## NiS<sub>1.03</sub> Hollow Spheres and Cages as Superhigh Rate Capacity and Stable Anode Materials for Half/Full Sodium-Ion Batteries

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*Keywords: hollow spheres and cages, sodium-ion batteries, anode material, ultrahigh performance, full cell* 

#### Abstract

Sodium-ion batteries (SIBs) are promising and attractive as next-generation battery candidates because sodium is abundant in the earth, its cost is low, and its intercalation chemistry is similar to that of Li. Nickle sulfides as promising anode materials for sodium-ion batteries have attracted tremendous attention owing to their large specific capacity and good electrical conductivity. However, the relative large volume changes during the sodiation/desodiation process usually result in a fast capacity decay, poor cycling stability, and sluggish electrode kinetics which hinder their practical applications.



Fig. 1, Rate performance of NiS<sub>1.03</sub> PHSs and NiS<sub>1.03</sub> PHCs electrodes in the voltage range of 0.01-2.3 V vs Na<sup>+</sup>/Na.

Herein, NiS<sub>1.03</sub> porous hollow spheres (NiS<sub>1.03</sub> PHSs) and porous NiS<sub>1.03</sub> hollow cages (NiS<sub>1.03</sub> PHCs) with high yield are designed and selectively fabricated via a simple solvothermal and subsequent annealing approach. As shown in Fig. 1, the obtained NiS<sub>1.03</sub> PHSs (605 mAh  $g^{-1}$  at 1 A  $g^{-1}$  and 175 mAh  $g^{-1}$  at 15 A  $g^{-1}$ ) and NiS<sub>1.03</sub> PHCs (577 mAh  $g^{-1}$  at 1 A  $g^{-1}$  and 100 mAh  $g^{-1}$  at 15 A  $g^{-1}$ ) display excellent rate performance. In addition, the analyses results of in situ and ex situ XRD patterns and HRTEM images reveal the reversible Na-ion conversion mechanism of NiS<sub>1.03</sub>. It is also worth noting that the NiS<sub>1.03</sub> PHSs//FeFe(CN)<sub>6</sub> full cell is successfully assembled and exhibits an initial reversible capacity of 460 mAh  $g^{-1}$  at 0.5 A  $g^{-1}$ , which further evidence that NiS<sub>1.03</sub> is a kind of prospective anode material for SIBs



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## Intelligent Casting Riser Optimization on TMCast Software Frame

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Keywords: Genetic Algorithm, Casting Riser, Software Develop, Defect Prediction

### Abstract

A modularized Software was developed by Shandong University Foundry Engineering Studio(FES) to test and apply new simulation and optimization algorithm. With well encapsulated API, researchers can easily develop unique simulation or optimization module. A well designed partition algorithm also improved the appearance of mesh generation process.

A riser design intelligent optimization module was also developed to test the accuracy of some defect prediction algorithm, including shrinkage prediction based on melting pool and fluidity, and porosity prediction based on modified Niyama. And possibility of practice application of this module is also considered. Riser graphic parameter identification and modify was implemented in a paralyzed calculate designed program frame to accelerate calculation.

In conclusion, the optimization module worked well on test mold, simulation and predict code perform well on large castings. Some code should be optimized to approach practice application.



Fig.1 GUI of TMCast







Author 1 Shao Anchen, started doctoral course in Nov. 2018 in School of Material Science & Engineering, Shandong University. Graduate as a Master student in 2018, and is the main designer and programmer of TMCast Software Program.

## Effect of Magnetic Field Imposition on Electro-deposition of ZnTe

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Keywords: ZnTe semiconductor, electro-depositing, magnetic field imposition,

#### Abstract

ZnTe is considered to be one of innovative semi-conducting materials because the theoretical energy band gap value is 2.26 eV suitable for solar cell and LED. And the further advantageous point is that the material of ZnTe is inexpensive and harmless. Among various synthesizing techniques, electro-deposition process has been investigated because the process is not expensive and suitable for mass production.

In this study, the optimum condition of electro-deposition of relatively thick ZnTe film under strong magnetic field. Fig.1 shows the schematic of experimental apparatus. The band gap value of obtained ZnTe film can be improved up to 2V in optimum conditions of electro-deposition and successive heat treatment.

The key technology to achieve high performance of energy band gap value, crystal orientation of ZnTe of cubic structure can be realized by electro-deposition of metal Te layer under strong magnetic field prior to ZnTe deposition.



2.5 2.26 ev Theoretical value of ZnTe 2.0 Band Gap (eV) 1.5 Value of ZnTe without Te film 1.0 0.5 0.0 3 5 15 Quantity of electricity (C)

Fig.1 Schematic view of electrodepositting cell set in the bore of a superconducting magnet.



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Fig.2 Effect of total quantity of electricity on energy band gap of ZnTe film

## Wear-Resistant Surfacing Layer Preparated by High Efficiency Twin-Wire Indirect Arc Welding

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*Keywords: Twin-wire indirect arc welding, wear-resistance surfacing layer, chromium carbide, droplet transfer, metallurgical reaction* 

#### Abstract

Twin-wire indirect arc welding (TWIAW) is a novel welding technology with high deposition efficiency and low dilution rate, which is especially suitable for wear-resistant surfacing. In this study, wear-resistant surfacing layer was prepareted on low-carbon steel using flux cored wire by TWIAW. The influence of welding parameters on droplet transition and the surfacing layers property were studied. In the TWIAW process, due to rapidly solidification of the weld pool, wear-resistant reinforced phase synthesized through metallurgical reaction mainly finished in the droplet transfer stage using the welding arc. The welding parameters not only affected the droplet transfer frequency and size, but also affected the microstructure of the surfacing layer. The main reinforcing phase in the surfacing layer was chromium carbide. "Lean carbon" phenomenon could be observed along the grain boundary in the matrix when the welding current was small. The increasing of the welding current could prompt the metallurgical reaction. The wear resistance of the surfacing layers depends on the distribution of the chromium carbide and the matrix microstructure.



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## Gas Sensing with metal oxide nanocrystals

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Keywords: gas sensor, nanocrystals, SnO<sub>2</sub>, diffusion, kinetics

#### Abstract

It is well known that the sensitivity of metal oxides is dependent on their morphology such as particle size, pore size, thickness, and surface states. We have been studying the effects of the particle- and pore-sizes of sensing films on sensitivity. In order to quantitatively analyze such effects, we fabricate SnO<sub>2</sub>-based films with different particle- and pore-sizes and study the sensor responses to three different gases, including H<sub>2</sub>, CO, and H<sub>2</sub>S with the different Knudsen diffusion coefficients. To fabricate SnO<sub>2</sub>-based films with different particle- and pore-sizes, we developed a seed-mediated growth approach using 4 nm SnO<sub>2</sub> nanocrystals as seed crystals. The developed method successfully produced nanocrystals

ranging from 9.5 to 17 nm in average diameter under hydrothermal conditions at  $250^{\circ}$ C. Using the SnO<sub>2</sub> nanocrystals, pore size of gas sensing films was successfully controlled from 2.8 to 5.5 nm in radius.



Fig. 1 Gas sensor structure and Sensor response to VOCs.

