

# ABSTRACT BOOK

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## Ratiometric Fluorescent Nanoprobe for ROS Detection Using Coumarin-3-Carboxylic Acid as a Detector

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Reactive oxygen species (ROS) are widely investigated for their features as they are highly reactive with biological materials, such as proteins, DNA, and RNA allowing them to produce oxidative stress (1). Hydroxyl radicals, one form of ROS, involve in some modifications that may cause clinical diseases, such as Alzheimer's disease, cancer, and cardiovascular diseases. Since the quantification of hydroxyl radicals has been the aim of researchers to develop nanoprobe combined with a delivery system that has a potential for treatment, yet there are some challenges affect designing nanoparticles with high selectivity and sensitivity toward hydroxyl radicals (2).

In this study, a ratiometric fluorescent nanoprobe was designed and prepared to detect hydroxyl radical by using coumarin 3-carboxylic acid (CCA) as the main detector and sulforhodamine B (SRB) loaded layered double hydroxide (LDH) as a fluorescent reference component. The coupling of CCA to bovine serum albumin (BSA) and the loading of BSA-CCA on the surface of LDH allowed the nanoprobe for ratiometric fluorescence detection of hydroxyl radical with high sensitivity and minimal interference from other biomolecules, ions, and ROS. The prepared BSA-CCA@SRB-LDH exhibited intense emission at 580 nm. In the presence of increased concentration of hydroxyl radical, a new emission peak at 444 nm was emerged and the intensity was increased according to the concentrations of hydroxyl radical, while the emission at 580 nm was maintained, allowing the nanoprobe for ratiometric fluorescence ( $I_{444}/I_{580}$ ) detection of hydroxyl radical. In addition, BSA@LDH-SRB used for cell culture experiments, cellular uptake showed a gradual increase in the MFI meaning more BSA@LDH-SRB NPs inserted into the cells. For cell viability, the result showed low cytotoxicity, even with high concentrations of NPs. Moreover, as the loading of the BSA protein on LDH surface, the biocompatibility, colloidal stability, and toxicity of fluorescent LDH nanoprobe were further improved allowing the future biological investigations of hydroxyl radical's evolution in vitro and in vivo.

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# Large-scale Silver Sulfide Nanomesh Membranes with Ultrahigh Flexibility

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The growth of flexible semiconductor thin films and membranes is highly desirable for the fabrication of next-generation wearable devices. In this work, we have developed a one-step, surface tension-driven method for facile and scalable growth of silver sulfide (Ag<sub>2</sub>S) membranes with a nanomesh structure. The nanomesh membrane can in principle reach infinite size but only limited by the reactor size, while the thickness is self-limited to ca. 50 nm. In particular, the membrane can be continuously regenerated at the water surface after being transferred for mechanical and electronic tests. The free-standing membrane demonstrates exceptional flexibility and strength, resulting from the nanomesh structure and the intrinsic plasticity of the Ag<sub>2</sub>S ligaments, as revealed by robust manipulation, nanoindentation tests and *pseudo*-in-situ tensile test under scanning electron microscope. Bendable electronic resistance-switching devices are fabricated based on the nanomesh membrane.

# Integrated Supramolecular Copolymerization of Hydrophobic and Hydrophilic Monomers in Liquid Crystalline Media

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Mixtures of hydrophobic and hydrophilic polymers are likely to cause macroscopic phase separation. Covalent linkage between the ends of the two types of polymers prevents macroscopic phase separation of them, resulting in an integrated structure formed by microscopic phase separation whose size corresponds to that of each polymer block, that have many important applications.<sup>1</sup> In contrast to covalent polymers, the monomers in supramolecular polymers are connected noncovalently. Therefore, we cannot force the two immiscible supramolecular polymers to form an integrated structure by covalently connecting two immiscible polymers and thus end up with macroscopic phase separation.

In this study, porphyrin-based hydrogen-bonding monomer pairs, <sup>C10</sup>P<sub>2H</sub> and <sup>TEG</sup>P<sub>Cu</sub>, bearing side

chains with cyanobiphenyl (CB) groups at the ends of hydrophobic alkyl chains or hydrophilic tetraethylene glycol, respectively, were synthesized. These monomers undergo self-sorting supramolecular polymerization in a highly diluted solution ( $[\text{monomer}] = 3.4 \times 10^{-9} \text{ mol\%}$ ) in nonpolar media due to side chain incompatibility. However, these monomers undergo supramolecular copolymerization in a medium of 4-cyano-4'-pentyloxybiphenyl (5OCB) at highly concentrated conditions ( $[\text{monomer}] = 7.7 \text{ mol\%}$ ) without macroscopic phase separation. This liquid crystalline (LC) system is designed based on our recent report of the formation of columnar LCs by supramolecular polymerization of disk-shaped monomer in a nematic LC medium composed of rod-shaped molecules.<sup>2-4</sup> We have previously reported disk-shaped porphyrin-centered monomer  $^{C10}P_{2H}$ .<sup>4</sup> In the present work, we newly synthesized porphyrin-centered  $^{TEG}P_{Cu}$ , bearing hydrophilic side chains. Surprisingly, when mutually incompatible  $^{C10}P_{2H}$  and  $^{TEG}P_{Cu}$  are polymerized together in 5OCB, the entire material formed a columnar oblique LC phase without macroscopic phase separation. The analysis by electronic absorption and fluorescence spectroscopy revealed that the individual column was formed by a supramolecular copolymer composed of both  $^{C10}P_{2H}$  and  $^{TEG}P_{Cu}$  monomers. Electron spin resonance (ESR) spectroscopy suggested that  $^{TEG}P_{Cu}$  partially aggregates with each other within the column, forming a block copolymer. The combination of CB termini in both monomers and a medium of 5OCB is essential for the two monomers to form an integrated structure in a condensed system. Our study paves the way to construct a microphase-separated structure in supramolecular copolymers by immiscible monomers for the diversification of supramolecular materials.

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## Joining of Carbon Fiber Reinforced Thermoplastic to Metal using Electrodeposited Film

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To protect the global environment through energy conservation, transportation equipment is becoming increasingly multi-material, combining lightweight materials and metals. Among lightweight materials, carbon fiber reinforced thermoplastic (CFRTP) has high strength and elasticity and can be mass-produced. Therefore, it is necessary to develop a process for joining dissimilar materials to realize the use of a combination of CFRTP and metals. We focused on a method joining CFRTP and metals using electrodeposited film with a special shape that forms minute irregularities, through the anchoring effect. In this study, the effectiveness of the joining method was investigated by evaluating the joint strength between the CFRTP and metal with the specially shaped electrodeposited and undercoated films by tensile shear test. The relationship between the joint strength and the deposition conditions of the specially shaped electrodeposited and undercoated films was also evaluated. Furthermore, fracture surface observation was performed after the tensile shear test.

