ORGANIC-INORGANIC HYBRID PEROVSKITES: SYNTHESIS, CHARACTERIZATION AND EVALUATION

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By

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ABSTRACT

The organic-inorganic hybrid perovskite materials emerged as a new class of semiconducting materials with a wide range of applications viz; optoelectronics, photovoltaics, etc. Among the various solution processed semiconductors, organometal halide perovskites represent a remarkable class of materials. Optical gap tunability, efficient charge transport, strong light absorption and favourable emission properties stand as the key features of these novel semiconductors. These properties make them a candidate for developing the new generation of low-cost solar cells and optical emitters. However, the fundamental properties of these materials remain unrevealed, making active discussions among the researchers.

In the thesis work, organic-inorganic perovskite materials are prepared using different strategies. Four different approaches of synthesis and characterization of tin and lead based perovskite were included in the thesis. The applications of the synthesised material were also attempted.

Layered organic-inorganic hybrid materials based on ionic liquid and lead chloride were studied for the first time. In this study, the synthesis, characterization and optical properties of hybrid materials formed from lead chloride ($PbCl_2$)-methylimidazolium chloride (MimCl) and $PbCl_2$-alkyl methylimidazolium chlorides (AmimCl) of varying alkyl chain lengths viz. ethyl (C_2mimCl), butyl (C_4mimCl) and hexyl (C_6mimCl) were evaluated. Complete structural characterisations of the synthesized materials were studied using single crystal X-ray diffraction, Raman spectroscopy, X-ray photoelectron spectroscopy. Apart from 3D structures, the presence of layered 2D structures was evident in all three structures. The interactions were studied using computational analysis and the results were correlated. The materials synthesized were non-hygroscopic and exhibited excellent thermal stability. The AmimCl-$PbCl_2$ shows absorption in the UV region with the onset extends to the visible range and exhibits good photoluminescence and exciton lifetime.

In the next chapter, organic dyes are introduced into a mesoporous perovskite layer and explored the contribution to light harvesting by co-sensitisation. Co-sensitisation has been investigated by using the bipyridyl based ruthenium dye-N719. These dyes absorb in the orange-red region of the visible spectrum and having a high molar extinction coefficient. Methyl ammonium lead bromide ($CH_3NH_3PbBr_3$) hybrid perovskites are doped with the bipyridyl based Ruthenium dye-N719 were synthesized. Doping with the dye on $CH_3NH_3PbBr_3$ exhibits a broad absorption peak in the visible region with a shift in the bandgap. The influence of doping on optical properties was studied using microscopic and spectroscopic analytical methodologies.

Tin halide perovskites are evolving as an alternate material to conventional lead based perovskites. The synthesis of methylammonium bimetallic bromide perovskites based on tin and copper ($MeSn_{1-x}Cu_xBr_{3-y}Cl_y$), where x and y = 0, 1, 2, etc. were carried out. Since tin (Sn) being highly sensitive to air, perovskite structure can be self-destroyed and Sn^{2+} forms Sn^{4+} oxidation state. As the copper is substituted against the tin, there is a tendency to form a 2D perovskite structure rather than a 3D structure. The thermal stability and environmental stability was investigated using Thermogravimetric analysis (TGA) and X-ray Diffraction (XRD), respectively. UV-Vis absorption spectrum exhibits optical absorption over the entire visible spectrum with a band gap of 1.60 eV which is comparable to that of lead based perovskites. Charge carrier lifetime and luminescence behaviour of the materials were determined using time-resolved fluorescence spectroscopy.

Polymeric encapsulants are proven defect passivating agents which render perovskite films robust against harsh environments. Here, we report the new synthesis approach of tin halide perovskite encapsulated by a transparent conducting oligomer, namely polysilsesquioxane (PSQ). The stability of the tin halide perovskite is improved using the modifier. PSQ has good electrical conductivity and HOMO-LUMO energy levels being suited for promoting the hole conductivity of the perovskite materials. The crystal structure, morphology, optical properties and current-voltage characteristics were studied for the PSQ encapsulated perovskite using microscopic, spectroscopic and photovoltaic characterization techniques.

Photovoltaic cells were fabricated under ambient atmosphere (RH: > 60%) over the fluorinated tin oxide (FTO) glass substrate by solution processing method using spin coating technique. All the cells exhibited photovoltaic responses when exposed to sunlight. As the layered AmimCl-$PbCl_2$ shows photocurrent in the UV region, these materials exhibit negligible power conversion efficiencies in solar cell devices. Photovoltaic power conversion efficiencies (PCEs) in the range of 4.8 - 6.8 % were observed for the dye-doped methylammonium lead bromide perovskites based active layer. Short-circuit current densities (J_{sc}) were in the range of 7-8 mA/cm^2 with open circuit potential (V_{oc}) ~ 0.96 V and fill factors (FF) in the range of 60 % under the 1 sun (100 mW/ cm^2) illumination. The tin and copper mixed perovskites exhibited PCE of ~ 2 % with an V_{oc} of ~ 0.95 V, Jsc of ~ 4.3 mA/cm^2 and a FF of ~ 0.55. The oligomer modified methylammonium tin bromide perovskites shows a PCE of ~2.2% with a J_{sc} of ~ 5.4 mA/cm^2, V_{OC} of ~ 1.0 V and a FF of ~ 40 % under 1 sun illumination. Compared to the commercial system though V_{oc} was comparable, the J_{sc} and the PCE was very low, which is probably due to the increase in resistance at the interface of the layers, defects, and increase in thickness of the layers. Further optimization of the fabrication condition can yield better PCE.