1&2DM

CONFERENCE & EXHIBITION

TOKYO (JAPAN) - JANUARY 28-29, 2020

1 & 2D MATERIALS INTERNATIONAL CONFERENCE



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FOREWORD

On behalf of the Organising Committee we take great pleasure in welcoming you to Tokyo for the second edition of the **1&2DM** International Conference.

A plenary session with internationally renowned speakers and an industrial forum featuring current and future Graphene, Nanotubes and other 1&2DM developments will be highlighted at the event.

1&2DM 2020 will bring together, from a global perspective, scientists, researchers, end-users, industry and policy makers in an environment of cooperation and sharing towards the challenges of 1&2DM commercialization.

We truly hope that **1&2DM 2020** serves as an international platform for communication between science and business.

We also would like to thank all the speakers and participants that join us this year.

One thing we have for granted: very few industries, one way or another, will escape from the influence of 1&2D Materials and the impact on businesses is here to stay.

Hope to see you again in the next edition of **1&2DM** to be held in 2021 in Tokyo (Japan).

MAIN ORGANISER





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Graphene Industry: Synthesis Determines Its Future

High quality graphene materials are the footstone of future graphene industry. As experienced in modern carbon fiber industry over last half century, the synthesis will certainly determine the future of graphene materials. Although great efforts have been done on synthesis since the first isolation of graphene in 2004, there still exists a big gap between the theoretical and realistic graphene. For the industry-level applications, one needs to consider the yield and cost issues in addition to purity, layer thickness and uniformity, domain size, lateral size of flakes, and defect density. The graphene synthesis calls for more technological innovations together with fundamental discoveries.

Over last ten years, we have made great efforts on the chemical vapor deposition (CVD) growth of high performance graphene films. We are working along two different directions towards commercial graphene materials. The first direction is the CVD growth of single crystal graphene wafers targeting electronic and optoelectronic purposes. We have realized a pilot level production of 4 inch single crystal graphene wafers using home-made CVD growth system with a capacity of 10,000 wafers/year. Using CuNi(111) alloy catalyst, we have succeeded in the ultrafast epitaxial growth of 6 inch single crystal graphene wafers with a growth rate of 50 times faster than on Cu(111), indicating the possibility of low cost production of high-quality graphene wafers. The second direction is the CVD growth of large scale graphene film using commercial Cu foil. We developed the first roll to roll continuous CVD growth system for this purpose. The production capacity reaches a level of 20,000m2/year with a domain size of 10-20µm. The cost has been reduced to 200 RMB/m2. To increase the growth quality, we also developed an A3-size static CVD growth system with a capacity of 10,000m2/year and an expected domain size of 0.5mm. Superclean graphene is our important contribution to produce high-performance graphene films. During CVD growth, there exists an inevitable contamination of graphene surface arising from amorphous carbon byproduct and not-well developed graphene seeds, which leads to the ordinary "dirty graphene". We have developed three effective techniques to grow the superclean graphene, including Cu-foam-aided growth, post-growth CO2 etching, metal-containing precursors and magic lint roller. Such kinds of superclean graphene exhibited the highest carrier mobility, the lowest contact resistance and sheet resistance, and the highest fracture strength. We designed two types of pilot CVD growth systems based on the CO2 etching technique, A3 size with a capacity of 10,000m2/year and 300nm x 100mm size with a capacity of 30,000 pieces/year. Moreover, we have made great efforts on directly growing graphene on traditional glass, optical fibers, glass fibers and sapphire wafers. Such kinds of growth products can be directly used for various applications without involving the difficult peeling off and transfer processes. Super graphene glass, graphene-tailored optical fibers and glass fibers using the direct growth technique have become our important research targets in the last few years. The talk will give a brief overview of our last 10 years studies on the industrial level synthesis and the killer applications of graphene materials.

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Hexagonal Boron Nitride single crystal as a two dimensional wide bandgap material

Hexagonal boron nitride BN (hBN) and cubic BN (cBN) are known as the representative crystal structures of BN. The former is chemically and thermally stable, and has been widely used as an electrical insulator and heat-resistant materials. The latter, which is a high-density phase, is a super-hard material second only to diamond.

Among those BN crystals, some progresses in the synthesis of high purity BN crystals were achieved by using Ba-BN as a growth solvent material at high pressure (HP) of 5.5GPa[1]. Band-edge natures (cBN Eg=6.2eV and hBN Eg=6.4eV) were characterized by their optical properties. The key issue to obtain high purity crystals is to reduce oxygen and carbon contamination in the HP growth circumstances. Then an attractive potential of hBN as a deep ultraviolet (DUV) light emitter [2] and also superior properties as substrate of graphene devices [3] were realized.

While the current subject is still to realize how the major impurities such as carbon and oxygen affect the properties of hBN and cBN, some progerss for the realization for the application of 2D's substrates and photonic materials have been achieved. In order to realize these newly developed potential of hBN crystals further, more precise insight for its quality control is important. So far qualitative study for residual carbon impurity was limited to SISM study where few ppm level is a detection limit, recent revist trials with EPR study could give further infomation with order of few ppb levels.

Also, controlling of boron and nitrogen isotope ratio (¹⁰B,¹¹B and ¹⁵N) in hBN and cBN crystals can be now carried out by metatheses reaction under HPHT.

In this paper, recent studies on BN crystals obtained at high pressure with respect to impurity / isotope controls and their functionalizations will be reported.

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Controlled synthesis and processing of 2D materials for future applications

Two-dimensional (2D) materials have attracted great interest because of their unique and excellent physical properties which promise a wide variety of applications. Hexagonal boron nitride (h-BN) is a key material which boosts physical and optical properties of various 2D materials, promoting the electronic and photonic applications. However, due to difficulty in synthesizing large-area h-BN, most of the current studies utilize exfoliated h-BN flakes made from bulk crystal.

In this talk, I will demonstrate the aligned growth of monolayer h-BN using epitaxial Cu(111) and Ni(111) films that are deposited on c-plane sapphire substrates [1,2]. In particular, the high temperature CVD growth on the Ni(111) gave very large and aligned monolayer h-BN grains with a lateral size up to 0.5 mm (Figure 1a,b).

Furthermore, we have developed a method to synthesize multilayer h-BN (Figure 1c,d) which is essential for developing applications of 2D The Fe-Ni alloy catalyst materials. allowed to tune the solubility of B and N atoms and also suppress the structural transformation seen in pure Fe metal catalyst. Monolayer WS₂ grown on our multilayer h-BN showed enhanced photoluminescence (PL) with narrow linewidth, indicating the effectiveness of the CVD-grown multilayer h-BN as a template of 2D materials.

Our recent studies on chemical doping of WSe₂ [4], and the controlled CVD synthesis and applications of monolayer and bilayer graphene [5-7] as well as their 2D heterostructures [8,9] will be also presented.



Figure 1: (a) CVD setup used to grow monolayer h-BN. (b) Very large monolayer h-BN grains grown on Ni(111)/sapphire surface. (c) Schematic of multilayer h-BN growth on Fe-Ni alloy catalyst. (d) Optical micrograph of multilayer h-BN transferred on SiO₂ substrate

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January 28-29, 2020

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Nanopipes: From Polymers to Nanocarbons. From 1D to 2D Hybrid Electrode Materials

Nanocarbons are very versatile materials providing conductive and capacitive matrices for the design of hybrid electrode materials and devices [1]

Nanopipes are template-grown nanostructures first reported for polypyrrole but that can be conformally turned into nanocarbon materials by pyrolysis under controlled atmosphere [2] (Figure 1). You could call them nanotubes (as it was initially done) if it wasn't because they feature diameters in the range of 50 to 200 nm.

In our group we have first synthesized these N-doped Carbon nanopipes [2] and have used them[2,3] as well as the precursor PPy Nanopipes [4,5] to prepare hybrid electroactive materials to be used in hybrid electrodes and devices. This conference will show recent results along this line both concerning supercapacitors, batteries and hybrid devices, including as well comparison with extended 2D graphene hybrids also developed in our laboratory.

