通过 S^{2-} 中间态将 CdSe 量子点有机配体转化为 ZnS 保护层及其器件光伏特性

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摘要: 通过 S^{2-} 中间态将有机配体三辛基氧磷(TOPO)转化为 ZnS 保护层, 显著改善了 CdSe 量子点(QDs)器件的转换效率. 配体交换后的傅里叶变换红外(FTIR)光谱结果表明, 有机配体已被 S^{2-} 离子配体取代; 离子反应后的 X 射线光电子能谱(XPS)结果表明 S^{2-} 离子配体反应生成了 ZnS, 紫外-可见(UV-Vis)吸收光谱结果表明量子点溶液吸收峰位没有发生明显改变, 透射电子显微镜(TEM)结果表明配体交换后量子点粒径减小. 电化学阻抗谱(EIS)结果表明光照条件下有机配体转化为 ZnS 保护层后 TiO_2 /QDs/电解质界面电阻减少, 证明该条件下正向电子传输增强; 强度调制光电压谱(IMVS)和强度调制光电流谱(IMPS)结果表明电子寿命和扩散速度增加. 相比于有机配体, 形成 ZnS 保护层后的量子点敏化太阳能电池(QDSC)效率由 0.98% 提高到 1.75%, 相对提高了 1.78 倍.

关键词: 量子点敏化太阳能电池; 无机配体; ZnS 层; 配体交换; 离子反应; CdSe 量子点
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Transforming Organic Ligands into a ZnS Protective Layer through the S^{2-} Intermediate State in *ex situ* CdSe Quantum Dot Devices

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Abstract: In this paper, the tri-*n*-octylphosphine oxide (TOPO) ligand on CdSe quantum dots (QDs) are changed to ZnS coating layer through S^{2-} intermediate state. After ligand exchange, the Fourier transform infrared (FTIR) spectra indicate that the long chain organic ligands are replaced by S^{2-} ions. After ionic reaction, the generation of ZnS is confirmed by X-ray photoelectron spectroscopy (XPS) measurements. In addition the UV-Vis absorption peaks did not move and transmission electron microscopy (TEM) results show that the diameters of the quantum dots decrease. Electrochemical impedance spectroscopy (EIS) results show that the interface resistance between the TiO_2 /QDs/electrolyte is reduced under illumination conditions, meaning that forward electron transport was enhanced. In addition, the intensity-modulated photovoltage spectroscopy (IMVS) and intensity-modulated photocurrent spectroscopy (IMPS) results reveal an increase in the electronic lifetime and diffusion rate increased. Finally, the conversion efficiency increases by 1.78 times from 0.98% (TOPO ligand) to 1.75% (ZnS coating).

Key Words: Quantum dot sensitized solar cell; Inorganic ligand; ZnS coating; Ligand exchange; Ionic reaction; CdSe quantum dot

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1 Introduction

Increasing demand for clean energy has promoted the exploration of efficient and cheap solar energy conversion devices such as quantum dot sensitized solar cells (QDSCs).^{1–3} Compared to traditional dyes used in dye-sensitized solar cells (DSCs), quantum dots (QDs) have quite a few advantages including size-dependent band gaps, large oscillator strengths, high cross sections for multi-photon absorption and multi-exciton generation.^{4–14}

In recent years, the most widely investigated topics of QDSCs are mainly focused on two kinds of methods for depositing QDs on a porous TiO₂ photoanode: *in situ* and *ex situ*. The *in situ* method is limited in its ability to control size distribution of QDs, resulted in the charge recombination centers formed on the surfaces of large QDs.^{15–18} In comparison, the *ex situ* method is of great importance in depositing QDs with a monodisperse-size and various structures such as core/shell structure,^{19–21} rod-like,^{21–23} tetrapod-like structure,²⁴ and multiple dot-in-rod hetero nanostructure.²⁵ It is note worthy that the high photoelectric conversion efficiency can also be achieved in *ex situ* method.²⁶

The *ex situ* QDs are normally synthesized in oil solution using oleic acid (OA), tri-*n*-octylphosphine oxide (TOPO) and trioctylphosphine (TOP) as ligands, which was firstly proposed in 1993.²⁷ In order to decrease the electron transfer distance between TiO₂ and QDs, small organic molecules, such as 3-mercaptopbenzoic acid (MPA),^{28,29} pyridine,³⁰ and 1,4-benzenedithiol,³¹ are widely used as linkers using aligand exchange method.

