

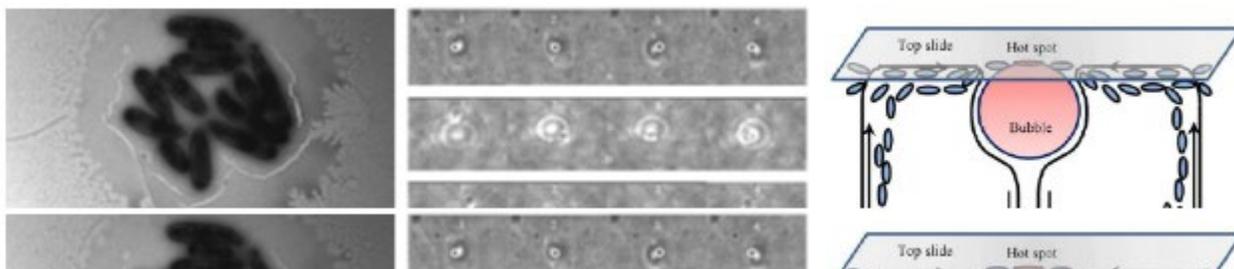
Soft-oxometalates: Patterning and Catalysis

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ABSTRACT



Soft-oxometalates (SOMs), oxometalates with soft-matter properties have been designed in recent times, and are gaining importance. Owing to their soft nature they can be tuned, activated and patterned deliberately. These properties thus render them as active catalytic model systems. In this review we highlight photo-active catalytic properties of oxometalates. Using oxometalates we synthesize larger SOMs in a controlled manner and use them in catalysis as well. For exercising even higher control we pattern the oxometalates using thermo-optical tweezers. Thereafter we use these patterned systems in catalysis. We also will discuss the factors controlling the self-assembly of SOMs and those controlling the patterning. The review will conclude with perspectives for future directions and applications.

Keywords: Soft-oxometalates, Photoactivity, Optical tweezers, Patterning, Catalysis.

INTRODUCTION

Recent discovery of soft-states of polyoxometalates leads to a new opportunities in polyoxometalate (POMs)¹⁻⁷ chemistry. Such entities, formed by self-assembly of polyoxometalates with soft properties are proposed to be termed as “Soft-oxometalates” (SOMs).⁸⁻¹⁰ SOMs exist as a dispersed phase in a dispersion, primarily in water, they have diffused boundary as well as can scatter light. Considering these properties, in accordance with de

Genes definition of soft matter,¹¹ the name “Soft-oxometalates” is convenient to understand and predict their behavior in terms of soft matter and colloids. SOMs can be formed either spontaneously¹²⁻¹⁴ or via directed route from well-defined nanoscopic POM precursors^{15,16} transcending the regime of translational periodicity.^{8,17} A huge numbers of POM building blocks are linked together via supramolecular interaction to form SOMs of diffused interface and colloidal scale-length. Control over their formation as well as their soft nature allow us to use SOMs to synthesize controlled pattern in microscale level with detailed structural information. This leads us to tune their properties in such a manner that SOMs can be activated for use in different applied fields e. g., as catalytic model.¹⁷ SOMs with photoactivity have been reported by us where we can also control their morphology by fine tuning the precursors. The photoactivity of these SOMs can be exploited in catalysis. Controllable rotation of an asymmetric SOM peapod also synthesized by us¹⁸ exploiting spin-orbit interaction of light designed to create exotic