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- [5] Deepak Dubal, Ajay Jagadale, Nilesh Chodankar, Do-Heyoung Kim, Pedro Gomez-Romero, Rudolf Holze. Energy Technology 2019 7, (2), 193-200. Polypyrrole Nanopipes as a promising cathode material for Li-ion batteries and Li-ion capacitors: Two-in-One Approach





January 28-29, 2020

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Emergent Transport in van der Waals heterostructures

The recent progress of van der Waals (vdW) heterostuctures enables new ways to study low dimensional transport by harnessing the unique features of atomically thin materials. The fabrication of vdW heterostructures are now extending from conventional transfer to chemical vapor deposition (CVD) and molecular beam epitaxy (MBE). Here, I will present two examples.

The first topic is on the symmetry control by vdW heterostructures. The nanomaterials is a good plat form of symmetry control. This is in sharp contrast with the bulk materials in which the crystal structure simply determines the symmetry. For instance, symmetry can be modified just by putting a different material on top of the bottom material. We will discuss the polar structure induced by the vdW heterostructures, and its spontaneous photovoltaic effect.

The second is the magnetic vdW heterostructure fabricated by MBE, in which we demonstrate that the magnetic anisotropy of 2D magnet can be modified by the material with the Zeeman-type spin-orbit interactions. We emphasize here that MBE should be a powerful tool for fabricating new van der Waals heterostructures.

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Graphene-based biosensors for diagnostics applications

Graphene oxide (GO) and graphene quantum dots (GQDs) display advantageous characteristics with interest for building innovative biosensing platforms and even smart devices such as nano/micromotors for a myriad of uses including sensing. Quenching of the fluorescence induced by GO or photoluminescence of GQDs can easily operate in synergy with various other nanomaterials and platforms opening the way to several unprecedented biosensing strategies and unique nanomotor technologies. Taking advantage of GO, GQDs we are developing simple, sensitive, selective and rapid biosensing platforms that include: a) GO – based microarray & laterals flow technologies taking advantages of high quenching efficiency of GO. A "turn ON by a pathogen" device will be shown as a highly sensitive detection system using plastics or paper/nanopaper substrates; b) GQDs–based sensors for contaminants detection based on the use of multifunctional composite materials that enable rapid, simple and sensitive platforms in connection to smartphone; c) A water activated GO transfer technology using wax printed membranes for fast patterning of a touch sensitive device with interest for electronic devices including sensing as well as for a cost-efficient nanomotor building technology for several applications. This work is supported by EU (Graphene Flagship), CERCA Programme / Generalitat de Catalunya. A.M. acknowledges also H2020 EU Project "INTCATCH" (Contract No. 689341).

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Conducting and Insulating Nanotubes as Platform for Rechargeable Batteries

Carbon nanotube (CNT) and boron nitride nanotube (BNNT) have small mass density, flexibility, and binding nature similarly to organic materials yet have very high thermal stability differently from organic materials. These characteristics are attractive in making rechargeable batteries lighter and safer.

Present batteries have many non-active components including binder, conducting filler, current collectors, and separator (Figure 1a). Innovative active materials have been extensively researched, but few of them are practically used because of the limited performance enhancement due to the non-active components used at large fractions. We have realized a full cell with CNT-based electrodes, in which 1 wt% CNTs held 99 wt% active materials without using any polymeric binders nor metallic foils [1]. The CNT-based electrode architecture is shown effective in making high-capacity negative and positive electrodes with Si [2] and S [3]. By introducing Li to the Si-CNT electrode, we realized a Li_xSi-CNT ||S-CNT full cell with high energy density (Fig. 1b) [4].

High energy cells should be safer. Conventional polyolefin separators shrink and melt, leading to overrun reaction when excessively heated. We developed self-supporting BNNT separator, and realized graphite-CNT|BNNT|LiCoO₂-CNT full cell without using any polymeric binders nor metallic foils (Figure 1c). The electrode/separator stack is thermally very stable, and a full cell made with the stack heated at 500 °C and a fresh electrolyte functioned correctly [5]. CNT and BNNT are a promising platform for innovative batteries.

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	(a) Conventional	(b) CNT-based	(c) CNT&BNNT-based
Binder	Polymers	CNTs	CNTs
Filler	Carbon materials	CNTs	CNTs
Collector	Metal foils	CNTs (+ Metal wires)	CNTs (+ Metal wires)
Separator	Polymers	Polymers	Polymers



Figure 1: Battery architectures. (a) Conventional architecture. (b,c) Proposed, nanotube-based architectures .

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Predictive Computational Modelling for Guiding Industrial Research & Development in 2D materials-based materials & devices

Abstract

I will illustrate today's capability of predicting physical properties of complex 2d materials-based materials and devices in the context of industrial applications, including gas sensing, composites materials, electronics, thermal management, energy-saving devices. A special focus will be given to scalable materials as produced in fab environment or production companies such as polycrystalline 2D materials and reduced oxide graphene, whereas simulations of amorphous forms of 2D materials will be presented in relation with recent breakthroughs in Asia. Recent results on gas sensors will be discussed within the context of the ULISSES European project which ambition to advance towards the most performant CO₂ gas sensors architecture and integrability into commercial products.

By computing charge and thermal conductivity on realistic models of disordered materials containing up to billion atoms, the supremacy of so-called order N computational algorithms will be presented, which together with machine learning approaches could further establish as essential tools for engineering highly performant materials and optimized device functioning.

This presentation has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 825272

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Nanoscale Investigation of Local optical Properties from Lowdimensional Materials using Electron Energy-loss Spectroscopy

Measurements of local optical properties are of great importance in designing nanoscale optoelectronic devices. Electron energy-loss spectroscopy (EELS) has been widely used for elemental identification in transmission electron microscopes (TEM) by using core-level excitations. Recent developments of monochromators after the e-beam guns has enabled us to access optical and vibrational ranges in the valence EELS regions from nanometric materials. Contrary to the core-level EELS, the valence EELS has a considerable delocalization effect which makes the local measurements intrinsically difficult. Here we show our continuous studies to develop the possibilities of valence EELS on low-dimensional materials. Attempts involve the local optical measurements of carbon nanotubes with atomic defects [1, 2], TMDC with various morphologies [3, 4], and individual quantum dots [5]. We will also show our challenge to use a TEM as a full phonon spectrometer with a nanometer spatial resolution even for non-polar materials [6].

This work is partially supported by KAKENHI (JP16H06333).

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Curious interaction of graphene with water and molecules

Water and ions show curious behavior when constricted by two-dimensional materials at the scales of few nanometers or less – the phenomena include the edge-enhance ionic current in graphene nanopores [1,2], anomalous ionic flow in nanotubes, and frictionless water transport in graphene [3] and graphene-oxide (GO) nanochannels [4, 5].

In this talk, I will present a systematic investigation of the ionic flow in nanopores, atomically-smooth graphene channels (height ranging from 0.7 - 3 nm), and chemically controlled GO channels. We identified several physical mechanisms governing ionic transport in different systems; armed with this insight we are able to rationally engineer new membranes of desirable properties. Finally, we will quantitatively unravel the interplay of hydrophobic and van der Waals interactions between graphene and organic molecules, revealing the transparency of graphene to the van der Waals interactions.

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Figures



Figure 1: Atomic force microscopy of ultra-clean, atomically-smooth graphene nanochannels with height ranging from 0.7 – 3 nm, and micrometers long.

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Creation of 2D topological insulating states on graphene and few-layer MoS₂

Topological insulating (TI) states have attracted large attentions from viewpoints of both basic physics and applications to innovative spintronic devices with topologically protected spins. Three dimensional (3D) TI materials have been well studied, while research of 2D TI states, in which bulks have band gaps while they disappear and the quantum-spin-Hall phases (QSHP) due to helical edge states appear at edges, was rare and only semiconductor quantum wells (e.g., HgTe and InAs/GaSb) were mainstream. However, significantly large topological gaps and high-temperature QSHP have been recently reported in atomically thin layers (e.g., \sim 0. 8eV bulk gap in bismuthene [1] and QSHP up to 100 K in short-channel WTe₂ [2]) and are attracting significant attentions.

