Synthesis and evaluation of composite TiO_2 @ ZnO quantum dots on hybrid nanostructure perovskite solar cell

Negin Pezhooli

Iran University of Science and Technology

Ali Maleki (✉ maleki@iust.ac.ir)

Iran University of Science and Technology

Farzam Hasti

Gorgan University of Agricultural Sciences and Natural Resources

Jamal Rahimi

Iran University of Science and Technology

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Abstract

This research is an interdisciplinary study aimed at helping the environment and producing clean energy. Therefore, one of the goals of this research towards the field of nanotechnology is the application of nanotechnology in the preparation of solar cells and the provision of optimal and efficient cells. Perovskite solar cells are of particular importance because of the high efficiencies that they have achieved in recent years. The use of quantum dots has also played an important role in the efficiency of these cells and their efficiency. The $\text{TiO}_2@\text{ZnO}$ nanocomposite was selected and synthesized for this study. The application of this nanocomposite with different ratios of TiO_2 and ZnO quantum dots was investigated and their efficiency was determined. Although the efficiency of the fabricated cell was reported to be about 5% in a solar cell made of $\text{TiO}_2@\text{ZnO}$ composite, the efficiency can be increased by optimizing conditions such as the optimal location for these cells or by compositing with other materials.

Introduction

With the widespread use of fossil fuels around the world, energy shortages have become a serious challenge. To solve these problems, the use of renewable energy such as solar energy has been studied (Sun et al., 2021; Xing et al., 2013; Stranks et al., 2013). Sun is a huge source of energy and solar energy is the unique renewable, convenient, and main source of all the available energy on Earth. Many efforts have been made today to exploit this great energy source. Solar cells are one way to use this energy. Nowadays, organometallic perovskite solar cells have become a powerful alternative to popular commercialized silicon solar cells due to their easy synthesis, inexpensive components, and low fabrication costs (Im et al., 2011; Noh et al., 2013).

In the past few decades, research activities on nanomaterials have grown rapidly since materials in nanosize exhibit completely different properties as compared to their bulk properties (Rajib et al., 2021). Quantum dots (QDs) grabbed lots of attention in recent years because of their amazing characteristics in optics. The energy gap of QDs depends on their sizes and synthesis methods. (Weimin et al., 2016; M.Sajimol et al., 2012; Y.H. Tong et al., 2004; D. Sun et al., 2008). Quantum dots (QDs) have the advantage of tunable bandgap as a result of size variation as well as the formation of intermediate bands (Jasim, 2018).

Since the application of perovskite light absorber with the formula $(\text{CH}_3\text{NH}_3\text{PbI}_3)$ in the construction of solid-state solar cells in 2012, a lot of research work has been done in the field of perovskite solar cells, so that in a few years the efficiency of these cells to increase by 25.5% (Shalan et al., 2021; Shalan et al., 2021; Khan et al., 2020). Studies show that the research into improving the efficiency of solar cells includes introducing new compounds or new methods of preparing these cells or improving existing compounds and methods. Since the solid-state perovskite cell consists of several layers consisting of compact TiO_2 , mesoporous TiO_2 , perovskite light-absorbing layer, a hole-transport layer, and electrode (Au) (Pourradi et al., 2019), these studies can be performed on any part of the cell (Lee et al., 2012). Nanotechnology and nanoscale materials can be introduced in some of these layers to increase the

efficiency of the solar cell. To review some of the research on the application of nanotechnology in the field of perovskite solar cells, the following can be referred to: A: Research cavity barrier layer (McDonal et al., 2019), B: Mesoporous TiO_2 research layer (Dar et al., 2014; Sun et al., 2015), C: Perovskite light-absorbing layer of research (Chueh et al., 2015; Hwang et al., 2015), d: study hole transfer layer (Malinkiewicz et al., 2014; Docampo et al., 2014).

Increase energy efficiency, can lead to the optimization of perovskite solar cell construction conditions, which can be used in the field of nanotechnology. Also, locating and optimizing the establishment of solar cell farms is another way to increase energy efficiency.

This research is an interdisciplinary study that aims to help the environment and produce clean energy, so one of the objectives of this research in the field of nanotechnology and the environment is the application of nanotechnology in the preparation of solar cells and the presentation of optimal cells and it is productive. In this regard, as an example, we will synthesize the $\text{TiO}_2 @ \text{ZnO}$ composite and study the electron donor properties, improve the gap band and material absorption coefficient, and its effect on the efficiency and flow-potential diagram in the perovskite solar cell. This article has been prepared in two parts. The second part of this research has discussed suitable locations for perovskite solar cells in Kurdistan province located in western Iran (Hasti et al 2022).

