ABSTRACTS OF CONTRIBUTED PAPERS

POSTER SESSION – I

MONDAY NOVEMBER 4

8:00 – 10:00 PM
Raman Studies of Nanostructured Catalysts: Laser-Induced Heating Effects in CeAl and NiAl Oxides

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Catalytic applications of nanostructured oxides have been carried out focusing on their vibrational properties [1,2,3]. Previous studies on the effect of laser heating over the nanostructured monoxides have indicated the occurrence of structural changes due to thermal effects [2]. The elucidation of the structural properties by Raman spectroscopy of monoxides has been an efficient resource to improve the catalytic performance of the solids [1,3].

In this work, Raman spectroscopy was used to evaluate the thermal stability of nanostructured catalysts based on CeAl and NiAl. The solids were prepared by a nanocasting route. The effects of laser-induced heating were evaluated by varying the incidente power of a laser with an initial power of 0.017 mW up to 4.0 mW as it can be seen in Fig. 1a and 1b. The laser-induced local heating effects on the solids surface influenced the particle size of CeAl causing the sintering of this binary oxide. In addition, CeAl nanostructure was affected by varying laser power from 0.017 mW to 4.0 mW, with defects appearing in the solid lattice. The formation of NiAl₂O₄ phase in NiAl was observed. The results may provide new insights in understanding the behavior of the solids in catalytic applications at the laser power variation measured.

Fig. 1. Raman spectra of CeAl a) and Raman spectra of NiAl b) from 0.017 mW to 4.0 mW.

Bottom-up One-step Photochemical Synthesis of Multifunctional Nickel-Carbon Catalysts

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Very few reports on metal nanoparticle synthesis from earth-abundant metal precursors involving laser plasma exist in literature [1]. Here in, we report the synthesis of multifunctional Nickel-Carbon catalysts using ultrafast femtosecond laser generated plasma in nickelocene/organic solutions. The syntheses were carried out under two different laser beam focusing conditions: tight focus and loose focus. Under both conditions, the reaction was determined to follow first order kinetics using UV-Vis absorption spectroscopy. The catalysts were characterized using FTIR, TEM, SEM, EDX, XPS, XRD instrumental techniques. The products were found to be catalytically active towards a model PNP reduction reaction and exhibited reasonable ORR performance. Further applications involving photocatalysis, OER and HER are underway.

Fig.1. (a) Representative SEM image, (b) TEM image, (c) XPS survey spectrum and atomic percentages and (d) FTIR spectrum of Nickel-Carbon catalyst.

Efficient Removal of Mercury and Phosphate Ions from Aqueous Solutions by Chemically Modified Metal-Organic Frameworks

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In this study, the novel adsorbent UIO-66-IT was synthesized to extract mercury and phosphate ions from contaminated water. The synthetic strategy has been accomplished by preparing the Metal-Organic Framework (UIO-66-NH₂) followed by post-synthetic modification using the chelating ligand 2-Imino-4-Thioburit to form the UIO-66-IT adsorbent. The structure and the morphology of the adsorbent were investigated by a variety of analytical techniques including FTIR, XRD, XPS, SEM, TEM and BET surface area measurements. The adsorption of mercury and phosphate were optimized by studying the effect of pH, initial concentration, contact time, temperature, and competitive ions. The results revealed exceptionally high adsorption capacities toward mercury and phosphate ions of 700 and 160 mg/g, respectively at pH = 5.5 from the initial concentration of 1500 mg/L. The adsorption isotherms showed excellent agreements with Langmuir isotherm model indicating that the formation of a monolayer on the surface of UIO-66-IT. The kinetics of adsorption fitted well with the pseudo-second order kinetics model which suggests the chemical adsorption of mercury ions through the nitrogen and sulfur functional groups of the adsorbent and the physical adsorption of phosphate negative ions through protonated functional groups on the surface of the UIO-66-IT adsorbent. The results of selectivity studies showed removal efficiencies of 98.9% Hg(II) from a solution containing a mixture of 25 mg/L mixed metal ions. The results of regeneration showed that the adsorbent can be regenerated several times by using different concentrations of nitric acid for mercury or sodium chloride for phosphate with removal efficiencies higher than 90%. Therefore, the UIO-66-IT is introduced as a unique adsorbent to remediate polluted water from mercury and phosphate ions selectively.
Probing the Surface and Exchange Kinetics of the Ligand Layer of Metallic Clusters through Nanopore-based Single Molecule Detection

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Water-soluble metallic clusters capped with thiolated organic ligands have been of increasing interest in many nano-medicinal fields involving imaging for diagnostics[1], virus detection[2], and immunosensors[3]. There has been increasing interest in ligand exchange on the surface of these clusters to functionalize them for medical use and alter their toxicity[4]. Despite recent advances there are still many questions left unanswered about these particles. The use of ligands to functionalize clusters is now standard practice but an exact understanding of how these ligands behave when bound to the cluster surface remains a topic of interest, particularly at the single particle limit where the chemistry and kinetics give rise to the clusters’ bulk properties. The activity of the cluster and ligand layer is of particular interest when confined within a biological nanopore as many proposed bioapplications would require the cluster to traverse through narrow biological channels. Recently we have shown that single-molecule nanopore spectroscopy can be used to probe the dynamic nature of the ligand layer on gold clusters approximately 2 nm in diameter[5]. Individual clusters trapped in an α-hemolysin (αHL) pore for extended periods exhibit discrete structural transitions within the pore dependent on the mass and structure of the capping ligand. To expand on this we have recently begun performing ligand exchange reactions on individual clusters held within the pore environment to better characterize exchange rates and ligand fluctuation kinetics. This presentation will discuss these results as well as our most recent work investigating isomers of mercaptobenzoic acid ligands on the kinetics of the passivating layer.

Roadmap for the design and synthesis of Cluster Assembled Multi-functional Materials

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Atomic clusters, due to their unique size- and composition-specific properties, could form the building blocks of a new class of cluster-assembled materials provided they can retain their structure and properties when assembled [1]. One such cluster that has been studied extensively is Al₁₃⁻. With a total of 40-valence electrons, Al₁₃⁻ is considered a magic cluster due to its enhanced stability and chemical inertness towards oxygen [2]. In addition, neutral Al₁₃, with 39 valence electrons, is classified as a superatom mimicking the chemistry of a halogen atom [3]. The stability of XAl₁₃ (X=K, Cs) salt, both as a molecular species [4] and bulk material [5], has resulted in conflicting results. While in KAl₁₃ cluster Al₁₃ behaves like a halogen, crystalline form of XAl₁₃ is unstable. We studied the crystal structure and stability of XAl₁₃ where X is an organic cation, N(CH₃)₄. While N(CH₃)₄ maintains its structure, Al₁₃ clusters begin to coalesce, thus destroying their initial icosahedral geometry. To see if a non-metallic superhalogen cluster such as B(CN)₄ could be a better building block of a cluster-assembled salt, we studied the crystal structure and stability of N(CH₃)₄⁺B(CN)₄⁻ using density functional theory and generalized gradient approximation for exchange-correlation potential. The lattice dynamic and thermal stability of this super-salt was also studied using ab initio phonon calculations and molecular dynamics. N(CH₃)₄⁺B(CN)₄ bulk prefers a nearly body-centered-cubic (bcc) crystalline geometry where both N(CH₃)₄⁺ cations and B(CN)₄⁻ anions retain their individual gas-phase identity. Ab initio molecular dynamical simulations further confirm its thermal stability at room temperature with a band gap of ~6.5 eV. Our conclusion is that jellium rule that accounts for the stability of nearly free electron metal clusters is less robust than the octet rule that governs the stability of covalently bonded clusters for the design and synthesis of cluster-assembled materials. More importantly, unlike the ordinary salt NaCl, which possesses a highly symmetric non-polar bcc geometry, the reduced crystalline symmetry of N(CH₃)₄⁺B(CN)₄⁻ bulk results in the separation of cation and anion centers, producing spontaneous electric polarization. Since the band gap and electric polarization can be tailored by varying the size of the cations and anions, a large class of cluster-assembled multi-functional materials can be designed and synthesized. Note that the cations and anions used here in the design of the stable salt are commercially available. We look forward to the synthesis of this supersalt.

