Second harmonic generation (SHG) spectroscopy is used to investigate the influence of salt concentrations and temperature on the adsorption properties of malachite green (MG) dye to the surface of polystyrene sulphate (PSS) microspheres in aqueous colloidal. The adsorption of MG to PSS microparticles in water is driven by the electrostatic attractions between the positively charged MG molecules and negatively charged PSS surface. Using dynamic light scattering, the hydrodynamic diameter of PSS particles is measured to be $1.1 \pm 0.1 \mu m$, in agreement with the transmission electron microscopy measurements. The SHG intensity increases as the added MG dye concentrations are increased, reaching a maximum as the MG adsorbate at the PSS interface approaches a saturation value. The experimental adsorption isotherms are fit using the modified Langmuir model to obtain the adsorption free energies, adsorption equilibrium constants, and the adsorbate site densities at different temperatures and salt concentrations. Corresponding temperature and concentration-dependent molecular dynamic (MD) calculations are performed in order to better characterize the adsorption process of MG molecules to the PSS surface. Overall, the combined approach of investigating the colloidal PSS microparticle interface with SHG spectroscopy and MD simulations provides a detailed foundation for understanding molecular interactions in different physical and chemical colloidal environments.

**Key Words:** Second harmonic generation, Microspheres, Adsorption Properties, Modified Langmuir model, Molecular dynamic simulations
Determining Single-Wall Carbon Nanotube Partition Conditions in Aqueous Two-Polymer Phase Extraction with Near-Infrared Fluorescence Spectroscopy (35)

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Aqueous two-polymer phase extraction (ATPE) is an effective, yet still developing, separation method for enriching or isolating single species of single-wall carbon nanotubes (SWCNTs), with control of individual SWCNT specie isolation usually achieved by competing two or more surfactants against the nanotube surface. However, methods for rapidly determining the aqueous surfactant concentration conditions that yield upper or lower polymer phase extraction for specific \((n,m)\) species SWCNTs in ATPE separations are a missing component limiting quicker development and optimization of the ATPE technique. Here, we demonstrate the use of near-infrared fluorescence emission from single-phase dispersions of multiple SWCNT specie mixtures to determine these partition coefficient conditions without performing ATPE separations. This new methodology enables rapid quantitative determination of partitioning conditions for individual \((n,m)\) species and their handed enantiomers, while using dramatically less material and without ambiguity of mass transfer limitations or interfacial adsorption present when conducting the ATPE separation itself. This methodology also enables swifter investigation of complicating factors such as temperature, polymer composition, and surfactant chemistry; variations of which are shown to strongly affect the amount of surfactant necessary to cause \((n,m)\) extraction using the ATPE method. These results provide additional insight into the underlying mechanisms behind ATPE-based SWCNT separations, towards further development and optimization of the ATPE method.

Key Words: carbon nanotube; separations; SWCNT; fluorescence

Thermodynamic Investigation on Halide Perovskite Nanocrystals via Isothermal Titration Calorimetry (79)

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Both organic-inorganic and all-inorganic halide perovskite nanocrystals \(ABX_3\) (Where \(A\) is an organic or inorganic cation and \(X\) is a halide e.g \(CsPbBr_3\)) have gained considerable attention over the last few years due to their ease of preparation, narrow emission widths, and high quantum yield. Although these materials have been identified as potential candidates for various commercial electronic materials such as sensors, solar cells, photodetectors, and light-emitting diodes (LEDs), their poor stability remains a major hurdle for their rational development. Also, an interesting phenomenon of this class of materials is their ease of anion exchange. Even though this property is often desirable because it allows for their bandgap tunability, it often results in a decreased stability and reduction in performance efficiency due to halide migration and phase separation. Thus, the science about the thermodynamically driven force for the ion/ligand exchange on the surface of these particles which is necessary to optimize their performance and
stability remains unclear. Here, using Isothermal Titration Calorimetry (ITC) technique, we study and quantify the thermodynamically driven force for different ligands and ion exchanges on the surface of these nanocrystals. Our result has provided more experimental investigation needed to understand the processes of these exchanges and to probe a better strategy for improved stability and optimization of these materials in different electronic applications such as tandem cells and white light-emitting diodes.

