COMPOSITES OF PbSe QUANTUM DOTS AND VERTICALLY ALIGNED TiO_2 NANORODS FOR NEXT GENERATION SOLAR CELLS

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ABSTRACT
A laser assisted spray (LAS) process was used to deposit surfactant-free PbSe quantum dots (QD) with diameters in the range of 2-3 nm onto vertically aligned TiO_2 nanorods that were fabricated on a quartz substrate by a hydrothermal process. Conductivity measurements demonstrated the enhanced carrier transport in surfactant-free PbSe QD films. Single crystal nature of the PbSe QDs and TiO_2 nanorods were observed via Transmission Electron Microscopy (TEM). LAS process has been used to fabricate the PEDOT (polymer)/PbSe QD/TiO_2 nanorod composite solar cell structures.

INTRODUCTION
Absorption of a UV photon with energy much higher than the band gap energy by an electron in the valance band excites it to a higher energy level in the conduction band, followed by thermal relaxation to the conduction band edge[1]. This one e-h pair per photon limitation is one of the major factors incorporated into determining the Shockley-Queisser theoretical efficiency limit in p-n junction solar cells. Possibility of suppressing the thermal relaxation in quantum confined systems such as quantum dots (QD) and imparting the excess energy of UV photons via an impact ionization process to generate additional e-h pairs (excitons) has been demonstrated in recent years[2]. Dissociation of excitons requires them to overcome the binding energy between the e-h pair, which is of the order of 0.01 eV. When embedded in a host material, dissociation via transfer of one or both charge types into the host material is possible based on the band alignment at the host/QD interfaces if QDs make a close contact with the host material. The advantage of using the LAS process for depositing PbSe QD on a substrate is that the surfactants are removed prior to deposition and thus QDs make close contact with the host material. Particular relevance to our research is the successful charge injection from PbS into a TiO_2 structures. It has been shown that excitons in quantum dots of PbSe that are under 2.5 nm in diameter can be dissociated at the QD-TiO_2 interface by transferring electrons to TiO_2. In this paper we present the structural characteristics and transport properties of the PbSe QD films, TiO_2 nanorods and PbSe QD-TiO_2 nanorod composite structures fabricated by the LAS process.

EXPERIMENTAL
Preparation of TiO_2 nanorods:

Titanium dioxide nanorods were synthesized via a hydrothermal process which utilizes an acid digestion bomb heated in an oil bath to a temperature of $160\,^{o}\mathrm{C}$. The nanorods are formed from nucleation sites on fluorine-doped Tin Oxide (FTO) coated glass substrate. It is the lattice mismatch between the FTO lattice and the nucleation sites of the TiO_2 that propagates the rod growth, each of which terminates upon reaching the first adjacent rod. XRD characterization showed that TiO_2 is formed in the rutile structure.

Deposition of PbSe QDs.

The growth process consists of two steps. In the first step a colloidal solution containing 2-3 nm PbSe nanoparticles was formed by a solvothermal technique[3]. This method offers the added advantage of using noncoordinating solvents. As-grown particles are coated with oleic acid that prevents agglomeration. The precipitated PbSe nanocrystals were re-dispersed in hexane. In the second step the hexane solution containing the PbSe nanoparticles was used as a precursor in the laser-assisted spray process. A schematic of the LAS apparatus is shown in Fig. 1. The aerosol produced by a nebulizer was carried by the SF_6 gas into the growth chamber through a nozzle that contained an inert gas at an ambient pressure of 200 Torr. The SF_6 gas has a high absorption coefficient at the 10.9μm wavelength of a CO_2 laser. A continuous wave (CW) 14W CO_2 laser beam focused at the nozzle exit increased the temperature of the aerosol-gas mixture. The high temperature causes the solvent and the surfactants to evaporate while surfactant-free PbSe nanoparticles were deposited on a substrate.

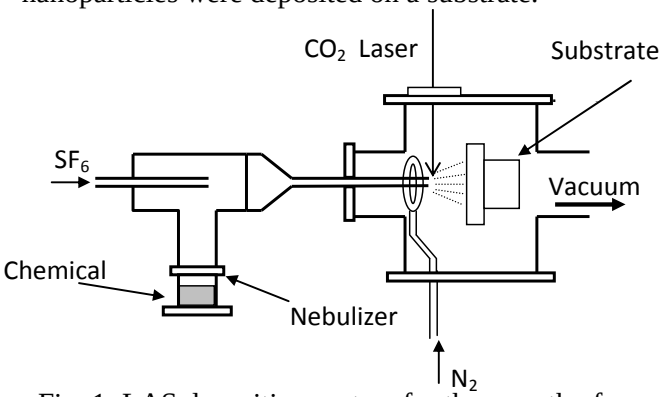


Fig. 1: LAS deposition system for the growth of surfactant-free PbSe QD films.

RESULTS AND DISCUSSION

In comparison to nanoparticle coatings prepared with caped PbSe QDs where the particles are separated by a 2-3 nm gap due to surfactants, the QDs in films prepared by the LAS process are uniformly distributed and are in contact with each other. The uniformity of the distribution of QDs and the single crystal nature of the particles are shown in Fig. 2.

