Abstract

During the past few decades, perovskite chemistry has emerged as a new space for promising light-harvesting materials. These unique materials provide outstanding optoelectronic properties, and as an outcome, it has been utilized as alternatives to the existing semiconductor materials. Perovskite materials are part of extensive studies because of their interesting properties such as high quantum yield, broad absorbance, tunable band gaps, etc. In the early stage, perovskite materials were used as a light sensitizer in a dye-sensitized solar cell. Later, in the year 2011, Park and co-workers fabricated a perovskite solar cell where TiO_2 acts as an electron transport layer and documented an efficiency of 6.5%. Till now, the highest efficiency achieved with the perovskite-based solar cell is 25.2%. Metal Halide Perovskites (MHPs) are known for their efficient light emitters because of their advancement in high photoluminescence quantum yield (80%), high external quantum efficiency (8%), and current efficiency of 43 cd A^{-1}. Due to the specific optoelectronic properties, perovskite-based materials are also utilized in broad photodetector applications. Also, the high quantum yield and efficient luminescence properties boost the perovskite materials to act as a sensor. Besides these applications perovskites are also a good candidate to act as a photocatalyst. Therefore, the prime motivation of this study is to explore the range of potential applications of perovskite-based materials as optical sensors (fluorescence and colorimetric), and as photocatalysts.

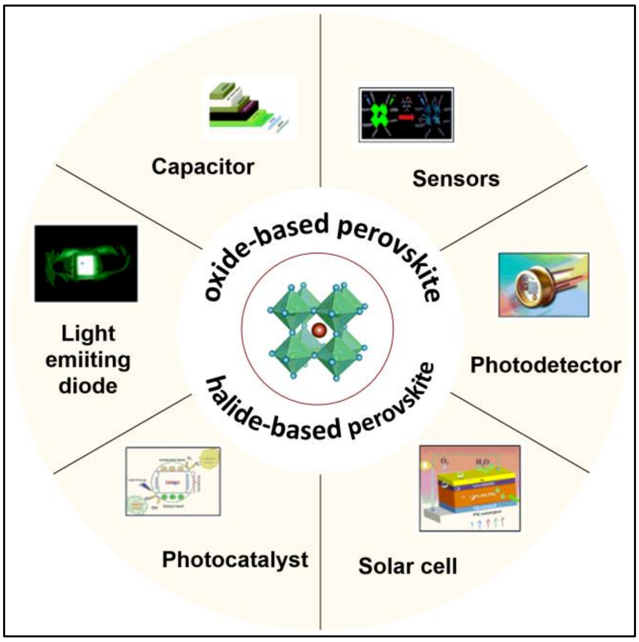

Figure 1. Schematic representation for different applications of perovskite materials

The Thesis

Chapter-wise summary of the thesis works is given below:

Chapter 1. General Introduction

This chapter deals with the general introduction to perovskite chemistry where the discussion is primarily focused on the motivation and background of the thesis research works. The classifications of perovskite-based materials, their properties, and their applications in different areas are reviewed in this chapter. The various preparative methods to synthesize perovskite materials are demonstrated. In addition, this chapter highlights the various applications of perovskite as an optical sensor and photocatalyst. The mechanism of studied perovskite materials to act as both fluorescence sensors and photocatalyst is also discussed.

Chapter 2. Cesium Lead Bromide: As a colorimetric and fluorometric sensing platform for selective detection of Uric Acid

This chapter discusses the design of a simple and very sensitive colorimetric fluorescent sensing probe for the detection of a biomolecule Uric Acid (UA, a heterocyclic organic compound generated during purine metabolism and a normal component of urine). For this purpose, easily synthesizable Cesium Lead Bromide ($CsPbBr_3$) is used as active perovskite material. With the gradual addition of analyte uric acid, the fluorescent emission peak of $CsPbBr_3$ at 520 nm shows quenching and thereby, the perovskite material is demonstrated as a fluorescent sensing probe. The devised probe in this study can be able to apply for an ultralow detection limit of 62.7 ppb and a fast response time of 30 sec in a linear range of (0.0031-1.33 μM). Along with the fluorescent technique, the same sensing platform can be utilized as a colorimetric sensing probe. A gradual colour changes from green to violet of the perovskite solution is observed upon interaction with UA, as a result, it makes this sensor probe a colorimetric sensing probe. The plausible mechanism for the detection of UA *via* $CsPbBr_3$ can be rationalized from the hydrogen-bonding interaction of UA with perovskite structure. In addition, the applicability of the proposed sensor is extended to a paper sensor probe for detecting UA. The selectivity of the sensing probe was performed in presence of different biologically relevant

interfering molecules and metal ions. Further, to validate the practical application the method is successfully applied for the detection of UA in human blood serum.

