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CsSnCl₃ nanocrystals as efficient lead-free perovskite: A combined experimental and theoretical study

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Introduction

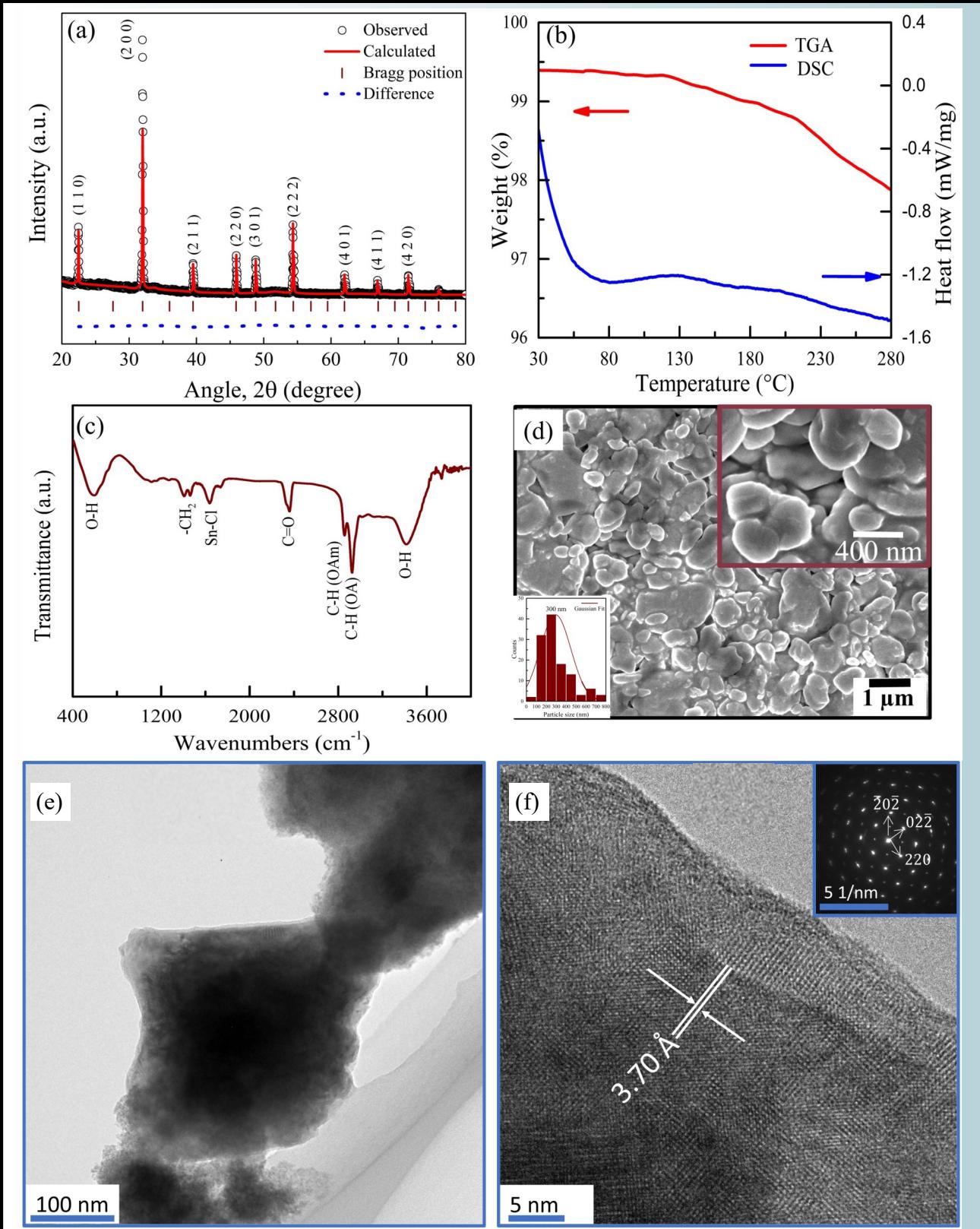
- Alternate lead-free halide perovskites have been gaining interest due to their non-toxic light-harvesting properties.
- This investigation aims towards a rapid synthesis of CsSnCl₃ nanocrystals and combined experimental and theoretical investigation of CsSnCl₃ nanocrystals.

Experimental Details

- A rapid hot-injection technique¹ was adopted to synthesize CsSnCl₃.
- The experimental characterizations were carried out using various techniques including TEM and FESEM imaging, TGA and DSC analysis, XPS spectroscopy etc. and theoretical analysis was conducted using DFT based GGA+U calculation.