Inorganic ligands such as the anion complexes Sn₂S₆⁴⁻ on ion-capped QDs were first reported by Talapin *et al.*³² Several inorganic-organic hybrid and inorganic ion ligands were later reported.^{33–35} This kind of ligands has smaller dimension than organic ligands such as MPA, and can further decrease the electron transfer distance. However, the inorganic ligands capped QDs have never been used as a sensitizer in QDSCs. The problem on the application may be due to the instability of inorganic-organic hybrid and inorganic ion ligands such as S²⁻ ions.

In this paper, S²⁻ ion ligands (transformed from TOPO) capping CdSe QDs is first used in QDSCs for obtaining a smaller transfer distance. However, the electron transfer in the devices can be retarded by the negative charge of the S²⁻ ions surrounding the QDs. Furthermore, the S²⁻ ion ligands will be unstable in QDSCs. To avoid these problems, the S²⁻ ion is stabilized by generation of ZnS protective coated by ionic reaction. It is note worthy that wide-bandgap ZnS as coating layer is widely used in QDSCs, which can efficiently solve the problem including the instability of the QDs and charges recombination.^{26,36–42} The power conversion efficiency (PCE) of QDSCs increases with the transformation from TOPO ligands to a ZnS layer. We report QDSCs using S²⁻ ions as a conversion agent to transform long chain organic ligands to ZnS protective layer, which open a new path to achieve both the removal of organic ligands and generation of a protecting layer.

2 Experimental

2.1 Preparation of CdSe QDs capped with S²⁻ ion ligands

The CdSe QDs were synthesized based on the method proposed by Zhong *et al.*⁴³ A Cd²⁺ solution was prepared by dissolving CdO (1.00 g, 7.8 mmol, Aladdin, 99.99%) in OA (12.0 mL, Alfa Aesar, 99%) and 1-octadecene (ODE, 60.0 mL, Alfa Aesar, 90%) at 250 °C to get a transparent solution and then cooled down to 60 °C. Typically, 10.0 g of octadecylamine (ODA, Alfa Aesar, 98%) and 10.0 g of TOPO (Alfa Aesar, 98%) were added to Cd²⁺ solution. The solution was heated to 280 °C with stirring, and then 9.0 mL of Se²⁻ solution (0.2 mol·L⁻¹) which included 0.158 g of Se powder (Aladdin, 99.99%), 4.572 g of tri-*n*-octylphosphinetop (TOP, Aladdin, 90%), and 3.425 g of ODE was injected quickly into the reaction flask. After the completion of particle growth, the reaction was stopped by injecting 10 mL of ODE and cooling to 60 °C in water bath. All the above reactions were carried out in argon protection. The QDs were extracted by *n*-heptane and precipitated by adding methanol. The further purification was carried out by repeated centrifugation and decantation. The QDs *n*-heptane solution was added to Na₂S saturated dimethylsulfoxide (DMSO) solution. The QDs were extracted in DMSO solution after the ligands exchange.

2.2 Preparation of photoanode

The TiO₂ colloid was synthesized with hydrothermal method which has been well documented in a previous report.⁴⁴ The QDs sensitized porous TiO₂ films were prepared through a step wise procedure as described elsewhere.⁴⁵ The TiO₂ films were immersed into S²⁻ ions capped CdSe QD solution for 1 h in the Ar protection. The films were subsequently bathed in a 0.1 mol·L⁻¹ Zn(Ac)₂ aqueous solution for 1 min. The film was immersed into water to remove redundant Zn²⁺ ion.

2.3 Assembly of the QDSCs

The composition of liquid polysulfide electrolyte was included as: 0.5 mol·L⁻¹ Na₂S, 2 mol·L⁻¹ S, 0.2 mol·L⁻¹ KCl, 7 mL of MeOH and 3 mL of deionized water. The PbS counter electrode was prepared by the method reported previously.⁴⁶ When assembling the QDSCs, the electrolyte was sandwiched by a sensitized TiO₂ electrode and a counter electrode.

