Project Title: Influence of Metal Incorporation on the Organizational Structure of Sulfonated Block Copolymers in Solution
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Progress of Research

The focus this research thus far has been a fundamental investigation of how organic charged polymers and small molecule chelator-type ligands impact the physical and chemical properties of metallic and metal oxide nanoparticles. The suite of ligands and polymers discussed herein are either produced through petroleum refining to fine chemicals processes or are under consideration and research for use in petroleum extraction processes. For example, carboxymethylcellulose materials have been studied as a hydraulic fracturing fluid additive to control viscosity. The aminophosphonic acid ligands used are common scale inhibitors in oil field operations and are produced via reactions that involve petrochemicals such as formaldehyde. The physical interactions of these polymers and ligands with metal/metal oxide surfaces are critical for a range of applications in the petroleum industry, from hydraulic fracturing to petroleum processing, scale inhibition, and catalytic chemical processes. The original intent of this proposal was to study sulfonated block copolymers and probe the interactions between specific block copolymers and metal/metal oxide nanoparticles. However, our initial work in the development of in situ techniques for probing polymer-nanoparticle interactions in aqueous and solvent environments suggested that the block copolymer system was quite complex, with physical and chemical behaviors difficult to delineate. Thus, two sets of polymers (i.e., two sizes of carboxymethyl cellulose (CMC)) and ligands (i.e., aminotrimethylene phosphonate (ATMP) and diethylenetriamine penta(methylene phosphonic acid) (DTPMP)) were chosen to study as a precursor to studying more complex charged polymers, such as the sulfonated block copolymers.

In this research, we are pursuing in situ quartz crystal microbalance (QCM) experiments to understand how the presence of a polymer or chelator ligand on the surface of a metal/metal oxide nanoparticle material impacts the adsorption and oxidation behavior of that nanoparticle material when exposed to a range of relative humidity and liquid water solution. As an example of this work, a set of results are presented in Figure 1 for 10%, 50%, and 90% relative humidity and 100% liquid water for four different iron/iron oxide nanoparticle materials. Each sample had a different polymer or chelator ligand on the surface of the nanoparticles. From these results, we observe several interesting trends. First, as the relative humidity increases, the overall mass of the adsorbed water increases, and there are distinct differences between the two different molecular weights of CMC (i.e., 250,000 g/mol or 476,000 g/mol) and the two chelators, ATMP and DTPMP. The difference

Figure 1. QCM experiments on ZVI nanoparticles at (a) 10% RH, (b) 50% RH, (c) 90% RH, and (d) oxygenated H_2O. Red lines correspond to ATMP stabilized ZVI nanoparticles, orange lines correspond to DTPMP stabilized ZVI nanoparticles, while dark blue and light blue lines correspond to CMC250 and CMC476 stabilized ZVI nanoparticles, respectively.

between the four samples is even more dramatic in the presence of liquid water (Figure 1d), where DTPMP on the iron/iron oxide nanoparticle surface completely prevents surface oxidation, while the larger CMC polymer reduces overall nanoparticle oxidation and both CMC250 and ATMP only delay nanoparticle oxidation. These results suggest that the properties of the polymer or ligand that is on the surface of the metal/metal oxide nanoparticles can have a strong influence on the adsorption and oxidation behavior of the nanoparticles. Further, it appears that the presence of a larger polymer or strongly-chelating ligand can in fact protect the metal/metal oxide nanoparticle surface from
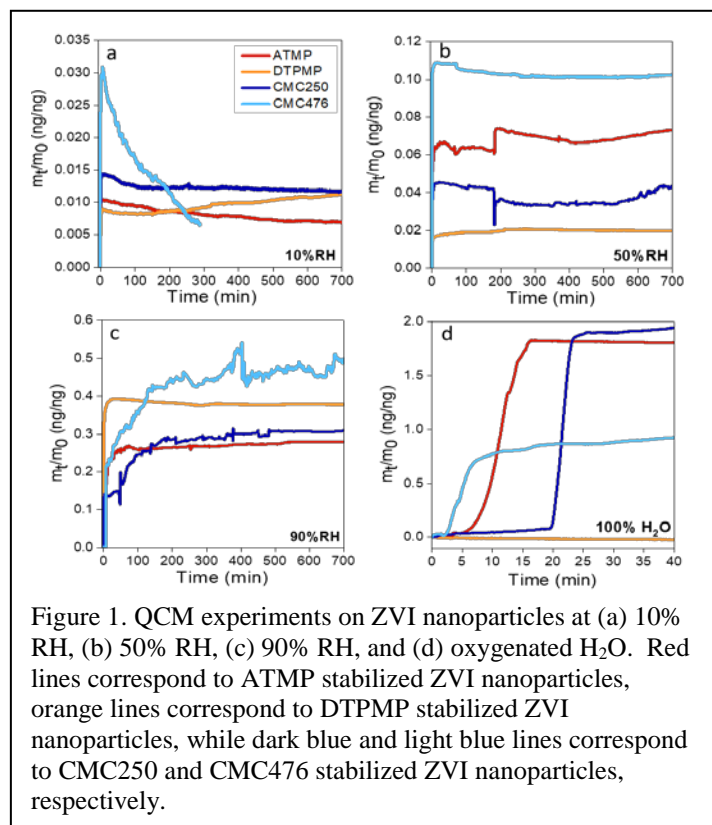
oxidation in oxygenated liquid water environments, even though the ligand or polymer might also enable increased water vapor sorption in relative humidity environments.

