1 Introduction

Colloidal quantum dots (QDs) have been widely studied as promising building blocks for applications in emerging optoelectronic technologies such as third generation photovoltaics, solar-driven photoelectrochemical (PEC) hydrogen production, light emitting devices, photodetectors, light emission displays and luminescent solar concentrators, due to their size/composition tunable band gaps, broad absorption spectra, multiple exciton generation and high extinction coefficients.1–10 Among various potential applications in solar technologies, solar driven solar cells and QDs sensitized solar cells (QDSSCs) constitute the most promising cost-effective and easy fabrication candidates for renewable and clean energy conversion.11–13 The main challenges for improving the performance of PEC cells and QDSSCs are the limited light harvesting range of QD sensitizers and charge separation/transport efficiency, which are largely influenced by the material’s band structure.14–17

Recently, various types of colloidal semiconductor QDs such as PbX and CdX (X = S, Se, Te) have been synthesized via wet chemical approaches. Among these, PbS QDs are becoming increasingly attractive due to their spectrally size-dependent broad absorption in the ultraviolet (UV)-visible-near infrared (NIR) region ranging from 300 to 2000 nm, rendering them useful as absorbers in solar technologies.18–20 For instance, the highest power conversion efficiency (PCE) of liquid-junction PbS QD based QDSSCs is over 7%21 and a photocurrent density of 11.2 mA cm$^{-2}$ was obtained for PbS based solar-driven PEC cells fabricated from an optimized heterostructured photoanode.2

In the above-mentioned applications, it is highly desirable to use high quality QDs presenting narrow size distribution, high quantum yield (QY) and good photo- and colloidal stability, which could be obtained by simple, well-controlled, environmentally friendly, large-scale colloidal synthesis approaches with low cost and non-toxic precursors. Typically, high quality PbS QDs can be synthesized via a hot injection organometallic approach.19 The most widely used sulphur precursors for the synthesis of PbS QDs include bis(trimethylsilyl) sulfide [(TMS)$_2$S] and sulphur (S). [(TMS)$_2$S] is very reactive, expensive, toxic, unstable and must be handled under an inert atmosphere.22 The use of S can enable a different synthesis route, to obtain high quality PbS QDs. However, the low reaction activity of S leads to limitations in the size control of QDs (first absorption excitonic peak $>$1000 nm). These drawbacks largely affect their use in solar technologies.

Recently, Hendricks et al. reported the synthesis of a series of metal sulfide QDs by using a library of inexpensive and air-stable substituted thioureas whose conversion reactivity can be
finely tuned by adjusting the organic substituents. This original approach involving thioureas was used to synthesize PbS QDs with the first absorption excitonic peak covering from 800 to 1700 nm, narrow size distribution, high yield and good batch-to-batch consistency. This synthetic method holds great potential in advancing the systematic development of solution-processed QD application.\(^\text{21}\) At this moment a glove box environment is needed to handle air-sensitive chemicals (e.g. trifluoroacetic acid and trifluoroacetic anhydride) for this type of synthesis. We therefore aim to synthesize PbS QDs without using a glove box by optimizing the reaction conditions, such as the solvent and lead precursors. On the other hand, to date most of the studies on PbS QDs for optoelectronic applications, such as solar cells and hydrogen production devices have been relying on synthetic routes involving \([\text{TMS}]_2\text{S}\),\(^\text{22,24,25}\) with only one report on the fabrication of PbS QD solar cells by using exclusively elemental sulphur synthesis.\(^\text{22}\) There is still no report on using PbS QDs synthesized with the thiourea approach for use in optoelectronic devices.