Results and Discussions

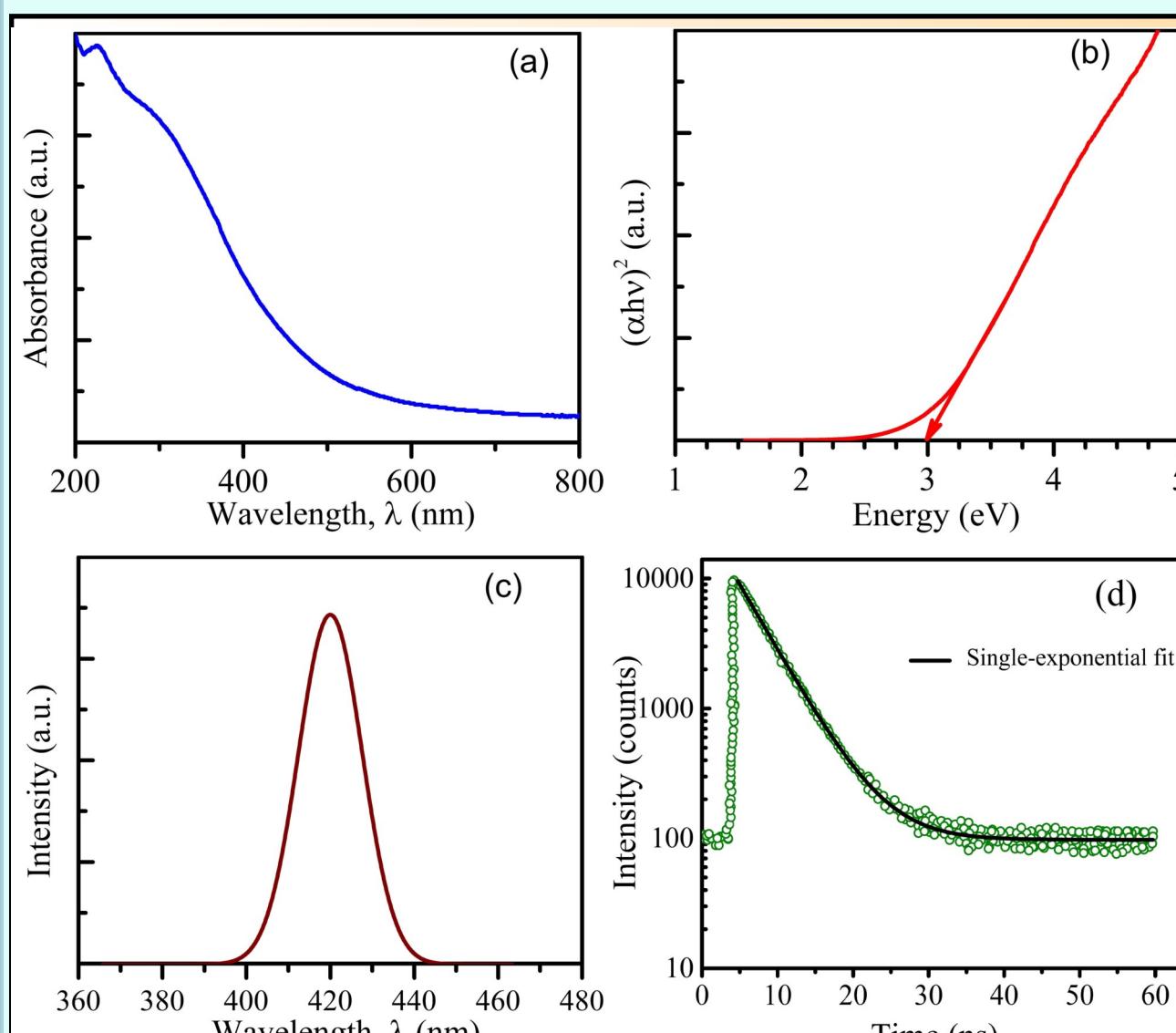
