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**Citation:** Thatheyus Peter. X, Geetha. D, Kamalarasan.V (2021). Study of Inorganic Halide (Cs<sub>2</sub>CuCl<sub>4</sub>) Perovskite Quantum dots for Energy Harvesting Devices. *Chemical Engineering*. v02i02, 08-12. <http://dx.doi.org/10.53709/CHE.2021.v02i02.002>

**DOI:**  
<http://dx.doi.org/10.53709/CHE.2021.v02i02.002>

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**Received on:** December 9, 2020  
**Revised on:** February 22, 2021  
**Accepted on:** June 02, 2021

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## RESEARCH ARTICLE

# Study of Inorganic Halide (Cs<sub>2</sub>CuCl<sub>4</sub>) Perovskite Quantum dots for Energy Harvesting Devices

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## ABSTRACT

*In recent days, there has been growing interest in metal halide inorganic perovskite quantum dots due to their promising diverse applications in the field of energy harvesting devices. Here, inorganic Cs<sub>2</sub>CuCl<sub>4</sub> perovskite quantum dots were prepared by facile re-precipitation technique at room temperature. Inorganic Cs<sub>2</sub>CuCl<sub>4</sub> QDs exhibited a quasi-spherical structure with a size of 5nm. As synthesized quantum dots indicate bright and broad bluish-green emission when the sample is excited below 300nm, inorganic perovskite QDs possess novel morphology and high quantum yield. These Inorganic perovskites provide a magnificent quantum yield (90%) more extensive than any other Quantum dots. The most crucial intent of this work is to investigate a novel material for various research applications and motivate the researchers to explore the potential of the material. These QDs make use of light-emitting diodes, photodetectors, and Solar cells are also highly motivated.*

**Keywords:** Colloidal processing, Perovskite Quantum dots, Solar energy materials, Metal halide, Electron microscope

## INTRODUCTION

Metal halides with the perovskite crystal structure, recently used as energy converting materials because of their power conversion efficiencies up to 22% [1-3]. Owing to the higher stability of inorganic material, it becomes frequently used, and it can be tunable up to 700nm and for high quantum yields. Hence the incorporation of QDs into bulk inorganic perovskite enabled decoupling of charge transport and light emission/sensitization heading to more efficient optoelectronic devices [4-6].

In these quantum dots, electrons and holes are confined three-dimensionally within the Bohr excitation radius. The specimen of Quantum dots is on the nanometer scale. As of this small-scale size of Quantum Dots, they contain distinct electronic energy, which results in individual optical properties [7]. High quantum yield, narrow and uniform emission spectra, and excitation due to we had these QDs have to use full over traditional inorganic quantum dots [8]. These quantum dots have narrow excitation and uniform emission spectra in a wide range of wavelengths, along with narrow full width at half maximum value (FWHM) [9-12]. By altering the basic structure of the quantum dots, they can emit from the UV to the NIR region in an absolutely facile mode; based on these aspects, quantum dots offer new opportunities in various fields. This combined property of nanomaterials results in developing new research areas of energy storage [13, 14].

Generally, Lot of approaches have been used to prepare QDs. But the precipitation approach is uncomplicated, cost-less, and eco-friendly. Also, it has some limitations viz., underprivileged properties and minimum luminescence intensity. To overcome with strategies like doped with inorganic halides. In the present work, novel perovskite quantum dots (Cs<sub>2</sub>CuCl<sub>4</sub>) were synthesized. A combination of inorganic halide group compounds having good absorption and emission. In this halide perovskite Quantum dots having high quantum yield and we can observe morphology,

Bandgap in future, we construct a goods solar cells, LED, Supercapacitor, Magnetic properties.

## Experimental details

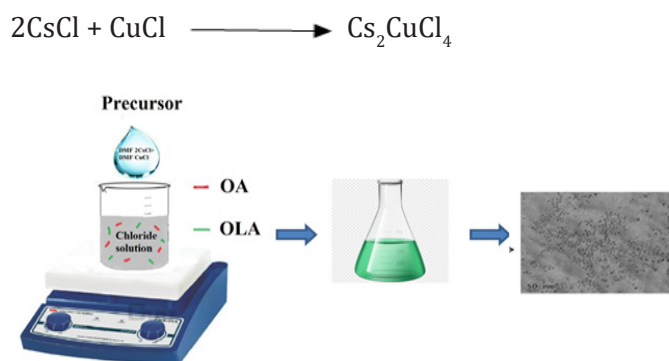
### Materials

Copper Chloride ( $\text{CuCl}_2$ ), Cesium Chloride ( $\text{CsCl}_2$ ), dimethylformamide (DMF), oleic acid (OA), and oleyl amine (OLA) were purchased from Sd. fine chemicals and were used without further purification.