Herein, we describe a facile and optimized approach based on lead oleate and substituted thiourea as lead and sulphur precursors to synthesize NIR PbS QDs. For lead oleate synthesis, we designed a simple reaction by using lead acetate as a lead source and without using air-sensitive chemicals during the overall reaction process. By adjusting the reaction parameters, size-tunable NIR PbS QDs (with absorption excitonic peaks in the 870–1400 nm range) were obtained via the hot injection method. To further improve the air-stable performance of the PbS QDs towards their applicability in solar technologies, a Cd post-treatment was performed to create a thin passivating layer on the PbS QD surface.\(^\text{26}\) We then explored their use in solar-driven hydrogen generation, obtaining a comparable photocurrent for PEC cells based on the QDs obtained from different sulphur precursors. The as-prepared NIR QDs were also employed as sensitizers in QDSSCs. For comparison, we fabricated QDSSCs with PbS QDs synthesized by using traditional \([\text{TMS}]_2\text{S}\) as a sulphur precursor. The devices sensitized by using QDs from thiourea show 43% higher PCE than the devices sensitized by using QDs from \([\text{TMS}]_2\text{S}\) under one sun illumination. These results indicate that our developed synthetic methodology is a promising alternative for preparing PbS QDs without using very toxic and expensive chemicals. Our approach represents a simple and low-cost strategy for the synthesis of colloidal PbS QDs for potential applications in photonic technologies.

2 Experimental

2.1 Materials

Aniline, 3,5-bis(trifluoromethyl)phenyl isothiocyanate, toluene, lead(II) acetate trihydrate \([\text{Pb(CH}_3\text{COO})_2\cdot3\text{H}_2\text{O}]\), oleate acid (OA), hexadecane, diphenyl ether, acetone, ethanol, methanol, cadmium oxide (CdO), 1-octadecene (ODE), \([\text{TMS}]_2\text{S}\), triocetylphosphine (TOP), cadmium nitrate tetrahydrate \([\text{Cd(NO}_3)_2\cdot4\text{H}_2\text{O}]\), cadmium acetate dihydrate \([\text{Cd(CH}_3\text{COO})_2\cdot2\text{H}_2\text{O}]\), diethylene glycol, acetonitrile, IPA, toluene, ethanol, acetone, methanol, acetonitrile, mixed hydrocarbons (such as decane), hexadecane, n-octadecane, diphenyl ether, diphenyl ether, cadmium acetate dihydrate, tetraethyl orthosilicate, zinc acetate dihydrate \([\text{Zn(CH}_3\text{COO})_2\cdot2\text{H}_2\text{O}]\), hydrochloric acid (HCl), sodium sulfide (Na\(_2\)S), and sodium sulfite (Na\(_2\)SO\(_3\)) were purchased from Sigma Aldrich. Brass was purchased from McMaster-Carr Company. Ti-Nanoxide BL/SC was obtained from Solaronix. Titania paste containing active anatase nanoparticles ~20 nm in diameter (18 NR-T) and a mixture of active anatase particle (~20 nm) and larger anatase scattering particle (up to 450 nm) paste (18 NR-AO) were purchased from Dyosol (Queanbeyan, Australia). Transparent fluorine doped tin oxide (FTO) coated conducting glass substrates with a sheet resistance of 8 Ω per square were bought from Pilkington glasses. All chemicals were used as purchased without any purification.

2.2 Synthesis of PbS QDs and further post-treated by using Cd(oleate)\(_2\)

Our modified synthetic route of PbS QDs consists of the following steps: first, for the synthesis of substituted thiourea, a solution of 1.7 mL aniline in 6 mL toluene was added to a solution of 5 g 3,5-bis(trifluoromethyl)phenyl isothiocyanate in 6 mL toluene. The solution was stirred for 30 minutes before the exothermic reaction ended. The product was thoroughly dried under vacuum to remove trace toluene, resulting in a white powder of substituted thiourea.\(^\text{23}\) Second, for the synthesis of lead oleate, 227.6 mg Pb(CH\(_3\)CO\(_2\))\(_2\cdot3\)H\(_2\)O and 0.4 mL oleic acid were mixed with 10 mL hexadecane in a 3-neck flask and flushed under a nitrogen gas flow for 5 min, then transferred in an oil bath at 160 °C under stirring held for 1 h in a Schlenk line. The temperature was then decreased to 95 °C. During this period, a mixture of 218.6 mg of the as-prepared thiourea and 1.61 g diphenyl ether was heated to 95 °C, then this clear solution was rapidly injected into the flask containing lead oleate at 95 °C. The solution was maintained at the latter temperature for 2 minutes, then cooled down to room temperature with cold water. Finally, the QDs were washed with ethanol/acetone and re-dispersed in toluene.