2.4 Characterization

The UV-Vis absorption spectra were used to measure the absorption of the QDs solution using a Hitachi U-3010 spectroscope. The morphology and size of QDs were characterized by high-resolution transmission electron microscopy (HRTEM, JEM-2010-FEG). The Fourier transform infrared (FTIR) spectrum was measured with a Perkin-Elmer Spectrum GX FTIR spectrometer. X-ray photoelectron spectroscopy (XPS) was measured with a PHI 5300ESCA instrument. Photoelement mapping was carried out using an energy dispersive spectrometer (EDS) equipped in HRTEM. Photocurrent–voltage (*J*–*V*), incident photon-to-current conversion efficiency (IPCE), electrochemical impedance spectroscopy (EIS) (ranging from 0.1

to 10^5 Hz), intensity-modulated photovoltage spectroscopy (IM-VS), and intensity-modulated photocurrent spectroscopy (IMPS) were measured by a ZAHNER CIMPS electrochemical workstation, Germany.

3 Results and discussion

3.1 S^{2-} ion ligand exchange and characterization

3.1.1 Reaction of S^{2-} ion ligand exchange

In QDSCs, electron transport between TiO_2 and the QDs depends on the distance and electronic coupling between TiO_2 and the QDs, and the electronic coupling is affected by the distance at the interface.⁴ Inorganic ligands exchange in *ex situ* QDs can decrease the electron transport distance. The as-synthesized QDs with TOPO ligands are transformed to S^{2-} ion ligands by extracting to a DMSO solution with sulfur sodium dissolved.³⁴

3.1.2 Molecule group characterization by FTIR

The FTIR analysis is used to investigate the removal of the TOPO ligand in perspective of the molecule group and the spectrum is shown in Fig.1. For the CdSe/TOPO QDs, the strong absorption of the C—H vibrations occurs at 2923 and 2853 cm^{-1} . When the TOPO is replaced with the S^{2-} ion, the absorption of C—H vibrations disappeared. We note that, in CdSe/ S^{2-} QDs, the two peaks near 2996 and 2913 cm^{-1} are considered as absorption of the symmetric and asymmetric C—H stretching vibrational frequencies of the methyl groups in the residual DMSO which is a high boiling solvent.⁴⁷ Therefore, it indicates that TOPO ligands have been removed by ligand exchange.

3.1.3 UV-Vis absorption of CdSe/TOPO and CdSe/ S^{2-} QDs

The UV-Vis absorption spectra of the TOPO and S^{2-} capped CdSe QD solutions are shown in Fig.2. The as-prepared CdSe/TOPO QD solution has an absorption peak located at 525 nm. After S^{2-} ion ligands exchange, a peak with a nearly identical location and full width at half maximum (FWHM) is observed, which indicates that the real sizes of QDs do not change. Under certain conditions, CdSe/CdS core/shell QDs generate through ion exchange at high temperature ranging from 60 to

Fig.1 FTIR spectra of CdSe QD heptone solution with TOPO ligand and QD DMSO solution with S^{2-} ligand

Fig.2 UV-Vis absorption spectra of CdSe QD solution before and after ligand exchange

260 °C, with a blue shift of UV-Vis absorption position.^{48,49} Therefore, the unchanged absorption peak can be considered as evidence that S^{2-} ions cannot replace Se^{2-} ions in given conditions.

3.1.4 TEM measurement of CdSe/TOPO and CdSe/ S^{2-} QDs

The TEM is used to characterize the sizes of CdSe/TOPO and CdSe/ S^{2-} QDs, as shown in Fig.3. Diameters of QDs are the average values through counting 100 particles in Fig.3, and the size distribution histograms of these measured diameters are shown in Fig.4. The diameter histogram of the CdSe/TOPO QDs is mainly concentrated in the size of 4.2 nm. After TOPO ligands are replaced with S^{2-} ion, the contrast of the QDs improves with an observable decrease in size, with the diameter histogram concentrated in the size of 3.6 nm. The decreases of QD size, but without changes in UV-Vis absorption position, are caused by the organic ligand with a larger steric value being replaced by an inorganic ligand. Tang *et al.*⁵⁰ ever reported

Fig.3 HRTEM images of (a) CdSe/TOPO QDs and (b) CdSe/ S^{2-} QDs

Fig.4 Size distribution histograms of (a) CdSe/TOPO QDs and (b) CdSe/S²⁻ QDs

that halide atoms did decrease the inter-dot spacing markedly compared to organic ligands. Therefore, it is reasonable to further conclude that the S²⁻ ligands in our case can shorten the space between QDs and TiO₂ to a greater degree than that achieved by the TOPO ligands.

