

# SUSTAINABLE GRAPHENE NANOPATELET HYDROGELS FOR ENHANCED SERS DETECTION OF PFAS CONTAMINANTS



MARYAM AGHILI

Surface-enhanced Raman scattering (SERS) spectroscopy offers rapid and efficient detection of chemical compounds, but conventional two-dimensional substrates limit the density of electromagnetic hotspots crucial for SERS effects. This study introduces a straightforward method for fabricating three-dimensional SERS substrates with high activity. Nanostructured silver (Ag) is electrochemically deposited onto conductive graphene nanoplatelet hydrogels (GNP-HGs), leveraging their unique three-dimensional structure and high conductivity. Departing from previous research on reduced graphene oxide (rGO) aerogels, GNP-HGs eliminate the need for freeze-drying. Their higher conductivity enables the deposition of silver morphology at a lower electrical field, thereby enhancing magnetic enhancement. The resulting substrates exhibit a strong SERS effect attributed to the high specific surface area of the GNP-HGs, facilitating molecular adsorption and supporting the creation of a dense network of electromagnetic hotspots. Optimized electrochemical growth of silver nanostructures on GNP-HGs yields substrates with exceptional sensitivity and low detection limits for per and poly-fluoroalkyl substances (PFAS) contaminants. This work highlights a sustainable and efficient approach to SERS substrate fabrication, showcasing the versatility and high sensitivity of GNP-HGs in chemical detection applications.

# ACETAMINOPHEN REMOVAL FROM FRESHWATER: A COMPARATIVE STUDY OF SYNTHETIC AND COMMERCIAL ADSORBENTS

**AMIR HOSSEIN BEHROOZI**

Acetaminophen, or paracetamol, is a common over-the-counter medication that relieves pain and reduces fever. Because of its widespread use, acetaminophen is now present in freshwater systems and poses potential environmental risks. Acetaminophen enters freshwater system from a variety of sources, such as wastewater treatment plant discharges, pharmaceutical manufacturing effluents, or improper disposal of medications. It can disrupt aquatic ecosystems, affect fish and other animals, and may contaminate drinking water sources. Such contamination is a growing concern in Canada, particularly near major cities and industrial areas, and especially because current treatment methods cannot effectively remove pharmaceuticals from water. Therefore, new treatment approaches are necessary. Adsorption may be an effective process to remove acetaminophen from contaminated water. However, the current findings describing sorption behaviour, pH-dependency, sorption material effectiveness, and optimal conditions are contradictory. Thus, the objectives of the present study are to develop novel graphene-oxide-, silica-, and chitosan-based sorption materials, and to characterize the main adsorption mechanisms and interactions with acetaminophen by comparing the performance of these new materials with that of commercial adsorbents, such as activated carbon, in aqueous solutions. Activated carbon is well-established in large-scale water treatments, whereas graphene oxide- and silica-, and chitosan-based adsorbents may deliver improved adsorption capacities and tunable surface properties.



Each of these adsorbents may have unique interactions with acetaminophen in aqueous solutions. In this study, the performance of selected materials, individually or in composites, is first evaluated at various pH to assess their adsorption performance. In the second step, the surface charge of each adsorbent is measured under various conditions of pH and acetaminophen concentrations to identify the dominant sorption mechanisms. Early results with an adsorbent concentration of 1 g/L suggest that commercial granular activated carbon (GAC) is the most efficient adsorbent with a removal efficiency of > 98% at neutral pH compared to other individual and composite adsorbents (e.g., graphene oxide-, silica-, and chitosan-based adsorbents with up to 70%, 10%, and 20% removal efficiencies at their corresponding optimal pH, respectively). Moreover, pore filling is the dominant mechanism for acetaminophen adsorption. These results indicate that porous adsorbents may be a suitable option for acetaminophen removal from freshwater systems. Further research is needed to improve the performance of selected composite material and to determine the optimal sorption conditions.

