

Tuesday Afternoon Poster Sessions

Graphene and Related Materials Focus Topic

Room: East Exhibit Hall - Session GR-TuP

Graphene and Related Materials Focus Topic Poster Session

GR-TuP2 Solution Plasma Assisted Surface Decoration of Chemically Converted Graphene Sheet with Various Metallic Nanoparticles, K. Sadasue, N. Zettsu, T. Ueno, O. Takai, N. Saito, Nagoya University, Japan

Like the other newly discovered carbon nanomaterials, such as fullerenes and carbon nanotubes, graphene, a monolayer graphite, and its composites have been widely applied to the field of electrocatalysis due to that graphene have unique structures and inherent properties including high specific surface areas, chemical and electrochemical inertness, easy surface modification, higher electron mobility and broad electrochemical windows. Thus, the use of graphene as substrates of catalysts provides a new opportunity for designing and constructing next-generation catalysts. Especially, graphene decorated with metallic nanoparticles can be employed as fuel cell electrocatalysts, in which they plays an important role in improving the charge-transfer efficiency and decreasing the overpotential of electrochemical reactions such as methanol oxidation and oxygen reduction.

However, there are still unresolved issues in practical use, such as durability. In situ growth method is the most widely used method for preparing graphene/metallic nanoparticle composites. Hydrophobic and/or electrostatic interactions are the main driving forces of adsorbing metallic nanoparticles on graphene surfaces. These relatively weak binding interaction often gave rise to desorption of the nanoparticles from the graphene surface during charging and discharging operation at high temperature.

Very recently, we reported a fabrication of Pt catalysts supported on carbon nanoballs, as well as characterization of their electrochemical activities (Saito et al.,

J. Vac. Sci. Technol. A, 27(4) pp.826-830). Plausible mechanism has remained a mystery, Pt catalysts were strongly attached to the carbon nanoball surface. The resultant products showed relatively higher durability compared with than that of catalysts prepared by conventionally used approaches. In this work, we demonstrate surface decoration of chemically converted graphene with various metallic nanoparticles by the originally-developed solution plasma processing. Structural characterization and electrochemical activities of the all product was performed by a combination with TEM, XRD, AFM, Raman spectroscopy, and measurements of oxidation-reduction potential [file:///C:/Users/%E5%AE%9A%E6%9C%AB%E4%BD%B3%E7%A5%90/AppData/Roaming/EdMax/Attachment/20110504_133844_dtub14/AVS%20%E3%82%A2%E3%83%96%E3%82%B9%E3%83%88%EF%BC%88%E5%AE%9A%E6%9C%AB%EF%BC%89_revised_zettsu0504.docx].

GR-TuP3 Synthesis of Carbon Nanoballs, Covered by CNTs with Metallic Conductivity, K. Ohno, N. Zettsu, T. Ueno, O. Takai, N. Saito, Nagoya University, Japan

Carbon nanostructures, due to their unique electronic and extraordinary mechanical properties, have been receiving much attention for a wide variety of applications. Especially, highly-conductive carbon nanostructures is a promising candidate supports for heterogeneous catalysts, for use in fuel cells and in metal-air sources of current. Synergetic interaction of the catalyst-nanoparticles with carbon nanostructures exhibits better catalytic parameters than application of carbonaceous materials.

Very recently, we demonstrated a fabrication of platinum catalysts supported on carbon nanoballs (CNBs), as well as characterization of their electrochemical activities (Saito et al., *J. Vac. Sci. Technol. A*, 27(4) pp.826-830). Originally-developed CNB is a highly crystallized nanosized carbon powder with spherical shape. The CNBs can be synthesized by thermal decomposition of ethylene and hydrogens under argon stream. Diameter of CNB can be tuned from 200 to 700nm by changing the mixing ratio of H₂. Platinum nanoparticles were densely loaded on the CNBs surface under modified solution plasma processing of CNBs and Pt ions with stabilizing agents. We obtained 1.6-fold increase in the electrochemical activity of Pt/CNBs system (0.26cm²/mg) compared with that of conventionally-used Pt/C system (0.16cm²/mg).

In this work, we propose newly developed CNBs, covered by carbon nanotubes (CNTs) with metallic conductivity in order to reduce contact resistance between neighboring CNBs in electrodes. We grew CNTs from various shaped Fe, Ni nanocrystals deposited onto an individual CNB, and subsequently decorated the surface of the CNBs with Pt nanoparticles as a

catalyst by using solution plasma processing. The ratio of metallic to semiconducting CNTs of our all products was evaluated by Raman spectroscopy.

