Supporting Information

High Performance PbS Quantum Dot Sensitized Solar Cells via Electric Field Assisted in-situ Chemical Deposition on Modulated TiO_2 Nanotube Arrays

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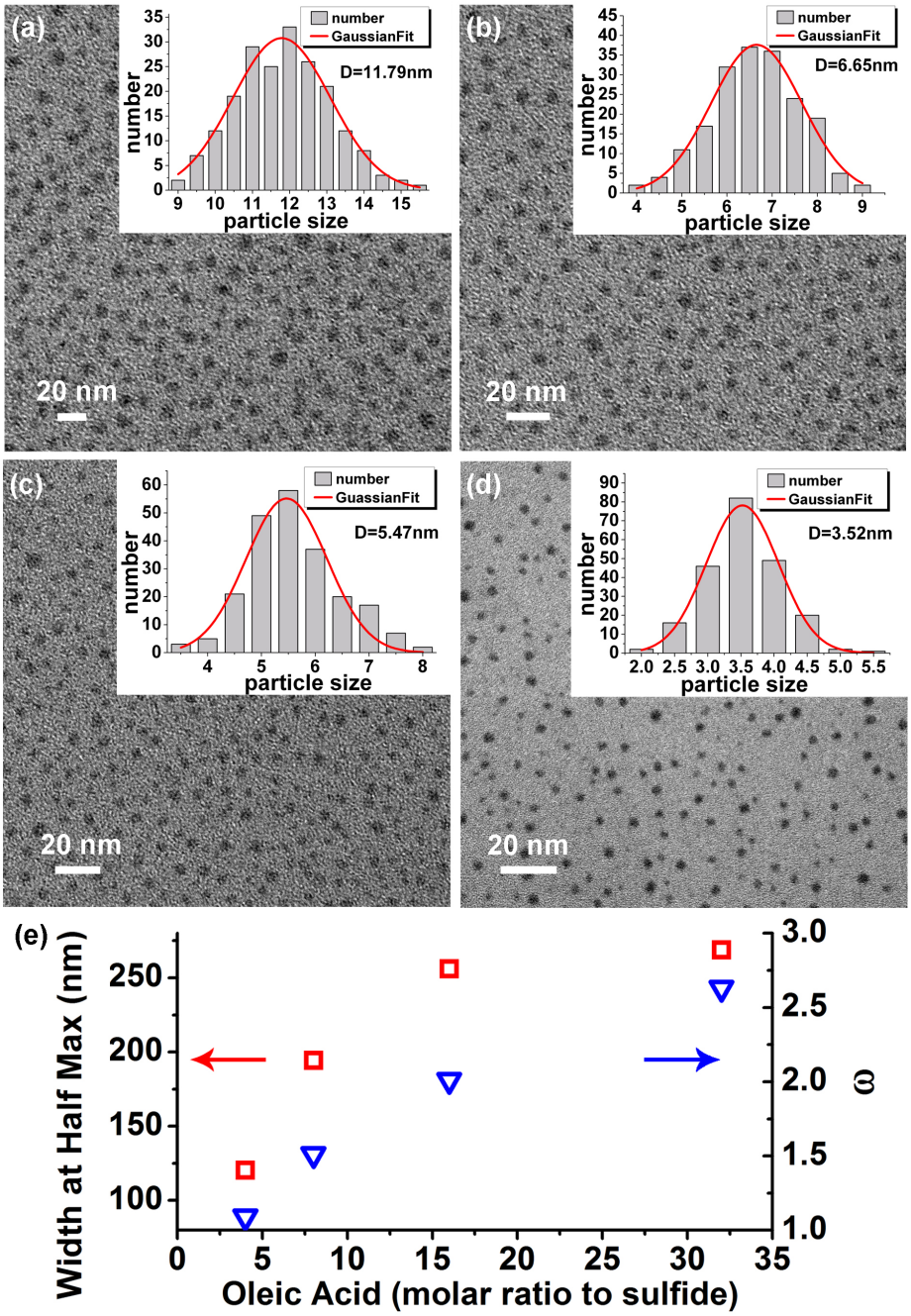

Figure 1S: SEM images of PbS QDs under different growth conditions and the statistics of particle sizes distribution. (a)-(d) Molar ratio of OA/Pb/S is from 32/2/1 to 4/2/1. Insets give the statistic information of corresponding particle size and their Gaussian fitting. (e) Consistent variation of QDs particle size distribution and QDs absorption FWHM ω.