The sensor response to  $H_2$  increased with decreasing the particle size probably due to the effective formation of electron depletion layers in the entire volume of nanosized crystals. In contrast, the responses to CO and  $H_2S$  increased with increasing the particle size and the resulting pore size. On the basis of the Knudsen diffusion-surface reaction equation, we simulated a gas concentration profile inside the films, which revealed that the diffusion of CO and  $H_2S$  is limited by small pores due to their lower diffusion rates than  $H_2$ . We found that controlling the pore size of sensing films is very effective to produce highly sensitive films toward larger weight gas molecules. In the presentation, our recent approaches to develop highly-sensitive sensors using oxide nanocrystals will also be given.



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## Effect of Buffer Layer on the Structural Properties of Tin Oxide Thin Film on Sapphire Substrate by Mist Chemical Vapor Deposition

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Keywords: Buffer layer, Single Crystal, Mist-CVD, Surface Morphology, Crystal Quality

#### Abstract

Tin oxide  $(SnO_2)$  is an n-type wide band-gap semiconductor material with excellent properties such as optical, electrical and chemical properties. The samples were deposited on m-plane sapphire substrates at various temperatures by lateral flow-type mist chemical vapor deposition. However, it has been difficult to deposit smooth surface with single crystal property, because of the large lattice mismatch and the large difference in the thermal expansion coefficient between the oxide film and the sapphire substrate. To improve the quality of SnO<sub>2</sub> films, we put a SnO<sub>2</sub> buffer layer for the purpose to solve the lattice mismatch problem between sapphire substrate and SnO<sub>2</sub> films. Surface morphologies of SnO<sub>2</sub> films with the buffer layer are much improved compared to the film without the buffer layer. The full width at half maximum of an X-ray  $\omega$ -rocking curve for the SnO<sub>2</sub>



Fig. 1 FWHMs of  $\omega$ -rocking curves for SnO<sub>2</sub> films with and without buffer layer

thin film was reduced from 0.99 deg to 0.13 deg by inserting the buffer layer between the sapphire substrate and  $SnO_2$  films. From these results, we can conclude that the crystal quality of  $SnO_2$  films was improved by introducing the buffer layers between the substrate and the thin films.



**Thant Zin Win** received the B.E and M.E degree in Electronics from Mandalay Technological University, Myanmar, in 2005 and 2008, respectively. He is currently a Ph.D. student in the Graduate of School of Science and Technology, Kumamoto University. His research interests include thin film deposition, optoelectronic devices and power devices.

## POMs Encapsulated in High-Nuclearity Silver Cluster

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*Keywords: silver cluster, anion template, polyoxometallate(POM), aesthetic structure, physicochemical property* 

#### Abstract

Polynuclear silver clusters have been very attractive due to their aesthetic structures as well as their physicochemical properties. The formation of a high-nuclearity silver cluster is a quite complicated process involving multiple small building blocks, and it is still challenging to arrange more than dozens of silver centers together in an ordered fashion; that is, a controllable synthesis is highly needed. In the past decade, the role of anions



Fig. 1 Some typical examples of anion templated silver clusters.

in determining the structures and properties of silver clusters appears very important. Recently, we have developed a series silver clusters based on the anion templates including small inorganic anions and large polyoxometallate(POM) anions such as  $[Mo_2O_8@Ag_{30}]$ ,  $[Mo_6O_{22}@Ag_{46}]$ ,  $[Eu(W_5O_{18})_2]_2@Ag_{72}$ ,  $[Mo_6O_{22}@Ag_{58}]$ ,  $[Mo_5O_{18}@Ag_{36}]$ ,  $[Mo_4O_{14}(SO_4)]_2@Ag_{73}$ . Among them, most of them are not classic species as observed in POM chemistry, indicating these species are highly active and can only be lived with the stability effects of outer silver shells.



**Di Sun** join the School of Chemistry and Chemical Engineering, Shandong University in 2011. His research interests include the rational design and synthesis of photoluminescent silver coordination complexes including clusters and polymers, crystal engineering of transition metal coordination complexes and so on.



**Zhi Wang** received her B.S. (2014) from Liaocheng University, and M.S. (2016) in Inorganic Chemistry from Shandong University under the supervision of Professor Di Sun. Currently, she is an doctoral student in Inorganic Chemistry, Shandong University. Her interests include the rational design synthesis of photoluminescent silver coordination complexes and clusters.

## The Study of Polymer Derived Silicon Oxycarbonitride for Anti-hydrolysis

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Keywords: aluminum nitride, hydrolysis; polymer derived silicon oxycarbonitride ceramic, core-shell structure

#### Abstract

Aluminum nitride (AlN) features an extremely interesting combination of very high thermal conductivity and excellent electrical insulation; therefore, it has been widely used in the high power electronic devices. The hydrolytic reaction of aluminum nitride powder decays the shelf-life and lowers the high power operating performance of the electronic devices. A protecting film of the polymer derived silicon oxycarbonitride ceramic is coated and fully wrapped on the surface of aluminum nitride powder against facilitating hydrolysis. Poly (organosilazane) precursor is incorporated with the commercial aluminum nitride powder pyrolyzed at 700 °C under argon environment for few hours to form a core-

shell structure with a film thickness, 10-20 nm of silicon oxycarbonitride (SiCNO) ceramic shell and the aluminum nitride core as shown in Fig.1. Measuring the pH value of SiCNO/AlN coreshell powder in deionized water at room temperature is to observe the hydrolytic behavior that its pH value is stable to maintain about 10 at ambient environment over ten days as shown in Fig.2. These results directly indicate that the polymer derived silicon oxycarbonitride ceramic film fully protects the aluminum nitride powder from hydrolysis. When the content of silicon oxycarbonitride shell reduces to reach certain value, the hydrolytic protection gradually vanishes for long time.



Fig. 1 SEM images EDS analysis of SiCNO/AlN core-shell powder structure



Fig. 2 the core-shell structure pyrolyzed at 700  $^{\circ}$ C with different content of SiCNO ceramic shell for testing hydrolysis (700-X SiCNO/AlN (X : the content of the commercial AlN)



**Lung-Hao Hu** received the B.S. degree in Mechanical Engineering from Tatung University, Taiwan in 2000. Then he received his M.S. and PhD. degrees in Mechanical Engineering from University of Colorado Boulder, U.S. in 2005 and 2010, respectively. He is currently an associate professor in the Department of Mechanical Engineering, Southern Taiwan University of Science and Technology. His research interests include Polymer Derived Ceramic, surface coating and 2D materials.

## **POSS Grafted Polybenzimidazole Hibrid Materials**

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Keywords: POSS, polybenzimidazole, grafted, packing, solubility

#### Abstract

Aromatic polybenzimidazoles (PBIs) possess a unique rigid structure containing  $\pi$ -conjugated benzimidazole groups. They are difficult to process because of their high melting temperature and poor solubility. N-POSS-substituted polybenzimidazoles (POSS-*g*-PBIs) were synthesized by grafting different amounts of polyhedral oligomeric silsesquioxane (POSS). X-ray powder diffraction analyses and Scanning electron microscope characterization revealed that POSS dispersed well in the polybenzimidazole matrix. The intermolecular face-to-face packing and hydrogen bonding between polybenzimidazole molecular chains were broken by the grafted pendant moieties POSS. As a result, POSS-*g*-PBIs showed better solubility than the pure polybenzimidazole because of less tight molecular chain packing. The mechanical properties, including Young's modulus, breaking strength and elongation at break, increased by introducing POSS into the polybenzimidazole backbone. POSS-*g*-PBIs also exhibited good thermal stability.





