



The 25<sup>th</sup> Iranian Conference on Optics and Photonics (ICOP 2019), and the 11<sup>th</sup> Iranian Conference on Photonics Engineering and Technology (ICPET 2019).  
University of Shiraz,  
Shiraz, Iran,  
Jan. 29-31, 2019



## سنتز پروسکایت دو بعدی و استفاده از لایه نشانی غوطه‌وری مناسب برای ساخت افزاره‌های الکترونیک نوری

پارسا درمان، سارا درباری

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چکیده- در این پژوهش سنتز پروسکایت دو بعدی رادلسدن پاپر که علاوه بر برخورداری از مزایای شناخته شده پروسکایت سه بعدی از جمله جذب نوری بالا و مشخصات انتقال حامل خوب عیب بزرگ ناپایداری را به طور قابل توجهی برطرف کرده است، گزارش می شود. در این مقاله از مولکول‌های بزرگ و پایدار و مقاوم به حرارت و رطوبت بوتیل آمین استفاده شد تا یک لایه از پروسکایت سرب تترایدید را احاطه کنند و مانع از نفوذ حرارت و رطوبت به لایه پروسکایت شده و پایداری را افزایش می دهند. وجود این مولکول‌های حائل باعث افزایش ثابت شبکه نسبت به حالت سه بعدی می گردد و محدود سازی کوانتومی در دو بعد باعث افزایش گاف انرژی می شود. این ماده به روش غوطه‌وری لایه نشانی شد و با انجام آزمایش‌های طیف جذب نوری و نورتابناکی گاف انرژی آن ۲/۵ الکترون ولت و بیشترین مقدار نورتابناکی ۲/۲۱ الکترون ولت اندازه گیری شد.

کلید واژه- افزاره های الکترونیک نوری، پروسکایت دو بعدی، پایداری، رادلسدن پاپر، لایه نشانی غوطه‌وری

### Synthesis of 2D Perovskite and Using Dip-coating Method Suitable for Fabrication of Optoelectronic Devices

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**Abstract-** In this paper synthesis of Ruddlesden-Popper two dimensional Perovskite (RPPs) is reported. Not only has this kind of Perovskite (PVK) its 3D counterpart advantageous such as high absorption coefficient and good carrier transport properties but also its stability has been improved. In this work BA molecule which is stable, heat and humid resistive and big enough to cover a mono layer of lead tetra iodide was used to prevent heat and humidity to reach PVK layer and stabilize it. The existence of spacer molecule increase lattice constant and quantum confinement enlarge band gap. After Dip-coating photoluminescence (PL) and photo absorption spectroscopy test was done and band gap was measured 2.5eV and PL pick was 2.21eV.

Keywords: Optoelectronic devices, 2D Perovskite, Stability, Ruddlesden-Popper, Dip-coating

## 1. Introduction

Organic–Inorganic Halide Perovskites (OIHPs) are a long time known materials which have been widely studied since 2009. Their optoelectronic properties have been investigated by numerous research groups in this decade, some of impressive ones are high light absorption coefficients, long charge carrier diffusion lengths, intense photoluminescence (PL), slow rates of non-radiative charge recombination, photoinduced polarization, high drift mobilities, and effective charge collection. Thus, they are attractive photoactive materials for developing high-performance optoelectronic devices[1]. These devices are also cheap and easy to be fabricated. Furthermore, recently, 2D Ruddlesden–Popper layered perovskites (RPPs) with good moisture resistance have been attracted attention for optoelectronic devices. This family of 2D layered OIHPs has a general formula of  $(\text{RNH}_3)_2(\text{CH}_3\text{NH}_3)_{n-1}\text{B}_n\text{X}_4$ , where R is a long chain alkyl or aromatic group, and  $n$  is the number of the metal cation layers between the two layers of the organic chains[2]. 2D semiconductors have quantum confinement and band gap tunability which are desirable in optoelectronic applications[3]. PVK photoactive layers should work effectively with other functional materials such as electrodes, interfacial layers and encapsulating films. Conventional two-dimensional (2D) PVKs are promising candidates for this purpose because of their unique structures and interesting optoelectronic properties[3].

Gustav Rose in 1839 discovered  $\text{CaTiO}_3$  and named it after Russian mineralogist Lev Perovski. nowadays perovskite also refers to the class of compounds which have the same type of crystal structure as  $\text{CaTiO}_3$  ( $^{XII}\text{A}^{2+}\text{VI}\text{B}^{4+}\text{X}^{2-}_3$ ), known as the perovskite structure[4]. The first series of Ruddlesden–Popper phase,  $\text{Sr}_2\text{TiO}_4$ ,  $\text{Ca}_2\text{MnO}_4$  and  $\text{SrLaAlO}_4$  were confirmed by powder X-ray diffraction (PXRD) in 1957[5]. Weber was the first to synthesize  $\text{MAPbX}_3$  in 1978[1]. In 2009, Miyasaka et al used PVK as sensitizer in solar cells and report 3.8% power conversion efficiency[1]. In

2015, Kanatzidis et al. synthesized 2D RPP using BA as spacer molecule to cover one layer of lead tetra iodide[2]. In 2016 Liu et al. synthesized 2D  $\text{MAPbI}_3$ [6]. During these 10 years solar cells, LEDs, PDs, X-ray detectors, and lasers were fabricated with OIHPs.