Experiments were conducted by following procedures. Stainless steel specimens (10 x 45 x 1.5 mm<sup>3</sup>) were used as the plated material. The stainless steel specimen with an aperture area of 5 x 10 mm<sup>2</sup> was subjected to base Ni electrodeposition and specially shaped electrodeposition. The



composition of the base Ni plating solution was prepared by mixing 200 g/L  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  and 100 ml/L HCl in pure water. The Ni electrodeposition conditions were as follows: solution temperature of 50°C, a current density of 50 mA/cm<sup>2</sup>, and plating time of 3 min. The compositions of the special plating solutions were prepared by mixing 15 g/L  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ , 150–450 g/L  $\text{Ni}(\text{NH}_4\text{SO}_3)_2 \cdot 4\text{H}_2\text{O}$ , 30 g/L  $\text{H}_3\text{BO}_3$ , and 0.2 g/L  $\text{C}_7\text{H}_4\text{NNaO}_3 \cdot 2\text{H}_2\text{O}$  in pure water. The specially shaped electrodeposition conditions were as follows: (1) a current density of 10 mA/cm<sup>2</sup> and plating time of 20 min, and (2) a current density of 100 mA/cm<sup>2</sup> and plating time of 2 min. The plated stainless steel and CF RTP (10 x 45 x 3 mm<sup>3</sup>) specimens were then joined using a joining machine. The joining conditions were set as follows: joining temperature of 200°C, a load of 5 N, and joining time of 5 min. The jointed specimens were then subjected to tensile shear tests using a tensile testing machine. The test conditions were as follows: room temperature and tensile speed of 10 mm/min. The test was conducted using three joint specimens per condition. The surface and cross-section of the specimens were observed by FE-SEM and EPMA after plating, joining, and tensile shear tests, respectively.

Results and discussions are presented below. Cross-sectional observation of the joint showed the electrodeposited film with dendritic structures at the interface between stainless steel and CF RTP resin. It is considered that the specially shaped electrodeposition forms the dendritic structures of minute irregularities which join the CF RTP resin to the stainless steel through the anchoring effect. From the observation of the fracture surface, it was found that the specially shaped electrodeposited film and the resin portion of the CF RTP were fractured.

## Deposition Mechanism and Water Repellency of Specially Shaped Plating Films

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To promote energy conservation, Al alloys are used in automotive heat exchangers because of their compact size and lightweight. In the heat exchangers, there is a problem that water droplets containing salts and chemical substances corrode Al alloy fins, resulting in reduced heat exchange performance. For this reason, a highly water-repellent technology with excellent water repellency, corrosion resistance, and self-cleaning properties is applied to Al alloy fins. We focused on the formation of Ni-Cu alloy plating on Al alloy fins. Ni plating has excellent corrosion resistance and Cu plating has high thermal conductivity. Ni-Cu alloy plating can form a water-repellent fine uneven plating film under specific Ni and Cu ion concentrations in the plating solution. In this study, the effect of electric potential on the formation of Ni-Cu alloy plating film and its time-dependent formation behavior were investigated using an electrochemical apparatus. In addition, the water repellency of the formed Ni-Cu alloy plating films was evaluated.

Al plates (20 x 20 x 1.0 mm<sup>3</sup>) were prepared as specimens. The Al plates were subjected to acid degreasing, etching, and zinc oxide treatment to form underlying Ni plating. Linear-sweep-voltammetry (LSV) was performed using an electrochemical apparatus to clarify the deposition principle of Ni-Cu alloy plating. The compositions of the solutions were as follows: 15 g/L  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ , 30 g/L  $\text{H}_3\text{BO}_3$ , 0.2 g/L  $\text{C}_7\text{H}_4\text{NaO}_3 \cdot 2\text{H}_2\text{O}$ , 150–450 g/L  $\text{Ni}(\text{NH}_4\text{SO}_3)_2 \cdot 4\text{H}_2\text{O}$ . LSV curves were obtained over a potential range of 0 V to -1.5 V and a sweep rate of 10 mV/s. The formation of Ni-Cu alloy plating was performed by fixing the potential to -0.5 V, -1.0 V, and -1.5 V, respectively. Subsequently, surface observation, surface roughness, and cross-sectional

microstructure of the Ni-Cu alloy plating film were performed using FE-SEM, a laser microscope, and EPMA, respectively. In addition, the water contact angle was measured by dropping 6  $\mu\text{L}$  of pure water onto the Ni-Cu alloy plating films using a contact angle meter.

Results and discussions are presented below. From the obtained LSV curves of the plating solution, Ni-Cu alloy plating is formed at a potential of -0.8 V or higher, and the amount of Ni precipitation increases as the potential increases. From the observation of the top surface and cross-section of the Ni-Cu alloy plating films formed at a constant potential using plating solution, the plating film had a smooth morphology at a potential of -0.5V and a dendritic morphology at a potential of -1.0 and -1.5 V. The water repellency of the specimen with the Ni-Cu alloy plating films formed at the ratio of the concentration of  $\text{Ni}(\text{NH}_2\text{SO}_3)_2 \cdot 4\text{H}_2\text{O}$  to that of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  in the plating solution was 450:15 (g/L) and a potential of -1.5 V was  $131^\circ$ , which was the highest among all the specimens prepared under different conditions.

## Brazing of Ferritic Stainless Steel with Al Using Cr-Free Brazing Filler Metal

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Recently, solid oxide fuel cells (SOFC) have attracted attention due to their various advantages, such as high power generation efficiency and the ability to use a wide variety of fuels. When power is generated by SOFC, the inside of the module is exposed under high temperature and steamy environment. Since the Cr oxide that is formed on the surface of stainless steel has a certain vapor pressure in high temperature environment, it is scattered and adheres to the object so that the performance of the cell is degraded. Thus high temperature oxidation resistance and Cr evaporation resistance are required to the SOFC materials. To satisfy such requirement, Al-containing ferritic stainless steel, which forms an aluminum oxide film on the surface, is generally applied for the SOFC materials.

In this study, we investigated the application of a Cr-free brazing filler metal to join 18Cr-1.5Al-Nb (mass%) steel, which is an Al-containing ferritic stainless steel, to suppress Cr evaporation from the brazed joint more. A Cu-23.5Mn-9Ni (mass%) alloy was prepared as the filler metal.

Two 18Cr-1.5Al-Nb steels were brazed with Cu-23.5Mn-9Ni (brazing temperature:  $990^\circ\text{C}$ , brazing time: 15 min) to fabricate the tensile shear specimen. The microstructure of the brazed joint was observed with an electron probe X-ray micro analyzer (EPMA). The tensile shear test was performed to investigate the joint strength. After tensile shear test, the fractured surface was observed with a scanning electron microscope (SEM), and the cross section was observed with an EPMA.

From the observation result of the cross section of the joint, it was found that the reaction layer, which is composed of component of the brazing filler metal and the base metal (steel), is formed at the joint interface. Cr-enriched phases were also formed in the reaction layer. The contents of

Mn and Ni in the reaction layer were relatively high, diffusion of Mn from the brazing filler metal part toward the base metal was widely observed. In contrast, diffusion of Ni into the base metal was not so much observed. This is due to high diffusion coefficient of Mn in Fe. Furthermore, it was clarified that the formation of the reaction layer is mainly caused by the diffusion of component of the brazing filler metal into the base metal.

The tensile shear test results showed that the strength of the brazed joint is approximately 180 MPa, which is a practical use level. From the fracture surface observation results, it was found that the main fracture mode was quasi-cleavage fracture at the interface between the reaction layer and the brazing filler metal.

