Design, Synthesis, and Multiscale Structural Investigation of Polymer-Grafted Nanoparticles (PGNs) for Application in Pyrolysis and Self-Assembly Processes

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Primary CNF Tools Used: Malvern Nano ZS Zetasizer, Dicing Saw, Zeiss Ultra SEM

Abstract:

The research team has made extensive strides in the study of polymer-grafted nanoparticles (PGNs) over the past year, utilizing the top-tier resources and support from the Cornell NanoScale Facility (CNF) as well as other facilities on campus. Two critical aspects of PGNs — self-assembly and pyrolysis to make polymer-derived ceramics (PDCs) — were investigated, providing key insights into how grafting density influences self-assembly and how varying pyrolysis conditions can tailor PGN-derived inorganic nanostructured materials. Our findings have the potential to transform various applications, including optical devices, magnetic devices, catalysis, energy storage, and the broader field of materials science.

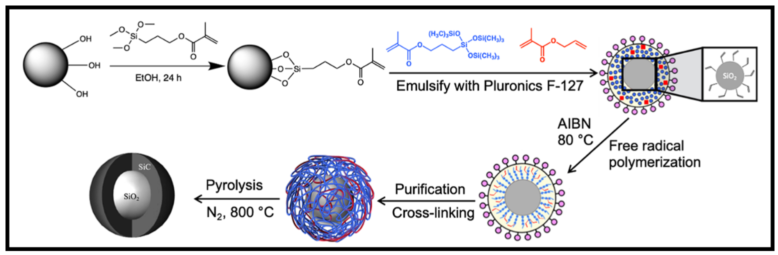

Figure 1: "Grafting-through" approach in mini-emulsion to covalently attach preceramic polymer chains to the silica surface, crosslinking of the preceramic polymer brushes via the allyl groups, and pyrolyze the PGNs to get SiO_2-SiC core-shell nanoparticles.

Summary of Research:

Synthesis, Functionalization and Self-Assembly of Polymer-Grafted Nanoparticles (PGNs). Our research began with the robust synthesis of PGNs with varied grafting densities [1]. A modified initiator, APTES-BIBB, was employed to functionalize silica nanoparticles (Ludox TM-40), which were then grafted with different polymers containing either hydrogen bonding donors or acceptors to create the PGNs. This process was optimized through iterative testing to yield PGNs with a range of grafting densities, thus enabling us to explore their impacts on self-assembly.

Utilizing transmission electron microscopy (TEM) and scanning transmission electron microscopy (STEM), we analyzed the PGNs' self-assembly behaviors. Our research established a direct link between the grafting density and self-assembly behavior of PGNs. This has opened a gateway to the predictable design of PGNs, enabling a more refined approach to their utilization in fields such as nanoparticle-based optical devices.

Pyrolysis of PGNs. In our other piece of work, we delved into the pyrolysis of preceramic polymer-grafted nanoparticles and its implications (Figure 1). Our objective was to understand how synthesis and pyrolysis conditions, impact the resultant structure, morphology, and composition of the preceramic PGN-derived nanostructured materials. CNF's state-of-the-art facilities enabled in-depth analysis and characterization of the outcomes.

Our findings, derived from thermogravimetric analysis, Fourier-transform infrared spectroscopy, scanning electron microscope (SEM) and high-resolution TEM, indicated that PGNs' pyrolysis led to the creation of SiO_2-SiC core-shell nanomaterials.

Future Plans:

Our groundbreaking progress over the past year paves the way for ambitious future research. We are particularly interested in investigating the influence of polymer chemistry on both the self-assembly behavior and pyrolysis outcomes of PGNs.

CNF's state-of-the-art facilities will enable us to take a deep dive into the structures derived from PGNs assembly and pyrolysis. Additionally, we're planning to focus our efforts on uncovering new applications of PGNs in areas such as optical and magnetic devices, as well as polymer-derived ceramic nanostructures.

References:

[1] Yuan, C., Käfer, F., and Ober, C. K. (2021). Polymer-Grafted Nanoparticles (PGNs) with Adjustable Graft-Density and Interparticle Hydrogen Bonding Interaction. Macromolecular Rapid Communications, 43(12), 2100629. https://doi.org/10.1002/marc.202100629