Here, I will talk about novel two creation methods of 2D TI phases; *i.e.*, Bi₂Te₃ nanoparticle decoration on graphene [3] and laser-beam irradiation to few-layer MoS₂ [4]. The former demonstrates that only 3 % coverage with Bi₂Te₃ nanoparticle leads to the bulk gaps and QSHP due to the extremely uniform graphene Dirac states. In the latter, on-demand patterning of the bulk gaps with the QSHP on few-layer semiconducting MoS₂ is shown by creation of the 1T' phase due to heat effect by laser-beam irradiation. Moreover, observation of the possible room-temperature (RT) QSHP will be presented, realized using the optimized conditions for laser irradiation. This method must establish the feasible application to RT topological quantum devices by easily patterning QSHP as one wants by laser beam irradiation, such as Majorana-fermion based topological quantum bits.

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Figure 1: Resistance plateau demonstrating a room-temperature quantum-spin-Hall phase. **Inset**; laser-beam patterned recranglar topological region with four electrodes for the resistance measurements in main panel.

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Quantum transport in van der Waals junctions of graphene and hexagonal boron nitride

We present our recent experiments on fabrication and quantum transport in van der Waals junctions of graphene and 2D materials: (i) We study mid-infrared/THz photoresponse in graphene/h-BN van der Waals heterostructures and discuss cyclotron resonance in monolayer, bilayer, trilayer, twisted bilayer graphene, and graphene under Moire superlattice potential. (ii) We have developed a robotic system that automatically searches exfoliated 2D crystals and assembles them into vdW superlattices. (iii) Hexagonal boron nitride (h-BN) crystals grown under ultrahigh pressures and ultrahigh temperatures exhibit a high crystallinity and are used throughout the world as ideal substrates and insulating layers in van der Waals heterostructures. However, in their central region, these crystals have domains, which contain a significant density of carbon impurities. We reveal that the carbon (C)-rich domain can exist even after exfoliation. Then, we study the carrier transport of graphene in h-BN/graphene/h-BN van der Waals heterostructures, precisely arranging the graphene to straddle the border of the C-rich domain in h-BN. We also study h-BN crystals synthesized with another method, i.e., via synthesis at atmospheric pressure and high temperature (APHT) using a metal alloy solvent in terms of its applicability in van der Waals heterostructures. (iv) We demonstrate 3D manipulation of 2D materials such as sliding, rotating, turning, folding, flipping, cleaving, and exfoliating by using micro-dome polymer.

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Development of graphene-based highly sensitive sensors

Rapid monitoring of biomolecules and gas molecules in liquid or in vapor is required in various applications, including clinical diagnostics, environmental testing, food analysis, bioterrorism detection technologies, etc.

In the talk, we will introduce highly sensitive electrical detection of biological molecules or gas molecules based on graphene field-effect transistors [1-6]. Since graphene has a perfect two-dimensional structure, the electrical characteristics in graphene devices are very sensitive for modulation of surface potentials in graphene channels, as shown in Fig. 1. In addition, for development of highly sensitive influenza-virus sensors, glycanmodified graphene devices were also fabricated [7]. We believe that label-free graphene-based highly sensors are a promising candidate for the development of hand-held multiplex biosensors in a home medical care system or for environmental testing.

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Figure 1: Detection of biomolecules using graphene-based devices

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Growth and characterization of in-plane heterostructures based on layered chalcogenides

Conventional semiconductor heterojunctions with two-dimensional (2D) interfaces have been an important topic, both in modern solid state physics and in electronics and optoelectronics applications. Recently, the inplane heterostructures based on two-dimensional materials (Fig.1a) are expected to provide a novel onedimensional (1D) interface with unique physical properties and applications. Even though there have been many reports on the growth and device studies of such heterostructures, it is still an important challenge to develop a sophisticated growth process of novel heterostructures/superlattices and high quality samples without interface degradation, contamination and/or alloying. Here, we report on our recent progresses of chemical vapor deposition (CVD) growth of transition metal dichalcogenide (TMDC) atomic layers and their heterostructures [1-8]. In particular, we have achieved the continuous heteroepitaxial growth of 2D multi-heterostructures (Fig.1a) and nanoribbons based on layered TMDC monolayers, employing metal organic liquid precursors (Fig.1b) [7]. This process can avoid air exposure during growth process, and enables the formation of in-plane heterostructures with atomically sharp and zigzag-edge straight junctions without defects or alloy formation (Fig.1c). We have also revealed the local electronic density of states of atomically sharp heterointerface by scanning tunneling microscopy and spectroscopy. These results demonstrate an approach to realizing diverse nanostructures such as atomic layer-based quantum wires and superlattices, and suggest advanced applications in the fields of electronics and opto-electronics.

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Figure 1: Schematic illustrations of (a) TMDC-based in-plane heterostructure and (b) the present CVD system with metal organic precursors. (c) STM image of MoS₂/WS₂ heterointerface.

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Atomically-precise 1D and 2D graphene nanoarchitectures

The manufacturing of 2D nanoarchitectures leads to materials with novel and highly tunable physico-chemical properties. On-surface reactions, via programmed interactions of molecular building blocks, has recently emerged as a promising route to synthesise atomically precise materials from the 'bottom-up'. This approach ensures exquisite atomic-scale control of the structural and chemical functionalization, allowing to design a vast number of carbon-based nanoarchitectures not available by traditional solution chemistry nor with the 'top-down' methodologies. In particular, 1D graphene nanoribbons (GNRs) with different structures can be synthesized with atomic precision and fine-tuned electronic band gap.

In this talk, I will describe the recent advances in the on-surface synthesis field. Then, I will discuss our recent results to synthetize atomically precise 2D nanoporous graphene [1], 1D graphene nanoribbons and their chemical functionalization and how to organize them into superlattices[2,3].

At the end of the day, this talk will demonstrate the full path to synthetize a semiconducting graphene material with a bandgap similar to that of silicon, its atomic-scale characterization, and its implementation in an electronic device. Further potential applications include in nanoelectronics, photonics and highly selective molecular filtration and sensing systems.

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Figure 1. STM images (bottom) and schematic representation (top) of the precursor, intermediates and final product of the hierarchical synthesis of nanoporous graphene.

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Giant Power Factors in Large-Area Graphene Films on a Flexible Plastic Substrate

Thermoelectric energy conversion based on flexible materials has attracted much attention over the years. To date, flexible large-scale thermoelectric conversion devices have been investigated in van der Waals materials, such as conducting polymers, carbon nanotubes, and graphene films. Among them, graphene films have indicated extremely high performances. More concretely, the best power factors for p-type and n-type devices were reported in micron-scale single-crystal graphene films [1], although they are too small to apply into practical devices. Moreover, centimeter-scale polycrystalline graphene films have been produced by chemical vapor deposition (CVD), which opened a pathway for the development of flexible large-scale thermoelectric conversion device. However, to the best of our knowledge, there is no report on the thermoelectric properties of large-area graphene films on a flexible substrate. Here, we investigated the thermoelectric properties of CVD-grown polycrystalline graphene films on plastic substrates.

To perform p- and n-type doping, we fabricated the measurement setup of thermoelectric properties using electrolyte gated transistors [2-6]. We used CVD-grown large-area graphene films on a polyethylene terephthalate (PET) substrate [7]. By combining thermoelectric measurements and the electrolyte gating technique, we continuously controlled the Seebeck coefficient (*S*) and electrical conductivity (σ) of the CVD-grown large-area graphene films on a PET substrate. As the results, we observed maximum power factors ($S^2\sigma$) of 6.93 and 3.29 mW m⁻¹ K⁻² for p- and n-type carrier doping, respectively. These results are the best values among large-scale flexible materials, such as organic conducting polymers and carbon nanotubes, suggesting that CVD-grown large-area graphene films have potential for thermoelectric applications.