## Observation of Early Fatigue Damage of Oxygen-Free Copper for Electric Power Application by EBSD Analysis

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In recent years, electric power equipment has been required to have high output and high voltage. As a result, the mechanical stress loaded on those components increases. Therefore, it is important to investigate fatigue properties in the low-cycle fatigue area by high stress. Copper has been used for conductor parts of the electric power equipment due to its high conductivity. Among them, oxygen-free copper has the advantage of low discharge of hydrogen gas and has been used in various types of power equipment. Investigation of slip behavior is important because the plastic deformation is considered to cause fatigue failure. The electron backscattered diffraction (EBSD) analysis has attracted attention as a fatigue damage evaluation method. Thus, the aim of this study is to investigate the slip behavior and fatigue damage behavior of the oxygen-free copper by the EBSD analysis.

C1020 oxygen-free copper was used in this study. The specimens were heat-treated at a temperature of 850 °C for 30 min. The heating period from room temperature (R.T.) to 850 °C was 7.4 h. The cooling from 850 °C to R.T. was conducted by natural heat radiation. After heat treatment, dog-bone shaped specimens with a thickness of 6 mm were cut by wire cutting. A fatigue test was conducted by load control using a triangular wave with a fatigue testing machine. The amplitude of load was 1.8–7.2 kN, which corresponds to the 50–200 MPa. The frequency, stress ratio, and test temperature were 10 Hz, –1, and R.T., respectively. Fracture surfaces were observed using a field emission scanning electron microscope. In addition, to investigate microstructural changes during fatigue deformation, the fatigue test was stopped at a predetermined number of cycles. An hourglass-shaped specimen with a thickness of 6 mm was also used in the fatigue test because the location of failure can be limited. The amplitude of stress was 75 MPa. Thereafter, optical microscope observation was conducted. To investigate the microstructures of the specimens before and after the fatigue test, the specimens were polished by #800–#4000 waterproof abrasive papers and were subsequently polished using 1 μm alumina powder suspension. The specimen after polishing with the alumina powder suspension was etched for 15–30 s with an etching solution. EBSD analysis was conducted to the surface of the specimen after etching.

The striations were observed in the fracture surfaces in the case of the stress amplitude less than

200 MPa. The quasicleavage fracture surface were observed in the fracture surfaces in the case of the stress amplitude above 150 MPa. The result of the EBSD analysis suggested that grain reference orientation deviation (GROD) map was useful to investigate the degree of fatigue damage in the grain by low cycle fatigue. In addition, accumulation of strain in the high misorientation regions and expansion of the high misorientation regions due to slip deformation were confirmed in the fatigue deformation process.

## Interfacial Reaction between Pd-Cu-Ni Alloy and Sn-58Bi Solder

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In the semiconductor manufacturing process, a needle-shaped pin material with a built-in spring, called a probe pin, is used to inspect the operation of semiconductor package with solder ball, such as Ball Grid Array and Chip Scale Package. The probe pin is pressed against the solder and an electric current is applied to determine the electrical connection. A probe pin is often damaged by repetition of inserting and conduction into a Sn-Bi solder ball of the semiconductor package. This is due to the low melting temperature of Sn-Bi solder, which causes a large amount of Sn-Bi solder to adhere to the probe pin. Pd-Cu-Ag alloys are generally used as inspection probe materials, which have excellent mechanical properties, electrical conductivity. In our previous study, the interfacial reaction between Pd-30Cu-29.5Ag-0.5Zn (mass%) alloy and Sn-58Bi (mass%) solder was investigated <sup>[1]</sup>. It was clarified that the reaction layer, which consists of the aggregate layer of Ag<sub>3</sub>Sn, the PdSn<sub>3</sub> + PdSn<sub>4</sub> + Cu<sub>6</sub>Sn<sub>5</sub> layer and the PdSn<sub>2</sub> + PdSn + Cu<sub>3</sub>Sn + Ag<sub>3</sub>Sn layer from the solder side to the probe pin side, forms at the interface. Moreover, the reaction layer became uneven by aging, with average thickness of approximately 50 μm after aging at 120°C for 1000 h. Thus in this study, a Pd-Cu-Ni alloy was prepared as the pin material to suppress the interfacial reaction with Sn-58Bi. A Pd-42Cu-10Ni (mass%) alloy and a Sn-58Bi solder were prepared. The interfacial reaction between the Pd-Cu-Ni alloy and Sn-58Bi solder was investigated by aging at 120°C up to 1000 h. As a result, it was found that aging at 120°C for the Pd-Cu-Ni alloy/Sn-58Bi solder joint results in the formation of a PdSn<sub>4</sub> layer at the joint interface, which grew on the solder side in the early stage in aging. Then, a (Cu, Ni)<sub>6</sub>Sn<sub>5</sub> layer was formed at the interface due to the reaction of Cu and Ni left over from the reaction with Sn. With the progress of aging, fine-grained (Cu, Ni)<sub>6</sub>Sn<sub>5</sub> was also formed in the PdSn<sub>4</sub> layer, and the reaction layer mainly grew on the solder side.

Finally, the PdSn<sub>4</sub>+Bi layer and the (Cu, Ni)<sub>6</sub>Sn<sub>5</sub> layer form from the solder side to the probe pin side at the joint interface as the reaction layers. In addition, the thickness of the reaction layers was reduced by less than half to approximately 20 μm after aging for 1000 h, and the formation of uneven shapes in the joint interface was suppressed. These effects can suppress the adhesion of Sn-Bi solder to the pin material and thus it is expected to prevent damage to the pin material.

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# Experimental Study on a Use of Metal Sputtered Cellulose Powder as the Codeposited Particle into Nickel Electroplating Film

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Recently, global efforts to protect the global environment have expanded, hence we have been studying on the development of Ni plating composited with cellulose fiber (CF) obtained from plants while effectively utilizing renewable resources<sup>[1]</sup>. Since defibrillated nano-scale CF; CNF is more than 5 times stronger than steel material, it is expected to have higher hardness by compositing CNF into plating films which can be applied to such parts as sliding parts of lightweight and compact products that are effective in saving energy. In our previous study<sup>[1]</sup>, it was reported that Vickers hardness of the surface of CNF composited Ni electroplated film improves by approximately 30% compared with that without CNF. On the other hand, codeposition of homogeneous CNF in the film remained a problem. The purpose of this study was to investigate the codeposition behavior of CF powder with metal species introduced by metal sputtering as codeposited particles into Ni electroplating films.

Experiments were conducted by following procedures. Au-Pd sputtering was applied to 0.5 g of CF powder (KC Flock W-100G, Nippon Paper Co. Ltd.) by a metal coater (MSP-1S, Shinku Device Co. Ltd.) for 7 min, while mixing the CF powder accordingly, to prepare the codeposited particles (Treated CF). Plating was conducted using Ni electroplating solution ( $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$  240 g/L,  $\text{NiCl}_2$  30 g/L,  $\text{H}_3\text{BO}_3$  30 g/L) with treated CF 1 g/L suspended in the solution. Acid cleaned copper plates (JIS C1100, Cu purity 99.9 mass% min.,  $10 \times 10 \times 0.3 \text{ mm}^3$ .) were used as the plated material. Plating conditions were as follows: current density  $2.5 \text{ A/dm}^2$ , charge density  $3000 \text{ C/dm}^2$ , solution temperature  $50^\circ\text{C}$ , solution volume 200 mL, and constant stirring was conducted in plating with a magnetic stirrer. Secondary electron (SE) image observation and elemental mapping analysis were conducted on the surface and cross-section of the obtained films using an electron probe micro analyzer.