3.2 Ionic reaction for ZnS coating and characterization

3.2.1 Ionic reaction between S²⁻ ligand and Zn²⁺ ion

The TOPO ligands were exchanged to S²⁻ ion by adding to Na₂S solution. To fabricate the photoanode, the TiO₂ porous film is soaked in the solution of CdSe/S²⁻ QDs. To resolve the problem of instability and further improve the electron transfer at the QDs/TiO₂ interface, a second step ligand reaction process has been developed, which could transfer S²⁻ ion to a protective layer of ZnS by immersing the sensitized film into a Zn(Ac)₂ aqueous solution. The reaction occurs as follows:

After the reaction, the device can be assembled in the air environment as the ZnS is stable in such environment. The inorganic ligands exchange and further ionic reaction can remove long chain organic ligands instead of using an annealing process.

A ZnS coating with a wide bandgap is often used in QDSCs aiming to solve the problems of QDs instability and charges recombination.^{40,42} The traditional method to produce ZnS layer adopts successive ionic layer adsorption and reaction (SILAR). However after the creation of ZnS coating, there are organic ligands remaining in the device between the QDs and the ZnS

coating, which limits the efficiency of electron transport in the traditional SILAR method.⁴² On the contrary, the two-step method developed in this work can achieve ligand-free QDs in QDSCs, which may improve the electron transport more efficiently compared to the traditional SILAR method.

3.2.2 XPS analysis for generation of ZnS coating

The XPS data in Fig.5 provide the significant information about the generation of ZnS by ionic reaction of ligands and Zn²⁺ ion. All of the peaks are calibrated using C 1s (284.8 eV) as the reference. The elements of the composite film are able to be identified in the XPS wide-scan survey spectrum shown in Fig.5(a). The binding energies of Zn 2p_{3/2} and Zn 2p_{1/2} are identified to be the peaks at 1022.0 and 1045.0 eV, respectively, and are shown in Fig.5(b). Fig.5(c) shows two distinct bands by fitting the S 2p, and the deconvoluted binding energies of 161.8 and 163.0 eV are assigned to the S 2p_{3/2} and S 2p_{1/2} of a

Fig.5 X-ray photoelectron spectroscopy (XPS) of (a) wide-scan survey, (b) Zn 2p and (c) S 2p patterns of TiO₂/CdSe/ZnS films

Zn–S bond, respectively.^{51,52} The S 2*p* spectra show that the sum curve is mostly fitted the raw intensity. Consequently, this shows that most of S^{2-} ligands are successfully transformed to ZnS.

3.2.3 UV-Vis absorption of $TiO_2/CdSe/TOPO$, $TiO_2/CdSe/S^{2-}$, and $TiO_2/CdSe/ZnS$ composite films

The absorption spectrum of TiO_2 film with CdSe/TOPO QDs is shown in Fig.6 (black line), and exhibits an absorption peak around 518 nm. While the absorption onset of CdSe/ S^{2-} QD film is located at 523 nm. This red shift is a result of the delocalization of electron and hole wave functions due to electronic coupling caused by the decreased distance between QDs. Moreover the $TiO_2/CdSe/ZnS$ film is in the absorption with onset around 530 nm. The red shift of the composite film with ZnS coating leads to a $\sim 10\%$ increase in QDs due to the loss of quantum confinement of the electron wavefunction.⁵³

The absorption intensities of $TiO_2/CdSe/S^{2-}$ and $TiO_2/CdSe/ZnS$ films are higher than that of $TiO_2/CdSe/TOPO$ film by 5.0% and 6.5%, respectively. The absorption intensity reflects the QD adsorption amount in the TiO_2 films. After S^{2-} ion ligands exchange with TOPO, the adsorption amount of CdSe QDs improves. One possible reason is that the reduced steric effects following ligand exchange lead to easier osmosis in TiO_2 porous films in the sensitized process. However, the higher adsorption amount indicates reduced steric influences.