PbS QDs were synthesized via a simple hydrothermal route using PbO in OA as the lead precursor and TMS in ODE as the sulfide precursor (see the experimental section for details). Corresponding low-magnification transmission electron microscopy

(TEM) images are shown in Figure 1S (a-d). Good dispersion can be seen for all of these QDs of various sizes. The size of as-fabricated PbS QDs obey the Gaussian distribution law, indicating that these PbS QDs have a relatively consistent and centralized diameter, as shown in the insets of Figure 1S (a) to (d). By altering the reaction conditions such as solvent molar ratio and temperature, the average particle size can be effectively controlled.

Moreover, the first excitonic absorption peak of QDs has a corresponding full width at half maximum (FWHM), which has been induced by a certain particle size distribution. As shown in Figure 1S (e), we calculated the normalized Gaussian fitting of QD size distribution under four different conditions and the FWHM value ω is 1.09, 1.51, 2.01, and 2.63, respectively. The increase of ω value illustrates that the more OA has been used in manufacturing QDs, the wider QD size distribution would result. Thus this method lays a good optical foundation for the application of PbS QDs, such as a spectrum matching AM1.5 for solar cell.

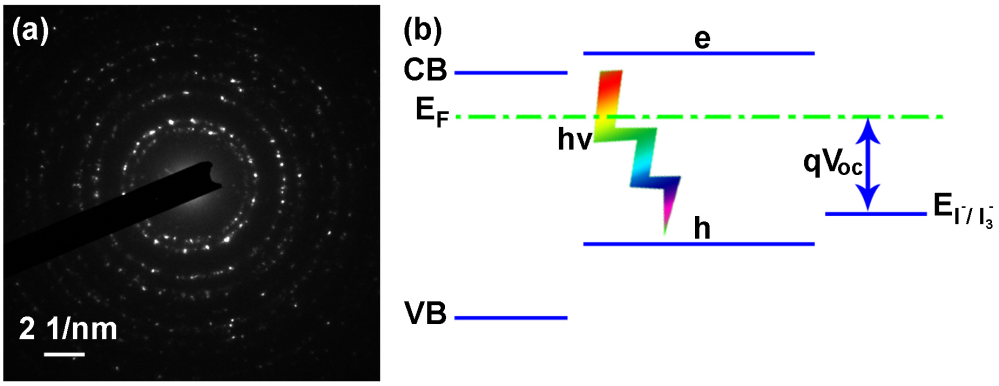

Figure 2S: (a) SAED pattern of PbS QDs. (b) Schematic illustration of energy levels for all parts of QDSSC.

Figure 2S (a) shows the SAED pattern of PbS QDs. The concentric circles illustrate the multiplicity of the crystal orientations, and the discrete diffraction spots indicate the nanocrystalline formation in the as-fabricated QDs. The operation mechanism of the QDSSC is presented in Figure 2S (b), showing energy levels of different parts of the cell, including the TiO_2 photoanode, QDs sensitizer, and iodide/triiodide electrolytes.