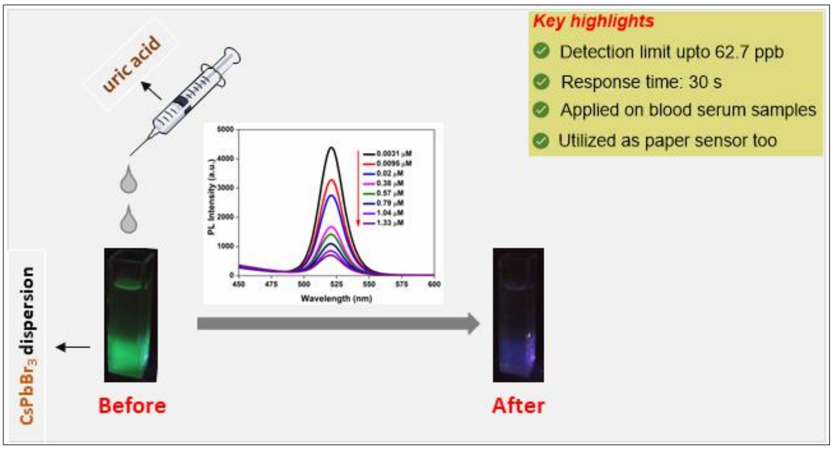

Figure 2. $CsPbBr_3$ as a colorimetric and fluorometric sensing probe for uric acid detection

Chapter 3. $CsPbBr_3$ Perovskites: A dual Fluorescence sensor to distinguish ethanol from methanol

This chapter describes the development of a fluorescence sensing system based on surfactant passivated $CsPbBr_3$ to monitor the alcohol. The chemical stabilities of different cationic [Cetyltrimethylammonium ammonium bromide (CTAB)], anionic [Sodium dodecyl benzenesulfonate (SDBS)], and non-ionic (Triton-x100) surfactant passivated $CsPbBr_3$ are studied. The most stable CTAB-passivated $CsPbBr_3$ (CTAB@$CsPbBr_3$) acts as a novel dual emission ratio-metric fluorescence sensing system and the designed sensor applies to detect the alcohol among different laboratory-used solvents. In this study, under a single excitation wavelength of 310 nm, the peak located at 550 nm can detect alcohols with turn-off fluorescence quenching behaviour; whereas the peak located at 432 nm can detect ethanol with turn-on fluorescence behaviour. As CTAB@$CsPbBr_3$ shows different modes of interaction with ethanol and methanol, therefore this sensing system is effectively applicable to discriminate ethanol from methanol. The designed sensing probe can detect alcohol with an ultra-low detection limit of 7.3 ppb for ethanol. In addition, the quantum yields of different passivated perovskites are calculated using rhodamine blue as a reference whereas the highest yield is found for CTAB passivated $CsPbBr_3$. To validate the applicability of the proposed sensor, the devised sensor is applied to determine the ethanol in easily accessible alcohol-containing samples such as cough syrup and petrol.

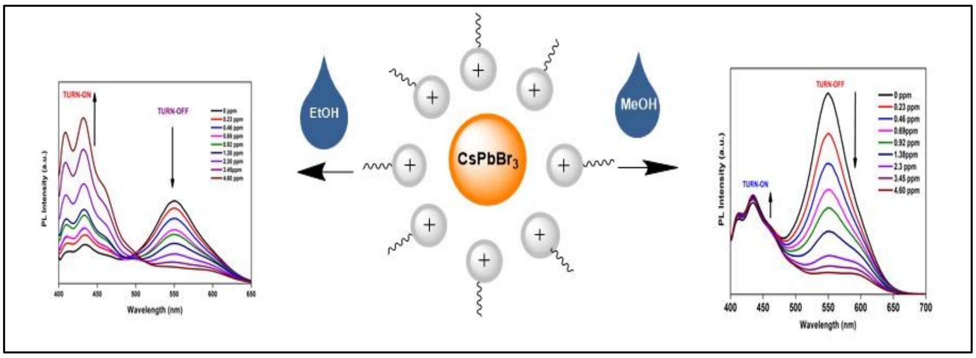

Figure 3. CTAB passivated $CsPbBr_3$ as sensors toward ethanol and methanol

Chapter 4. *p*-Thiocresol functionalized Cesium Lead Bromide (PTC@$CsPbBr_3$): As a fluorometric sensing probe for the detection of Cholesterol

In this chapter, the work highlights the synthesis of functionalized perovskite material and its application in the detection of cholesterol (responsible for diseases related to the heart and arteries in the human body). This study mentions the chemical stability of *p*-thiocresol, and oleic acid passivated Cesium Lead Bromide (PTC@$CsPbBr_3$) and the designed method can be applied as a colorimetric and fluorescence sensing probe. For the fluorescence probe, the luminescence intensity of PTC@$CsPbBr_3$ at 530 nm exhibits quenching with the gradual addition of cholesterol molecules under the excitation of 380 nm. The detection limit of cholesterol under the fluorescence sensing probe is 0.24 ppm with a fast response of 10s. The selectivity of the sensing probe was performed in presence of different biologically relevant interfering molecules and metal ions. The mechanism of the