Results and discussions are presented below. SE images of the surface of the plated film fabricated with treated CF showed that treated CF was dispersed and attached to the surface of the plated film. SE image observation and elemental mapping analysis of the contact area between treated CF and electrodeposited Ni showed that Ni grows over treated CF, and it was confirmed that it is not merely an attachment, but is fixed to the surface. Similarly, in SE image observation and elemental mapping analysis of the cross-section of the film, it was confirmed that treated CF is completely incorporated into the electrodeposited Ni layer. Such a morphology was not confirmed in the previous study<sup>[1]</sup>. On the other hand, with untreated CF as received, codeposition to the plating film was not observed. In addition, no significant amount of Au or Pd was detected on the surface of codeposited treated CF. This indicates that even a very low amount of sputtering is effective to codeposite CF into an electroplating film.

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# Effect of Durability Improvement of Steel/Al alloy Adhesive Joints by Ti-based Conversion Treatment

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In recent years, in order to prevent global warming, the automotive industry has been required to reduce the weight of car bodies to reduce CO<sub>2</sub> emissions. In order to achieve the weight reduction of automobiles, it is strongly desired to use the right materials in the right places to maximize the effect of various materials by taking advantage of their unique characteristics. Therefore, the realization of a hybrid structure of steel and Al-alloy for car bodies is attracting attention. Adhesive bonding is a bonding method that has many advantages over conventional mechanical bonding, such as weight reduction, high fatigue strength, excellent damping characteristics, improves aerodynamic characteristics, and simplifies machining operations. In this study, adhesive bonding was performed between an Al alloy with Ti-based conversion treatment and a steel plate. The durability of the joints under high temperature and high humidity environment was investigated.

Al-Mg-Si aluminum alloy A6016 (hereafter referred to as A6016) and high-tensile strength steel 980 were used as specimens. The specimen sizes were 25x80 mm<sup>2</sup> and the plate thicknesses were 1.0 mm and 1.2 mm for A6016 and the steel, respectively. The adhesive bonding area was 12.5x25 mm<sup>2</sup>. Ti-based conversion treatment was conducted to the surface of A6061. For a comparison, the specimen without Ti-based conversion treatment was also prepared (hereafter referred to as “blank”). A one-component thermosetting epoxy-based structural adhesive was used to prepare tensile shear specimens. The curing of the adhesive was conducted at 180°C for 20 min. The specimens were aged at 85°C, in 85%R.H., for 360 h and 500 h. The unaged and aged specimens were subjected to tensile shear tests at a cross head speed of 5 mm/min. X-ray photoelectron spectroscopy (XPS) analysis was conducted to the fracture surface of A6061 in the specimen which was fractured at the A6016/epoxy interface by the tensile shear test.

The results of the tensile shear tests showed that the effect of Ti-based conversion treatment on the joint strength is negligible in the unaged specimens. The fracture mode was mainly cohesive fracture within the epoxy resin regardless of the Ti-based conversion treatment. In contrast, the tensile shear strength of the Ti-based conversion treated specimen was higher than that of the blank specimen after aging. In the blank specimens, main fracture modes were cohesive fracture and the A6016/epoxy interfacial fracture. In the Ti-based conversion treated specimens, the steel/epoxy interfacial fracture was also detected in addition to those two fracture modes. The results of XPS analysis for specimens aged for 360 h showed that the fracture occurs in the aluminum oxide film (Al<sub>2</sub>O<sub>3</sub>) in the blank specimen and in the mixed film of Al<sub>2</sub>O<sub>3</sub>+TiO<sub>2</sub> in the Ti-based conversion treated specimen. It was clarified that such change in fracture mode by applying Ti-based conversion treatment to A6016 is effective to improve the joint durability under high temperature and high humidity conditions.

The results of this research have been obtained as a result of the commissioned work (JPNP14014) by the New Energy and Industrial Technology Development Organization (NEDO).

# Interfacial Dipole for Suppressing Charge Recombination in Perovskite Solar Cells under Low-Intensity Indoor Lights

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In this presentation, we propose a strategic interface engineering method to optimize the power conversion efficiency of perovskite solar cells in low-light indoor lighting environments.

Indoor light harvesting technologies based on perovskite solar cells have attracted considerable attention due to their promising photovoltaic properties as indoor generators.

By inserting a polar basocuproin (BCP) interfacial layer between the electron transport layer and the electrode, the photovoltaic characteristics were significantly improved under low-illuminance conditions. It effectively inhibits interfacial charge recombination and improves interfacial charge transfer, enabling sustained charge counting in low-light conditions. Based on systematic characterization of surface trap states and carrier dynamics using Kelvin probe force microscopy, we show that BCP promotes efficient charge carrier separation and electron extraction under low-intensity illumination due to surface passivation and dipole-induced suppressed charge recombination. shows that said. The beneficial role of BCP has enabled excellent indoor power conversion efficiencies of 27.04% and 35.45% respectively in low light-emitting diode (LED) and halogen lighting. Electron transport layer interfacial modification with polar molecules is a simple but highly effective method to optimize the indoor performance of perovskite solar cells.

## The introduction of Gd<sup>3+</sup> and its effect on the luminescent properties of $\alpha$ -Al<sub>2</sub>O<sub>3</sub>:Mn phosphors

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In recent years, there has been an increasing impetus of studies undertaken on Mn<sup>4+</sup> activated red-emitting phosphors due to their promising applications in optical data storage, dosimetry, computed radiography, and phosphor-converted light emitting diodes (LED) [1, 2]. This study presents the structural and photoluminescence (PL) properties of red-emitting submicron  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>:0.4 atom% Mn<sup>3+</sup> co-doped with Gd<sup>3+</sup> ions (2 and 4 atom%). The phosphors were successfully synthesized via a facile combustion reaction method at 600°C in air. We observed the enhancement of photoluminescence emission of tetravalent manganese ions at 678 nm (spin-forbidden <sup>2</sup>E →

$^4A_2$  electronic transition), which can be attributed to the  $Gd^{3+} \rightarrow Mn^{4+}$  energy transfer process. The integrated PL intensity of  $Mn^{4+}$  ions showed a linear relationship with co-dopant concentration with the 4 atom%  $Gd^{3+}$  phosphor displaying the maximum luminescence intensity. To study the effect of X- irradiation on the phosphors, the PL intensities of  $\alpha-Al_2O_3:0.4 \text{ atom\% } Mn^{3+}, xGd^{3+}$  ( $x=2$  and 4 atom%) were measured as a function of accumulated soft X-rays from 0.015 Gy to 330 Gy. The generation of  $Mn^{4+}$  ions in  $\alpha-Al_2O_3$  could be observed upon X-rays exposure due to  $Mn^{3+} + Mn^{5+} \rightarrow 2Mn^{4+}$  mechanism. Under 470 nm blue light illumination, the photoinduced disproportion (back reaction) of  $2Mn^{4+} \rightarrow Mn^{3+} + Mn^{5+}$  was observed. The temperature dependence of the R lines was also investigated for  $\alpha-Al_2O_3:0.4 \text{ atom\% } Mn^{3+}, 4 \text{ atom\% } Gd^{3+}$  from 45 to 294 K; with increasing temperature, the R-lines were red shifted and subject to temperature broadening. The present outcomes show some potential for the development of photoluminescent materials with improved  $Mn^{4+}$  luminescence properties by energy transfer from a co-dopant.