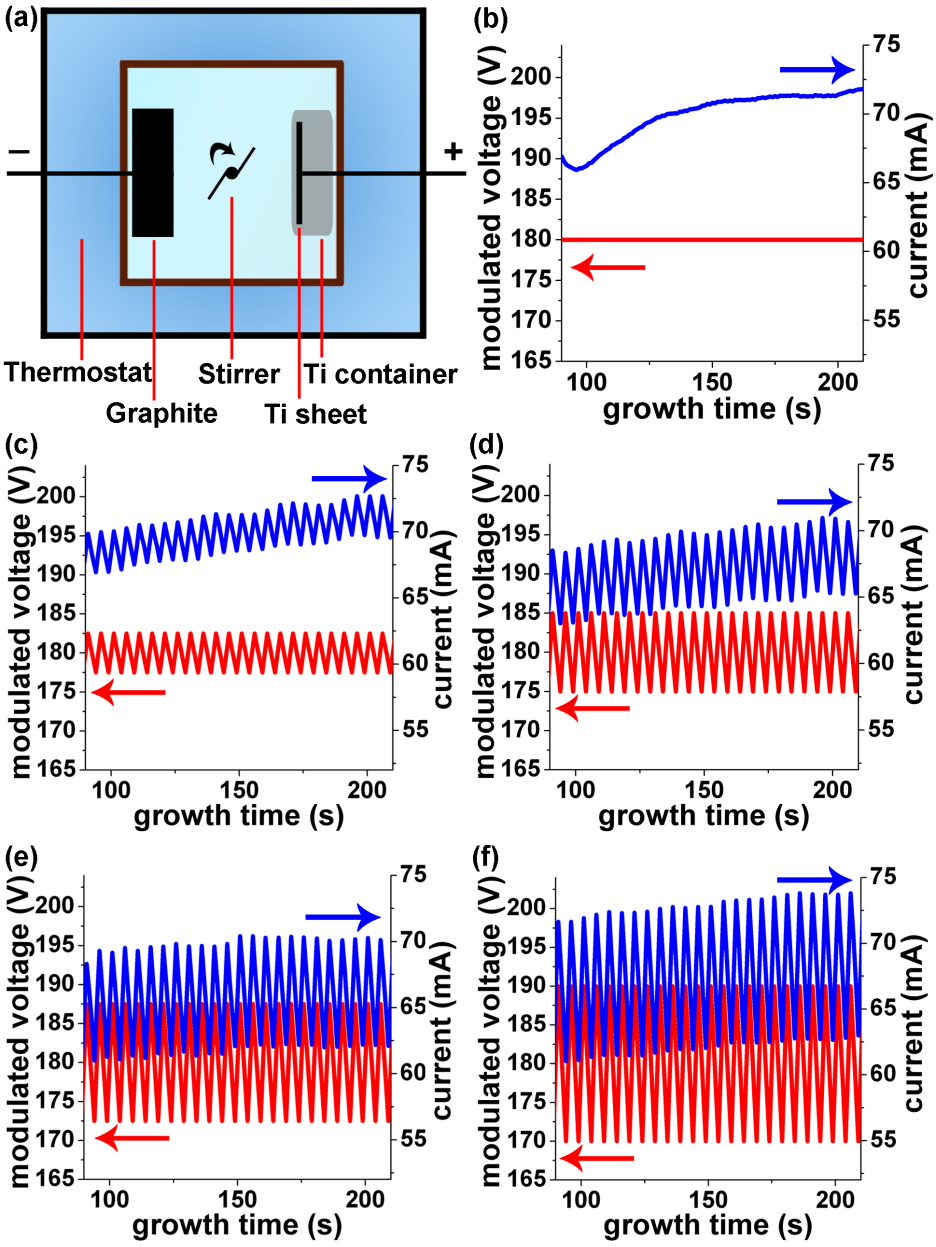

Figure 3S: (a) Schematic description of the experimental setup for modulation process with the top view. (b)-(f) Voltage-time curve with a series of modulation methods and corresponding current-time curve under different modulation amplitudes.

Electrochemical anodization was performed in a two electrode configuration as shown in Figure 3S (a), using a direct current power supply (Agilent 5720) and a Keithley 2400 source meter to measure the resulting current. In order to reach the best modulation effect, a mechanical stirrer was placed between the graphite electrode and

the Ti sheet with the constant stirring rate of 100rpm. The temperature of reaction solution was controlled at 5^{o}C by the thermostat.

Figure 3S (b-f) show the results from the experiments with periodical modulation voltages. Only part of the results (100-200s) were shown in the illustration for the purpose of displaying more clearly, while the whole growth time was 300s. As can be seen in the red curves, the modulation voltage was triangular shaped and its period was set to 5s. From Figure 3S (b) to (f), the modulation amplitude was 180±0V, ±2.5V, ±5.0V, ±7.5V, and ±10.0V, respectively. As shown in the blue curves, the corresponding current curve shows similar oscillation behavior to the modulation voltage.

