Efficiency Enhancement of Perovskite Solar Cells Based on Graphene Nanocomposites as Electrons and Holes Transport Layers

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Abstract
This study investigates the use of TiO$_2$/G and ZrO$_2$/G transport layers in perovskite solar cells. The hydrothermal technique was used to synthesize the transport layers. According to the results, using TiO$_2$/G as an electron transport layer enhances the transfer of negative charges from perovskites, which increases the efficiency of the solar cell. This is thanks to improved electrical conductivity and less loss of negative charges in the transport layer. The positive gap transition from the perovskite layer to the gap transport layer was enhanced using ZrO$_2$/G. The chemical and physical properties of ZrO$_2$/G help to build a strong interface with perovskite, which promotes gap crossing and reduces the loss of positive charges. Regarding the photonic layer, the efficiency of the solar cell increased significantly when CsPbBr$_3$ quantum dots were used as the active element due to their strong abilities to absorb light from the visible light spectrum according to absorption spectrometry measurements. The efficiency of converting light into electrical charges increases because they can absorb more sunlight, including low-level solar energy. Quantum dots have efficient charge transfer paths, which reduces charge loss and improves conversion efficiency. CsPbBr$_3$ quantum dots are chemically and crystallographically stable. These factors work together to increase the efficiency of the perovskite solar cell when using CsPbBr$_3$ quantum dots from 10.004% to 10.425%.

1. Introduction
A recent forecast predicts that photovoltaics will contribute nearly a third of new electricity generation capacity globally between now and 2030. This is due to recent significant reductions in manufacturing costs of mainstream solar cell technology [1]. On all fronts, a new generation of hybrid organic-inorganic halide perovskites provides enticing possibilities [2]. The lead has been a significant component of all highly effective perovskite cells to date, raising toxicity concerns throughout device production, deployment, and disposal, is one drawback of perovskites. Additionally, they typically degrade when exposed to moisture and ultraviolet light, sometimes rather quickly.

Perovskites have many advantageous properties that make them suitable as materials for photons in solar devices. Importantly, it is possible to install the perovskite layer using inexpensive coating and printing methods, indicating that improvements gained for polymer solar cells would apply to this new material system. In fact,
there are reliable fabrication methods for perovskites [1]. Perovskite absorbers have a good absorption coefficient over a large wavelength range [3]. Due to a significant variety of applications, including electrochromic, photovoltaic, and microelectronic devices, TiO$_2$ thin films have attracted a lot of interest [4]. TiO$_2$ has a wide energy bandgap, which means it has a good ability to separate electrical charges. This enhances the efficiency of electron transfer from perovskite to TiO$_2$ and reduces charge loss. It has high chemical stability, which means it can withstand the harsh operating conditions of perovskite solar cells, such as exposure to humidity and high heat. TiO$_2$ is available in large quantities, and its cost is reasonable compared to other materials used in perovskite solar cells [5, 6]. Zirconium dioxide (ZrO$_2$) is used as a hole transport layer (HTL) in perovskite solar cells because it is a material that has a suitable energy level that allows the holes to be transferred effectively from the perovskite layer to ZrO$_2$. ZrO$_2$ has the ability to form a good interface with the perovskite layer, which contributes to improved gap transport and reduced charge loss. It has a low refractive index, which helps reduce light loss when passing it through the different layers in the solar cell and increases absorption efficiency [7, 8].

A single layer of atoms bound in a two-dimensional crystalline structure makes up the nanocomposite material known as graphene (G). In terms of transmitting charges, graphene offers a number of unique characteristics. Given its extraordinary capacity for efficiently transferring electrical charges, it is regarded as one of the most well-known electrical conductors. It also has excellent thermal conductivity, which means it can transfer heat very effectively. It has an exceptional ability to withstand high electrical current without losing its efficiency in transporting charges [9].

This study aims to prepare nanocomposites TiO$_2$/G and ZrO$_2$/G in the form of thin films by the hydrothermal method as electron and hole transport layers, as well as to prepare perovskite CsPbBr$_3$ and CsPbBr$_3$QDs as effective materials in the manufacture of solar cells from inorganic perovskites as follows: (FTO/TiO$_2$-G/CsPbBr$_3$/ZrO$_2$-G/Pt) represents the first perovskite solar cell (PSC1) and (FTO/TiO$_2$-G/CsPbBr$_3$QDs/ZrO$_2$-G/Pt) represents the second perovskite solar cell (PSC2).