Fig. 1 Scheme of N-POSS-substituted polybenzimidazoles

Fig. 2 XRD of POSS-g-PBIs



**Qingzeng Zhu** received his M.S. and Ph.D. degree from Shandong University, China in 1997 and 2003, respectively. Then he spends two years as a postdoctoral at State Key Laboratory of Polymer Physics and Chemistry, China. In 2007, he worked at Max-Planck-Institute for Polymer Research as a visiting scholar in Prof. Hans-Jürgen Butt group. He is currently a professor in the School of Chemistry and Chemical Engineering, Shandong University. His research interests include the investigation of organosilicon materials and high performance polymer materials.

#### Necklace-shaped Dimethylsiloxane Polymers Bearing POSS Cages

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Organosilicon polymer compounds with siloxane bonds as the main skeleton have structural diversity comparable to that of organic compounds. Among the large degree of structural freedom of siloxane-based molecules similar to that of carbon materials, discrete nanostructures such as polyhedral oligomeric silsesquioxane (POSS) molecules, which possess nanocage structures, have been studied extensively for both basic research and industrial applications. We have focused necklace-shaped POSS-dimethyl siloxane (DMS) alternating polymers, in which POSS cages are alternately connected to short soft chains, for purposes of the development of synthesis methods with structural control and understanding of the correlation between nanostructure and physical properties. Two major synthetic methods based on polycondensation and ring-opening polymerization with a bifunctional POSS have been reported for the synthesis of necklace-shaped POSS-DMS polymers. The stepwise synthesis allows us hierarchical control of the primary structures of the necklace-type polymers.

Necklace-shaped POSS-DMS polymers show very good solubility in common organic solvents. The polymers generally possess an amorphous structure and flexible and transparent polymer films are prepared by simple casting. By crosslinking at the ends of the polymers with a cross-linker agent, insoluble polymers, in which original structural features and thermal properties of the thermoplastics are almost maintained, are also obtained as thermosetting plastics. The polymers reveal extremely high heat resistance. The 5% decomposition temperature (Td<sub>5%</sub>) of POSS-DMS polymers exceeds over 400 °C (The highest Td<sub>5%</sub> was 470 °C) compared to about 350 °C of polydimethylsiloxane (PDMS) in air. Such remarkably high heat resistance performance is considered to result from the extremely high-volume ratio and high homogeneity of POSS cages in the polymer matrix, which is allowed by the necklace-shaped polymer structures.

It was also found that these thermoplastic POSS-DMS polymers exhibit very strong adhesion in the glassy state after hot melt press, indicating the potential of the polymers as a hot melt adhesive. Strong adhesion of the polymers was observed not only to an intact hydrophilic glass but also to a modified hydrophobized glass, metal like a stainless, metal oxides and some polymers. Additionally, the easy and reversible peeling off was able to be achieved by heating up above the glass transition temperature. From the aspects of the shape of the POSS-DMS polymer, only the van der Waals force between the phenyl groups on the POSS cage and the substrate surfaces can be considered for the force involved in adhesion. The key of unexpected strong adhesion based on van der Waals force will be due to the good wettability of the POSS-DMS polymer at lubberly state. Siloxane soft chains connecting POSS cages would provide the conformability of the polymers against atomic rough substrate surfaces to support the nanoanchoring effect of POSS cage units.



Adhesive area 7x5 mm<sup>2</sup>

Figure 1. Basic chemical structure and the space-filling model of POSS-DMS necklace type polymers and hot-melt adhesion test using stainless steels

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## Activity of slip and twin systems in pure titanium polycrystals

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Keywords: titanium, polycrystals, slip system, twin,

## Abstract

Tensile tests of pure titanium polycrystals with different grain sizes and different tensile direction were carried out and the activity of slip and twin systems at each strain stage was investigated. Slip and twin

systems of each grain was identified by comparing the angle of a slip line that observed by an optical microscope (Fig. 1) with the initial crystal orientation that measured by EBSD. Prismatic slip was activated with the grains of 80% or more until  $\varepsilon$ =1%. First order pyramidal slip and second order pyramidal slip were activated with 10% grains after  $\varepsilon$ =1%. On the other hand, activities of {1012} twin and {1122} twin increased with increasing grain size and the activities depended on tensile direction.



Fig. 1 Optical micrograph after  $\varepsilon$ =4.3% deformation in the d=85µm specimen.



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## Local Deformation Behavior of Pure Mg, Zn and Ti Single Crystals using Ball Indenter

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Keywords: pop-in, basal slip, pyramidal slip, {10-12} twin

#### Abstract

Indentation tests were performed to pure Mg, Zn and Ti single crystals to investigate crystal orientation dependence of local indentation behavior. Indented planes were (0001), (10-10) and (11-20), and indentation tests were carried out using a ball indenter at room temperature. Figure 1 (a) and (b) show optical micrographs of indentations and load-penetration curves when indented on (a) (10-10) in pure Mg and (b) (0001) in pure Zn. In Mg single crystals, pop-in was observed in (10-10) and (11-20) indentations. When indented on (0001) in Zn, pop-in was observed and the indentation showed isotropic morphology. Also, twins were scarcely observed. When indented on (10-10) and (11-20) indentations, indentations elongated to [0001]. In Ti single crystals, no pop-in was observed in this study.

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Fig.1 Optical micrographs of indentations and load-penetration curves when indented on (a) (10-10) in pure Mg and (b) (0001) in pure Zn.



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## Mist-CVD deposition of AlTiO thin films for potential applications in AlGaN/GaN MOS-HEMTs

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Keywords: AlTiO, mist chemical vapor deposition

#### Abstract

GaN-based metal-oxide-semiconductor (MOS)-highelectron-mobility transistors (HEMTs) are promising for high-power switching devices, owing to a high blocking voltage and a low on-state resistance. For a gate insulator of the MOS-HEMTs, Al<sub>2</sub>O<sub>3</sub> is an attractive material due to its large bandgap  $E_g$  (~ 7 eV) and relatively high permittivity  $\varepsilon_r$  (~ 9). On the other hand, high- $\kappa$  dielectric such as TiO<sub>2</sub> ( $\varepsilon_r \sim 50$ ) is also attractive for achieving large transconductance in the MOS-HEMTs. However, the TiO<sub>2</sub>/AlGaN/GaN MOS-HEMTs showed large leakage currents owing to the small  $E_g$  of TiO<sub>2</sub> (~ 3 eV). Therefore AlTiO, alloys of TiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>, is one of effective solutions to realize a large bandgap and high dielectric



constant. In this study, AlTiO thin films were grown by mist chemical vapor deposition (CVD), which allows film growth even at atmosphere pressure using a simple system with low cost and environmental friendliness. The AlTiO films grown at 400 °C with aluminum acetylacetonate  $(Al(C_5H_7O_2)_3)$ , titanium isopropoxide  $(Ti[(CH_3)_2CHO]_4)$  and methanol, without a post deposition annealing process, showed an excellent film density (not shown here). In addition, bandgap of obtained AlTiO films are in good agreement with reference samples as shown **Fig. 1**.