The Cd post-treatment of QDs was performed as follows: typically, CdO (100 mg), OA (2 mL) and ODE (10 mL) were heated to 240 °C under N\(_2\) atmosphere for 30 min. The clear solution was then cooled down to 140 °C under vacuum for 15 min. The flask was then reopened and the N\(_2\) flux was restored. The PbS QD suspension in toluene was diluted in 10 mL toluene, purged with N\(_2\) for 30 min and then immediately heated to 100 °C. The Cd/OA mixture was added \(\text{via}\) a syringe. The solution was maintained at 100 °C for 5 minutes and then cooled down to room temperature with cold water. Then the QDs were washed with ethanol and re-dispersed in toluene.\(^\text{27}\) PbS and Cd-treated QDs synthesized by using \([\text{TMS}]_2\text{S}\) were also prepared for comparison, according to previous reports.\(^\text{28,29}\)

2.3 Fabrication of QDSSCs and PEC cells

2.3.1 TiO\(_2\) film preparation. A compact TiO\(_2\) thin blocking layer was deposited on an ultrasonically cleaned transparent FTO-coated glass substrate (sheet resistance 8 Ω per square) by spin coating (5000 rpm for 40 s), using the commercial solu-
tion Ti-nanoxide BL/SC.30 The samples were then annealed at 500 °C under an ambient atmosphere for 30 minutes. TiO2 mesoporous transparent and scattering layers were prepared by the tape casting method as reported in previous work.2,3 In brief, a transparent layer was tape casted on the above-prepared TiO2 compact blocking layer. The drying process was followed for 15 min under an ambient atmosphere at room temperature and then at 120 °C for 6 min. Subsequently a scattering layer was tape casted, followed by the same drying process. After drying, all the samples were annealed at 500 °C for 30 min under an ambient atmosphere, forming a mesoporous film with a thickness of about 12–14 μm, as measured by contact profilometry.

2.3.2 TiO2/QDs anode preparation. The above-prepared TiO2 films were sensitized with PbS QDs by using electrophoretic deposition (EPD) as follows: a pair of TiO2 films grown on FTO were vertically immersed in the QD solution facing each other with a distance of around 1 cm. A voltage of 200 V was applied for 2 hours.32 The samples were then rinsed with toluene and dried with N2 at room temperature twice.

2.3.3 Fabrication of the PEC devices. For use in PEC devices, the PbS QD sensitized TiO2 anode via the EPD process and subsequently two ZnS cycles were performed by the successive ionic layer adsorption and reaction (SILAR) method. An insulating glue was then used to cover the sample’s non-active area to avoid the direct contact between the electrolyte and conducting back-contact. The PEC performance was evaluated in a three-electrode configuration with the photoanode, Pt and saturated Ag/AgCl as the working, counter and reference electrodes, respectively. The electrolyte consists of 0.35 M Na2SO3 and subsequent two ZnS cycles were performed by the successive ionic layer adsorption and reaction (SILAR) method. An insulating glue was then used to cover the sample’s non-active area to avoid the direct contact between the electrolyte and conducting back-contact. The PEC performance was evaluated in a three-electrode configuration with the photoanode, Pt and saturated Ag/AgCl as the working, counter and reference electrodes, respectively. The electrolyte consists of 0.35 M Na2SO3 and 0.25 M Na2S as sacrificial hole scavengers to prevent photo-corrosion.

