

The 3rd Postdoctoral Research Symposium & Conference for International Students

November 26, 2021

Room 112, Chemistry Building and Zoom(Live)

Pusan National University (PNU)

Organized by

Department of Chemistry, PNU

Education and Research Center for Molecular Materials (BK21), PNU

Chemistry Institute for Functional Materials, PNU

The 3rd Postdoctoral Research Symposium & Conference for International Students (November 26, 2021)

09:50 – 10:00 **Registration**

<1st Session>

Chair: Syed Asad Abbas

10:00 – 10:20 **Dr. Vedikuyilazhagan Muniraj** (Division of Analytical Chemistry; Prof. Hyun Deog Yoo)

“Na⁺-Pillared Lithium Cobalt Oxide as an Efficient Cathode for Thermally Stable and Fast-Charging Batterie”

10:20 – 10:40 **Dr. Sagar Arepally** (Division of Organic Chemistry; Prof. Jin Kyoong Park)

“Regiodivergent Ni-mediated Paired-Electrochemical [2+2+2] Cyclotrimerizations to 1,3,5- and 1,2,4-Trisubstituted Benzenes”

10:40 – 11:00 **Dr. Jae-Ho Jang** (Division of Organic Chemistry; Prof. Do-Hoon Hwang)

“Thermally cross-linkable host materials based on Diels-Alder reaction for solution-processed OLEDs”

11:00 – 11:10 **Coffee Break**

<2nd Session>

Chair: Vedikuyilazhagan Muniraj

11:10 – 11:30 **Dr. Syed Asad Abbas** (Division of Analytical Chemistry; Prof. Ki Min Nam)

“Synthesis of Fe₃C@C core-shell catalysts with controlled shell composition for robust oxygen evolution reaction”

11:30 – 11:50 **Dr. Atanu Naskar** (Division of Bio Chemistry; Prof. Kwang-sun Kim)

“Black Phosphorus based nanocomposites for biomedical applications”

11:50 – 12:10 **Dr. Seonhwa Park** (Division of Analytical Chemistry; Prof. Haesik Yang)

“Electrochemical Detection of Porphyromonas gingivalis in Saliva for Diagnosis of Periodontitis”

12:10 – 13:00 **Lunch & Discussion (Conference for International Students)**

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Abstracts

Na⁺-Pillared Lithium Cobalt Oxide as an Efficient Cathode for Thermally Stable and Fast-Charging Batteries

Vedikuyilazhagan Muniraj, Fuead Hasan, Hyun Deog Yoo*

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Abstract: Despite the high theoretical capacity, the layered lithium cobalt oxide (LiCoO₂; LCO) cathode suffers from unfavorable phase transitions at higher working potential, causing severe capacity fading, particularly at elevated operating temperatures. Pillaring the layered structure can improve the structural stability and the capacity retention by binding the layers with pillaring ions. In addition, the inherently expanded structure can facilitate the intercalation kinetics as well. Herein, we implemented the pillaring strategy by ion-exchange of Na_xCoO₂ with Li⁺ ions, which produced Na⁺-pillared lithium cobalt oxide with expanded interlayer spacing. And the Na⁺-pillared LCO cathode exhibited improved specific capacity, rate capability, and cycling stability. X-ray diffraction revealed the formation of layered Li_{0.75}CoO₂ (space group: R-3m; hexagonal phase) and OP4-Li_{0.37}Na_{0.31}CoO₂ (space group: P63/mmc; 2H phase). The Na⁺-pillared LCO delivered a maximum specific capacity of 145 and 140 mAh g⁻¹ at 25 °C and 60 °C, respectively, which was larger than pristine LCO by 10 mAh g⁻¹. In terms of rate capability, the Na⁺-pillared LCO secured 54% capacity at 10C, whereas pristine LCO retained 0.06%. The improved cycling stability at high temperature of 60 °C was represented by 92% capacity retention after 100 cycles at 0.5C rate, whereas operation of pristine LCO failed at 60 °C. Especially, the cells operated at 60 °C retained 95% of the initial capacity even after 100 cycles at 25 °C, suggesting the thermo-electrochemical structural reconstruction or surface stabilization during the initial formation cycling at the raised temperature. In addition, the structural and electrochemical properties of the Na⁺-pillared LCO were fully explored by a variety of analytical tools, in comparison with pristine LCO.