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Atomic-layer Rashba superconductor protected by dynamic spin-momentum locking

The recent discovery of superconductivity in atomic-layer materials has attracted extensive attentions from the viewpoint of fundamental physics, materials science, and device applications [1]. Particularly, when atomic layers are epitaxially grown on a substrate surface, the space inversion symmetry breaking should affect superconductivity in general through the manifestation of Rashba effect. In this talk, I will focus on metal atomic layers on semiconductor surfaces prepared in ultrahigh vacuum (UHV) environment, which can be directly probed with state-of-the-art surface science techniques [2-4]. Indium atomic layers on silicon surface, Si(111)- ($\sqrt{7} \times \sqrt{3}$)-In, was found to have a spin-split Fermi surface through laser-based angle-resolved photoemission spectroscopy (ARPES). Intriguingly, the direction of spin polarization in the momentum space is determined by the orbital angular momentum, unlike the conventional Rashba effect [5]. The superconducting transition of this surface atomic layer was studied with a home-developed electron transport measurement apparatus under the UHV environment and strong magnetic fields. The in-plane critical magnetic field was found to exceed the Pauli-limit by a factor of 3-4 at zero temperature, which indicates a strong suppression of the paramagnetic pair breaking effect (Figure 1). This is attributed to a *dynamic* spin-momentum locking, where the spin of an electron is forced to flip by every elastic impurity scattering [6]. This mechanism is complimentary to the *static* spin-valley locking in terms of robustness of superconductivity against magnetic field [7].

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Figure 1: Temperature dependence of in-plane and out-of-plane critical magnetic fields of Si(1111)-($\sqrt{7}\times\sqrt{3}$)-In.

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Spin-valleytronics in bilayer graphene

Two-dimensional layer materials have electrically tunable intrinsic properties. These properties allow us to control and connect varieties of quantum degrees of freedom including spin and valley. Graphene and transition metal dichalcogenide (TMD) atomic layers have two valleys, K and K'. Using the valley for information carrier is called valleytronics. One of advantages of TMD for valleytronics application is that the spin current can be generated through the valley contrasting intrinsic Hall conductivity and strong spin-orbit interaction in the valence band. On the other hand, graphene has the advantage of large valley relaxation length owing to the high crystal guality. In this talk, we present our recent attempt to interconnect spin and valley in a graphene device [1].

It was theoretically established that a gapped layer anti-ferromagnetic state appears near the charge neutrality point of bilayer graphene owing to the spontaneous symmetry breaking induced by electron-electron interaction. In this gapped state, non-zero spin and valley contrasting Berry curvature leads to anomalous transport, where the valley current flows opposite direction between the layers hosting opposite spin [2]. We detect experimentally such anomalous transport using dual-gated bilayer graphene encapsulated by hexagonal-Boron Nitride and performing non-local resistance measurement. Since this anomalous transport naturally allows conversion between the valley current and the spin current, being combined with the valley Hall effect [3, 4], it may be used to generate electrically the spin current with high efficiency in bilayer graphene.

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INDUSTRIAL FORUM

January 28-29, 2020

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Graphene Products Commercialization in Malaysia

Abstract

Launched in 2014, NanoMalaysia continues relentlessly in developing a local graphene-based industry through a number of product development and pilot production projects focusing on 5 key applications namely rubber additives, plastic additives, energy storage, nanofluids and conductive inks. These 5 applicatins have been translated into products with commercialization strategies. Academia-Industry partnerships form the basis of the aforementioned projects with investment from NanoMalaysia. The 4th Industrial Revolution demands a shift in the action plan's focus towards graphene-based connected devices.

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MEIJO ARC and MEIJO eDIPS

We discuss our company and products **MEIJO ARC and MEIJO eDIPS**. **MEIJO NANO CARBON** is the carbon nanotubes venture company established in April, 2005. We started under the lead of Prof. Yoshinori Ando of Meijo University who contributed to Prof. Iijima's CNT discovery¹). Main business is manufacturing and sales of carbon nanotubes. We mainly provide MEIJO ARC and MEIJO eDIPS. The product MEIJO ARC is single-walled carbon nano tubes(SWNT) with a narrow diameter distribution by arc discharge method. The product MEIJO eDIPS is the mass produced and high quality SWNT by CVD method. The feature of these products is high purity and crystalline. Moreover, we provide various forms of SWNT such as dispersion liquid, coated film and yarn. We aim to realize industrialization of SWNT.

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Figures



Figure 1: Actual image of MEIJO eDIPS

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Nano-carbon Bendable Terahertz Camera: a Tool for Multi-view Inspection

Terahertz (THz) imaging technology is highly promising for the use in powerful non-destructive and non-contact inspections due to its abilities of high penetration and fingerprint spectra of various materials and molecules. My talk will present our recent development of two types of THz imaging systems: carbon-based THz flexible cameras [1-3] and plasmon-based near-field spectroscopic imagers [4-8]. Most real objects have various three-dimensional curvatures; however, conventional THz imaging technologies are mainly limited to flat samples, resulting in blind areas. The use of carbon nanotube films has enabled multi-view THz visualization and inspection without bulky optical components and systems (Fig. 1). The latter part of my talk explains plasmonic structures for sub-wavelength spectroscopy and imaging. I introduce novel resonant frequency tunable plasmonic structures and their applications to medical examination (Fig. 2).

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Figure 2 Resonant frequency tunable THz plasmonic structure and medical spectroscopy.

Figure 1: (a) Multi-view THz inspection of syringe with nano-carbon flexible camera. (b) Finger-wearable THz glove.

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Synthesis and commercialization of graphene and related materials by plasma CVD

It is necessary to establish high-quality and high-throughput graphene synthesis technique for the practical application of graphene transparent films. In this talk development of high-throughput plasma-enhanced CVD for high quality graphene and its commercialization will be discussed. The plasma CVD is characterized by high-growth rate graphene atomic membrane compared with conventional thermal CVD (fig.1), which is suitable for the high-throughput production for the industrial use [1,2,3]. We have achieved a graphene membrane with a transmittance of 95% (two-layer) for visible light and sheet resistance of 130 Ω (gold chloride doped) in A4 size by developing an original plasma CVD method. The grain boundary and residual strain in graphene synthesized by plasma CVD with high-growth rate is analyzed by scanning transmission electron microscopy (STEM) and Raman spectroscopy [4]. The connection between the grains of graphene by high-throughput synthesis was confirmed. The compressive strain remained in graphene, which affects electrical conductivity, was observed. (fig.2).

Very thin graphite film is expected for higher specification thermal management which cannot be attained by using current TIM materials. We have developed fast synthesis of thin graphite film with high-performance thermal and electrical properties grown by plasma CVD using polycrystalline nickel foil at low temperature [5].

We have established a start-up company for the commercialization of high-throughput synthesized graphene.

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Figure 1: Temperature dependence of graphene growth rate for thermal CVD and plasma–assisted CVD which are normalized by CH4 partial pressure.



Figure 2: Grain boundary of graphene synthesized by high-throughput plasma CVD

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High-Responsivity Graphene Infrared Sensors

Abstract

High-responsivity graphene infrared sensors have been developed operating in the middle-wavelength infrared (MWIR) or long-wavelength infrared (LWIR) region by exploiting the photogating effect [1, 2]. The photogating effect is induced by photosensitizers that are located around the graphene and couple incident light to generate a large change in electrical current (Fig. 1(a)). For the MWIR and LWIR regions, InSb [3] and LiNbO3 [4] were ued as a photosensitizer, respectively. The MWIR and LWIR photoresponses were more than 10 times higher than those for conventional quantum IR sensors (Fig. 1(b)). In particular, room temperature operation was realized in LWIR due to pyroelectric effect. Moreover, low dark current and high responsivity have recently been demonstrated using amplification of injected photo-carries by photogating [5]. The results obtained in this study are expected to contribute to the development of high-performance graphene-based IR image sensors.

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Figure 1: (a) Schematics of graphene IR sensors using photogating. (b) Photoresponse with and without photogating

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Application of 1 & 2D nanocarbon materials to heat dissipation and sensing

We work on growth and application of nanocarbon materials, such as carbon nantubes (CNTs), graphene, and graphene nanoribbons (GNRs). The applications include transistors [1], interconnects [2], sensors [3], and thermal interface materials (TIMs) [4].

We first describe our recent efforts to grow edge-functionalized graphene nanoribbons [5]. The electronic states of GNRs can be modulated by changing their edge-terminating atoms/molecules. We are actually trying to synthesize armchair-edged GNRs with methylene-dioxy (Medioxy) functional groups, as shown in Figure 1. We have found that the edge structures of resulting GNRs is affected by the growth conditions.

