

## **Introduction**

Polyoxometalates (POMs) are a large class of anionic metal-oxygen clusters mainly composed of early transition metals ( $\text{Mo}^{\text{VI}}$ ,  $\text{W}^{\text{VI}}$  and  $\text{V}^{\text{V}}$ ) in their highest oxidation state. The diversity in structure and controllable redox properties of POMs are attractive for wide range of applications in numerous fields such as catalysis, materials science and medicine. Amongst the different types of POMs exist, the Keggin type due to their structural symmetry, stability and tunable composition have been utilized in majority of the catalytic and optical applications. However, owing to high soluble nature of pure POMs in many polar solvents and lower surface area ( $<10 \text{ m}^2\text{gr}^{-1}$ ) their processability for various applications has been severely limited. Therefore, functionalization of POMs is crucial in order to exploit the potentiality of these materials. In this context, there have been various techniques developed such as heterogenization via impregnation on a suitable support, and ion-exchange to convert soluble POMs into their insoluble salts. However, there are issues related to these methods like slow reaction rates, leaching of active species and decrease in activity during the reaction. Alternatively, in recent years, functionalization of inorganic POMs with organic moieties has received significant attention to fabricate novel hybrid architectures. This involves covalent or noncovalent interactions of organic ligands such as surfactants, ionic liquids, polymers and dendrites. However, compare to covalent interactions the noncovalent interactions are more preferable for preparation of such POM hybrids, as it can provide controlled ways for functionalization without impeding their intrinsic properties.

## **Statement of problem**

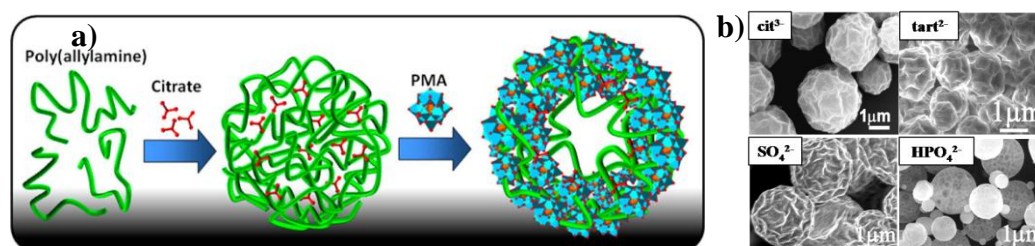
- There is a need to improve POM stability in the heterogenized structure and in most cases the non-environmentally-friendly synthesis processes have been detrimental to the progress in this field and their wider exploitation in general.
- For catalytic applications the methods to heterogenize POM via noncovalent interactions often require either multiple time-consuming steps or toxic solvents and harsh reaction conditions that can result in loss of materials during each step and during the reaction.
- It is also desirable to use organic component for functionalization of POM, which can provide suitable hydrophobicity/hydrophilicity in the hybrid system

to facilitate accessibility of the active sites for organic reactants during the catalytic reaction.

- In photochromic applications, especially the formation of POM based films or coating on flexible substrates necessitates mild reaction conditions, while it is also important to extend their application to visible-light for wider exploitation.

## Approach

In a bio-inspired assembly approach, the role of cationic polyamines in assembling the negatively charged POMs was investigated to fabricate hybrid structures under mild synthesis conditions. These polyamines are known to be responsible for the biosilicification of diatoms in which they facilitate silica formation and assembly under extremely mild conditions to generate intricately assembled structures. Herein, poly (allylamine hydrochloride) (PAH) was used for the assembly of POM. It involves supramolecular aggregation of PAH with multivalent anions (citrate) to form spherical aggregates, which then allows the assembly of negatively charged phosphomolybdic acid (PMA) into microcapsules (MCs) in an aqueous medium under ambient conditions (Figure 1a).

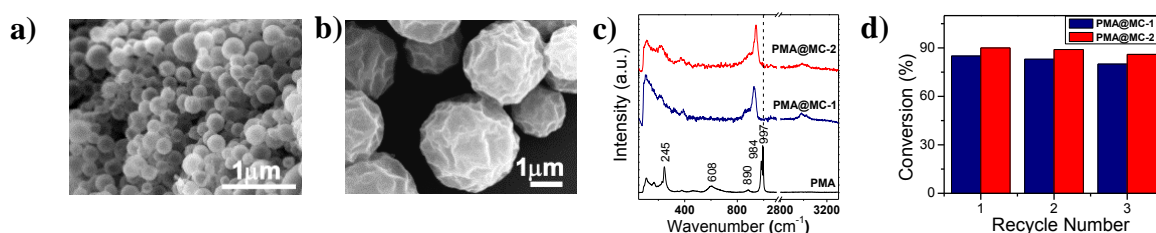


**Figure 1:** a) Schematic representation of polyamine-mediated PMA assembly; b) FE-SEM images of MCs prepared using different multivalent anions.

