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Synthesis and Characterization of Methyl Ammonium Lead Halide Perovskite $MAPbI_3$ for Applications in Photodetector Devices

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ABSTRACT

Methyl ammonium lead iodide ($CH_3NH_3PbI_3$) Perovskite was synthesized by a mixing method in one and two steps. The ethanol solvent was also used to dissolve CH_3NH_3I that is compared with isopropanol solvent. The characterizations of synthesized perovskite samples include the structural properties, morphological characteristics, and optical properties. The intensity and orientation in X-ray diffraction patterns appear clearly in ethanol solvent. Additionally, the ethanol solvent increases the grain size of perovskite which is homogeneous of the surface morphology. It causes a decrease in the wavelength of absorbance edge in addition to an increase in the energy bandgap value. The photodetector parameters for MAPbI3 perovskites cover the PbS nanocrystal which was prepared on the FTO glass dissolved by Isopropanol and DMF where the responsivity Rλ= 0.0037 and the quantum efficiency QE=1.016% was under λ nm =650 nm and V_{bias}=0V. These values were decreased by using Ethanol solvent.

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تحضير وتشخيص بيروفسكايت ميثيل أمونيوم هاليد الرصاص MAPbI3 للتطبيقات في نبائط الكشف الضوئي

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الـــخُـــلاصـــة:

تم تحضير بيروفسكايت ميثيل امونيوم يوديد الرصاص $CH_3NH_3PbI_3$ بطريقة تدمج بين خطوة واحدة و خطوتين. تم استخدام مذيب الإيثانول أيضًا في إذابة CH_3NH_3I مع المقارنة بمذيب الأيزوبروبانول. تتضمن تشخيص عينات البيروفسكايت المُحضرة الخصائص التركيبية والخصائص المورفولوجية والخصائص البصرية. تظهر الشدة والاتجاه في أنماط حيود الأشعة السينية بوضوح في مذيب الإيثانول. بالإضافة إلى ذلك ، يزيد مذيب الإيثانول من

الكلمات المفتاحية:

البيروفسكايت
التقنيات الفوتوفولتائية
حيود الأشعة السينية

حجم حبيبات البيروفسكايت المتجانسة لتشكل السطح. يتسبب في انخفاض الطول الموجي لحافة الامتصاص بالإضافة إلى زيادة قيمة فجوة الطاقة. تغطي معاملات الكاشف الضوئي لـ MAPbI$_3$ perovskites البلورة النانوية PbS التي تم تحضيرها على زجاج FTO المذاب *بواسطة* Isopropanol و DMF حيث كانت الاستجابة R = 0.0037 والكفاءة الكمية QE = 1.016 ٪ كانت أقل من نانومتر = 650 نانومتر و V_{bias} = 0V. وتم تقليل هذه القيم باستخدام مذيب الإيثانول.

1. Introduction

The perovskite refers to chemical components which have been discovered in 1839 by the German mineralogist Gustav Rose for the first structure of calcium titanium oxide CaTiO. Then, it has been classified by the Russian mineralogist Lev A. Perovski after which perovskite is attributed name, and in 1926, the crystal structure of the perovskite has been described by Victor Goldschmidt [1-3]. The general structure of perovskite has ABX_3 as chemical formula where A is a cation organic group (NH_4^+, $CH_2NH_3^+$(MA), $CH_2CH{=}NH_2^+$ (FA) or inorganic which can be either Alkali metal cations A^+(Li^+, Na^+, K^+, etc.), alkaline earth metal cations A^{2+} (Mg^{2+}, Sr^{2+}, Ba^{2+}, etc.), or lanthanide A^{3+} (Pm^{3+}, Ce^{3+}, etc.), which generally have low charge and occupy a cube-octahedral site shared with 12X anions. B is a transition metal cation (Cr^{3+}, Mn^{3+}, Fe^{3+}, etc.) or metal cation (Pb^{2+}, Sn^{2+} and Bi^{3+}), in which B has sizes smaller than A and it is stabilized in an octahedral site shared with 6X anions. X is an anion which binds both cations, like halogen e.g. chloride Cl^-, bromide Br^- and iodide I-. The structure of perovskite is shown in Figure 1 [4].

