

University of Louisville  
Department of Chemistry

## Rajiv Singh Research Seminar

When: August 28, 2023

Time: 3:00 p.m.

Location: CBL-16

### Synthesis, Characterization, and Catalytic Activity Study of Gold Nanoparticles Inside Hydrogel Beads

#### Abstract:

In recent years, noble metal nanoparticles (NPs) with sizes of less than 20 nm have garnered a great deal of interest in the field of catalysis due to their size dependent catalytic activity.<sup>1</sup> Gold (Au) originally thought to be catalytically inactive, was later recognized as very active as NPs and could be an exceptional green catalyst.<sup>2</sup> Metal NPs in general have greater activity compared to bulk metals because they have greater surface area-to volume ratio (SA/V)<sup>3</sup> which leads to higher number of low coordination surface metal atoms available to bind substrate and catalyze reactions relative to the same volume of larger bulk material. The downside is that the high surface energy of the metal NPs leads to aggregation or ripening, which is due to the thermodynamic driving force to lower the SA/V. This lowers or deactivates the activity completely, making separation or reuse of the catalyst very challenging. A support material is often useful to inhibit aggregation or ripening for improving long term stability. Solid supports improve stability to protect metal NPs from aggregation or ripening, allow high catalytic activity due to the high-water content, and easy separation of catalyst and allow easy separation of the catalyst from the reaction products due to the hydrogel insolubility. Alginate, which forms the main constituent of brown algae, is a well-known biopolymer belonging to the polysaccharide family. It is composed of homo polymeric blocks of 1-4-linked  $\beta$ -D-mannuronic acid (M) and R-L-guluronic acid (G). Two acid units M and G are connected with regions of alternating structure in varying proportions of GG, MG, and MM blocks.<sup>4</sup> The sodium salt of alginate is water soluble and forms a hydrogel with divalent metal cations especially  $\text{Ca}^{2+}$ . Ca-alginate hydrogels behave as support for metal NPs for a variety of biological, sensing, and catalytic applications.<sup>5,6</sup>

This talk describes the synthesis, characterization, and catalytic activity of Au, Ag, and AuPd NPs or nanoclusters (NCs) incorporated into Ca-alginate hydrogel beads ( $\mu\text{m}$  to  $\text{mm}$  size). Combining Na-alginate and metal NPs/NCs and adding the solution dropwise led to successful synthesis of various Ca-alginate metal NPs/NCs beads of  $\sim 2$ -3 mm diameter. The metal NPs/NCs include  $\sim 2$  nm glutathione (SG)-stabilized Au and AuPd NCs (Ca-*alg*-AuSG and Ca-*alg*-AuPdSG), citrate (cit)-stabilized Au NPs of various size (Ca-*alg*-cit-Au NPs), 9 nm cit-stabilized Ag NPs (Ca-*alg*-cit Ag NPs) and aggregated cit-stabilized Au NPs. Additionally, the cleaning procedures of the noble metal nanoparticles incorporated hydrogel beads will be discussed. Further, the chemical activities of noble metal nanoparticles inside the alginate hydrogel beads will also be discussed. Finally, the catalysis of borohydride reduction of 4-nitrophenol to 4-aminophenol, reusability and recyclability of these metal incorporated beads will be discussed.

#### References:

- (1) Ishida, T.; Murayama, T.; Taketoshi, A.; Haruta, M. *Chem Rev* **2020**, *120* (2), 464-525.
- (2) Stratakis, M.; Garcia, H. *Chem Rev* **2012**, *112* (8), 4469-4506.
- (3) Ilgin, P.; Ozay, O.; Ozay, H. *Appl Catal B-Environ* **2019**, *241*, 415-423.
- (4) Saha, S.; Pal, A.; Kundu, S.; Basu, S.; Pal, T. *Langmuir* **2010**, *26* (4), 2885-2893.
- (5) Supriya; Pal, C. K.; Sengupta, S.; Basu, J. K. *Can J Chem Eng* **2021**, *99* (1), 359-373.
- (6) She, T. T.; Niu, L. B.; Nie, S. L.; Li, H. F.; Qiao, X. L.; Ma, Y. Y.; Han, X.; Chen, G. F.; Bai, G. Y. *J Mater Sci* **2020**, *55* (24), 10482-10491.