We also explain the application of CNTs to TIMs [4]. We fabricated TIMs consisting of bundles of vertically aligned CNTs. After being removed from a substrate, the vertically-aligned CNTs were annealed at 2600 °C, making CNT of high-quality. A scanning electron microscope image of the CNTs is shown in Figure 2. The thermal conductivity of the CNT film (TIM) was estimated to be ~80 W/mK including the contact thermal resistance with Cu blocks. This value was higher than that of Indium measured in a similar setup.

We recently developed a graphene-gate transistor, where the gate of a Si transistor was replaced with monolayer graphene [3]. This graphene-gate transistor can be used for gas sensing if the graphene-gate is exposed. In fact, when gas molecules adsorb on the graphene-gate surface, the Fermi level or work function of graphene can change, thus shifting the threshold of the Si transistor. This leads to changes in the drain current. This graphene-based sensor is very sensitive to NO₂ and NH₃. In fact, we found that the sensor can detect NO₂ with concentrations less than 1 ppb, and NH₃ down to a few tens of ppb.

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Figure 1: Sheme for synthesysing AGNRs with methylene-dioxy functional groups



Figure 2: Vertically aligned CNTs after being annealed at 2,600 °C.



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Optical Properties of Atomically-thin MoS₂ Semiconductor Nanocrystals: Effects of Lateral Quantum-Confinement

Atomically-thin layers of semiconducting MoS_2 exhibit strong light emission resulting from radiative recombination of coupled electron-hole pairs (excitons). The pronounced electrostatic interaction between electrons and holes² imposes strict constraints on inducing spatial-quantum-confinement to the motion of excitons lying in the crystal plane. Strong quantization can only be achieved with lateral sizes below ~3 nm that challenges the fabrication of well-defined atomically-thin MoS_2 nanocrystals (NCs).

Here, by using a novel top-down approach², we have fabricated genuine MoS₂ NCs with typical lateral sizes of ~2 nm, and thicknesses varying from one- to four-layers². We employed Raman, steady-state photoluminescence (PL), time-resolved PL, polarized-resolved PL and excitation spectroscopy (PLE) to characterize diluted ensembles. We show that at low-temperature (T = 10 K), the optical emission takes place at ~2.5 eV (~485 nm), which is ~500 meV higher than the exciton luminescence in micro-sized MoS₂ monolayers (Fig. 1). The PL spectrum is composed of an unusually narrow zero-phonon-line in colloidal II-VI quantum dots. Time-resolved PL experiments reveal the ultrafast decay of the luminescence explaining for the bright light-emission of the colloidal nanostructures. We, therefore, attribute the zero-phonon line in MoS₂ NCs to the radiative recombination of laterally-confined (bright) excitons. More importantly, we resolve its fine-structure, arising from strong spin-orbit and electron-hole exchange interactions in MoS₂ that drastically affects the optical polarization of the nanocrystal.

Our results on high-quality MoS₂ NCs clearly demonstrate pronounced in-plane quantum-confinement effects in atomically-thin semiconductors³, showing novel optical properties as compared to monolayer MoS₂ and/or to II-VI NCs. This newly produced colloidal nanostructures are of fundamental interest and also hold potential as stable near-UV single-photon sources.

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Figure 1: Low-temperature (T = 10 K) photoluminescence spectra of MoS₂ monolayer (red curve) and MoS₂ nanocrystals (orange and blue curves).

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Theoretical Study of Electronic Structure for Heterogeneous Nanostructures

Various nanostructures have shown interesting physical and chemical properties because of intriguing dependence of electronic structure on morphology. Despites enormous advances in theoretical calculations, a reliable description by first principle is still challenging due to an enhanced electron-electron interaction in reduced dimension and a significant coupling between constituents of hetero-nanostructures. Here I present electronic structures for two heterogeneous nanostructures, (i) 1D zigzag-edge graphene nanoribbons with heterogeneous edge passivation along the edge [1], (ii) atomically thin van der Waals multiferroicity [2]. If allowed, I will present some results of other on-going studies and further theoretical development towards description of exotic phenomena.

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Figures



Figure 1: (Left) electron transmission probability as a function of mixing ratio of dihydrogen passivated edge carbon atoms. (Right) van der Waals stack of ferroelectric In₂Se₃ monolayer and ferromagnetic Cr₂Ge₂Te₆ monolayer, illustrating forbidden (b) or allowed (c) long-range ordering of Cr spins for upward or downward electric polarization, respectively.

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Solid State Actuators based on Helical CNT yarns: structure, properties and applications

Abstract:

It has been demonstrated^{1,2,3} that highly twisted carbon nanotube and polymeric fibers are also capable to generate impressive tensile actuation, providing large strokes and vastly exceeding the work and power capabilities of natural skeletal muscle. More than 10 million cycles of actuation were performed without significant loss of performance. These actuators are also can operate as torsional motors: a single fiber can rotate heavy rotors at up to 55,000 rpm. Actuation can be driven by electrical signals or by relatively small variation in environmental temperature, which can be converted into mechanical work.

A novel method to manufacture composite carbon nanotubes yarns by spinning vertically aligned nanotube forests allows the large-scale manufacturing of multifunctional yarns which are flexible and robust enough to be introduced into textiles using conventional techniques. The porous nature of these yarns allows the addition of a variety of guest materials such as polymers, ceramics, metals or even biological agents. Such hybrid yarns can be used as electrodes for batteries, supercapacitors and fuel cells, catalytic membranes, magnets, highly porous absorbers, and strong structures containing biomedical agents. When spun with elastomers and submitted to a special twisting process, CNT yarns can be also used as actuators capable to respond either to electrical or chemical stimuli. By applying electrical pulses, contractions up to 33 % and a mechanical work capacity of 1.36 kJ/kg were achieved, which exceed by two orders the performance of biological muscle. When driven chemically by absorption of solvents CNT yarns containing silicon rubber can generate up to 50% stroke and 1.2 kJ/kg work capacity at an efficiency of chemical to mechanical energy conversion of 16%³. **References**

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Thickness dependent phase diagram up to *B* = 60 T in graphite

Bulk graphite, a stacked form of 2D graphene layers, shows a phase transition when the very high magnetic field (around B = 30 T) is applied orthogonal to the plane [1]. Such high magnetic fields realize the so-called quasiquantum limit in graphite. This phase transition was studied for several decades, but the origin of it is still under discussion. Recently, we found that this phase transition is controllable by reducing the thickness below d = 200 nm [2]. In the thinner system, the temperature dependence of the critical magnetic field B_c becomes small, and the value of B_c becomes higher. Our calculation based on the density-wave state model, where the quantum-size effect is taken into account, successfully reproduces this phase diagram. Hence we concluded that the phase transitions were reported at higher magnetic fields of B = 53 T [3] and 75 T [4], but the origin of them remains controversial. In order to understand the physics in the quasiquantum limit, the magnetic-field evolution of the electronic state in graphite should be clarified.

In this study, we experimentally determine the effect of thinning on the second phase transition at B = 53 T. Mechanically exfoliated thin-film of graphite crystals were transferred onto an insulating silicon substrate, and inplane resistance up to 60 T was measured by using a non-destructive pulse magnet. Figure summarizes the phase diagram determined by the anomaly in magnetoresistance (an example is shown in the inset). In contrast to the 30-T transition, the thickness dependence of the 53-T transition is observed only below d = 70 nm. We conclude that this behavior qualitatively supports the realization of the density-wave state in the region between 30 and 53 T.

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Figure: Magnetic-field – temperature phase diagram of graphite for several thicknesses. Inset: Magnetic-field dependence of in-plane resistance in 77-nm-thick graphite. The transition field is determined by the anomaly around 30 and 50 T.

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Giant streaming currents in 2D nanopores

A nanopore is a pore in a membrane whose radius is comparable to some relevant physical quantities (screening length, hydration radius, molecule size...) leading to qualitatively different behaviors then expected from bulk fluidics and ionic.[1] We explored a new class of nanopores, 2D pores made in atomically thin 2D materials, whose channel length is much smaller than their radius, leading to emergence of new phenomenon.[2] We will present observations of the pressure-driven ionic currents (as figure 1 shows) for different ions and physical parameters. The observed streaming currents show giant enhancement, and qualitatively different behaviors, compared to the nanochannels.[3] Finally, we will present theoretical model and discuss different applications of this new phenomenon.