Perovskite materials are widely used as photon absorbers in perovskite based on solar cells. The interest in organic-inorganic hybrid perovskite materials has been due largely to their useful characteristics of the inorganic components, which include thermal stability [5] and the high degree of structural order. It is also due to the properties of the organic components such as the functional versatility, mechanical flexibility and low-cost process ability [6, 7]. Hence, the possibility of merging the properties of typical inorganic crystals with those of molecular organic solids has stimulated the recent research into the versatile properties of organic-inorganic hybrid perovskite materials. In more details, organic-inorganic hybrid perovskite materials have some enticing potential for applications in photovoltaic devices [8]. There are two basic methods for synthesizing perovskites, one and two steps. In this research, perovskites have been synthesized as a method that includes combining the two methods. The research aims at synthesizing perovskites from MAPbI$_3$ on PbS, there is a study of compositional and optical properties and their application as a photodetector.

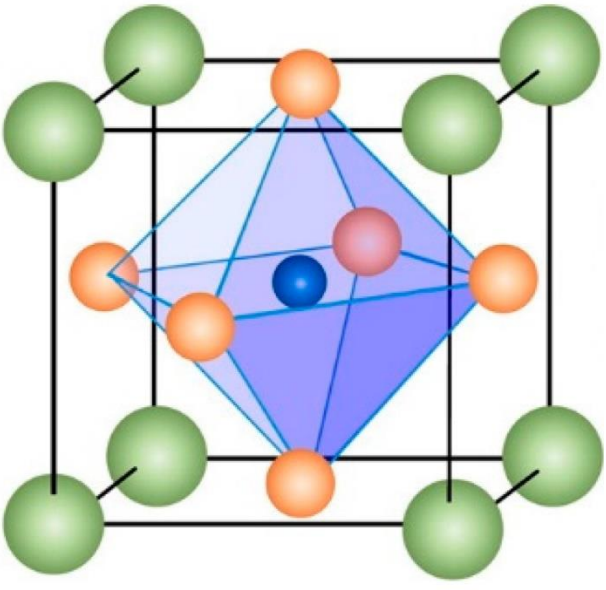

Figure 1: The ideal structure of perovskite.

2. Experimental part

Materials

The materials which were used in this work are as follows: FTO glass, Ethanol, Acetone,

Thiourea, Sodium hydroxide, Methylammonium CH_3NH_2 (MA), Hydroiodic acid HI, Diethyl ether $(C_2H_5)_2O$ (DEE), Lead nitrate $Pb(NO_3)_2$, Potassium iodide KI, Dimethyl formamide DMF and Isopropanol.

PbS Preparation

The lead sulfide films were prepared using 0.331 g of lead nitrate and 0.180 g Sodium hydroxide in 100 ml of double distilled water and 0.071 g of thiourea in 10 ml of double distilled water. The mixture has been placed at a room temperature for 24 hours.

Preparation of Salts MA Methylammoniom

Briefly, reacting 11ml of CH_3NH_2 with 12ml of Hydroiodic acid HI in a three-neck round bottom flask that has been placed in mixture down the ice bath at about 0°C for one hour with stirring to obtain a brown mixture of CH_3NH_3I(MAI). The mixture has been turned from liquid phase to the solid phase by placing it on a drying system to evaporate at 60°C for an hour. MAI has been washed with a Diethyl ether DEE 8 times. Finally, the powder is dried by evaporating at 80°C for three hours to obtain the salt of MAI.

Preparation of Lead Halides

To prepare PbI_2 (2 g) of lead nitrate, $Pb(NO_3)_2$ and potassium iodide KI were dissolved in 50 ml of deionized water for each substance. The aqueous $Pb(NO_3)_2$ was mixed with the aqueous KI. After that, the precipitate was formed at the bottom of the beaker, and by the process of filtering the mixture and drying it to reach a yellow powder of PbI_2.

