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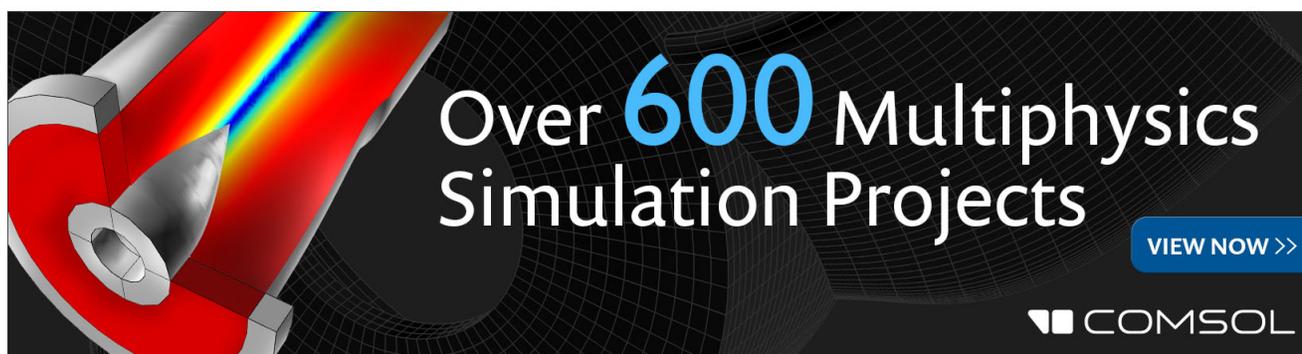
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PbS quantum dots prepared by pulsed laser deposition for photovoltaic applications and ligand effects on device performance

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In this research, PbS quantum dots (QDs) were assembled directly on ternary metal oxide nanowires by pulsed laser deposition (PLD) for photovoltaic applications, which avoided the difficult ligand exchange processing needed in typical colloidal synthesis processes. Different ligands including oleic acid, oleylamine, and 3-mercaptopropionic acid (MPA) were used to cap the PbS QDs after PLD deposition, and Fourier transform infrared spectroscopy was used to characterize their coverage. The ligand effect on solar cell performance was also investigated, and it was found that the device treated with oleic acid exhibited a significantly improved performance.

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Quantum dot sensitized solar cells (QDSSCs) have been widely studied due to their potential to circumvent the Shockley-Queisser efficiency limit through the multiple exciton generation effect,^{1–3} the ability to match the solar spectrum by employing quantum dots with different sizes,⁴ and improved stability due to the nature of the semiconductor materials compared to organic dye molecules.⁵ Typical QDSSCs are based on colloidal QDs that are prepared and assembled in organic solvents involving capping ligands.⁶ Ligands such as 3-mercaptopropionic acid (MPA) can limit the growth of the QDs under a desired size and keep them dispersed in the solution.⁷ However, the ligands are also associated with some disadvantages. First, for certain types of colloidal QDs, in particular, the PbS QDs that have shown the important multiple exciton generation effect, the ligand exchange processing is nontrivial and time-consuming and is not always reproducible.⁵ Second, the ligands introduce additional transport barriers in the carrier transfer process between the QDs and the photoanodes, and such effect has not been fully understood. In our previous study, we have developed a one-step QD synthesis and assembly approach that is based on a physical, pulsed laser deposition (PLD) technique.⁸ In this work, we further applied this method to the deposition of PbS QDs on Zn₂SnO₄ nanowires and examined their photovoltaic applications. In addition, previous research has shown that certain ligands can modify the QD surface defect states that are detrimental to QDSSC performance,⁹ and thus it is desirable to cap the PLD-coated QDs with these ligands and investigate their effects on device performance. In this work, we utilized common ligands such as oleic acid, oleylamine, and MPA that have been widely used in colloidal QD synthesis and ligand exchange process to cap the PLD deposited PbS QDs in order to modify the surface defects and possibly improve solar cell performance.

