CHARGE GENERATION AND SELECTIVE SEPARATION AT PbS-QUANTUM DOT / METAL OXIDE INTERFACES

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ABSTRACT: Charge separation and transfer at the interface between layers of oleic acid capped PbS quantum dots (QDs) and Titanium and Indium Tin oxide (TiO_2 and ITO) films were investigated by surface photovoltage (SPV) measurements. Photoluminescence (PL) measurements were performed in order to check for excitonic transitions and determine the QD band gaps. The QDs diameter of 4.2 nm and 5.0 nm were estimated by using the PL band gaps and the theoretical equation derived by Wang et al. [J. Chem. Phys. 87 (1987) 7315]. The SPV spectra of the PbS-QDs/TiO_2 system reveal a positive charge on the PbS film surface and show three distinguished regions which demonstrate: (i) the charge separation across QDs, (ii) the electron-injection from QDs into TiO2 and (iii) the fundamental absorption in TiO_2. The on-set of the electron injection depends on the QD size (QD band gap): it shifts to lower photon energies for lower QD dimensions (for higher QD band gaps). Thus, a better conduction band alignment is achieved in the latter case. In contrast to PbS-QDs/TiO_2, the SPV spectra of the PbS-QDs/ITO structure reveal the negative charge on PbS surface. Moreover, the charge transfer at this interface is not observed. Instead, the SPV peculiarities in the photon energy range 1.4–3.0 eV point out to trapped holes on the ITO surface states.
Keywords: PbS, ITO, TiO_2, Quantum Dots, Interfaces, Photoluminescence, Surface photovoltage.

1 INTRODUCTION

The preparation of quantum dots (QDs) provides the possibility to tailor several materials properties to match the desired application needs. Besides the increase of the surface area of the material, a very important change in material properties is the fine adjustment of the band gap width for semiconducting materials. Due to the quantum confinement effect, particles in the nanometre range show a strong increase in band gap energy with a decrease of particle size [1]. For optical applications, this allows to adjust the absorption edge energy which has to be surpassed to achieve absorption and exciton generation in the material.

As the band gap increases, also the energetic positions of the valence and conduction bands will change. This effect can be used to achieve better band alignment to other materials. By band gap engineering potential barriers at interfaces could be tuned. This in turn will influence the charge carrier transport.

In this work PbS particles of different sizes were prepared and deposited on TiO_2 and ITO surfaces. We demonstrate that by adjusting the particle size and therefore the band gap energy and position of the bands, the photoinduced charge transfer can be strongly influenced.

2 PbS NANOPARTICLE PREPARATION AND DEPOSITION

2.1 Synthesis and nanoparticle size

A mixture of PbO and oleic acid (OA) was heated up to 150°C for one hour to allow for a complete reaction and removal of the water generated by the reaction. Subsequently, the mixture was cooled down to the reaction temperature between 30°C and 120°C. The temperature of the solution is the parameter used to influence the size of the grown nanoparticles. By the injection of the bis(trimethylsilyl)sulphur ((TMS)2S) solution in octadecene-1 (ODE) under intense stirring, the reaction to form PbS nanoparticles was started. The reaction was stopped after 10 s by cooling down the mixture by ice water. The PbS nanoparticles were dispersed by adding chloroform to the reaction product. The resulting dispersion was purified by a precipitation of particles with methanol and a re-dispersion in chloroform for 4 times. More details about the preparation procedure can be found in Ref. 2. The end product of this procedure was a stable dispersion of PbS nanoparticles. The size of nanoparticles depends on the reaction temperature where higher temperatures result in larger particles. In this work PbS particles were prepared at temperatures of 55°C and 100°C labelled hereafter PbS-55 and PbS-100, respectively.

The resulting particle sizes were estimated by means of photoluminescence (PL) measurements. The PL measurements of the PbS-55 and PbS-100 dispersions show band gap energies of 1.28 eV and 1.12 eV, respectively (see figure 1), while single crystalline bulk PbS shows a band gap of 0.41 eV.

By application of the theoretical equation derived by Wang *et al.* [3]

$$\Delta E = \frac{\hbar^2 \pi^2}{2R^2}\left(\frac{1}{m_e}+\frac{1}{m_h}\right) - \frac{1.8e^2}{\varepsilon R} + polarisation\ \ term, \quad (1)$$

where R is the particle radius, ε is the dielectric constant, m_e and m_h are the effective masses of the electron and hole, respectively, the size of the particles can be estimated. As the equation (1) overestimates the band enlargement related to the quantum confinement term, the results were also compared to the fit of experimental data by the hyperbolic band model. By this, the diameter of the grown particles were identified to be 4.2 nm for PbS-55 and 5.0 nm for PbS-100.