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Figures



Figure 1: Schematic figure of pressure-driven ionic currents in 2D nanopore.

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Cost effective and highly ordered nanopillar array meta-surface for optical biosensing application

Nano-structure-based biosensors have been developed recently with the merits of high resolution and sensitivity, benefitting from their large antibody binding number of sites resulting from high aspect ratio and larger surface area.[1][2] In this letter, a highly ordered nanopillar array meta-surface is developed for optical biosensing application via an anodic aluminium oxide (AAO) template. AAO template with highly-ordered nanopore structure has been widely employed to fabricate nanodots array and nanowire array resulting from the advantages of the controllable size and thickness, the easiness of fabrication, the low cost, and the chemical stability. Therefore, a nanopillar array meta-surface is fabricated via the AAO template with a thickness of 1500 nm. an interpore distance of 500 nm. and a diameter of pore of 300 nm using poly (vinylidenefluoride-cotrifluoroethylene) [P(VDF-TrFE)].[3] The SEM figures of top view(a) and cross-section(b) for the fabricated nanopillar meta-surface are illustrated in figure 1. During the nanopillar meta-surface fabrication process, the P(VDF-TrFE) solution is prepared by dissolving P(VDF-TrFE) powder in DMF with a ratio of 7:3, and then coated by 1 min spin-coating after dropped on the AAO template using a pipette. Next, the DMF solvent is evaporated in a drying oven for overnight. Afterward, the prepared P(VDF-TrFE)/AAO is put in the Muffle Furnace for 1 h, in order to melt the P(VDF-TrFE) into nanopores of AAO membrane to form the nanopillar structure. At last, the AAO template is removed via employing NaOH solution and mixture solution of CuCl₂ and HCI to get pure nanopillar array meta-surface. To construct the biosensor, the fabricated nanopillar array is transferred onto a glass substrate that is used to hold the soft membrane. Prostate Specific Antigens (PSAs) are immobilized on the surface of the nanopillar array with the support of APTS and Glutaraldehyde (C₅H₈O₂). Incident light is emitted on the meta-surface of the nanopillar array, and the reflected light is detected and measured via reflectance optical probe and spectrometer. The detection of the antigen-antibody recognition on the meta-surface is observed by the change in optical wavelength with respect to the change in refractive index. Owing to the utilization of the AAO template, the proposed nanopillar array meta-surface for optical biosensor shows the advantages of easy fabrication, cost-effectivity, and high selectivity.

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Figure 1: Top view(a) and cross-section(b) of SEM figure of highly-ordered nanopillar array meta-surface



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Energy absorption performance of nano filler reinforced polymer composites for crashworthiness applications

During the past few decades, the automobile manufacturing industry has expended significant effort to develop lightweight structures from novel materials like polymeric nano-composites. These materials have been particularly attractive because they can increase fuel efficiency and reduce overall weight of the vehicle and greenhouse gas emissions [1]. The utilization of nano filler reinforced polymer composites in vehicle structures is expected to improve vehicle speed, enhance energy absorbing capacity, promote recycling, and reduce weight. Unlike metals, nano filler reinforced polymer composites do not typically exhibit plastic deformation, although their stress–strain relationships may show signs of other types of nonlinearities, but they are superior to metals for specific energy absorption [2]. Polymer based nano-composites offer the potential for simultaneous improvement of several properties, including toughness, and energy absorption [3]. Hence this article focuses on the improvement of the energy absorption performance of polymer composites reinforced with different fibres and various nano-fillers, with better understanding of the energy absorption mechanism in these materials. The attained outcomes indicate an important influence of the filler and the matrix material on the mechanical properties and energy absorption capabilities of the polymer composites for crashworthiness applications.

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Figure 1: Constituents of polymer nano-composite

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Laser Scribing of Graphene Oxide Yielding Multipurpose Stamped Nano Films

We have designed a new method for the fabrication and easy patterning of flexible exfoliated reduced graphene oxide (rGO) nano films for different applications. Combining high resolution laser annealing with the stamping technique, isolated rGO films up to 30nm thick with a conductivity of 10² S/m were produced in a three-step process: filtering the graphene oxide (GO) solution through nitrocellulose membranes, reduction of GO surface using laser and transfer of the resulting rGO pattern onto new substrates via pressure-based mechanism. This technique has been already applied in the field of sensing and biosensing, where it proved to offer better performance compared to other commonly used materials. The technology was tested using a wide variety of substrates, and its applicability as back electrode in an electroluminescent lamp was demonstrated. Furthermore, since it is a stamping technique, the substrate is not affected by any solvent or temperature, which increases its usability. [1]

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Lateral collapse behaviour of hybrid basalt fabric reinforced MW-CNT dispersed epoxy composite tubes

Thin-walled cylindrical tubes have been well-known as an ultimate energy absorbing structures employed in car manufacturing industries for their light-weight prospective and superior energy dissipating capability [1-4]. In this research study, systematic examinations on the lateral collapse behaviour and energy absorption characteristics of basalt fabric reinforced epoxy composite tubes were performed. Detailed experimental studies on the Multi-Walled Carbon NanoTubes (MW-CNT) dispersed epoxy composite cylindrical shaped tubes under lateral quasi-static loading have been carried out. The lateral crushing force-deformation histories obtained were analyzed. The quasi-static impact collapse response of the proposed MW-CNT blended epoxy composite tubes and the proposed tubes deformed gradually and absorbed more energy than the traditional cylindrical tubes. In conclusion, it was observed that the hybrid basalt fabric reinforced MW-CNT blended epoxy composite cylindrical tubes are very substantial in lateral direction as energy absorbing structures, as they show suitable crushing force–deformation characteristics.

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Figure 1: Lateral deformation response of MW-CNT dispersed epoxy composite tubes

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Effect of nano graphene on the energy absorbing capacity of aluminium-glass fabric reinforced composite hybrid tubes

In the past few decades, hybrid aluminium-composite tubular components, which combine the uniform and continuous plastic buckling of the metal with light-weight composites, are gaining better attention for meeting the requirements of crashworthiness characteristics [1-3]. This research article presents the experimental outcomes of aluminium cylindrical tubes wrapped with glass fabric reinforced nano graphene dispersed epoxy composites subjected to quasi-static axial force. The influence of number of fabric layers in the composite segment are investigated experimentally. The overall results exposed that the crashworthiness characteristics of crushing force consistency and specific energy absorption of the proposed hybrid tubes are superior to those of the traditional aluminium and aluminium-composite tubes. When the nano graphene particles are blended with glass fabric/epoxy composite-aluminium cylindrical tubes, the specific energy absorption increases about 10-20%. An additional advantage of the composite-wrapping approach is that the composite could be retro-fitted to aluminium tubes, and the energy absorption ability is shown to be considerably improved by such utilization. Such a hybrid tubular structures would be of enormous potential to be employed as effective energy-absorbing elements in automotive applications [4].

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Figure 1: Progressive deformation of aluminium-glass fabric reinforced composite hybrid tube

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Enhancement of ballistic properties by reinforcing nano-fillers in hybrid twill woven fabric polymer composites

The defense industry in conjunction with the scientific community has continued to show great interest in the development of protective armor systems (for both equipment and people) against threats in combat operations [1]. One of the foremost threats is the impact of projectiles at medium and high speed. The efficiency of these systems depends strongly on their ability to resist impulsive loads and absorb energy [2]. Currently, the commercially available, ballistic armor plates in the world market are heavy and with thickness exceeding 25 mm [3]. Therefore, it is critical to find new ways to improve the impact resistance of materials for protective armor application with reduced weight. Hence improving the ballistic impact resistance of hybrid twill woven fabric polymer composites through addition of nano-particles as fillers is the main objective of this study. Development of lightweight ballistic plates, made of hybrid nano composites with improved ballistic resistance, can offer a solution of shielding with lighter, thinner, stronger and less expensive materials than the conventional ballistic plates. The use of nano-particles in low concentrations can achieve this goal without compromising the density or strength of the new armor plates.