Zn₂SnO₄ nanowires with length of $\sim 200 \mu\text{m}$ and diameter of $\sim 80 \text{nm}$ were used as the photoanode, which were grown on silicon substrates following the procedure published elsewhere.¹⁰ After growth, the nanowires were

removed from the substrate in ethanol solution by ultrasonication and transferred to Transmission Electron Microscopy (TEM) grids for QD deposition and structural characterization. For solar cell fabrication, the PbS QDs were deposited on Zn₂SnO₄ nanowires that had been previously transferred to fluorine-doped-tin-oxide (FTO) coated glass substrates by a printing transfer process. A Zn₂SnO₄ precursor film was used as an adhesion layer between the transferred wires and the FTO substrate, which also created a good electric contact between the two after annealing. This precursor film was first spin-coated on the FTO substrate, and the Zn₂SnO₄ nanowires on a silicon substrate were faced down and pressed to the precursor-coated FTO substrate with a pressure of 1000g/cm^2 , which was maintained for 1 min before release. The FTO substrate with nanowires was then annealed at 500°C for 5 h to transform the precursor into a Zn₂SnO₄ film. The deposition of PbS QDs on nanowires was performed using the pulsed laser deposition technique. A Nd:YAG laser (wavelength: 266 nm; pulse repetition rate: 10 Hz) with a laser fluence of 12.6J/cm^2 was used for the experiment. The deposition was carried out under a pressure of 10^{-6} Torr in a vacuum chamber with a quartz window that allowed the UV laser beam to pass through. Before entering the chamber, the laser beam also went through a lens with a 30 cm focal length, which focused the laser energy on the target. The target was a dense solid piece of PbS purchased from Alfa Aesar. The distance from the target to the substrate was 6 cm, and the deposition time was 3 min. After PLD deposition, the Zn₂SnO₄ nanowires coated with PbS QDs were dipped successively into ligand solution (oleic acid, oleylamine, or MPA) and pure ethanol or methanol, 2 min for each dipping, for ligand coating and washing, respectively. Such a coating cycle was repeated five times for each ligand studied here. The size, size distribution, and morphology of the PbS QDs were analyzed by TEM using a JEOL 2010 microscope equipped with EDAX DXPrime energy dispersive x-ray spectroscopy (EDS). For QDSSC fabrication, an FTO substrate with QD-coated Zn₂SnO₄ nanowires and a Cu₂S counter electrode were bonded together through a hot-melt spacer (Bynel, Dupont, $75 \mu\text{m}$) to form a sandwiched structure, and polysulfide electrolyte

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consisting of 0.25M Na₂S and 0.1M NaOH in de-ionized water was injected into the device space through pre-drilled holes on the Cu₂S counter electrode. The Cu₂S counter electrode was made by immersing a brass plate in 36% HCl at 60 °C for 10 min and then in the polysulfide electrolyte for another 10 min at room temperature. Incident-Photon-to-Electron Conversion Efficiency (IPCE) spectra in the wavelength range of 400–1400 nm were acquired using a two-electrode configuration with a platinum wire as the counter electrode. A 100 W Quartz Tungsten lamp was used as the light source, and the monochromatic light was realized by a motorized grating monochromator. The lock-in technique was used to acquire the photocurrent at short-circuit condition. Current density-voltage (*J-V*) curves were obtained by a source-measurement unit under dark or a simulated sunlight using a setup with a Xenon lamp (100 mW/cm², calibrated with a KG-5 filtered silicon photodiode).

