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Colloidal Synthesis of Lead Oxide Nanocrystals and their Optoelectronic Properties

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Experimental Methods

Chemicals: Lead (II) acetate tryhydrate, oleic acid 90% grade, octadecene 90% technical grade and anhydrous methanol, anhydrous acetonitrile and anhydrous ethyl acetate were purchased from Sigma Aldrich. Oleylamine 70% CG was purchased from Fisher Scientific.

Synthesis of PbO NCs: For this investigation, a 5mmol, 1:1 ratio of oleic acid and lead acetate trihydrate ($Pb(CH_3COO)_2(H_2O)_3$) crystals were placed in a three neck flask with 3ml of octadecene. The reagents were degassed under a nitrogen flow and then heated to 150ºC for 1hour whilst being continuously stirred, into this 5mmol of oleylamine was injected.. After mixing the reagents thoroughly, the temperature was rapidly increased to 190ºC at which point the nitrogen gas purge was halted and replaced with high purity oxygen gas. The colour change from, clear to yellow, witnessed upon the introduction of oxygen signified the start of the nucleation phase. This temperature was maintained for 5 minutes after which the solution was rapidly cooled in an ice bath to a temperature below which no noticeable nucleation had occurred (150ºC). This temperature was then maintained for 1hour to allow for sufficient ageing of the nanoparticles. The nanocrystals produced with this method had a mean diameter of 7nm (±0.5nm) with a 0.8nm deviation from this mean value.

Post synthesis processing of PbO NCs: The product solution was transferred to a 50ml plastic centrifuge tube. Ethyl-acetate (20ml) was then added in order to precipitate any of the un-reacted reagents out of the solution. The cloudy solution that formed was centrifuged at 4000rpm for 2 minutes to separate the organic waste products from the solution. The PbO NCs were then precipitated from the reaction solution by adding 40ml of a premade 3:1 volume ratio mixture of ethyl aceate: methanol followed by a 10 minute centrifuge at 4000rpm. The supernatant solution was then removed and the yellow/brown NC precipitate was either redissolved in hexane for device fabrication or was further cleaned using a 2:1 volume ratio mixture of Ethyl acetate: Acetonitrile (denoted as EAA). This EAA solution was used to further clean the PbO NCs after the first cleaning step and before redissolving the NCs in hexane. In this second cleaning step, the EAA solution was added in the centrifuge tube, dissolving residues of oleic acid, oleylamine from the tube's walls and the precipitate though without redissolving the PbO NCs of the precipitate. To enhance this effect when adding the EAA solution the tube was gently shaken then all solution was removed. This procedure was repeated 2 times before final drying of the NCs and re-dispersing in hexane.

TEM and XRD analysis: TEM samples were prepared by dipping a holeycarbon copper grid in hexane/NC light solutions, then leaving them dry for 1 minute. Low magnification TEM and HREM were performed with a 4000HR JEOL microscope equipped with a Gatan camera.

XRD samples were prepared by grinding dried lead oxide NCs in a pestle and mortar to form fine powders that were then compressed on to 25x25mm silicon wafers; chosen for their reduced background signature, enabling the detection of the characteristic peaks of the nanocrystals.

Device fabrication: For device fabrication 14mmx12mm ITO/glass substrates, with a nominal ITO thickness of 120-160nm, were acquired from Delta Technologies. Black plastic tape was used to mask a 2mm wide ITO strip along the length of each substrate. An etchant solution, with a 25:15:2 mixture, of H_2O:HCl:HNO_3 was heated to 60^oC into which the masked substrates were suspended for 7minutes. The substrates were subsequently cleaned in ultrasonic baths of deionised water, isopropanol and acetone for 5 minutes each at 70^oC. The substrates were then placed in a Gallenkamp vacuum oven overnight at 40° to ensure the removal of any moisture. Finally, the substrates were oxygen plasma treated for 10 seconds, using a Nanotech PLASMOD plasma chamber, to remove any remaining organic material[85].