Effect Of Graphene Oxide (GO) In Synthesis of Gold Nanoparticles (AuNPs) Through Femtosecond And Nanosecond Laser Irradiation

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In this work we demonstrate the synthesis of reduced graphene oxide (rGO) supported gold nanoparticles (AuNPs) dispersed in water through femtosecond and nanosecond laser irradiation. This “green method” synthesizes mono-dispersed rGO-AuNPs that are stable at high temperatures without the use of any harmful chemical reducing agents or surfactants. The fast heterogeneous electron transfer kinetics, along with the high thermal, chemical, and mechanical stability of the rGO-AuNPs make them optimal for a variety of applications including catalysis, drug delivery, and photothermal therapy. UV-vis spectra were taken throughout the irradiation processes that produce rGO-AuNPs. Analysis of the resulting reaction kinetics shows two distinct mechanisms of [AuCl₄]⁻ reduction using femtosecond and nanosecond laser pulses when GO is absent. The addition of GO can be utilized to control the reduction kinetics of the precursor [AuCl₄]⁻ in the irradiation process. A change in mechanisms can also be established by increasing the concentration of GO, where the reaction mechanisms for femtosecond and nanosecond pulses converge at sufficiently high GO concentration. For both methods, the first step in synthesis of rGO-AuNPs is the reduction of GO. The rGO has a large surface area that contains several vacancies and defect sites where ultra small AuNPs can be stabilized. A distinct change in size of the anchored AuNPs can be observed through tuning the time required to completely reduce the GO, which can be achieved by varying the concentration of GO in the irradiated solution. Due to the change in mechanisms induced by the addition of GO, with an increase in GO concentrations in the precursor, a decrease in AuNP size is observed with femtosecond pulses, while an increase in AuNP size is observed with nanosecond pulses. Further characterization of rGO-AuNPs synthesized through both femtosecond and nanosecond pulses show that they outperform graphene oxide supported gold nanoparticles synthesized by traditional methods as catalysts for NaBH₄ reduction. This project will further explore the effects of GO on the femtosecond and nanosecond laser synthesis of AuNPs.
Synthesis of Ge\textsubscript{0.92}Sn\textsubscript{0.08}/SiO\textsubscript{2} Core-Shell Nanocrystals with Visible to Near-IR Photoluminescence

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The utility of semiconductor nanocrystals is often limited by toxicity, expense, or crude synthetic routes [1]. Low-cost, low-toxicity, colloidalysynthesized Ge\textsubscript{0.92}Sn\textsubscript{0.08} alloy nanocrystals are a convenient alternative, displaying attractive features such as bandgap tunability, solution processability, and silicon compatibility [2]. However, these materials have a notoriously low photoluminescent quantum yield (PLQY), due to the high probability of nonradiative surface recombination [3]. This happens because defects along the surface of the nanocrystal have a high affinity for excited electrons. The PLQY must be improved for Ge\textsubscript{0.92}Sn\textsubscript{0.08} particles to find applications in photonic devices or as biosensors. An intuitive solution is to coat the particles with a transparent, amorphous, inorganic material, such as silica (SiO\textsubscript{2}) to passivate the surface. Here, we have shown that Ge\textsubscript{0.92}Sn\textsubscript{0.08} nanocrystals can be functionalized with SiO\textsubscript{2} shells by employing a modified Stöber process [4], that is, the base-catalyzed hydrolysis of tetramethyl orthosilicate (TMOS) in a heterogenous mixture of dimethyl sulfoxide (DMSO) and toluene.

Figure 1: Ge\textsubscript{0.92}Sn\textsubscript{0.08} nanocrystals before (a) and after (b) growth of an SiO\textsubscript{2} shell

Crystal Phase Dependence on HER Water Splitting Performance of Earth-Abundant Ni$_{1-x}$Mo$_x$ Electrocatalysts

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Economical hydrogen production via renewable-energy-powered water splitting is only feasible with earth-abundant electrocatalysts exhibiting low over-potentials (<150 mV @ 10 mA/cm$^2$). Nickel-molybdenum alloys, as earth-abundant electrocatalysts, have been reported to show competitive HER activity over the past years. Herein, alkaline hydrogen evolution reaction (HER) over-potentials and polarization curves are presented for multiple stoichiometric ratios (Mo at.% = 0–11 %) and crystal phases (cubic and hexagonal) of Ni$_{1-x}$Mo$_x$ alloy NPs. Typically, alkaline media lends to higher transition metal stabilities over acidic media but limits low over-potentials. In our case, specific phases of Ni$_{1-x}$Mo$_x$ showed competitive over-potentials to platinum-based electrodes regardless of the alkaline electrolyte.

Colloidal nanocrystals were synthesized and drop-casted onto titanium foil to form pure-phase Ni$_{1-x}$Mo$_x$ electrodes. Electrodeposited, instead of drop-casted, films might result in good electrode stability and performance but does not easily elucidate experimental crystal phase dependence on HER over-potential. In particular, alloy NPs can differentiate between phase and composition dependence on HER activity whereas amorphous films cannot.

Structural crystal phase differences between different colloidal nanocrystal alloy compositions will be presented as x-ray photoelectron spectroscopy (XPS) spectra and x-ray powder diffraction (XRD) patterns. Electrochemical data, including polarization curves and Tafel plots, will also be presented. Specific insights into over-potential differences of alloys with similar elemental composition was gained and a discussion connecting higher valent surface states to low over-potentials will take place.

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Electrolysis-enabled water splitting presents an exciting and sustainable route to produce environmentally benign fuel to power human activities. However, fundamental technological challenges remain for its economical and widespread use. Nobel metal (Pt, Pd, Ru, Ir) catalysts show high catalytic activity and durability for water splitting, however their high cost and rare existence remain as main obstacles for commercialization of this technique. Low-cost, earth abundant transition metals (Ni, Mo, Co, and Fe) and their phosphides (Ni₂P, MoP, Co₂P, and FeP) are emerging as promising candidates to replace precious noble metals. Their activity can be further improved by alloying with a second transition metal because of the bifunctional synergistic effects. [1] Recently, our group reported the synthesis of Ni-Mo alloy NPs with varying crystal structures and elemental compositions as high efficiency, durable water splitting catalyst either comparable or superior to noble metal catalysts. [2] Incorporation of phosphorous is expected to further improve the catalytic activity due to changing the geometry and creating localized negative charges that attract protons and facilitate their coupling for hydrogen production. [3] Herein, we have used colloidal synthesis to produce two distinct crystal structures of Ni-Mo alloy NPs with a varying Mo composition (0-11.4%) and studied their chemical transformation into ternary Ni-Mo-P NPs with variable crystal structures, morphology, and compositions at moderately high temperatures. In addition, structure and composition dependent electrocatalytic activity and durability of Ni-Mo and Ni-Mo-P alloy NPs for water splitting was investigated using linear sweep voltammetry (LSV) and chronoamperometry. In this presentation, effect of synthetic and physical parameters on catalytic activity and water splitting efficiency will be discussed.

Rat Surfactant Replacement Therapy Using Enhanced Excipient Growth

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Rational: Surfactant is composed of lipids and proteins and its purpose is to keep the airways open and prevent them from collapsing by reducing the surface tension of airway surface liquid. The lungs are one of the last organs to develop, hence infants that are born prematurely may suffer from surfactant insufficiency. This lack of natural surfactant often leads to infant respiratory distress syndrome, IRDS, which affects about 6-7% of newborns [1] and it is more prominent with premature infants born 6 weeks early or more. To remedy IRDS, infants are put on breathing support and other therapies to keep the airway open. In addition to ventilation, surfactant replacement therapies such as Curosurf and Survanta have clear clinical benefits, however these biologicals are given in liquid form, which requires a large liquid volume in order to reach the alveolar region. Instillation of a large volume of liquid into already injured lungs has been associated with several unwanted side effects causing some to suggest the use of aerosolized surfactant. Our group is developing an excipient enhanced growth (EEG) aerosolized surfactant approach for the rapid and high efficiency delivery of surfactant powders to the alveolar.