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## X-ray-induced $Sm^{2+}$ Ions in $SrF_2:Sm^{3+}$ Nanocrystals

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$Sm$  ion-doped materials have been the focus of numerous studies due to their considerable potential in the field of spectral hole-burning based data storage, solid-state lasers, and in applications as ionizing radiation storage phosphors. Specifically, the valence conversion ( $Sm^{3+} \rightarrow Sm^{2+}$ ) upon exposure to ionizing radiation or light which yields narrow f-f or broad  $4f5d1 \rightarrow 4f6$  of  $Sm^{2+}$  emission lines has been of interest. We have investigated the  $Sm^{3+} \rightarrow Sm^{2+}$  conversion upon blue-violet light and vacuum UV-,  $\beta$ ,  $\gamma$ -, X- irradiation in  $Sm$ -doped alkaline earth fluorohalide MFX nanocrystals ( $M = Ca, Ba, Sr$ ;  $X = Br, I, Cl$ ), 1-4  $Sm$  -doped alkaline earth fluoroperovskites nanocrystals of composition  $BaLiF_3$ , 5 and  $Sm$ -doped alkaline earth fluoride  $CaF_2$  with promising applications in the fields of dosimetry, medical imaging, and optical data storage. However, to the best of our knowledge, the  $Sm^{2+}$  generation by X-irradiation has not been reported in  $SrF_2:Sm^{3+}$  nanocrystals. In this study, we present results demonstrating the X-irradiation-induced  $Sm^{3+} \rightarrow Sm^{2+}$  reduction in  $SrF_2:Sm^{3+}$  nanocrystals and its potential as an X-ray storage phosphor. The nanocrystalline  $SrF_2:Sm^{3+}$  was prepared by coprecipitation of  $SrCl_2 \cdot 2H_2O$ ,  $SmCl_3 \cdot 6H_2O$ , and  $NH_4F$  (0.5 mol% of  $Sm$  relative to  $Sr$ ). The X-ray diffraction (XRD) characterization results an average crystallite size of  $42 \pm 1$  nm with a fluorite-type cubic structure with the  $Fm\bar{3}m$  space group. The photoluminescence spectra with a 462 nm laser diode excitation were measured on a Spex 500 M monochromator, equipped with an Andor iDus Model DV401A-BV CCD camera. The  $Sm^{3+}$  emission lines of  $4G_5/2 \rightarrow 6H_J$  ( $J = 5/2, 7/2, 9/2$ , and  $11/2$ ) f-f transitions were observed in a non-irradiated sample. Interestingly, a relatively intense  $Sm^{2+}$  emission line assigned to the  $4f6 \ 5D_0 (A_1) \rightarrow 7F_1 (T_1g)$  transition appeared upon X-irradiation. The study was conducted up



to 300 Gy (Cu-K $\alpha$  X-irradiation) by monitoring the photoluminescence intensities of both Sm<sup>3+</sup> and Sm<sup>2+</sup> ions. The generation and reduction of Sm<sup>2+</sup> and Sm<sup>3+</sup> intensities as a function of X-ray dose can be rationalized within a dispersive first-order kinetics approximation. Preliminary results indicate the potential of Sm doped SrF<sub>2</sub> as an X-ray storage phosphor i.e. a material for nanocrystals dosimetry and computed radiography applications.

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## Nanoengineering of Printable Graphene Electrocatalyst for Sustainable Fuel Cells

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Currently, 85% of the global energy supply is derived from fossil fuels (i.e. coal, oil and gas). To save the world from ever-increasing energy needs and environmental problems, clean and highly efficient renewable energy sources must be developed. Among various renewable energy technologies, fuel cells are recognized as one of the most promising clean energy sources due to their emission-free nature and high energy conversion efficiency. In fuel cells, chemical energy from the reactants (e.g. hydrogen or methanol) can be directly converted into electrical energy through electrochemical reactions. While splitting of hydrogen molecules at the anode (into positively charged protons and negatively charged electrons) is relatively easy, the sluggish kinetics of the cathodic oxygen reduction reaction (ORR) impedes the overall performance of fuel cells, requiring a high loading of efficient electrocatalysts to overcome the activation energy. Platinum-based electrocatalysts have long been established as the industry standard for ORR, since they offer excellent electrocatalytic activity. However, their exorbitant cost and low stability to methanol crossover prevent fuel cells from becoming commercially viable. There for, the development of metal-free electrocatalysts with efficient catalytic performance and long-term stability is highly desired for fuel cells applications.

Herein, a novel solution-processable and printable graphene-based electrocatalyst for oxygen reduction reaction (ORR) is developed by interfacing graphene with amphiphilic conductive polymers *via* exfoliation-assisted noncovalent functionalization. The interfacial interactions between pristine graphene and amphiphilic conductive polymers molecules, and the intrinsic colloidal structure of their dispersions at the nanoscale were studied using ultra-small/small angle neutron scattering (U/SANS) with contrast-variation for the first time. It is found that the strong noncovalent  $\pi$ -stacking interaction between graphene and the hydrophobic rings of conductive polymers disrupts the  $\pi$ - $\pi$  interactions holding the graphite layers and promotes

exfoliation. Such strong  $\pi$ -stacking interactions between graphene basal plane and conductive polymers chains induce the conformational change of the resonant structures to facilitate charge transport, contributing to higher conductivity. The intermolecular electron transfer from graphene to the hydrophobic rings of conductive polymers creates net positively charges at the C atoms of graphene flakes, facilitating its electrical conductivity and electrocatalysis activity. The printable graphene inks were utilized to fabricate metal-free electrocatalyst layers for ORR, which reduces  $O_2$  molecules to  $OH^-$  ions via the highly efficient four-electron pathway and exhibits superior stability ( $\sim 97\%$  retention after 10,000 cycles). This printable graphene electrocatalyst provides a breakthrough for the new green chemistry and advanced techniques for fabrication of low-cost and sustainable fuel cells.