2.3.4 Fabrication of the QDSSCs. After the EPD process, five cycles of CdS and four cycles of ZnS were subsequently deposited by SILAR.33,34 Specifically, the QD-sensitized TiO2 film was treated with five cycles of CdS by immersing in 0.1 M Cd(CH3COO)2·2H2O and 0.1 M Na2S aqueous solutions for one min alternately, then four cycles of ZnS by immersing in 0.1 M Zn(CH3COO)2·2H2O and 0.1 M Na2S aqueous solutions for one min alternately. Silica coating was then performed by immersing the sample in 0.01 M ethanolic solution of tetraethyl orthosilicate at 35–40 °C for 2 h. The Cu2S counter electrode was obtained by immersing brass foil in a 37% HCl solution at 75 °C for 10 min. The foil was then Vulcanized by immersing it in a polysulfide electrolyte solution for 10 min to generate the active Cu2S. The polysulfide electrolyte solution composed of 2.0 M sodium sulfide, 2.0 M sulfur, and 0.2 M sodium hydroxide in distilled water and methanol (3 : 7, v/v) was injected into the cell. The QD-sensitized TiO2 film photoanode and the as-prepared Cu2S counter electrode were sandwiched together with a Teflon spacer (25 μm thickness) for the fabrication of QDSSCs. Devices were then clamped for functional performance analysis. For each type of QDSSC, at least two samples were prepared and evaluated in parallel.

The prepared water-soluble QDs from thiourea were obtained by using TGA as the phase transfer agent via the ligand exchange method.21 The specific synthesis method and the following corresponding fabrication of QDSSCs are described in the ESI.†

2.4 Characterization

2.4.1 Material characterization. The morphology of the Cd-PbS QDs was characterized using a JEOL 2100F transmission electron microscope (TEM). The composition of the films was measured on a freshly cleaved cross-section of the photoanode and imaging by field emission scanning electron microscopy (FE-SEM) using a JEOL JSM-6300F FE-SEM equipped with an energy-dispersive X-ray spectrometer (EDS). Absorption spectra were acquired with a Cary 5000 UV-visible-NIR spectrophotometer (Varian) with a scan speed of 600 nm min−1. The Cd/Pb ratio was measured by using inductively coupled plasma optical emission spectrometry (ICP-OES) (PerkinElmer Model Optima 7300 DV).

2.4.2 Device characterization. The PEC performance of the photoanode was evaluated in the three-electrode configuration described above, using a CHI 760D electrochemical workstation. The potential during electrochemical measurement was converted to the reversible hydrogen electrode (RHE) scale according to the equation

\[
V_{\text{RHE}} = V_{\text{Ag/AgCl}} + 0.197 + \text{pH} \times 0.059 \quad (\text{V RHE})
\]

The measurement was carried out at AM 1.5 with an intensity of 100 mW cm−2. A silicon reference diode (Sciencetech) was used to adjust the distance between the photoanode and the solar simulator before each measurement to guarantee the standard one sun illumination on the photoanode. The typical distance from the sun simulator to the PEC cell is 20 cm. The current-voltage characteristics of the QDSSCs were determined using a digital Keithley as a source meter under one sun simulated sunlight calibrated with the silicon reference diode. Transient photovoltage decay measurements were carried out under one sun simulated illumination as a light source to illuminate the devices to an open circuit voltage (Voc), then the light was shut down and the transient photovoltage decay was recorded. The transient photovoltage values continuously decrease with time from the open circuit voltage to nearly 0 V in the dark. The electrochemical impedance spectroscopy (EIS) measurements were carried out under dark conditions using a SOLARTRON 1260 A Impedance/Gain-Phase Analyzer at forward bias ranging from 0 to 650 mV over the frequency range of 10−3 Hz to 300 kHz with an applied AC amplitude of 10 mV.