Methods: After anesthesia, Sprague Dawley rats were surfactant depleted using two 1x phosphate buffer saline lavages. Lung ventilation mechanics (LVM) were taken before depletion and after depletion. Those mechanics included compliance (expansion of the lung due to pressure), elastance (elastic deformation of the lungs) and resistance (relationship between pressure and airflow rate). After surfactant depletion, rats were given either EEG Survanta (3, 5, 10, and 20 mg) using a custom aerosolization device or liquid Survanta (2 ml/kg) through typical liquid instillation down an endotracheal tube followed by 10 minutes of mechanical ventilation at 8 ml/kg. After surfactant administration and ventilation, LVM were again taken. The inflammation was assessed via cytospin of bronchoalveolar lavage fluid onto microscope slides.

Results/Discussion: Groups receiving EEG Survanta had LVM that were closer to healthy conditions compared with the liquid Survanta groups. Moreover, lower doses of EEG Survanta (such as 3 mg) was better at improving mechanics than higher EEG Survanta doses, potentially due to better delivery to the deep lung from the custom device when delivering a lower powder dose. In addition, inflammation assessment using cytospin show no significant differences among all treatment groups and all groups also had a low neutrophil count. Overall, spray dried EEG Survanta significantly improved compliance and elastance of lungs compared to commercially available Survanta and did not lead to increase neutrophil count.

Thermal Impact on Emission and Structure of GaAs/AlGaInAs Heterostructures with InAs Quantum dots covered by strain reduced capping layers

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InAs quantum dots (QDs), grown by MBE in the Stransi-Krastanov growth mode, attracted the great attention as an active medium for low threshold lasers, photodiodes, solar cells and memory devices. The development of InAs QD structures with a high QD density, uniform QD sizes and significant thermal stability, was a primary goal for InAs QD structures in the last decades.

InAs QDs embedded in MBE grown GaAs/Al₀.₃₀Ga₀.₇₀As/AlGaInAs/Al₀.₃₀Ga₀.₇₀As/GaAs heterostructures have been investigated in as grown state and after thermal annealing at 710°C. Three types of QD structures with the different compositions of AlGaInAs capping layers for QDs: GaAs (#1), Al₀.₃₀Ga₀.₇₀As (#2) and Al₀.₁₀Ga₀.₇₅In₀.₁₅As (#3) and the same buffer layers (In₀.₁₅Ga₀.₈₅As) are compared and studied by means of photoluminescence (PL), X-ray diffraction (XRD) and high resolution HR-XRD methods. XRD and HR-XRD techniques are applied to control varying the crystal structures, material compositions and elastic strains in quantum wells at thermal annealing.

The highest PL intensity, smaller PL band half width and lower energy of ground state (GS) emission are detected in the structure with the Al₀.₁₀Ga₀.₇₅In₀.₁₅As capping. Thermal annealing leads to the shift of PL spectra into higher energy range and the value of this shift is more essential for Al₀.₁₀Ga₀.₇₅In₀.₁₅As capping as well. The GS peak variation versus temperature has been monitored within the range of 10-450K and compared with thermal shrinkage of band gap in the InAs crystal. It permits to reveal that the QD composition in #3 is closer to InAs, and the efficiency of Ga/In intermixing at annealing in #2 is less than in #1 and #3. Composition varying the QDs and QWs at annealing has been modeled by the simulation of HR-XRD results with Xpert Expitaxy software.

Finally, the reasons of PL spectrum transformation at annealing, the mechanism of PL thermal decay, and the advantages of the QD structure with Al₀.₁₀Ga₀.₇₅In₀.₁₅As capping layer have been analyzed and discussed.
Applications of Interferometry to Medicine on the Nanoscale

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Interferometry has long been used to measure surface imperfections in lens and mirrors at the nanoscale. The same capabilities for measuring changes in distance with great precision can be applied to biological substrates to measure changes in the homeostasis of biological material within a living cell over time. These dynamic measurements can inform us of how cells regulate their biomass in response to stress, and potentially inform a patient’s response to drug treatment.

High-Speed Live Cell Interferometry (HSLCI) incorporates interferometric measurements into a scanning platform that enables the tracking of the changes in biomass for thousands to tens of thousands of cells at once. This higher throughput makes it possible for HSLCI to become a screening platform for drug sensitivity testing. HSLCI has shown promise by predicting the relative sensitivity to carboplatin of three patient derived xenograft (PDX) triple negative breast cancer (TNBC) mouse models [1]. When single cells from tumors were exposed to carboplatin, many of those cells from tumors that were sensitive began losing mass or stopped growing. In contrast, single cells from resistant tumors continued growing. The single cell sensitivity of HSLCI enabled the identification of resistant single cells in the sensitive tumors which could be the source of resistant cancer recurrence in patients. Such single cell sensitivity is unavailable to most screening methods which average a signal from thousands of cells.

An additional barrier to application in the clinic is the acquisition of patient material. Patient samples must be acquired with the minimum invasiveness to the patient which necessitates the use the fine needles and limits the possible number of live cells to the low thousands. The precise nanoscale measurements of HSLCI maximize the information obtained from these small samples. In four separate biopsies of the HCI09 TNBC tumor, HSLCI was able to screen enough cells to demonstrate HCI09’s in vivo resistance to carboplatin.

Thermophysical properties of ethylene glycol-based nanofluids containing magnesium oxide: possible applications in heat exchanging systems

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Nanofluids are stable suspensions of nanoparticles in liquids. Those class of nanomaterials exhibit higher, than pure base fluid, thermal conductivity as reported for the first time by Choi and Eastman [1]. According to this physical properties it seems to be a nice engineering material that could find many industrial applications [2]. However, beside the thermal conductivity enhancement, there is observed also viscosity increase which leads to less effective use of those materials in the above-mentioned systems.

The main goal of this paper is to perform measurements of the thermal conductivity and dynamic viscosity of ethylene glycol based nanofluids containing magnesium oxide nanoparticles (MgO-EG) and compare the experimental results with predictions of the theoretical models. All measurements were performed in strictly controlled conditions. Later, those results are applied to evaluate the benefits of using those materials to enhance the heat exchange in advanced energy systems. Two possible flow types has been considered: (a) laminar flow (by check the Prasher criterium) and (b) turbulent flow (by calculating Mouromtseff number and its’ ratios). The detailed description of the used materials and techniques used in this study could be found in Ref. [3].

Strategic Design of Highly-Efficient Solar Water Purification System with rGO-Modified Plasmonic Nanocomposite

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ABSTRACT
Solar energy based water purification system has been considered as a great solution to clean the sewage water. Traditional technologies provide the complicated solar water purification system with high cost and very low efficiency. Here we have offered a very simple and state-of-the-art solar water purification system by utilizing graphene and plasmonic nanocomposite as a promising component to improve the efficiency. We have synthesized the graphene-plasmonic nanocomposite by using sol-gel technique. Advanced graphene-plasmonic nanocomposite has been implemented for contaminated water to design the water purification system under the sun light. The nanocomposite has been combined with water in the presence of sunlight, it captured the contaminated components, and pure water converted into vapors, which have been collected on another chamber. We have achieved the purification rate of 2.6 kg h⁻¹m⁻¹g⁻¹ and efficiency of about 80% under the sunlight. Results showed that a competent nanocomposite provides an ideal change in solar water purification system by using simple technique. The morphology and chemical composition of advanced graphene-plasmonic nanocomposite have been studied by field emission scanning electron microscope (FE-SEM) and energy-dispersive X-ray spectroscopy (EDX) respectively. Crystal structure and absorption spectra were analyzed by X-ray diffraction (XRD) and UV/Vis Spectroscopy. Furthermore, pure drinkable water has been achieved from sea water under normal environmental conditions.