## Passivation Performance of ALD-NiOx Thin Film Using Ni(dmb)<sub>2</sub> Precursor in Si Solar Cells

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NiOx is one of the materials used as hole transport layer (HTL) in perovskite solar cell (PSC). NiO in PSCs has shown many advantages such as valence band matching with most perovskite absorbers, excellent electron blocking, high transparency, and thermal stability. Recently, NiOx thin films for HTL are growing by atomic layer deposition (ALD) using Ni(dmamb)<sub>2</sub> precursor and H<sub>2</sub>O, O<sub>3</sub> oxidants. We investigated the passivation characteristics of silicon solar cells in addition to the HTL characteristics of NiOx thin films. The physical, electrical and chemical characteristics such as, carbon concentration within NiO thin film, Ni/O atomic ratio, NiO bandgap control by Al doping, NiO conductivity, were studied by x-ray photoelectron spectroscopy (XPS), Ultraviolet photoelectron spectroscopy (UPS), UV-Vis, Reflection Electron Energy Loss Spectroscopy (REELS), and tunneling electron microscopy (TEM) etc. In XPS analysis, it is found that Ni<sub>2</sub>O<sub>3</sub> phase was dominant at the initial growth below 70 cycles and NiO phase is increased as the thickness of NiO increases over 150 cycles. Ni2p peaks has also shown the same change of NiO states as the NiO thickness increases. The ratio of Ni to O was increased as ALD cycle increased and it was 0.5 at approximately 110 cycles. ALD NiOx energy bandgap was measured 3.8 eV by UV-Vis.. Finally, we will compare the passivation characteristics of the ALD NiO thin film with the Al<sub>2</sub>O<sub>3</sub> thin film used in PERC solar cells.

## Neutron Reflectivity Study for Diffusion Dynamics of Polymer-Graphene Composite Films

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For graphene-based composites, the dynamics of polymers confined between graphene sheets are a key parameter governing the overall mechanical properties of bulk materials. In this work,

we used neutron reflectivity (NR) to measure the diffusion dynamics of polymer melts confined between graphene oxide (GO) surfaces. From the NR results, we found that the diffusion coefficients of poly(methyl methacrylate) (PMMA) between the GO sheets were dramatically reduced by more than 1 order of magnitude when the film thickness was less than  $\approx 3$  times the gyration radius of the bulk polymer ( $R_g$ ), whereas the diffusion of the polystyrene (PS) films sandwiched between GO sheets was only three times slower as the PS thickness decreased from  $\approx 8 R_g$  to  $1 R_g$ . This difference was due to the fact that the polymer-GO interaction significantly influences the dynamics of confined polymer melts.

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## Influence of substrates on Liquefied Petroleum Gas Sensing Performance of Electrochemically deposited Cuprous Oxide Thin Films

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The Cuprous oxide thin films were electrodeposited on Titanium (Ti) plates, Fluorine-doped Tin Oxide (FTO) pre-deposited glass substrates, Indium Tin Oxide-coated glass substrates and thin Cu plates in an acetate bath ( $\approx 60^\circ\text{C}$ ) to investigate their influence on the surface structural morphological variation and wetting nature against Liquefied Petroleum gas (LPG). Mott-Schottky plots and spectral response measurements were carried out to confirm n-type conductivity in the resulting films electrodeposited in an acetate bath of pH 6. X-ray diffraction (XRD) and scanning electron microscopy (SEM) were performed to investigate the crystalline structure and the surface morphology of Cu<sub>2</sub>O thin films. The wetting nature of films was observed with contact angle measurements. SEM images showed the presence of well-defined cubic crystallites with sharp edges in n-Cu<sub>2</sub>O deposited on Ti, and a network-like porous structure is predominant in Cu<sub>2</sub>O films deposited on FTO, ITO, and Cu substrates. The preferred orientation along the (111), (200), and (220) planes verified the visible distribution of cubical shapes among the porous natured n-Cu<sub>2</sub>O films. The film structure on FTO is inhomogeneous due to preferential orientation of grains with slightly different peak intensities as observed in the XRD patterns. Inter-planer spacing of dominant plane, (311) of n-Cu<sub>2</sub>O on Cu has a relatively high compact nature yet low contacting surface area due to the high particle size. In this work, grain diameters were evaluated using Debye-Scherrer formula and d spacing using Bragg's Law considering the peak intensities of XRD spectrum. This analysis gives evidence in support of the grain size variations which emphasized, Ti and ITO have the lowest grain sizes of 24 nm and 30.9 nm respectively. Contact angle measurements carried

out by using  $\sim 10 \mu\text{l}$  water droplets revealed different wetting behaviors in Cu<sub>2</sub>O film, depending on the substrate. Based on the grain size, grain distribution, contact angle measurements and their wetting natures, films were subjected to LP gas (5 cc min<sup>-1</sup>, 100%) detecting evaluations. The stable resistances of these films which were initially under ambient atmospheric conditions at different levels, increased upon exposure of LPG. This behavior is caused by the changes in resistance induced by the adsorption and desorption of LPG molecules (C<sub>n</sub>H<sub>2n+2</sub>) on the film surface. Electrodeposited n-Cu<sub>2</sub>O films on FTO, ITO, and Ti showed improved gas sensor performances due to their moderate wetting behaviors. Under steady sensing conditions, ITO showed the most enhanced LPG response with 32.63% at 700C, with reasonable recovery, and stability over time. It is attributed to the high surface area facilitated by the porous structure, small grain size, and slightly non-wetting nature of the film. On the other hand, Cu deflects from ideal sensing behavior due to the difficulty in recovering at its' ambient state with time. The findings in this work are directed toward the relationship that possibly optimizes the fabrication process of Cu<sub>2</sub>O in an acetate bath depending on the substrate, which could be useful to make the perfect combination for Nano-structured Cu<sub>2</sub>O thin films for various fields such as gas sensing and many other applications.

## Rational Design of Mesoporous AuCu Nanospheres Using Polymeric Micelles

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Owing to the large surface area and high degree of accessible pores with good stability, nontoxicity, and good resistance to poisoning effects during the course of reaction, mesoporous gold (Au) NPs with large pores, and surface dominated by active low-coordinated atoms have significant enhancement as an electrode in the catalytic reaction of small organic molecules.<sup>1</sup> Modifying the composition by introducing such cheap metals like copper (Cu) to prepare bimetallic Au-based catalyst is expected to improve the surface adsorption/desorption properties and increase the catalytic activity.<sup>2</sup> Although Au-based nanoporous alloy have been synthesized via various approaches, however, these methods typically require multi-step procedures and harsh conditions, leading to difficult control over the resulting compositions and morphology. The high reduction potential and high mobility of Au ions in the solution also hinders the simple templating method to be performed. Therefore, here we focused on fabrication bimetallic mesoporous AuCu NPs and evaluating the catalytic activity towards ethanol oxidation reaction. In this study, we describe experiments to prepare mesoporous AuCu NPs with ultra large pores of 16 nm and narrow size distributions. Mesoporous AuCu NPs is synthesized by an effective and simple co-reduction of two metal precursors through chemical reduction method in the presence of the di-block copolymers of polystyrene-*block*-poly(oxyethylene) (PS-*b*-PEO) and L-Cysteine is employed. L-Cysteine serves as a ligand to form the intermediate meta-stable metals nanoclusters that allow reduced metals to grow around the spherical micelles of PS-*b*-PEO. The mesopores and the final metals composition can be controlled by the size of used polymeric micelles and the metal precursors ratio in the initial electrolyte solution, respectively. The mesoporous AuCu NPs exhibit high electrochemical surface area due to the advantages of open porous architecture and low-coordinated atoms as multi-active sites over the framework. Consequently, the mesoporous



AuCu NPs possess a superior electrocatalytic activity in the ethanol oxidation reaction with the maximum current density of 730.7 mA mg<sup>-1</sup>, and  $I_f/I_b$  value of 4.9 for 1M ethanol with 1M NaOH solution. Thus, our mesoporous AuCu NPs shows excellent potential for high performance electrocatalyst for direct alcohol fuel cell.