Perovskite Preparation

$MAPbI_3$ perovskites were prepared as a method by mixing of 0.553g from MAI in 2ml of Isopropanol the first time and ethanol the second time at 70 c with stirring 0.753g lead of halides pbI_2. Moreover, with 2ml of Dimethyl Formamide DMF at 70 °C with stirring, the solvent has been heated at a temperature of 70°C for one hour with stirring. The mixture has been deposited on a FTO glass and PbS with spin coating. Finally, the perovskites film has been formed after annealing.

3. Results and discussion

Figure (2) shows the XRD pattern of the PbS particles indexed as follows: 25.7°, 30.2 °, 43.1 °, 51.1 ° and 53.5 ° corresponding to (222), (111) (200), (220) and (311), and consistent to the cubic rock salt structure.

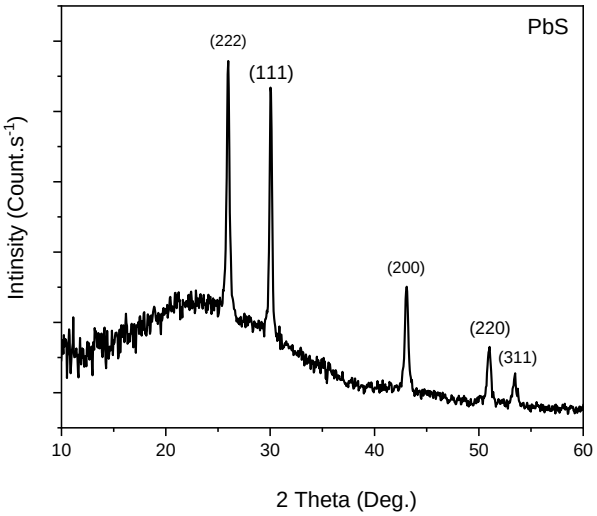

Figure 2: The X-ray diffraction (XRD) of PbS.

Figure (3) shows the X-ray diffraction (XRD) patterns of $CH_3NH_3PbI_3$ film substrates that are indicated by triangles. The main peaks are located at 14.319° ,16.263 °, 16.777 °, 25.199 °, 28.66 °, 32.081 °, 38.04 °, 40.682 ° ,43.41 ° and 50.34 ° for 2θ axis has been observed which is corresponding to the planes of (110), (112), (211), (202), (220), (222), (224), (314) and (404). The latter is in agreement with [9-10]. XRD indicates that the films are highly crystallized phases [11-12]. Meanwhile, it is a weak diffraction.

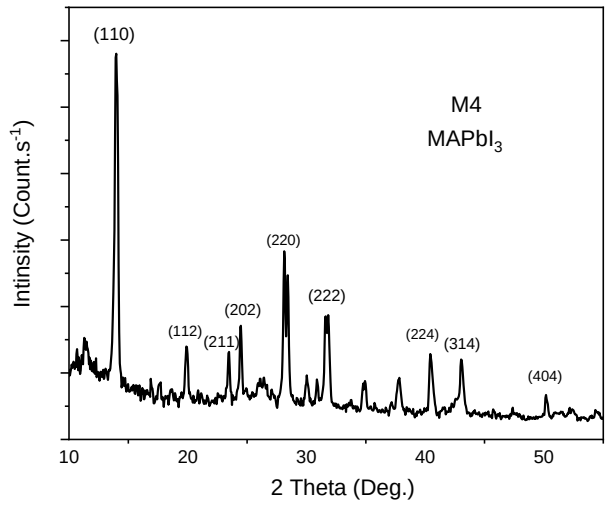

Figure 3: The X-ray diffraction (XRD) of $CH_3NH_3PbI_3$ dissolved by isopropanol and DMF.