Figures 1(a) and 1(b) are low and high magnification TEM bright-field images of an axially periodic Zn₂SnO₄ nanowire coated with PbS QDs by PLD deposition, respectively. It can be seen that the PbS QDs were deposited on the nanowire surface when a laser fluence of 12.6 J/cm² was used. The deposition time was 3 min, much shorter compared to that used for conventional ligand exchange assembly methods. In addition, these PbS QDs were directly coated on the nanowires without any linker molecules, which presented a direct, clean interface. EDS data are shown in Figure 1(c), confirming that the material deposited on the nanowire surface was PbS. Figure 1(d) is a high-resolution TEM image

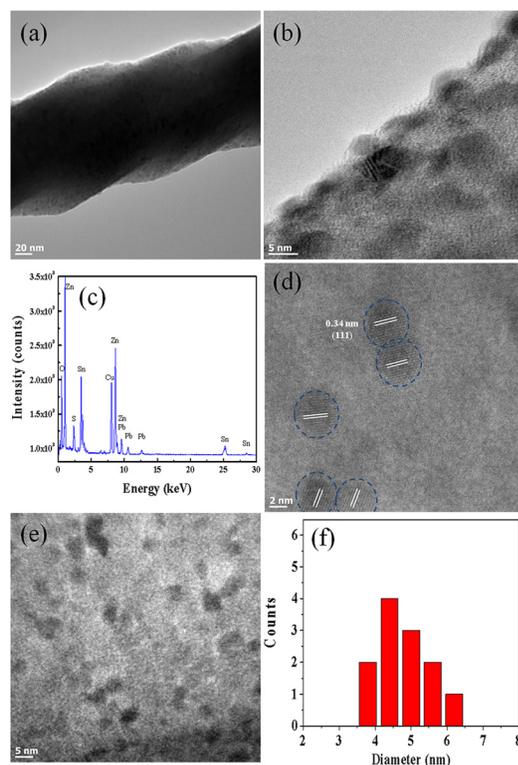


FIG. 1. (a) and (b) are low and high magnification TEM images of a Zn₂SnO₄ nanowire coated with PbS QDs via PLD deposition. (c) EDS spectrum of Zn₂SnO₄ nanowires coated with PbS QDs. (d) High-resolution TEM image of PbS QDs. The (111) crystal planes of the PbS QDs are indicated. (e) and (f) are the TEM image and corresponding size distribution of PbS QDs on a carbon grid.

that shows the (111) lattice planes of the PbS QDs. In order to study the size distribution of PLD-coated QDs, TEM images of the QDs deposited on amorphous carbon grids were taken, and Figure 1(e) shows one of them. Figure 1(f) shows the QD size distribution, and from this statistical analysis, it was concluded that the PbS QDs had a mean diameter of ~4.5 nm. The deposition of PbS QDs on Zn₂SnO₄ nanowires most likely followed the Volmer-Weber (island) growth mechanism due to the large lattice mismatch and the low wettability between the coating material (PbS) and the substrate (Zn₂SnO₄).¹¹ In this growth process, the formation of three-dimensional adatom islands can be attributed to the adatom-adatom interactions since the interaction between the adatoms and the substrate surface is weak.¹¹

The surface of the PbS quantum dots prepared by PLD could be passivated by ligands through the ligand attachment processing described previously. Figure 2 shows the FTIR spectroscopy measurement data that confirmed this surface ligand modification. For bare samples without ligand modification, no vibrational mode was observed in the wavenumber range of 700 and 4000 cm⁻¹. However, for the samples with ligands attached (oleic acid, oleylamine, and MPA), the surface passivants exhibited IR vibrations as shown in Figure 2. In Figure 2(a), the C=O stretching peak at 1710 cm⁻¹ was obvious in the IR spectrum of oleic acid in solution,¹² but it