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## Machine Learning Study on Screening and Prediction of CO<sub>2</sub> Reduction Reaction Electrocatalysts

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## Strategic Design of ZIF-8-Derived Hierarchically Porous Carbons for Superior ORR Electrocatalyst: From the Perspective of Nanoarchitectonics

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With large surface area, good electrical conductivity, and abundant nitrogen dopants, ZIF-8-derived porous carbons have been heavily exploited to synthesize PGM-free ORR catalysts. Its highly microporous structure, however, severely restricts the efficient diffusion of substances, hence rendering a significant portion of the surface area electrochemically redundant. In this regard, the nanoarchitecture of ZIF-8-derived porous carbons must be designed and synthesized in more strategic and meticulous ways to maximize the exposure of their surface area to the surrounding electrochemical environments.<sup>[1]</sup> Herein, a novel ZIF-8-derived hierarchically porous carbon with a unique double-shelled structure is synthesized by applying mesostructured polymeric coating on ZIF-8 prior to the direct-carbonization process.<sup>[2]</sup> To highlight the structural advantage of the ZIF-8-derived hierarchically porous carbon, ZIF-8-derived microporous carbons and hollow microporous carbons are also synthesized. Based on the impedance spectroscopy and the cyclic voltammetry analyses of the as-synthesized three types of ZIF-8-derived porous carbons of different porosities, the specific role of each class of nanopores is better elucidated. Our study confirms that mesopores play an important role in maximizing the electrochemically wettable and accessible surface areas by alleviating the electrical double-layer overlapping often taking place in small micropores. Moreover, macropores contribute to the rate capability of the carbon samples by serving as a reservoir for the electrolyte ions, thus achieving the efficient usage of the surface area at high charge-discharge rates. The findings are largely translatable to their ORR electrocatalytic activity, especially, with respect to electron transfer number. As ZIF-8-derived

hierarchically porous carbon is found to be an ideal nanoarchitecture in this study, it is further doped with Fe atoms to form highly active Fe-N<sub>x</sub> sites, hence achieving dramatic improvement in ORR catalytic activity comparable to that of the commercial 20 wt% Pt/C in alkaline electrolyte.

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## Self-Assembling of Metal Ions and Melem through Selective Coordination

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Supramolecular self-assembly is formed by molecular aggregation based on non-covalent interactions between molecules, which is a conversion process of molecules from disorder to order and from individuals to complex advanced structures. The various types of intermolecular interactions, such as hydrogen bond, van der Waals force, coordination bond and  $\pi$ - $\pi$  interactions, result in the types of supramolecular self-assembly are also different. Especially, the energy of coordination bonds is stronger than other intermolecular interactions and coordination bonding is directional interaction, leading to organic-inorganic supramolecular aggregates driven by coordination bonds playing an important role in the field of supramolecular chemistry in recent years.

The structure of melem contains a tri-s-triazine ring, which means three terminal amino groups can provide more hydrogen bond receptor sites and rich nitrogen atoms in the molecule also support the convenience for coordination with metal ions. However, the supramolecular structure with melem as ligand is almost not reported. On the other hand, transition metals have various coordination configurations and appropriate ionic radii. Therefore, it is widely used in organic-metal complexes, such as silver ions. In this project, we found that adjusting the concentration and volume ratio of melem and silver ions in pure water can fabricate a stable microcube crystal with an average diameter of about 18 $\mu$ m. And fiber crystals can appear as intermediate products in the reaction process. Through a series of experiments, the reaction conditions are very harsh, which not only needs high optimization for the concentration and volume of reactants, but also the melem calcined at different temperatures also has an obvious influence on final complexes. In addition, under the certain condition, the single crystal structure of Melem-Ag was presented, and the space group is P $\bar{4}$  b 2. Silver ions and nitrogen atoms from heptazine rings construct this 3D structure link via silver–nitrogen coordination bonds. Finally, by introducing extra other transition metal ions such as Zn<sup>2+</sup>, Co<sup>2+</sup>, Cu<sup>2+</sup> and Ni<sup>2+</sup> respectively with Ag<sup>+</sup> in melem suspension. Surprisingly, melem will selectively self-assemble only with silver ions. This unique characteristic of melem may have certain potential in practical applications.

## LUCID: Inside View of Organs and Tissues, Enabler of 3D Imaging

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Cells are composed of organelles such as the nucleus, Golgi apparatus and mitochondria, and these organelles are surrounded by cytoplasm composed mainly of water.[1] In general, biological tissues made of cells are opaque in the visible light range, and it is not easy to observe their internal structure. However, if three-dimensional observation of the internal structure becomes possible, it will not only provide a great deal of new bioscientific knowledge, but also bring about innovations in pathology.

When considering the optical properties of cells and tissues, it is necessary to consider the structure of the cell. A cell is about 10 $\mu$ m in size, and is composed of organelles as well as cytoplasm, where very little absorption of visible light occurs. In a cell, each organelle is surrounded by cytoplasm, and the scale of its spatial disorder is less than 1 $\mu$ m. The refractive index of organelles ranges from 1.53 to 1.55, whereas that of water-based cytoplasm is 1.33. As a result of this difference in refractive indices, random spatial variations in refractive index, of the order of wavelengths, occur in cells. This spatial randomness in the refractive index causes light scattering in biological tissues, and the tissues become opaque. If the cytoplasm could be replaced with a liquid that has the same refractive index as that of the organelles, the refractive index mismatching would be suppressed, and tissues would become transparent and observable.

Based on this idea, we developed a reagent, LUCID (ilLUmination of Cleared organs to IDentify target molecules method) with a refractive index of 1.53 to 1.55.[2] It is observed that mm-size tissues of stomach, lungs, intestines, muscles, and other organs become transparent after just a few hours of immersion in LUCID, and we confirmed that LUCID can easily replace cytoplasm without damaging cells and tissues. We would like to stress that transparent biological samples do not deteriorate and dissolve, and secular change of the samples has not been observed over a period of more than 10 years. It is noteworthy that LUCID has cleared the 10-year retention requirement for pathology specimens.

LUCID is expected to open up new learning in the field of bioscience with its ability to easily make biological samples transparent quickly, and thereby enabling 3D imaging. Furthermore, since LUCID allows long-term preservation for more than 10 years, 3D diagnostic techniques can be introduced into pathology and 3D pathology can be expected to improve diagnostic accuracy and speed, and hopefully also contribute to the relatively new field of remote diagnostics.

[1] Geoffrey M. Cooper and Robert E. Hausman, *The Cell*, 7th edition, Oxford University Press, (2015).

