RSC Advances

Optimizing the deposition of CdSe colloidal quantum dots on TiO₂ film electrode *via* capping ligand induced self-assembly approach

Xinxin Meng, Jun Du, Hua Zhang, and Xinhua Zhong*

Key Laboratory for Advanced Materials, Institute of Applied Chemistry, East China University of Science and Technology, Shanghai 200237, China

E-mail: zhongxh@ecust.edu.cn

Fax/Tel: +86 21 6425 0281

Abstract

The deposition method for immobilizing quantum dots on TiO$_2$ film electrode is crucial for the photovoltaic performance of the resulting quantum dot sensitized solar cells (QDSCs). The recently developed capping ligand-induced self-assembly approach has been demonstrated to be an effective deposition route with fast, dense and uniform immobilization of pre-prepared colloidal QDs on TiO$_2$ film electrode. In order to make this technique more reproducible and applicable, the influences of variable experimental parameters, including pH, free ligand, deposition temperature, and QD concentration, on the loading amount and photovoltaic performance of the resulting cell devices have been systematically investigated with use of CdSe QDs as a model. The intrinsic mechanism of the effects from these investigated variables have been elaborated primarily. An averaged power conversion efficiency of 6.49% (J_{sc} = 15.91 mA/cm^2, V_{oc} = 0.618 V, FF = 0.660) under the irradiation of full one sun (AM 1.5G) has been obtained for the CdSe-based QDSCs under the optimum QD deposition conditions.

1. Introduction

Quantum dot sensitized solar cells (QDSCs) have been regarded as a promising candidate for low-cost third-generation solar cells because of the distinguished advantages of colloidal QDs such as tunable band gap, high extinction coefficient, multiple exciton generation (MEG), large dipole moment, and solution processability.[1-5] Whereas, the current best power conversion efficiency (PCE) of QDSCs is only in the level of 7-8%,[6-8] inferior to those of its analogue dye sensitized solar cells (DSCs, in the level of 12-13%).[9,10] The current moderate performance of QDSCs is partially ascribed to the low QD loading on TiO_2 film electrode, which plays an crucial role in determining the light-harvesting capability, and therefore directly relates to the photocurrent and PCE of the resultant cell devices.

Tethering QDs on TiO_2 mesoporous film electrode at monolayer or sub-monolayer coverage is a prerequisite for high light-harvesting capacity and therefore a high photocurrent and high PCE of the resultant cell device.[11] Traditionally, two general approaches have been developed to tether QDs on TiO_2 film electrodes: 1) direct growth of QDs through chemical bath deposition (CBD),[12-15] successive ionic layer adsorption and reaction (SILAR) techniques,[16,17] or electrodeposition;[18] 2) post-synthesis assembly using pre-synthesized colloidal QDs via the direct attachment,[19-21] electrophoretic deposition (EPD),[22-24] or linker-assisted assembly route.[6-8,25-27] The linker-assisted assembly approach can be divided into two methods.[28,29] In the first method, TiO_2 film electrode is firstly functionalized with bifunctional linker molecules and then immersed into a QD dispersion in nonpolar solvents. In the second method, *i.e.* capping ligand-induced self-assembly (CLIS) method, bifunctional ligand molecules (mainly thiolcarboxylic acid) capped water-soluble QDs are immobilized onto the untreated TiO_2 film electrode surface induced by the affinity between terminal carboxylic group of the capping molecules and TiO_2.[30-33] In this method, the deposition of QD on TiO_2 film electrode is similar to the case of carboxylic terminated molecular dyes absorbed onto TiO_2 electrode in DSC system. The CLIS method for sensitization of TiO_2 electrode has become more and more popular in the construction of high efficiency QDSC recent years because the superior electronic properties of the pre-synthesized colloidal QDs after bound on TiO_2 substrate can be retained by this method.[29] Furthermore, the interfacial properties between QDs and TiO_2 substrates could be flexibly designed by CLIS method. Benefited from the CLIS method for the electrode sensitization, the PCE of QDSCs has been improved steadily from 4-5% to 8-9%.[6-8,34-38]

Although the CLIS method has been adopted for the construction of a series of record efficiency QDSCs, the influence of experimental parameters in the QD deposition process on the performance of the resulting cell devices has not been investigated and optimized systematically. Furthermore, some divergent viewpoints and even paradoxical conclusions exist in this sensitization method. For example, some previous literatures have demostreated that the CdSe QDs loading amount could be effectivly enhanced when the pH value match the point of zero charge of TiO_2 nanoparticles (low to pH 7).[31,39] While, in some other reports, [40,41] higher pH (10-12) has been demonstrated to favor the loading of CdTe QDs on TiO_2 film electrodes. Based on these results, it is imperative that the experimental parameters for QD deposition *via* CILS method should be investigated and optimized systematically, since these parameters affect the amount of QDs loading and the photovoltaic performance of the resultant cell devices.