3 Results and discussion

The previously reported PbS nanocrystals synthetic route by Hendricks et al. involved a series of substituted thioureas as a sulphur precursor instead of the “traditional” [(TMS)2S], which is toxic and expensive. The new procedure also increased the extent of crystal nucleation by exploiting the conversion kinetics of thiourea, which is faster.23 However, in the synthetic route of PbS nanocrystals, a complex reaction was performed with the assistance of a glove box to prepare lead precursors.
The specific synthetic route is shown in the ESI.† For instance, a complex reaction was used to synthesize powder lead (oleate)₂. In addition, several air-sensitive chemicals were used, which should be stored and handled under an inert atmosphere. Here we modified the synthetic route by replacing the air-sensitive chemicals. Specifically, our optimized synthetic route was based on lead acetate as a lead source. This can be easily obtained without using a glove box. On the other hand, OA was used directly to react with lead acetate to prepare the precursor solution rather than preparing the lead oleate powder.23 The overall synthetic methodology avoided toxic [(TMS)₂S] while applying a facile approach for lead precursors. The yield of PbS QDs is up to 140 mg for one batch. The as-synthesized PbS QDs present a well-controlled absorption spectrum with a narrow absorption peak width (Fig. 1). The QDs show the typical first absorption excitonic peak ranging from 870 up to 1400 nm by a simple variation of the reaction parameters, such as reaction time, injection temperature etc.

After the synthesis, we explored the applicability of the prepared QDs in PEC cells and QDSSCs. Two types of QDs with similar sizes of around 3 nm from different sulphur precursors of thiourea and [(TMS)₂S] were chosen for comparison. However, colloidal PbS QDs capped with pure organic ligand shells suffer from surface oxidation which has an adverse effect during the fabrication of solar energy devices in an air atmosphere. Cd post-treatment was implemented before device fabrication since a thin CdS layer can protect the PbS core from surface oxidation during photoanode fabrication under ambient conditions.2,21 Fig. 2a and b display representative TEM images of Cd-PbS QDs obtained from [(TMS)₂S] and thiourea, respectively, indicating that the sizes of both types of Cd-PbS nanocrystals are very uniform. The epitaxial CdS layer is difficult to image by TEM because of the very similar crystalline structure and lattice constant of CdS and PbS.21 High-resolution TEM (HRTEM) images in the inset of Fig. 2a and b show crystal lattice fringes with a spacing of 0.34 nm, corresponding to the interplanar distance of the (111) planes of rock-salt lead sulfide. The size distributions of colloidal Cd-PbS QDs obtained from [(TMS)₂S] and thiourea are displayed in Fig. S1a and S1b† relative to TEM images, which show that the prepared QDs exhibit a uniform size distribution. The average diameter of the QDs obtained from [(TMS)₂S] and thiourea are both around 3.0 nm. To further investigate the shell thickness of the CdS layer, we measured the Pb-to-Cd atomic ratio by using ICP-OES. Based on this ratio and the overall diameter measured from TEM images, the calculated shell thickness is about 0.2 nm for QDs synthesized using [(TMS)₂S] or thiourea.

Fig. 2c and d report the UV-Visible-NIR absorbance spectra of the as-prepared PbS and Cd-PbS QDs from [(TMS)₂S] and thiourea, respectively. Pure PbS QDs from [(TMS)₂S] exhibit an absorption excitonic peak at around 918 nm, which occurs at around 875 nm for PbS from thiourea. The blue-shift of the absorption curve after cation exchange is apparent due to the slight decrease of the PbS core size during the replacement of Pb²⁺ by Cd²⁺.18,37 In Fig. 2d, the disappearance of the first-excitonic absorption peak for the thiourea sample after Cd treatment is due to the broad PbS core size distribution, consistent with our previous report on small-sized PbS/CdS QDs.29