Regiodivergent Ni-mediated Paired-Electrochemical [2+2+2] Cyclotrimerizations to 1,3,5- and 1,2,4-Trisubstituted Benzenes

Sagar Arepally[†], Alina Dzhaparova[†], Gyeongho Kim[†], Ponnusamy Nandhakumar[†], Gisela A. González-Montiel[‡], Haesik Yang^{*†}, Paul Ha-Yeon Cheong^{*‡}, and Jin Kyoong Park^{*†}

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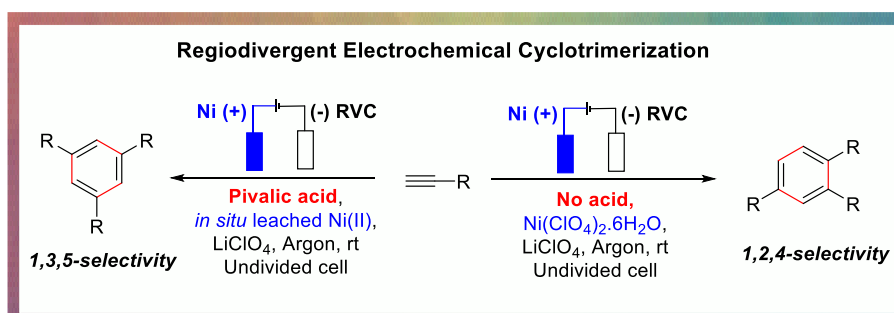
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Abstract:

Since the development of cyclotrimerization of terminal alkynes by Reppe, strong efforts have been made on the design and development of metal catalyst to achieve the regioselective formation of 1,2,4- and 1,3,5-isomers with a clear mechanistic understanding. Thus far, many of cyclotrimerizations have been developed with high level of regioselectivity, however, a divergent regiocontrol of both cyclotrimerizations still remains elusive. Mechanistically, the typical regioselective metal-catalyzed reactions are known to be initiated by metal(0) species which is *in situ* reduced by external reductant. Herein, we report the regiodivergent paired-electrochemical [2+2+2] cyclotrimerizations of terminal alkynes to access trisubstituted benzene derivatives via the direct alkyne reduction mediated by Ni(II). It was revealed that the regiocontrol was depending on how to stabilize alkyne radical anion species by additives. The exclusive 1,3,5-isomers were synthesized by adding carboxylic acid, while the formation of 1,2,4 isomers were achieved with an external Ni(II) additive under non-acidic condition. The plausible Ni-mediated reduction of alkyne and Ni-catalyzed radical pathways were proposed and supported by a series of investigations involving electron paramagnetic resonance, cyclic voltammetry, deuterium exchange, and computational studies.

Graphical abstract:



References:

- (a) Yoshida, J.-I.; Kataoka, K.; Horcajada, R.; Nagaki, A. Modern Strategies in Electroorganic Synthesis. *Chem. Rev.* **2008**, *108*, 2265. (b) Kingston, C.; Palkowitz, M. D.; Takahira, Y.; Vantourout, J. C.; Peters, B. K.; Kawamata, Y.; Baran, P. S. *Acc. Chem. Res.* **2020**, *53*, 72. (c) Siu, J. C.; Fu, N.; Lin, S. *Acc. Chem. Res.* **2020**, *53*, 547.
- (a) Reppe, W.; Schlichting, O.; Klager, K.; Toepel, T. *Justus Liebigs Ann. Chem.* **1948**, 560, 1. (b) Roglans, A.; Pla-Quintana, A.; Solà, M. *Chem. Rev.* **2021**, *121*, 1894.

Thermally cross-linkable host materials based on Diels-Alder reaction for solution-processed OLEDs

Jae-Ho Jang^a, Jeong Yong Park^a, and Do-Hoon Hwang^{a*}

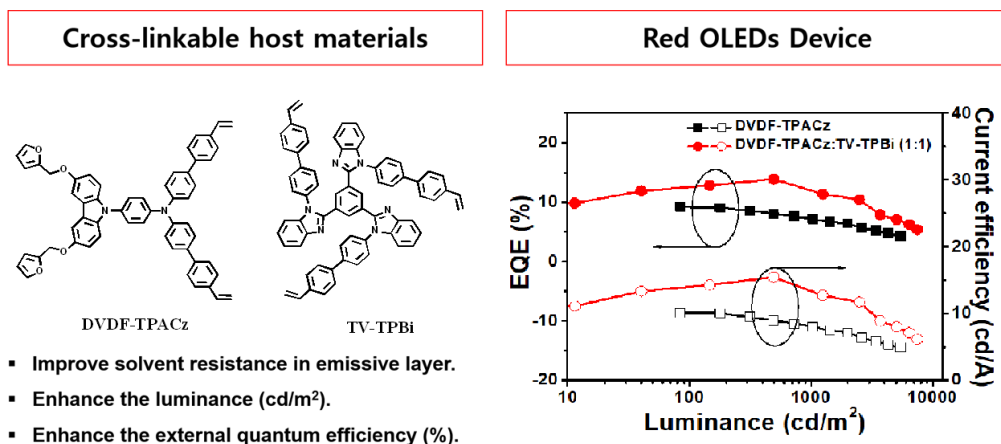
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Abstract:

Thermally cross-linkable host materials containing carbazole and triphenylamine were designed and synthesized for solution-processed organic light-emitting diodes (OLEDs). The host materials with styryl- and furyl- groups can be thermally cross-linked by curing at 120 °C without any polymerization initiator. Excellent solvent resistance was observed for all the host materials. The highest occupied molecular orbital energy levels of 5.6 eV are estimated for these host materials, which indicates low injection barrier from the hole transport layer. A current efficiency of 15.4 cd/A, power efficiency of 8.81 lm/W, and external quantum efficiency of 13.8 % were achieved for solution-processed (MPHMQ)₂Ir(tmd)-based OLEDs by using the thermally cross-linkable host material.

Graphical abstract:



Keywords: organic light-emitting diodes, cross-linkable, host, low temperature

Synthesis of Fe₃C@C core-shell catalysts with controlled shell composition for robust oxygen evolution reaction

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Abstract:

In this study, iron carbide (Fe₃C) particles were encapsulated in graphitic carbon shells by a facile carbonation process. These core-shell carbides, in which iron carbide is encapsulated in graphene-like layer (Fe₃C@C) and nitrogen doped graphene-like layer (Fe₃C@C-N) were investigated as oxygen evolution reaction (OER) catalysts to investigate the effect of the carbon shell on catalyst activity and stability. Due to the protective effect of the graphitic carbon shells, the performance of Fe₃C@C and Fe₃C@C-N were considerably better than the bare Fe₃C nanoparticles. The OER activity of Fe₃C@C-N is comparable with that of carbon-supported ruthenium oxide (RuO₂/C), and this core-shell carbide has a remarkable stability and high turnover frequency under alkaline conditions. To elucidate the real active sites of these core-shell carbides, the role of the Fe₃C core, Fe-N_x active sites, and effect of nitrogen doping in the shell were investigated in detail.

The major purpose of this study was to investigate the real active sites between Fe-C and Fe-N moieties in the catalyst. The importance of graphitic shell was also investigated for the stability of the catalyst with Fe-C moieties. Graphitic Shell enhanced the stability of the catalyst and the presence of doped nitrogen in the carbon support increased the number of active sites due to its unstable nature at higher pyrolysis temperatures subsequently creating vacancies for extra Fe metal incorporation in the catalyst. Furthermore, catalytic performances were also evaluated using basic and neutral electrolytes to fully understand the reaction mechanism at the surface of the catalyst.

Graphical abstract:

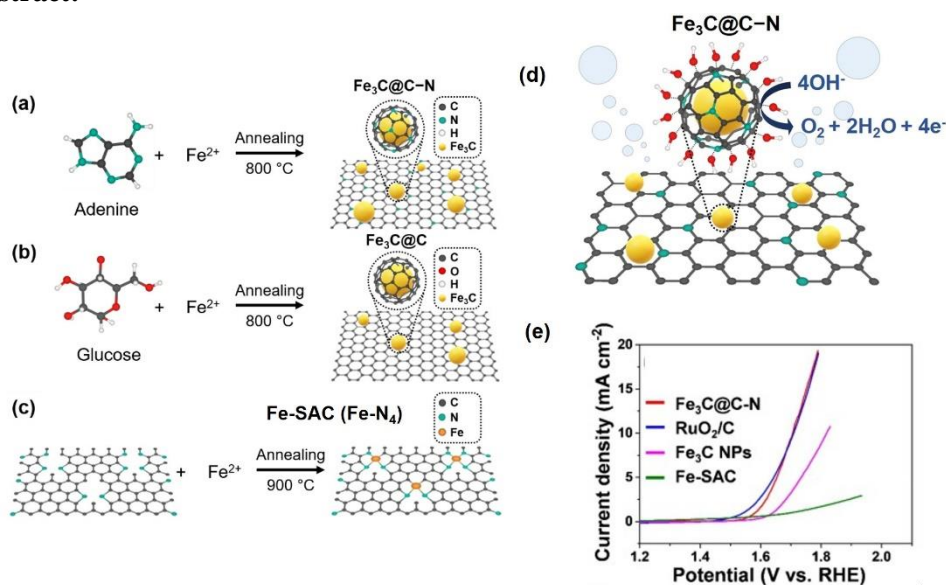


Figure 1. Synthetic scheme of (a) Fe₃C@C-N, (b) Fe₃C@C, (c) Fe-SAC, (d) proposed reaction mechanism of OER and (e) LSVs to observe the catalytic performances at the scan-rate of 10mV/s.