Herein, we focus on the investigation of the influences from experimental parameters in the process of CdSe QD deposition with use of CILS method, on the amount of QD loading and photovoltaic performance of the resultant cell devices. The investigated experimental variables include: pH of QD solution, free ligand, deposition temperature, and concentration of QDs. The experiment results demonstrate that both the deposition temperature and concentration of QD solution have nearly no influence, while the free capping ligand, and pH play heavy effects on the amount of QD loading and the performance of the resultant cell devices. Under the optimum deposition conditions, an average PCE of 6.49% has been obtained for CdSe based QDSCs. It is expected that this work could pave a way for the construction of high efficiency QDSCs.

2. Experimental section

Chemicals

Oleic acid (90%), and 3-mercaptopropionic acid (MPA, 98%) were received from Alfa Aesar. Oleylamine (OAm, 95%), trioctylphosphine (TOP, 90%), selenium powder (200 mesh, 99.99%), 1-octadecene (ODE, 90%), and cadmium oxide (CdO, 99.99%) were obtained from Aldrich. All reagents were used as received without further treatments.

Preparation of CdSe QDs and sensitization of photoanode

The TiO_2 mesoporous film electrode with use of fluorine doped SnO_2 (FTO) glass substrate consists of 9.0 ± 0.5 μm transparent layer and 6.0 ± 0.5 μm scattering layer was prepared according to our previous report.[42] The original oil-soluble OAm-capped CdSe QDs with the first excitonic absorption peak at ~ 618 nm was synthesized through the hot-injection method.[43] The optical properties and the TEM image of the OAm-capped CdSe QDs were shown in Fig. S1 of ESI.† The water soluble MPA-capped CdSe QDs were obtained from the original oil-soluble OAm-capped CdSe QDs *via* ligand exchange procedure with use of MPA as the phase transfer reagent.[44] The purified MPA-capped CdSe QDs were re-dispersed in deionized water with resulting QD concentration of 3.6 μM (corresponding absorbance at 618 nm is 2.0). Then MPA was added into the above solution with MPA concentration of 0.1 M and the pH value of the solution was adjusted to 10.0 with the use of 10% NaOH solution. The obtained QDs solution can be used for the sensitization of TiO_2 film electrode by dipping the mesoporous films into the QDs solution and keeping for 2 h at room temperature of $25^{o}C$. Then the film was rinsed by water and ethanol and dried. The resultant film were further overcoated with ZnS layer by dipping into 0.1 M $Zn(OAc)_2$ and Na_2S solutions alternately for 1 min per dip with four cycles and SiO_2 layer by immersing in a tetraethoxysilane (TEOS) solution at 35 ^{o}C for 2 h.[7] The CdSe-sensitized photoanodes were achieved. In the controlled experiments, QD solutions with different compositions were adjusted accordingly.

Assembly of solar cells

The solution of polysulfide electrolyte was prepared by adding Na_2S (2.0 M), S powder (2.0 M), and KCl (2.0 M) into deionized water. The Cu_2S/brass counter electrodes were obtained

by immersing a brass foil in HCl solution (1.0 M) at 70 ^{o}C for 5 min, followed by immersing in polysulfide electrolyte solution (2.0 M) for 10 min. The cell devices were assembled by clamping the Cu_2S counter electrode and QD-sensitized photoanode using a binder clip followed by injecting 10 μL of electrolyte.

Characterization

The UV-vis absorption and PL emission spectra were measured on an UV-visible spectrophotometer (Shimadzu UV-3101 PC) and a fluorescence spectrophotometer (Cary Eclipse Varian) respectively. Current-voltage characterization (*J–V* curves) was carried out on a Keithley 2400 source meter and an AM 1.5G solar simulator (Oriel, Model No.94022A) was used with the illumination intensity at 100 mW/cm^2. The photoactive area was settled at 0.237 cm^2 by covering a black metal disk. Incident photon-to-current conversion efficiency (IPCE) spectra were measured using a Keithley 2000 multimeter, and a spectral product DK240 monochrometer with 300 W tungsten lamp. Transition electron microscopy (TEM) images were obtained on a JEOL JEM-2100 microscope with an accelerating voltage of 200 kV. The analysis of dynamic light scattering (DLS) of the QDs aqueous solution was measured through a Zeta Sizer nano series laser light scattering system (Malvern Instrument Corporation)

3. Results and discussion

In order to achieve high efficiency QDSCs, the dense and uniform distribution of QDs on TiO$_2$ film electrode is crucial. Due to the relative chemical stability and short carbon chain length, MPA is the most used bifunctional molecule linker molecule in capping ligand-induced self-assembly (CLIS) method to tether QDs onto mesoporous TiO$_2$ film in the construction of high efficiency QDSCs. To demonstrate the influence of the experimental variables in the process of CLIS on the performance of the resulting CdSe cells and therefore get the optimal experimental conditions and best photovoltaic performance, the deposition experimental parameters, such as the pH of QD solution, presence of free ligand, deposition temperature and QDs concentration, have been systematically investigated. CdSe QD with the first absorption peak at 618 nm was selected as the sensitizer due to the excellent photovoltaic performance of the resulting QDSCs and the reproducibly synthetic method for it.[45] All adopted CdSe QDSCs were constructed employing polysulfide electrolyte as redox media and Cu$_2$S/brass as counter electrode. To minimize the sampling deviation, average photovoltaic performance of five cells in parallel under each studied condition was used to evaluate the effect from the studied variables.