2.2 Layer deposition

PbS nanoparticles were deposited on TiO_2- and ITO-coated glass substrates by dipping the substrates into dispersion. For the dipping process a robot was used to

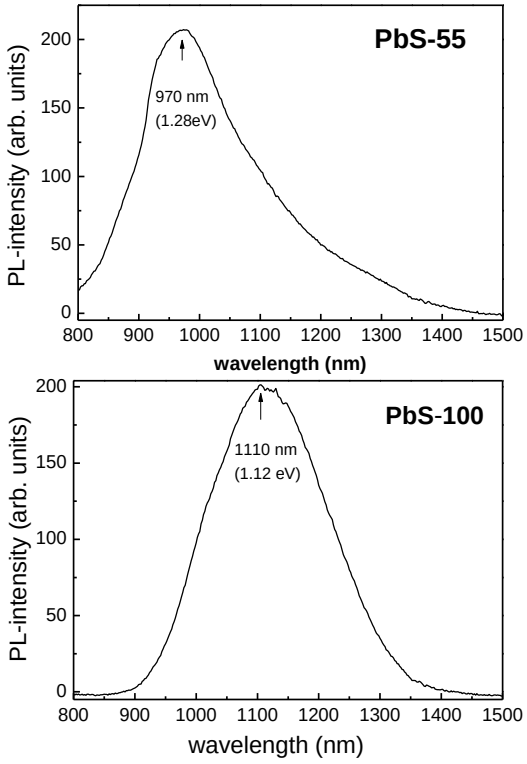

Figure 1: PL spectra of samples PbS-55 and PbS-100.

achieve a constant dipping speed. The substrates were vertically dipped into the PbS dispersion with a speed of 1 mm/s. The substrates were pulled out with the same speed after a waiting time of 5 s. Finally, the as-deposited PbS nanoparticle layers were dried at 100°C for 5 minutes to remove the dispersion solvent. The whole process of dipping and drying was performed under a nitrogen atmosphere to prevent the particles from being oxidised.

3 SURFACE PHOTOVOLTAGE MEASUREMENTS

3.1 Surface photovoltage setup

Surface photovoltage (SPV) measurements were carried out by the fixed capacitor setup in figure 2. In this setup, the sample is illuminated by chopped light of varying wavelengths through a quartz electrode and a slice of mica. The quartz electrode and the sample form the capacitor plates separated by the mica as the dielectric isolating layer. The resulting voltage signal between the quartz electrode and the sample is measured by a lock-in amplifier, resulting in an in-phase signal (x) and a 90° phase-shifted signal (y). The x:y ratio characterises the limiting recombination processes; the larger the x:y ratio is the faster the processes are and vice versa. The x-signal shows the response of the SPV during the illumination phase, while the y-signal is related to delayed SPV reply during the dark phase.

3.2 SPV results and discussion

In figure 3(top panel) the SPV spectra of the PbS-QDs/TiO_2 system are shown. The SPV signal shows three maxima at different photon energies of the incident light which can be attributed to three different electronic processes in this system. For all processes, the in-phase signal is positive indicating that holes move to the surface

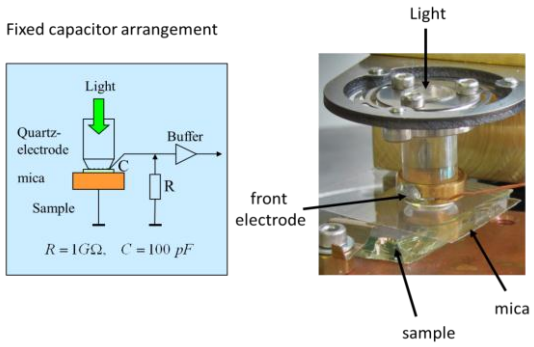

Figure 2: SPV setup.

of the sample (figure 3(bottom panel)). In the sub band gap region (1) both particle sizes show charge release effects from surface defect states, resulting in a positively charged surface. Due to the band sloping the electrons in the conduction band move away from surface and therefore the fraction of recombined holes on surface is reduced.

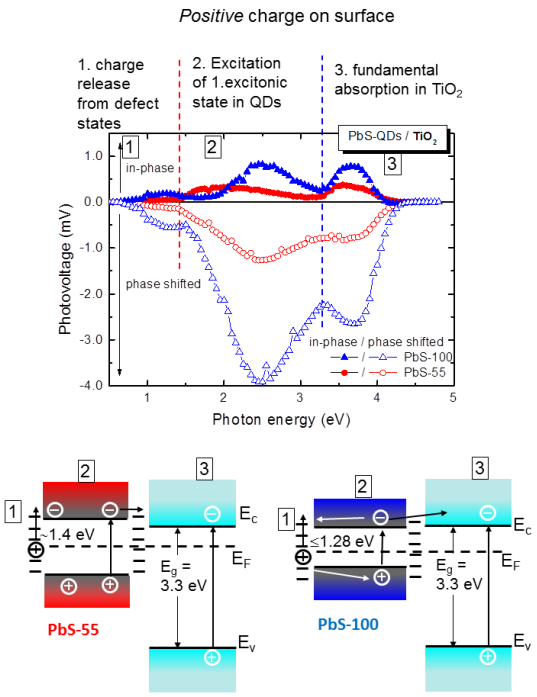

Figure 3: Top panel: SPV spectra of the PbS-QDs/TiO_2 system. Bottom panel: Energetic band diagram of the PbS-QDs/TiO_2 system.