GR-TuP5 Soluble Precursor Synthesis of Grapheme and Graphene Nanoribbons, L.M. Tolbert, C.L. Henderson, J. Vargas, J. Baltazar, J. Kowalik, Georgia Institute of Technology

Graphene is currently produced typically through one of three routes: (1) some combination of mechanical and chemical exfoliation of graphite, (2) high temperature processing of SiC, or (3) through high-temperature catalytic methods on metal surfaces using simple carbon precursors such as methane. We are investigating and developing methods for synthesis of graphene through a molecular approach, in which the molecular precursors used already possess most of the C=C bonds necessary for graphene formation. A limitation of such approaches is that many of the precursors, e.g., pentacene, are only sparingly soluble and thus have difficulty being solution coated or have low volatility that prevent vapor phase deposition. Thus we have been investigating the use of soluble precursor molecules which form the graphene templates at higher temperatures or in the presence of catalysts. In particular, one approach toward solubilization that is under investigation is the use of reversible Diels-Alder chemistry to produce soluble grapheme precursor adducts. After solution coating of the materials onto appropriate substrates, the cycloaddition can be reversed at modest temperatures to produce the desired polyaromatic precursor and subsequently processed into grapheme through a further chemical or thermal consolidation. This presentation will review our progress to date in developing such techniques and will demonstrate the ability to form graphene from such approaches at relatively moderate temperatures. A discussion of the effect of choice of precursor on the ability to consolidate the material into graphene and its resulting quality will be presented.

GR-TuP6 Formation of Graphene Films and Patterned Structures through Deposition of Graphene Oxide on Patterned Aminosilane Monolayers, C.L. Henderson, L.M. Tolbert, H.-W. Chu, J. Baltazar, J. Kowalik, Georgia Institute of Technology

Graphene is currently produced typically through one of four routes: (1) some combination of mechanical and chemical exfoliation of graphite, (2) oxidation of graphite to form grapheme oxide which is subsequently deposited onto surfaces and reduced to grapheme, (3) high temperature processing of SiC, or (4) through high-temperature catalytic methods on metal surfaces using simple carbon precursors such as methane. Some applications for grapheme would benefit from low temperature methods (<400 °C), and the first two methods mentioned above can inherently provide access to such low processing temperatures. However, simple exfoliation of graphite has only been demonstrated to produce relatively small, poorly controlled grapheme flakes that are not easily processed due to their limited solubility in solvents and lack of methods for further assembly into larger structures. Therefore, we have been investigating the ability to utilize grapheme oxide (GO) flakes as a soluble grapheme precursor that can be assembled onto surfaces to form both continuous grapheme films and directly form patterned grapheme microstructures. We will present a process in which we deposit and pattern aminosilane monolayers on a substrate, pattern them using lithographic techniques, and utilize such aminosilane patterns to control where GO assembles on the surface and subsequently is reduced to form grapheme. It will be demonstrated that by producing aminosilane monolayers that are dense and which possess a large fraction of non-hydrogen bonded amine terminal groups, continuous grapheme oxide and grapheme films and microstructures can be assembled on substrates. It will be shown that by subjecting the resulting assembled grapheme on such aminosilane layers to modest thermal treatments, that stable n-doped grapheme can be produced. The materials produced via such methods will be discussed in terms of their spectroscopic (e.g. Raman) and electrical properties (e.g. I-V curves for FET devices, carrier concentrations, mobilities, etc.)

GR-TuP7 Graphene Layer-By-Layer Growth on Co₃O₄ (111) at 1000 K by Molecular Beam Epitaxy, M. Zhou, F. Pasquale, J. Kelber, University of North Texas, A. Boosalis, M. Schubert, P.A. Dowben, University of Nebraska - Lincoln

We report layer-by-layer growth of macroscopically continuous and uniform graphene sheets on Co₃O₄(111) at 1000 K by carbon molecular beam epitaxy (MBE) from a graphite rod source. The direct growth of graphene on dielectric substrates is an essential step in the practical and scalable production of graphene-based devices. Co₃O₄(111) films 3 monolayers (ML) thick were formed from surface segregation of dissolved oxygen after deposition ~ 40 Å Co grown on Al₂O₃(0001) substrates at 750 K in UHV. Epitaxial Co₃O₄(111) films, as characterized by Auger

spectroscopy and LEED, were formed by subsequent annealing to 1000 K in UHV, and exhibit th a O-O surface nearest neighbor distance of 2.8 Å, in good agreement with literature. The evolution of the Auger electron C(KVV) lineshape during carbon MBE indicates sp² hybridization, and layer-by-layer growth up to at least 3 ML average thickness. LEED spectra indicate that the sp² (111) graphene overlayer is incommensurate with the Co₃O₄(111) substrate. The graphene-related diffraction spots remain sharp from a coverage of 0.4 ML up to 3 ML, indicating that the graphene sheets are azimuthally in registry with each other. Exposure of the 3 ML graphene/Co₃O₄(111)/Co(111) sample to ambient results in no observable change in Auger or LEED spectra, indicating macroscopically continuous graphene sheets. Subsequent acquisition of XPS spectra in a separate chamber yields a graphite-characteristic asymmetric C(1s) peak at 284.9 eV binding energy, indicating graphene → oxide charge transfer, as observed for graphene/SiC and graphene/MgO. A $\pi \rightarrow \pi^*$ satellite feature is also observed. Spectroscopic ellipsometry measurements carried out in a separate system confirm the presence of a $\pi \rightarrow \pi^*$ resonance, and similarities with the optical absorption of graphene/SiC are observed. Raman spectra acquired at different, macroscopically separated sample areas indicate a uniform 3ML graphene film thickness. These results also strongly suggest that other non-polar (111) transition metal oxide surfaces with similar O-O nearest neighbor distances may act as suitable substrates for graphene growth at moderate temperatures, opening the way to controlled direct growth of high quality graphene on a variety of dielectric substrates, with materials and processing temperatures readily compatible with Si CMOS integration.

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