Physical and Chemical Properties of High Quality Three Dimensional Nanoporous Graphene

These articles provide a new concept of introducing three-dimensional (3D) porous structures into a single two-dimensional (2D) graphene sheet with well-preserved 2D graphene characters.[21] The conventional 2D graphene constructed with perfect, honeycomb-like carbon bonding inside a single atomic carbon sheet has essential problems of limitation for their physical chemistry and applications. It means that the 2D graphene sheet itself is no volume and no 3D structures, and then it is not suitable for practical 3D devices which require some thickness (i.e. single layer graphene is not always required for applications) and quick mass transport inside graphene

sheets. Indeed, the stacked 2D graphene sheets with certain volume cannot avoid short circuit between uncontrollable layers and also cannot provide effective mass transport pathways inside and outside graphene sheets due to no porous (space) structures. Thus, it is widely recognized that the 2D graphene sheets are not suitable for applications which require ions/molecules injections for carrier doping or chemical reactions. Therefore, many researchers have been challenging to introduce open 3D porous into a single 2D graphene sheet for applications. Here I would like to report a novel 3D nanoporous graphene sheet with preserved 2D electronic nature, tunable pore sizes and high electron mobility for electronic applications, successfully synthesized by using nanoporous metal based chemical vapor deposition (CVD) method. The complex 3D network comprised of interconnected graphene whose structure was exactly duplicated from the morphology of nanoporous metal having periodic structures confirmed with transmission electron microscope (TEM) tomography remains to be a 2D coherent electron system of the mass-less Dirac fermions investigated with angle-resolved photoemission spectroscopy. The transport properties of the nanoporous graphene show a semiconductor-like behavior and strong pore size dependence together with unique angular independence. The 3D nanoporous graphene keeps high electron mobility of ca. 5000 $cm^2/(Vs)^{-1}$ by a semiclassical model analysis. These results will contribute the understanding of physics of constricting electrons on 2D periodic sheet structures.

Another interesting points are chemical properties of 3D nanoporous graphene. Graphene is known as a very stable materials without any defective structures so that graphene shows no chemical activities. Here I focused geometric defects to form the curved graphene layer and considered that the geometric defects on the curved part can be a host of chemical dopants, enhancing chemical activity and tuning their electronic density of state. With this idea, I and colleagues have successfully investigated 3D chemically doped nanoporous graphene for applications of oxygen reduction reaction[21], hydrogen evolution reaction[6,12], supercapacitor[3], lithium-air battery[1,5,7], steam generation by heat localization[8], photodetector[4]. Most remarkable results here are renewable energy devices and we have discovered the interesting chemical properties of 3D nanoporous graphene chemically doped with nitrogen and nitrogen-sulfur. The chemically doped graphene have greatly promoted chemical activities towards both oxygen reduction reaction and hydrogen evolution reaction with an aid of easy mass transport inside and outside nanoporous graphene sheet. Their performances are very close to platinum catalysts and it can be called as metal-free energy harvesting graphene devices. I strongly believe that the 3D nanoporous graphene will bring a breakthrough on physics, chemistry and industrial applications which 2D graphene devices cannot be achieved.

List of Publications

1. Xianwei Guo, Jiuhui Han, Pan Liu, **Yoshikazu Ito**, Akihiko Hirata, Mingwei Chen, Graphene@nanoporous nickel cathode for Li-O2 battery, *ChemNanoMat*, **2015**, DOI:10.1002/cnma.201500214.
2. Takeshi Fujita, Hideki Abe, Toyokazu Tanabe, **Yoshikazu Ito**, Tomoharu Tokunaga, Shigeo Arai, Yuta Yamamoto, Akihiko Hirata, Mingwei Chen, Earth-Abundant and Durable Nanoporous Catalyst for Exhaust-Gas Conversion, *Adv. Funct. Mater.* **2015**, DOI: 10.1002/adfm.201504811.
3. Hamzeh Kashani, Luyang Chen, **Yoshikazu Ito**, Jiuhui Han, Akihiko Hirata, Mingwei Chen, Bicontinuous Nanotubular Graphene-Polypyrrole Hybrid for High Performance Flexible Supercapacitors, *Nano Energy* **2016**, 19, 391–400.
4. **Yoshikazu Ito**, Wenfeng Zhang, Jinhua Li, Haixin Chang, Pan Liu, Takeshi Fujita, Yongwen Tan, Feng Yan, Mingwei Chen, Three-dimensional bicontinuous nanoporous reduced graphene oxide for highly sensitive photodetectors, *Adv. Funct. Mater.* **2015**, DOI: 10.1002/adfm.201504146.
5. Jiuhui Han, Xianwei Guo, **Yoshikazu Ito**, Pan Liu, Daisuke Hojo, Tsutomu Aida, Akihiko Hirata, Takeshi Fujita, Tadafumi Adschiri, Haoshen Zhou, Mingwei Chen, Effect of chemical doping on cathodic performance of bicontinuous nanoporous graphene for Li-O2 batteries, *Adv. Energy Mater.* **2015**, DOI: 10.1002/aenm.201501870.
6. H.-J. Qiu, **Yoshikazu Ito**, Weitao Cong, Yongwen Tan, Pan Liu, Akihiko Hirata, Takeshi Fujita, Zheng Tang, Mingwei Chen, Nanoporous Graphene with Single-Atom Nickel Dopants: An Efficient and Stable Catalyst for Electrochemical Hydrogen Production, *Angew. Chem. Int. Ed.* **2015**, 54, 14031–14035. (Hot Paper)
7. Xianwei Guo, Pan Liu, Jiuhui Han, **Yoshikazu Ito**, Akihiko Hirata, Takeshi Fujita, Mingwei Chen, Three-dimensional nanoporous nitrogen-doped graphene with encapsulated RuO_2 nanoparticles for Li-O_2 battery, *Adv. Mater.,* **2015**, 27, 6137–6143.
8. **Yoshikazu Ito**, Yoichi Tanabe, Jiuhui Han, Takeshi Fujita, Katsumi Tanigaki, Mingwei Chen, Multi-functional porous graphene