1.1 Background on nanocomposite and perovskite solar cell

One of the goals of this research in the field of nanotechnology is to provide optimal and efficient solar cells. As an example, we will synthesize the $\text{TiO}_2 @ \text{ZnO}$ composite and study its electron-giving properties in the perovskite solar cell. To do this, we used the quantum dots of TiO_2 and ZnO . Quantum dots are semiconductor crystals in the nanoscale (1–10 nm). Semiconductors are materials whose electrical conductivity is the interface between the electrical conductivity of conductive and non-conductive materials. Titanium dioxide due to its many properties including high refractive index, Lewis acid property, semiconductor and as an absorber of ultraviolet and visible light in photocatalytic applications and cheapness, high chemical stability, and non-toxic nature among other important metal oxides has special importance. Zinc oxide is also an important semiconductor with a band gap of 3.37 electron volts and high excitation energy of 60 mV at room temperature. In recent years, zinc oxide has attracted much attention mainly due to its unique optical, electronic, and piezoelectric properties, as well as its potential application in solar cells, blue light emitting diodes, sensors, and dimmers. This material can be used in optical instruments in ultraviolet and visible regions. At the nanoscale, it is also a highly transparent semiconductor with strong luminescence at room temperature, making it an ideal choice for a variety of sensors, laser diodes, displays, and transparent electrodes. Zinc oxide is biocompatible and safe and can be used in medicine and solar cells. Composite refers to solids that have more than one component used in their structure. A composite material is a physical, not a chemical, mixture on a macroscopic scale of two or more different materials. These materials retain their physical and chemical properties, but in general, the mixture has better properties than each of its components (Ajayan et al., 2003). The bonds that small material makes with its surrounding phases are much stronger than on larger scales.

Accordingly, a new branch of composites called nanocomposites has been introduced and developed. The nanocomposite is a composite material in which at least one of its constituent phases has nano dimensions (between 1 and 100 nanometers) (Luo & Daniel, 2003). Nanocomposites have a wider range of applications compared to other composites due to their more desirable physical, mechanical, and chemical properties (Theng, 2012). In general, there are three generations of solar cells, of which the perovskite solar cell is a third generation solar cell. The general formula for perovskite compounds is ABX_3 , in which (A) can be a mono-valent organic or inorganic cation surrounded by twelve anions. (B) is a divalent cation of the group of four principal bonds with six anions that forms an octagon. The combination of these octahedrons has created cavities that are occupied by a cation of organic or inorganic capacity and a perovskite structure. And X represents halogen atoms. The total oxidation number of cations and anions is equal to three, which has contributed to the charge balance and stability of the crystal structure (Prakash Singh & Nagarjuna, 2014). Synthesis of the $MAPbI_3$ compound performed by Weber and proposed a cubic structure for this compound and showed that the methyl ammonium group or C_{3v} symmetry must be twisted to provide the necessary symmetry to form the facet octagon. As mentioned, in these compounds, phase change occurs with temperature change, and the combination, $MAPbI_3$, also changes phase with temperature change from cubic to tetragonal. In addition to sensitivity to temperature and pressure, perovskite compounds are highly sensitive to moisture, which should be taken into account when preparing these compounds, so that they are not exposed to moisture because water enters the crystal structure of these compounds. These compounds change from black with the formula $MAPbI_3$ to yellow with the formula $MA_4PbI_6 \cdot 2H_2O$ (Baikie et al., 2013). The results of the research indicate the sensitivity of these compounds to temperature, pressure, and humidity, and this evidence suggests that when preparing these compounds, temperature and humidity control should be considered to obtain a perovskite compound with the appropriate phase.

Material And Method

2 – 1 Laboratory equipment and chemicals

Laboratory equipment

The products were identified using infrared spectra by Shimadzu infrared spectrometers in the form of potassium bromide tablets. FE-SEM (Field Emission Scanning Electron Microscope) images were taken using the MIRA3 TESCAN device.

Chemicals

All materials include potassium hydroxide, zinc acetate, titanium isopropoxide, tetra isopropyl ortho-titanate, high purity iodide, dry ethanol solutions, ethyl acetate, hydrochloric acid, methylamino acid, hydrochloric acid, and hydrochloric acid Supplied by Merck and Aldrich companies.

2–2 Synthesis of materials

Synthesis of ZnO quantum dots

They were first agitated by a magnetic stirrer in various containers of KOH in ethanol and $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ in ethanol, and then ultrasonic at room temperature for one hour. Then drop by drop of a container containing KOH solution was added to the container containing the solution of acetate for two hours by magnetic stirring at room temperature.

Ethyl acetate was then added to obtain ZnO quantum dot precipitate. Finally, the resulting solution was washed with additional ethanol and placed in an oven at 70°C to dry (Geng et al., 2017).

