Hot Injection Synthesized Lead-free $CsSnCl_3$ Nanocrystals: An Experimental Investigation

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Introduction

In this current investigation, we have demonstrated a rapid synthesis technique of thermally stable cubic phase non-agglomerated cesium tin chloride ($CsSnCl_3$) nanocrystals (NCs) with an average crystal size of 300 nm via the hot-injection method and characterized the optical and photocatalytic properties experimentally.

Synthesis

1. $CsSnCl_3$ perovskite nanocrystals was synthesized by adopting a facile, low temperature hot-injection technique[1].

2. Stochiometric amount of $C_{18}H_{36}$, Cs_2CO_3 and $C_{18}H_{34}O_2$ was taken into a beaker and dried for 1 hour in a vacuum drier at 120 °C. The mixturer is then heated for 1 hour at 180 °C in Ar atmosphere. Thus Cs-oleate was prepared.

3. In another beaker stochiometric amount of $SnCl_2.2H_2O$, $C_{18}H_{36}$, C_{18},$H_{37}N$ was tak -en and dried for 1 hour in a vacuum dri -er at 120 °C. The prepared Cs-oleate is then quickly injected and the resultant mixture is heated for 1.5 hours at 200 °C. Finally, the CsSnCl3 nanocrystals are separated by centrifugation.

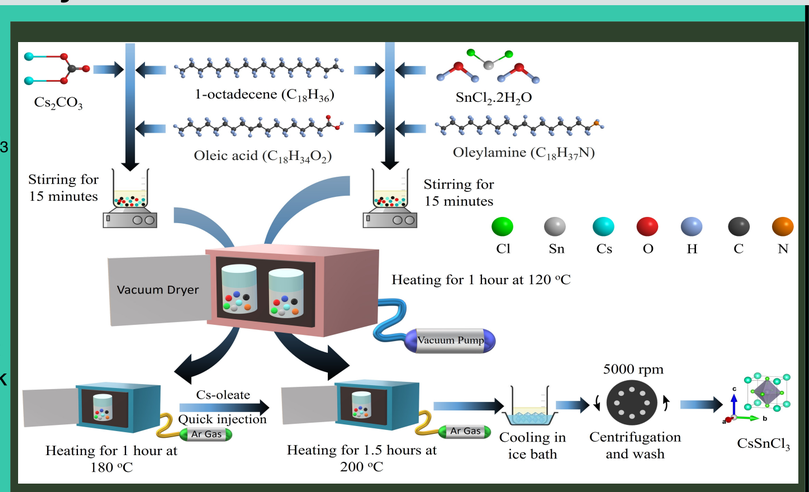

Figure 1: Schematically the synthesis steps of $CsSnCl_3$ perovskite using hot-injection technique

Crystal structure, FTIR, Morphological and Elemental Analysis

1. The Rietveld refined powder XRD spectrum, confirms the as-synthesized NCs were cubic crystals with a space group of pm3m and no undesired peak was found.

2. The atomic positions and bond length of as prepared CsSnCl3 NCs and the reliability (R) factors of Rietveldrefinement were inserted in Table 1.

3. The thermal stability of the $CsSnCl_3$ NCs were investigated by conducting TGA and DSC me -asurements. The weight loss of $CsSnCl_3$ pero -vskite due to the increase of temperature from 30 °C to 280 °C was only 2.15 % which is an indication of its excellent thermal stability. The observed nominal percentage of weight loss can be attributed to the decomposition of the binding surface ligands of the sample i.e. oley -lamine and oleic acid. Also, no endothermic and exothermic peak was observed which co -nfrims the crystallographic phase stability of the as-prepared NCs.

4. FTIR spectroscopy was conducted and no unexpected absorption band was observed which conforms to the phase pure formation of the prepared NCs.

5. No agglomeration was seen in the FESEM image and the sample was homogenous and non-porous which is bettwr than the previously reported results[2]. Here, the distribution of the size of as-prepared NCs is presented in the inset image. We can see that the average crystal size was 300 nm which lies in the sub-micrometer regime.

6. The elemental composition of as-prepared $CsSnCl_3$ nanocrystals was obtained from EDX analysis at room temperature. The mass and atom percentages of each element in $CsSnCl_3$ as obtained by EDX are demonstr -ated in Table 2.