Keywords: Oxygen Evolution Reaction, Fe-N and Fe-C active sites, Core shell structure.

Black Phosphorus based nanocomposites for biomedical applications

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Abstract

The immense success of graphene has motivated researchers to discover additional 2D nanomaterials such as hexagonal boron nitride, transition metal dichalcogenide, and layered double hydroxide etc. with new advantageous functions in biomedical applications. Among emerging post-graphene scenarios, black phosphorus (BP) has arisen as a new beneficial 2D nanomaterial for various biomedical applications including photothermal therapy, drug delivery, biosensing, and bioimaging. Due to its excellent physicochemical properties such as layer dependent band-gap, thermodynamic stability and non-toxicity, BP can be easily utilized for various biomedical applications. Moreover, after combining with other favourable metal and metal oxides, BP based nanocomposite can be the answer to various problem in biomedical sector. Here, we prepared four different BP assembled nanocomposites (γ -Fe₂O₃ based: 2, ZnO based: 2) consisting of metal- and metal-oxides. The preparation was performed with low temperature solution synthesis method and resulting materials were characterized by X-ray diffraction, transmission electron microscopy with elemental mapping, and X-ray photoelectron spectroscopy studies. The prepared materials were evaluated for their efficacy of biocompatibility and antibacterial activity which showed great potential to solve the nanomaterial toxicity and bacteria killing. Therefore, our newly prepared BP-assembled metal- and metal-oxide based nanoplatform could be used for overcome the limitations of metal- and metal-oxide in the usage of biomedical applications.

Keywords: black phosphorus, nanocomposite, cell viability, antibacterial, 2D material

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Electrochemical Detection of *Porphyromonas gingivalis* in Saliva for Diagnosis of Periodontitis

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Abstract:

Indirect detection of *Porphyromonas gingivalis* in saliva, based on proteolytic cleavage by gingipain, has traditionally been used for simple, diagnosis of periodontitis. To accurately detect *P. gingivalis*, the development of a simple biosensor that can measure the exact concentration of *P. gingivalis* is required. However, electrochemical detection in saliva is challenging, due to the presence of various interfering electroactive species. Here, we report a washing- and separation-free electrochemical biosensor for sensitive detection of *P. gingivalis* in saliva. Glycine-proline-arginine conjugated with 4-aminophenol (AP) was used as an electrochemical substrate for trypsin-like gingipain. The electrochemical signal of AP was increased using electrochemical-chemical (EC) redox cycling, and the electrochemical charge signal was corrected using the initial charge obtained before a 15-min incubation period. The proteolytic cleavage of the electrochemical substrate was specific to *P. gingivalis*. The calculated detection limit for *P. gingivalis* in artificial saliva was 5×10^5 CFU/mL, and the concentration of *P. gingivalis* in human saliva could be measured. The developed biosensor can be used as an initial diagnosis method to distinguish between healthy people and patients with periodontal diseases.

Graphical abstract:

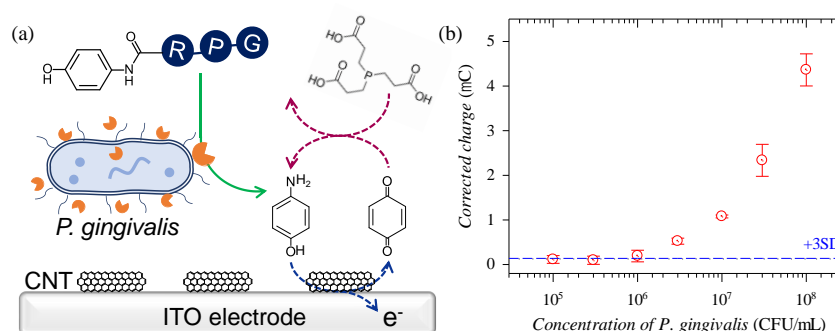


Figure 1. (a) Schematic diagram of *P. gingivalis* detection based on proteolytic reaction and EC redox cycling. (b) Calibration plot obtained matrix-corrected charges obtained using the scheme in artificial saliva containing various concentrations of *P. gingivalis*.

Keywords: Electrochemical biosensor, *Porphyromonas gingivalis*, gingipain, proteolytic reaction, electrochemical-chemical redox cycling.