For both PEC cells and the QDSSC anodes, a ZnS layer was applied by SILAR following the QDs tethered on TiO₂. In the case of PEC cells, electron recombination is suppressed by the ZnS layer coating, which acts as an energy barrier prohibiting photoexcited electron transfer into the electrolyte, thereby increasing the photocurrent.2 For QDSSCs, charge recombination at the interface of the photoanode and electrolyte in devices could be effectively and significantly reduced via the
wide band ZnS barrier layer capped around the QD sensitized photoanode. To further investigate the distribution of QDs tethering on the TiO₂ mesoporous film and the ZnS passivation layer on the surface of QDs, cross section analyses of the prepared fresh TiO₂/QD anode capped with a ZnS layer were performed by SEM, EDS 2D mapping and line mapping. Fig. S2a† displays a cross-sectional SEM image of the QDs on the TiO₂ mesoporous film capped with a ZnS layer. Fig. S2(b–i)† show the EDS mapping images of different elements, indicating the presence of Ti, O, Si, Sn, Cd, Zn, Pb and S elements and the homogeneous distribution of the adsorbed QDs and ZnS layer in the mesoporous TiO₂ film. Fig. S2j† displays the EDS spectra, in which the semi-quantified element weight percentage is labeled. Fig. S2k† reports the EDS line mapping presenting the relative weight ratio of elements along the blue highlighted line in Fig. S2a† which comprises both the glass/FTO substrate (initial 1.5 μm) and photoanode (remaining 13.5 μm). The Cd-PbS QDs are distributed homogeneously in the TiO₂ film, resulting in high quality TiO₂/QD anodes.

The anode was then used to fabricate PEC cells for solar driven hydrogen generation. The schematic illustration of PEC cells with the prepared QDs as light harvesters is shown in Fig. 3. Upon illumination, the QDs absorb solar light, generating excitons. Photoexcited exciton dissociation occurs at the QDs/TiO₂ interface, and the electrons that were photoexcited in the conduction band of the QDs can be effectively injected into the conduction band of TiO₂. Electron transport occurs in the TiO₂ mesoporous film and charges are collected by the FTO film, then transferred to the Pt counter electrode, where hydrogen generation takes place. Na₂S and Na₂SO₃ hole scavengers in the electrolyte provide a shuttle for the photoexcited holes.

PEC solar-driven hydrogen generation was carried out in a three electrode system under 100 mW cm⁻² AM 1.5 G illumination in 0.25 M Na₂S and 0.35 M Na₂SO₃ (pH = 13) aqueous solution. A set of linear-sweep voltammograms were obtained by using different photoanodes in the dark and under simulated solar illumination. The photocurrent density of light gradually increases with the increase in the voltage, until a saturated current density is obtained. Fig. 4a and b show the photocurrent response measured with the PEC cell in the dark, under

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**Fig. 3** Schematic illustration of PEC cells with the prepared QDs as light harvesters. Energy levels (at pH = 13) of TiO₂, prepared QDs (3 nm in diameter) and related characteristic redox potentials. The arrows indicate the electron and hole transfer process.

**Fig. 4** Photocurrent density versus the applied voltage (vs. RHE) curves of PEC devices assembled using our as-prepared QDs from (a) [(TMS)₂S] and (b) thiourea in the dark (blue line) under chopped (black line) and constant one sunlight illumination (red line). (c) measured current density as a function of time for the devices of PbS QDs from [(TMS)₂S] and thiourea at 0.4 V versus RHE under one simulated sunlight illumination (AM 1.5 G, 100 mW cm⁻²).
one simulated sunlight illumination condition and under chopped discontinuous one sun simulated sunlight illumination. A saturated photocurrent density of 2.03 mA cm$^{-2}$ was observed for the PEC cell made of QDs from thiourea, which is very similar to that of [...] (1.97 mA cm$^{-2}$).

To identify the contribution of bare TiO$_2$ to the observed efficiency of PEC cells, we fabricated devices only using TiO$_2$ as the photoanode (without using QDs). The photocurrent density is only 0.3 mA cm$^{-2}$ which is much less than that obtained in the PEC cell based on the QDs/TiO$_2$ system ($\sim$2 mA cm$^{-2}$) [see Fig. S4 in the ESI†].