**Koshi Nishiyama** received the B.E. degree in engineering from Kumamoto University, Japan, in 2017. He is currently the second year of master course in the Department of Computer Science and Electrical Engineering, Kumamoto University. His research interests are wide band gap semiconductors formed by mist chemical vapor deposition.

## **Electrochemical Hydrogen Separation using a Graphene Oxide Membrane**

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Keywords: Graphene Oxide, Hydrogen Separation, Hydrogen pump

#### Abstract:

In recent years, hydrogen energy has attracted much attention as clean energy because combustion of hydrogen emits only water as a by-product. To produce pure hydrogen, several hydrogen separation methods have been developed. In this study, we focused on graphene oxide (GO) membrane as a proton conducting material. GO is a carbon nanosheet synthesized from inexpensive graphite, which shows high proton conductivity that is comparable to that for Nafion. However, the low mechanical stability of GO membranes made by laminating GO nanosheets limits their practical use. Therefore, we incorporated metal ions into GO membranes to improve the stability.

GO nanosheets were synthesized by the Hummers' method from a commercial graphite powder and GO membranes were prepared by a filtration mixed with Ceion nitrate. Firstly, we measured the proton conductivity of the GO and Ce-GO membrane by the impedance measurement under 25-100 °C. The results on proton conductivity measurements is shown in Fig.1. The proton conductivity of the GO membrane decreased as the temperature increase. However, the Ce-GO membrane maintained the proton conductivity even at high Secondly, we attempted to separate temperature. hydrogen from mixed gases by an electrochemical hydrogen pumping method using the GO membrane.  $H_2$ in Ar was introduced to the one side of the membrane and permeated H<sub>2</sub> in the other side was detected by gas chromatography. We measured the amount of permeated  $H_2$  by applying potential from 0.5 to 4.0V. The results on electrochemical hydrogen pumping experiments showed that the permeation rate of hydrogen was linear to the currents flowed, in good agreement with the Faraday's law. Therefore, it can be concluded that pure hydrogen was produced by electrochemical permeation through the GO membrane.



Fig.1 Proton conductivity of GO and Ce-doped GO membrane as a function of temperature.



Fig.2 The dependence of hydrogen permeation rate on currents flowed through the GO membrane.

## Synthesis of Lead-free Perovskite Quantum Dots for by an emulsion method

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Keywords: Perovskite Quantum Dots, lead-reduce, crystal structure,

#### Abstract

Lead halide perovskites are attracting much attention as excellent optical materials for various applications such as phosphors, displays, solar cells, and bioimaging. In particular,  $CsPbX_3$  (X = Cl, Br, I) quantum dots show an excellent quantum yield exceeding 90% with a sharp emission peak (Full width half maximum <25 nm). Other benefits are that they are inexpensive and the emission wavelengths can be controlled from infrared to ultraviolet. However, their stability is poor; they decompose immediately when being in contact with water or polar solvents. Furthermore, the hazardous nature of Pb is a major disadvantage. In this study, we attempted to develop lead-free or lead-less perovskite quantum dots. We focused on using Sn in place of Pb and investigated a change in the luminescence characteristics by the substitution.

The crystal structure, particle size and optical properties of the synthesized perovskite quantum dots were analyzed by TEM, PL and UV-vis, respectively. The obtained PL spectra are shown in Fig.1. Pb-derived peaks (530 nm) and Sn-derived peaks (460 nm) can be observed in samples with 90% and 50% Sn substitution in CsPbSnBr<sub>3</sub>. The presence of the two-phases, CsPbBr<sub>3</sub> and CsSnBr<sub>3</sub>, is suggested. The XRD pattern confirmed that the cubic phase changed to the tetragonal phase as the amount of Sn substitution increased. This suggests that in Sn-rich samples the structure changed from a two-phase mixture to a single phase. It should be noted that even when the Pb content was suppressed, good emission intensity was obtained. The above results show the possibility of developing lead-free luminescent quantum dots by further composition control.



Fig.1 PL emission peaks for CsPb<sub>1-</sub>xSn<sub>x</sub>Br<sub>3</sub>

## Formation of N-doped ZnO thin films formed by annealing in NH<sub>3</sub> gas ambient

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Keywords: annealing, p-type ZnO thin film, Mist-CVD

#### Abstract

Light-emitting diode devices (LEDs) have characteristics of high efficiency, long life, low power consumption. However, GaN LEDs are expensive because they are fabricated by the metal organic chemical vapor deposition (MOCVD) which needs expensive toxic gases and vacuum components. In the present study, ZnO thin films with high exciton binding energy (60 meV) were grown by using Mist-CVD that can form thin films at atmospheric pressure. After that nitrogen doping and p-type conversion of ZnO thin films were attempted by annealing in NH<sub>3</sub> gas ambient. As shown in Fig. 1, analysis of nitrogen element was carried out by X-ray fluorescence (XRF). Doping of nitrogen into the ZnO thin

film was confirmed by annealing in NH<sub>3</sub> gas ambient. However, Hall measurement showed n-type conductivity. This is probably because holes were compensated by compound of nitrogen and hydrogen. Therefore, rapid thermal annealing (RTA) was performed for the purpose of desorption of hydrogen. From the XRF analysis results in Fig. 1, nitrogen as a p-type dopant was observed in ZnO thin films, but n-type conductivity in the Hall measurement was kept probably because large number of residual electrons. Therefore, it is necessary to reduce the residual electron density.







**Takumi Furukawa** received the B.E. degree in engineering from Kumamoto University, Japan, in 2018. He is currently the first year of master course in the Department of Computer Science and Electrical Engineering, Kumamoto University. His research interests are wide bandgap semiconductors formed by Mist-CVD.

## Fabrication of single crystals of organic semiconductors in hydrogel capillaries

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Keywords: phase diagram, heterogeneous nucleation at air/liquid interface, agarose hydrogel Abstract

The patterning the single crystals of organic semiconductors on desired regions has attracted much attention in organic electronics. One of the single crystallization strategies are based on inducing the polynuclear at the one side of the desired regions followed by converting to a single crystal in crystal growth condition at the one direction. We have reported phase diagrams of organic semiconductors to know critical crystallization conditions and found that an air/liquid interface has different crystal nucleation conditions.<sup>1</sup> In this study, we fabricate



Figure 1. Optical microscope image of a C8-BTBT single crystal on a substrate.

single crystals in capillaries by air/liquid-induced heterogeneous nucleation and crystal growth in super cooling conditions which are adjusted with temperature. The single crystals are transferred on Si substrates by fabricating capillaries with hydrogels and then dissolving.

