1
Introduction

1.1 Purpose of the study

Energy – a commodity essential for the development and survival of humankind. Energy is also a criterion for gauging the growth of a country by measuring its consumption and is an important parameter for economic growth.(Lu 2016) It has become of vital importance to cater to the energy requirements of an exponentially increasing population. The result of which is utilizing and over-exploitation leading to depletion of non-renewable fossil fuels and also simultaneously increasing anthropogenic CO_2 emission leading to a major crisis of climate change. Thus, the immediate requirement of a paradigm shift towards sustainable means of renewable sources of energy and the effect of climate change has brought about a major transformation in the way energy is perceived and utilized globally today. The resultant of which is the invention of sustainable technologies such as solar-based systems leaving less carbon footprint. Therefore, the use of an already existing inexhaustible solar energy is of prime obligation. The tapping and harvesting sun's enormous power can be of in the form of direct conversion by solar cell or from its secondary sources such as wind, hydro power, etc. Of the 123000 TW solar power that the earth receives only a fraction amounting to 15 TW is consumed worldwide.(Graetzel, Janssen et al. 2012) Statistically, the global PV capacity rose from 15 GW in the year 2007 to 400 GW a decade later whereas the global wind capacity increase from 50 GW in 2005 to 590 GW in 2018. However, the global share of renewable in electricity accounts for only a small increase from 18% in 2000 to 25% in 2019.(IRENA 2019) It is inevitable to find materials and resources that can boost the renewable energy sector which will comprise the harnessing of solar energy by converting into useful electricity and its storage. Some of the methods that have been growing int the field of solar energy conversion includes solar cells – from first generation Si solar cells, thin film photovoltaics to dye sensitized and perovskite solar cells in most recent years.

Certain other factors that needs to be addressed with the utmost urgency is that of pollution. Burning fossil fuels increases the amount of carbon dioxides and sulphur dioxides, damaging the environment.(Chen, Seo et al. 2013) Engines running on petrol and diesel contribute a major part of global pollution increasing the global temperature and CO_2 concentration in the atmosphere. The unburnt fuels or soot from these engines are released into the atmosphere thereby contributing hugely to global phenomena such as warming and climate change. Consequently, health-related issues such as breathing troubles, asthma, bronchitis lung cancer and skin-related allergies are caused by soot emitted from the exhaust of diesel-based engines. To curb these, a catalytic converter is installed in these engines. Without the use of a good catalytic converter the oxidation of soot occurs at very high temperature over 600 °C. However, the current converters utilizes material such as Pt that are expensive and suffers catalytic poisoning rapidly and needs to be replaced frequently. The process of burning the soot is generally an exothermic process occurring at a high temperature and holds high risk of destroying the filter in the process and thus, it is of major concern to develop a catalyst that will perform regeneration efficiently and conveniently. Existing technologies in catalytic soot oxidation uses expensive material such as Pt which are expensive and also suffers greatly from catalytic poisoning. Apart from this CeO_2 have been investigated because of its switchable oxidation states from 4+ to 3+. However, Ceria is reported to have low stability when operated at high temperature. One of the major criteria of improving the efficiency is to increase the contact and interaction points among the soot particles and the catalyst. Also, of equal importance is the existence of oxygen vacant and acid sites for active conversion of carbon soot into oxidized products such as CO_2. Following the present invention, we aim to develop materials with high oxygen vacant sites with active oxygen species for decreasing the temperature of soot oxidation to a range between 300 °C to 450 °C. We aim to achieve this by annealing hierarchically synthesized nanomaterials in a hydrogen atmosphere. The reducing ambience provided by the hydrogen will help to create and generate oxygen vacant sites which will act as active sites on the catalyst. Thus, when interacted with the soot particles will oxidize to soot to products such as CO_2. The hierarchical structure of the nanomaterial will favourably increase the surface area of the nanomaterial and increase the number of contact points between the soot particles and the catalyst nanomaterial. This will not only help reduce the temperature of the reaction but will also fasten the rate of reaction.