The onset of the excitation of the first excitonic states within the PbS-QDs (region 2, figure 3(top panel)) occurs at 1.4 eV. The signal is related to the strong response due to the excitation of the first excitonic state in QDs. However, for the PbS-100 particles, the in-phase signal starts to rise only at higher energy of about 2.0 eV, while the phase-shifted signal starts to rise much earlier. As there cannot be a phase-shifted SPV signal without an in-phase signal, we deduct a fast overlaying process with opposite sign (opposite direction of charge separation) between 1.4 eV and 2.0 eV, in that the generated charge carriers recombine along defect states at the surface. In our proposed band diagram in figure 3(bottom panel) we can explain this effect as a recombination at surface

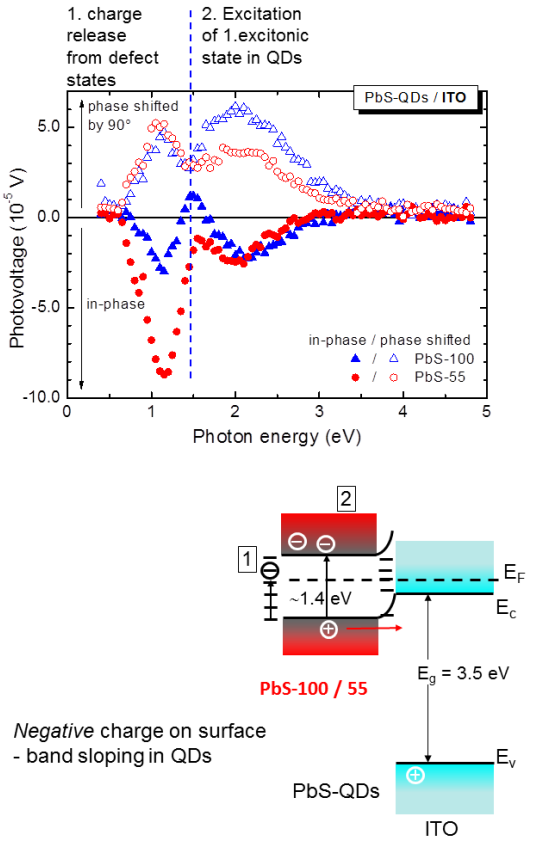

Figure 4: Top panel: SPV spectra of the PbS-QDs/ITO system. Bottom panel: Energetic band diagram of the PbS-QDs/ITO system.

defects which is intensified by the barrier between the excitonic states of the PbS-QDs and the conduction band of TiO_2. This barrier hinders the charge transfer to the TiO_2. For the smaller PbS-55 particles, we do not observe the delayed onset of the in-phase signal for the first excitonic transition. This is explained with the wider band gap of the smaller particles, resulting in a better band alignment removing the barrier and therefore the high recombination probability at interface states.

At higher energies above the bang gap of the TiO_2, fundamental absorption in TiO_2 is observed, resulting in holes moving to the interface between the two materials and therefore generating a positive x-signal.

The SPV in-phase signal for the PbS-ITO system in figure 4(top panel) shows a negative value indicating electrons moving to the surface of the sample. Due to the high doping level of ITO and therefore of a high position of the Fermi level, we expect sloping of the PbS-QD bands down to the surface. This results in a movement of the generated electrons to the sample surface (figure 3(bottom panel)). This holds true for electrons released from the defect states as well as for the electrons generated by excitation of the first excitonic states of the PbS-QDs. In general, the effects in this material system are much smaller than in the PbS/TiO_2 system. This is related to the fact that the PbS-QD/ITO interface forms a recombination contact.

When comparing the data obtained from both PL and SPV measurements, a slight difference of about 0.10-0.15 eV for the determined band gap energies can be observed. This could be related to shallow defect states.

4 CONCLUSION

- It was shown that by varying the reaction temperature for the PbS nanoparticle synthesis the size of the resulting particles can be fine tuned.
- The PbS nanoparticles deposited on a TiO_2 surface show a strong positive in phase SPV signal, displaying a transfer of electrons away from the surface and a charge transfer to the TiO_2 material. It was shown that for PbS nanoparticles smaller than 4.2 nm the charge transfer to the TiO_2 was clearly improved which was attributed to a better band alignment resulting in the removal of an energy barrier for the electron transfer.
- For the PbS nanoparticles on the ITO substrate, only a small negative in phase SPV signal was measured explained by the band setup of this material system. No charge transfer to the ITO could be observed.

5 REFERENCES

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