Key Words: Halide perovskite nanocrystals, isothermal titration calorimetry, stability, thermodynamics

Understanding the Effects of Polar and Non-Polar Surfactants on the Oxidation Performance of Copper Nanoparticles (86)

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Copper nanoparticles (Cu-NPs) have garnered attention due to their high electrical and thermal conductivity, high melting point, and relatively low cost compared to other metals (i.e., gold and silver). The widespread usage of Cu-NPs is hindered due to their susceptibility to oxidize and corrode, as well as the difficulty to achieve an synthetic route that easily scalable with controlled morphology and does not encompasses parasitic conditions (i.e., harsh reactants, high temperature). Many of the published routes involve harmful/toxic compounds and reducing agents, as well as very high temperatures/long reaction times, and despite the harsh synthetic conditions the nanoparticles are extremely susceptible to oxidation. Therefore, developing a cost effective and green synthesis that can produce Cu-NPs that is resilient/controllable to oxidation and corrosion environments is critical for Cu-NPs to be usable in industrial and commercial usage. In this work, a novel microwave-assisted synthetic route is demonstrated using an organometallic precursor (Copper (I)-Mesityl) and a variety of green solvents (glycols) and surfactants (hexadecylamine [HDA]). Numerous synthetic parameters (i.e., solvent/surfactant combinations) were systematically investigated to evaluate their effect on the particle size and morphology as well as how the solvent/surfactant prevent oxidation/corrosion in atmospheric corrosion environments. The various surfactant/solvent coated nanoparticles were subjected to a variety of environments such as 100% relative humidity (RH) and 10 ppm H2S/50% RH. Results show the combination of glycols/HDA yielded a synergistic effect that lead to a reduction in the oxidation kinetics upon exposure to atmospheric corrosive environments, yielding oxidative resistant nanoparticle (> 14 days).

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Key Words: Copper nanoparticles, microwave synthesis, oxidation resistant, surfactants

Engineering porous nanocomposite particles via aerosol-assisted synthesis as solid adsorbent for CO2 Capture (88)

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Effects of global warming on climate change has called for the development of technologies for the reduction and removal of atmospheric greenhouse gases such as CO2. The adsorption of CO2 onto solid adsorbents is of great interest as an alternative carbon capture technology to the liquid amine absorption process due to its potential for less energy consumption. Solid adsorbent used in this technology are highly porous materials that have large surface areas such as zeolites, MOFs and mesoporous silicas. The CO2 capture capacity and selectivity of these adsorbents are further amplified by impregnating or functionalizing the adsorbents with amine functional groups that allow for the reversible chemisorption of CO2 under dry and humid conditions. Progress has been made in incorporating polymeric amine molecules into mesoporous supports such as MCM-41, however CO2 capture efficiency diminishes at high amine loading concentrations due to the diffusion limitations within the tight pores of such solid adsorbents. In this work, we demonstrate new strategies for the design of highly porous adsorbents with improved diffusivity for CO2 capture using a one-step aerosol assisted synthesis technique. In this process, precursor solutions containing reactants and structure templating molecules are atomized by an inert gas leading to the formation of micro droplet mists that are transported to a tubular furnace heating zone where hydrothermal reaction occurs rapidly in each droplet leading to the deposition of solid particles. We present results on how this strategy has been employed to synthesize nanocomposite porous silicas and amine containing polymers for CO2 capture. This facile method for synthesizing hollow and mesoporous nanoparticles is a semi-continuous process with short residence time, high throughput and yields highly reproducible particles which makes this technique attractive for industrial scale-up.

Key Words: Carbon capture, porous solid adsorbents, aerosol-assisted synthesis

Kinetic Control of Quantum Dot Gel Formation via Oxidative Assembly: The Role of Metal Ion Solubility and Surface Energy (99)

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The assembly of quantum dots (QDs) into three-dimensional architectures is a promising strategy to enable facile communication between particles for solid-state applications. Among QDs, metal chalcogenides are among the most studied an exhibiting composition, size and shape dependent electro-optical properties resulting from the quantum confinement effect. The oxidative assembly method pioneered by the Brock group provides a robust three-dimensional network of QDs based on three main steps; (1) oxidation induced irreversible ligand removal, (2) dissolution of metal ions into the solution and
(3) oxidation induced formation of di- or poly-chalcogenide bonds between particles. This method also permits the assembly of multicomponent QD systems to enable applications requiring different functional QDs integrated together such as in photocatalysis, photovoltaics and sensors. Thus, understanding the parameters that dictate the kinetics of gelation of single component QDs is compulsory to tune the reactivity and control the heterogeneity of multicomponent systems produced by oxidative assembly method. Prior work in our lab has revealed that factors such as native structure (hexagonal vs cubic), ligand chain length, particle size, chalcogenide identity and oxidant concentration all contribute to the kinetics of assembly. Here, we hypothesize that the gelation kinetics may also be governed by (1) the solubility of the metal ions and (2) facet-dependent surface energy effects because the solubility of metal ions and the oxidation of surface ligands from surfaces are key steps in the formation of gels. The Presentation will describe a comparative study of CdS vs ZnS gelation kinetics as well as CdSe particles of different shapes.

**Key Words:** Oxidative assembly method, Quantum dots