### Preparation

The  $\text{Cs}_2\text{CuCl}_4$  quantum dots were prepared by an improved ligand-assisted re-precipitation (LARP) technique at room temperature. Copper chloride ( $\text{CuCl}_2$ ) 1 mM, cesium chloride ( $\text{CsCl}$ ) 2mM, DMF, and oleic acid-OLA were purchased without further purification. (0.168g) of  $\text{CsCl}$  and (0.067g) of  $\text{CuCl}_2$  were loaded into a mixture of 2ML DMF and then stirred. Octylamine and oleic acid as ligands added perovskite precursors then formed Quantum dots. The resultant QDs were quasi-spherical with a means size of 5 nm. The reaction mechanism of as-prepared samples is given below.

The mechanism of  $\text{Cs}_2\text{CuCl}_4$  QDs formation reaction can be express



## Results and Discussion

### Structural analysis (XRD)

To know about structural parameters, we recorded the x-ray diffraction pattern of quantum dots  $\text{Cs}_2\text{CuCl}_4$ . Obtained x-ray diffraction spectra for Quantum dots are presented in Fig. (1), which shows a thin film pattern of the inorganic perovskite  $\text{Cs}_2\text{CuCl}_4$  quantum dots [QDs]. The QDs diffraction peaks observed at  $2\theta = 11.0, 16.4, 18.6, 20.5, 23.3, 29.0, 31.0, 34.2,$  and  $37.4^\circ$  corresponds to the planes of (101), (111) (200), (112), (103), (122), (302), (204) and (024) respectively. All diffraction peaks are well indexed to the orthorhombic crystal structure of  $\text{Cs}_2\text{CuCl}_4$  QDs and space group  $\text{Pnma}$  with a lattice constant of

$a=9.769$   $b=7.607$  and  $c=12.381$  [JCPDS card no 79-1321]. No impurity is found in the pattern. Thin-film XRD pattern of mixed halide [Cl]  $\text{Cs}_2\text{CuCl}_4$  QDs was inferred with the powder XRD pattern of [ $\text{Cs}_2\text{CuBr}_4/\text{I}_4$ ] QDs and exhibiting orthorhombic crystal structure [15-16]. These characterizations are accurately proved that the  $\text{Cs}_2\text{CuCl}_4$  quantum dots formed when the precursor ratio is 2:1. Here, using Scherer's equation were calculated the particle size of QD.

$$D=0.9\lambda/\beta\cos\theta \quad (1)$$

Wherein the crystallite size,  $k$  -shape factor,  $\lambda$  -wavelength of the x-ray ( $\lambda=1.5406 \text{ \AA}$ ),  $b$ -full width at half maximum (FWHM) of the peak and  $q$ -angle of the diffraction. these samples could be assessed the lattice parameters. The lattice parameters for tetragonal structure  $\text{Cs}_2\text{CuCl}_4$  QDs are calculated from the following equation.

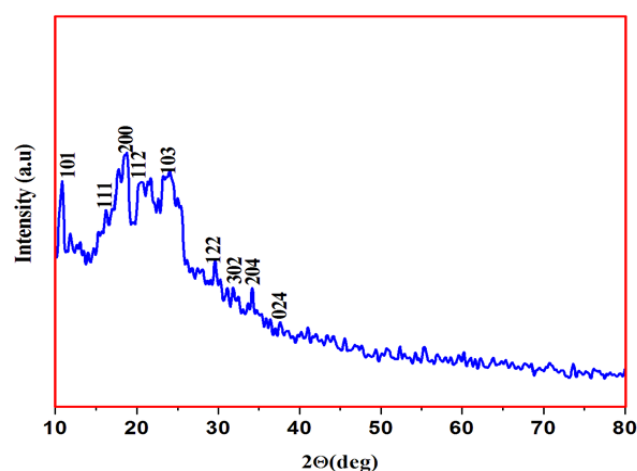
$$\delta=1/D^2 \quad (2)$$

The above formulae calculate crystallite size, dislocation density, and lattice parameters, then its tabulate in table 1.