3.3 Photovoltaic performance of QDSCs

3.3.1 *J*–*V* properties of QDSCs

As shown in Fig.7, the photocurrent density–voltage (*J*–*V*) curves are measured under one sun illumination (AM1.5, 100 $mW \cdot cm^{-2}$). The characterizing parameters are summarized in Table 1. There are only a few studies of the inorganic ion ligands QDSCs, and they show the PCE of the device is relatively low at 0.9%.⁴⁵ Compared with the $TiO_2/CdSe/TOPO$ device, $TiO_2/CdSe/S^{2-}$ device shows an increased open circuit voltage (V_{oc}) and fill factor (FF), but a lower J_{sc} . The improvement of V_{oc} and FF may be because of the reduced resistance of photo-injection and electron recombination. However, the S^{2-} ligands are unstable in electrolytes and tend to be oxidized, which may cause degradation of the QDs in electrolytes. After ZnS is

Fig.6 UV-Vis absorption spectra of $TiO_2/CdSe/TOPO$, $TiO_2/CdSe/S^{2-}$, and $TiO_2/CdSe/ZnS$ films

Fig.7 *J*–*V* curves of $TiO_2/CdSe/TOPO$, $TiO_2/CdSe/S^{2-}$, and $TiO_2/CdSe/ZnS$ devices

Table 1 Photovoltaic parameters of QDSCs involved in Fig.7

Sample	$J_{sc}/(mA \cdot cm^{-2})$	V_{oc}/V	FF	PCE/%
$TiO_2/CdSe/TOPO$	4.16	0.46	0.51	0.98
$TiO_2/CdSe/S^{2-}$	2.82	0.49	0.58	0.80
$TiO_2/CdSe/ZnS$	5.01	0.57	0.61	1.75

formed, the J_{sc} increases to more than that of the $TiO_2/CdSe/TOPO$ device and the $TiO_2/CdSe/S^{2-}$ device. Meanwhile the V_{oc} further increases from 0.49 to 0.57 V. This method through ionic ligands exchange and ionic reaction could get a structure without organic ligand such as TOPO. However the CdSe/ZnS core/shell QDs contain organic ligand in synthesis process. The organic ligand between QDs and TiO_2 leads a relatively lower PCE and instabilities.²⁰

3.3.2 Stability of QDSCs

As shown in Fig.8, the stability of the devices is studied by efficiency attenuation spectra. After 90 min, the PCE retention of the $TiO_2/CdSe/TOPO$ device is still around 100%. However, the PCE of $TiO_2/CdSe/S^{2-}$ device decreases to less than 30%, which may result from the strong reductive property of S^{2-} ions, and thus to less stability than that of $TiO_2/CdSe/TOPO$ QDSCs. Sambur suggests that the stable and wide band gap material coating on QD surface could enhance the stability of QDs.²⁰ The XPS results verify the existence of ZnS. Prior to the ionic reaction of S^{2-} into ZnS, the TOPO ligands are exchanged to S^{2-} ligands, and S^{2-} should surround the QDs uniformly. This means that the subsequent ionic reaction would happen on the surface of QDs, and the produced ZnS coats the CdSe QDs. In the field of solar cell development, much research focuses on the generation of ZnS from ionic reaction and commonly defines the ZnS as a protective layer.^{15,20} The ZnS layer created by S^{2-} ion have a bandgap of 3.6 eV, which is larger than the bandgap of the CdSe QDs employed in this work. The transfer of S^{2-} ions to ZnS may be a very useful tool to enhance the stabilities of S^{2-} ligand capped QDs. The stability test of $TiO_2/CdSe/ZnS$ device clearly showed that the PCE exhibited no decrease in 90 min. Therefore the generation of ZnS through ionic reaction that induces a transfer from the unstable S^{2-} ligand to a stable semiconductor material greatly enhances the device stability.

Fig.8 Stability test spectra of $\text{TiO}_2/\text{CdSe}/\text{TOPO}$, $\text{TiO}_2/\text{CdSe}/\text{S}^{2-}$, and $\text{TiO}_2/\text{CdSe}/\text{ZnS}$ devices