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optical potentials in an optical trap has been shown by our group.¹⁹ Such motion of SOMs can be deliberately used for inducing dynamics in coordination chemistry. Achieving structural control in mesoscopic scale in oxometalate research is a challenge. We have in recent times also achieved such control by inducing soft-to-crystalline phase transition aided by controlled nucleation of SOM nanotubes under thermo-optic tweezers. Typically, on interaction with a thermo-optical component of an externally applied field, SOMs can be led to undergo continuous pattern formation via self assembly, caused by controlled nucleation on any surface. Formation of such directed mesoscale patterns also opens up the possibility of exploration of SOMs towards highly efficient catalysis. Recently, we have successfully shown such pattern formation on a glass substrate by using irreversible self-assembly leading to nucleation by the help of an external trigger of a laser beam in an optical tweezer.²⁰ SOMs as well as other functional molecules, loaded on SOMs, such as carbon nanotubes, paracetamol and fluorescent dye like perylene have been used in this approach for patterning. We have seen continuous permanent pattern formation leading to nucleation as we have created a “hot spot” on the surface around which a bubble grows. This pattern formation also exploits the high absorptive property of SOMs and much lower laser power is employed than usual laser-induced nucleation.²¹⁻²³ When functionalized SOMs are exposed to laser beams of optical tweezers, due to high absorptivity of SOMs stemming from ligand to metal charge transfer (LMCT) type transitions controlled nucleation of SOM core takes place and crystalline patterns of oxometalates are formed. Patterning with SOMs employing thermo-optical tweezers allows us to write pattern in microscopic scale-length in a pre-defined manner. This opens up enormous possibility of creating channels of micro-dimension to use them in channel catalysis. In this review article we have explored these topics in detail. We will here first describe synthesis and photo-catalytic properties of gold nanoparticle SOMs (AuNP-SOMs). From photo-chemical activity of SOMs we will move on to describe photo-physical property of another type of SOMs: the SOM peapods. We will describe their controlled complex motions in designed trajectories under exotic optical potentials in an optical field. We will also show catalysis by these dynamic particles in such optical fields. We will further exploit photo-physical properties of SOMs and pattern them using thermo-optic tweezers. We will finally conclude with open perspectives within the context of SOMs in patterning and catalysis.

PHOTOACTIVE SOMS: SYNTHESIS AND PROPERTY IN CATALYSIS

Recently, our group has reported synthesis of photoactive gold nanoparticle-SOM (AuNP-SOM) composite following a very facile and green synthetic route starting from POM building blocks viz., $[Mo_{132}]$.¹⁷ The work also demonstrated that one can control the morphology of the AuNP-SOM nanostructure by varying the ratio of the precursors in solution. Here we have taken the directed route to synthesize SOMs keeping in mind the goal to exploit its photoactivity. Redox reaction between $[Mo_{132}]$ and $HAuCl_4$ is employed which in turn produces oxidised oxometalate fragments absorbed onto AuNP surfaces. This produces AuNP-