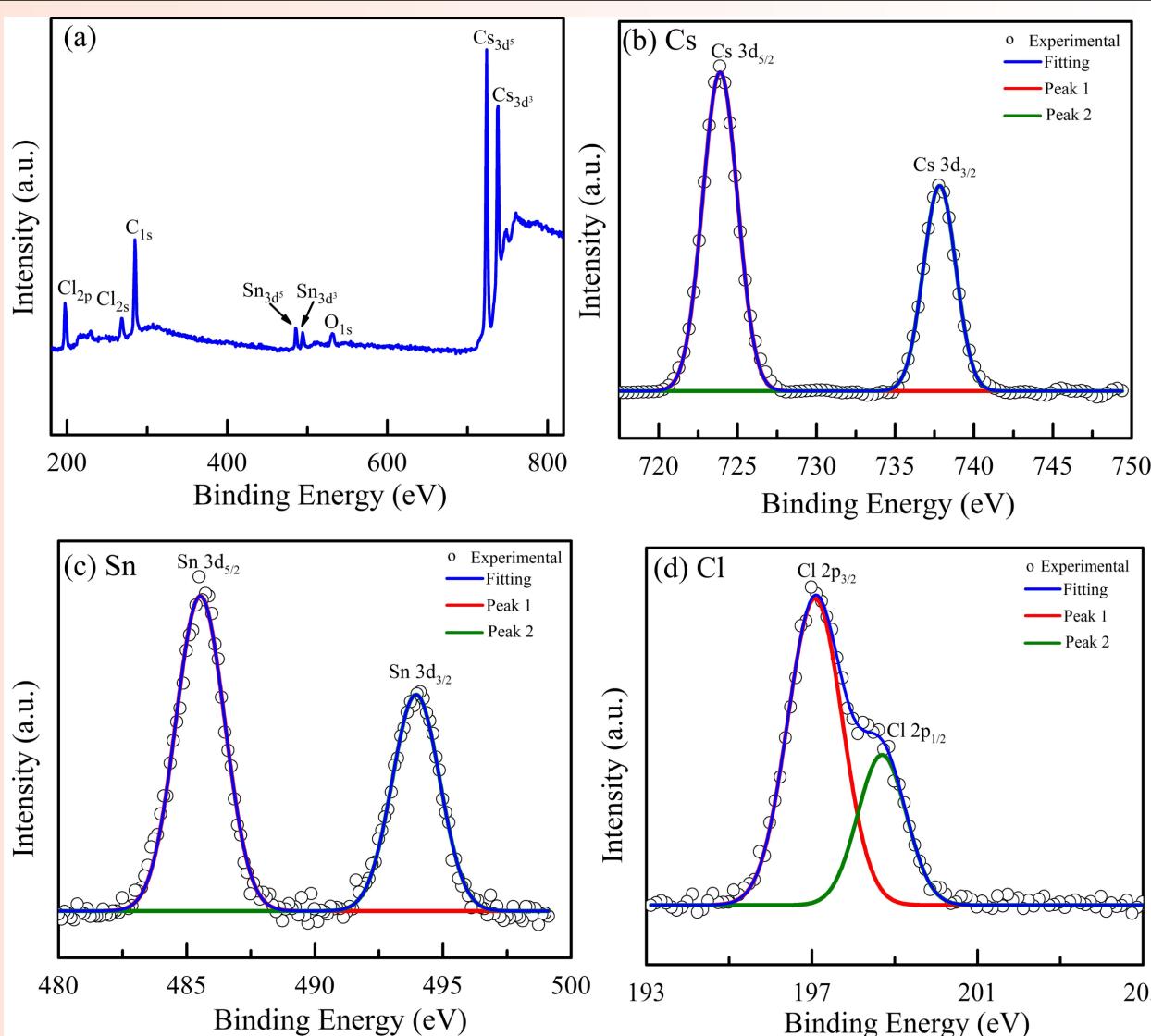
Experimental Results