Keywords: Graphene, plasmonic nanocomposite, solar water purification system.
Repetitively Coupled Chemical Reduction/Galvanic Exchange as a Synthesis Strategy for Largest Ever Pt Nanoparticles Encapsulated inside Dendrimers

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Recently, we reported the controllable synthesis of Pt dendrimer-encapsulated nanoparticles (DENs) having up to 1320 Pt atoms without being compromised by the fixed number of complexation sites for Pt²⁺ precursor ions in the dendrimers.[1] In the new synthetic approach, the synthesis of Pt DENs is achieved in a short period of time (i.e., ~10 min) simply by the co-addition of appropriate amounts of Cu²⁺ and Pt²⁺ precursors into aqueous dendrimer solution and subsequent addition of reducing agents such as BH₄⁻. This results in fast and selective complexation of Cu²⁺ with the dendrimers and subsequent chemical reduction of the complexed Cu²⁺ while uncomplexed Pt²⁺ precursors remain oxidized. Interestingly, the chemical reduction of Cu²⁺, leading to the formation of Cu nanoparticles encapsulated inside the dendrimers, is coupled with the galvanic exchange of the Cu nanoparticles with the nearby Pt²⁺. This coupling repetitively proceeds until all of the added Pt²⁺ ions form into Pt nanoparticles encapsulated inside the dendrimers. In contrast to the conventional method utilizing direct chemical reduction, this repetitively coupled chemical reduction/galvanic exchange enables a substantial increase in the applicable number of Pt atoms up to 1320 in Pt DENs while maintaining unique features as DENs. The significance of the expanded number of atoms in Pt DENs is also demonstrated with the catalysis of Pt DENs for the hydrolytic dehydrogenation of ammonia borane, which is found to be sensitive to the subtle changes in the number of Pt atoms in the expanded range of small sizes.

**In Silico Design of Fullerene-Based Nanovectors for Transport of Anticancer Drugs Through the BBB**

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In this work we present a computational study and *in silico* design of sixteen fullerene-based nanovectors as carriers of certain anticancer drugs that seek to improve their passage through the blood-brain barrier (BBB). C₆₀ molecules were functionalized with four different organic linkers and thereafter combined with four anticancer drugs: 5-Fluorouracil (Fig. 1), chlorambucil, carmustine and 1-methyl-1-nitrosourea¹². The selected free drugs can penetrate the BBB at minimum percentages, and we show that the formation of the nanovectors can improve that capacity. The calculations were made at the Density Functional Theory (DFT) level of theory, with the M06-L³ functional, the 6-311G(d, p) basis set, and the PCM model to account for the solvent. On the other hand, chemoinformatic calculations were also performed to predict the free drugs and nanovectors penetration of the BBB, using a computed QSAR model⁴. The results suggest that the set of sixteen nanovectors studied possess the physicochemical properties required for the transport of drugs through the BBB, which we evaluate through computation of the conceptual DFT³ global descriptors of reactivity, the dipole moment and the Gibbs free energies of solvation in water and in n-octanol. The QSAR model results are in good agreement with the DFT results, showing that the percentage of crossing through the BBB of the designed nanovectors increases in comparison with the free drugs.

![Optimized structure of the 5-Fluorouracil drug linked to a C₆₀ fullerene molecule.](image)

**Figure. 1.** Optimized structure of the 5-Fluorouracil drug linked to a C₆₀ fullerene molecule.

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One-Step Synthesis of Catalytically Active “Naked” Palladium Nanoparticles via Femtosecond Laser Irradiation in Aqueous solution

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We report the one-step synthesis of naked palladium nanoparticles (PdNPs) via femtosecond laser irradiation of aqueous palladium solutions. Intense femtosecond laser pulses in H₂O result in the photolysis of water which, in turn, generates solvated electrons and reactive species that aid in the reduction of the palladium salt precursor [1]. To understand and optimize the formation of the colloidal PdNPs, we investigated the effect of adding different acids (HCl and HNO₃) to different palladium salt precursors (K₂PdCl₄ and Pd(NO₃)₂). Analysis of TEM images reveals that PdNPs synthesized with both Pd(NO₃)₂ and K₂PdCl₄ produced isolated nanoflower shapes with products from Pd(NO₃)₂ being smaller and more monodisperse. The naked PdNPs were catalytically active toward the model para-nitrophenol reduction by sodium borohydride reaction. The synthesis, characterization and formation mechanisms of catalytically active PdNPs will be discussed.

![Figure 1](image1.png)

Figure 1. PdNPs synthesized with (a) K₂PdCl₄ and HCl (b) Pd(NO₃)₂.

![Figure 2](image2.png)

Figure 2. k_app values of nanoparticles followed over time for Pd NPs synthesized with K₂PdCl₄ and HCl (red squares), Pd(NO₃)₂ (green triangles) and Pd(NO₃)₂ and HNO₃ (cyan diamonds).

**Supported Copper Nanocatalysts for Selective CO\(_2\) Hydrogenation**

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We report the synthesis and characterization of supported copper oxide nanoparticles exhibiting selective CO\(_2\) hydrogenation. These nanocatalysts are generated from a one-step femtosecond reactive laser ablation in liquid (fs-RLAL) technique [1]. By combining two laser-assisted approaches for generating nanoparticles- ablation and photochemical reduction- into one step, we are able to generate various composite nanomaterials efficiently. For example, copper nanoparticles (Cu NPs) stabilized in a silica matrix were generated by focusing fs laser pulses onto a silicon wafer immersed in an alkaline copper (II) nitrate solution. Figure 1a shows a TEM image with histogram of the 3.52 nm Cu NPs stabilized throughout an amorphous matrix. When the fs-RLAL technique was carried out in more acidic Cu(NO\(_3\))\(_2\) solutions (pH 5.6, 2.9), very little copper was detected in the silica matrix, determined by SEM-EDX and XPS analysis. This pH-dependent interaction between the Cu\(^{2+}\) ions and the ablated silicon atoms in solution was observed when the catalytic activity of the products was tested using a model para-nitrophenol reduction reaction [2]. Figure 1b shows the relationship between the catalytic rate constant (\(k_{\text{app}}, \text{s}^{-1}\)) and the wt.% of Cu determined from XPS. The Cu-silica nanocatalyst exhibits up to 75% CO\(_2\) conversion by 750ºC, with 100% selectivity to methane formation. This presentation will discuss the versatility of the fs-RLAL approach to different support materials and the effect on the catalytic activity toward CO\(_2\) hydrogenation.

![Figure 1](image)

**Figure 1.** TEM image with histogram of Cu-SiO\(_2\) nanocatalyst (a). Catalytic rate constant versus wt.% Cu detected from XPS analysis of Cu-SiO\(_2\) samples generated from different solution pH's (b).

Reax-Simulation and *in vitro* Assessment of Differentially charged PEGylated Polymeric Nanoparticles as Platelet Anti-aggregant Drug Delivery System

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Nanotherapeutics is a promising field for numerous diseases and represents the forefront of modern medicine [1]. Polymeric nanoparticles are a special kind of carriers used in drug delivery systems mainly because of their biodegradation and biocompatibility properties [2,3]. In the present work, full atomistic computer simulations were applied to study cilostazol-loaded (antiaggregant compound) hybrid poly(lactic) acid (PLA) and polyethylene glycol (PEG) polymeric nanoparticles with a different surface charge (positive, negative and neutral) using the reactive polarizable force field ReaxFF. An *in silico*/experimental strategy was carried out, which provided the molecular characterization of the nanosystem, its synthesis, and the assessment of the nanoparticle-drug influence on the inhibition of platelet function.

The results suggest that the combination of molecular dynamics ReaxFF simulations and blind docking techniques can be used as an explorative tool prior or as a complementary approach to experiments, which is useful for rational design of new drug delivery systems. We designed differentially charged PEGylated lipid-polymer nanoparticles with ideal properties for biomedical use in terms of morphological and structural features, like a size range 100-120 nm and a negative charge of ~ -40 mV [4,5]. However, only the carboxy-terminated (negative) hybrid nanoparticles comprises a feasible nanosystem for cilostazol release in terms of human platelet compatibility *in vitro*, while methoxy-terminated (neutral) nanoparticles were not. The cilostazol-loaded negative nanoparticles have an antiaggregant activity induced by ADP 4 μM and does not interfere with platelet activation process. The obtained results are consistent with the hypothesis that the hemocompatibility of nanoparticles is governed by the combination of size, composition and surface charge [6]. The present work provides evidence to continue the research, design, and optimization of a new nanosystem with therapeutic approaches for cardiovascular diseases.

From Molecules to Mono-layers: A Study in Evolution

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One of the primary motivations for studying clusters has been to answer a fundamental question: when does a cluster become a crystal? More than half a century and 200,000 papers later, no satisfactory answer to this question has emerged. The main reason is that the nature of evolution depends not only on the systems under consideration but also on the properties being studied. For example, the structures of metal and non-metal clusters evolve differently, the former exhibiting icosahedral pattern while the latter clusters such as those of C and B exhibit, respectively, linear and planar structures at small sizes.