A p-type thienoacene-based organic semiconductor (C8-BTBT) derivative and o-dichlorobenzene as good solvent were used. Agarose gel capillaries were fabricated by solidifying agarose sols with templates followed by removing the templates. C8-BTBT solutions were injected in the gel capillaries and one of the solution was filled with air. These samples were cooled down to and kept at the temperature which was the nucleation temperature at air/oil interface and the super-cooling temperature in bulk liquid phase. Single crystals were transferred on Si substrates by dissolving the gel capillaries.

Figure 1 shows optical microscope image of a C8-BTBT crystal on a Si substrate. The width of the crystal was same and the thickness was smaller than the capillary sizes. Crossed-Nicol microscopy showed that the crystals had the extinction position by rotating 45 degree in plane direction, indicating the formation of single crystals. X-ray analysis revealed that edge-on and herring bone structures were formed in out-plane and in-plane direction of crystals.

1) S. Watanabe, R. Urata et al., *Langmuir* 2017, 8906-8913.



**Ryota Urata** received the B. E. degree (2017) and now is in master course students in Science and Technology from Kumamoto University, Japan. His research interests include Colloid and interface Science, and Organic Electronics.

## Electrochemical CO<sub>2</sub> reduction using metal modified carbon electrodes

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Keywords: electrochemical, carbon, catalyst, carbon dioxide, reduction

#### Abstract

In recent years, much attention has focused on the reduction of carbon dioxide into valuable compounds. Among the methods so far reported, electrochemical reduction of  $CO_2$  is one of the most promising routes because of its good yield, simplicity, and room temperature operation. However, the low selectivity of products is one major issue. As such, further development of electrocatalysts is needed. In this research, we aimed to prepare carbon-based electrodes to electrochemically reduce carbon dioxide into organic compounds.



Fig. 1 Cell structure.

In the experiment, the activity of the electrode was examined by Liner Sweep Voltammetry (LSV), and then

electrochemical carbon dioxide reduction was carried out with Chronoamperometry (CA). The electrode was fabricated by depositing carbon colloids and metal (or oxide) nanoparticles on Ni mesh electrodes. We used a platinum plate as the counter electrode and Ag / AgCl as the reference electrode. KHCO<sub>3</sub> was used as the electrolyte solution and Nafion membrane was used as the ion exchange membrane. A two-compartment cell was used, as shown in Fig.1 The reduction was conducted at -1.2 V for 0.5, 1.0, and 1.5 h.

The results showed the formation of formic acid, acetic acid, and ethanol under electrolysis in a  $CO_2$  flow. In all cases, reaction time for 0.5 h gave the best results, showing a gradual change of product distribution. We found that the control of thickness of the carbon layer and nanoparticle size is critically important to obtain better conversion yields. The results suggest that our carbon electrodes have a potential to convert carbon dioxide to value-added compounds in a short time.



**Yudai Hirano** received the B.E.degrees in applied chemistry from Kumamoto University, Japan, in 2017. He is currently a graduate student in the second grade in the Department of Science and Technology, Kumamoto University. His research interests include electrochemical, carbon and metal catalyst.

## Epitaxial growth of non-polar ZnO films on buffer layers on sapphire substrates by mist chemical vapor deposition

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Keywords: ZnO, mist chemical vapor deposition

#### Abstract

ZnO is a II-VI compound semiconductor that has attracted much attention because it has superior properties such as a wide direct band gap (3.37eV) and a large exciton binding energy (60meV). Therefore, ZnO is expected as a new material for light emitting diodes (LEDs). As a final goal, we aim to realize low cost LEDs by using ZnO and mist chemical vapor deposition (mist-CVD). In our former study, we have developed a new mist-CVD system of high-speed rotation-type. We have obtained uniform ZnO epitaxial films over 2-inch sapphire substrates by this system[1]. In this study, we aim to improve crystal quality of ZnO films on sapphire substrates by introducing buffer layers. Fig.1 shows

XRD  $\omega$ -rocking curve of ZnO films. It was found that full wide at half maximum (FWHM) of XRD  $\omega$ -rocking curve decreased by inserting the buffer layer between the sapphire substrate and the ZnO film. From this result, crystallinity of the ZnO film has been improved. In addition, the buffer layer greatly contributed to improvement of the crystal quality especially along the lateral direction in which the lattice mismatch was large.



Fig.1 XRD ω-rocking curve of ZnO films

### [1] H. Tanoue, et al., Appl. Phys. Express 8, 125502 (2015).



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## Enhancing the Stability of CsPbX<sub>3</sub> Quantum Dots by Metal Oxide Coating

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Keywords: CsPbX<sub>3</sub>, perovskites, quantum dots, nanocrystals, photoluminescence

#### Abstract

 $CsPbX_3$  (X = Cl, Br, I), all inorganic perovskites, are newly-emerging semiconducting materials, which can be applied to various optoelectronic devices, such as solar cells, photodiodes, and perovskite light-emitting diodes (LEDs), and lasers. These applications rely on their remarkable optical properties such as high photoluminescence quantum yields (PLQY), extremely narrow bandwidths (full width at half maxima (FWHM) of the PL spectra, tunability of the emission spectra, and short radiative lifetimes. Although CsPbX<sub>3</sub> perovskite Quantum Dots (QDs) are highlighted as excellent optical materials, CsPbX<sub>3</sub> suffers from serious issues; it is instable against moisture, at elevated temperatures, in polar solvents, and under UV light.

Thus, this study focusses on improving the stability by encapsulation of perovskite QDs with a silica shell. The silicacoated CsPbX<sub>3</sub> QDs (SiO<sub>2</sub>-QDs) were synthesized by a reprecipitation-encapsulation method assisted with amine functional silane. Specifically, amino groups of silane take part in the crystallization of perovskite QDs, while alkoxysilane groups undergo hydrolysis and condensation, resulting in the encapsulate of QDs.

The morphology of the resulting SiO<sub>2</sub>-QDs was characterized by transition electron microscopy (TEM). Fig.1 shows a representative TEM image of SiO<sub>2</sub>-QDs. The formation of spherical particles was confirmed, suggesting that several QDs were covered with silica. We next studied the optical properties of the QDs. The SiO<sub>2</sub>-QDs have a narrow green emission peak at 511 nm with a FWHM of 20 nm and a PLQY of 90.9%. The silica coating did not degrade the excellent optical properties of CsPbX<sub>3</sub> Fig.2 shows the PL intensity of the QDs in ethanol as a function of time. We found that the silica coating significantly improved the stability.



Fig.1 TEM image of CsPbBr<sub>3</sub>/SiO<sub>2</sub>.



Fig.2 PL intensity of CsPbBr<sub>3</sub>/SiO<sub>2</sub> in ethanol after storage for different times.

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## Gas sensing properties of pn junction films using ZnO nanorods and CuO nanocrystals

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Keywords: Gas sensor, Colloidal quantum dots, Nanorods, ZnO, pn junction films

#### Abstract

Hydrogen sulfide ( $H_2S$ ) is known as a colorless, flammable and highly toxic gas with strong odor. Therefore, to avoid the risk of its leakage, continuous monitoring of  $H_2S$  is extremely important. Semiconductor gas sensor is promising for such application because of its high sensitivity, selectivity, fast response, and good stability. It has been reported that CuO and Cu<sub>2</sub>O deposited on SnO<sub>2</sub> show high sensitivity to  $H_2S$ . In this study, we deposited p-type CuO and Cu<sub>2</sub>O nanocrystals on n-type ZnO nanorod films to develop a new type  $H_2S$  sensor.