# MODELING OF A HEAT-INTEGRATED BIOMASS DOWNDRAFT GASIFIER WITH CONSTRUCTION AND DEMOLITION WASTE AS FEEDSTOCK

**HOUDA HAIDAR**

A mathematical model for a heat-integrated biomass downdraft gasifier is extended to account for use of construction and demolition (C&D) waste as a feedstock. Model equations are updated to account for the relatively high proportion of inerts in C&D waste compared to pine wood. Statistical subset selection methods are used to select 11 out of 39 model parameters for estimation using data from 13 experimental runs. Model is validated using additional data and gives better noticeably predictions than when pine-wood model parameters are used. Simulations reveal that a lower volumetric feed rate of C&D waste is required to generate the same energy as pine wood, due to the higher density of the C&D particles fed to the gasifier. Using C&D feedstocks results in lower predicted H<sub>2</sub>/CO ratios and more tar in the producer gas than when pine wood is gasified. Simulations show that it is important to select an appropriate solids removal rate at the bottom of the gasifier so that sufficient high quality producer gas can be generated. Reducing the moisture content of the C&D waste from 8.1 wt% to 5.0 wt% is predicted to increase the CO and H<sub>2</sub> mole fractions by 4.3% and 3.6%, respectively, and to reduce the tar content in the producer gas by 0.475 g m<sup>-3</sup> to nearly zero. Experimental and simulation results confirm that C&D waste is a promising feedstock for biomass gasification and subsequent electricity generation.

# DATA-DRIVEN GAUSSIAN PROCESS OUTPUT REGULATION FOR A CLASS NONLINEAR SYSTEMS

TELEMA HARRY

We solve the adaptive output regulation problem of a class of nonlinear systems using a data-driven approach to reconstruct the internal model unknown nonlinear continuous map online from some input and output data. The data-driven model is then used to estimate the ideal feed-forward steady-state control inputs obtained by solving the regulator equation instead of implementing it with an extended observer as in previous studies. Secondly, we implement an output feedback stabilizer that does not rely on the complete knowledge of the system but on output measurement of the regulated output, making the proposed approach suitable for systems with modeling errors. Finally, we showed through detailed Lyapunov analysis that under certain conditions the closed-loop system is practically asymptotically stable.

# STRUCTURE-ACTIVITY RELATIONSHIPS OF PBAE-BASED POLYMERIC NANOPARTICLES FOR *IN VIVO* DRUG DELIVERY

**MANPREET KAUR**

For targeted delivery in gene therapy, nucleic acids need to be protected by drug delivery carriers to overcome extracellular and intracellular barriers. Among other types of drug delivery carriers, polymeric nanoparticles show immense potential for gene therapy due to their various tunable properties. Poly ( $\beta$ -amino acids) (PBAEs) have gained enormous interest in the scientific community due to their ability to target various cell lines.

PBAEs are a class of polymers synthesized via Michael addition of acrylates and amines in an organic solvent without the production of any by-products. These polymers possess various advantages including biocompatibility, biodegradability, pH responsiveness, and facile tunability of structures. The acrylate backbone of PBAEs is responsible for their biodegradability and tertiary amines make these materials pH-responsive. The goal of this study is the development of a novel, inexpensive and versatile engineered design of PBAEs with structure and surface modifications to heighten *in vivo* efficacy and to apply these materials to cell lines targeting the lungs and brain. Some of our polymer nanoparticles have shown a 100-fold increase in transfection efficiency to the lungs compared to the current gold standard.

# ULTRASMALL GOLD NANOCRYSTALS AND CONJUGATED POLYMER WRAPPED SINGLE-WALLED CARBON NANOTUBES COMPOSITES FOR CATALYZING CO<sub>2</sub> ELECTROREDUCTION