for high-efficiency steam generation by heat localization, *Adv. Mater.,* **2015**, 27, 4302–4307.
9. **Yoshikazu Ito**, Christos Christodoulou, Marco V. Nardi, Norbert Koch, Mathias Kläui, Hermann Sachdev, Klaus Müllen, Tuning the Magnetic Properties of Carbon by Nitrogen Doping of its Graphene Domains, *J. Am. Chem. Soc.*, **2015**, 137, 7678–7685.
10. Takeshi Fujita, Yasuhiro Kanoko, **Yoshikazu Ito**, Luyang Chen, Akihiko Hirata, Hamzeh Kashani, Osamu Iwatsu, Mingwei Chen, Nanoporous Metal Papers for Scalable Hierarchical Electrode, *Adv. Sci.* **2015**, *2*, 1500086.
11. Jiuhui Han, Yu-Ching Lin, Luyang Chen, Yao-Chuan Tsai, **Yoshikazu Ito**, Xianwei Guo, Akihiko Hirata, Takeshi Fujita, Masayoshi Esashi, Thomas Gessner, Mingwei Chen, On-Chip Micro-Pseudocapacitors for Ultrahigh Energy and Power Delivery, *Adv. Sci.* **2015**, *2*, 1500067.
12. **Yoshikazu Ito**, Cong Weitao, Takeshi Fujita, Zheng Tang, Mingwei Chen, High Catalytic Activity of Nitrogen and Sulfur Co-Doped Nanoporous Graphene in the Hydrogen Evolution Reaction, *Angew. Chem. Int. Ed.* **2015**, *54*, 2131–2136.
13. Yongwen Tan, Pan Liu, Luyang Chen, Weitao Cong, **Yoshikazu Ito**, Jiuhui Han, Xianwei Guo, Zheng Tang, Takeshi Fujita, Akihiko Hirata, Mingwei Chen, Monolayer MoS2 Films Supported by 3D Nanoporous Metals for High-Efficiency Electrocatalytic Hydrogen Production, *Adv. Mater.,* **2014**, *26*, 8023–8028.
14. Prince Ravat, Yulia Borozdina, **Yoshikazu Ito**, Volker Enkelmann, Martin Baumgarten, Crystal Engineering of Tolane Bridged Nitronyl Nitroxide Biradicals: Candidates for Quantum Magnets, Cryst Growth Des., **2014**, *14*, 5840–5846.
15. Takeshi Fujita, **Yoshikazu Ito**, Yongwen Tan, Hisato Yamaguchi, Daisuke Hojo, Akihiko Hirata, Damien Voiry, Manish Chhowalla, Mingwei Chen, Chemically Exfoliated ReS2 Nanosheets, *Nanoscale*, **2014**, *6*, 12458–12462.
16. **Yoshikazu Ito**, Hidetoshi Ohta, Yoichi M. A. Yamada, Toshiaki Enoki, Yasuhiro Uozumi, Transfer Hydrogenation of Alkenes with a Ni/Ru/Pt/Au Heteroquatermetallic Nanoparticle Catalyst: Sequential Cooperation of Multiple Nano-Metal Species, *Chem. Commun*., **2014**, *50*, 12123–12126.
17. H.-J. Qiu, **Yoshikazu Ito**, Mingwei Chen, Hierarchical nanoporous nickel alloy as three-dimensional electrodes for high-efficiency energy storage, *Scripta Materialia*, **2014**, *89*, 69–75.
18. Prince Ravat, Yoshio Teki, **Yoshikazu Ito**, Elena Gorelik, Martin Baumgarten, Breaking the Semi-Quinoid Structure: Spin-Switching from Strongly Coupled Singlet to Polarized Triplet State, *Chem. Eur. J.*, **2014**, *20*, 12041–12045.
