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ZnO photoluminescent quantum dots with down-shifting effect applied in solar cells.

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Abstract. We report the synthesis of Zinc Oxide (ZnO) quantum dots (QDs) and their influence on the power conversion efficiency of photovoltaic devices. With an excitation wavelength of 340 nm the down-shifted emission peaks were observed to be located at 510 and 540 nm for colloidal solutions with pH values of 10 and 12, respectively. The largest PCE variation was observed to increase from 14.60\% to 15.49\% when dispersing the QDs extracted from a 4 mL colloidal solution that were subsequently dispersed in PMMA. This represents an improvement of ~6.1\%.

1. Introduction  
The solar spectrum comprises wavelengths extending form the infrared to ultraviolet, however, in silicon electron-hole pairs are only produced by photons that fall within the visible range [1-2], obviating the need to extend the range of photons producing electron-hole pairs. Specifically, Zinc Oxide (ZnO) quantum dots have the capability to absorb photons in the UV region of the solar spectrum and subsequently emitting a photon within the region of interest for silicon photovoltaic structures. The colloidal ZnO quantum dots were synthesized in ethanol-based solutions obtaining different sized nanoparticles, i.e., emitting different wavelengths. The emission wavelength of the synthesized ZnO quantum dots can, in fact, be tuned by adjusting the pH value of the corresponding solution. Subsequently, the quantum dots were collected by adding hexane to the ethanol solution to promote their sedimentation [3]. Different concentrations of zinc oxide quantum dots were collected and dispersed in Poly methyl methacrylate (PMMA) to be deployed on the window side of solar cells using a standard spin coating approach.
2. Experimental details.

2.1. Synthesis of ZnO quantum dots.
Colloidal Zinc Oxide Quantum Dots (ZnO QDs) were synthesized employing a controlled-precipitation method [4]. In a typical synthesis, 0.02M zinc acetate solution was made by dissolving 0.256 gr of zinc acetate (99.99%, Sigma-Aldrich) in 70 mL of pure ethanol, and 0.01M lithium hydroxide solution was prepared separately by dissolving 0.125 gr of LiOH (≥ 98.0% Sigma-Aldrich) in 30 mL of pure ethanol. The reaction was carried out at room temperature by dropwise addition of LiOH solution to zinc acetate solution under constant stirring until the pH values of 10 and 12 were reached. Once the sought pH values were obtained, the solution was placed in an ultrasonic bath for 3 hours and it was observed to be transparent. In order to elucidate the process of reaction in the synthesis, a chemical reaction model was proposed where the interaction between zinc acetate and ethanol carries an esterification reaction that promotes the formation of water, ester and also the growth of nanoparticles of ZnO, according to the following reaction [5].

\[ \text{Zn(CH}_3\text{COO)}_2 + 2R\text{-OH} \rightarrow \text{ZnO + 2CH}_3\text{-CO-R + H}_2\text{O} \]

The size of the produced quantum dots is determined by the pH of the solution during the reaction synthesis, as previously discussed.

2.2. Collection of ZnO quantum dots.
Once the reaction was brought to completion, the synthesized quantum dots were purified by extracting the unreacted products and collecting the nanoparticles from the ZnO solution. Several groups have reported the utilization of organic "nonsolvents" such as heptane and hexane to promote the precipitation of the particles in the solvent [3, 6]. However, in this exercise hexane was added to the ZnO QD solution in a volume ratio of 3:1 and allowed to stand for 24 hours. Subsequently, the supernatant was removed and the precipitated ZnO QDs were washed three times in ethanol and redispersed also in ethanol for storage.

2.3. Application of ZnO quantum dots over solar cells.
After collecting the quantum dots, several QD samples with different concentrations of the purified ZnO QDs were prepared. The purified samples were centrifuged in order to promote the precipitation of the ZnO particles suspended in ethanol, after that, the solvent was removed leaving only ZnO quantum dots precipitated at the bottom of the vial. In order to incorporate the synthesized QDs to solar cells, they needed to be dispersed in a polymer matrix. Polymethylmethacrylate (495 PMMA A2 from Microchem) was selected for its properties of transparency, resistance to ultraviolet light, and its reported low brittleness. Thus, 1 mL of PMMA was added to the vials with the precipitated QDs. Polycrystalline silicon, commercial solar cells, with dimensions of 52mm x 38mm and a thickness of 200μm were employed to quantify the influence of the synthesized ZnO QDs. The PMMA+QD films were spin cast on the window side of the aforementioned solar cell. The spin coating was carried out starting with 300 rpm for 10 secs, followed by 4,000 rpm for 45 seconds [7]. After spin coating the solar cells with PMMA + QDs, they were placed on a hot plate at 200 °C for 60 secs to promote the evaporation of the solvents within the PMMA. Device characterization was carried out before and after the deployment of the aforementioned PMMA+QD film.