- The Rietveld refined powder XRD spectrum (Fig. a) confirms the as-synthesized nanocrystals were cubic crystals with a space group of $pm\bar{3}m$ and no undesired peak was found.
- The thermal stability of the CsSnCl₃ nanocrystals were investigated by conducting TGA and DSC measurements (Fig. b) and the nanocrystals were found to be thermally stable.
- FTIR spectroscopy was conducted and no unexpected absorption band was observed (Fig. c) which conforms to the phase pure formation of the prepared nanocrystals.
- The surface morphology of the nanocrystals was better than the previously reported results². The average crystal size was 300 nm. (Fig. d)
- TEM bright field image showed the nanocrystals were cubic in shape. (Fig. e)
- The high-resolution TEM (HRTEM) image showed the crystallinity of this nanocrystal with a 3.70 Å interplanar spacing. The selected area electron diffraction (SAED) pattern demonstrated the crystals had face-centered cubic phase. (Fig. f)

(a) XPS full spectra of CsSnCl₃ nanocrystals illustrating the existence of constituent elements (Cs, Sn and Cl) in the fabricated sample. Core level XPS spectra for (b) Cs 3d (c) Sn 3d (d) Cl 2p demonstrating the purity of the sample and valence states of the constituent elements, respectively.

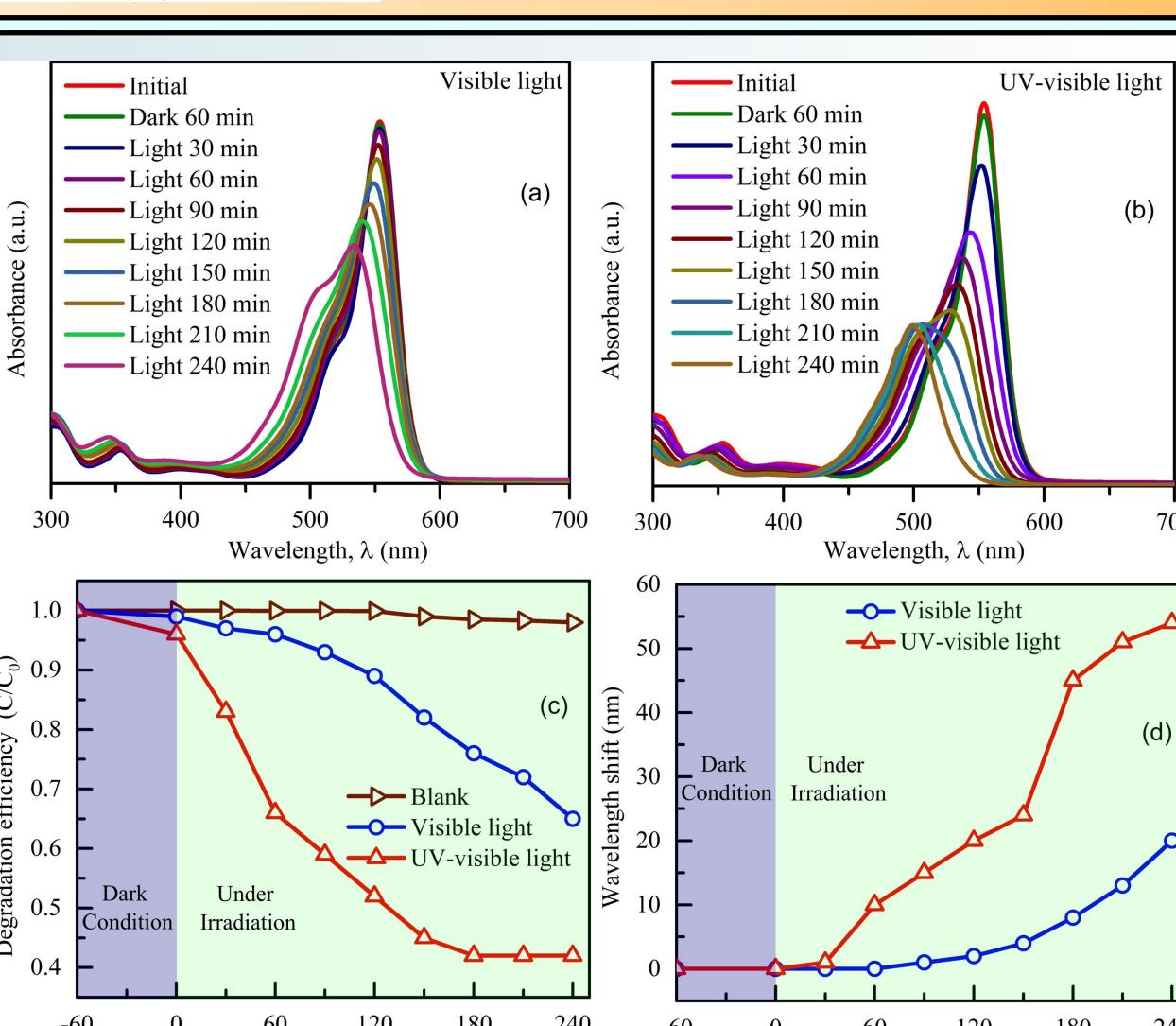
- The XPS spectroscopy was performed to assess the surface purity of the sample.
- No unexpected peaks other than Oxygen (O) and Carbon (C) was obtained because of the adsorption of O and C from the environment³.