1.2 Objectives and scope

The main objectives laid out on all the chapters in this thesis are focused on engineering and synthesis of nanomaterials with different morphological, structural, physical, chemical, optical and electrochemical properties. The idea is to use these materials for various applications relating to sustainable technologies for energy harvesting and remedying environmental pollution such as water and air. However, there exists certain limiting factors that restrict its wide usability, such as – finding highly efficient materials with perfect bandgap alignment absorbing the visible IR region. This is important as it comprises the major portion of the solar spectrum, finding economically viable and environmentally benign materials to ensure its wide usability and production. The study undertaken in this thesis attempts to address some of these issues. The main objectives for the thesis work are listed below:

1. The idea of the study lies in exploring new nanomaterials with enhance properties using facile synthesis techniques in an ambient environment of temperature and pressure.
2. To study and analyse the properties of the synthesized materials using various characterization techniques.
3. Utilize these nanomaterials for applications relating to energy harvesting and environmental remediation withcareful use of the combination of the hierarchical morphological structure of environmentally benign and easily available TiO_2 nanomaterials with more stable mat
4. The aforementioned nanomaterials and its subsequent annealing in reducing hydrogen atmosphere are expected to create defect sites and oxygen vacant sites which will reduce the optical band gap during the synthesis HfO_2 doped black TiO_2 and HfO_2.
5. It is also the aim of this study to use sustainable local Rajasthani clay materials by modifying it for use as a catalyst for application in soot oxidation.
6. One of the most studied material known to mankind is Carbon. A part of this study aims to explore a particular carbon nanomaterial – N doped spherical carbon and explore it for applications such as energy harvesting and CO_2 capture.
7. A new perovskite quantum dots of $CsPbBr_3$ is explored for applications relating to water splitting.

1.3 Brief results and future perspective of the work

To achieve the objectives laid out in the study presented in this thesis, a combination of synthesis, characterization and application methods have been employed for carrying out various relevant experiments. The aim is to synthesis functional nanomaterials which are economically viable, ecologically benign and sustainable for applications relating to environmental remediation such as solving problems of dye contaminants in water, soot particle from fumes and diesel-run engines, energy harvesting using dye sensitized solar cell and photocatalytic splitting of water to generate a clean source of fuel.

HfO_2/TiO_2 Spherical Nanoparticles for Visible Photocatalytic Water Remediation of Industrial Dyes. (chapter 3: published as Laishram, et al., 2018; Materials Letters)

The study in this chapter was undertaken to understand and synthesize nanomaterials which can degrade common industrial dyes. In this study, a non-toxic and inexpensive wide band gap TiO_2 semiconductor was synthesized by doping with hydrogen and tuning the morphological features to spherical nanomaterials confirmed with TEM images. A simple two-step process of sol-gel synthesis followed by a hydrothermal process whereby nanospheroids of hydrogen and HfO_2 doped TiO_2 were synthesized. The modified TiO_2 has its optical bandgap tuned to about 2.94 eV which increases towards the visible spectrum compared to the generic TiO_2 having an optical bandgap of 3.14 eV. These nanomaterials were tested for its photocatalytic activity for applications in the degradation of five common industrial dyes namely, methyl orange, methylene blue, cresol red, thymol blue and solochrome black at different pH conditions – acidic, neutral and basic. It was observed that among all the dyes methylene blue degraded rapidly under basic condition very fast within 10 minutes of the reaction. Recyclability tests were successful and degradation activity was accounted for by HPLC. It can be concluded that the structural and morphological assembly of the synthesized nanomaterials greatly enhances attachment of dye molecules and in turn the degradation activity. The findings from this study might be a development in finding better and wide absorbing catalysts for photocatalytic applications. Additionally, this study might be able to provide a good photocatalyst for the degradation of industrial dyes polluting the water bodies.

