# RAFT AGENT PRIMED MESOPOROUS SILICA PARTICLES FOR SELECTIVE GRAFTING OF POLYMER CHAINS AND THEIR APPLICATIONS

## ABSTRACT

Cutting-edge achievements have been made towards controlled synthesis of different types of mesoporous silica nanoparticles (MSNs) using variety of structure directing agents. The possibility of organically functionalizing interior and exterior surfaces of MSNs utilizing various organoalkoxysilanes is one of the most interesting and challenging areas in the field of surface engineering today. MSN's superlative properties such as high surface area, ordered pore structure and uniform pore size distribution has been the motivation for further modification, functionalization, and application of MSNs. Thus, depending on the functional organic groups present inside or outside the surface of MSNs, they have been widely used in catalysis, sensors, absorbents, and drug delivery. The main pathway for these processes includes post functionalization in which an organic group is covalently attached to the inorganic surface after the synthesis of the MSNs, or by co-condensation which involves incorporation of the organic group during the synthesis of MSNs. Utilizing these pathways further for the surface modification of MSNs with polymers can alter the inherent properties of the MSNs and makes it compatible for different applications.

In this thesis, synthesis of RAFT agent functionalized MSNs *via* co-condensation and further grafting of different polymers [poly(*N*-isopropyl acrylamide), poly(acrylic acid) and poly(acrylamide)] from RAFT primed MSNs *via* surface initiated RAFT polymerization was carried out. Further, these polymers grafted MSNs were utilized for controlled drug delivery and nanoconfinement of ammonia borane application studies. Two different types of organoalkoxysilane-based RAFT agent having two different types of R group such as isobutyric

acid and phenylethyl group were synthesized and characterized by $^{1}H$ NMR, $^{13}C$ NMR and UV-visible spectroscopy. For the preparation of RAFT functionalized MSNs, different mmol % of both organoalkoxysilane-based RAFT agent was chosen with respect to silica precursor (TEOS) such as 6, 12.8 and 18 mmol %. The synthesis of RAFT functionalized MSNs was confirmed by UV-visible spectroscopy, FTIR, TGA and solid-state NMR. The morphological analysis of the RAFT agent functionalized MSNs was carried out utilizing SEM and TEM. Different morphology of the RAFT agent functionalized MSNs was observed such as spherical shape for isobutyric acid group containing MSNs and short-rod shape for phenylethyl group containing MSNs. Following such morphological changes, it was also observed that isobutyric acid group containing RAFT agent were preferentially functionalized outside the surface of MSNs and phenylethyl group containing RAFT agent were preferentially functionalized inside the pores of MSNs. Consequently, different polymers (PNIPAM, PAA, PAM) were then grafted preferentially outside and inside the surface of MSNs.

To practically understand the applicability of the stimuli responsive polymers such as poly(*N*-isopropyl acrylamide), poly(acrylic acid) grafted MSNs, in-vitro loading and release of drug doxorubicin (Dox) was performed at different pH and temperature. Further ex-vivo assay was performed in MCF-7 cancerous cell line of the Dox loaded polymer-grafted MSNs. An efficient Dox loading was observed in both cases of PAA and PNIPAM grafted MSNs. In-vitro Dox release from both the systems was demonstrated effectively via changing pH or temperature of the surrounding environment. The cell viability assay clearly showed the pH responsiveness of the PAA chains allows the release of Dox at pH 7.4 with a good efficacy to kill MCF-7 cells. From these studies, it was concluded that polymer-grafted MSNs synthesized from in-built RAFT agent containing MSNs can be effectively used in different therapeutic applications.

Similarly, poly(acrylamide) grafted MSNs were efficiently utilized as an organic-inorganic hybrid material for nanoconfinement of ammonia borane (AB). The nanoconfinement of AB was successful established by FTIR, $^{11}B$ solid-state NMR, XPS and XRD. It was observed that dehydrogenation temperatures of AB confined MSNs generally agreed with theoretical predicted trend based on surface tension provided by nanoconfinement. However, AB nanoconfined in PAM-COOH-MSNs had even lower dehydrogenation temperature ($T_d$). This was observed possibly due to synergistic effect of AB nanosize, as well as strong interaction between AB and the functional groups present in these inorganic structures which was proved by XPS. For justifying the effect, kinetics at temperature near to the $T_d$ was also performed and it was observed that higher equivalent of hydrogen was released at temperature near to $T_d$ from AB confined PAM grafted MSNs. Hence, utilization of these polymer-grafted organically modified MSNs with active organic functional groups would possibly widen its window to be used as a catalyzing material for thermolysis of AB for generation of hydrogen.