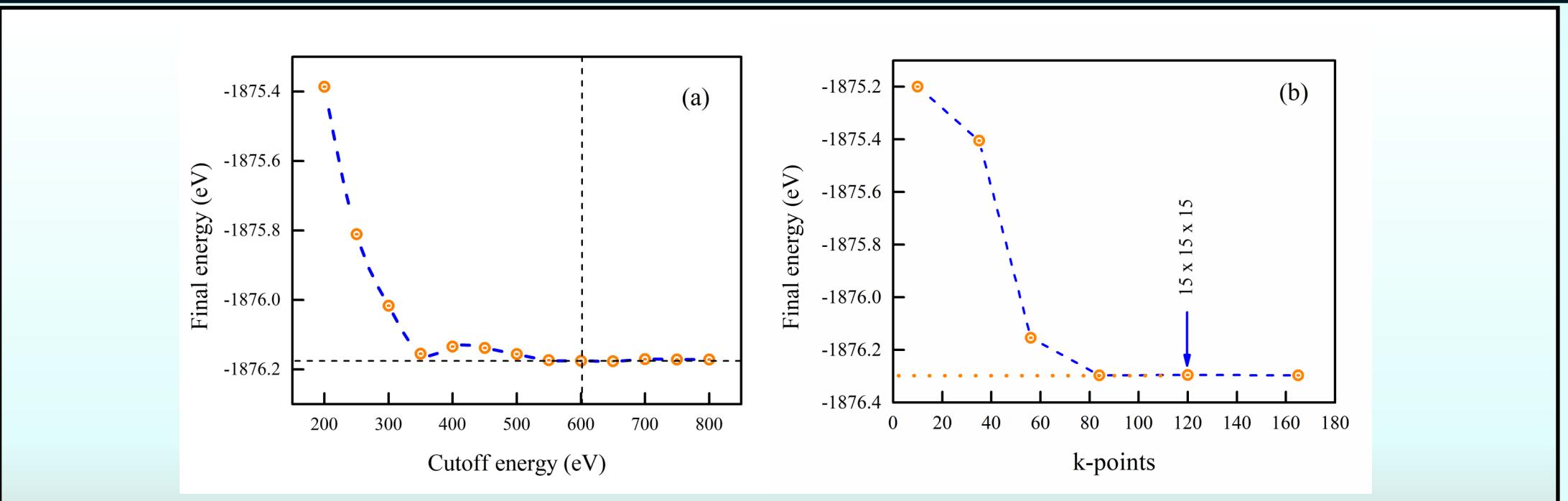
The absorption spectrum of the as-prepared CsSnCl₃ nanocrystals. (b) Tauc plot demonstrate the direct band gap of the CsSnCl₃ perovskite to be ~2.98 eV. (c) PL spectrum of the perovskite nanocrystals shows the peak wavelength at 420 nm. (d) Time-resolved PL decay curve under pulsed 440 nm excitation at room temperature for CsSnCl₃ nanocrystals.

- A strong absorption is observed in the UV-visible region
- From the Tauc plot from fig. (b), we have determined the direct bandgap of ~2.98 eV
- The bandgap from the PL spectra was also found to be ~2.96 eV.
- Time resolved photoluminescence spectra demonstrated the quantum efficiency of 91%.