## 2. Methodology

### 2.1. BAI synthesis

n-butylammonium iodide (BAI) was synthesized by neutralizing 924  $\mu\text{L}$  n-butylamine (BA) and 5 mL 57% w/w aqueous hydriodic acid (HI) with stirring for four hours at 0 °C. The solvent was then evaporation using rotary evaporation at 60 °C and washed by diethyl ether three times followed by dried at 70 °C for 12 hours.

### 2.2. $(\text{BA})_2\text{PbI}_4$ synthesis

500 mg  $\text{PbO}$  powder was dissolved in a mixture of 3 mL 57% w/w aqueous HI solution and 1 mL 50% aqueous  $\text{H}_3\text{PO}_2$  by heating to boiling under constant magnetic stirring for about 5 min, which formed a bright yellow solution. Subsequent addition of liquid. Addition of 500mg n- $\text{CH}_3(\text{CH}_2)_3\text{NH}_3\text{I}$  (BAI) powder to the  $\text{PbI}_2$  solution initially produced a black precipitate, which was subsequently dissolved under heating the combined solution to boiling. The stirring was then discontinued, and the solution was left to cool to room temperature during which time orange rectangular-shaped plates (flakes) started to crystallize. The precipitation was deemed to be complete after ~3 h.

### 2.3. Deposition

The resulting product of synthesis was colloidal suspension in which the solid particles were  $(\text{BA})_2\text{PbI}_4$  and solvent was  $\text{H}_3\text{PO}_2$ . For deposition substrates were cleaned by sonication in deionized water, soap water, and 2-propanol and then treated by oxygen plasma. Substrates were carefully entered in the mixture without hitting 2D flakes on top of solvent and then after putting flakes on the

substrate, it was gotten out of mixture and left out in room temperature to dry.

### 3. Results and discussion.

The size of RPP flakes that was deposited using Dip-coating varies from 15  $\mu\text{m}$  to 5000  $\mu\text{m}$ , therefore it can be used in fabrication of micro optoelectronic devices, Fig 1 a) shows 2000  $\mu\text{m}$  RPP flake under optical microscope. The size of flakes were evaluated by comparison between RPP flakes and a 500  $\mu\text{m}$  printed line b) Field Emission Scanning Electron Microscopes (FE-SEM) has shown RPP's crystals has indeed been formed.

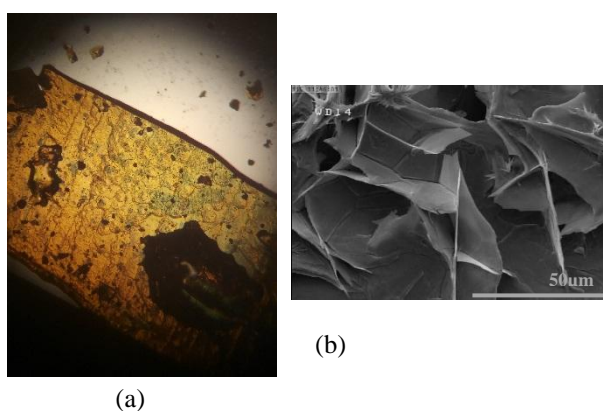


Fig. 1: a) optical microscope image b) FE-SEM views of the resulting layer.

The photo absorption spectroscopy is shown in Fig 2. that is an approximate match with previous works[7, 8].

The exciton absorption happened in 2.35eV and band gap (absorption pick) has been measured 2.5eV that indicates exciton energy of 150meV while in previous literature exciton absorption and band gap were reported 2.35eV and 2.43eV respectively so exciton energy was 80meV.

Therefore, excitonic absorption matched perfectly with previous works but measured band gap is 0.7eV blue-shifted.

It should be noted here that Cao et al. have also observed dramatic change in deposited sample's absorption spectrum[8].their excitonic absorption almost disappeared and their absorption pick blue shifted a bit so they reported their absorption edge as band gap which was 2.24eV.