19. **Yoshikazu Ito**, Hidetoshi Ohta, Yoichi M.A. Yamada, Toshiaki Enoki, Yasuhiro Uozumi, Bimetallic Co-Pd Alloy Nanoparticles as Magnetically Recoverable Catalysts for the Aerobic Oxidation of Alcohols in Water, *Tetrahedron*, **2014**, *70*, 6146–6149. (highlighted by *Synfacts* **2014**, *10*, 1222.)
20. **Yoshikazu Ito**, Christos Christodoulou, Marco Vittorio Nardi, Norbert Koch, Hermann Sachdev and Klaus Muellen, Chemical Vapor Deposition of N-Doped Graphene and Carbon Films: The Role of Precursors and Gas Phase, *ACS Nano*, **2014**, *8*, 3337–3346.
21. **Yoshikazu Ito**, H.-J. Qiu, Takeshi Fujita, Yoichi Tanabe, Katsumi Tanigaki, Mingwei Chen, Bicontinuous Nanoporous N-doped Graphene for Oxygen Reduction Reaction, *Adv. Mater.* **2014**, *26*, 4145–4150.
22. **Yoshikazu Ito**, Yoichi Tanabe, H.-J. Qiu, Katsuaki Sugawara, Satoshi Heguri, Ngoc Han Tu, Khuong Kim Huynh, Takeshi Fujita, Takashi Takahashi, Katsumi Tanigaki, Mingwei Chen, High Quality Three-Dimensional Nanoporous Graphene, *Angew. Chem. Int. Ed.* **2014**, *126*, 4822–4826.
23. **Yoshikazu Ito***, Kazuyuki Takai, Akira Miyazaki, Vajiravelu Sivamurugan, Manabu Kiguchi, Yoshihiro Ogawa, Naotake Nakamura, Suresh Valiyaveettil, Tomofumi Tada, Satoshi Watanabe, Toshiaki Enoki*, Anomalous metallic-like transport of Co–Pd ferromagnetic nanoparticles cross-linked with π-conjugated molecules having a rotational degree of freedom, *Phys.Chem.Chem.Phys.*, **2014**, *16*, 288–296.
24. Prince Ravat, **Yoshikazu Ito**, Elena Gorelik, Volker Enkelmann, Martin Baumgarten. Tetramethoxy-Pyrene Based Biradical Donors with Tunable Physical and Magnetic Properties. *Org. Lett.*, **2013**, *15*, 4280–4283.
25. **Yoshikazu Ito**, Akira Miyazaki, Kazuyuki Takai, Vajiravelu Sivamurugan, Takashi Maeno, Takeshi Kadono, Masaaki Kitano, Yoshihiro Ogawa, Naotake Nakamura, Michikazu Hara, Suresh Valiyaveettil, Toshiaki Enoki. Magnetic Sponge Prepared with an Alkanedithiol-bridged Network of Nanomagnets. *J. Am. Chem. Soc.,* **2011***, 133,* 11470–11473.
26. **Yoshikazu Ito**, Kazuyuki Takai, Toshiaki Enoki. Ferromagnetic Enhancement in the Clusters of Co–Pd Magnetic Nanoparticles Induced by the Formation of Cross–linkage *J. Phys. Chem. C*. **2011**, *115*, 8971–8975.
27. Akira Miyazaki, **Yoshikazu Ito**, Toshiaki Enoki. Classes of Nanomagnets Created from Alkanethiol-Coated Pt or Pd Nanoparticles and Their Alloys with Co. *Eur. J. Inorg. Chem.* **2010**, 27, 4279–4287.
28. **Yoshikazu Ito**, Akira Miyazaki, Suresh Valiyaveettil, Toshiaki Enoki. Magnetic Properties of Fe-Pd Alloy Nanoparticles. *J. Phys. Chem. C* **2010**, *114*, 11699-11702.
Yoshikazu Ito, Akira Miyazaki, Kenichi. Fukui, Suresh Valiyaveettil, Toshihiko Yokoyama, Toshiaki Enoki. Pd Nanoparticle Embedded with Only One Co Atom Behaves as a Single-Particle Magnet. *J. Phys. Soc. Jpn.* **2008**, *77*, 103701.