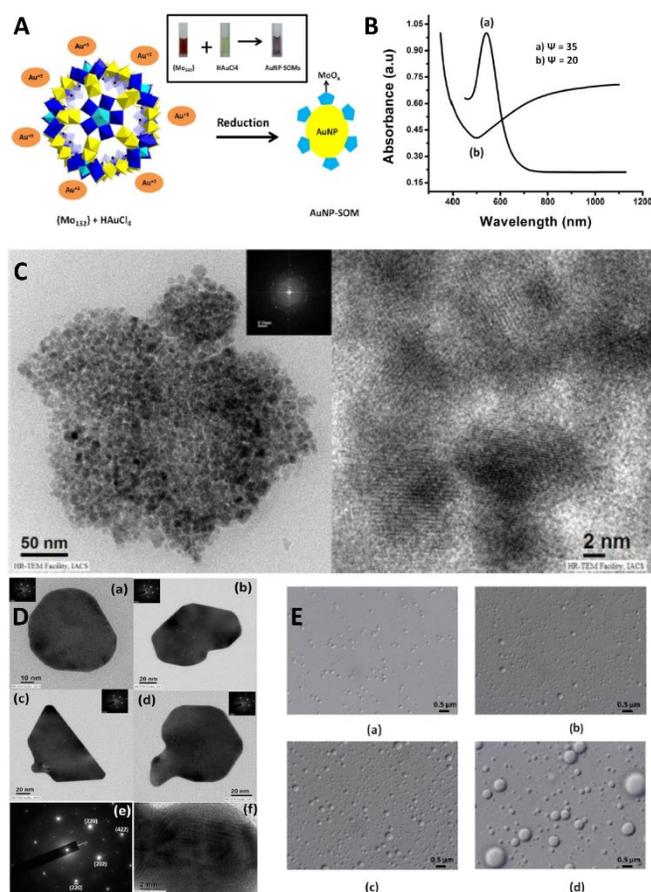


Figure 1. (A) Schematic of formation of AuNP-SOMs, (inset) color changing from brown to violet indicating formation of AuNP-SOMs. (B) SPR spectra of AuNP-SOM with different values of excess parameter ψ . (a) $\psi=35$; (b) $\psi=20$. (C) TEM images of AuNP-SOM (left) and the SAED pattern (inset), lattice spacing in nanoparticles (right) for $\psi=35$. (D) TEM images of AuNP-SOM (a-d); the SAED pattern of the hexagonal plate (e); lattice spacing in nanoparticles for $\psi=20$ (f). (E) Polystyrene microspheres obtained using different initial monomer concentrations, (a) 200 μ l, (b) 500 μ l, (c) 700 μ l and (d) 1000 μ l.

SOMs which get stabilized by virtue of electronic interaction between the components. A synthetic route of AuNP-SOM preparation is demonstrated in Figure 1. Quantum confinement of AuNPs deliver unique electronic as well as photo-catalytic properties dependent on the size, shape and morphology of the AuNP-SOM nanostructures.²⁴⁻²⁶

CONTROL OVER MORPHOLOGY

To check whether we can control the morphology of the AuNP-SOM nanostructure, we ran a series of concentration dependent experiments where we vary the molar ratio (ψ) of the reactants $\{C_{HAuCl_4} / C_{[Mo_{132}]}\}$ from a value of 20 to 40 by keeping concentration of $[Mo_{132}]$ fixed. We have observed that at low ψ value the resultant colloidal dispersion exhibits a very large and wide surface plasmon resonance (SPR) band extending from the near-IR into the whole visible range in the UV-VIS spectrum where the absorbance abruptly increases around 500 nm and keeps

on increasing indicating in-plane plasmon resonance band. (Figure 1) This phenomenon along with the transmission electron microscopy (TEM) images (Figure 1) of the AuNP-SOMs for $\psi = 20$ leads us to conclude the formation of anisotropic AuNP-SOM nanostructures.²⁷⁻²⁹ Spherical and crystalline nanostructures have been observed at $\psi = 35$ evidenced by the broad SPR band centered at 520 nm in the UV-VIS spectrum, indicative of a typical dipole resonance associated with spherical or quasi spherical Au nanoparticles. TEM images and select area electron diffraction (SAED) patterns confirm the spherical shape and crystalline nature of the AuNP-SOMs, respectively. No effect on the SPR band and size or shape of the nanostructures have been observed on increasing ψ value from 35 to 40 and for ψ greater than 40, no nanoparticle at all is detected.

Thus we have shown that it is very much possible to exercise a control over the overall formation of SOM nanostructures by controlling the operational parameters of the system which empowers us to control the morphology of the AuNP-SOM nanostructures.

AuNP-SOMs AS PHOTOCATALYST

As synthesized AuNP-SOMs have been shown to be effective as photopolymerization catalyst of vinylic monomers as they are employed successfully to polymerize styrene under UV irradiation.¹⁷ We have also been able to control the size and morphology of the polymerization product in this reaction by varying the loading of the monomer, i.e., styrene. As the monomer concentration for a fixed amount of catalyst has been increased, dimension of the polymeric sphere also increases. (Figure 1)

OPTICAL RESPONSE OF SOM-PEAPOD AND ITS CATALYTIC ACTIVITY

Now we want to see whether SOMs are optically responsive. We also ask whether we can induce and control the dynamics of SOMs using optics. Physical methods for inducing controlled motion in mesoscopic objects can mimic the transport system in a living body where transport is carried out by motor proteins. Thus, by monitoring such an induced motion, it may be possible to reproduce transport system of a living being synthetically. SOM-peapod, synthesized by our group, may play important role in this aspect since its intrinsically asymmetric shape can be responsive towards designed circular optical fields.¹⁸ With this end in view we place SOM peapods in designed optical fields created by optical tweezers.