2. Materials and Methods

2.1. Preparation of TiO$_2$/G Thin Film as ETL

Using the drop casting method, a paste made of TiO$_2$/G nanoparticles was created and evenly distributed over an FTO substrate. 1 g of TiO$_2$ was combined with 0.03 g of graphene in 5 ml of ethanol, followed by 40 ml of deionized water, and cooked hydrothermally for 72 h at 180°C in an autoclave. The autoclave was cooled to room temperature following the reaction. To create the nanocomposite TiO$_2$/G powder, the precipitate was filtered, repeatedly washed with distilled water and ethanol, and then overnight dried at 50°C. The TiO$_2$/G nanocomposite was combined with 5 ml of ethanol to make the TiO$_2$/G paste. The mixture was then stirred with a magnetic stirrer for 48 h at room temperature while 0.25 g of ethyl cellulose and 0.1 cc of citric acid were added. TiO$_2$/G film is produced using the drop casting method by drizzling a solution droplet onto the FTO glass with an effective area of 2 cm$^2$, and the film is then allowed to dry at room temperature. These as-fabricated TiO$_2$/G films ETL are then annealed at 450°C for better film-to-FTO adhesion (See Figure.1).
2.2. Synthesis of ZrO$_2$/G Nanocomposite as HTL

To make ZrO$_2$/G Nanocomposite, 50 ml of distilled water was mixed with 0.5 g of graphene and 25 g of ZrO$_2$, and after 5 h of ultrasonication, the suspension was placed into a 100 ml Teflon-lined stainless-steel autoclave. Following that, the autoclave was maintained for 10 h at a preset temperature of 180°C. The dark product was rinsed many times with distilled water after reaching room temperature. Then, ZrO$_2$/G was filtered out and dried in a vacuum for 12 h at 80°C.

2.3. Synthesis of CsPbBr$_3$ and CsPbBr$_3$ QDs Thin Films

We used a pipette to add 5 ml of DMF: DMSO (4:6) to 1.835 g of PbBr$_2$ to create a 1M PbBr$_2$ solution. We then sealed the bottle with sealing tape and set it on the magnetic stirrer at 100 °C with continuous stirring until the white powder was entirely dissolved. We next made a 0.07M CsBr solution (1.491 g of CsBr) and added methanol before transferring the beaker to the ultrasonic apparatus to dissolve the white powder entirely. To make perovskite films, the TiO$_2$/G layer was treated with drops of PbBr$_2$ solution at 2000 rpm for 40 s, dried at 80 °C for 30 min, and then treated with drops of CsBr solution at 2000 rpm for 40 s. For five minutes, the film was heated to 250 °C. A perovskite-based CsPbBr$_3$ film was created by carrying out the CsBr deposition four times. As for the synthesis of CsPbBr$_3$ QDs, we followed the same methods used by Taolin et al [10]. We added 0.18 g of PbBr$_2$ and 0.10 g of CsBr to 10 ml of N, N-dimethylformamide (DMF). The mixture was transferred to a 150 ml beaker until the solid powder dissolved completely. At room temperature, a magnetic stirrer was used to stir the liquid. Continuous for 5 h. Next, we added 0.5 ml of oleic acid (OA) surfactant and 0.5 mL of oleylamine (OAm). Then 10 ml of the ethyl acetate solution was transferred to a 100 ml beaker. After mixing the solution well, 1 ml was withdrawn and then quickly injected into the ethyl acetate solution. The transparent solution immediately took on a yellow-green color, and this color indicates the formation of the CsPbBr$_3$ QDs solution. To purify and clean the QDs, the solution was extracted using a centrifuge for 3 min. After decanting the supernatant, the precipitate was suspended in an n-hexane solution for storage (See Figure 2).

![Figure 2](image-url) Schematic of synthesis of CsPbBr$_3$ QDs.

2.4. Fabrication of Devices

We deposited droplets of perovskite CsPbBr$_3$ on the electrons transport layer (TiO$_2$/G thin film) by two-step spin coating, after which the substrate was annealed at 250 °C for 30 min, then deposited droplets of ZrO$_2$/G solution applied as holes transport layer (HTL). Using a spin-coating method the substrate was annealed at 100 °C. Then, the counter electrode (CE) is prepared using TEV technology. By placing a Platinum (pt) wire at a pressure of (10$^{-5}$) Torr and with a surface area of the CE film of (2 cm$^2$) to make (PSC1). Figure (3) shows the structure of the manufactured solar cell. The perovskite layer was replaced by a perovskite QDs layer to form (PSC2).
3. Results and Discussion