**Table 1:** Structural parameters of  $\text{Cs}_2\text{CuCl}_4$  Quantum Dots

Material	Crystal-lite size (nm)	Dislocation density ( $\delta$ ) $\times 10^{14}$ lines/ $\text{m}^2$	Lattice parameters ( $\text{\AA}$ )		
			a	b	c
$\text{Cs}_2\text{CuCl}_4$	18	214.6	9.769	7.607	12.381

**Fig. 1.** XRD pattern of  $\text{Cs}_2\text{CuCl}_4$  QDs

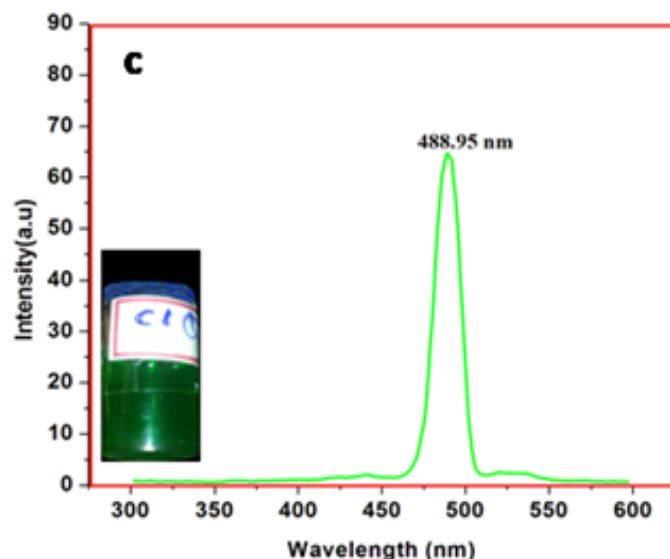
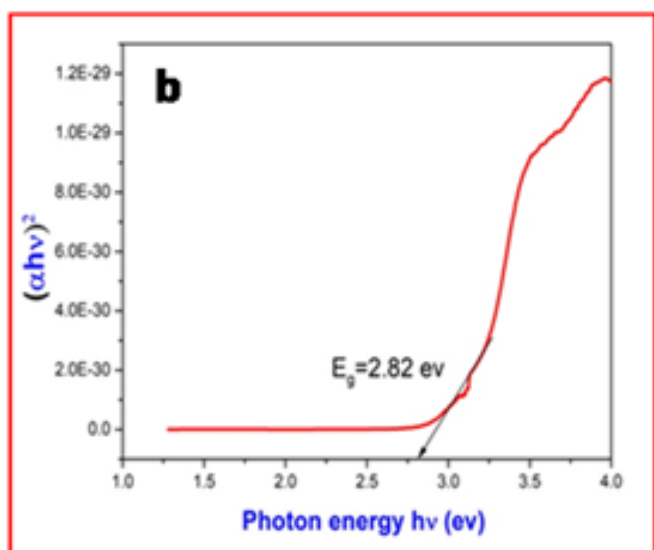
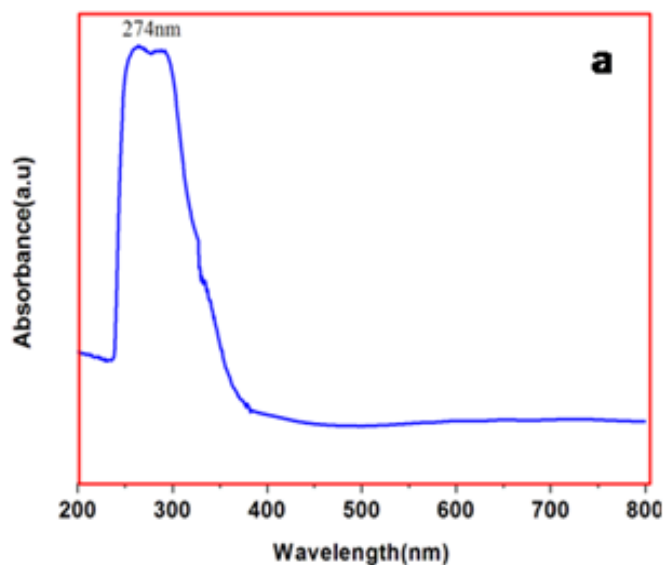