Figure (4) shows the X-ray diffraction patterns of $MAPbI_3$ film, which is dissolved by Ethanol and DMF on PbS substrate. The main peaks are located at 11.4 °, 14.0 °, 20.1 °, 23.5°, 24.5 °, 26.3 °, 28.3 °, 29.9 °, 32.1° 35,1°,38.0 °,40.7 °, and 43.3 ° for 2θ axes that have been observed corresponding to the planes of (110), (112), (211), (202), (220), (222), (224), (314) and (404). The ethanol pattern has the highest orientation and intensity compared to isopropanol; this refers to the best crystal structure. It was also due to the different polarity between solvents. Ethanol has a polarity about 5.2 and is greater than isopropanol 3.9 [13].

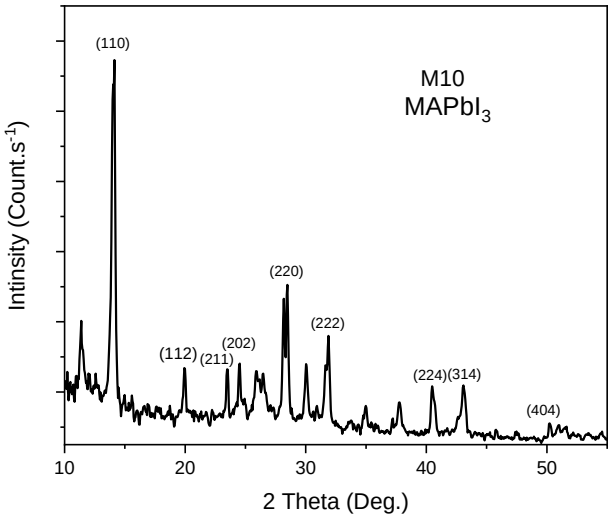

Figure 4: The X-ray diffraction (XRD) of CH3NH3PbI3 dissolved by Ethanol and DMF.

Figure (5) presents UV- Vis spectra of PbS nanoparticle. A further characterization of PbS nanoparticle was confirmed by studying the optical properties. The absorption edge was found at ~790 nm (1.56 eV) which is strongly blue shifted from the corresponding bulk value (0.41 eV) indicating strong quantum confinement.

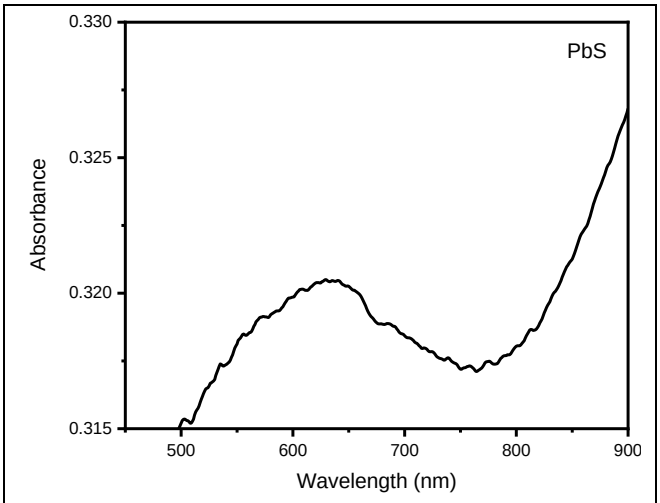

Figure 5: UV- Vis spectra of PbS nanoparticle.

Figure (6) indicates that the absorbance peak equals to 810 nm and energy band gap Eg=1.53 eV. The iodine is the main component of this type of perovskite; therefore, it affects the absorbance and energy bandgap by displacing towards redshift. These results agree with refs [14].