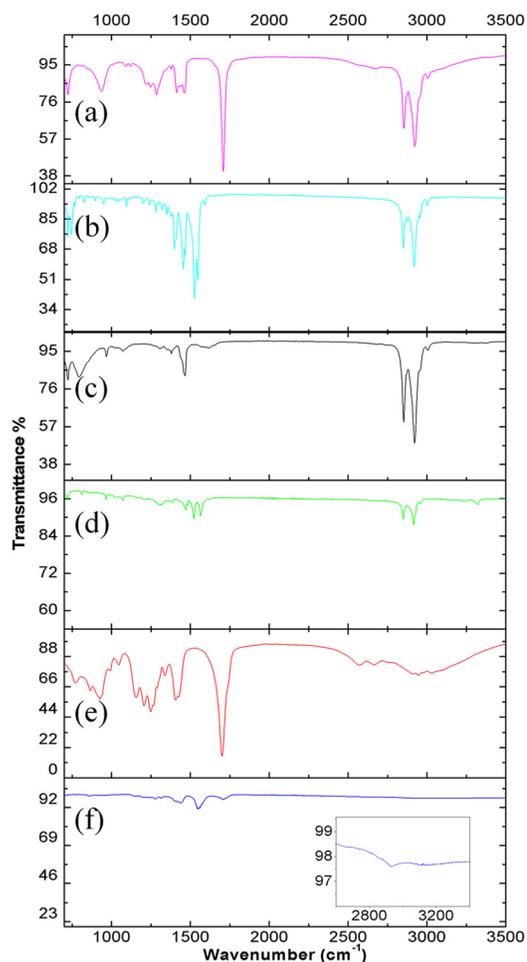


FIG. 2. FTIR data of the ligands in solution and after coating on PbS QDs. (a) and (b) oleic acid; (c) and (d) oleylamine; (e) and (f) MPA. The inset in (f) is the magnified plot in the wavenumber range of 2600–3400 cm⁻¹.

disappeared in the spectrum of the capped QDs shown in Figure 2(b), indicating that the capping ligand was attached to the PbS QD surface not by physical adsorption but instead through a complete chemisorption process.¹² The presence of oleic acid on the surface of PbS QDs was evidenced by the IR bands at 2850 and 2920 cm^{-1} in Figure 2(b) as compared with the peaks at 2853 and 2922 cm^{-1} for pure oleic acid shown in Figure 2(a), which correspond to the symmetric and asymmetric C-H stretching modes of the CH_2 groups of oleic acid, respectively.¹² This blue shift of the symmetric and asymmetric C-H stretching modes of the CH_2 groups after oleic acid adsorption on QD surface was caused by the binding of the CH_2 groups to the PbS surface.¹² Similar FTIR results were also obtained for oleylamine and MPA capped samples, which were shown in Figures 2(c)–2(f). The peaks that were associated with the symmetric and asymmetric C-H stretching modes of the CH_2 groups in oleylamine were also observed in the IR spectrum of the PbS QDs capped with this ligand, revealing that oleylamine was bound to the PbS surface [Figures 2(c) and 2(d)].¹² However, for MPA modified PbS QDs, as shown in Figure 2(f) and inset, these two peaks were not as obvious as the ones discussed above, indicating that only a very small amount of MPA molecules were bound to the PbS surface, which was manifested by the low peak intensities in the FTIR spectrum.

Figures 3(a) and 3(b) show the IPCE spectra, in different wavelength ranges, of Zn_2SnO_4 nanowires coated with PbS QDs with and without the capping ligands. All of the IPCE spectra showed monotonic increase as the incident photon energy was increased from 1400 to 400 nm, without exhibiting distinctive excitonic feature at ~ 1200 nm that is associated