To address this question, we considered two simpler systems - two dimensional (2D) graphene with zero band gap and boron nitride with 4.46 eV band gap. We studied the evolution of geometry, energy gap between the highest molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO), electron affinities (EA) and ionization potentials (IP) by starting with the most fundamental unit – benzene and borazine molecules and systematically building larger complexes by adding concentric rings, \( n \) as shown in Fig. 1. The dangling bonds of these complexes are saturated with H, F, BO, and CN ligands. The corresponding clusters studied are \( \text{C}_n \text{X}_n \) and \( (\text{BN})_n \text{X}_n \) (\( n=1-5, \text{X}=\text{H, F, BO, CN} \)). The geometries were optimized using the density functional theory with generalized gradient approximation and hybrid functionals.

![Fig. 1 The geometries of \( \text{C}_n \text{X}_n \) (left) and \( (\text{BN})_n \text{X}_n \) (right) complexes](#)

The HOMO-LUMO gaps of \( \text{C}_n \text{X}_n \) clusters are found to decrease steadily as the number of concentric hexagonal rings, \( n \) increases, but does not vanish even when the number of C atoms reach 150. However, the effect of ligands on the HOMO-LUMO gap diminishes by this size. The IP values show the same evolutionary pattern as the HOMO-LUMO gaps.

The evolution of the \( (\text{BN})_n \text{X}_n \) complexes shows a somewhat different pattern. While the HOMO-LUMO gaps decrease with size, they approach the monolayer limit by the time there are five concentric rings of B and N atoms. However, the IP values converge to the 2D limit rather slowly. Based on these results, we conclude that it is difficult to answer “when a cluster becomes a crystal?” even in simple systems where clusters, like their 2D counter parts, are planar.
Laser Synthesis of Metal Oxide Nanostructures as Catalyst Support for Pd Nanoparticles for Suzuki Cross-Coupling Reactions

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Laser Irradiation in Solution (LIS) was used to deposit Pd nanoparticles on SiO₂, TiO₂, ZrO₂, and ZnO nanostructures prepared by the laser vaporization-controlled condensation (LVCC) technique. A 100% conversion to the biphenyl product form the reaction of bromobenzene and benzeneboronic acid was achieved by the LIS Pd-LVCC TiO₂ catalyst within 5 min under microwave reaction conditions at 60 °C. Also, more than 70% conversion to the biphenyl was achieved within 15 min under room temperature reaction condition. The surface areas of the oxides synthesized by LVCC were measured by BET analyses, and TiO₂ was shown to have a significantly higher porosity than the other oxides. Pd nanoparticles were also deposited on the oxides using the microwave-assisted chemical reduction method (MWI). The LIS reduced catalysts were found to be superior due to the smaller Pd particles’ size (5.2 ± 2.7 nm) compared to the MWI reduced Pd catalysts (6.7 ± 3.6 nm). The LVCC TiO₂ support was also compared with hydrothermally prepared TiO₂. The LIS method was used to deposit Pd on hydrothermally prepared TiO₂ supports. The anatase-to-rutile phase characteristics were tuned by TiO₂ hydrothermal syntheses to model an ideal ratio for the Suzuki Cross-Coupling reaction. The LIS Pd-LVCC TiO₂ catalyst was found to be superior among all the catalysts studied with turn over frequency (TOF) as high as 933 h⁻¹.
Laser Synthesis of Carbon Supported Bimetallic Au-Pd Catalysts for Benzyl Alcohol Oxidation

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The laser synthesis of Au-Pd bimetallic nanoparticles supported on oxidized Darco G60 activated carbon by pulsed Laser Irradiation in aqueous Solution (LIS) is demonstrated for the catalytic oxidation of benzyl alcohol. The Laser synthesis process is a tunable, effective and green process for the synthesis of heterogeneous catalysts. A series of catalysts were prepared with different Au/Pd ratios and varying the laser irradiation times. The effect of consecutive and simultaneous preparation of the Au-Pd nanoparticles was also investigated. In the consecutive synthesis process, Au nanoparticles were deposited on 3%Pd/C catalyst whereas, in the simultaneous synthesis process, Au and Pd nanoparticles were deposited at the same time on the carbon support. The effect of the irradiation time to reduce the metal precursor on the support was also studied. It is found that as the laser irradiation time for the preparation of 3%Pd/C decreases from 12 minutes to 1 minute, the average Pd particle size decreased from 5.5 nm to 4.3 nm. The catalytic activities of the various catalysts were tested for benzyl alcohol oxidation. The 3%Pd/C (LIS) 1 min catalyst proved to be the most active among all the catalysts studied. This catalyst achieved 100% benzyl alcohol conversion within 3 hours with a turn-over frequency (TOF) 16,784 h⁻¹. The 3%Pd/C (LIS) 12 min catalyst showed decreased activity with a TOF of 4,825 h⁻¹ due to larger average Pd particle size. Simultaneously prepared 5%Au/3%Pd/C achieved 100% conversion in 4 hours with a TOF as high as 9,555 h⁻¹ while maintaining high selectivity towards benzaldehyde. The consecutively prepared 5%Au/3%Pd/C catalyst achieved 100% conversion in 7 hours. The highest catalytic activities correlates with the smallest particle size of the Pd nanoparticles.
Iron Phosphide Doped-porous Carbon as an Efficient Electrocatalyst for Oxygen Reduction Reaction in Alkaline Fuel Cells

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The increase in energy demands [1] and the environmental concerns, has required researchers to make the development of clean and sustainable energy conversion devices a priority. Pt-loaded carbon substrate is the catalyst of choice in fuel cells for anodic oxidation of H₂ and cathodic reduction of O₂ but large-scale production is restricted by its cost, limited supply, weak durability and easy loss of activity through methanol poisoning. [2]

Dual-dopants combination of heteroatom and transition metal doped porous carbon materials are the highly considered candidates and are well researched because of their high abundance and low cost. Electrocatalyst composed from transition metals and nitrogen doped carbon materials or solely nitrogen doped carbons have shown competitive performance towards the ORR. [3] In contrast to nitrogen, phosphorus has a larger atomic radius and higher electron-donating ability making it a promising dopant capable of modifying the electron transport properties of the graphitized porous carbon. Incorporation of iron into a phosphorus-doped carbon matrix through high temperature carbonization led to the formation of various Fe-P compounds giving rise to a series of ORR active electrocatalysts having enhanced kinetics. [4]

Here we report a viable synthesis of P and Fe-doped porous carbon (PFeC) using triphenylphosphine as a single source precursor for both carbon and phosphorus through a simple one-step carbonization-chemical activation route using anhydrous ZnCl₂ and FeCl₂. The electrocatalytic activity towards ORR was studied using a rotating ring-disk electrode technique. PFeC showed high activity towards ORR. PFeC electrocatalyst selectively catalyzes oxygen to water via a direct four-electron pathway also showed to be inert toward alcohol oxidation and had superior long-term stability.

Wetting Translucency of Conducting Graphene in Polar and Nonpolar Liquids

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Contact angle measurements revealed that the underlying substrate can exert a significant effect on the contact angle, CA, of graphene, a phenomenon called wetting transparency or translucency. CA measurements conducted on the suspended graphene compared to the supported one, as well as molecular dynamics simulations on submerged graphene fragment in water have consistently shown the CA reduction when graphene was wetted from both sides, but the magnitude of the effect varied. So far, computer simulations of CA for water on graphene relied on simplified force fields ignoring the material’s conducting properties. We improved the graphene model by incorporating the conductivity of graphene sheet by applying the fluctuation charge technique of Constant Potential Molecular Dynamics (CPMD). We evaluated the wettability by measuring the contact angle of cylindrical water drops on a conducting graphene sheet. We found that the contact angle of a water droplet on a graphene sheet submerged in water is lower than in the absence of water under graphene. Our calculations reveal effective attractions between partial charges of equal sign across the conducting graphene sheet. Attractive correlations are attributed to the formation of the highly localized image charges on carbon atoms between the partially charged sites of water molecules on both sides of graphene. By performing additional computations with nonpolar diiodomethane, we confirm that graphene is transparent to both polar and dispersive interactions. These findings are important in applications including sensors, fuel cell membranes, and water filtration, and graphene-based electrode material to enhance the supercapacitor performance.
Atomically Precise, Thiolated Copper-Hydride Nanoclusters as Single-Site Hydrogenation Catalysts for Ketones in Mild Conditions

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Copper-hydrides are known catalysts for several technologically important organic reactions such as hydrogenation of CO, hydroamination of alkenes and alkynes, and chemoselective hydrogenation of unsaturated ketones to unsaturated alcohols. Stabilizing copper-based particles by ligand chemistry to nanometer-scale is an appealing route to make active catalysts with optimized materials economy, however, it has long been believed that the ligand-metal interface, particularly if sulfur-containing thiols are used as stabilizing agent, may poison the catalyst.