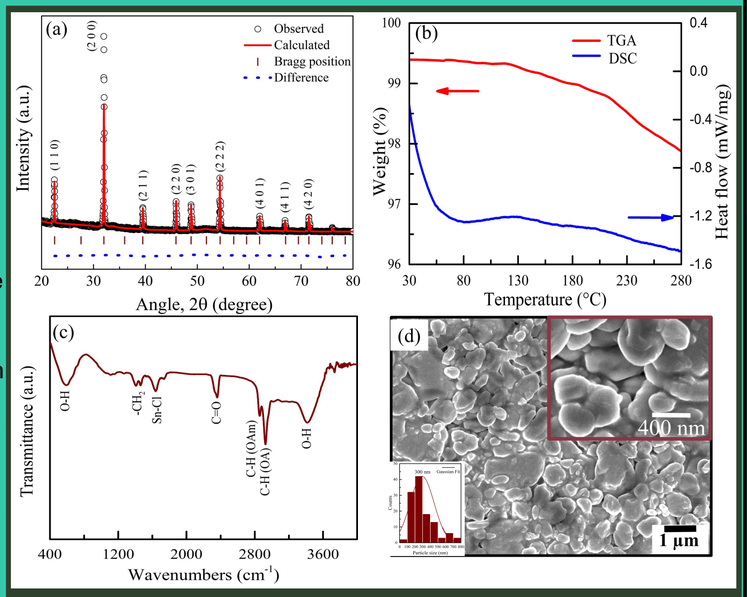

Fig. 2 (a) Rietveld refined powder XRD patterns of CsSnCl3 perovskite. (b) TGA and DSC curves of cubic CsSnCl3 perovskite. (c) FTIR spectrum recorded at room temperature. (d) FESEM image of $CsSnCl_3$ perovskite nanocrystals. Inset: A magnified view of the as-synthesized nanocrystals. The crystal size distribution is shown in inset

Table 1: Structural parameters of $CsSnCl_3$ nanocrystals and the value of R factors.

Atom	Wyc. Positions	x	y	z	a (Å)	α	volume (Å^3)	Bond length (Å)	R factors
Cs	1a	0.0	0.0	0.0					R_{exp}=5.48
Sn	1b	0.5	0.5	0.5	5.583	90°	174.02	Sn-Cl = 2.791	R_{wp}=7.24
Cl	3c	0.0	0.5	0.5					χ^2=2.53

Table 2: Mass and atomic percentages of $CsSnCl_3$ nanocrystals as obtained by EDX analysis.

Element	Mass (%) (Theoretical)	Mass (%) (Experimental)	Atom (%) (Theoretical)	Atom (%) (Experimental)
Cs	37.13	45.91	20	23.43
Sn	33.16	29.48	20	18.59
Cl	29.71	24.61	60	57.98
Total	100	100	100	100

Chemical State Analysis

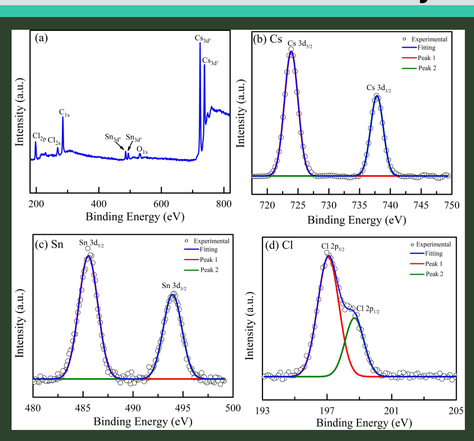

Fig. 3 (a) XPS full spectra of $CsSnCl_3$ nanocrystals illustrating the existence of constituent elements (Cs, Sn and Cl) in the fabricated sample. Core level XPS spectra for (b) Cs 3d (c) Sn 3d (d) Cl 2p demonstrating the purity of the sample and valence states of the constituent elements, respectively.

1. The XPS spectroscopy was performed to asses the surface purity of the sample.
2. No unexpected peaks other than Oxygen and Carbon was found.
3. The peaks due Oxygen (O) and Carbon (C) was obtained beacuse of the adsorption of O and C from the environment[3].