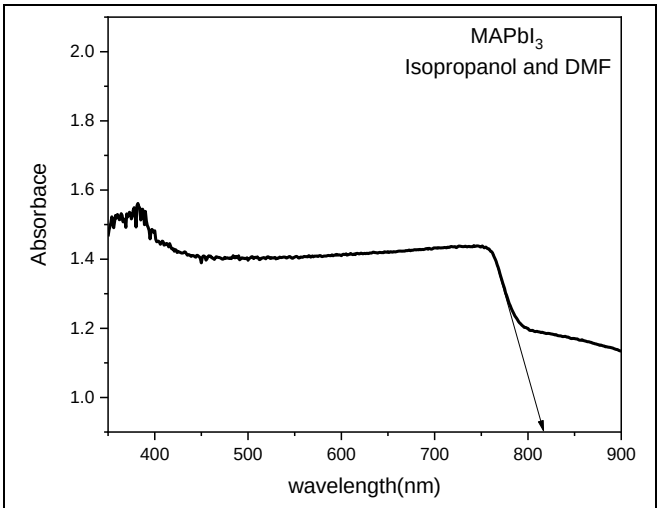

Figure 6: The absorbance peak of $MAPbI_3$ film dissolved by isopropanol and DMF

Figure (7) demonstrates the optical characteristic for $MAPbI_3$ by ethanol and DMF;

the absorbance edge is at 730 nm with corresponding energy bandgap around 1.59 eV perovskite. A decrease was seen in the wavelength of absorbance edge in addition to an increase in the energy bandgap value. This is due to the presence of ethanol which is used in preparation of perovskite.

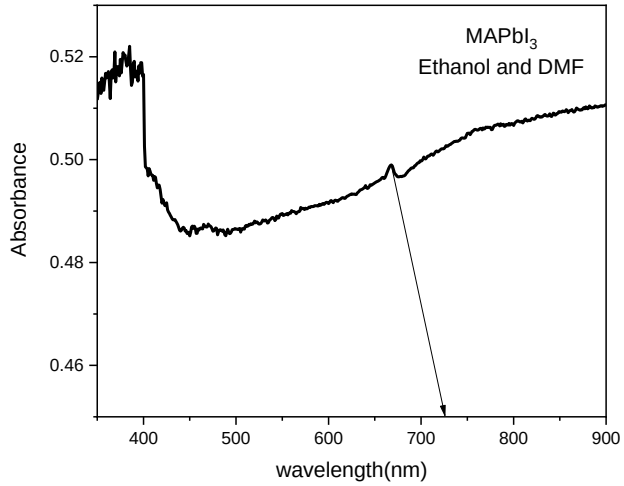

Figure 7: The absorbance peak of $MAPbI_3$ film dissolved by Ethanol and DMF.

The morphology and nanostructure of PbS thin films were characterized by using field-emission scanning electron microscopy (FESEM), as shown in Fig 8. The pristine PbS thin film exhibits a porous nature and has a granular shaped morphology with an approximately 170 nm grain size.

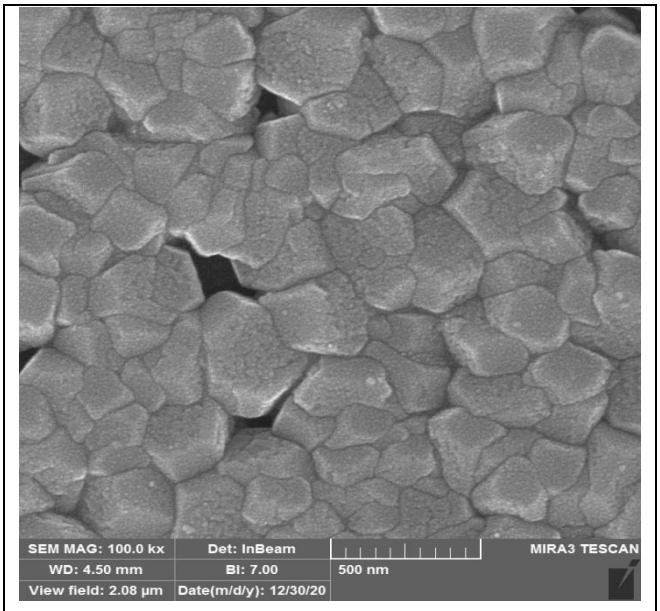

Figure 8: The morphology of PbS thin films.