The stability of the PEC cells was carried out in a three electrode system. A photocurrent versus time evolution of the PEC system at 0.4 V vs. RHE is shown in Fig. 4c. For the photoanode based on PbS QDs synthesized via thiourea, the photocurrent density gradually decreased. After 2 h illumination under one sun (100 mW cm$^{-2}$), the photocurrent density still maintains 56% of its initial value. In the photoanode based on PbS QDs synthesized via [(TMS)$_2$S], the photocurrent density decreased rapidly in the first 5 minutes and then gradually decreased during 2 h illumination. After 2 h, the current density decreases to 41% of its initial value. The results show that the as-prepared PbS QDs obtained from thiourea as the sulphur precursor are suitable for use in PEC hydrogen generation. The measured H$_2$ generation rate by gas chromatography (GC) [details in Fig. S5 in the ESI†] is around 0.50 mL cm$^{-2}$ h$^{-1}$ (equal to 12 mL cm$^{-2}$ day$^{-1}$) in the anode based on QDs synthesised via thiourea which is higher than that of 0.38 mL cm$^{-2}$ h$^{-1}$ (equal to 9.1 mL cm$^{-2}$ day$^{-1}$) in the anode based on QDs synthesized via [(TMS)$_2$S].

In a separate set of experiments, the QDs synthesized via different sulphur precursors were employed as sensitizers in QDSSCs. Fig. S3† illustrates the operating mechanism of QDSSCs based on the as-prepared QD sensitized TiO$_2$ mesoporous film as the photoanode, $S^{2-}/S_n^{n-2}$ redox couple as the electrolyte and Cu$_2$S as the counter electrode. Under one sun illumination, photoexcited excitons yield at the interface between QDs and TiO$_2$, QDs and the $S^{2-}/S_n^{n-2}$ redox couple electrolyte. The electrons are injected from the conduction band of QDs to the conduction band of TiO$_2$ and then transported to the external circuit, while holes in the valence band of QDs are collected by the electrolyte. The electrons finally reach the counter electrode to participate in the reduction reaction of the counter electrode and electrolyte interface.45

The current density versus voltage (J–V) curves of the fabricated QDSSCs are shown in Fig. 5a and the corresponding functional parameters are reported in Table 1. The device based on QDs synthesized via thiourea yields a short circuit current ($J_{sc}$) of 7.84 mA cm$^{-2}$, a $V_{oc}$ of 0.52 V, a fill factor (FF) of 0.49 and a PCE of 2.00%, showing an overall better photovoltaic (PV) performance compared to the device sensitized by using QDs based on [(TMS)$_2$S] with a $J_{sc}$ of 6.95 mA cm$^{-2}$, a $V_{oc}$ of 0.48 V, a FF of 0.42 and a PCE of 1.40%, respectively.

To identify the contribution of bare TiO$_2$ to the observed PCE of QDSSCs, we fabricated devices by using bare TiO$_2$ as a photoanode material (without sensitizing with QDs). The
device exhibits only 0.023% PCE. This is significantly lower as compared to the PCE of 2% obtained from the devices based on QDs/TiO$_2$ (see Fig. S6†). This demonstrates the promising role of QDs as sensitizers, to increase the PCE of QDSSCs.

Transient photovoltage decay measurements were carried out to investigate in greater detail the carrier dynamics of devices based on QDs synthesized by using different sulphur precursors. In this measurement, both devices were illuminated under one sun simulated sunlight (100 mW cm$^{-2}$) until we obtained a steady voltage (open circuit voltage of the device) and then the sun-simulator shutter was closed and we measured the voltage decay rate of the devices under dark conditions. Fig. 5b shows the systematic comparison of the transient photovoltage decay of the devices based on QDs synthesized by using different sulphur precursors. The results demonstrated that the device sensitized with QDs from [TMS$_2$]S shows a rapid drop of photovoltage as compared to the device sensitized with QDs from thiourea, which means that the carrier recombination at the QDs/TiO$_2$ interface is higher in the former device as compared to the latter one. The electron lifetime ($\tau$) values were derived from the transient photovoltage decay measurement by using the following equation:$$\tau = -(k_bT/e)(dV_{oc}/dt)^{-1}$$
where $k_b$ is Boltzmann’s constant, $T$ is the absolute temperature, and $e$ is the electronic charge.