In addition to these QCM experiments, we have also designed, constructed, and tested an in situ cell for performing Raman spectroscopy measurements in liquid and electrochemical environments. The purpose of designing and using this cell (Figure 2a,b) is to be able to probe metal/metal oxide materials and their dynamic chemistry in aqueous, solvent, and humid environments, as well as when the experimental materials are held under an applied potential. An initial set of experiments are shown in Figure 2c-e, where Raman spectroscopy measurements were taken on a series of iron-nickel oxide/hydroxide nanoparticles as a function of iron-nickel composition and applied electrochemical potential. All measurements were performed in an aqueous electrolyte solution of 1 M NaOH. These spectroscopy measurements not only demonstrate that we have successfully set up our desired experimental system but that we are able to probe changes to the nickel-oxygen chemistry as a function of material composition and applied potential. In Figure 2, we observe that as the nickel content in the nanoparticles decreases, the emergence of nickel oxyhydroxide features (peaks at 478 and 559 cm^{-1}) shifts to higher voltages. We plan to continue research in this area to further understand how surface-functionalized ligands, including charged polymers, impact the metal oxide chemistry in aqueous environments.
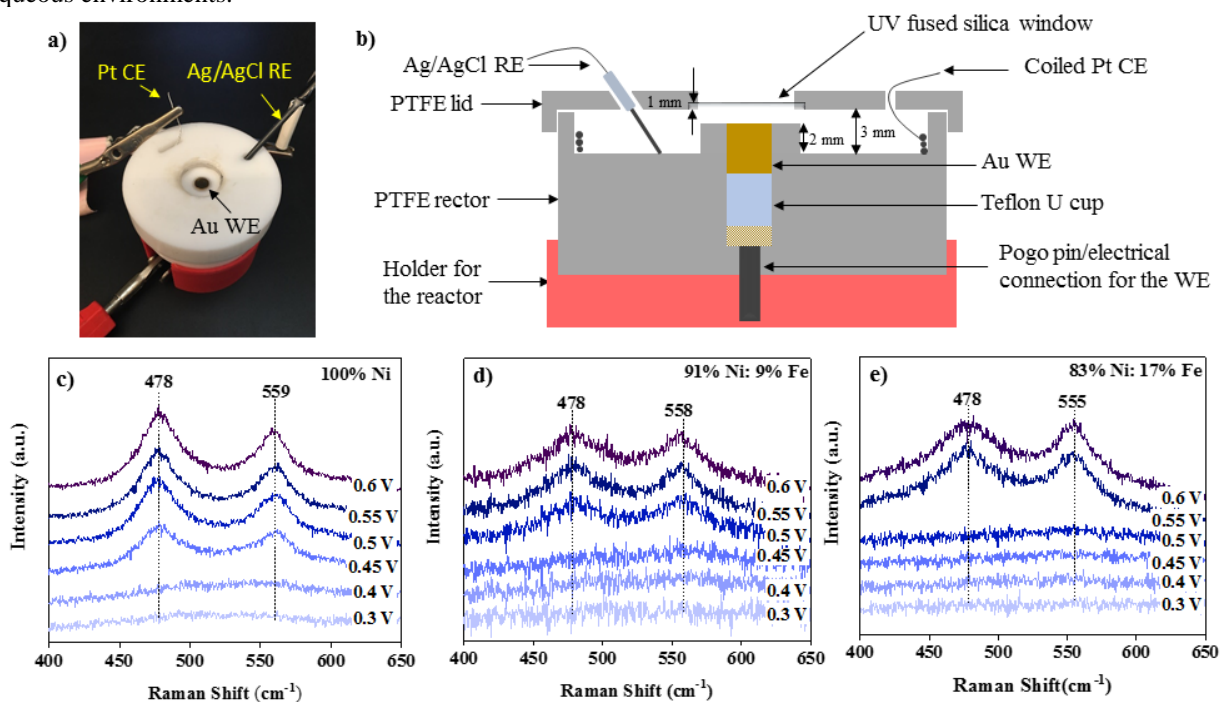

Figure 2. (a) Digital photograph and (b) schematic of the in situ Raman setup. WE-Working electrode, CE-Counter electrode, RE – Reference electrode. In situ Raman spectra of Ni:Fe alloy nanoparticles acquired while running a LSV from -0.1 to 0.8 V vs Ag/AgCl reference electrode; (c) 100% Ni (d) 91%Ni: 9% Fe and (e) 83%Ni:17%Fe nanoparticles. Peaks at 478 and ~558 cm^{-1} are due to Ni-O vibrations in NiOOH formed by the oxidation of Ni(OH)$_2$ in Ni:Fe alloy nanoparticles. Note the increase of the potential at which NiOOH peaks first appear in Raman spectra with increasing Fe content from 0 to 17%. Nanoparticles with higher Fe contents up to 50% followed the same pattern obtained for 17% Fe (not shown in this figure).

Impact on the Careers of the PI and Students

This grant has enabled the PI's research group to develop several in situ measurement techniques, including QCM, Raman spectroscopy, and more recently, Fourier transform infrared spectroscopy. The grant has supported a significant effort to develop these techniques and the cells and setups required, and it is expected that the PI's research group will continue to use these techniques across all projects to conduct fundamental research on metal/metal oxide materials and ligand-metal interactions. The postdoc who has been funded has expanded her expertise to new fields, such as electrochemistry, and will have several high impact publications from this work. The undergraduate student was able to spend a summer in the laboratory and has learned how to conduct research on nanomaterials, which will further his academic career and goal of attending graduate school.