YUEYING LI

Gold (Au) is one of the most active and selective catalysts for electrochemical CO<sub>2</sub> reduction reaction (eCO<sub>2</sub>RR). For practical application, lowering Au loading while maintaining good activity and selectivity is important. With the development of nanotechnology, metal electrocatalysts with various sizes and morphologies and with remarkably improved CO<sub>2</sub> reduction performance have been demonstrated. Higher surface-to-volume ratio, larger surface area, and more active sites are considered the main reasons for the good electrochemical performance of metal nanocrystals. Today, the syntheses of metal nanocrystals, especially ultrasmall particles, are usually energy-demanding or involve multiple steps. Using polymer-wrapped semiconducting single-wall carbon nanotube (sc-SWCNT), ultrasmall gold nanocrystals (AuNCs) could be produced at room temperature and in an ambient environment within minutes. A conjugated polyfluorene (PF) group polymer with a bipyridine (BPy) unit at the backbone was employed in this system, where the BPy unit plays a role in anchoring the Au<sup>3+</sup> and AuNCs. Since Au<sup>3+</sup> ions near the BPy are easily reduced to metallic Au by using the excited electron from SWCNTs, the local concentration of Au<sup>3+</sup> near each BPy unit is relatively low. This enables the formation of ultrasmall AuNCs in which the density of AuNCs on the CNT surface can be adjusted by changing the ratio between the precursors and the polymers. In addition, the size of AuNCs on the CNT matrix is controlled by modulating the diffusion rate and local concentration of Au<sup>3+</sup>. This method allows us to synthesize ligand-free AuNCs stabilized in a polymer/CNT matrix and study their size-dependent activity in CO<sub>2</sub> reduction. The AuNCs stabilized in polymer/CNT exhibited a high CO Faradaic efficiency of up to 86% at 25 mA/cm<sup>2</sup> and a high mass activity of up to 5.61 A/mgAu at 100 mA/cm<sup>2</sup>, which is the highest value up to date in AuNCs electrocatalysts for CO<sub>2</sub> reduction. In addition, other metal nanocrystals could be synthesized by using a similar method. This opens doors for exploring CO<sub>2</sub>RR or other reactions on various types of ultrasmall metal NCs.

# PROCESS KNOWLEDGE FOR DRUG SUBSTANCE PRODUCTION VIA KINETIC MODELING, PARAMETER ESTIMABILITY ANALYSIS AND REACTION OPTIMIZATION

IMAN MOSHIRITABRIZI

A fundamental model is developed to study production of 2-fluoroadenine-9-THP from starting material 2,6-dichloropurine-9-THP. The 2-fluoroadenine-9-THP product is an intermediate used to make the drug Islatravir (MK-8591). Kinetic parameters are estimated from 26 batch reactor experiments. An Error-in-Variables-Model (EVM) approach is used for parameter estimation because initial concentrations of trimethylamine (TMA) in the reactor are uncertain. A parameter subset selection method that accounts for uncertainty in independent variables is used to determine that 33 out of 39 model parameters should be estimated along with uncertain initial concentrations. The remaining 6 parameters are kept at their initial values to prevent overfitting of the available data. EVM parameter estimates are compared with estimates obtained using a traditional weighted-least-squares approach that neglects input uncertainties. The EVM estimates provide a better fit to the data and better accuracy for model predictions, which was assessed using cross-validation. The resulting model and EVM parameter values are used to find reactor conditions that maximize the product yield while obeying constraints on temperature, the initial ratio of TMA to starting material, batch time, and the volume of solvent. An optimal yield of 92.04 % is predicted, which is higher than the largest yield of 90.26 % corresponding to the best experimental conditions used to generate the data. Contour plots are used to determine that optimal yield is not very sensitive to batch time and solvent volume, so a yield of 91.83 % could be obtained using a 50 % lower batch time and 33 % less solvent.