Fig. 1 shows the IV curve of the ZnO/CuO (or Cu<sub>2</sub>O) pn junction film device in air and air containing H2S at 150 oC. The clear rectifying property has been confirmed in the ZnO nanorod/CuO (Cu<sub>2</sub>O) nanocrystal film. In H<sub>2</sub>S atmosphere, the rectifying property of the device was deteriorated; the reverse current increased, suggesting the formation of CuS. However, in air, the rectifying property recovered. The results indicate the promising capability of the device to detect H<sub>2</sub>S with diluted concentrations in air.



**Fig.1** IV curve of the ZnO nanorod/CuO device in air and H<sub>2</sub>S (150°C)



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## Synthesis and Application of Necklace Shaped Inorganic Polymers

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Keywords: POSS, inorganic polymer, adhesion

### Abstract

Polymers having "polyhedral oligomeric silsesquioxane (POSS)", which is a rigid cage structure, have recently attracted attention. We have developed a series of necklace shaped dimethylsiloxane (DMS) polymers bearing POSS cages. In the polymers, POSS cage units and soft DMS chains are connected alternately (Fig.1). The polymers are synthesized by two different synthetic methods, "polycondensation" and "ring-opening polymerization" with a bifunctional



Fig.1 Hierachiral synthesis of POSS-DMS polymers

POSS molecule. High molecular weight polymers are able to produce by the both methods. Moreover, we have achieved systematic control of primary polymer nanostructures, such as the average siloxane chain length and arrangements between POSS cages. The synthesized POSS-DMS alternating polymers are a transparent, flexible films with extremely high heat resistance ( $T_{d5\%} > 400$  C). In addition, glassytransition temperature of the polymer can be designed freely by changing the chain length.

Furthermore, we have found that un-crosslinked POSS-DMS thermoplastics exhibit very robust hotmelt type adhesive properties, although the considered adhesion force will be only van der Waals forces. The unique adhesion mechanism will be introduced in the presentation.



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## Preparation and Properties of anodizing film on 5XXX aluminum alloy

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Keywords: Anodizing, Aluminum alloy, Corrosion resistance, Sulfuric acid bath

#### Abstract

This study was focused on preparing high quality anodic aluminum oxide film by studying the anodic oxidation conditions of aluminum alloy to produce porous, high wear resistance, high corrosion resistance and decorative aluminum alloy anodic oxide film. Anodic aluminum oxide film was prepared by using AA5XXX aluminum alloy as substrate and 180g/L sulfuric acid as anodizing electrolyte at different anodizing voltage and different anodizing temperature.

Increasing the anodizing voltage increased the rate of oxide formation and aluminum oxide film got rough under the higher anodizing voltage condition. Through sealing treatment, anodizing voltage range

of 16V~22V for all specimens had good film properties like thickness, wear resistance and corrosion resistance. This voltage range could be used as an appropriate operating voltage for the anodic oxidation process.

The anodic aluminum oxide film prepared was examined by SEM, film thickness analysis, hardness analysis and corrosion resistance analysis. The results showed that the anodic aluminum oxide film was prepared with the optimum conditions of the anodizing: Voltage of 18V, anodizing time of 1hour and anodizing temperature of 20°C ; Sealing treatment after the same procedure as exhibited the best uniform and the largest number of holes, the film thickness of 21µm, hardness of 276.8HV<sub>0.1</sub> and corrosion resistance of 6254  $\Omega$  / cm<sup>2</sup>(Fig.1).







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# Thermal and Optical properties of graphene nanocomposites for Green Architectures

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**Keywords:** green architectures, thermal insulated glass, spray-coating, electrochemically exfoliated graphene, Al<sub>2</sub>O<sub>3</sub>, heat conduction and radiation

### ABSTRACT

Graphene provides good and stable thermal conductivity in-plane but poor thermal conductivity out-of-plane[1,2]; however, this drawback can be regarded as an advantage for the application of green architectures (thermal insulated glass, TIG). The bi-layer or few-layer graphene used in this research is manufactured by the electro-chemically exfoliated method, called ECG (electro-chemically exfoliated graphene, commercially available from Nitronix Nanotechnology Corporation) incorporated with the aluminium oxide, an electrical insulator but has a relatively high thermal conductivity (40 W/m K), commercially available Aerosil [3]. The graphene ink is made of mixing of ECG with NMP solvent in a fix ratio and spray-coated with the different concentration of ECG (wt %) onto single side of the glass in a range of nm thick as shown in Fig.1(a,b)[4]. The Raman spectra shown in Fig.1(c) represents the quality of ECG is higher than that of reduced graphene oxide (RGO)[5]. The spraying ink is made of mixing nano  $\gamma$ alumina powder with ECG in NMP solvent at fixed ratio of Al<sub>2</sub>O<sub>3</sub> and ECG solution, and the Al<sub>2</sub>O<sub>3</sub>/ECG ink sprayed on a single side of the glass with different concentrations of ECG / Al2O3 (wt%) as shown in Fig. 1 (d). Transmittance and absorptivity were measured using different concentrations of ECG and ECG/Al2O3 coated glass. Obviously, the higher graphene concentration applied, the lower transmittance and the higher absorptivity detected; however, if the higher amount of nano  $\gamma$  alumina is added, the higher the transmittance and the lower the absorbance can be detected .In order to investigate the effect of heat conduction and radiation, the setup for thermal measurement is shown in Fig.2 (a) that the temperatures at  $T_1$ ,  $T_2$  and  $T_3$ are measured in transient state and the location of T<sub>3</sub> is simulated in an adiabatic system for heat flux insulation, such as a car parking under sunshine and the green glass window of a building as the barrier to prevent from heat flux (the both cases are not ideal adiabatic systems). The result shows that as single side coated with Al<sub>2</sub>O<sub>3</sub>/ECG

layer,  $T_3$  temperature can be kept at a lower temperature even after prolonging exposure to high temperatures as shown in Figure 2 (b). The results show that the spraying graphene with alumina in a specific proportion of solvent can insulate the heat flux through the green building glass.



Fig.1(a) spray-coating of ECG on glass with different concentrations.(b) spraying different proportions of graphene-alumina on the glass. (c) AFM image of ECG thickness.(d) Raman spectra of ECG.



Fig.2(a) the experimental set-up for thermal measurement. (b) the comparison of  $T_3$ 

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## Highly Concentrated Aqueous Electrolyte for High Voltage Liion Hybrid Supercapacitor

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Keywords: Highly concentrated aqueous electrolyte, Hybrid supercapacitors, LiTFSI, LiMn<sub>2</sub>O<sub>4</sub>

#### Abstract

Aqueous hybrid supercapacitors raise safety, high energy density, high power density and long cycling life .The use of aqueous alternatives is limited by their narrow electrochemical stability window(1.23V), which sets an intrinsic limit on the practical voltage. Highly concentrated aqueous electrolyte reduces the average number of water molecules available to cation ions that suppresses hydrogen evolution to push well beyong the limit. And lithium bis(trifluoromethane sulfonyl)imide (LiTFSI) was chosen as the salt because of its high solubility in water and high stability against hydrolysis.