Optical Properties

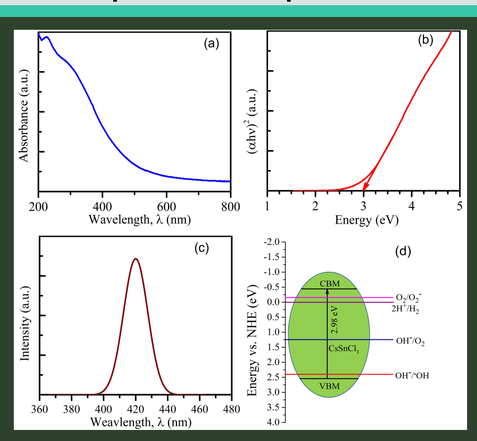

Fig. 4 (a) The absorption spectrum of the as-prepared $CsSnCl_3$ nanocrystals. (b) Tauc plot demonstrate the direct band gap of the $CsSnCl_3$ perovskite is 2.98 eV. (c) PL spectrum of the perovskite nanocrystals shows the peak wavelength at 420 nm. (d) Band edge positions adopted from Mulliken electronegativity approach conveying the potential use of fabricated $CsSnCl_3$ as an efficient photocatalyst.

1. A strong absorption is observed in the uv-visible region as seen in fig. 4(a).
2. From the Tauc plot from fig. 4(b), we have determined the direct bandgap of ~2.98 eV
3. The bandgap from the PL spectra was also found to be ~2.96 eV.
4. The band edge position was calculated where the VBM >2.38 eV and CBM < -0.16 V which predicts the photocatalytic capability.

Photocatalytic Degradation Capability

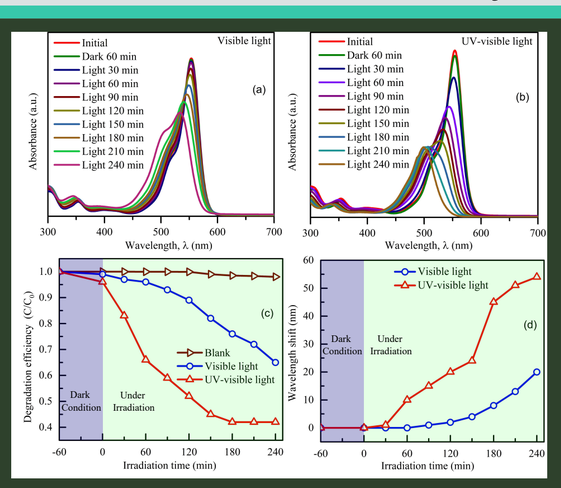

Fig. 5 Time-dependent absorption spectra of RhB solution for diff -erent times up to 240 minutes under the irradiation of the (a) visible and (b) UV-visible light. (c) Degradation efficiency of RhB as a function of the irradiation time for CsSnCl3 photocatalyst. (d) The wavelength shifts of the absorption spectra of the RhB dye solution under identical conditions of figure (c).

1. The photocatalytic performance of the $CsSnCl_3$ nano crystals was investigated towards the degradation of RhB under both visible and UV-visible illumination.
2. 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 negligiblefor RhB mollecules.
3. Under the irradiation of visible light, a ~35% degeradation of RhB dye after 240 minutes is achieved.
4. When irradiatied under uv-visible light, a 58% degradation after 240 minutes is achieved.
5. Under visible light irradiation, the decomposition was due to cleavage of its whole conjugated chromophore structure.
6. But under uv-visible light, the main degradation pathway was N-deethylation.

Concluding Remarks

1. We have demonstrated a new way of the synthesis of lead-free $CsSnCl_3$ perovskite via hot injection method.
2. The as-prepared sample is non agglomerated and non porus, resulting in a superior surface morphology.
3. The synthesized $CsSnCl_3$ has a cubic structure with pm3m space group and has crystal phase stability over a large temperature window.
4. The calculated bandgap of the $CsSnCl_3$ was ~2.98 eV.
5. The as-synthesized sample showed highest ~58% photocatalytic degradation efficiency under UV-visible irradiation.

References

1. C. B. Murray, D. J. Norris and M. G. Bawendi, J. Am. Chem. Soc., 1993, 115, 8706–8715.
2. T. Xia, Y. Li, L. Huang, W. Ji, M. Yang and X. Zhao, ACS Appl. Mater. Interfaces, 2020, 12, 18634–18641.
3. T. C. Jellicoe, J. M. Richter, H. F. J. Glass, M. Tabachnyk, R. Brady, S. E. Dutton, A. Rao, R. H. Friend, D. Credgington, N. C. Greenham and M. L. Böhm, J. Am. Chem. Soc., 2016, 138, 2941–2944.