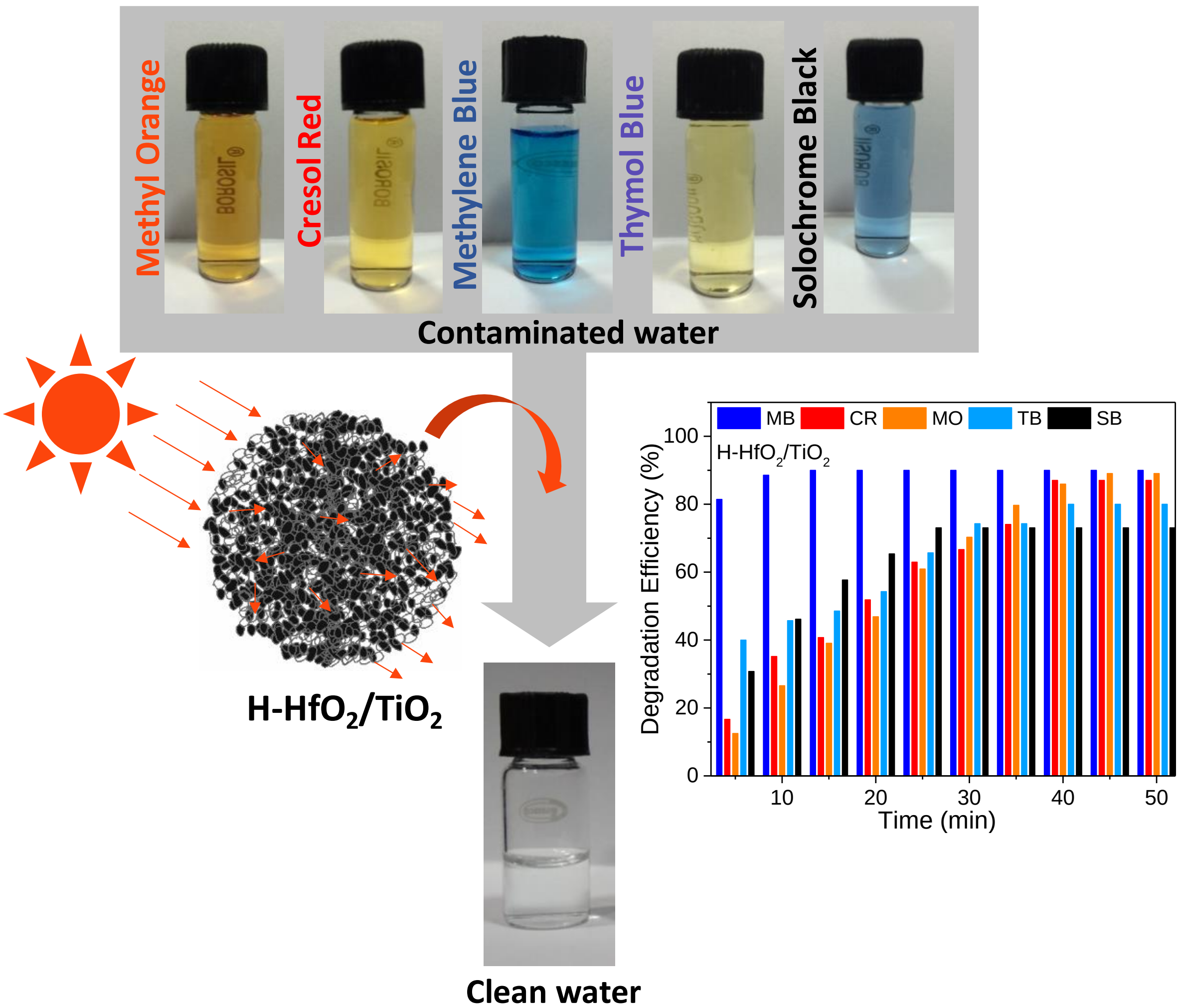

Figure 1.1: Photocatalytic degradation of five different industrial dyes using the synthesized hydrogen and HfO_2 doped TiO_2 nanomaterials.

