Synthesis of Pb-doped CdS quantum dot using SILAR method on mesoporous TiO$_2$ layer

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Abstract. This research focuses on the fabrication of CdS quantum dot-sensitized solar cells (QDSCs). CdS quantum dots (QDs) were fabricated on a mesoporous TiO$_2$ electrode using a successive ion layer adsorption and reaction (SILAR) method and Pb doping concentrations (0, 2, 4, 10, 15, 20, 25 and 30 %mol) were varied. The change in optical properties of CdS QDs was found to be affected by Pb doping. The Pb-doped CdS QDSCs were determined under the illumination of 100 mWcm$^{-2}$, which indicated the highest power conversion efficiency (PCE) was 1.73% at 20% Pb dopant.

1. Introduction
Quantum dots (QDs) have been received attention as a sensitized material for solar cells due to tunable energy bandgap depending on the size of the quantum, high extinction coefficient, oxygen and water stability, and multiple exciton generation (MEG). The theoretical power conversion efficiency (PCE) of solar cells can reach up to 42%, which is exceedingly higher than PCE of first-generation solar cells (32.9%) [1-3]. Among the various QDs, Cadmium sulfide (CdS) is mostly used for quantum dot sensitized solar cells (QDSCs) since CdS has a high potential for light-harvesting in the visible light region [4]. However, CdS does not utilize a full solar spectrum because of its absorption ability. CdS has an energy band gap of 2.42 eV (515 nm) [5], which may absorb the light with wavelengths shorter than 600 nm and limits to get a higher PCE of CdS QDSCs. One of the interesting techniques to enhance the efficiency of CdS QDSCs is doping. Li Tianxing et al developed CdS by doping manganese (Mn) into CdS thin films for use in solar cells. The variation of absorbance was found, and the PCE of solar cells exceeded 1.51% [6].

This research proposes to extend the light absorption ability of CdS QDSCs for achieving higher PCE. To provide electrons in long-wavelength regions, CdS QDs were doped with lead (Pb) since Pb has been known as an excellent material that absorbs the light through all visible and near-infrared. The PCE of Pb-doped CdS QDSCs showed 1.73% under the illumination of one sun with the optimum Pb doping concentration in the precursor (20%mol).

2. Research methods
Titanium Dioxide (TiO$_2$) electrodes were prepared using TiO$_2$ pastes via doctor blading on fluorine-doped tin oxide (FTO) coated glass and then heat TiO$_2$ electrodes under air temperature 500°C for 30
min. Then, Pb-doped CdS QDs were grown on the TiO$_2$ surface using a successive ionic layer adsorption and reaction (SILAR) method. The mixing of cadmium acetate dihydrate [(CH$_3$COO)$_2$Cd$\cdot$2H$_2$O] and Lead (II) acetate [(CH$_3$COO)$_2$Pb$\cdot$3H$_2$O] 0.04 M in deionized (DI) water was used as the cationic solution. This experiment has eight different mixing percentages of Lead (II) acetate (Pb doping concentrations) with cadmium acetate dihydrate, including 0, 2, 4, 10, 15, 20, 25, and 30 %mol in the precursor. 0.04 M sodium sulfide nonahydrate (Na$_2$S$\cdot$9H$_2$O) dissolved in DI water was used as the anionic solution. The TiO$_2$ electrode was first dipped in a cationic solution for 2 min then rinsing with DI water and ethanol. Successively, the electrode was dipped into the anionic solution for 2 min then rinsing with DI water and ethanol. The sequence of dipping cationic solution - washing - anionic solution - washing is one SILAR cycle. In this experiment, Pb-doped CdS QDs were synthesized by SILAR for three cycles. The structure and the sample of QDSCs from this research were shown as figure 1.

The optical properties were analyzed using ultraviolet-visible spectrophotometry (UV-Vis). The photovoltaic properties of the solar cells were evaluated under the illumination of one sun (AM 1.5, 100 mW·cm$^{-2}$). The active area of the solar cells was 0.2375 cm$^2$. In this research, four samples were prepared and measured for each condition of Pb doping concentration.

![Figure 1](image)

**Figure 1.** (a) Schematic of quantum dot sensitized solar cell and (b) The sample of CdS quantum dot sensitized solar cell.

### 3. Results and discussion

In this study, the SILAR method was used to directly fabricate CdS and Pb-doped CdS quantum dot as sensitizer on the mesoporous TiO$_2$ electrode.

The absorbance spectra of photoelectrodes were measured by ultraviolet-visible spectrophotometry (UV-Vis) at wavelength 200-2000 nm. As shown in figure 2(a), the photoelectrode gradually darkened, and the optical absorbance increased as the percentage of Pb doping concentration increased. With higher Pb doping concentration, the absorption edge shifts to higher wavelength (redshift) from 460 nm to 660 nm, which means an increase in wavelength of absorbance. This result indicates that the light absorption range can be improved with Pb doping into CdS QDs. Absorbance increasing also causes the bandgap to decrease, which the energy bandgap calculation of QD growth with different percentages of Pb doping concentration is discussed further. Li Tianxing et al deposited the Mn-doped CdS quantum dots with different doping ratio of Mn:CdS (1:1, 1:10, 1:100). After doping Mn into CdS QDs, They found the noticeable redshift in the UV-Vis absorption spectra, which meant CdS quantum dots could provide electron in the long-wavelength region of the spectrum due to the introduction of midgap states between the conduction band and the valence band of TiO$_2$ QDs by Mn doping [6].