3.1. X-Ray Diffraction

TiO$_2$/G thin films' XRD diffraction patterns are displayed in Figure (4a). The findings and the references [11, 12] are in good agreement. Since every diffraction peak has an index, they all coincide with the typical peaks (JCPDS NO. 21-1272). The TiO$_2$/G thin film has a polycrystalline anatase structure [13] in the X-ray spectrum, which may be directly attributable to the presence of rutile TiO$_2$ (JCPDS Card No. 21-1276) and contains seven peaks in the diffraction and (211) plane. The (101) direction is where the X-ray's peak is located. The addition of graphene to TiO$_2$ does not alter the final crystalline structure, according to the XRD data. Although the graphene peak at 2θ = 26.5° may have been covered by TiO$_2$ nanoparticles, this may be because the strong peak at 2θ=25.3°, which is attributed to the anatase phase of TiO$_2$, often masks the graphene peak in TiO$_2$/G nanocomposites. The crystallite size values of TiO$_2$/G films were estimated using FWHM and 2θ of the directions' peaks using the Debye-Scherer equation.

Figure (4b) exhibits crystalline diffraction peaks that closely resemble the standard peaks (JCPDS NO. (37-1484) and (41-0017)) and can be used to analyze the crystalline phase of the ZrO$_2$/G nanocomposite. The graphene nanosheets' XRD pattern shows a peak at 2θ = 26.48° [14, 15]. The cubic structure is indexed to each and every diffraction peak. Debye Scherrer's equation (Eq.1) is used to determine crystallite size. The dimension of nanostructures determined from the TEM results accords with the average crystallite size of 43 nm.

\[ D = \frac{K\lambda}{\beta \cos \theta} \]  

(1)

The X-ray diffraction pattern of the CsPbBr$_3$ and CsPbBr$_3$ QDs thin films, respectively, is shown in Figure (4c, d). The experimental peaks are consistent with earlier published literature [16, 17] and closely resemble the conventional CsPbBr$_3$ peaks (JCPDS file No. 054-0752). The cubic phase in the space was indexed to each peak (a = b = c = 5.83 Å). The film showed a significant amount of crystallinity. The CsPbBr$_3$ QDs XRD pattern then showed strong, identifiable peaks. The XRD patterns of all the perovskite QDs are comparable and nicely crystallized in the cubic phase. The findings were in good accord with those reported by [18]. At 30.7°, the (200) plane's diffraction was quite strong. Its appearance suggested a highly crystalline, pure, and defect-free cubic phase, together with the secondary diffraction peak of the (100) plane. PbBr$_2$ or CsBr precursor peaks were absent from the pattern. Cs ions occupy the cube's vertices in the space group's cubic symmetry, while Pb and Br ions make up the octahedral \{PbBr$_3$\}_4 building blocks. We note that the quantum dot example has a smaller crystal size.
Figure (4). XRD spectra of (a) TiO$_2$/G film, (b) ZrO$_2$/G film, (c) CsPbBr$_3$, and (d) CsPbBr$_3$ QDs perovskite.

3.2. Morphological Properties
Figure (5) shows the TEM images of the prepared TiO$_2$/G nanocomposite, this image showed that the nanoparticles were quasi-spherical or spherical aggregates with an average TiO$_2$/G particle size of about 40–50 nm. Graphene is characterized by its unique chemical composition, which is a thin layer of carbon that consists of carbon atoms arranged in a specific geometric pattern. TiO$_2$ contains titanium and oxygen atoms bonded in a specific way. Because there is chemical compatibility between the structure of graphene and TiO$_2$, it contributes to achieving homogeneity and good bonding between them. Because graphene has high bond strength, great flexibility, and good thermal and electrical conductivity. These properties enhance graphene ability to interact and bond with other compounds such as TiO$_2$ at the nanoscale interface. Since graphene is very thin and consists of only one layer of carbon atoms, it increases the interaction area with TiO$_2$. This enhances the potential for chemical interaction and bonding between molecules and leads to reliable homogeneity at the nano-level. These factors contribute to achieving strong and stable bonding between molecules and forming a homogeneous nanostructure that is effective in various performances and applications. This may lead to increased current density ($J_{sc}$) and improved cell power conversion efficiency (PCE).
The TEM image shows the homogeneity of ZrO$_2$/G as a nanocomposite in Figure (6). The microscopic images confirm the formation of well-defined spherical nanoparticles with different sizes from 20–40 nm. The homogeneity of ZrO$_2$ with graphene as a nanolayer in perovskite solar cells is considered a promising option to improve cell performance and increase its efficiency because graphene is an electrical conductive material, and therefore it can be used as a nanolayer to conduct charge in a perovskite cell. The efficiency of solar energy conversion is increased by the graphene because it enhances charge conduction from the perovskite layer to the counter electrode (pt). Due to ZrO$_2$ excellent oxidation resistance, corrosion, and long-term performance deterioration are prevented in graphene as a nanostructure. The solar cell's stability and longevity are both improved by doing this. By enhancing charge conduction, decreasing charge loss, and enhancing the absorption rate, all of these characteristics help the cell become more effective and function better.