In this work [1], we have discovered an ambient-stable thiolate-protected copper-hydride nanocluster \([\text{Cu}_{25}\text{H}_{10}(\text{SPhCl}_2)_{18}]^{3-}\) that readily catalyzes hydrogenation of ketones to alcohols in mild conditions. A full experimental and theoretical characterization of its atomic and electronic structure shows that the ten hydrides are instrumental not only for the stability of the nanocluster but also play an active role in the catalytic process by being the source of hydrogen for the reaction. The \(\text{H}^+\) ions are continuously consumed and replenished during the hydrogenation reaction. Density functional theory computations suggest, backed up by the experimental evidence, that the hydrogenation takes place only around a single site of the ten hydride locations, rendering the \([\text{Cu}_{25}\text{H}_{10}(\text{SPhCl}_2)_{18}]^{3-}\) one of the first nanocatalysts whose structure and catalytic functions are characterized fully to the atomic precision.

Understanding of a working catalyst at the atomistic level opens doors to further optimization of its properties and provides fundamental new insights into the controversial issue why a stable, ligand-passivated, metal-containing nanocluster can be at the same time an active catalyst.

Towards Atomically Precise Supported Catalysts from Monolayer-Protected Clusters: The Critical Role of the Support

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Controlling the size and uniformity of metal clusters with atomic precision is essential for fine-tuning their catalytic properties, however for clusters immobilized on porous supports such control is exceptionally challenging. Here by combining X-ray absorption spectroscopy and density functional theory calculations, we demonstrate that supports play a crucial role in the evolution of monolayer-protected clusters into supported catalysts.

We find that on Brønsted acidic supports such as SiO₂, under mild conditions, cluster-support interactions lead to oxidative fragmentation of a phosphine-stabilized Auₙ cluster into isolated Au-ligand species, while on Lewis acidic supports such as CeO₂, the cluster-support interactions lead to the formation of ligand-free metallic Au⁰ nanoclusters. The latter transformation, as demonstrated for various sizes of the Auₙ cluster, occurs with the preservation of the size of the cluster, yielding atomically precise and ligand-free supported nanoclusters. These findings represent an important step towards the synthesis of atomically precise nanocatalysts with tailored physico-chemical properties.

Fig. 1 A schematic summarizing the evolution pathways of a phosphine-stabilized \([Auₙ(PPh₃)₈]^{3+}\) cluster. The cluster remains unchanged upon heating or immobilization on supports at 25 °C, however, it undergoes a transformation on the supports upon heating to 120 °C.
There’s a whole lot of nano down there!
Exploring the capabilities of high-speed atomic force microscopy

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Traditional methods of microscopy have an inherently limited field of view that often decreases rapidly with increased resolution. Many devices are limited to a sub-micron field of view to achieve their best resolution. While the quality of information obtainable by many modern tools such as scanning or transmission electron microscopes, or atomic force microscopes (AFM) is constantly getting better with an ever increasing array of imaging modes; the limited sample throughput of these tools demands the assumption that every sample is homogenous from a few select data points. This is of course never true at the nanoscale. AFMs are capable of high-resolution imaging of structures and the measurement of mechanical properties at nanometre scales within gaseous, liquid and vacuum environments. The contact mode high-speed AFM (HS-AFM) developed at the University of Bristol \cite{1} operates at speeds orders of magnitude faster than conventional AFMs, capturing multiple megapixel frames per second. These speeds enable three distinct capabilities for HS-AFMs that set them apart from their conventional counterparts. Firstly, their microsecond temporal resolution allows for the direct observation of dynamic nano and microscale events in real-time \cite{2}. Secondly, regions hundreds of microns square can be scanned, and their nanoscale surface structures characterised in minutes. This can be used to provide significantly greater statistical confidence when measuring distributions and populations of nanostructures. Finally, millimetre and even centimetre-sized areas can be mapped in hours, collecting data on the long-range ordering and distribution of nanoscale features across the macroscale object or surface. I will present examples of these three capabilities using recent studies including the characterisation of 2d materials \cite{3,4}, the measurements of degradation in stainless steels \cite{2,5}, and next generation genome sequencing \cite{5}.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{phosphorene_nanoribbons.png}
\caption{High-speed atomic force microscopy topography maps of 1 to 5 layer thick sections of 2d phosphorene nanoribbons.}
\end{figure}

Induced Magnetic Field in Thiolated Polyhydrides Copper Nanoclusters

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Copper hydrides have received increasingly attention due to the fascinating activity as intermediates in catalysis and hydrogen storage [1-3]. In this work we compute the NMR shifts of $^1$H copper hydrides for three different Cu protected nanoclusters, $\text{Cu}_{20}$H$_{11}$($\text{S}_2\text{PH}_2$)$_9$, $\text{Cu}_{25}$H$_{10}$($\text{SCHCl}_2$)$_{18}$ and $\text{Cu}_{32}$H$_{20}$($\text{S}_2\text{PH}_2$)$_{12}$, as coded in deMon2k employing the auxiliary density functional theory (ADFT). Two different GGA xc-functionals (BP86 and PBE) and two basis sets (def2-TZVP and aug-cc-pVDZ) are employed to test the reliability of the NMR shifts in comparison with the experimental values [1-3]. To evaluate the response to a 1T external magnetic field we plot the contour planes of the induced magnetic field (IMF). We show the direct correlation between shielding and de-shielding observed for the hydrides in the three different systems. Additional Born-Oppenheimer Molecular Dynamics (BOMD) have been recorded for 10ps to demonstrate the evolution on time of the $^1$H shifts and the dependence of the induced magnetic field response.

Hydroxyapatite Nanoparticle Density not Nanoscale Topography Regulates Osteoblastic Differentiation and Integrin Expression

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Introduction: Manipulating substrate nanotopography to regulate osteogenesis has extensive clinical implications. Previous studies have shown a correlation between the substrate characteristics such as roughness and hydrophobicity and the substrates ability to regulate osteogenesis [1,2]. Despite this, a singular characteristic has not been shown to consistently regulate osteogenesis on a host of substrates, suggesting another factor may be more significant in regulating osteogenesis [2]. In this study, we evaluated various substrates of similar surface properties to determine if particle density positively regulates osteoblastic differentiation.

Materials & Methods: Polycaprolactone (PCL) was dissolved in chloroform at a 2.5% wt./vol ratio. 200nm carbonated hydroxyapatite nanoparticles (HA) were suspended in solution at a 5%, 30%, and 50% wt./wt. ratio with PCL. A 200nm thick coating was then created on glass coverslips using a dip coating technique. The substrates created were then characterized for roughness, \(z\)-range, hydrophobicity, and particle density with PCL without HA used as a control. Each substrate was then seeded with hFOB 1.19 cells, a fetal osteoblastic cell line. After 48 hours integrin expression for integrin \(\alpha_2, \alpha_3, \alpha_5, \beta_1, \) and \(\beta_3\) was examined on the various substrates using flow cytometry. After 7 days alkaline phosphatase (ALP) activity, a marker of osteoblastic differentiation was examined for all substrates.

Results & Discussion: All substrates had similar \(z\)-range, roughness, and contact angle (°) values of approximately 1000nm, 20-25 nm, and 80-85° respectively. The PCL, 5%, 30%, and 50% substrates did however have a significantly different particle density of 3, 16, 56, and 155 particles per centimeter respectively. ALP activity increased roughly 2-fold on the 30% substrate compared to all other variants and roughly 3-fold compared to PCL controls. No other substrate exhibited significant changes in ALP activity compared to all other substrates. Expression of integrins \(\alpha_5, \beta_1, \) and \(\beta_3\) were all down regulated on the 30% substrate compared to PCL controls but not compared to any other substrate we examined. This data suggests that nanoparticle density is a main factor in the regulation of osteoblastic differentiation and may be regulating osteogenesis through integrin expression. It has been shown that integrin expression is highly regulated based on nanoscale properties and in turn regulates cell mechanotransduction.