Optical tweezers are perfect tools to examine controlled motion by SOMs as they can apply well-defined forces on mesoscopic materials confined within it.³⁰ As we change the angle of polarization of the linearly polarized laser beam, trapped particles start moving. But when we use thicker cover slip instead of the more common one used in optical trap, this enhances the possibility of spin-orbit interaction of the material with the beam as it affects the distribution of electric field near the material³¹ (Figure 2).

We also load POMs on the surface of the SOM peapods and perform catalysis under optical forces. We examine the catalytic property of SOM-peapods under optical fields. SOM peapods successfully act as catalyst carriers in the oxidation reaction of

benzaldehyde to benzoic acid. Here the SOM peapods carry $[\text{PMo}_{12}\text{O}_{40}]^{3-}$ to catalyze the reaction. The loading of $[\text{PMo}_{12}\text{O}_{40}]^{3-}$

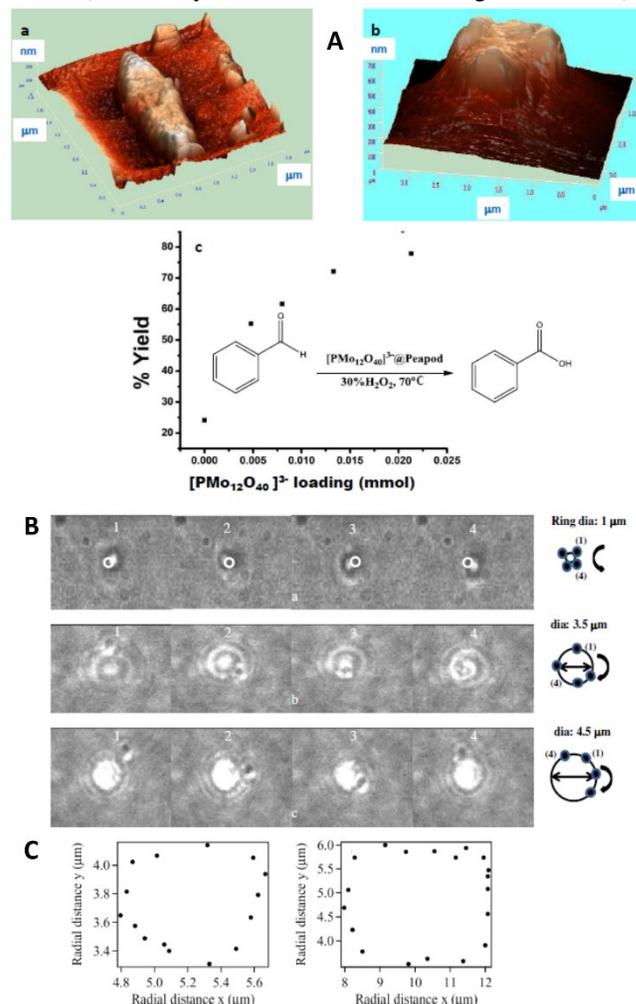


Figure 2. A. SOM Peapods as catalyst carrier. (a) shows the AFM image of a single peapod, (b) shows clear change in topology and dimensions of $[\text{PMo}_{12}\text{O}_{40}]^{3-}$ loaded catalyst and (c) shows the catalytic activity of the catalyst as function of catalyst loading on SOM peapod carrier from a spectroscopic analysis. The catalyzed reaction is also shown schematically. B. The actually controlled motion of an optically trapped single optically along the periphery of the intensity maxima ring having diameter 1 μm , 3.5 μm , and 4.5 μm , respectively. C. It shows the quantified values of the particle trajectories as obtained from a commercial particle tracking software.

on peapod is evident from the AFM image where it is clearly been shown that on loading the topology of the peapod changes. Gravimetric and spectroscopic results suggest that the loaded peapods catalyze the reaction and with an increase in the extent of loading, yield of the reaction increases.