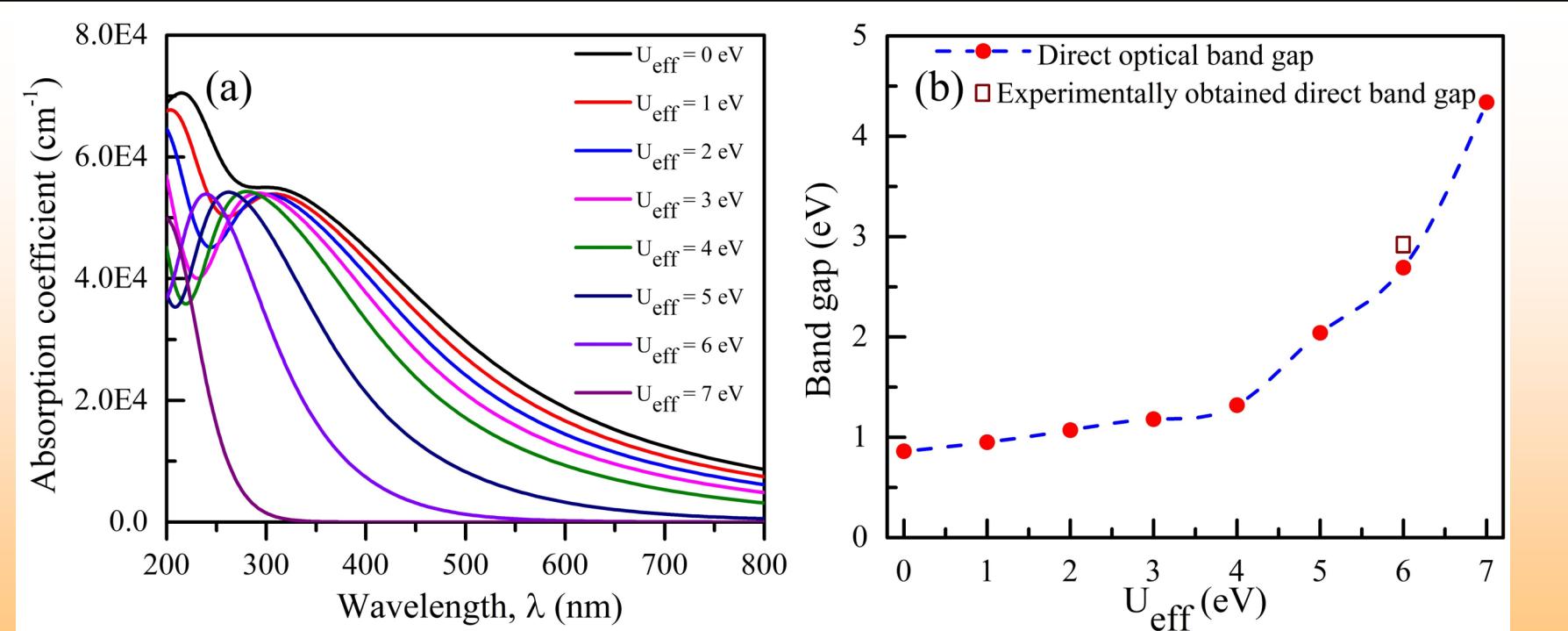
- The photocatalytic performance of the CsSnCl₃ nano crystals was investigated towards the degradation of RhB under both visible and UV-visible illumination.
- From the blank test and dark adsorption test, we confirmed the due to self photolysis and chemi adsorption potential of the RhB dye molecules is negligible for RhB molecules.
- Under the irradiation of visible light, a ~35% degradation of RhB dye after 240 minutes is achieved.
- When irradiated under uv-visible light, a 58% degradation after 240 minutes is achieved.
- Under visible light irradiation, the decomposition was due to cleavage of its whole conjugated chromophore structure. But under uv-visible light, the main degradation pathway was N-deethylation.



Theoretical Results



The DFT based first-principles calculation was carried out using the Cambridge Serial Total Energy Package (CASTEP) with GGA and GGA+U approximation. The optimized cut-off energy of 600 eV and k-points 15 × 15 × 15 is sufficient to obtain the ground state energy of CsSnCl₃ perovskite.



(a) Absorption coefficient variation as a function of wavelength for various U_{eff}. For U_{eff} = 6 eV the theoretically calculated direct optical band gap matches well with the experimentally obtained direct band gap of 2.98 eV (square marked).

Variation of the absolute effective masses of holes and electrons in terms of the electron rest mass, m₀ with the increase of U_{eff} values were calculated using the following equation.³