Figure (9) showa FESEM of $MAPbI_3$ perovskites dissolved by isopropanol and DMF. It appears that the perovskites had a size that ranges from nanometers to micrometers. These perovskites cover the PbS nanocrystal which was prepared on the FTO glass dissolved by isopropanol and DMF. The image of FESEM appears as a rough surface as a star due to insolubility of primary components in the solvent. In addition, it seems inhomogeneous due to using spin–coated method which does not distribute the solution regularly.

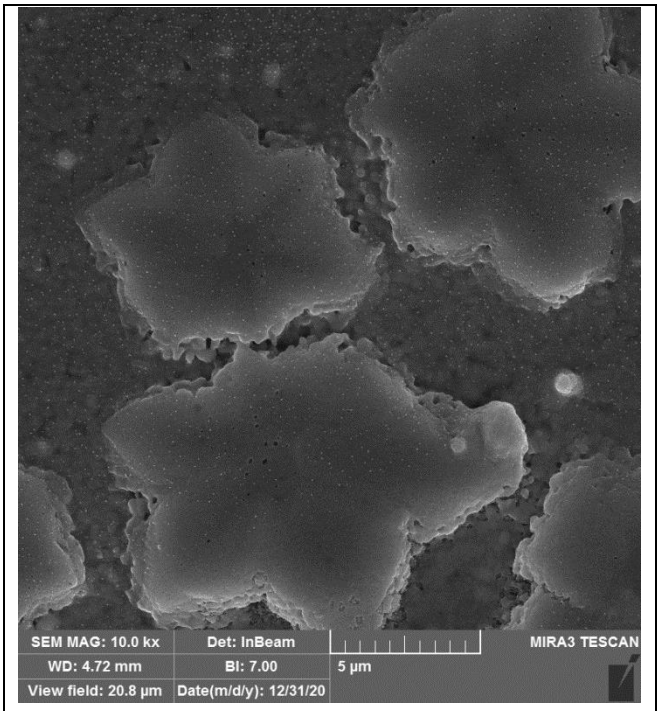

Figure 9: The morphology of MAPbI3 perovskites dissolved by isopropanol and DMF.

Figure (10) displays the perovskite covered the PbS nanocrystal which was prepared on the FTO glass dissolved by Ethanol and DMF. When ethanol was used as a solvent, the surface in most of the particles can be homogeneous and clearly defined. This is due to the increased grain size when using ethanol as a solvent compared to the grain size when using isopropanol.

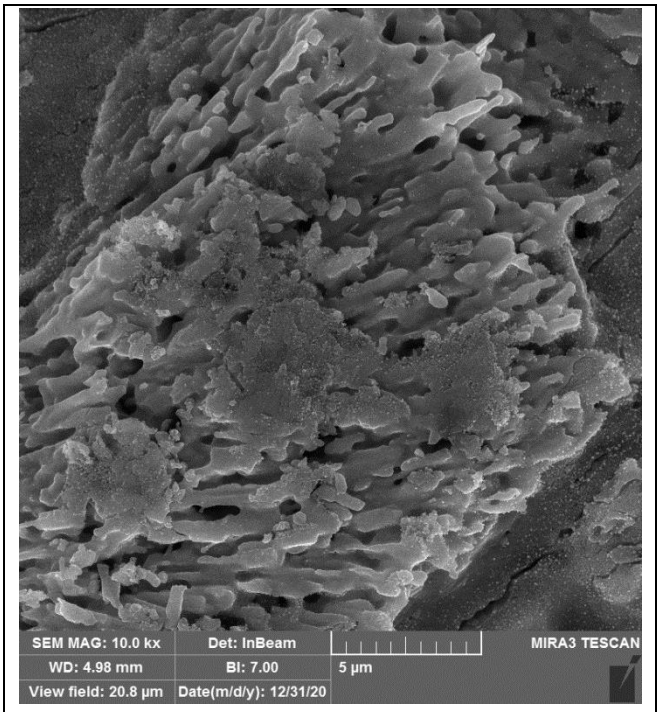

Figure 10: The morphology of $MAPbI_3$ perovskites dissolved by Ethanol and DMF.