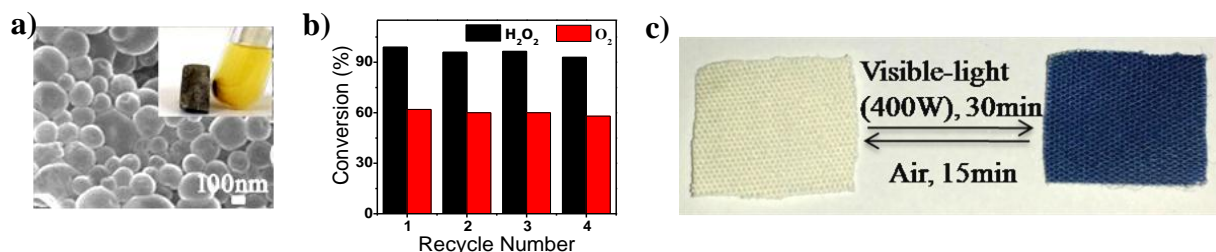
## Results and discussion

**Assembly:** Studies were carried out to understand the effect of various parameters such as negative to positive charge ratio ( $R$ ), pH, various multivalent anions (citrate, tartarate, sulphate, and phosphate) and other Keggin POMs on the PMA-assembly process (Figure 1b). As observed, the assembly process provides structural stability to the PMA and facilitates an interesting transition from a smooth to a wrinkled surface depending on the pH of the medium. The surface structure and size of the MCs are also influenced by the multivalent anion depending on its interaction with the PAH.

**Catalysis:** The assembled PMA hybrid structures were utilized for application as heterogeneous catalysts in oxidation reactions. Apart from the surface morphology, the change in pH from 4.0 (PMA@MC-2, smooth surface) to 8.0 (PMA@MC-1, wrinkle surface) during the synthesis also resulted in a change in the Keggin structure to lacunary form (Figure 2(a-c)). Irrespective of the Keggin type, the isolation of PMA units as found in the assembled MC structure was effective as catalyst in solvent free aerobic oxidation of alkenes (Figure 2d). Whilst the Keggin type promoted the acid catalyzed cleavage of the epoxide, the lacunary form being less acidic was selective for epoxide formation. The MCs were structurally stable and could be reused without any apparent loss in activity. In another experiment, Phosphotungstic acid (PTA) was used for the MC assembly process and for a facile recovery of the catalyst, citrate functionalized magnetic ( $\text{Fe}_3\text{O}_4$ ) nanoparticles were encapsulated during the synthesis. Thus assembled structures as catalyst for aerobic oxidation of alcohols exhibited efficient activity and recyclability. The microcapsules could be separated from the reaction mixture via magnetic separation using an external magnet (Figure 3(a-b)).



**Figure 2:** a, b) FE-SEM images, c) Confocal micro-Raman spectra of PMA@MC synthesized at pH 4 and 8 (PMA@MC-2 & 1); d) Catalytic activity of PMA@MCs as catalyst in different reaction cycles for oxidation of styrene (Styrene (10 mmol), TBHP (0.2 mmol),  $\text{O}_2$  at 1atm,  $70^\circ\text{C}$ , catalyst (0.89  $\mu\text{mol}$  of PMA) respectively.



**Figure 3:** a) FE-SEM image of magnetic PTA@MCs and (inset) magnetic separation of the MCs; b) Catalytic activity and reusability of PTA@MC in oxidation of benzyl alcohol using different oxidants ((benzyl alcohol (0.2mmol),  $\text{H}_2\text{O}_2$  (0.2mmol), solvent  $\text{CH}_3\text{CN}$  (5mL),  $\text{O}_2$  at 1atm,  $80^\circ\text{C}$ , catalyst (2  $\mu\text{mol}$  of PTA)); c) Reversible visible-light (400W) photochromism of PMA(6mM) coated on cotton fabric (PMA@CF) in presence of air.

**Photochromism:** The reducing behaviour of POM in the presence of light can generate a mixed valence coloured species called heteropoly blues via ligand-to-metal charge transfer (LMCT). This photochromism phenomenon can have applications in photo-switching memory devices, smart windows, cosmetics, multicolor smart painting, and UV sensors. It has been shown that the combining POMs with proton donor organic counter-ions can result in improved photochromic reversibility, color intensity and response time. For practical photochromic applications these POMs usually fabricated into thin films or coat on suitable matrices. Herein the polyamine-mediated assembly process was further extended to coat PMA clusters on a flexible substrate like cotton fabric. The presence of polyamine not only allows effective coating of PMA on the fabric (PMA@CF), but also facilitates reversible photochromism under visible-light (Figure 3c). The functionalities remain stable even after washing several times with water further indicating the importance of polyamine in stabilizing PMA on the fabric surface. Furthermore, the photo-reducible behavior of PMA@CF allowed to be used as an efficient photocatalyst for aerobic oxidation of benzyl alcohol under visible-light at room temperature.

### **Summary**

Herein in the thesis work, a polyamine-mediated method to assemble Keggin type polyoxometalates into microcapsule structures was demonstrated. The use of polyamines not only leads to an environmentally friendly synthesis route, but also their noncovalent interactions provide stability for the assembled structure suitable for catalytic and optical applications. Moreover, this bioinspired method of POM assembly represents can as well be an effective way for heterogenization of POM-based materials for applications in a wider hybrid-cluster field.