3.3.3 IPCE characterization

The incident-photon-to-carrier conversion-efficiency (IPCE) is recorded at different incident light wavelengths ranging from 420 to 620 nm for $\text{TiO}_2/\text{CdSe}/\text{TOPO}$, $\text{TiO}_2/\text{CdSe}/\text{S}^{2-}$, and $\text{TiO}_2/\text{CdSe}/\text{ZnS}$ QDSCs, as shown in Fig.9. All of the samples show a maximum photocurrent response located at around 527 nm, which matches with the absorption spectra. Compared to the $\text{TiO}_2/\text{CdSe}/\text{TOPO}$ device, the $\text{TiO}_2/\text{CdSe}/\text{S}^{2-}$ QDSCs shows a decrease of photocurrent response, presumably because of the unstable S^{2-} ligand, which is agreement with J_{sc} in $J-V$ curves. After the ionic reaction, the $\text{TiO}_2/\text{CdSe}/\text{ZnS}$ device shows great improvement, and IPCE result boosts to 60% at 530 nm wavelength, which is also reflected by J_{sc} in $J-V$ curves. Compared with $\text{TiO}_2/\text{CdSe}/\text{TOPO}$ device, the IPCE of $\text{TiO}_2/\text{CdSe}/\text{ZnS}$ device increases from 40.1% to 60.5%, which is an increase of 50.9%. The IPCE can be expressed by the following formula (2):⁵⁴

$$\text{IPCE}(\lambda) = \text{LHE}(\lambda) \varphi_{\text{mi}} \eta_c \quad (2)$$

where, $\text{LHE}(\lambda)$ is the light-harvesting efficiency for photons of wavelength; φ_{mi} is the quantum yield for electron injected from the excited sensitizer in the conduction band of TiO_2 ; and η_c is the electron collection efficiency.

For the whole conversion starting from TOPO ligands and ending with the ZnS coating, the IPCE increase of 50.9% is much larger than the absorption intensity increase of 6.5%. The absorption intensity results also indicate the values of $\text{LHE}(\lambda)$ are almost same. The ZnS layer is not reacted with TiO_2 , thus η_c values will also remain unchanged. Therefore the increase of IPCE is caused by the enhancement of the quantum yield for electron injected process represented by φ_{mi} . The reasons for the increase in φ_{mi} increase may include two aspects. First, the electron transfer distance between QDs and TiO_2 is reduced. And second, ZnS coating decreases the recombination at the interface between TiO_2 and electrolyte.⁴²

3.3.4 EIS measurement

Electrochemical impedance spectroscopy (EIS) measurements are carried out to further confirm the interface resistance to forward electron transport in $\text{TiO}_2/\text{CdSe}/\text{TOPO}$, $\text{TiO}_2/\text{CdSe}/\text{S}^{2-}$ and $\text{TiO}_2/\text{CdSe}/\text{ZnS}$ devices. The illumination condition is

Fig.9 IPCE spectra of $\text{TiO}_2/\text{CdSe}/\text{TOPO}$, $\text{TiO}_2/\text{CdSe}/\text{S}^{2-}$, and $\text{TiO}_2/\text{CdSe}/\text{ZnS}$ QDSCs

an air mass (AM) of 1.5 G under a forward bias with a frequency range from 0.1 to 100 kHz to explore the electron transfer in the QDSC devices. The resistance at the $\text{TiO}_2/\text{QDs}/\text{electrolyte}$ interface reflects by the value of R_2 (the R_2 in the equivalent circuit represented in Fig.10 can be determined by the middle frequency (10–100 Hz) semicircle in the Nyquist plots).⁵⁵ The values found for R_2 are 278.1, 113.4, and 75.4 Ω for $\text{TiO}_2/\text{CdSe}/\text{TOPO}$, $\text{TiO}_2/\text{CdSe}/\text{S}^{2-}$, and $\text{TiO}_2/\text{CdSe}/\text{ZnS}$ devices, respectively. When the TOPO is replaced by S^{2-} the R_2 decreases by less than half. A smaller ligands such as S^{2-} ions improve the forward electron transport, which is consistent with the conclusions in Ref. 50. Fortunately the generation of the ZnS layer further decreases the interface resistance. It is possible that the S^{2-} ions are unstable and the charges of ions impede the electron transport. Theoretically, reduction of interface impedance can improve the FF and V_{oc} in $J-V$ analysis,^{56,57} the similar variations are found in this work and pointed out in the discussion.