Solution Processed Hafnia Nanoaggregates: Influence of Surface Oxygen on Catalytic Soot Oxidation. (chapter 4: published as Laishram, et al., 2018; ACS Sustainable Chemistry & Engineering)

This chapter attempts to address one of the major issues of soot particle pollution by developing a nanomaterial for catalytic oxidation of soot. Herein, a new and unconventional synthetic protocol to prepare HfO_2 with high porosity and surface area to be used for catalytic applications. HfO_2 is used as a support system for catalytic oxidation followed by the investigation of the role of surface oxygen by comparing the pristine with hydrogenated HfO_2. In this, nanohafnia prepared by a two-step process involving a sol-gel and hydrothermal route followed by annealing under hydrogen for different time intervals. The HfO_2 was then characterized by various methods to study the influence of hydrogen annealing on structural, optical, and catalytic properties. It was found via the TEM image that compared to the pristine HfO_2 when it is annealed under hydrogen the porosity, and the structure opens up which increases with annealing time from 2h to 6h. This nanomaterial, which is robust and stable is used as a catalyst for soot oxidation and found that after recycling and under accelerated thermal tests it is stable with the light off temperature as low as 551 °C for HfO_2 annealed for 2h. This study might provide a more stable soot oxidation catalyst compared to the conventionally reported Pt and CeO_2 based catalysts.