After successful manipulation of the motion employing the interaction of optical component of SOMs with that of laser beam, we ask whether it is possible to exploit the responsiveness of SOMs to light to self-assemble them and write patterns using them? Can we get higher control over the formation of SOMs in different scale lengths and also over the thermo-optical properties

to design a model system for catalysis? We discuss these options next.

PATTERNING OF SOMS WITH LIGHT

Formation of induced pattern can open up a new direction in different catalytic reactions. SOMs being photo-active and soft in nature can be ideal candidates to induce patterns. This might be an optimal way to exploit their catalytic activities. Here we discuss the patterning technique of SOMs developed by us in detail.²⁰

In our patterning technique, the sample chamber consists of a slide on top and a coverslip attached to it from bottomside. On irradiation of the SOMs inside sample chamber a hotspot is formed on the slide region where the laser beams are focused around SOMs due to its high absorptivity at the wavelength of the laser. As a result a bubble is formed. This bubble acts as a nucleation site, and induces a convection current around of SOMs around it. On moving the laser beam the hot-spot also moves but deposits at the base of the bubble do not and thereby forming patterns at the base of the bubble on the glass slide. For pattern formation we have used mainly molybdenum based SOM nanotube and also organic molecule functionalized SOM nanotubes. Certain materials such as CNTs do not show patterning due to poor attachment with the surface due to their physical interaction with the surface unlike functional molecules like perylene with coordination centres or supramolecular bonding sites ensuring proper interaction with SOMs. SOMs play important role in patterning by assisting nucleation and also forming composite mesoscopic structure. Use of water as solvent enhances accessibility of this technique being greener and cheaper. Materials used are soluble in water, SOMs also form dispersion with water.

NUCLEATION OF BUBBLES

On irradiation of laser on the sample chamber with dispersed SOMs a hotspot is formed as mentioned above. At the vicinity of which several microbubbles formed in few millisecond timescale. Bubbles are also formed at the bottom surface but immediately pulled up to upper surface owing to buoyant forces. A single bubble grows very quickly on nucleation of all the small bubbles at the upper slide. Liquid particles or SOMs start flowing around the bubble in accordance with Gibbs–Marangoni convection flow as the difference in temperature of upper and lower slide comes into play which is accompanied by a capillary flow on evaporation of water.³² These combined flows draw the SOM particles towards the bubble resulting self-assembly at bubble base to form a ring like deposition.³³ We have demonstrated the bubble nucleation evidenced by Ostwald ripening incorporating a 670 nm detection laser and a photodiode. As the laser is moved to a new spot, it is energetically more favourable for the hot-spot to move leaving the deposit of nucleated SOMs to oxometalates at the base of the bubble or on the glass-slide. Thus moving the laser hot-spot or in fact moving the microscope stage of the optical tweezer a pattern can be written. The nucleation and phase transition from SOMs to crystalline oxometalates have been shown by Raman spectroscopy and TEM Electron diffraction studies. Various laser powers have been used for bubble growth and to control the thickness of the trail of the pattern. The width of the trail can also

be controlled by varying the speed of the stage of the microscope.²⁰

NUCLEATION OF CRYSTAL

On turning off the laser, the ring like material deposited at the base of the bubble undergoes a phase transition transforming into crystalline phase from soft SOM-structure.³⁴ As the laser on-time is increased gradually, the diameter of the deposited ring increases (Figure 3). Dimension of the material ring follows bubble formation. A plot of ring diameter against time generates a power law behaviour which fits in with Ostwald ripening. These data are well agreed with the two-stage crystal nucleation theory in which the first stage ends with phase transition from a viscous soft state to a crystalline hard state of matter.³⁵⁻³⁷ Two steps describe the complete process of nucleation; firstly, SOMs are absorbed in dispersion by the trapping laser, and secondly, dispersed SOMs undergo phase transition to form crystalline oxometalates on switching off the trapping laser. Raman Spectroscopy has been employed to characterize the complete procedure of crystallization. Raman spectra of SOM nanotubes in dispersion shows strong spectral band at 938 cm^{-1} due to the breathing mode of $\text{Mo-O}_{\text{br}}\text{-Mo}$. This band vanishes almost completely in case of crystalline state with the significant appearance of Mo=O_l band at 963 cm^{-1} implying optical field induced crystallization of oxometalates. (Figure 3).