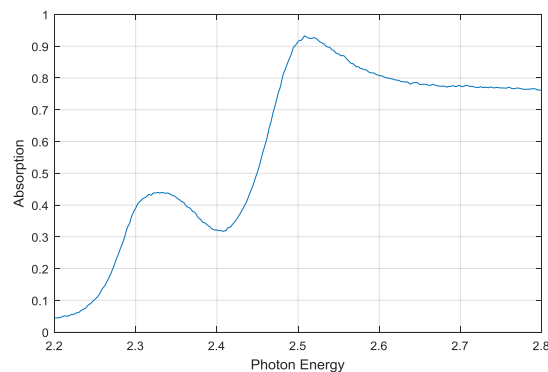


Fig. 2: Dip-coated Si- (BA)<sub>2</sub>PbI<sub>4</sub> absorption spectrum

PL pick observed at 2.21 eV in Fig 3. Shows 140meV mismatch with other work's[7, 8] but it again proves not only was the synthesis of 2D RPP successful, but also it does have wider band gap.

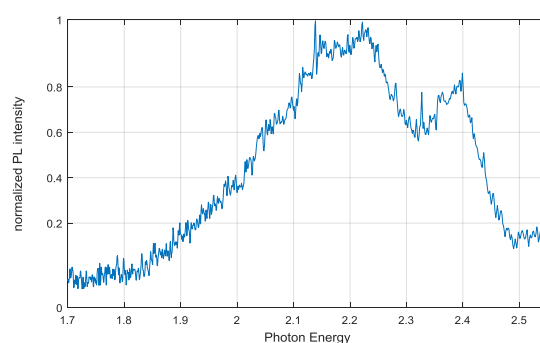


Fig. 3: PL spectrum of dip-coated Si-perovskite thin films of the (BA)<sub>2</sub>PbI<sub>4</sub>

In 2D MAPbI<sub>3</sub> (non RP method) the band gap was reported 1.8 eV[6], which is larger than 3D MAPbI<sub>3</sub> due to Quantum confinement in RP method in addition of Quantum confinement, the existent of big spacer molecule such as BA increase the lattice constant and it result in larger band gap which was previously seen in (BA)<sub>2</sub>PbBr<sub>4</sub>[2].

### 4. Conclusion

The aim in this paper was synthesis of 2D Ruddlesden Popper Perovskite and using dip-coating deposition method to fabricate micro optoelectronic devices.

Previously (BA)<sub>2</sub>PbI<sub>4</sub> was synthesized and was deposited using spin coating method[7, 8]. in this

work we compared absorption spectrum and Photoluminescence to see whether the synthesis and its deposition method were correctly done.

In table 1 exciton Pick is 2.35 eV which is exactly the same as reported before [7]. PL and  $E_g$  is 2.21eV and 2.5eV respectively while they were reported 2.35eV and 2.41eV respectively[7]. Genuinely it can be claimed that synthesis was successful and crystals were transferred well by dip-coating method specially by taking absorption spectrum changes in Cao et al. work [8]into account.

(BA)2PbI4	Band gap	Exitonic absorption	photoluminescence
This paper	2.5eV	2.35eV	2.21eV
Stoumpos et al.[7]	2.43eV	2.35ev	2.35eV

Table I. comparison between measured data and reported data

It is also demonstrated here that by Dip coating it is possible to fabricate 2D RPP based Micro optoelectronic devices and its advantage is that it is done without using Suction (vacuum) filtering and DMF.

## References

[1] T. M. Brenner, D. A. Egger, L. Kronik, G. Hodes, and D. Cahen, "Hybrid organic—inorganic perovskites: low-cost semiconductors with intriguing charge-transport properties," *Nature Reviews Materials*, vol. 1, no. 1, p. 15007, 2016.

[2] Y. Chen, Y. Sun, J. Peng, J. Tang, K. Zheng, and Z. Liang, "2D Ruddlesden–Popper perovskites for optoelectronics," *Advanced Materials*, vol. 30, no. 2, p. 1703487, 2018.

[3] S. Chen and G. Shi, "Two-Dimensional Materials for Halide Perovskite-Based Optoelectronic Devices," *Advanced Materials*, vol. 29, no. 24, p. 1605448, 2017.

[4] H.-R. Wenk and A. Bulakh, *Minerals: their constitution and origin*. Cambridge University Press, 2016.

[5] S. Ruddlesden and P. Popper, "The compound Sr<sub>3</sub>Ti<sub>2</sub>O<sub>7</sub> and its structure," *Acta Crystallographica*, vol. 11, no. 1, pp. 54-55, 1958.

[6] J. Liu *et al.*, "Two-dimensional CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> perovskite: synthesis and optoelectronic application," *ACS nano*, vol. 10, no. 3, pp. 3536-3542, 2016.

[7] C. C. Stoumpos *et al.*, "Ruddlesden–Popper hybrid lead iodide perovskite 2D homologous semiconductors," *Chemistry of Materials*, vol. 28, no. 8, pp. 2852-2867, 2016.

[8] D. H. Cao, C. C. Stoumpos, O. K. Farha, J. T. Hupp, and M. G. Kanatzidis, "2D homologous perovskites as light-absorbing materials for solar cell applications," *Journal of the American Chemical Society*, vol. 137, no. 24, pp. 7843-7850, 2015.