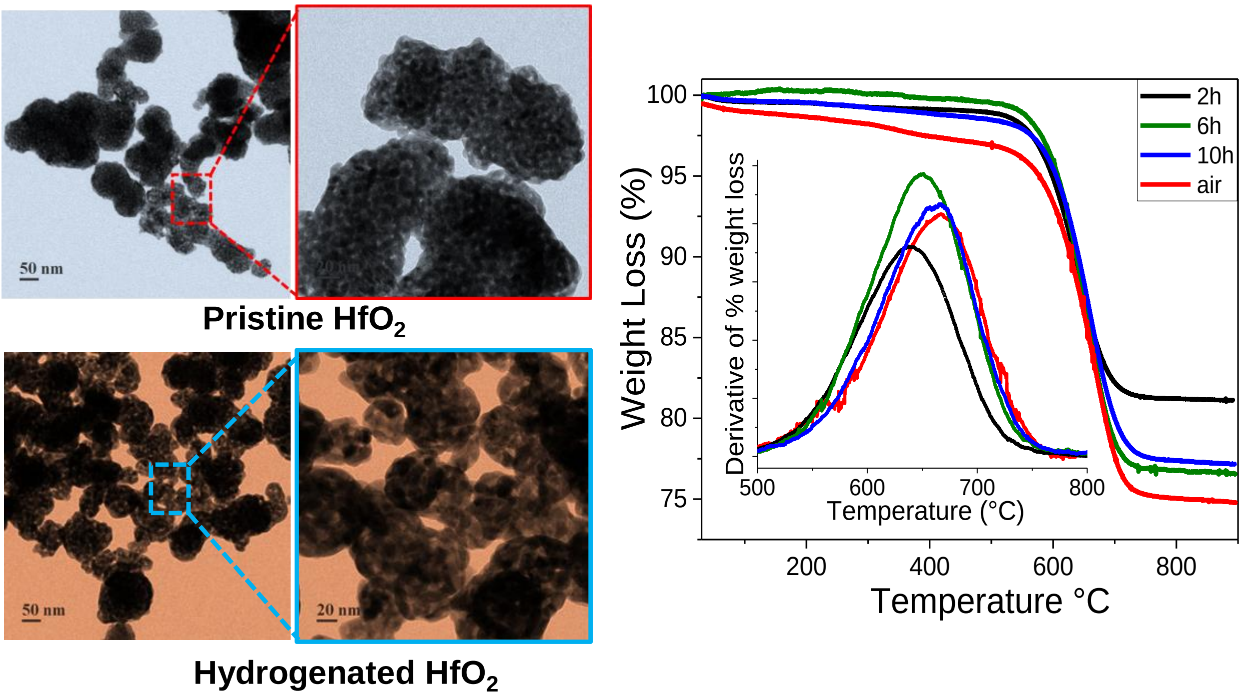

Figure 1.2: Accelerated soot oxidation activity of hydrogenated HfO_2 nanocatalysts a result of annealing under hydrogen giving rise to enlarge of pores in the synthesized nanomaterials compared to the pristine.

Natural Clay Transfiguration using Ni/Co Nanoparticle as Green Catalyst for Efficient Low-Temperature Catalytic Soot Oxidation.

In this chapter, we are proposing modified Rajasthani local clay as a suitable catalyst for another soot oxidation application. The use of clay is suitable as it offers interlayers in the nanometre range that can be tuned and engineered to make them active and green catalyst. Clay as a material has inherent properties such as large surface area, broken edge bonds, ion exchange which increases the adsorption, absorption and catalytic properties. This study investigates natural clay used along with non-noble metal – Ni and Co composition. The clay material acts as good support for Ni and Co, while the metal provides high reactivity. The use of a bimetal mixed oxide is expected to enhance the catalytic property of the system by a compound effect of improvement in terms of redox property, textural improvement, increasing basic sites, and increasing surface oxygen vacant sites. This is the first time that bimetal incorporation of Ni and Co in clay has been carried out for soot oxidation application. The findings in this study might help find an inexpensive and sustainable alternative to the commercially available ones.

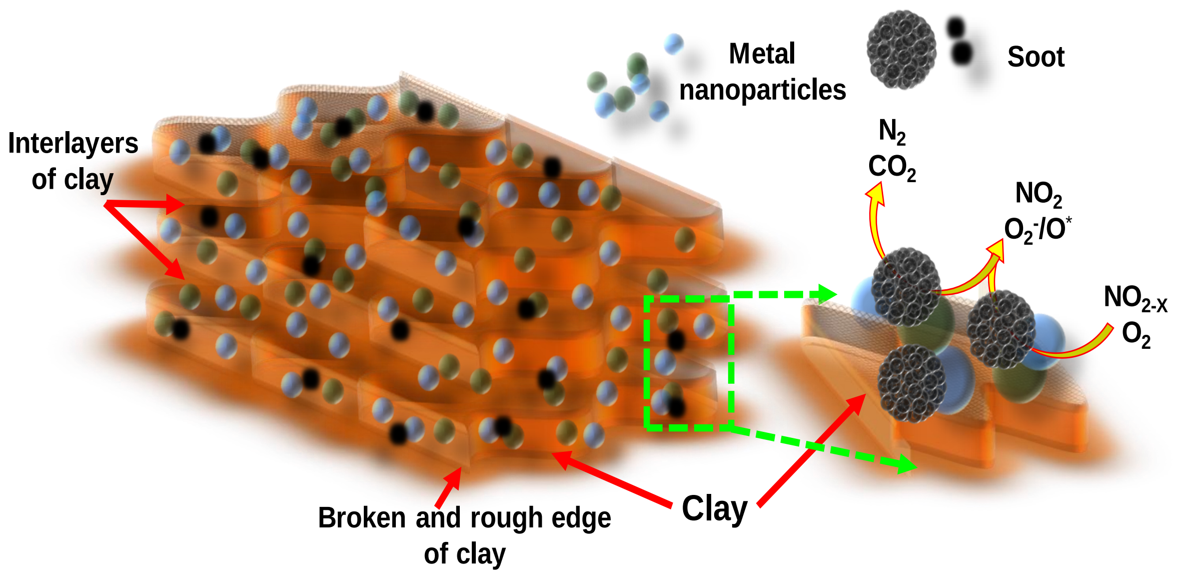

Figure 1.3: Use of sustainable local Rajasthani clay incorporated with Ni and Co oxides for use as catalysts in soot oxidation.