### Optical studies

Fig 2(a) shows the UV-Visible spectra of perovskite QDs of  $\text{Cs}_2\text{CuCl}_4$ . The absorption spectrum was recorded for

these perovskite Quantum Dots has been detecting by the UV-Visible spectrum. The corresponding band gap obtained is 2.82 eV. The onset of the blue absorption shift is obtained due to bandgap edge shift 2.82 eV. In General, the blue-shifted optical spectra can be caused to the concentration of the perovskite, and it is best leading to the more vital interaction between Cu and Cl orbital [17]. The lesser conduction band of the copper halide perovskite is composed of the Cu 3d orbitals and Cl 3p orbitals. The respective absorption band edge shifts from 200 to 400 nm. The absorption band edge shifts to the higher wavelength increases when the size of the Nps.

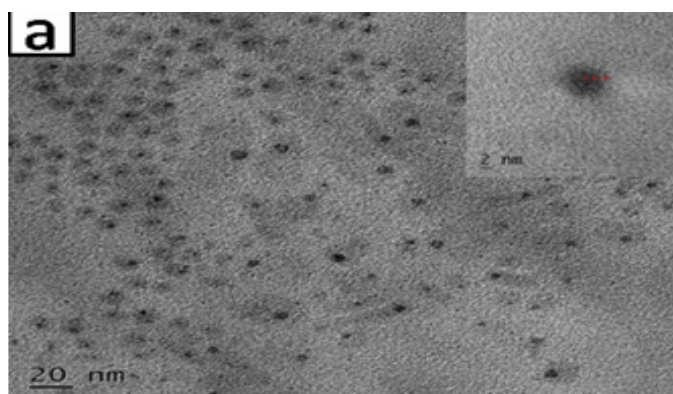
The PL-emission spectrum of the QDs was measured for the  $\text{Cs}_2\text{CuCl}_4$  solution as shown in Fig 2 (b), remaining details of the optical behavior of PL as shown in Fig 2 (c). The observed 274nm wavelength of excitation reflects the bright, broad emission peak between 400 to 520, which was confirmed by 300nm wavelength of excitation energy, and It was observed the sharp peak of broad bright blues green emission was monitored at 488nm. The sharp peak of the emission of FWHM is 19.2, for  $\text{Cs}_2\text{CuCl}_4$  quantum dots