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Figure 1: Carbon kevlar twill woven fabric

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Thermoelectric characteristics of Graphene for Recovery of Low Temperature Waste Heat

I .Introduction

Thermoelectric generation is a method of converting waste heat into energy by using the Seebeck effect of matter. High temperature exhaust heat recovery is progressing, but not at low temperature. In addition, the materials used for thermoelectric devices are inorganic materials and there are problems such as heavy, expensive and hard. In this reserch, we focused on graphene that exhibits high electron mobility even near room temperature. Graphene is a lightweight and flexible material suitable for thermoelectric devices.

II .Methods

Figures.1 shows the transfer method of graphene film deposited by plasma CVD method^[1]. Graphene synthesized on copper foil by plasma CVD was transferred to PET substrate. The Seebeck coefficient and the electrical conductivity of the deposited graphene film were measured using a thermoelectric characteristic evaluation device.(ZEM-3:ADOVANCE RIKO,Inc). Moreover, the power factor (PF) was calculated from the obtained Seebeck coefficient and the thermoelectric characteristic.

III.Results and Discussion

Figures.2 shows the Seebeck coefficient measurement results of the deposited graphene film.Seebeck coefficient was 56 μ V/K at 309 K, 70 μ V/K at 376 K respectively.the electrical conductivity was 6.30×105 S/m.The PF calculated from these values is 1.97 mW/mk2 at 309 K.This material exhibited relatively high performance compared to the reported thermoelectric properties of the Organic material system^[2].In the future, it can be expected to further improve the thermoelectric characteristics by doping.

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Figure 2: Seebeck coefficient of bilayer graphene film

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DFT study of Oxygen Reduction Reaction on various edge structure of graphene nanoribbon

Electrocatalyst plays important role in increasing the efficiency of batteries, and producing eco-friendly resources such as hydrogen or oxygen via water splitting reaction. Many researchers are trying to enhance the efficiency of electrocatalyst with cheaper materials. Especially, in case of Oxygen Reduction Reaction(ORR), transition perovskite oxides, single-metal atom embedded graphene, and metal-free electrocatalyst are mainly investigated and tested its catalytic activity these days. Not only the experimental accomplishments, but theoreticians develop various descriptors which represent a certain reaction activity of given materials to reveal reasons of occurrence of reduction or evolution reaction. For example, existence of e_{α} orbital is known as the descriptor of perovskite oxide materials[1], and d-band center is the descriptor of transition metals in ORR activities.[2] However, metal-free catalyst does not have appropriate descriptor for ORR activities like transition metals or perovskite oxides. Researchers widely use correlation plot between ΔG_{OH} and ΔG_{OH} , which are indicated as Potential Determining Step(PDS), or only ΔG_{*OH} because metal-free catalysts such as doped graphene have PDS in ΔG_{OH} region. Other descriptors using density of state[3] or electron affinity and electronegativity[4] have been suggested consistently, but these descriptors are not suitable for whole metalfree catalyst. In this study, we investigated various graphene nanoribbon structures with chiral edge, straight zigzag edge, graphitic nitrogen doped zigzag edge using DFT method. Unlike straight zigzag edge graphene nanoribbon, chiral graphene edge localizes electrons in edge site[5] which can enhance ORR activity than other metal-free catalyst. We are going to show the DFT calculation about ORR catalytic activity of graphene nanoribbon structures mentioned above via Gibbs free energy plot, and compare calculation results with other descriptors such as density of state to figure out descriptor is able to describe the property of structures we investigated..

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Recent progress of nano particle reinforcements in enhancing the toughness of polymer composites

Impact strength is one significant measure of material's mechanical toughness or resistance to fracture [1]. As polymer composites are increasingly finding more applications which are prone to impact force, more work has focused on identifying their fundamental toughening mechanisms [2]. Epoxy resin is extensively employed as the matrix in high-performance polymer composites for aeronautical and automobile applications. Synthetic fibre, as one of the stiffest and strongest fiber reinforcements, is generally selected to reinforce such epoxy matrices [3]. However, one serious problem for these safety-critical applications is the brittle mechanical performance and poor toughness of synthetic fabric reinforced epoxy composites, especially under high velocity impact loading in low temperature environment. Accordingly, there has been a concerted effort in recent years to improve the impact and low-temperature toughness of such epoxy polymer matrix. Hard nano-fillers such as graphene nano-sheets, carbon nanotubes are commonly used to enhance the low-temperature toughness of polymer composites. Hence in this study, influence of nano fillers as secondary reinforcements to enhance the toughness of polymer in composites and their recent progress in developments has been discussed elaborately.

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Figure 1: Sketch map of failure mechanism subjected to impact

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Staircase-Like Transfer Characteristics in Multilayer MoS₂ Field-Effect Transistors

Layered semiconductors such as MoS₂ have attracted as a channel material for transistors in post-silicon and beyond-CMOS electronics [1]. Much attention has been devoted to the monolayer limit, but the monolayer channel is not necessarily advantageous in terms of the performance of field-effect transistors (FETs) [2,3]. Therefore, it is important to investigate the characteristics of FETs possessing multilayer channels. In this presentation, we report on staircase-like transfer characteristics of exfoliated MoS₂ FETs, which are frequently observed with exfoliated multilayer MoS₂ flakes as shown in Figure 1. Atomic force microscope (AFM) characterizations reveal that the presence of thinner terraces at the edges of the flakes accompanies the staircase-like characteristics. The anomalous two-tiered characteristics are ascribable (i) partly to a stronger gate electric field at the edges due to a fringing field and (ii) mainly to a difference in threshold-voltage shift by charge transfer from surface adsorbates. The difference in the shift is caused by the difference in film thickness between the channel center and the thinner terrace at the edge. This study reveals the importance of the uniformity of channel thickness.

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Figure 1: Transfer characteristics of fabricated FETs based on exfoliated multilayer MoS₂. (a) Commonly observed onetiered characteristics. (b) Anomalous two-tiered staircase-like characteristics. The insets show an AFM image and a line profile of the edge of the flake in the measured FET.

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Tunable Interlayer Spin-Spin coupling in 2D Magnetic Material : Fe₃GeTe₂

Recently van der Waals (vdW) type 2D magnetic materials attract great interest. Many researches have been performed for the semiconductor type such as CrX_3 (X = CI, Br, I), CrGeTe₃ and FePS3. In our research we focused on the weak interlayer coupling of metallic 2D magnetic material, Fe₃GeTe₂ with DFT calculation.

In experiment [1], Fe₃GeTe₂ was observed to have very high Curie temperature (~220 K) and the ferromagnetic interlayer spin alignment. To unravel the microscopic origin of interlayer spin coupling, we performed the total energy and band calculations for ferromagnetic (FM) and anti-ferromagnetic (AFM) alignment with the bulk phase. The FM stability is found to be in a good match with the interlayer hopping from our controlled calculations. The idea of tuning the interlayer spin alignment is explored with altering the interlayer hopping, where we consider the external vertical electric field to the bilayer of Fe₃GeTe₂. A finite electric field generates the potential difference between the FM bilayers, thus the interlayer hopping is reduced, which can lead to the AFM preference (Fig. 1). Our study can provide insight for various instabilities occurring in weakly coupled vdW metallic system

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Figure 1: FM/AFM stability regard to vertical electric field

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Hydrogen adsorption on atomic vacancies in Epitaxial Graphene toward Hydrogen storage

Defect introduction is one of the important strategy to tune graphene properties. Especially, for hydrogenated atomic vacancies, the theoretical calculation shows a low energy barrier and little adsorption heat for the additional adsorption of hydrogen molecules [1], suggesting an efficient hydrogen storage and release in this system [2]. In this study, hydrogenated atomic vacancies are formed by ion-beam irradiation and subsequent molecular / atomic hydrogen adsorption on epitaxial graphene, and the amount of hydrogen and carrier scattering related to vacancies are evaluated. Atomic vacancies were introduced into the surface of epitaxial graphene grown on SiC by Ar ion beam sputtering at 100 eV after pre-annealing, followed by exposing to molecular / atomic hydrogen or oxygen molecules. Raman spectroscopy and Elastic recoil detection analysis (ERDA) were measured by LabRAM HR Evolution (532 nm) and Van der Graaff accelerator AN2500, respectively. XPS spectra reveal that the chemical structure of defects in epitaxial graphene can be tuned by the subsequent adsorption of hydrogen and oxygen molecules after defect formation by ion-beam irradiation. Interestingly, the smaller Raman D-band for hydrogenated vacancies than that for oxygen terminated vacancies suggests the inter valley scattering depends on the chemical structure of defects in graphene. This is explained by E_F dependence of the carrier scattering probability, tuned by chemical doping through the termination atoms on vacancies. ERDA profile indicates that the increment of hydrogen in epitaxial graphene after the ion beam irradiation and hydrogen adsorption, is comparable to the upper limit for the number of vacancies introduced by the irradiation.