The absence of surfactants and the ensuing proximity of the particles enhanced the transport properties of the film by promoting carrier hopping between adjacent QDs. Comparison of the I-V characteristics of PbSe QDs with and without the surfactants is presented in Fig. 3. The power law dependence indicates a 2D percolation transport path for these films.

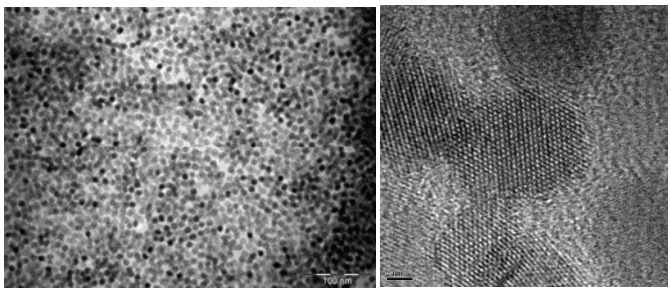


Fig. 2: TEM images of surfactant free PbSe QDs deposited by LAS process.

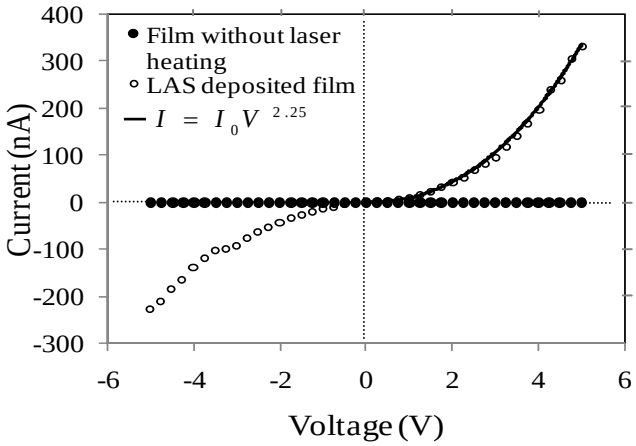


Fig. 3: I-V characteristics of a PbSe QD coating with and without surfactants.

The next step in the process was to deposit PbSe QDs on vertically aligned TiO_2 nanorods. Fig. 4 (a) shows a SEM image of nanorods grown on a FTO conducting film. QDs of PbSe were deposited on nanorod s by the LAS process. Single crystal nature of the TiO_2 nanorod and an attached PbSe QD is shown in Fig. 4 (b). The outline of the QD is indicated by the circle.

Subsequently, a layer of the p-type polymer PEDOT was spin-coated over the QD layer to form the composite device structure shown in Fig. 5. The photocurrent generated by the composite structure was investigated by exposing the device to different light

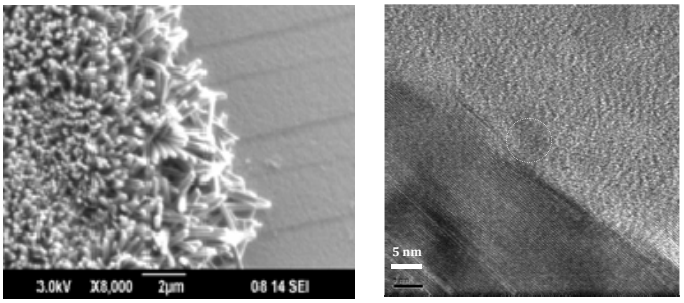
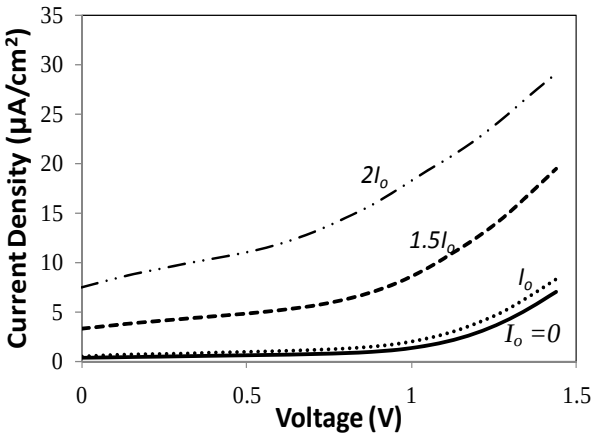


Fig. 4: (a) SEM images of vertically aligned TiO_2 nanotubes and (b) TEM image of a TiO_2-PbSe composite. The circle indicates the position of a QD.



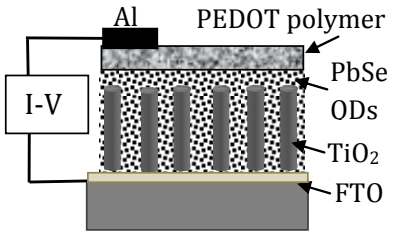


Fig. 5: TiO_2-PbSe QD-polymer composite cell structure and photocurrent at different illumination intensities.

intensities from a white light source. As shown in the graph in Fig. 5 a significant photocurrent was generated by the cell.

CONCLUSION

A laser assisted spray process was used to deposit PbSe QDs on crystalline TiO_2 nanorods grown by a hydrothermal process. Absence of surfactants enhanced exciton dissociation and charge transport. A significant photocurrent was produced by the composite TiO_2-QD-polymer structures.

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