Thin films of PbO NCs were fabricated with the dip-coating method described elsewhere[2] using 0.007gr/ml NC/hexane solutions and a second 0.01M ethyldithiol in acetonitrile solution. For a 10nm monolayer deposition each ITO/glass substrate was vertically dipped by hand (holding the substrate by its edges) in the NC solution, then was slowly (~0.3cm/sec) retracted out of the solution and left dry for 10sec. The film was subsequently dipped quickly into the EDT solution for 3sec then retracted quickly (~1cm/sec) and left drying for 20sec.

60-100nm thick Al contacts were thermally evaporated on the film at a 0.1nm/sec rate using shadow metallic masks. All NC film fabrication took place in a fumehood. Aluminium electrode deposition took place in an evaporator attached to a nitrogen glovebox. The top electrodes were 1.5mm wide stripes across the short substrate axis. Three $0.03cm^2$ area device pixels at the overlapping spots of the bottom and top stripe electrodes were formed on each substrate.

Device testing: Current-voltage (IV) characteristic measurements were carried out using an 8 point-probe measuring box positioned within a hermetically sealed device holder connected to a Keithley 2400 Sourcemeter via an 8-way junction box. A voltage loop was measured in the dark and under applied 1-sun test conditions (100 ± 5 mW cm-2) white light to measure the open circuit voltage (Voc) and short circuit current (ISC) of each 0.03cm2 cell. Light intensity was adjusted using a Thorlabs S210A - Thermopile Sensor for optical power measurements.

Table 1. XRD Data for PbO Nanocrystals:

d-spacing [Å]	Pos. [°2Th.]	Rel. Int. [%]	Plane
3.06916	29.092	69.75	111
2.97684	30.315	50.07	020
2.77059	32.607	27.68	200
2.39526	37.818	33.45	210
2.28933	39.528	4.21	121
2.01855	45.116	36.46	220
1.97887	46.209	8.9	030
1.85939	49.212	36.75	022
1.80255	50.765	45.34	202
1.73042	53.078	70.85	131
1.64793	56.029	52.68	311
1.60502	57.716	8.13	230
1.54184	60.285	48.95	222
1.48148	63.013	56.32	040
1.41133	66.335	5.2	312
1.36813	68.825	19.4	141
1.33042	71.092	9.71	232
1.30282	72.87	18.15	240
1.29224	73.396	26.03	331
1.2566	75.941	25.21	042
1.20741	79.631	32.29	133
1.19251	80.842	22.41	004
1.17774	82.011	27.7	313
1.14332	85.11	22.27	114
1.12291	86.907	33.89	151
1.10518	88.694	35.66	422

Thin film thickness and roughness data:

A Veeco DEKTAK 6M stylus profiler was used to determine the thickness and roughness of each thin film device. The average roughness (Ra) values for each device were calculated using the Veeco 32m profiler software. To measure surface thickness, a strip of thin film was removed across the width of the device using a sharpened wooden cotton-bud stick. Three separate 8µm profiles were taken across this strip to determine the step height of the thin film. These values were then averaged to arrive at a final value. All measurements were taken along the ITO electrode of each device in order to determine a more accurate impression of the physical characteristics of the active cell region. The inherent error in the profiling apparatus was too small (±1A) to be displayed on the graphs below. However, the roughness of the film at any given thickness greatly affected each thickness measurement and so both sets of data have been plotted together, for each device.

Figure 1 highlights the approximately linear increase in thickness and roughness with every dip coat step, exhibited by the 1,2-ethanedithiol substituted PbO thin film devices; with an increase in thickness of ~26nm/dc.

By measuring the change in thickness and roughness with changing 1,2-ethanedithiol concentration it can be seen from Figure 2 that an increase in thickness of approximately ~100nm is achieved for every additional 200µls of 1,2-ethanedithiol added to the dip coat solution. This would suggest that exposure to a more concentrated 1,2-ethanedithiol solution only increases the volume of 1,2-ethanedithiol deposited on the film.