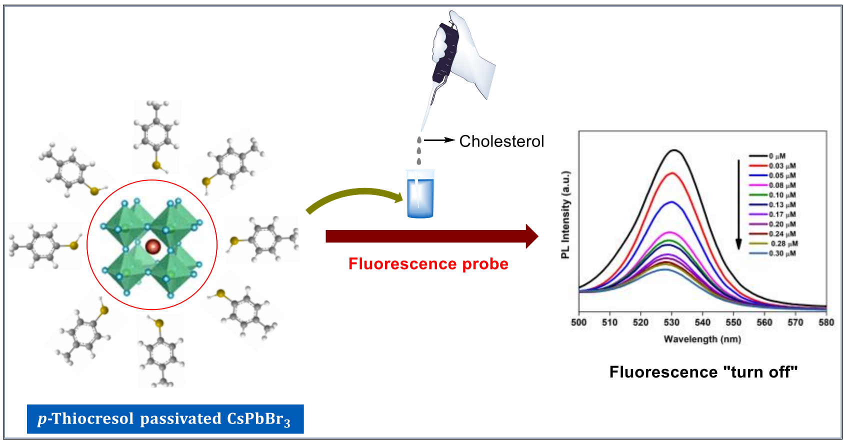

Figure 4. Detection of Cholesterol *via* *p*-thiocresol passivated $CsPbBr_3$

sensing process is investigated in this study. Finally, the applicability of the sensing method is established with the successful detection of cholesterol in human blood serum.

Chapter 5. Synthesis of $Ca_xCu_{3-x}Ti_4O_{12}$ Perovskite Materials and household LED light-mediated degradation of Rhodamine Blue dye

This chapter is about the synthesis of different compositions of Calcium Copper Titanate (CCTO) and the exploration of their photocatalytic activities for the degradation of Rhodamine Blue dye using household blue LED light. The quadrupole perovskite photocatalyst CCTO and its compositions ($Ca_xCu_{3-x}Ti_4O_{12}$) with varying x = 1, 1.5, 2 are synthesized and their defect density are studied to determine the suitable photocatalyst. The best defect density featured material is found with $Ca_xCu_{3-x}Ti_4O_{12}$ possessing a composition of x=1. Later, under the illumination of a 20-Watt LED light, the degradation of Rhodamine Blue dye is successfully demonstrated with these materials as a photocatalyst. The higher photocatalytic activity is achieved with the material with composition x = 1 and it shows effective degradation of Rhodamine Blue dye up to 99.43% within 5 hours. The rate constant of the degradation process is studied where a first-order reaction kinetics with the composition (x=1) is found higher than the other compositions. The possible reason for the different photocatalytic activity is most likely due to the larger defect density in composition (x=1). Finally, the mechanistic understanding of the degradation process is rationalized with different scavengers.

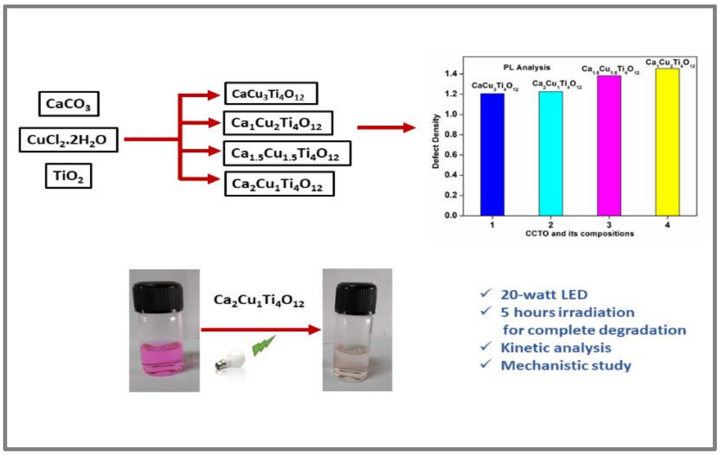

Figure 5. CCTO and its compositions towards the degradation of Rhodamine Blue dye

Chapter 6. Conclusion and future scope

The chapter-wise concluding remarks, major findings, and future scopes from this thesis work are summarized in this chapter. The primary goal of the studied research works is to explore the application of perovskite-based materials as a sensor and photocatalyst. Since the halide-based perovskite materials exhibit stability issues, different ligands have been successfully passivated on the halide-based perovskites to improve their stability. The different analytes such as alcohols, uric acid, and cholesterol are studied by applying both fluorescence and colorimetric sensing methods. Furthermore, another key outcome of these sensing methods is that the probe can be applied to practical samples having those analytes.