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Figure 1: Hydrogen amount in defects layers obtained by ERDA in Epitaxial graphene

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Characterizing Fracture Behavior of Monolayer Graphene

The fracture behavior of a monolayer graphene, containing a center crack (length of 2a) was characterized based on the atomistic simulation and the concept of continuum mechanics. Two distinct failure modes, i.e., opening mode (Mode I) and sliding mode (Mode II), were examined by applying remote tensile and shear loading, respectively, on the monolayer graphene. In the atomistic simulation, the equilibrium configurations of the cracked graphene subjected to the applied loadings, before and after the crack extension, were determined respectively through molecular dynamics (MD) simulation, from which the variation of the potential energy and the strain energy release rate of the discrete graphene structure was calculated accordingly. It is noted that because of the discrete attribute, there is no stress singularity near the crack tip, and thus, the concept of stress intensity factor which is generally employed in the continuum mechanics may not be suitable for characterizing the crack behavior in the monolayer graphene. For the sake of comparison, the continuum finite element model with the same geometric parameters and material properties as the monolayer graphene was constructed, and the corresponding strain energy release rate was calculated from the modified crack closure method. Results indicated that the strain energy release rates obtained from the continuum model exhibit good agreement with those obtained from discrete atomistic model. Thus, it is suggested that the strain energy release rate is an appropriate parameter to characterize the fracture behaviors of the covalently bonded monolayer graphene no matter from the atomistic point of view or from the conventional continuum mechanics.

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Perovskite Solar Cells with ZnO Nanowall as Electron-Transporting Materials

This study reports on the fabrication of ZnO nanowalls for use as an electron collecting layer (ECL) in CH₃NH₃PbI₃ perovskite solar cells (PSCs). Two-dimension ZnO nanowalls were grown using a low-temperature chemical bath method with a thin Al film as a seed layer. We compared electron collecting layers based on nanowalls and sol-gel derived ZnO thin film in PSCs and sought to identify the mechanism underlying the collection of electrons. The proposed ZnO nanowalls achieved a fill factor significantly higher than that of ZnO thin films, which translated into a remarkable improvement in power conversion efficiency, reaching 13.6% under AM 1.5G illumination.

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Figures



Figure 1: SEM images of CH3NH3PbI3 deposited on (a) ZnO NWs in top-view and (b) cross-section; (c) ZnO thin films in top view and (d) cross-section.

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Intermittent CDW current switching of one dimensional ring crystal in TaS₃

A one dimensional metal is unstable toward the formation of a periodic lattice distortion associated with a spatially periodic modulation of the electronic charge density, which called a charge density wave (CDW). The CDW was pinned by the interaction with impurities or lattice. The pinned CDW, however, display response in an electric field and overcome the pinning energy, resulting in a current carrying sliding CDW.

A number of inorganic linear-chain compounds have been discovered which display a CDW ground state. The materials were transition metal trichalcogenide MX_3 (M = Nb, Ta X = S, Se). Topological crystals of MX_3 , known as ring and Möbius strips, have been reported since 2002 [1]. In general, MX_3 crystal forms a monocrystalline whisker. If a hole was made in the whisker crystal, the conduction-chain is destroyed. Hence the CDW order is destroyed near the hole. For this reason, a CDW loop, over which the continuity of the CDW order is maintained, should be employed to argue about transport properties. Ring crystals are the only materials providing such a CDW loop. The chain axis of a CDW directs itself along the circumferences of the ring without losing the CDW order.

We report current switching between two states in a time-dependent fluctuation, which observed only in the ring crystal. The CDW condensate maintained macroscopic phase correlation over tens of micrometers. The samples TaS_3 were synthesized by the chemical vapor transport method. We prepared ring crystal and whisker crystal with a hole pierced by heavy-ion irradiation. Two gold electrodes were fabricated on these samples in a symmetrical position. Then the dc electric current were measured at 79 K under the Peierls transition temperature. Figure 1 shows time-dependence of the current when constant voltage is applied for 500 seconds. As a result, we observed two values of the current in the ring crystal. Assume that a soliton pair is created when the CDW slides [2]. When a soliton pair is created, a voltage is generate between the solitons. Thus, the soliton pair is accompanied by a voltage different from the initial voltage due to the relaxation of CDW strain, which may drive a circulating current in the CDW loop.

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Figure 1: Time dependence of the current for applying constant voltage. (Top) ring and (Bottom) whisker.

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Realization of label-free PSA biosensor with highly-ordered nano-pore array using AAO template

Nano-structure-based biosensors have been developed recently with the merits of high resolution and sensitivity, benefitting from their large antibody binding number of sites resulting from high aspect ratio and larger surface area. Especially the nanopore array structure based on anodic aluminium oxide (AAO) template is attractive for optical biosensor implementation.[1] In this study, we produce a high-selectivity prostate-specific antigen (PSA) biosensor with highly-ordered nanopore array based on AAO membrane. AAO membrane can be easily fabricated using the two-step anodization process and the parameters of the membrane, such as the diameter of pores and thickness of membrane, are controllable via the tuning of processing parameters.[2] The biosensor proposed in this letter is constructed by an ultra-thin AAO membrane and Ag-deposited glass substrate with the thickness of 500 µm and the refractive index of 1.457, which has a potential application for optical filter. The ultra-thin AAO film is transferred to the Ag-deposited substrate in acetone solution after hydrophilic treatment by H₂O₂ and 3MPT solvent, which is used to enhance the adhesive force. The PSA antibodies are immobilized on the AAO surface that is utilized to bind with PSA to achieve high selectivity. The performance of the developed biosensor is evaluated via measuring the change in the wavelength with respect to the changes in the refractive index of the AAO resulting from the antigen-antibody binding.[3][4] The best sensitivity can be achieved by tuning the parameters of AAO film, such as the length and diameter of pores. The AAO membrane and glass substrate are bought from the commercial company resulting in reduced fabrication time and simplified process. Based on this optical filter structure, the proposed biosensor shows the merits of easily fabrication process, shortened fabrication time, and good performance of high selectivity and good sensitivity, enabling a potential application in biosensor for different kinds of antigens.

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Figure 1: SEM figure of fabricated AAO membrane surface

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Ion-beam irradiation effects on the structure and electronic properties of MoS₂

In view of verifying the influence by defects on the structure and electronic properties, the monolayer MoS₂ is irradiated with low energy Ar⁺ ion beam in order to introduce defects under a well-controlled condition, and then evaluated by Raman spectroscopy, photoluminescence (PL), and electric conductivity.

After Ar^+ ion irradiation, both of the line widths of E_{2g} and A_{1g} peaks for Raman spectroscopy increase and become broader as increasing of irradiation time. The observed increase of the line width is considered mainly because of the increase of the satellite peaks' contribution caused by the introduction of defects [1]. Interestingly, the effect of the irradiation is more significant for E_{2g} in spite of less influence of charge transfer by molecular adsorption, where A_{1g} peak is much more sensitive due to its large electron-phonon coupling [2].

As for photoluminescence (PL), after Ar⁺ ion irradiation, as increasing of irradiation time, the intensity of the peak at 1.84 to 1.88 eV decreases significantly with the emerging of a tail at the lower energy side. Interestingly, the peak around 1.35 eV assigned to the emission related to impurity levels also rapidly decreases upon ion beam irradiation.

The shift of the threshold voltage for MoS₂-FET " V_g shift" increases upon the irradiation time, suggesting hole doping by the Ar⁺ ion irradiation.

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Figure 1: V_g shift for monolayer MoS₂ irradiated with Ar⁺ ion beam for 0, 10, 30, and 100 sec.