Nitrogen Enriched Carbon Nanobubbles and Carbon Spheres: A Study Involving Versatile Energy Harvesting, Storage and CO_2 Adsorption Applications. (chapter 6: published as Laishram, et al., 2020; ACS Applied Nano Materials)

This chapter attempts to engineer nanomaterials with the high surface area. N doped carbon spheres (CS) and N doped carbon hollow spheres (CNB) are synthesized that are used as support material in DSSC fabrication by using other metal oxides such as TiO_2. These carbon spheres and carbon nanobubbles are a result of a modified Stöber process. These are used in integration along with highly efficient variations of TiO_2 having different morphology, namely, rod-shaped TiO_2 synthesized at sub-zero temperature and spherical heterostructure TiO_2 with ZnO. The introduction of carbon spheres promotes better dispersion in TiO_2 nanoparticles eventually reducing agglomeration. This will lead to enhancement of porosity, scattering of the light which will improve the amount of light, dye absorption ideal for fabrication of DSSC device. This study highlights the differences between CNB and solid carbon spheres CS. Illustrations of diverse and significant properties of these synthesized materials focusing on the chemical, physical and morphological architecture have been detailed using various techniques such as XPS, TPD, BET, TEM and FESEM. Consequently, the effect of these materials when used for applications as electrode materials for DSSC, supercapacitor application and as an adsorbent for CO_2 adsorption has been thoroughly examined. High photoconversion efficiency was observed for the synthesized material when used as both photoanode and counter electrode for DSSC application with PCE of 10.4 % and 6.8 % respectively. It also showed good carbon dioxide adsorption with 2 mmol/g for the CS sample. This study may provide a new material not only for the aforementioned studies for various other application such as energy storage and fuel cell applications as well.

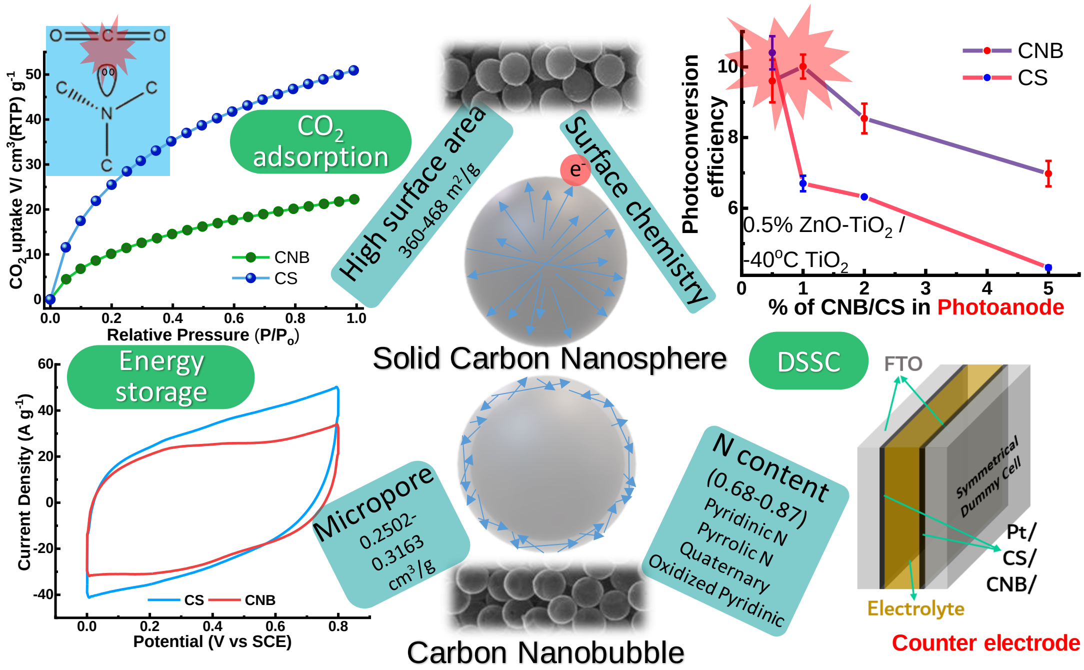

Figure 1.4: Nitrogen doped hollow carbon nanobubbles and solid carbon spheres for use as photoanode and counter electrode in DSSC, CO_2 capture and as a material for supercapacitor application.