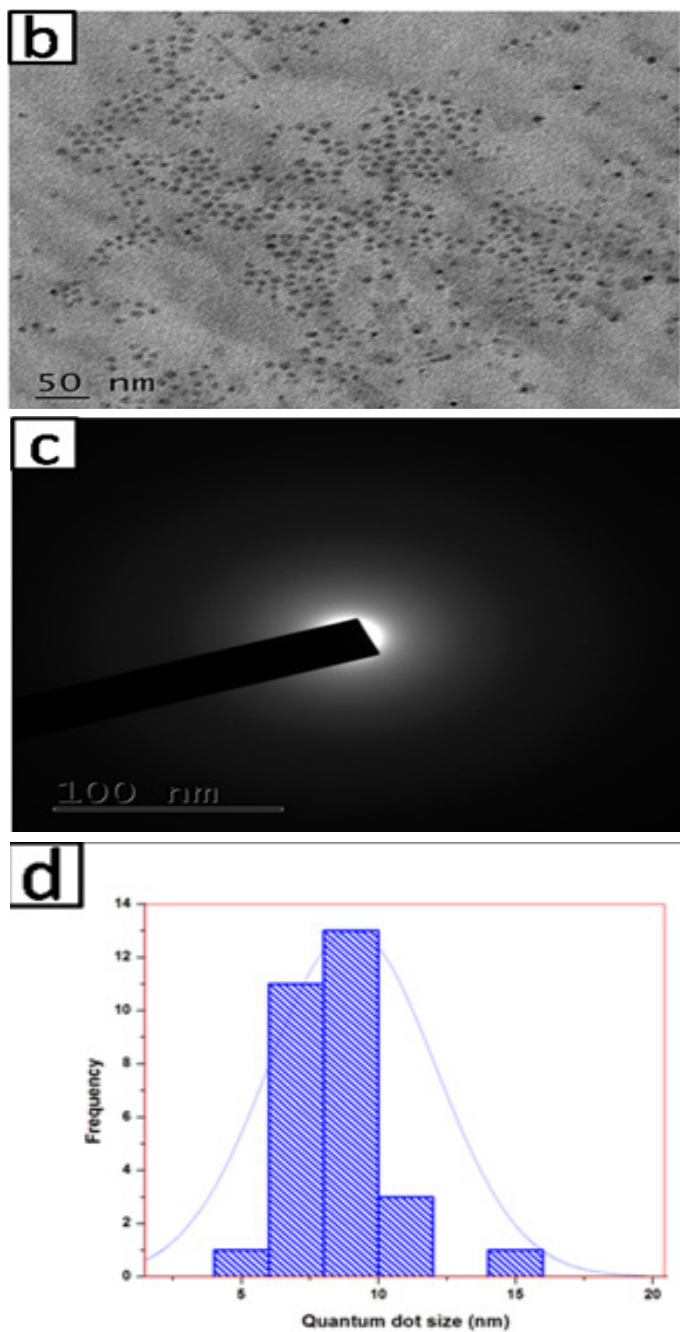


**Fig. 2.** (a) Optical absorption spectra (b) Band gap energy of the  $\text{Cs}_2\text{CuCl}_4$  QDs (c). Photoluminescence Spectra of  $\text{Cs}_2\text{CuCl}_4$  QDs

### Morphological studies (HR-TEM)

The surface morphological studies of the as-synthesized perovskite quantum dots [QDs] have been investigated by HR-TEM, representative HR-TEM image of the QDs is portrayed in Fig 3 (a & b). In this TEM, images clear that the prepared samples are single particles [dots] having the size of 5 to 10 nm.  $\text{Cs}_2\text{CuCl}_4$  QDs were quasi-spherical in shape and distributed homogeneously. The presented typical HR-TEM Image and the size distribution of synthesized  $\text{Cs}_2\text{CuCl}_4$  QDs. The images confirm that the synthesized sample was a halogen component inorganic perovskite quantum dot. Fig 3 (b) shows 9.10 is the average particle size of  $\text{Cs}_2\text{CuCl}_4$  QDs It is gained from HR-TEM analysis, which is slightly higher than the crystallite size calculated from XRD analysis. Further Fig 3 (d), represents the size distribution of the histograms graph. From the HR-TEM images of the  $\text{Cs}_2\text{CuCl}_4$  QDs can be calculated the lattice spacing and found to be 0.20 nm, which corresponds to (112) lattice plane. The crystal nature of the samples can be determined from the selected area (electron) diffraction pattern [Fig3 (c)], and the selected area electron diffraction (SAED) pattern indicates the single-crystalline nature of the  $\text{Cs}_2\text{CuCl}_4$  nanoparticles.