3. Results and discussions.
During ZnO quantum dot synthesis, the pH of the solution was adjusted to different values before submitting to reaction process in order to obtain different sizes as well as different luminescent and absorption effects. The pH values selected during synthesis were approximately 10 and 12.
3.1. Photoluminescence characterization. Employing an excitation wavelength of 340 nm, the produced ZnO QDs exhibited photoluminescence spectra extending from approximately 420 nm to 650 nm and with luminescence peaks at 510 and 540 nm for pH values of 12 and 10, respectively. Figure 1-a shows the normalized spectra obtained by dividing the collected spectra obtained by the maximum of their excitonic emission obtained in luminescence measurements for different characterized samples. It can be observed that the maximum luminescent peaks in the samples have a wavelength difference between them of 30 nm, centred around 525 nm, evincing that the luminescent characteristics of the produced particles, as well as their size, are directly linked to the reaction conditions related with the rate of pH in the solution during the synthesis and the luminescence effects can be tunable. The yellow-greenish and blue-cyan photon emission for the pH values of 10 and 12, respectively (see figure. 1-b) [8], were observed using a handheld UV lamp light over the synthesized samples.

![Figure 1. (a) Synthesized ZnO QDs photoluminescence spectra with an excitation wavelength of 340 nm. (b) Visible light emission of samples with pH values of 10 and 12 when the samples are exposed to UV light.](image)

3.2. Absorption characterization. The UV/Vis absorption spectra were characterized with a UV-VIS-NIR Cary 5000 spectrometer. Absorption measurements of ZnO quantum dots in ethanol exhibit a spectrum starting around ~250 nm and extending up to ~400 nm, except for the sample made with a pH value of 12, which shows a gradual downward curve to ~800 nm (see figure 2). This behaviour may be attributed to the turbidity of the solution at the end of the synthesis process in contrast to the transparency observed on the samples with pH values of 8 and 10. The solutions of ZnO quantum dots show their spectra centred around ~ 300 nm and an approximate width of ±50 nm consistent with values reported elsewhere [9].

![Figure 2. Absorption spectra for ZnO quantum dots synthesized with different pH values](image)

3.3. Solar cell characterization. To measure the performance of the solar cells, we used a solar simulator (Oriel Sol2A) to evaluate the major values of the photovoltaic device related with open circuit voltage ($V_{oc}$), short circuit current ($J_{sc}$), Fill Factor (FF%) and Power Conversion Efficiency (PCE%). The collected measurements are
shown in Table 1. [10-12]. All measurements were made before and after deploying the synthesized quantum dots on the window side of the solar cells with a film of PMMA + ZnO QDs obtained by spin casting.

Table 1. Summary of measured performance of photovoltaic devices before and after deploying PMMA layers with different ZnO QD concentrations.

<table>
<thead>
<tr>
<th></th>
<th>2 mL of ZnO QDs</th>
<th>4 mL of ZnO QDs</th>
<th>6 mL of ZnO QDs</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Before</td>
<td>After</td>
<td>Before</td>
</tr>
<tr>
<td>Voc (V)</td>
<td>0.62</td>
<td>0.62</td>
<td>0.63</td>
</tr>
<tr>
<td>Jsc (mA/cm²)</td>
<td>36.90</td>
<td>36.59</td>
<td>37.03</td>
</tr>
<tr>
<td>FF (%)</td>
<td>67.06</td>
<td>67.58</td>
<td>63.10</td>
</tr>
<tr>
<td>PCE (%)</td>
<td>15.40</td>
<td>15.42</td>
<td>14.60</td>
</tr>
</tbody>
</table>

4. Conclusions
The size and, therefore, the emission wavelength of Zinc Oxide quantum dots can be tuned by varying the pH value of the solution during synthesis. The largest PCE variation was observed to increase from 14.60% to 15.49% when dispersing the QDs extracted from a 4 mL colloidal solution that were subsequently dispersed in PMMA. This represents an improvement of ~6.1%.

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