In this work, we report a nanostructured spinel  $LiMn_2O_4$ and carbon nanotube (CNT) composite with much enhanced electrochemical performance as the cathode for aqueous hybrid supercapacitors, which was synthesized by ball milling. For the as-prepared composite , two couples lithiarion/delithiation process was observed from 0 to 1.1V in 1M  $Li_2SO_4$  aqueous electrolyte. When replacing with 5M LiTFSI, the working window can extend from 1.1V to 1.8V, which vastly promoted the energy density of aqueouse hybrid supercapacitors.



Fig.1 CVs of the LiMn<sub>2</sub>O<sub>4</sub>@CNT//AC hybrid supercapacitor coin cell in 1M Li<sub>2</sub>SO<sub>4</sub> aqueous electrolyte at different sweep rates.



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## NH<sub>3</sub> Combustive Decomposition over Various Supported Catalysts

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Keywords: Ammonia, Combustive decomposition, Supported catalysts

#### Abstract

Although  $NH_3$  has been considered as a renewable and carbon-free energy, it has a high ignition temperature and its use results in the production of  $N_2O/NO_x$ . In this study, we focused on  $NH_3$  combustive decomposition properties of various supported catalysts to suppress  $N_2O/NO_x$  production.

Various supported catalysts were synthesised via impregnation. The as-prepared catalysts were thermally aged at 900 °C for 100 h in air. The catalysts before and after reactions were characterised via XRD, XPS, and so on. Catalytic NH<sub>3</sub> combustive decomposition was conducted in a flow reactor. The O<sub>2</sub> excess ratio of NH<sub>3</sub> combustion was expressed as  $\lambda = (pO_2/pNH_3)_{exp}/(pO_2/pNH_3)_{stoichiom}$ .

Figure 1 shows the temperature dependence of product selectivities for catalytic NH<sub>3</sub> combustive decomposition over Cu/3A2S at  $\lambda = 0.90$ , over Cu/Al<sub>2</sub>O<sub>3</sub>, Pt/Al<sub>2</sub>O<sub>3</sub> and Rh/Al<sub>2</sub>O<sub>3</sub> at  $\lambda = 0.75$  and over Ir/Al<sub>2</sub>O<sub>3</sub> at  $\lambda = 0.60$ . For all catalysts, it is clear that NH<sub>3</sub> conversion reached approximately 100% without the production of N<sub>2</sub>O. The light-off curves of NH<sub>3</sub> for Cu/3A2S at  $\lambda = 0.90$  and Cu/Al<sub>2</sub>O<sub>3</sub> at  $\lambda = 0.75$  appeared to be similar to those previous reports for  $\lambda = 2.0$ . After NH<sub>3</sub> conversion reached approximately 100%, although the production of NO was slightly observed for Cu/3A2S, those concentration for Cu, Pt and/or Rh/Al<sub>2</sub>O<sub>3</sub> at  $\lambda = 0.75$  and Ir/Al<sub>2</sub>O<sub>3</sub> at  $\lambda = 0.60$  were considered negligible even with high activity. Therefore, NO production after NH<sub>3</sub> conversion reaches approximately 100% can be suppressed by controlling the O<sub>2</sub> concentration.





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## Catalytic NH<sub>3</sub> Combustion over CuO<sub>x</sub>/3Al<sub>2</sub>O<sub>3</sub>·2SiO<sub>2</sub>

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Keywords: Ammonia, Catalytic combustion, Copper oxides, Aluminum silicates

#### Abstract

Recently, NH<sub>3</sub> has been regarded as a renewable and carbon-free energy source due to its high energy density. However, NH<sub>3</sub> fuel has issues including high ignition temperature and N<sub>2</sub>O/NO<sub>x</sub> production. In this study, we focused on copper oxides (CuO<sub>x</sub>) catalysts supported on composite oxides of  $3Al_2O_3 \cdot 2SiO_2$  (3A2S) to investigate catalytic properties for the combustion of NH<sub>3</sub>.

3A2S was prepared using an alkoxide method. Supported  $CuO_x$  was prepared by an impregnation. As-prepared catalysts were thermally aged at 900 °C for 100 h in air. The catalysts were characterized by XRD, H<sub>2</sub>-TPR, and so on. Catalytic NH<sub>3</sub> combustion was conducted in a flow reactor.

Table 1 summarizes the catalytic properties of supported CuO<sub>x</sub> before and after thermal aging.  $T_{10}$  increased in the following order: CuO<sub>x</sub>/3A2S < CuO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub>(aged) < CuO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> < CuO<sub>x</sub>/3A2S(aged) < CuO<sub>x</sub>/SiO<sub>2</sub>  $\approx$  CuO<sub>x</sub>/SiO<sub>2</sub>(aged). This finding is almost consistent with the order of the reduction temperatures observed in the H<sub>2</sub>-TPR experiments, suggesting that the reduction of CuO<sub>x</sub> is closely associated with the combustion activity. In addition, it is considered that the lattice oxygen of the CuO<sub>x</sub> surface acts as a reactant for adsorbed NH<sub>3</sub>, and catalytic NH<sub>3</sub> combustion over supported CuO<sub>x</sub> proceeds *via* the Mars–van Krevelen mechanism. The supported CuO<sub>x</sub> with smaller particle sizes tended to exhibit lower reduction temperatures. N<sub>2</sub> selectivity at  $T_{90}$  decreased in the following order:

 $CuO_x/3A2S(aged) > CuO_x/SiO_2(aged) > CuO_x/Al_2O_3 > CuO_x/Al_2O_3(aged)$ . Therefore, it is suggested that  $CuO_x/3A2S$  before and after thermal aging exhibited improved the performance for catalytic NH<sub>3</sub> combustion than  $CuO_x/Al_2O_3$  and  $CuO_x/SiO_2$ .

 $\approx$ 

 $CuO_x/SiO_2$ 

> Table 1 Catalytic properties of supported CuO<sub>x</sub> before and after thermal aging.