Conclusion: The nanotopography of substrates plays a critical but complex role in mediating osteoblastic differentiation with many factors contributing to the overall response. This study suggests that in addition to other characteristics, the density of nanoparticles on the surface may significantly influence the substrates ability to induce osteoblastic differentiation and in turn osteogenesis.

Nanoporous Organic Polymers for Revisable Capture of Radioactive-Volatile Iodine

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Fossil fuels constitute the primary source of energy today. While they are energy dense and reliable, they have taken a massive toll on the environment. Both the extraction and combustion of fossil fuels emit harmful greenhouse gases, most prominently, carbon dioxide, which is believed to be the main cause of climate change and global warming. Nuclear energy is considered as one of the most prominent alternative to fossil fuels given its high energy density and low carbon footprint. However, exhaust fumes coming off nuclear power plants contain high percentage of radioactive materials such as $^{129}$I and $^{131}$I isotopes that have half-lives of about 8 days and 15.7 million years, respectively, and thus impose major environmental and health concerns. As a result, there is a great need to develop novel materials that are capable to capture and store iodine vapor before its release into the atmosphere.

Porous organic polymers (POPs), made of covalently bonded-light atoms such as C, N, O, and S, are considered one of the most promising iodine sorbents given their high surface areas, remarkable thermal and chemical stabilities, and tunable functionality. In this work, we report on the synthesis and characterization of two nitrogen-rich, highly porous organic polymers, employing a metal-free, one-pot synthesis, by reacting 9,10-bis(3,5-diaminotetrazine)anthracene and 1,4-dibenzaldehyde or thieno[2,3-b]thiophene-2,5-dicarbaldehyde in DMSO at 180 °C, to afford NRPOP-1 ($S_{BET} = 544 m^2 g^{-1}$) and NRPOP-2 ($S_{BET} = 424 m^2 g^{-1}$), respectively. The two polymers display high iodine uptake (NRPP-1, 281 wt. %) and (NRPP-2, 271 wt. %) and able to release more than 98 % of the loaded iodine when immersed in polar organic solvent at room temperature. The exceptional performance of these polymers in iodine removal ranks among the best of POPs and makes them very promising materials in solving a major environmental concern.
Fabrication and Electrical Characterization of a Flagella-Scaffolded Metallic Nanocluster Network

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Bacteria produce rotary filamentous appendages, known as flagella, for propulsion through their environment in response to various chemical signals. The flagella, of nanoscale width and of microscale length, can be easily isolated from the microorganisms at low cost and in large quantities. Once isolated, these nanofilaments of uniform size distribution can be deposited onto desired surfaces in controlled quantities (Figure 2) and can act as novel templates for nanostructures. Flagella placed on a surface prior to deposition of soft-landed nanoclusters could act as scaffolds in the construction of nanoparticle networks. We will present on the progress towards the fabrication and characterization of nanocluster chains supported by bacterial flagella in a suspended micro-trench device design. Future work with these organized nanocluster/flagella devices with varying cluster material and tuned size-selection could then be used to investigate various unique quantum and nanoscale properties exhibited by finite-size systems. These include enhanced surface plasmon resonance, catalytic applications, charge tunneling junctions, and Josephson current in potential superconducting arrays.

\textbf{Figure 2: Atomic force microscope height image of isolated bacterial flagella deposited on silicon oxide.}

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Polyamidoamine Dendrimer Gene Delivery via Complexation with a Nuclear Localization Sequence Peptide

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Introduction: Polycationic polymers have been widely studied for their use as alternatives to viral gene delivery. However, limitations to transfection still pose a significant challenge to polymer gene transfection vehicle design. The electrostatic interaction that very effectively condenses the nucleic acid for successful intracellular transport also represents its transfection drawback. Once in the cytosol, little dissociation takes place, thereby hindering the genetic material’s nuclear translocation. This work addresses the transfection performance of plasmid-carrying polyamidoamine (PAMAM) dendrimers by further interaction with a nuclear-localization sequence (NLS) peptide to promote the entire complex’s translocation [1].

Materials and Methods: G4 ethylenediamine core PAMAM dendrimers, a custom NLS-containing peptide (NLS sequence: PKKKRKV) [2], and a GFP-expression plasmid were used for complex characterization and transfection assays. Fluorescein isothiocyanate (FITC)-labeled G4, Tetramethylrhodamine (TAMRA)-labeled NLS peptide, and Cyanine (Cy3)-labeled plasmid were used for intracellular trafficking. G4 and NLS-peptide were first mixed and equilibrated, followed by the addition of plasmid DNA and a 2nd equilibration (30 min each at room temperature). Gel shift assays and dynamic light scattering were performed to assess G4/NLS/plasmid complex ratios. Confocal and transmission electron microscopy (TEM) were used to track nuclear translocation and to confirm complexation, respectively. Transfection was assessed via fluorescence microscopy in mouse embryonic fibroblasts (NIH3T3) and head and neck squamous cell carcinoma (HN12). Safety was assessed using a WST-1 cell proliferation assay.

Results and Discussion: Gel shift data showed stable complexes forming at 0.5:30:1 G4/NLS/pGFP weight ratios, relative to a 1:0:1 ratio in the absence of NLS. Intracellular trafficking confirms the nuclear translocation of the G4 and G4/plasmid complexes when NLS peptide is present, which corresponds to an increase in the number of GFP-expressing cells (Fig 1).

Optimization of Pt/C Catalyst Nanofibers Electrospun on Nafion 117 Membranes in Polyelectrolyte Membrane Fuel Cells

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Polyelectrolyte Membrane Fuel Cells (PEMFCs) have been of great interest as a potential source of alternative energy due to their high power output and zero-emission activity, yet their low cost efficiency relative to combustion engines has impeded commercial success. While the Pt/C catalyst is traditionally deposited on the electrodes of the PEMFC, this study explores electrospinning Pt/C onto the commercially used Nafion 117 membrane and finely tuning the deposition and composition of the nanofiber structures to increase electrochemically active surface area and proton conductivity in the fuel cell. Catalyst ink solutions were made from Nafion 117, poly(acrylic acid), and Pt/C as solutes in an isopropanol-water solvent, with Pt/C catalyst wt. % varying from 20.0% to 40.0%. Solutions were then electrospun onto Nafion 117 membranes at a voltage of 15.0 kV, maintaining a Pt loading of approximately 0.10 mg/cm². Flow rates of 0.5 mL/hr and 1.0 mL/hr were employed at each Pt/C wt. %. SEM and 3D laser microscopy imaging revealed that flow rate and Pt/C wt. % were positively correlated with platinum agglomeration and nanofiber diameter, respectively (Fig. 1). The peak power density achieved by the 32.5% wt. Pt/C nanofibers indicated an optimal fiber diameter of approximately 1.25 μm. At all Pt/C wt. %, the 0.5 mL/hr nanofiber-coated membranes performed better than or equal to the 1.0 mL/hr nanofiber-coated membranes in terms of power density, supporting the agglomeration reduction theory derived from SEM imaging. Overall, tests showed a 62% increase in maximum power density with 32.5% wt. Pt/C nanofibers extruded at 0.5 mL/hr onto Nafion 117 membranes when compared with commercially used Nafion 117 membranes (Fig. 2).
Antibody impact on Emission and Energy band profile of bioconjugated CdSeTe/ZnS quantum dots

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The commercial core/shell CdSeTe/ZnS quantum dots (QDs), covered by the PEG polymer, with emission at 705 and 800nm, have been studied by means of photoluminescence (PL), its excitation power dependence and Raman scattering methods in the non-conjugated state and after conjugation to different antibodies (Ab): i) mouse monoclonal [8C9] human papilloma virus Ab, anti-HPV 16-E7 Ab and ii) pseudo rabies virus (PRV) Ab.