Cesium Lead Halide Perovskite ($CsPbBr_3$) Nanocrystal Composites with Graphitic Carbon Nitride ($g\text{-}C_3N_4$) and Metal Oxide for Photoelectrochemical Application (chapter 7: this work was carried out at University of Alberta as a part of the SERB OVDF)

The main objective of the work carried out in this chapter is to attempt to synthesize stable quantum dots of all inorganic perovskites (AIP). However, this compound is known to be highly unstable in the ambient atmosphere and thus in order to increase its stability graphitic carbon nitride ($g\text{-}C_3N_4$) and metal oxides are introduced as composites. The $g\text{-}C_3N_4$ is a novel 2-D material synthesized by the Shankar's group at the University of Alberta (Kumar, Vahidzadeh et al. 2019) and oxides of Mo, Ti, Ta and Sn are further explored to act as a casing in the $CsPbBr_3$ compound. The synthesized materials were found to be stable for longer than 3 weeks (in comparison to the pristine $CsPbBr_3$) and are successfully implemented as electrode material for photoelectrochemical water splitting with the $g\text{-}C_3N_4$ and $CsPbBr_3$ composite giving enhanced photocurrent density.

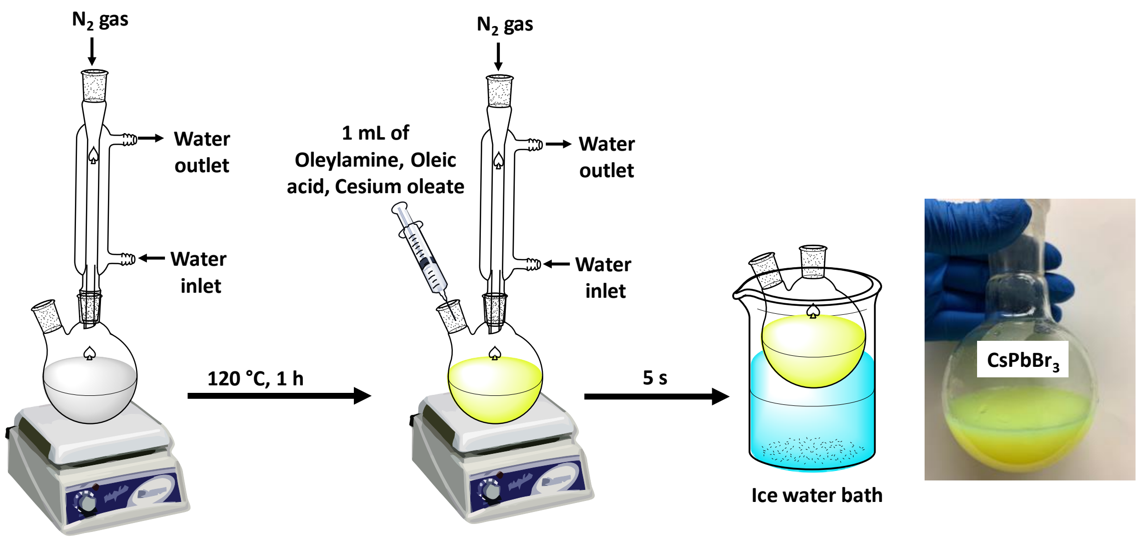

Figure 1.5: Schematic representation of synthesis of cesium leads halide all inorganic perovskite.

...