Catalyst		Phase	$T_{10}$	$T_{90}$	Selectivity			Reduction	Cu
					at $T_{90}$ <sup><i>a</i></sup> /%			temperature	particle
			$^{a}/^{\circ}\mathrm{C}$	<i><sup>a</sup></i> /°C	$N_2$	$N_2O$	NO	<sup>b</sup> ∕ °C	size <sup>c</sup> / nm
Cı	uO <sub>x</sub> /3A2S	CuO/3A2S	292	484	97	<1	3	209	3.1
C	uO <sub>x</sub> /3A2S(aged)	CuAl2O4/3A2S	326	570	94	3	3	234	43
C	uO <sub>x</sub> /Al <sub>2</sub> O <sub>3</sub>	$CuAl_2O_4/\gamma$ - $Al_2O_3$	303	476	92	6	2	185	2.4
C	uO <sub>x</sub> /Al <sub>2</sub> O <sub>3</sub> (aged)	$CuAl_2O_4/\alpha, \gamma$ - $Al_2O_3$	295	450	91	8	1	155	1.8
C	uO <sub>x</sub> /SiO <sub>2</sub>	CuO/SiO <sub>2</sub>	334	490	97	1	2	220	9.4
C	uO <sub>x</sub> /SiO <sub>2</sub> (aged)	CuO/SiO <sub>2</sub>	335	557	93	4	3	234	17
a ,	Temperature at	which NH3 conver	sion r	eached	10%	and	90%.	<sup>b</sup> Temperat	ture of the

first H<sub>2</sub> consumption peak determined by H<sub>2</sub>-TPR.  $^c$  Calculated from H<sub>2</sub>-TPR after H<sub>2</sub> reduction and subsequent N<sub>2</sub>O reoxidation.



 $CuO_x/3A2S$ 

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## C-C coupling and structural control of metalloporphyrin derivatives with halogen substituents

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Keywords: electrochemistry, surface science, coordination chemistry, self-assembly

#### Abstract

The construction of characteristic nanoarchitectures on surfaces in particular has been the subject of considerable levels of interest. From the viewpoint of surface science, supramolecular assembly based on non-covalent interaction such as hydrogen bonding, dipole coupling, and metal-organic coordination, has been studied to control surface properties and to construct two-dimensional (2D) nanoarchitectures on metal surfaces. The 'bottom-up' strategy is an attractive and promising approach for construction of nanoarchitectures. Recently, 'on-site' covalent bond formation on surfaces has been also explored to produce 1D graphene nanoribbons and organometallic 2D nanosheets including metalloporphyrins because metalloporphyrins are promising materials such as electrocatalysts, electronic devices, and light harvesting system.

In the present study, we focus on C-C coupling of metalloporphyrins such as tetrabromophenylporphyrin cobalt (II) (CoTBrPP) on Au(111). Characteristic nanoarchitectures were

controlled by elevating temperature. The obtained nanostructures were observed in  $0.05 \text{ M} \text{ H}_2\text{SO}_4$  using an electrochemical scanning tunneling microscope (EC-STM).

CoTBrPP adlayer was prepared by immersing into 10 u CoTBrPP benzene solution. The CoTBrPP-modified Au(111) substrate was heated at 350 °C for 1 h under high vacuum. Typical STM image observed in 0.05 M  $H_2SO_4$  is shown in Fig. 1. On the terrace, a small molecular network structure was observed, suggesting the formation of thermal condensation of CoTBrPP molecules. The similar structure was obtained at iodine-modified Au(111). We have explored better condition to form the greater molecular network.



**Fig. 1** STM image of CoTBrPP adlayer on Au(111) after heating at 350 °C.



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## Fabrication and Nanoscale Characterization of Nanographene Monolayers Using Aromatic Micelle

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Keywords: EC-STM, solid-liquid interface, scanning tunnering microscopy, Nanostructures

#### Abstract

Polycyclic aromatic hydrocarbons (PAHs) having various chemical structures have excellent donor properties by a  $\pi$ conjugated system and are promising as building blocks for creating molecular functions having new functions and electrode catalysts. However, since PAHs are hardly soluble in water and many organic solvents, it's difficult to form adlayer on the electrode surface. In this research, we tried to solubilize various PAHs by aromatic micelle utilizing V-shaped amphipathic molecules with anthracene ring<sup>1</sup>, and investigated their electrochemical behavior and interface adsorption state. Encapsulation into micelles was carried out by grinding on



**Fig. 1** Typical EC-STM image of (Dic) adlayer on Au-(111) observed in 0.1 M H<sub>2</sub>SO<sub>4</sub>.

amphiphilic molecules and Dic agate mortar which is one type of PAH. Evaluation of encapsulation was carried out by UV-Vis spectrum. We searched for the conditions to introduce the guest molecule to the Au (111) surface and succeeded in observation of a clear Dic molecular sequence by introducing the dicoronylene encapsulated micelle solution into 0.1 M sulfuric acid solution. (Fig. 1) Several kinds of PAH other than Dic have been successfully arranged on the electrode surface by the same method, and a method of arranging the sparingly soluble molecules on the substrate surface became clear.

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# Edible bird's nest protein hydrolysates decrease melanogenesis in B16F10 mouse melanoma cells

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Keywords: Bird's nest protein hydrolysates, melanogenesis, proliferation

#### Abstract

Bioactive peptides could be produced by enzymatic hydrolysis of food proteins. Edible Bird's Nest (EBN) is a valuable functional food and is believed to have a therapeutic function in herbal medicine that has been used for hundreds of years in China. Potential bioactive peptides in protein rich Edible Bird's Nest (EBN) might possess some bioactivity.



Fig.1 Colloclia and Bird's Nest. (picture source: 黃祥華, 2010)

In the present study, the effect of edible bird's nest protein hydrolysates on melanogenesis and the inhibition proliferation of B16F10 murine melanoma cell were investigated.

Conclusion: These results shows that the 10mg/mL of EBN protein hydrolysates could inhibit 24% of B16F10 murine melanoma cell proliferation during 72h, and 0.1mg/mL EBN protein hydrolysates could decrease 29% of melanin biosynthesis in B16F10 murine melanoma cells whitening activities. These findings showed the EBN protein hydrolysates own the potential to become a raw material for health foods and beauty products.



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## Photocatalytic activity of Rh-doped oxide nanosheet

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Keywords: Photocatalyst, Nanosheet, Hydrogen, Water splitting, Oxide

#### Abstract

Hydrogen production using semiconducting photocatalysts has attracted attention as a clean solar hydrogen-generation system. High crystallinity and high surface area are important properties required for high efficiency photocatalysts. A two-dimensional single crystal sheet (nanosheet) prepared by exfoliation of a layered metal oxide is an ideal material that can satisfy both of these requirements. The photocatalytic activity is strongly dependent on the co-catalyst and the loading method or process, so that a catalyst without co-catalyst or with too much co-catalyst has poor photocatalytic activity. The role of these co-catalysts is the introduction of active sites and the promotion of charge separation. However, doping of novel metal in catalysts without co-catalyst loading does not generally cause a significant improvement in activity compared to that with



 $Ca_2Nb_3O_{10}$  nanosheet

co-catalyst loading. One reason for this could be that most of the dopants in bulk such as have an indirect effect on the reaction on the surface, because almost all of the dopants are present within the catalyst, rather than on the catalyst surface. In contrast, all dopants in a nanosheet are present very close to the surface, because the thickness of the nanosheet is approximately 1 nm. Fig. 1 shows the AFM image of Rh-doped  $Ca_2Nb_3O_{10}$  nanosheet. Therefore, most of the dopants in a nanosheet can be expected to be directly involved in the catalytic reaction and cause a significant improvement in photocatalytic activity in the same manner as co-catalyst loading. In this study, we report on photocatalytic properties of Rh-doped oxide nanosheets, which exhibited high activity for  $H_2$  production from a water/methanol system without co-catalyst loading.



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