# CO<sub>2</sub> ELECTROREDUCTION IN AQUEOUS FED SYSTEMS TO C<sub>1</sub> AND C<sub>2</sub> PRODUCTS

**BEHNAM NOURMOHAMMADI KHIARAK**

Carbon dioxide (CO<sub>2</sub>) emissions contribute significantly to global warming and climate change. One promising way to tackle these emissions is using carbon capture and conversion such as electrochemical CO<sub>2</sub> reduction (ECR). Conventional gas-phase ECR enables CO<sub>2</sub> reduction at industrially relevant reaction rates but faces challenges, including low product concentration in the output stream which requires extensive energy for product separation and flooding and salt precipitation which lead to low system stability. In this study, we address these challenges by developing ECR systems that use liquid CO<sub>2</sub> feed. Traditional liquid-phase CO<sub>2</sub> electrolysis has limitations, such as low CO<sub>2</sub> reduction rates and poor selectivity for both C<sub>1</sub> (e.g., CO and CH<sub>4</sub>) and C<sub>2</sub> products (e.g., ethylene and ethanol) at high current densities, primarily due to limited CO<sub>2</sub> availability. To overcome these limitations, we used membrane electrode assembly (MEA)-based flow cell with bipolar membrane as reactor and large-pore silver (Ag) and copper (Cu) meshes as catalysts to enhance selective CO<sub>2</sub> conversion into C<sub>1</sub> and C<sub>2</sub> products, respectively, from an aqueous bicarbonate solution. Our findings show that activating the Ag surface through oxidation/reduction cycles creates highly porous surfaces, optimizing it for CO<sub>2</sub>-to-CO conversion. We achieved over 85% Faradaic efficiency for CO production at a high current density of 100 mA/cm<sup>2</sup>, maintaining stability for over 100 hours. In the case of the Cu catalysts, specific heat treatment conditions improve selectivity for C<sub>2</sub> products. We observed over 65% Faradaic efficiency for C<sub>2</sub> products (such as ethylene, ethanol, and acetate) at 150 mA/cm<sup>2</sup> and stable operation at 100 mA/cm<sup>2</sup> for more than 100 hours. These results underscore the potential of large-domain metal mesh catalysts for efficient, stable ECR in aqueous systems, offering a pathway toward sustainable CO<sub>2</sub> mitigation solutions.

# AMBIPOLAR ION TRANSPORT MEMBRANES FOR CO<sub>2</sub> ELECTROLYSIS

HUY PHAM

Electrochemical carbon dioxide (CO<sub>2</sub>) reduction (ECR) is a promising approach for enabling the conversion of greenhouse gas CO<sub>2</sub> into valuable products with electricity from renewable sources to achieve net-zero CO<sub>2</sub> emission. ECR simultaneously reduces carbon emissions and dependence on fossil-based fuels and chemicals. Membrane electrode assemblies (MEAs), which often comprise an anion exchange membrane (AEM) and a precious iridium oxide (IrO<sub>x</sub>)-based anode, have been extensively studied in the last few years. However, challenges such as salt precipitation on cathodic gas diffusion electrodes (GDEs), high cell voltage and the need to use noble metal anodes have hindered ECR's practical applications. Herein, we introduce a new design of MEA cells using an Ambipolar Ion Transport Membrane (AITM) and a Nickel (Ni) foam instead of AEM and IrO<sub>x</sub>, respectively. The AITMs with high water permeability lower the full-cell voltage and eliminate the salt accumulation on the GDE in neutral-pH conditions. Using copper and silver sputtered on polytetrafluoroethylene (Cu/PTFE or Ag/PTFE) as cathodes, we demonstrated a stable conversion of CO<sub>2</sub> to ethylene (C<sub>2</sub>H<sub>4</sub>) and carbon oxide (CO) at current densities over 100 mA/cm<sup>2</sup>. In neutral-pH anolyte with Cu/PTFE, the average C<sub>2</sub>H<sub>4</sub> FE was sustained at around 45% for 950 hours with a cell voltage of 3.1 V at the current density of 110 mA/cm<sup>2</sup>. Using Ag/PTFE as a cathode, this system showed 180 hours of stability of CO<sub>2</sub>-to-CO conversion: the CO FE was maintained above 90% with the cell voltage of 3.25 V at 110 mA/cm<sup>2</sup> current density. Our research provides a solution for achieving stable ECR operation at a relatively high current density using Earth-abundant materials. This work opens opportunities for energy-efficient and stable CO<sub>2</sub> conversion without needing expensive and rare elements, which are crucial for practical applications.