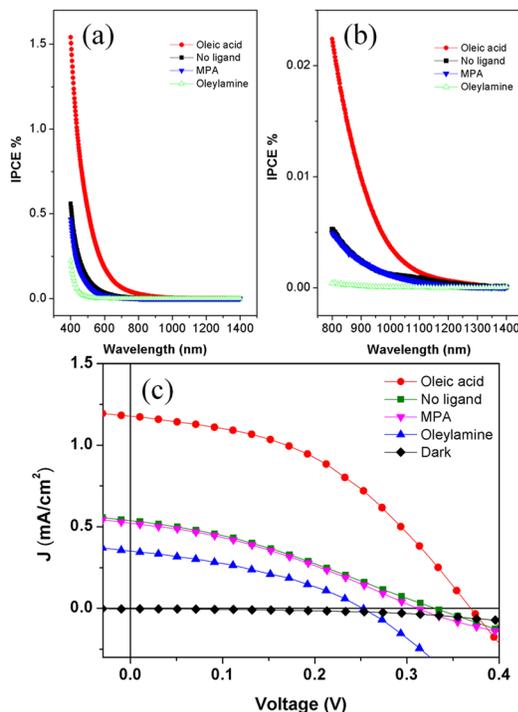


FIG. 3. (a) IPCE measurement results of PbS QD-coated Zn_2SnO_4 nanowire photoanodes with and without ligand modification. (b) Same IPCE data in the wavelength range of 800–1400 nm. (c) J - V characteristics of the QDSSCs with and without ligand treatment. A typical J - V in dark is also shown.

with the light absorption by 4.5 nm PbS QDs.¹³ The absence of the PbS excitonic features in the IPCE spectra could be explained by the broad size distribution of the PLD deposited QDs,⁸ which has also been widely observed in QDSSCs prepared by, for example, the successive ionic layer adsorption and reaction approach and is not critical to the performance of QDSSCs.^{14–16} It can be seen from Figure 3(a) that after ligand attachment the samples showed different behavior compared to the device without undergoing the surface modification. The sample treated with oleic acid exhibited the highest IPCE efficiency, while the sample treated with MPA did not show improvement and the one treated with oleylamine instead showed significantly decreased IPCE. It was reported that oleic acid has a strong binding capability, which could lead to more oleic acid attached onto the QD surface and significantly decrease the surface defect states that could trap the photo-generated electrons.^{17,18} This explains the improved IPCE of the sample treated with oleic acid, which was also confirmed by the strong intensities of the characteristic FTIR peaks compared to those treated with oleylamine or MPA, as shown in Figure 2. After the sample was treated with oleylamine, the IPCE decreased substantially, which could be attributed to the oleylamine etching effect. For example, it has been reported that high concentration of *n*-butylamine could cause the etching of CdSe QDs and lead to the quenching of their photoluminescence behavior.¹⁹ Ligand etching effect was also reported for dodecylamine capped gold nanoparticles.²⁰ Therefore, we anticipate that the excess oleylamine in the dipping solution could cause the etching of PbS QDs during the ligand attachment process, which subsequently leads to the decreased IPCE. For the MPA capped sample, from the FTIR data shown in Figure 2, it could be concluded that there was only limited amount of MPA attached to the surface of PbS QDs, which explains the similar IPCE level between this sample and the one without ligand modification. The thiol group of MPA typically shows a strong binding capability during ligand exchange processing in base environment.²¹ However, in this study, pure, weak acidic MPA solution was used, which could lower its binding capability and cause a reduced MPA attachment. It has been reported that the thiol-QD bond is not stable for MPA capped QDs, which could be another reason for the low MPA coating observed here.^{22–24} In addition, the low IPCE could be related to the ligand's weak ability to passivate the QDs' surface states. QDSSCs based on PLD-coated PbS QDs and different capping ligands were also fabricated, and Figure 3(c) shows the J - V measurement results. Same trend was observed for the solar cell performance, which could be explained by the reasons discussed above. In particular, the sample treated with oleic acid exhibited a substantially improved performance, with both short-circuit current and power conversion efficiency being almost doubled. However, even after ligand modification, the device efficiency is still low ($\sim 0.2\%$), which could be due to the low coverage of PbS QDs on the nanowires and other issues, and efforts are being undertaken to further improve the solar cell performance.

In summary, in this work, using the pulsed laser deposition technique, PbS QDs were deposited on ternary metal oxide nanowires for photovoltaic applications. TEM examinations have been carried out to study the morphology and size distribution of the deposited QDs. Different ligands

including oleic acid, oleylamine, and MPA were used to modify the surface defects of the PbS QDs, and the sample treated with oleic acid exhibited a significantly improved performance. Further studies are needed in order to obtain a better understanding of the issues that limit the performance of these photovoltaic structures, which include QD coverage, electrolyte etching effect, etc.

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