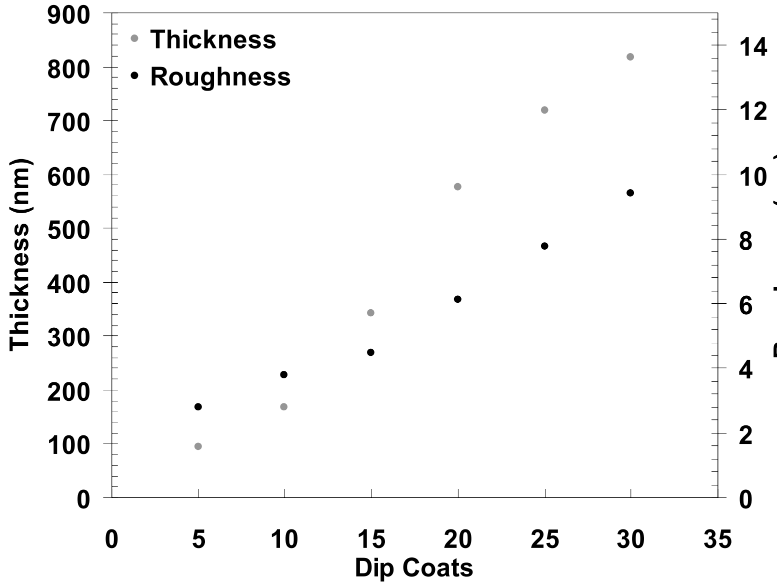

Figure 1: DEKTAK analysis of the change in thickness and roughness, of PbO nanocrystal thin films, with increasing dip coat steps using 0.5M [800µl] 1,2-ethanedithiol.

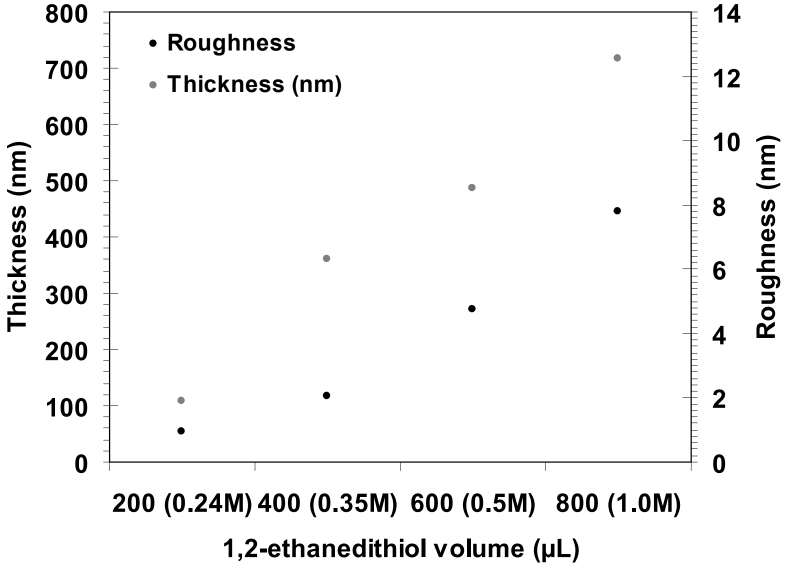

Figure 2: DEKTAK analysis of the change in thickness/ roughness of PbO nanocrystal thin films with increasing 1,2-ethanedithiol concentration (1,2-ethanedithiol volume per 20ml solution with acetonitrile- 25 dip coat steps).

The effect of number of dip coats on device efficiency is shown in the table below and shows that at a certain point number of dips does not change efficiency but increases open circuit voltage and decreases fill factor.

Table 2: A summary of the J-V photovoltaic device characteristics as a function of dips.

Dip Coats	**PCE (%)**	**J_{SC} (mAcm^{-2})**	**V_{OC} (V)**	**FF (%)**
10	0.0003	0.00208	0.4021	24
15	0.00047	0.00272	0.7317	19
20	0.00048	0.00299	0.7622	16

[1] G. D. Scholes M.A. Hines, "Colloidal PbS Nanocrystals with Size-Tunable Near-Infrared Emission: Observation of Post-Synthesis Self-Narrowing of the Particle Size Distribution," Advanced Materials **15** (21), 1844-1849 (2003).

[2] Joseph M. Luther, Matt Law, Matthew C. Beard et al., "Schottky Solar Cells Based on Colloidal Nanocrystal Films," Nano Letters **8** (10), 3488-3492 (2008).

[3] National Research laboratories (NREL) Renewable Research Data Centre, http://rredc.nrel.gov/solar/spectra/am1.5/.