[2] "LUCID brings organs and tissues into clear view", <https://www.nature.com/articles/d42473-021-00185-5>

## Influence of Various Binder Initiators of Low-Temperature Silver Electrode Materials on Wire Bonding Strength for Hjt Solar Cell

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Ag paste sintered at a high temperature ( $\geq 200$  °C) cannot be used for the fabrication process using c-Si heterojunction (HJT) solar cell due to the hydrogen evolution from a-Si:H thin films which could dramatically deteriorate the passivation quality of dangling bond on c-Si surface. Therefore, the development of Ag pastes cured at low temperatures under 200 °C with excellent electrical conductivity has been demanded for a long time. In this study, we have developed Ag pastes for busbar electrodes capable of solder interconnection which can be solidified with a low curing temperature and short curing time. First, the characteristics of the Ag paste depending on the types and contents of the initiators were studied. We tested four types of initiators and then the pastes were fabricated by mixing Ag flakes. They were analyzed for thermal, rheological, and electrical properties. The thermal property was investigated by differential scanning calorimetry (DSC). And the electrical property was calculated from the line resistance and the wire area. The peel strength bonded to the HJT cell with was measured by a digital force gauge and we obtained a peel strength of 0.5N/mm or higher.

## Dependence of the Ratio of Oligomers and Monomers in Acrylic Binders for Electrically Conductive Adhesives and their Properties

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Electrically conductive adhesives (ECAs) for photovoltaic (PV) cells are applied on the prepared silver (Ag) electrode to connect divided shingled PV cells in series, leading to PV strings and modules. In general, ECAs consist of Ag powders called filler, oligomer and monomer resins, initiators, cross linkers, and others. Initiators have an important role in starting interconnections between organic materials, forming large polymers. The properties of the large polymer with Ag fillers, which is an ECA, depend on the molecular structures of the materials in the ECA. Oligomers and monomers in the ECA are most important materials to decide the properties. In this report, we fabricate ECAs with various oligomer and monomer ratios. Increase of the monomer content reduces the resistivity to  $10^{-4} \sim 10^{-5} \Omega \cdot \text{cm}$ . It is assumed that high ratio of monomer content leads to low viscosity of ECA paste and degree of polymerization is also increased because of that. Eventually, Ag fillers can be very close each other after thermal curing.

## Leaching Rate of Silver Nanoparticles by Reactive Molecular Dynamics

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Silver nanoparticles (nanosilver) exhibit high antibacterial activity, with promising applications in biomedicine (Pulit-Prociak et al., 2015). However, concerns about nanosilver toxicity arise when such nanoparticles are dispersed in liquids due to leaching of Ag<sup>+</sup> ions in aqueous solutions. These Ag<sup>+</sup> ions originate from the silver oxide layer that is believed to be formed at the nanoparticle surface. However, this hypothesis of the formation of a surface silver oxide layer has not been proven and, so, the mechanism related to the toxicity of nano silver is poorly understood. Here, a reactive force field (Lloyd et al., 2016) is used to simulate the leaching of silver nanoparticles by molecular dynamics (MD) simulations. Oxidation during flame synthesis of 2 – 6 nm silver nanoparticles at various temperatures (600 and 900 K) is simulated and the fraction of Ag<sup>+</sup> in the resulting oxidized silver nanoparticles is quantified as a function of the nanosilver size. The results reveal that the fraction of Ag<sup>+</sup> decreases as particle size increases, consistent with experiments of flame-made and wet-made nanosilver in aqueous solutions (Sotiriou et al., 2012) obtained by ion selective electrode measurements. Moreover, the results fall in-between the Ag<sup>+</sup> fraction estimated (Sotiriou et al. 2011) by assuming one layer and two layers of silver oxide on the nanoparticle surface. In addition, the mechanism of leaching is explored. The oxidized silver nanoparticles of various sizes are dispersed in water and the amount of Ag<sup>+</sup> ion released from the nanoparticle surface is tracked as a function of time. The effect of nanoparticle characteristics, including nanosilver size, crystallinity, composition, and thickness of the silver oxide layer, on the leaching rate is quantified. The reactive MD method can reveal the underlying mechanism of leaching and can facilitate linking the leaching rate with cytotoxicity experiments of nanosilver. Understanding the mechanism of Ag<sup>+</sup> leaching, as well as the effect of particle characteristics (particle size, oxidation state) and environmental conditions on the Ag<sup>+</sup> release rate, can facilitate the evaluation and control of nanosilver toxicity.

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## Future Mutli-analyser Upgrade for Thermal-Neutron Triple-axis Spectrometer Taipan at ANSTO

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Taipan is a high-flux thermal-neutron triple-axis spectrometer with a traditional single-detector design. Taipan has been the power horse for thermal neutron inelastic neutron scattering experiments in *Australian Centre for Neutron Scattering at Australian Nuclear Science and Technology Organisation* (ANSTO) for the last ten years,<sup>[1]</sup> generating numerous beautiful scientific highlights, ranging from phonon dispersion in thermoelectric materials<sup>[2]</sup>, to spin-wave spectrum in multiferroics<sup>[3]</sup>, and to magnetic diffractions in 100nm BiFeO<sub>3</sub> thin films<sup>[4,5]</sup>. Following the current trend for the neuron instrumentation worldwide,<sup>[6]</sup> it is interesting to consider a future upgrade of Taipan to increase its data-acquisition efficiency with a multi-analyser design. In this work, a flexible multi-analyser design is proposed for Taipan, and the advantages of such an upgrade are

discussed via simulations. In contrast to the current Taipan with the single-detector design, the multi-analyser Taipan with 21 analyser channels will be able to simultaneously collect 21 different Q positions at the same energy transfer, providing at least one order of magnitude faster in data-acquisition rate. The splitting angle of the neighbouring channels is flexible and able to change from 1.5° to 2.5°. The energy and Q resolutions of all the channels are simulated at two different final energy configurations,<sup>[7]</sup> namely,  $E_f = 8.07$  meV and 14.87 meV, to determine the optimized splitting angle for the most efficient data acquisition. The simulated results demonstrate that the data-acquisition efficiency on Taipan can be enhanced to one order of magnitude higher by implementing the new multi-analyser design. Different splitting angles are suitable for different types of scans depending on the purpose of the experiments. The changeable splitting angle extensively enhances the flexibility of Taipan, on which similar high data-acquisition efficiencies as demonstrated on the cold-neutron triple-axis spectrometer Sika<sup>[8,9]</sup> at ASNTO are expected.

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## Extraordinary Non-linear Optical Interaction from Strained Nanostructures in van der Waals CuInP<sub>2</sub>S<sub>6</sub>

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Local strain engineering and structural modification of 2D materials furnish benevolent control over their optoelectronic properties and provide an exciting approach to tune light-matter interaction in layered materials. Application of strain at the nanoscale is typically obtained through permanently deformed nanostructures such as nano-wrinkles, which yield large bandgap modulation, photoluminescence enhancement and surface potential. Ultrathin transition metal

dichalcogenides (TMDs) have been greatly analyzed for such purposes. Herein, we extend strain induced nano-engineering to emerging 2D material, CuInP2S6 (CIPS) and visualize extraordinary control over nonlinear light-matter interaction. Wrinkle nanostructures exhibit ~160-fold enhancement in second harmonic generation (SHG) compared to unstrained regions, which is additionally influenced by change in dielectric environment. The SHG enhancement was significantly modulated by the percentage of applied strain which was numerically estimated. Furthermore, polarization dependent SHG revealed quenching and enhancement in the parallel and perpendicular directions, respectively, due to the direction of the compressive vector. Our work provides an important advancement in controlling optoelectronic properties beyond TMDs for imminent applications in flexible electronics.

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