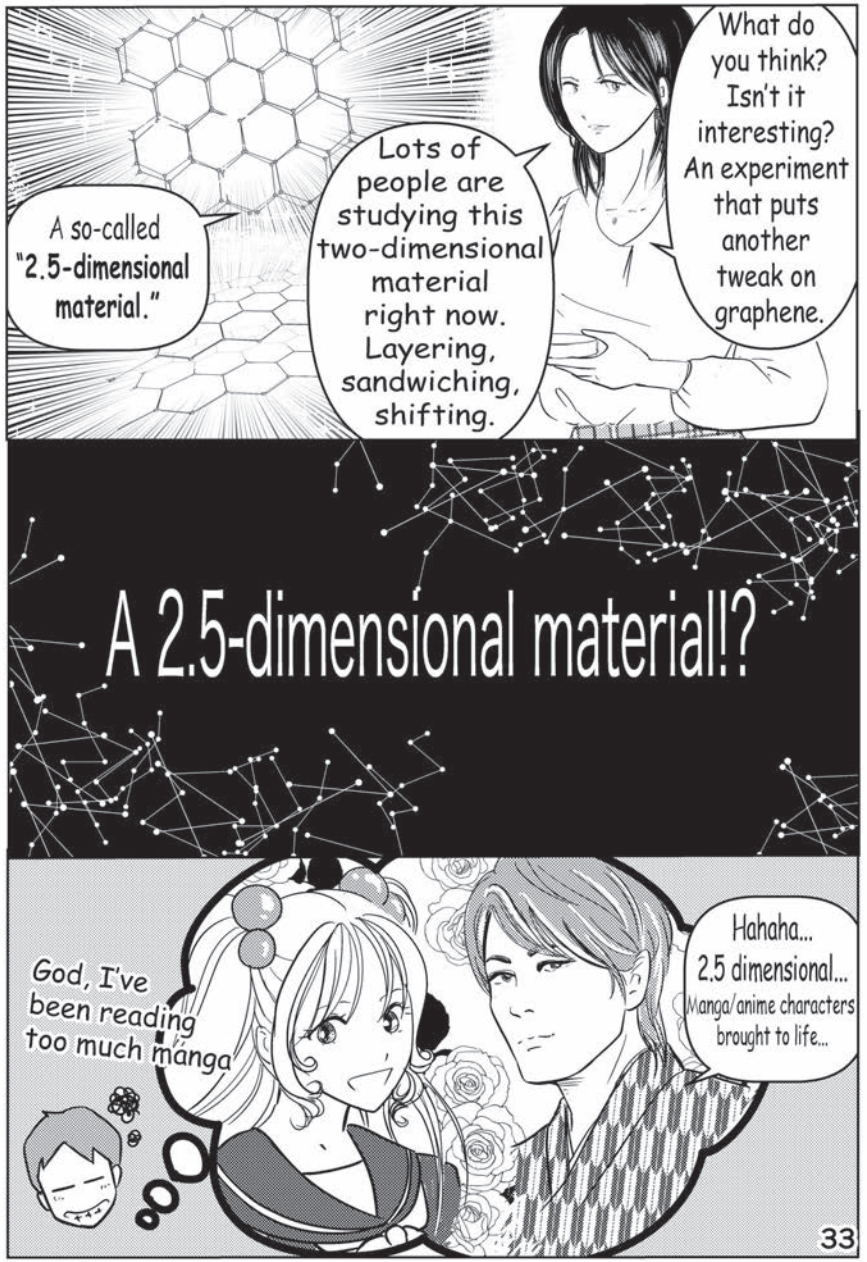
A so-called "2.5-dimensional material."
Lots of people are studying this two-dimensional material right now. Layering, sandwiching, shifting.
What do you think? Isn't it interesting? An experiment that puts another tweak on graphene.
A 2.5-dimensional material!?
God, I've been reading too much manga
Hahaha... 2.5 dimensional... Manga/anime characters brought to life...
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