Synthesis of TiO_2 quantum dots

Titanium isopropoxide ($\text{C}_{12}\text{H}_{28}\text{O}_4\text{Ti}$) was added to ethanol and stirred for 20 minutes at room temperature to form a precursor solution with a magnetic stirrer. Then aqueous ethanol solution (ethanol/water 1: 1) was added drop by drop to the precursor solution under ultrasound and then the solution was stirred with a magnetic stirrer for one hour at room temperature. Finally, the whole solution was placed in an autoclave at 150°C for 12 hours.

The resulting precipitate was cooled to room temperature and then centrifuged. The solution was then washed with water and ethanol and placed overnight at 50°C to dry. The precipitate was then collected and calcined at 45°C for 2 hours (Kaur et al., 2015).

Synthesis of $\text{CH}_3\text{NH}_3\text{I}$

The methylamine was stirred with the hydriodic acid in a 250 ml round bottom flask at 0°C (ice bath) for two hours. The solution was then rotated at 50°C to remove solvents, which precipitated. The crude white to slightly yellow $\text{CH}_3\text{NH}_3\text{I}$ product was washed three times with diethyl ether to give a white powder. After filtration, the solid was collected and dried in a vacuum oven at 60°C for 24 hours. The resulting white solid was used without purification (Chen et al., 2015).

Synthesis of $\text{CH}_3\text{NH}_3\text{PbI}_3$ nanoparticles

To obtain $\text{CH}_3\text{NH}_3\text{PbI}_3$ nanoparticles, two compounds, $\text{CH}_3\text{NH}_3\text{I}$ and PbI_2 , were each separately dissolved in isopropanol. The manufacturing steps are as follows: First, 0.25 M $\text{CH}_3\text{NH}_3\text{I}$ solution was sonicated for 30 seconds. Then 0.25 M PbI_2 solution was added dropwise to $\text{CH}_3\text{NH}_3\text{I}$ solution for 30 minutes. A color change from yellow to dark brown was observed after the addition of two precursors and their mixing, indicating the occurrence of a chemical reaction. In this experiment, the purity of PbI_2 is very important because if it is not pure enough, a good result will not be obtained (Bhooshan Kumar et al., 2016).

Composite synthesis of TiO_2 @ZnO quantum dots

2–3 Identification analysis and determination of efficiency

In the synthesis of this composite, different amounts of TiO_2 with ratios of 1:1, 2:1, and 1:2 to the quantum dots of ZnO were used. In a 1:1 ratio in separate containers, KOH in ethanol and zinc acetate along with quantum dots of TiO_2 in ethanol was first stirred with a glass stirrer and sonicated at room temperature for one hour. Then drop by drop of KOH-containing solution was added to the zinc-containing solution for two hours by magnetic stirring at room temperature, and then ethyl acetate was added to precipitate ZnO quantum dots. The resulting solution was washed with excess ethanol and water and placed at 70° C to dry. A 2:1 ratio and a 1:2 ratio of TiO_2 and ZnO were used in the same manner as previously. Finally, the perovskite solar cell was fabricated by spin coating deposition and immersion (Liang et al., 2015; Hwang et al., 2015; Barrows et al., 2014).

Investigation of the infrared (FT-IR) spectra of TiO_2 and ZnO quantum dots and their composites:

Figure 1 shows the infrared spectrum of TiO_2 and ZnO quantum dots and their composite. Infrared spectrum related to ZnO quantum dots, peak 447 cm^{-1} related to Zn-O vibration, peak 705 cm^{-1} related to Zn-OH, peak 1352 cm^{-1} related to C = O bond Zinc acetate, spectrum 1487 cm^{-1} Related to the C = C bond of zinc acetate, the peak of 1577 cm^{-1} corresponds to the stretching vibration of C-H zinc acetate and the peak of 3294 cm^{-1} corresponds to the O-H bond.

In the case of the infrared spectrum of the wide peak TiO_2 quantum dots observed at $3000\text{ to }3400\text{ cm}^{-1}$, it is related to the stretching vibration of the hydroxyl group (-OH), which represents water as moisture. The peak observed in 1627 cm^{-1} is related to the stretching C = O of titanium carboxylate, which is due to the presence of titanium isopropoxide and ethanol as a precursor. The weak peak observed in 1047 cm^{-1} belongs to the Ti-O-C group and the peak observed in 474 cm^{-1} and 800 cm^{-1} is due to the presence of stretching Ti-O in TiO_2 .