Fig. 5c shows that the electron lifetime is higher for the device based on QDs from thiourea as compared to the device based QDs from [TMS$_2$]S, which is consistent with the obtained PV performance of the respective devices. At a particular value of $V_{oc}$ (~0.25 V), the calculated electron lifetime values for the device based on QDs from thiourea is almost double as compared to the device based on QDs from [TMS$_2$]S. These results confirmed that the QD-thiourea device has reduced non-radiative carrier recombination at the QD/TiO$_2$/electrolyte interface due to fewer surface traps in the respective QDs as compared to its counter-part QDs based on [TMS$_2$]S. As these surface trap-states act as active sites for recombination during device operation, the overall functional performance of the device degrades. These results are further confirmed by electrochemical impedance spectroscopy (EIS).

EIS characterization (Fig. S7†) was also carried out to investigate the carrier recombination for the devices sensitized with QDs from thiourea and [TMS$_2$]S respectively. The detailed analysis is described in the ESI†.

We also fabricated QDSSCs by using QDs with an overall size of 3.2 nm and a shell thickness of 0.2 nm, produced using either thiourea or [TMS$_2$]S as precursors. The results further confirm that the QDSSCs using QDs synthesized via thiourea exhibit a better performance compared to that of the QDSSCs using QDs produced by [TMS$_2$]S. The $J$–$V$ curves are shown in Fig. S8† and the corresponding functional parameters are reported in Table S1†.

To further improve the PCE of the QDSSCs, the oil soluble QDs were transferred into water (the method is described in the ESI†). The $J$–$V$ curves of the QDSSCs sensitized by using water-soluble QDs are shown in Fig. S9† and the corresponding functional parameters are reported in Table S2.† The device based on water soluble QDs yields a $J_{sc}$ of 10.72 mA cm$^{-2}$, a $V_{oc}$ of 0.55 V, a $FF$ of 0.50 and a PCE of 2.95%, demonstrating better functional performance compared with the device sensitized by using oil-soluble QDs.

### Table 1  Functional parameters of QDSSCs sensitized with QDs from different sulphur precursors

<table>
<thead>
<tr>
<th>QDs from different sulphur precursors</th>
<th>$J_{sc}$ (mA cm$^{-2}$)</th>
<th>$V_{oc}$ (V)</th>
<th>FF</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[TMS$_2$]S</td>
<td>6.95 ±0.08</td>
<td>0.48 ±0.05</td>
<td>0.42 ±0.03</td>
<td>1.40 ±0.03</td>
</tr>
<tr>
<td>Thiourea</td>
<td>7.84 ±0.16</td>
<td>0.52 ±0.04</td>
<td>0.49 ±0.01</td>
<td>2.00 ±0.07</td>
</tr>
</tbody>
</table>

### 4  Conclusions and perspectives

We designed a simple approach to synthesize NIR colloidal PbS QDs by using lead acetate and thiourea as lead and sulfide sources, respectively. By adjusting the reaction parameters, the size-tunable NIR PbS QDs (with absorption excitonic peaks from 870 to 1400 nm) were obtained with a narrow size distribution (<10%). Further Cd post-treatment was conducted to generate a passivating layer to improve the stability of the QDs. The as-prepared QDs were employed for application in both solar-driven hydrogen generation and QDSSCs. Under identical measurement conditions, the as-prepared devices using thiourea as a new inexpensive and air-stable precursor show a comparable or better performance with respect to QDs synthesized using the commonly used toxic and air-sensitive [TMS$_2$]S precursor. This work provides a simple methodology for PbS QD synthesis and holds potential and promising applications in PbS-QD based optoelectronic devices, such as solar cells, PEC solar-driven hydrogen production cells, photodetectors, sensors, light emitting devices, luminescent solar concentrators, etc.

### Conflicts of interest

There are no conflicts to declare.

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