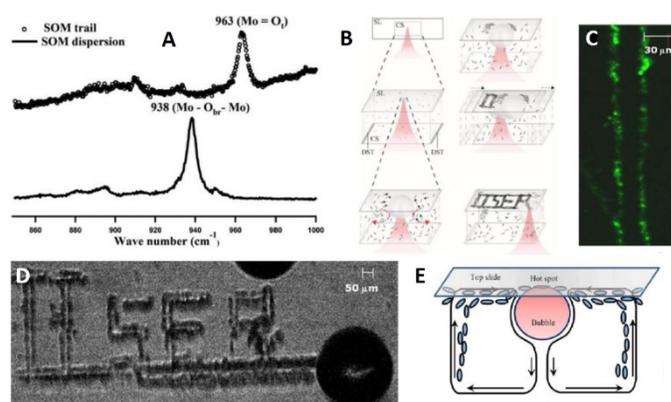


Figure 3. (A) Raman spectra of SOMs in an aqueous dispersion (solid line) and Raman spectra of the trails in a bubble-induced trail (open circles). (B) Schematic of the technique used for patterning. (C) SOM assisted patterning in presence of perylene, (D) Pattern “IISER” written on the top slide with deposited SOM crystals using a single bubble shown at the lower right corner of the picture, (E) Schematic representation of phenomenon involved in patterning.

FORMATION OF PATTERNS

During patterning, the bubble, trapped by the focused laser beam owing to the temperature gradient around it,³⁸ actually follows the laser beam as it is scanned through different areas by moving the stage. This phenomenon follows Gibbs–Marangoni convection of thermo-optic bubble migration. Combined trapping forces along with optically induced thermocapillary effect empowers us to translate the bubble with a high velocity that can not be obtained employing optical forces alone.³⁹ As the bubble is

moved by displacing the microscope stage, materials start to be self-assembled and then subsequent crystallization occurs, which then forms the desired pattern. Pre-determined pattern can thus be written with controlled movement of the stage. When SOMs are loaded with organic molecules such as glycine and paracetamol, continuous trails form by deposition of materials. Similar pattern is seen when SOMs are loaded with carboxylate substituted perylene accompanied with green fluorescence in the trail, which is higher at the edges. This phenomenon proves that self-assembly occurs at the bases of the bubbles than the centre.

To show the effectiveness of this technique in controlled pattern writing, we have written a pattern 'IISER' on a glass slide with SOMs with a length of around 1 mm and thickness of 50 μm .²⁰

POTENTIAL OF SOM TRAILS IN CATALYSIS

Optically-driven patterns made from SOMs have huge potential in catalysis, specially in catalysis. They can pave way for design of new micro-chip catalytic reactors, conducting circuitry, comprising of POM or any loaded material trails prepared from SOMs via laser irradiation. Reaction media can be loaded onto these trails which would act as catalysts and give products in high yield due to their extremely high surface area and high proximity with reactions. Such potentials of SOM trails in catalysis are now being investigated in our laboratory.

CONCLUSION

To conclude, we have shown that transformation of building blocks of POMs into SOMs opens up new opportunities as we go beyond crystalline regime of POMs. Owing to their soft nature, they can be easily tuned by externally applied forces like light to induce motion in them. Hence we are able to transfer structural information from molecular scale of starting well-defined precursor POMs to mesoscopic SOMs and further manipulate their properties like inducing dynamics. We can also render SOMs photo-active and do catalysis with them. We are able to exploit the photo-physical properties of SOMs to make patterns of crystalline oxometalates from them. Options exist to do catalysis and design circuitry using such patterns. SOMs and organic moiety loaded SOMs can be used for patterning and nucleation which have huge prospect in the field of catalysis and electronic circuit design just to name a few.

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