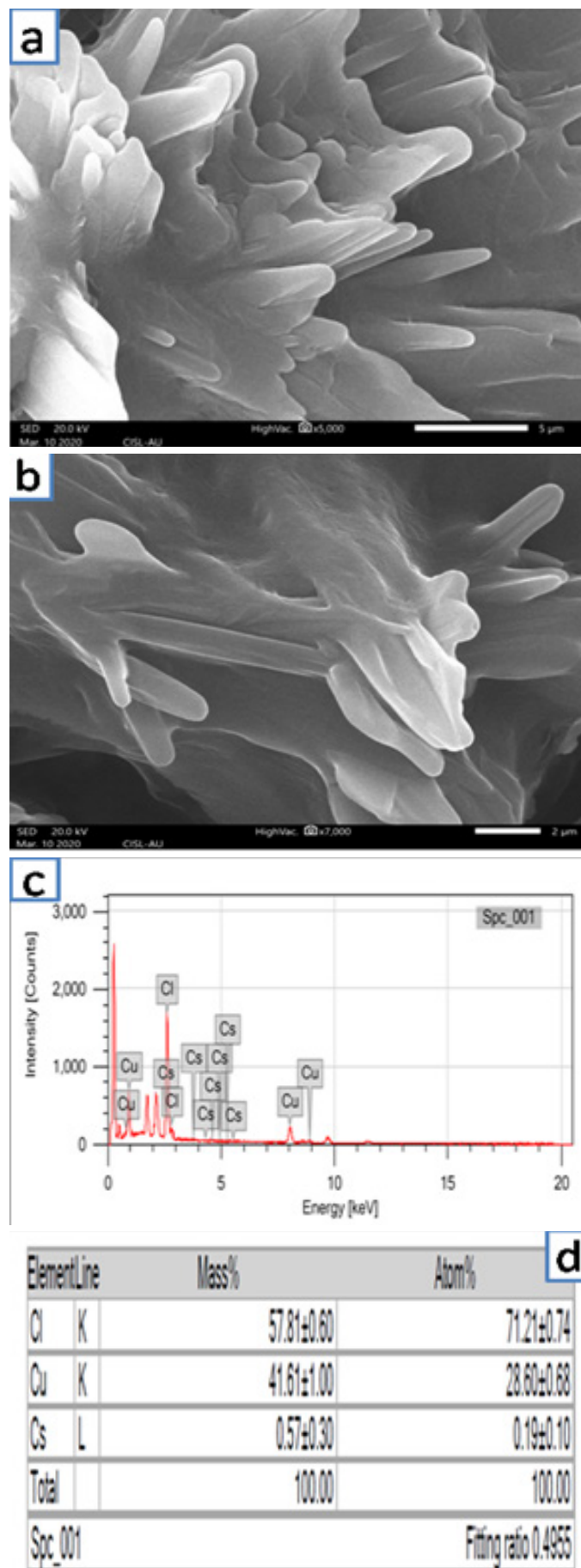


**Fig. 3.** HR TEM images of Cs<sub>2</sub>CuCl<sub>4</sub> QDs (a) 20nm (b) 50nm (c) SAED pattern (d) Histogram of particle size distribution of Cs<sub>2</sub>CuCl<sub>4</sub> QDs

**Morphological analysis (SEM/EDS)**

The SEM micrographs of perovskite QDs of Cs<sub>2</sub>CuCl<sub>4</sub> particle prepared by the re-precipitation method as shown in fig 4. (a). From that characterization, Fig 4(a, b) shows a morphology image at different magnification which reveals flower-like structures with precursor dependent petal shapes. When the petal is a tapered QDs self-assembled from lots of nanorods. The EDX spectrum is composed the Cu, Cs, Cl elements. The perovskite Quantum dots cannot be visualized in SEM images, discarding the dots are agglomerate in low magnification. HR-TEM study will help to confirm the quantum dot. Fig.4 (c) Shows the typical EDX spectrum of various elements in the Cs<sub>2</sub>CuCl<sub>4</sub> sample. EDX spectrum is composed of CS, Cu,

Cl elements. The element Cl, Cu present in K shell and Cs element present in L shell, the EDX shows fitting ratio 0.495.



**Fig.4.** (a, b) SEM image of Cs<sub>2</sub>CuCl<sub>4</sub> QDs (c) EDX spectra (d) Mass and atomic value of Cs<sub>2</sub>CuCl<sub>4</sub> QDs

## CONCLUSION

In summary, a novel inorganic halide perovskite ( $\text{Cs}_2\text{CuCl}_4$ ) quantum dots are prepared successfully by the reprecipitation method is proposed, wherein each molecule is capable of coordinating the cations and anions. As synthesized samples were characterized the optical and structural properties were examined XRD UV-Vis, and PL techniques showed that the sample has unique optical properties. By optimizing the halide composition and the ratio of the precursors (2:1), uniform quantum dots were harvested (visualized in HR-TEM). These Quantum Dots showed broad bluish-green emission upon excitation with 274 nm. These advantages will promote this new material in the field of energy harvesting devices viz., LED, solar cell. The simple synthesis for preparing perovskite Quantum Dots is the innovative research with few more transition metals-based perovskite nano crystals in the next level.

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