From the above, Pb doped into CdS, and Mn-doped into CdS yielded the same promising results, in which the light absorption range was extended due to redshift.
Figure 2. (a) UV-visible spectra curves of Pb-doped CdS QDs with different percentage of Pb doping concentration and (b) Tauc plot of CdS QDs.

Tauc plot [7] relation was used to evaluate the optical band gap energy, as illustrated in figure 2(b). The energy bandgap of CdS quantum dots, shown in figure 3(a), had no significant change during 0 - 10 %mol Pb dopant (2.68±0.01 eV). The energy band gap was found to decrease slightly after 15 %mol Pb dopant onward. Due to their unique properties, quantum size effect, energy bandgap can be tuned depending on the quantum size variation [8]. The previous work can confirm the size of the quantum variation dot affects the energy bandgap [9], and the relation between the energy bandgap and the size of the QD is an inverse relationship. Thus, the decrease in energy bandgap of CdS quantum dots is caused by increases in the size of QDs. This result can signify the change of Pb doping concentration effect on the size of CdS QD and energy bandgap when the concentration is 15 %mol onward due to the shift in bandgap energy.

Figure 3. (a) The energy bandgap of quantum dots calculated by Tauc relation and (b) The J-V characteristic of different samples based on the concentration of Pb dopant.

Photocurrent density-voltage (J-V) characteristics, shown in figure 3(b), used to characterize Pb-doped CdS QDSCs under the illumination of one sun (AM 1.5, 100 mW·cm⁻²). The parameters of photocurrent density-voltage (J-V) characteristics, which is the average value from each condition, are shown in table 1. Pb-doped CdS QDSCs revealed an increment in the PCE from 0.44% to 1.73%, compared with undoped CdS QDSC. 20 %mol Pb dopant was the optimum Pb doped amount due to the
highest PCE in this experiment. As higher Pb doping concentration, short circuit current ($J_{sc}$) increased from 2.63 mA/cm$^2$ (0 %mol) to 12.04 mA/cm$^2$ (20 %mol). However, the performance of the QDSCs began to decline when the concentration continuously increased (more than 20 %mol). Simultaneously, the fill factor (FF) had no significant change, and open-circuit voltage ($V_{oc}$) slightly decreased since Pb doping. The reason behind the enhancement of $J_{sc}$ is midgap states created by Pb doping, which improved the capture for electrons and also screened the charge recombination partly with the hole and electrolyte. However, $J_{sc}$ decreased when the Pb dopant ratio reached some point. A decrease in $J_{sc}$ may be caused by a large number of recombination centers, which have been introduced along with the Pb ions doped on the CdS QDs. Li Tianxing et al and other previous research also described the phenomenon of midgap states that affected J-V characteristics of QDSCs [6,10,11].

| Pb doping concentration (%mol) | $V_{oc}$ (V) | $J_{sc}$ (mA/cm$^2$) | FF | PCE (%) |
|-------------------------------|-------------|----------------------|----|---------|
| 0                            | 0.412       | 2.63                 | 0.41| 0.44    |
| 2                            | 0.385       | 3.09                 | 0.50| 0.59    |
| 4                            | 0.385       | 3.10                 | 0.59| 0.70    |
| 10                           | 0.362       | 6.31                 | 0.58| 1.09    |
| 15                           | 0.325       | 8.04                 | 0.56| 1.48    |
| 20                           | 0.318       | 12.04                | 0.55| 1.73    |
| 25                           | 0.293       | 9.10                 | 0.53| 1.27    |
| 30                           | 0.282       | 6.43                 | 0.53| 0.82    |

4. Conclusions
CdS quantum dots (QDs) were directly fabricated on the mesoporous TiO$_2$ electrode with different Pb doping concentration (%mol) using the SILAR method. The doping of CdS QDs with Pb successfully enhanced the light absorption range of CdS QDs. The absorption edge moves to the higher wavelength from 460 nm to 660 nm, which is related to the decrease in energy bandgap when the doping concentration increases. The PCE and $J_{sc}$ of solar cells improve after doping of Pb compared with pure CdS QDSCs. The highest PCE is 1.73% at 20 %mol Pb dopant in the precursor. However, the properties of QDSCs started to decrease when the Pb doping concentration increased further (> 20 %mol), and the $V_{oc}$ continuously decreased after doping. Further studies are needed to determine which parameter may affect decreasing in $V_{oc}$. The passivation layer, such as ZnS, can apply to QDSCs for achieving higher efficiency.

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