# SELECTIVE ELECTROCHEMICAL NITRATE REDUCTION TO AMMONIA OVER OXIDE-DERIVED CO CATALYSTS

LAURA QUINONES-GOMEZ

The electrocatalytic synthesis of ammonia ( $\text{NH}_3$ ) offers a sustainable alternative to the traditional Haber-Bosch process. The benefit is amplified when ammonia is produced from nitrate reduction ( $\text{NO}_3^-$ -RR) because it simultaneously addresses  $\text{NO}_3^-$  pollution in water sources. Given that the  $\text{NO}_3^-$ -RR to  $\text{NH}_3$  is a complex eight-electron transfer process, developing highly active, selective, and stable catalysts is crucial. In this study, we developed cobalt (Co)-based catalysts for  $\text{NO}_3^-$ -RR to  $\text{NH}_3$  under alkaline conditions. The catalysts were synthesized by growing a layer of cobalt oxide on the surface of metallic Co foam, followed by electrochemical reduction of Co oxide to form pre-reduced catalysts (i.e., PR-Co/ $\text{Co}_3\text{O}_4$ /CoO). We found that, without oxide layer, bare Co foam exhibits a Faradaic Efficiency (F.E.) of 97.4% at -0.4 V versus the Reversible Hydrogen Electrode (RHE), with a  $\text{NH}_3$  partial current density of 213.5  $\text{mA cm}^{-2}$ . In comparison, the PRCo/ $\text{Co}_3\text{O}_4$ /CoO electrode attains an F.E. of 97.1% under the same conditions but with a markedly higher  $\text{NH}_3$  partial current density of 433  $\text{mA cm}^{-2}$ , corresponding to an  $\text{NH}_3$  yield rate of 2.2  $\text{mmol h}^{-1} \text{cm}^{-2}$ . This considerable improvement is attributed to the increased electrochemical surface area after the thermo-oxidation and pre-reduction processes, which is 29 times higher than that of bare Co. Furthermore, XRD patterns reveal that the oxide phase undergoes a surface reconstruction to a  $\text{Co}(\text{OH})_2$  phase, which enhances the electrode surface properties by promoting active hydrogen adsorption while preventing  $\text{NO}_2^-$  desorption at low overpotentials. This lowers the overpotential required for efficient  $\text{NH}_3$  production. This work offers valuable insights into the synergy between Co and  $\text{Co}(\text{OH})_2$  to produce high ammonia yields, as well as a facile method for catalyst optimization through the synthesis of Co-oxide-derived pre-catalysts.

# ENHANCING PERFORMANCE OF PLA/CNCS COMPOSITES: SURFACE MODIFICATION, COMPATIBILIZATION, AND BLENDING STRATEGIES

**MOHAMED WAHBI**

There is growing interest in developing sustainable materials as replacements for conventional petroleum-based plastics. For a number of different applications, poly(lactic acid) (PLA) has emerged as the most promising biobased and biodegradable polymer; however, there are still several shortcomings hindering the practical uptake and widespread industrial use of PLA. In particular, some of the main disadvantages include slow crystallization rate, low thermal resistance, and poor flexibility. Although much research has been performed aiming to incorporate plasticizers and nanoparticle filler into PLA matrices, most of these solutions have not resulted in property improvements that would make the resulting composites viable for commodity and highvalue-added applications. To this end, cellulose nanocrystals (CNCs), rigid rod-shaped nanoparticles derived from cellulose, the most abundant natural polymer on Earth, have gained interest as sustainable fillers. Incorporating CNCs into PLA matrices has the potential to enhance both mechanical properties and crystallinity. Unfortunately, achieving good dispersion while maintaining flexibility remains a significant challenge, limiting the widespread use of these composites. This study investigates the potential of using epoxidized canola oil (ECO) as a compatibilizing agent to facilitate CNC dispersion and thus improve the mechanical properties of the composites.

This study investigates the potential of using epoxidized canola oil (ECO) as a compatibilizing agent to facilitate CNC dispersion and thus improve the mechanical properties of the composites. We successfully modified CNCs with ECO using a one-step base-mediated epoxide ring-opening reaction to improve the affinity between the PLA matrix and CNCs. CNC modification was analyzed using FTIR, contact angle, thermal gravimetric analysis, and light scattering measurements. CNCs were then blended/compounded with PLA following multiple protocols. Additionally, we investigated the effect of incorporating ECO into the PLA/CNC composites directly during compounding. Although modifying CNCs can enhance dispersion by increasing interactions between the PLA matrix and CNCs, the compounding approach used also significantly affects filler dispersion within the polymer matrix. In this regard, a hybrid blending technique combining solution and melt blending was employed to ensure homogeneous dispersion of CNCs within the polymer matrix. Preliminary findings suggest promising improvements in crystallinity, mechanical, and thermal properties, attributed to the improved microstructure of the resulting composites. We anticipate that our approach, being sustainable, scalable, and compatible with existing industrial blending processes, could lead to a significant uptake of PLA use in emerging applications