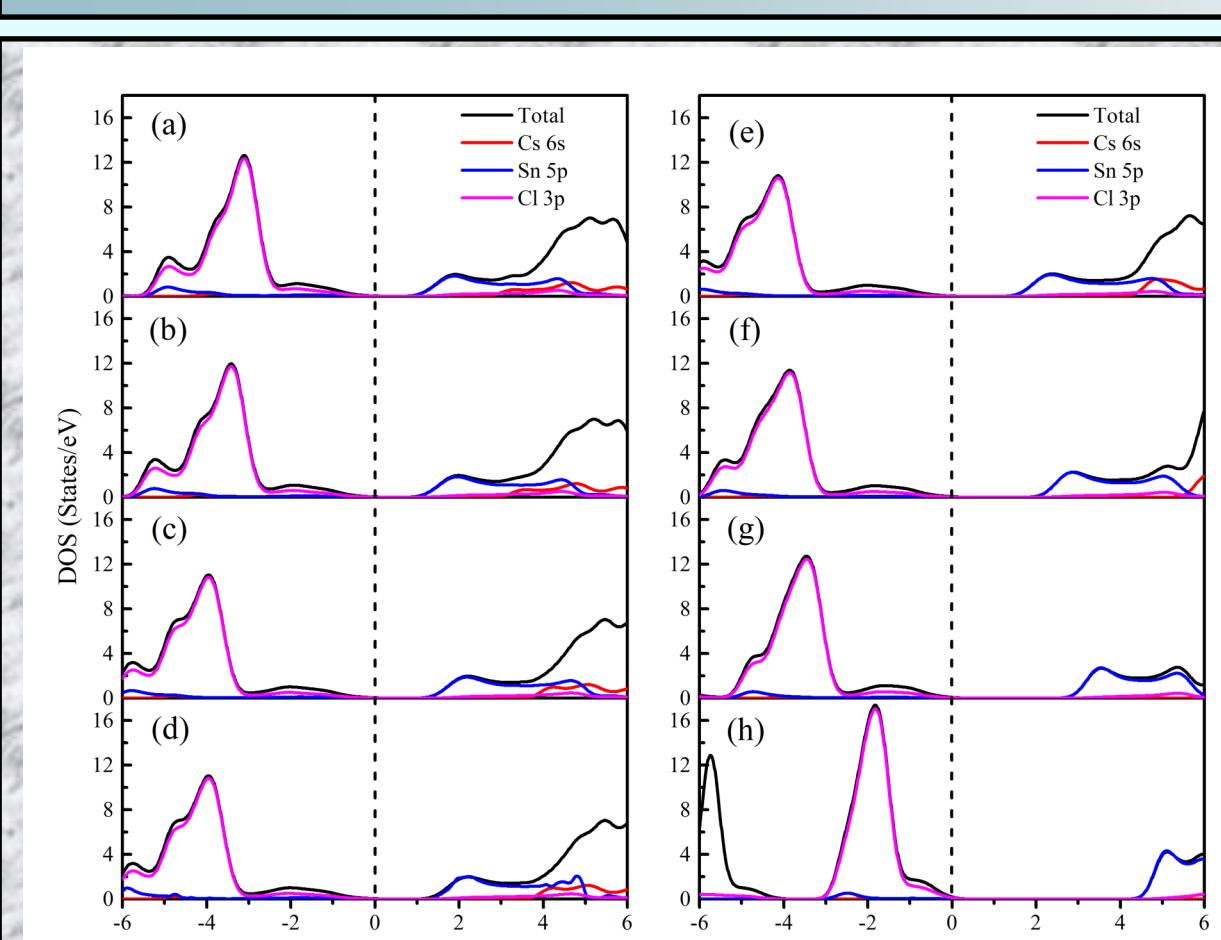
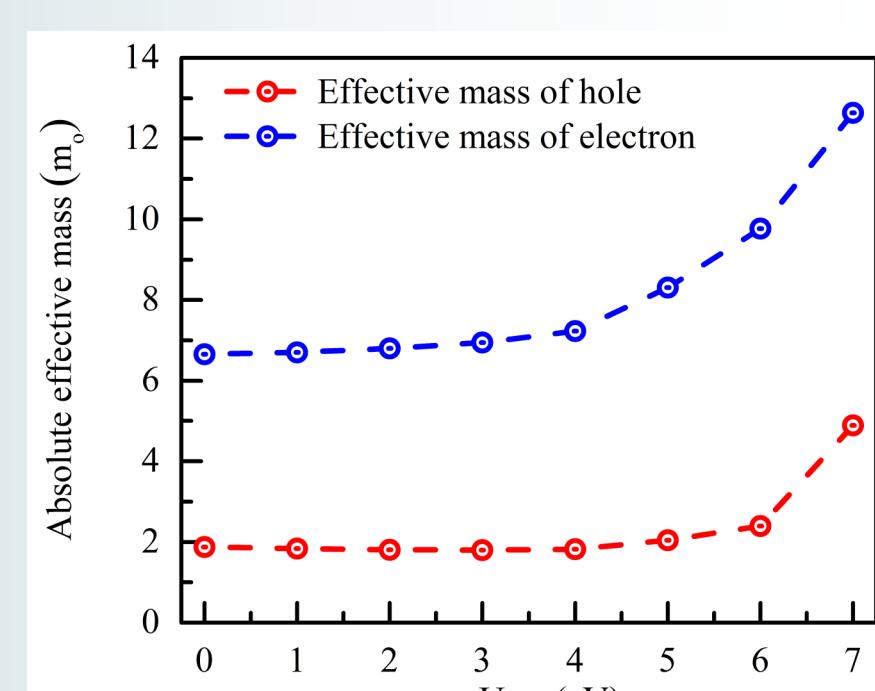
$$m^* = \hbar^2 \left(\frac{d^2 E}{d K^2} \right)^{-1}$$

The ratio of the effective mass of holes and electrons (D) can be used for the indication of low recombination rate of photogenerated electrons and holes:

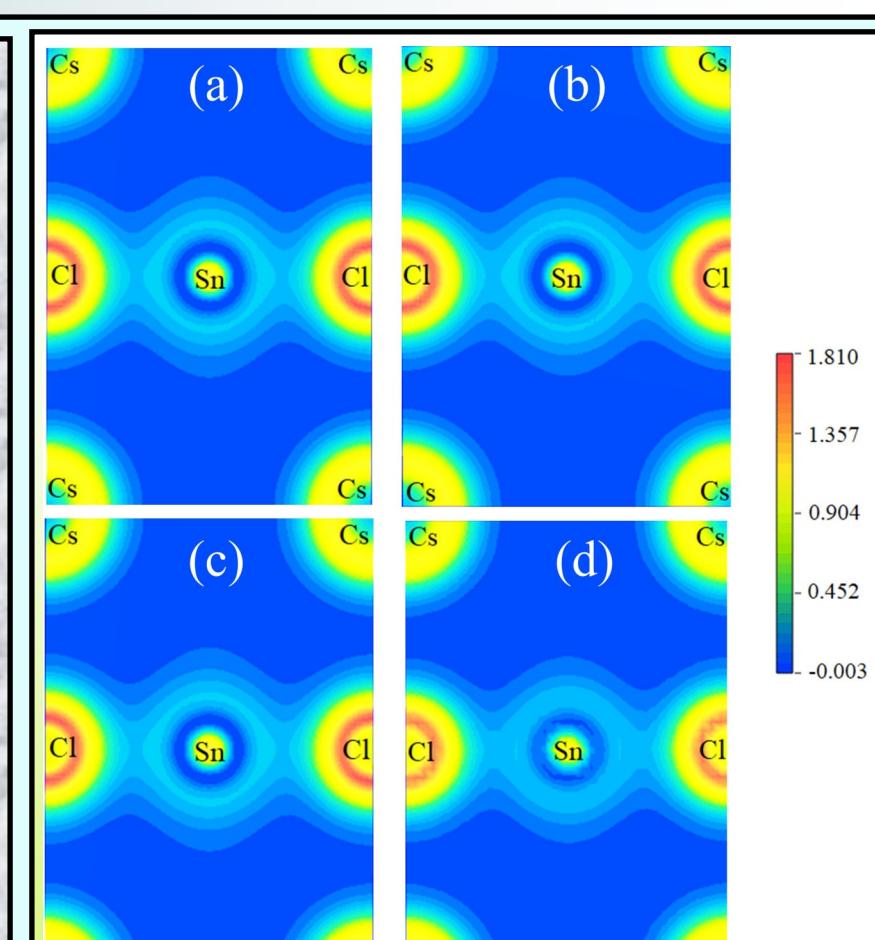
$$D = \frac{m_h^*}{m_e^*}$$

Here, unlike conventional photocatalysts the “D” value of CsSnCl₃ was less than 1 and CsSnCl₃ demonstrated up to 58% degradation without any reagents.

So we think that a “D” value either greater or smaller than 1 can be the indication of promising photocatalytic performance.



The valence and conduction bands are formed via the hybridization of the Cl 3p, Sn 5p and Cs 6s orbitals, respectively as seen from the density of states figure.



The covalent type band is formed in Sn and Cl atoms, while Cs atoms make an ionic bond.

Conclusion

- We have demonstrated a new way of the synthesis of lead-free CsSnCl₃ perovskite via hot injection method.
- The as-prepared sample is non agglomerated and non porous, resulting in a superior surface morphology.
- The synthesized CsSnCl₃ has a cubic structure with pm₃m space group and has crystal phase stability over a large temperature window.
- The calculated bandgap of the CsSnCl₃ was ~2.98 eV.
- The as-synthesized sample showed up to ~58% photocatalytic degradation efficiency under UV-visible irradiation.
- Our theoretical calculation demonstrated a 90% accurate estimation of the previously reported experimentally observed optical band gap when U_{eff} = 6 eV was considered in the “GGA+U” method.
- The hybridization of Cl 3p and Sn 5p orbitals with a major contribution from Cl 3p states contributed to the formation of the valence band while the Sn 5p orbital with a minor contribution from Cs 6s orbital contributed to the creation of the conduction band of the CsSnCl₃.
- The concentrated overlapping electron cloud between Sn and Cl atoms demonstrates that a sigma-type covalent bond prevails between the Sn and Cl atoms, and the degree of the bond covalency reduces when a strong on-site coulomb interaction is considered.

References

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