Investigation of FE-SEM images of TiO_2 and ZnO quantum dots

FE-SEM images show TiO_2 and ZnO quantum dots, particle size distribution, and particle morphology. As shown in Fig. 2, TiO_2 quantum dots have a spherical morphology and have a particle size distribution between 6–8 nm. The particles are slightly agglomerated, resulting from the agglomeration of small quantum dots. In the case of ZnO quantum dots, it is also observed that the particles have a spherical morphology and have a particle size distribution between 5–9 nm.

Investigation of TEM images of TiO_2 and ZnO quantum dots and $\text{TiO}_2\text{@ZnO}$ composite

Figure 3 shows the TEM images of TiO_2 and ZnO quantum dots and their composite. The average particle size of TiO_2 quantum dots is about 7 nm. This indicates that different sizes of irregular shapes of TiO_2 quantum dots have grown in large quantities in the agglomerate state and the average of ZnO quantum dots is 6 nanometers.

XRD characterization of TiO₂ and ZnO quantum dots and TiO₂@ZnO composite

As shown in Fig. 4, diffraction peaks at 25.3°, 38.0°, 48.1°, 54.2°, 55.1°, 62.8°, 68.9°, 70.4° and 75.3° (2 θ) marked in XRD pattern are well indexed with crystal planes of anatase (101), (004), (200), (105), (211), (204), (116), (220) and (107) indices of TiO₂, respectively. This observation confirms the existence of anatase phase which matches well with the reference card (JCPDS-#21-1272). (Amandeep Kaur et al., 2015; P. Kundu et al., 2014; S. Sood et al., 2014)

Diffraction peaks at 31.68°, 34.35°, 36.09°, 47.36°, 56.48°, 62.70°, 66.23°, 67.87°, 68.99° and 76.77° marked in XRD pattern with crystallographic planes (1 0 0), (0 0 2), (1 0 1), (1 0 2), (1 1 0), (1 0 3), (1 1 2) and (2 0 1) are well indexed wurtzite phase of ZnO respectively which is well compatible with the reference card (JCPDS No 36-1451) (Weimin Yang et al., 2016).

Investigation of I-V diagram of Perovskite solar cell in 2:1 ratio of TiO₂ @ZnO composite

Current-voltage analysis is the first and most basic analysis of a solar cell. In this analysis, cell efficiency as well as open circuit voltage, short circuit current and cell filling factor are determined. Three perovskite solar cells for each ratio were fabricated and three tests were taken from each to obtain the best performance. The best yield for 2:1 TiO₂: ZnO ratio was 5.21%, for 1:1 TiO₂: ZnO was 2.3 and for 2:1 ZnO@TiO₂ was 3.7. Results of Fig. 5 were obtained from the calculation of current and voltage according to the calculations performed.

Discussion And Conclusion

Due to the growing energy consumption, limited current energy production resources, increased productivity of solar-powered equipment, the simplicity of installation, commissioning and use of equipment and the low cost of equipment with solar energy the use of solar energy is becoming more widespread day by day. Perovskite solar cells are of particular importance because of the high efficiencies they have achieved in recent years. The use of quantum dots has also played an important role in the efficiency of these cells and their efficiency. The TiO₂@ZnO composite was synthesized for the first time and the application of this composite with different ratios of TiO₂ and ZnO quantum points was investigated and the efficiency was determined. Although the efficiency of the cell was reported to be about 5% in a solar cell made of 2:1 ratio TiO₂@ZnO composite, the efficiency can be increased by optimizing the conditions or by composing with other materials. In order to increase the efficiency, it is possible to optimize the construction conditions of the perovskite solar cell (in terms of layering, layer thickness, rotational layering time, etc.); Improving the stability of ZnO quantum dots by composing TiO₂@ZnO composites with other materials (such as PbS and materials that affect the efficiency of the solar cell) are other ways to increase efficiency. Also, the use of TiO₂@ZnO composite in core-shell composites, the use of TiO₂@ZnO composite in multiple (tandem solar cells), and finally locating and optimizing the establishment of solar cell fields are other ways to increase efficiency.

Declarations

Conflicts of interest

The authors declare no conflict of interest.

Data availability

All data generated or analysed during this study are included in this published article.

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Figures

Figure 1

FT-IR spectra of ZnO and TiO_2 quantum dots and their composites

Figure 2

FE-SEM of TiO₂ quantum dots and ZnO quantum dots

Figure 3

TEM of TiO₂ quantum dots, ZnO quantum dots and TiO₂@ZnO composite

Figure 4

XRD pattern of TiO_2 quantum dots, ZnO quantum dots and TiO_2 @ZnO composite

Figure 5

I-V graph a) 1:1 $\text{TiO}_2@ \text{ZnO}$, b) 2: 1 ratio of $\text{TiO}_2@ \text{ZnO}$, c) 2:1 ratio $\text{ZnO}@ \text{TiO}_2$ composite