Figure (11) shows the photo response of $MAPbI_3$ perovskites dissolved by (A) Isopropanol (B) Ethanol and DMF. According to the analysis, the highest values of the photo response and response time were recorded in the wavelength 640nm. This is due to the illumination light of the 640 nm that has a higher energy than the bandgaps for types of fabricated Perovskite devices in addition to the PbS layer that absorbs incident light at this wavelength. For these reasons, the perovskite devices have best results in the λ=640nm; these show clearly when the photodetector parameters are calculated in the equation below.

$$\boldsymbol{R_\lambda = \frac{I_{ph}}{P_{in}}\ (AW^{-1})} \ldots\ldots\ldots (1)$$

$$\boldsymbol{QE = \ R_\lambda \frac{1240}{\lambda}} \ldots\ldots\ldots \textbf{(2)}$$

$$\boldsymbol{D^* = \frac{R_\lambda}{\sqrt{2q\,(\frac{I_d}{A})}}} \ldots\ldots\ldots\ldots \textbf{(3)}$$

Where $\boldsymbol{R_\lambda}$ responsiveness is the ratio of the I ph produced photocurrent to the Pin light incident power provided by [15].

The external quantum efficiency related to the responsivity [16] The external efficiency of quantum QE is occasionally characterized as the pair flux ratio between the photodetector and the photon.

The standard guidance D* is the most essential metric for photo-detector characterization as it enables direct comparisons between photo-detector performance employing technologies and operating techniques that are extremely different at first sight [17]. The relationship between response and dark current.

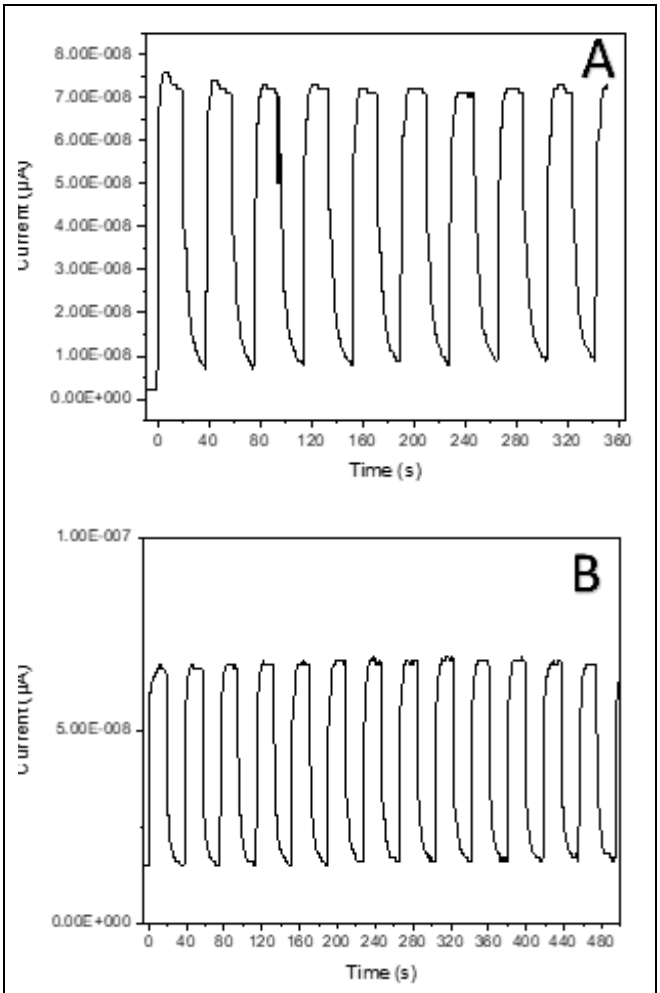

Figure 11: Photoresponse of MAPbI3 perovskites dissolved (A)Isopropanol (B) Ethanol and DMF.