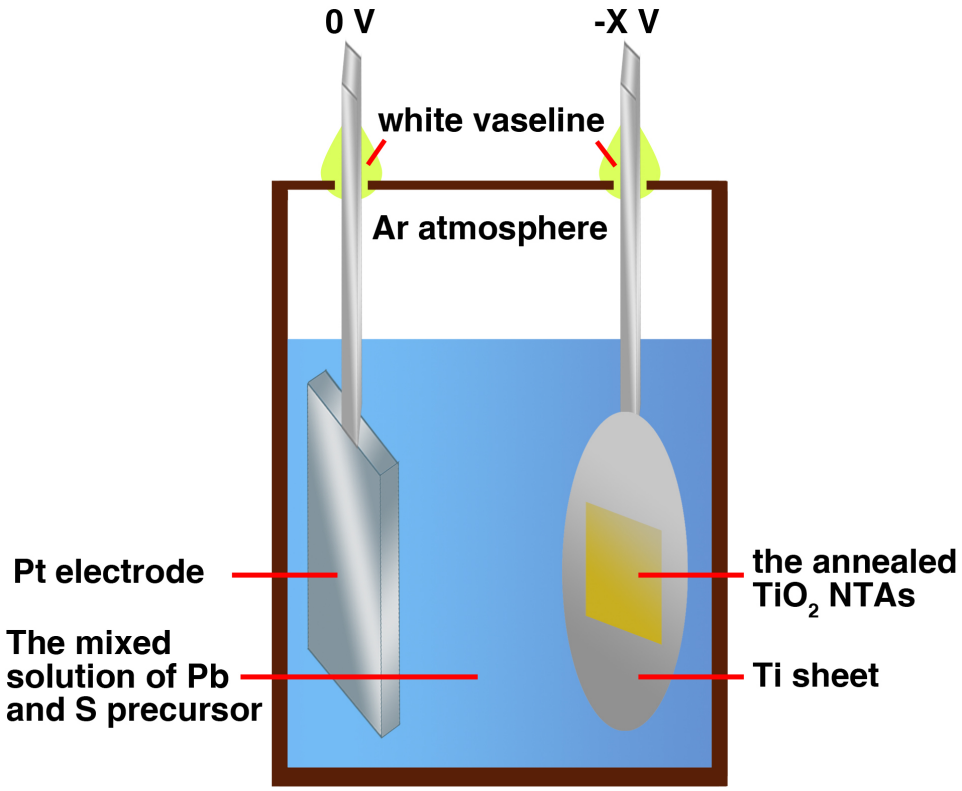

Figure 4S: Schematic description of the experimental setup for the situ growth process with the lateral view.

The negative bias situ growth process was performed in an oxygen-free container with two electrode configuration as shown in Figure 4S, using the annealed TiO_2 NTAs as the low potential electrode and the Pt electrode as the high potential electrode. We first prepared the two precursor solution by dissolving the Pb/S solute into the solution independently at high temperature, the same as the preparation for soaking process. But the concentration of both solutions has been reduced to one-tenth. After sufficient dissolution, they were mixed into the oxygen-free container and the container was filled with Ar atmosphere, followed by sealing with white vaseline. The two electrodes were set up a very low electric circuit by -5~0 V bias from a Keithley 2400 source meter. The PbS QDs tends to be formed at the low potential electrode because the Pb source is excessive. The growth process lasted for 24 h.

Table 1S. Photovoltaic characteristic information of QDSSCs with different film thickness at 50 V. [a]

Growth Time (min)	Film Thickness (μm)	η (%)	Jsc (mA)	Voc (V)	FF
20	1.4	0.65	1.74	0.60	0.62
30	2.1	0.95	2.61	0.61	0.60
60	3.5	1.69	4.47	0.63	0.60
75	4.4	2.08	5.25	0.64	0.62
90	6.4	1.65	4.21	0.63	0.62
120	6.7	1.58	3.94	0.64	0.63
150	7.7	1.53	3.83	0.64	0.62
180	8.3	1.46	3.61	0.65	0.62

[a] All of the effective areas of solar cell are 0.25 cm^2.

Table 2S. Photovoltaic characteristic information of QDSSCs with different field intensity of EACBD. [a]

EACBD Voltage (V)	Film Thickness (μm)	η (%)	Jsc (mA)	Voc (V)	FF
0	4.4	0.36	1.48	0.47	0.52
-1	4.4	0.80	2.82	0.64	0.44
-2	4.2	3.15	7.69	0.65	0.63
-2.5	4.2	3.41	8.48	0.64	0.63
-3	4.4	3.30	9.30	0.64	0.55
-3.5	4.3	3.19	7.69	0.65	0.64
-4	4.1	2.92	8.24	0.65	0.54
-5	4.3	0.72	2.72	0.62	0.43

[a] All of the effective areas of solar cell are 0.25 cm^2.