The QD bio-conjugation to antibodies stimulates the “blue” energy shift of PL bands related to exciton emission in the CdSeTe cores. The energy band diagram of core/shell CdSeTe/ZnS QDs has been designed that helps to analyze the PL spectra. It is shown that the core structure in CdSeTe/ZnS QDs is complex and includes the type II quantum well. The last fact permits to explain the nature of infrared (IR) optical transitions (1.55-1.60 eV) and high energy PL bands (1.88-1.94 eV) in the non-conjugated and bio-conjugated 800nm QDs, respectively.

A set of physical models has been analyzed and discussed with the aim to explain the PL spectrum transformation in the bio-conjugated QDs. Finally, it is shown that two factors are responsible for the PL spectrum transformation at the bio-conjugation to antibodies: i) the change of energy band profile in QD cores and ii) the shift of QD energy levels for the strong quantum confinement case. Both these effects are appeared due to the stimulation by the excitation light the electric dipoles in antibodies and owing to the dipole electric field impact on the energy levels in QDs. The effect of PL spectrum transformation at the bio-conjugation to specific antibodies can be a powerful technique for early medical diagnostics.
A Novel Nanohybrid for Potential Utilization in NIR Photocatalysis: A combined experimental and DFT Study

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Utilization of full solar spectrum to minimize the energy crisis is of major importance nowadays. Solar light driven photocatalysis is one of the prime interests for efficient conversion of solar light. Solar light consists of ~4% UV, 46% Visible and 50% near infrared (NIR) lights. The difficulty of NIR usage is its associated low energetic photons, which can lead to exciton generation only for low band-gap semiconducting systems, which shows low yield in photocatalytic process. Moreover low bandgap systems pose very fast charge recombination process. Forming a heterostructure with one low band gap semiconductor and wide bandgap semiconductor could be an option to overcome the problems. Herein, we report a novel CuS-ZnO nanohybrid, attached by a cysteine ligand, to exhibit efficient photocatalytic performance using the NIR part of the solar light spectrum. Picosecond resolved studies and raman spectroscopy have been utilized to confirm the formation of the nanohybrid. We have observed an improved photocatalytic activity towards degradation of methyl orange (MO) by the nanohybrid compared to its pristine counterparts under NIR light illumination. Ab initio studies have been carried out in DFT framework to obtain the insight to the photocatalytic process. Theoretically predicted band alignment indicates that the newly synthesized nanohybrid forms a type II heterojunction. An increment of significant charge separation from the conduction band of CuS to those of ZnO is the key mechanism behind the enhanced photocatalysis. This material can be very much useful to harvest NIR light efficiently.

References:
Roles of the MOFs Incorporated with Semiconductors in CO₂ Photoreduction

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The photoreduction of CO₂ is a promising strategy to generate renewable energy. The efficient CO₂ photoreduction process requires photocatalysts possessing several critical properties, including high gas adsorption capacity, good molecule activation ability, and efficient separation of charge carriers. The emerging family of metal-organic frameworks (MOFs) has drawn great attention in CO₂ photoreduction mostly because of their high surface area and huge porosity, which can significantly boost the CO₂ adsorption capacity for the photocatalytic process. However, the inherently low migration rate of charge carriers inside MOFs greatly limits the photocatalytic efficiency of MOFs in CO₂ reduction, rendering MOFs less efficient than the conventional semiconductor photocatalysts. On the other hand, the unique properties of MOFs are vital keys to further improving the efficiency of the semiconductor photocatalysts by promoting CO₂ adsorption. Based on this rationality, several MOF/semiconductor composite photocatalysts have been reported and demonstrated enhanced CO₂ photocatalytic efficiency than the individual components.

Despite the numerous successful cases of MOF/semiconductor composites for CO₂ photoreduction, the roles of the incorporated MOFs are still unclear, which is of great importance to study. Here, we will show two examples of efficient MOF/semiconductor composite photocatalysts for CO₂ photoreduction, including HKUST-1/TiO₂ and HKUST-1/TiO₂/Cu₂O (HKUST-1 is a typical MOF).[1, 2] The results demonstrated that the pure MOF showed no obvious ability to reduce CO₂ under the flow condition. But the incorporation of MOF to the semiconductors could significantly promote the photocatalytic efficiency meanwhile result in preferential formation of CH₄. In-depth analysis (e.g., charge carrier density, band alignment, activation of adsorbed molecules, and photocatalytic intermediates) was conducted with the aid of systematic measurements. From the results and analysis, it has been clearly demonstrated that the incorporated MOF acted as a co-catalyst and played several vital roles, including enhancing adsorption, activation, and charge migration. The results from abstract are of great interest to both the MOFs community and renewable energy community and shall offer mechanical insights into both CO₂ photoreduction and future design of efficient photocatalysts.

Yeast-derived Carbon Nanotube Li-S Batteries

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Carbon nanotubes (CNTs) are finding more applications in batteries, sensors, thermal electronics, and high-strength composites. Low-cost high throughput production capacity of CNTs is needed. We demonstrate that CNTs can be derived from yeast with biomass (wheat flour, cotton, recycled cardboard and corncob) as carbon source via a simple, green, and sustainable activation process without using any additional catalysts. Such CNTs were used to construct cathode for lithium–sulfur (Li–S) batteries. The assembled Li–S cells exhibited excellent cyclic performance, with a well-retained capacity of \( \sim 450 \text{ mA h g}^{-1} \) even after 1500 cycles at a high charge/discharge rate of 1 C. A “self-catalysis” growth mechanism is proposed to explain the formation of the yeast-derived CNTs [1]. Our new findings represent a paradigm shift in developing CNTs and provide a promising solution to obtain advanced renewable carbon materials from natural and abundant biomass materials for use in energy storage applications.

Multilayer Graphene As Highly Performance Electrodes For GaN Nanorod Array LED

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GaN-based nanowire LEDs have been known to suffer from the poor Ohmic contact and injection current distribution [1]. Meanwhile, it has been reported that graphene demonstrates superior conductivity and high optical transmittance. In this regards, we report a systematic study on the characteristics of graphene as a transparent current spreading layer in GaN nanorod LED.

Four nanowire LED samples are fabricated. Figure 1 shows the measured IV curves. It can be seen that all samples with graphene electrode appears to have lower contact resistance than the one with conventional ITO films. Also it can be observed that the multilayered graphene electrode has lower resistance than the single layered graphene electrode, this is caused by the reduced resistance for multilayer graphene films. However, the 5-layer sample shows a better IV characteristic than the 10-layer sample. This can be explained by reduced electron quantum tunneling effect between p-GaN and graphene film for thicker graphene film. Measured EQE also shows that 5-layer sample has the best performance, as shown in Figure 2. Moreover, it is worth mentioning that a higher optical transmittance for the 5 layers sample compared with 10 layers sample can also contribute to higher optical power output under same injection level. A complex theoretical model has been constructed to explain this enhanced optical and electrical properties for the first time.

Prediction of Room-Temperature 2D Ferromagnetic Semiconductors via Isovalent Alloying

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Owing to the spontaneous net magnetization, the moderate electrical resistivity at finite temperature and unique potentials for applications, two-dimensional (2D) ferromagnetic (FM) semiconductors with layered structures have attracted considerable research interest. Since the pioneering experimental works of exfoliating 2D FM Cr₂Ge₂Te₆ and CrI₃ [1,2] layers in 2017, more and more new phenomena and materials have been reported. However, their Curie temperatures (T_C, ~30 K and ~45 K for Cr₂Ge₂Te₆ and CrI₃ thin layers, respectively) are lower than the liquid nitrogen temperature (77 K), which greatly restricts their practical applications in spintronics. Thus, it is necessary to develop new ferromagnetic 2D crystals with robust long-range spin ordering, which can survive above room temperature. Here, through isovalent alloying, we propose that the semiconducting ferromagnetism of 2D MnS₂ can be significantly enhanced with T_C above room temperature. Based on first-principles calculations, we systematically studied the properties of original MnS₂ and the isovalent alloying systems MnₓRe₁₋ₓS₂. The spin coupling is significantly enhanced by introducing Mn–Re virtual bonds, and the highest T_C of the system reaches 360 K. Besides this, a tensile strain can further enhance the ferromagnetic couplings as well as the uniaxial magnetic anisotropy, which is important for the stabilization of long-range ferromagnetic order in a 2D system. Our results not only broaden the family of 2D ferromagnetic semiconductors but also provide direct clues for preparing such high temperature magnetic materials with promising applications in spintronics.