3.3.5 IMVS and IMPS measurement of QDSCs

To explore the influence of ligand exchange and ionic reaction on the electron lifetime and diffusion in QDSCs, the IMVS and IMPS spectra are collected. The IMVS experiment uses the same intensity perturbation as used in IMPS, but measures the periodic modulation of the photovoltage, giving the information of electron lifetime under open-circuit conditions.⁵⁸

Fig.10 Typical Nyquist plots of $\text{TiO}_2/\text{CdSe}/\text{TOPO}$, $\text{TiO}_2/\text{CdSe}/\text{S}^{2-}$, and $\text{TiO}_2/\text{CdSe}/\text{ZnS}$ QDSC devices under illumination conditions

The electron lifetime can be obtained from the IMVS plot by defining the life time (τ_d), to be,⁵⁹

$$\tau_d = (2\pi f_{\min}(\text{IMVS}))^{-1} \quad (3)$$

where, $f_{\min}(\text{IMVS})$ is determined by the frequency of the minima in types of IMVS plots. As shown in Fig.11(a), the electron lifetime of the $\text{TiO}_2/\text{CdSe}/S^{2-}$ device increases compared with the $\text{TiO}_2/\text{CdSe}/\text{TOPO}$ device, and improves further when the S^{2-} ions react and create the ZnS layer. The enhancement of electron lifetime is due to the stronger effect of retarding charge recombination. It indicates that the ZnS layer has a more strengthened effect of retarding dark reaction than that of S^{2-} ligand. The results are also accorded with the results of V_{oc} .

The IMPS measures the periodic photocurrent response of the device to a small sinusoidal perturbation of the light intensity superimposed on a larger steady background level. This provides information about the dynamics of charge transport and back-reaction under short-circuit conditions.⁶⁰ An order of magnitude estimate of a mean transit time (τ_c) for photogenerated electrons can be obtained from the frequency minimum in the complex plane IMPS plot, and the value of τ_c follows the formula (4):⁵⁹

$$\tau_c = (2\pi f_{\min}(\text{IMPS}))^{-1} \quad (4)$$

where, $f_{\min}(\text{IMPS})$ is determined by the frequency of the minima in types of IMPS plots. As shown in Fig.11(b), the collection time of the $\text{TiO}_2/\text{CdSe}/S^{2-}$ device is increased compared with $\text{TiO}_2/\text{CdSe}/\text{TOPO}$ device, which means that the electron diffusion in TiO_2 film is slowed. To some extent, the S^{2-} ions on the TiO_2 surface create a large negative charge density and

influences the electron diffusion. For this reason, the J_{sc} and IPCE values of $\text{TiO}_2/\text{CdSe}/S^{2-}$ QDSCs are lower than those of $\text{TiO}_2/\text{CdSe}/\text{TOPO}$ QDSCs. When the S^{2-} ions are reacted to ZnS layer, the collection time decreases markedly, and the electron diffusion in TiO_2 film is faster than that in $\text{TiO}_2/\text{CdSe}/\text{TOPO}$ and $\text{TiO}_2/\text{CdSe}/S^{2-}$ devices. From the discussion concerning the EIS values, we found that the ZnS layer is the most favorable to the electron injection process. The results indicate that of all the samples the $\text{TiO}_2/\text{CdSe}/\text{ZnS}$ QDSCs should have the best performance in J_{sc} , which is also reflected by IPCE data.

4 Conclusions

In summary, the CdSe QDs with inorganic ligands are exchanged from TOPO ligands and successfully used in *ex situ* QDSCs. A ZnS layer created through ionic reaction is adopted to improve the stability of the device. The fabricated $\text{TiO}_2/\text{CdSe}/\text{ZnS}$ device shows a reduced resistance of 75.4Ω as is expected from the shorter functional ligand, compared with 278.1Ω in the reference $\text{TiO}_2/\text{CdSe}/\text{TOPO}$ device, and the corresponding efficiency increases from 0.98% to 1.75%. Stabilization of the device is accomplished by ZnS coating, and the efficiency attenuation experiment shows 100% performance remaining prolonged to 90 min. We have therefore supplied an efficient method to improve device performance using inorganic ion ligand and also to stabilize the QDs by ionic reaction to create a protective coating.

Supporting Information: available free of charge via the internet at <http://www.whxb.pku.edu.cn>.

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Fig.11 (a) IMVS and (b) IMPS spectra of $\text{TiO}_2/\text{CdSe}/\text{TOPO}$, $\text{TiO}_2/\text{CdSe}/S^{2-}$, and $\text{TiO}_2/\text{CdSe}/\text{ZnS}$ devices

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