The SEM image shows the homogeneous distribution of CsPbBr$_3$ quantum dots and we observe the presence of consistent small particles on the surface of the sample. Quantum dots are composed of (Cs), (Pb) and (Br) ions, and are characterized by their small size that can be clearly seen using an SEM. We also note that quantum dots are regular in size and shape, and can be homogeneous. The CsPbBr$_3$ nanocomposite is expected to be
homogeneous in composition. Coordinated and homogeneous quantum dots consisting of the component elements of the compound (cesium, lead and bromine) can be seen on the surface of the sample (See Figure 7).

**Figure (7).** The SEM images for CsPbBr₃ quantum dot

### 3.3. Optical Properties of CsPbBr₃ and CsPbBr₃ QDs

Figure (8) shows the absorption spectra of the CsPbBr₃ and CsPbBr₃ QDs. Quantum dots are small aggregates of nanocomposite atoms. This small size leads to remarkable quantum effects, including increased efficiency of absorption of light at a specific wavelength. Quantum dots have a very high surface-to-volume ratio as a result of their small size and two-dimensional shape. This leads to increased interactions with light and improved absorption efficiency, as there are more opportunities for photons to interact with quantum dots on their surface. Although these factors play an important role in increasing the absorption of light by CsPbBr₃ nanocomposite quantum dots, it should be noted that the precise explanation of these phenomena is complex and still requires further study and research.

**Figure (8).** Absorption spectrum of CsPbBr₃, CsPbBr₃ QDs.
3.4. The Photovoltaic Performance

From Figure (9) and Table (1) we notice that the $J_{sc}$ value for the cell (PSC1) has increased compared to the solar cell (PSC2) (from 8.30 to 8.42 mA.cm$^{-2}$) as well as in $V_{oc}$ values (from 1.47 to 1.51 V), respectively. This increase leads to an increase in the energy conversion efficiency from 10.004% to 10.425% when using quantum dots of the CsPbBr$_3$ nanocomposite in the perovskite solar cell. This means that the CsPbBr$_3$ nanocomposite quantum dots can more efficiently absorb light in the visible and near-visible range which is important for solar power generation. The quantum dots of the CsPbBr$_3$ nanocomposite interact better with light and increase the chances of absorbing it, which contributes to increasing the efficiency of converting light into electrical energy in the perovskite solar cell. These features can contribute to increasing the energy conversion efficiency of the perovskite solar cell when using CsPbBr$_3$ nanocomposite quantum dots.

Table (1). Photovoltaic Parameters of perovskite solar cells.

<table>
<thead>
<tr>
<th>Device</th>
<th>$J_{sc}$ (mA.cm$^{-2}$)</th>
<th>$V_{oc}$ (V)</th>
<th>FF</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PSC 1</td>
<td>8.30</td>
<td>1.47</td>
<td>0.82</td>
<td>10.004</td>
</tr>
<tr>
<td>PSC 2</td>
<td>8.42</td>
<td>1.51</td>
<td>0.82</td>
<td>10.425</td>
</tr>
</tbody>
</table>

Figure (9). Performance of all perovskite Solar Cells.

4. Conclusions

In conclusion, we manufactured two solar cells and comparing the results improved the optoelectronic properties of CsPbBr3 by converting it into CsPbBr3 QDs as the photoactive layer active material in perovskite solar cells. The fabricated device reached the highest power conversion efficiency of 10.425%, which is 10.004% higher than the original device based on CsPbBr3 as the active material in the photonic layer. Our study included a comprehensive understanding of the use of TiO2/G as the electron transport layer and ZrO2/G as the hole transport layer.

Conflict of Interest: The authors declare that there are no conflicts of interest associated with this research project. We have no financial or personal relationships that could potentially bias our work or influence the interpretation of the results.
References