Figure (12) illustrates the rise time and fall time for $MAPbI_3$ perovskites dissolved (A) Isopropanol (B) Ethanol and DMF. The photodetector parameters, which include: responsivity R_λ, external quantum efficiency QE, and normalized detectivity D*, were calculated by the equations 1, 2, and, 3. Table 1. shows the photodetector parameters for MAPbI3 perovskites covered the PbS

nanocrystal which is prepared on the FTO glass dissolved by Isopropanol and DMF where the responsivity R_λ= 0.0037 and quantum efficiency QE=1.016% under λ nm =640 nm and V_{bias}=0V. These values are decreased by using Ethanol solvent.

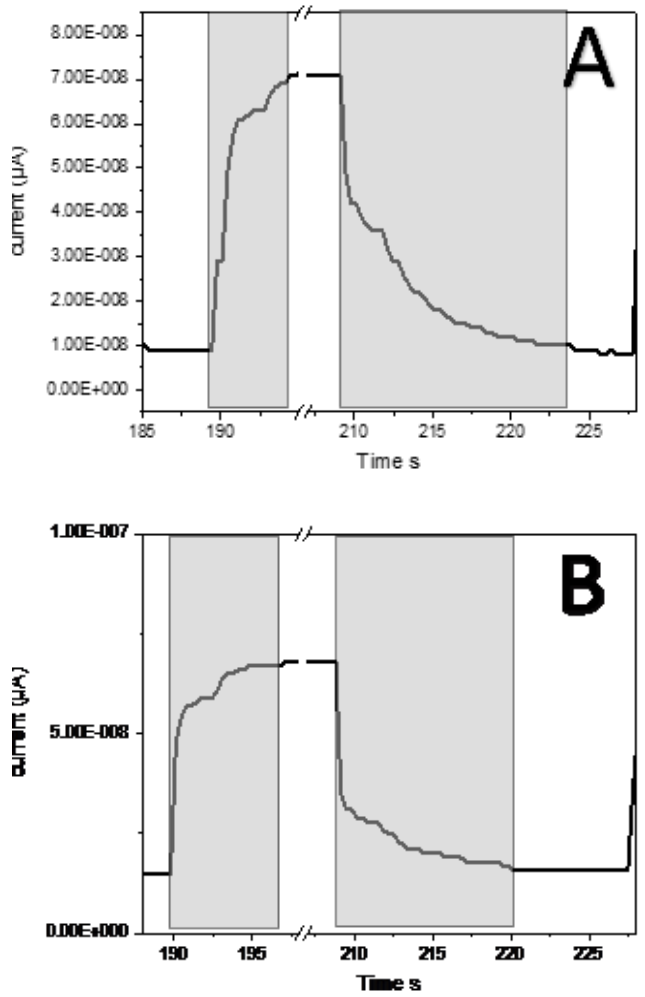

Figure 12: The rise time and fall time for MAPbI3 perovskites dissolved (A) Isopropanol (B) Ethanol and DMF.

Table 1: The photodetector parameters for MAPbI3 perovskites.

perovskite	Solvent	λ nm	t_{rise} (s)	t_{fall} (s)	R_λ ($A.W^{-1}$)	QE %	D* Jones
$MAPbI_3$	Isopropanol	640	5.3	11.1	0.0037	1.016	$1.79E^{-10}$
$MAPbI_3$	Ethanol	640	5.1	10.9	0.0032	0.865	$1.16*10^{-11}$

4. Conclusion

$MAPbI_3$ low cost has been successfully synthesized by using a new method that based on mixing between one and two step and using a solvent (Ethanol). In addition, its application as a photodetector has been studied. Through numerous experimental techniques and practices of X-ray FESEM and UV, the results reveals that the usage of ethanol provides improved results for X-ray diffraction, high homogeneity, and solubility for FESEM. A shift relative to the absorption edge occurs on optical characteristic.

5. Acknowledgment

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