Research statement

Introduction and Background

I am Shivendra Singh, currently working under the guidance of Dr. Tushar Kanti Mukherjee at the department of chemistry IIT Indore. My research focuses on the photophysical study of self-assembled nanoparticle-polymer nanocomposite and their applications in environmental remediation and photocatalytic organic and inorganic transformations. Coacervate nanodroplets (NDs) are spherical polymer rich nanocomposite of oppositive charged polycations and polyanions formed via electrostatic interactions. They have a membrane-free structure with a large number of aqueous compartments making them a new class of efficient nanocages to trap or encapsulate different organic and inorganic molecules. Similarly, hybrid coacervates with embedded nanoparticles inside its structure make them inherit its photophysical properties as well as making them a prospective photocatalytic nanoreactor keeping its earlier membrane-free properties intact. The combined effect of these properties makes coacervate droplets an efficient biosensor as well as a capable nanocage for efficient environmental remediation of various pollutants whereas the embedded nanoparticles inside these coacervate droplets makes them a new class of efficient photocatalytic nanoreactor.

Summary of previous work

At the beginning of my Ph.D., I started with synthesizing ligand-capped luminescent CdTe quantum dots (QDs) in aqueous medium. After thorough characterization, the photophysical and physicochemical properties of bare QDs and its nanocomposite with a positively charged polymer have been explored in detail using various spectroscopic and microscopic techniques. Subsequently, these robust photostable coacervate nanocomposites have been utilized for ultrasensitive detection and simultaneous removal of environmentally toxic Hg^{2+} ions from aqueous medium. This work (Quantum Dot-Based Hybrid Coacervate Nanodroplets for Ultrasensitive Detection of Hg^{2+}) was published in **ACS Applied Nano Materials (***ACS Appl. Nano Mater.* **2020**, *3*,3604-3612**)**.

Current work, its objectives and results

Post Covid lockdown, during my second year of Ph.D. I started working with these nanoparticle-embedded coacervates toward its photocatalytic applications. Presently, utilization of visible-light to carry out various chemical transformations has become a fascinating field of research and particularly important in the current environmental and economical context. However, bare photocatalysts often undergo photodegradation or agglomeration, which limits their recyclability. To avoid this problem, researchers have recently focused on designing and fabrication of artificial photocatalytic nanoreactors. The confinement of catalysts and substrates inside a small volume of nanoreactor often modulates their chemical reactivity, which results in enhancement of reaction kinetics and conversion yields. Steering incompatible reactions to completion under nanoconfinement inside the nanoreactor finds particular importance in various applications. In this regard, designing of robust and flexible artificial photocatalytic nanoreactors with embedded catalytic units finds tremendous importance in recent times. However, the synthetic routes for earlier reported photocatalytic nanoreactors are often complex and require harsh experimental conditions for its fabrication. To overcome these shortcomings, we have developed a facile methodology for the fabrication of a new class of unique nanoparticle-embedded hybrid coacervate nanodroplets just by simple mixing of oppositively charged inorganic NPs and polyelectrolyte in aqueous medium.

The membrane-free structure of the coacervate droplets with embedded-nanoparticles makes it a potential photocatalytic nanoreactor. The presence of metal, carbogenic or semiconductor nanoparticles in these systems may provide many accessible and confined catalytic sites, which can result in enhanced catalytic activity for various important organic and biological transformations in an effective and economical way. With the aim to study and explore the photocatalytic properties and efficacy of these hybrid coacervate droplets we first fabricated metal free carbon dot (CD)-embedded nanodroplets (NDs). After an extensive characterization of their physiochemical and optoelectronic properties these CD-embedded NDs were utilized as a confined photocatalytic nanoreactor to drive the visible-light driven one electron photoredox reaction of ferricyanide to ferrocyanide. During our study we observed that while bare CDs failed to catalyze the photoredox reaction, the membrane-less architecture of these NDs provides an ideal microenvironment to drive the incompatible reaction in the confined space by regulating the surface charge density and effective concentrations of reactants. Our findings indicate that the visible light-generated electrons and holes in the CDs can be utilized efficiently inside these NDs to drive a wide range of photoredox conversions. The catalytic activity of the present CD-embedded NDs can be attributed to the symbiotic effect between the modulation of the surface charge density of individual CDs and the nanoconfinement effect inside the spherical NDs. This work was recently published in **ACS Applied Material and Interfaces** (*ACS App. Mater. Interfaces* **2021**, *13*, 43, 51117-51131). I further extended this work with QD-embedded NDs taking same model reaction of photoconversion of ferricyanide to ferrocyanide. The main aim of the present work was to shed some light on the versatility of these NDs as well as to show how the change in embedded nanoparticles affects the kinetics and photocatalytic efficiency of these NDs. This work is still under preparation.

Future plan and its scope

In the future I plan to fabricate different nanoparticle-embedded coacervate droplets as apart from the confinement effect these embedded nanoparticles are the major unit which decides the catalytic performance of these nanoreactors for various organic and inorganic transformations. So, the fabrication of appropriate nanoparticle-polymer nanocomposite is the key to carry out majority of photocatalytic transformations. I further plan to utilize these NDs to carry out various organic transformations like C-H oxidation, alcohol oxidation, C-C coupling etc. Furthermore, these coacervate droplets can also be utilized for various complex enzymatic reactions which may be realized easily in an effective and economical way inside these photocatalytic nanoreactors.

I also plan to study the applicability of these NDs towards various environmental problems and its remediation. The removal of various pollutants from the aqueous source as well as their degradation still remains to be a reason for concern. The photocatalytic properties of these NDs as well as the confinement effect might be effective for various pollutant degradation as well as their removal from the water source making them effective for environmental remediation. I believe the optimized performance of these coacervate NDs can help us to effectively control and regulate the environmental pollution level.