Influence of pH value in the absence of free ligand

Since the protonation and de-protonation of the capping ligand around QD surface and the surface electronic charge of TiO$_2$ substrate are heavily dependent on pH value of the solution media,[46] the pH value in QD aqueous solution is expected to influence the deposition of QD on TiO$_2$ electrode and the performance of the resultant cell devices consequently. The effect of pH in QD aqueous solution with the absence of free MPA ligand was studied, while all the other parameters such as TiO$_2$ film electrode thickness and configuration, the compositions in each QD solutions except the pH values, and the deposition temperature are kept constant as specified in the Experimental section in the process of QD sensitization *via* CLIS method. Acknowledged from the literature report,[43,47] MPA-capped CdSe QDs are well-dispersed in weak basic media, while show a progressive agglomeration and precipitation in strong basic or acidic media. Our own experimental results also indicate that the obtained MPA-capped CdSe QD aqueous dispersion can be stable only in the pH range of 8-12, therefore in this

6

study, the investigated pH value of QD solution is set at the range of 8.0 to 12.0. In the experiment, to each QD aqueous solutions with different pH (8.0, 9.0, 10.0, 11.0 and 12.0), 5 pieces of TiO_2 film electrodes from the same batch were immersed for certain period, and corresponding absorption spectra were measured to reflect the loading amount of CdSe QDs on TiO_2 film electrode. It is noted that in the absorption spectra study, in order to avoid the scattering effect from the large sized particle, the used TiO_2 film electrodes, which are different from those used for the construction of cell devices, contain only 5.0 μm transparent layer with dimension of 2.0×1.0 cm^2. The temporal evolution of the absorption spectra of the sensitized film electrodes under CdSe QD solution with different pH values were measured to monitor the amount of CdSe QD loading. From these absorption spectra, the temporal evolution of absorbance at the first absorption excitonic peak (herein 618 nm) was then obtained and illustrated in Fig. S2a of ESI. † It was found that the absorbance (i.e. the loading amount of CdSe QD sensitizers) approached the saturation values in a period of 2 h under each pH condition and no further enhancement was observed with over extending the deposition time. It was found that saturation adsorption time is 2 h and no more QDs can be anchored onto TiO_2 film after then. The absorption spectra with maximum loading amount under different pH conditions are shown in Fig. 1a with corresponding photographs of the film electrode in the inset. The absorption peaks of five sensitized film electrodes stay at nearly the same position as that of colloidal QD solution at around 618 nm. This indicates that the agglomeration of QD particles has not occurred. As can be seen from Fig. 1a, the intensity of the absorption peak of different pH based QD-sensitized TiO_2 films are in the sequence of pH 12.0 > pH 11.0 > pH 10.0 > pH 9.0 > pH 8.0 with normalize ratio of 3.04 : 2.89 : 2.67 : 2.28 :1. Due to the absorbance is directly related to the loading amounts of QDs onto TiO_2 films, the amount of QD loading also obey the same sequence of pH 12.0 > pH 11.0 > pH 10.0 > pH 9.0 > pH 8.0 with relative ratio of 3.04 : 2.89 : 2.67 : 2.28 :1. Furthermore, systematically deepen coloration of the sensitized electrodes as shown in the inset of Fig. 1a also demonstrates this variation trend. From this result, it is clearly demonstrated that high pH value in QD solution favors the QD loading on TiO_2 electrode.

Due to the large size of QD particle related to the mesoporous channel in the film

electrode, the prerequisite for the high QD loading is the availability of the well-dispersible QDs aqueous solution, *i.e.* QD is dispersed in the form of isolated particle without agglomeration. The average hydrodynamic diameter of QD under different pH solutions were measured by dynamic light scattering (DLS), and the results are shown in Fig. 1b. It was found that the average hydrodynamic diameter of QD turns larger with decreasing pH value of QD solutions. This means that agglomeration of QD in solution occurs with decreasing pH in solution. This result primarily indicates that the dispersibility of QD determines the amount of QD loading on TiO_2 film electrode. High pH value in QD solution favors the dispersibility of QD, and consequently benefits the QD loading. The reason is ascribed to the de-protonation of the carboxylic group from the QD surface binding MPA ligand at high pH and render the surface of QD negative charged. The mutual electrostatic repulsion of QD particle therefore improve the colloidal stability and dispersibility undoubtedly. Another factor for the effect of pH is that the high pH value favors the de-protonation of the thiol group in MPA and the formation of thiolate group. The interaction between MPA ligand and CdSe QDs could be considered as a coordination bond. According to previous reports, [47-50] the binding strength for thiolate (deprotonated products of thiols) to Cd atom at the QD surface is about 40 times higher than that for the thiol group to Cd. The strengthen interaction between capping ligand and QD surface would improve the colloidal stability and dispersibility of the resultant QD, and therefore enhance the QD loading amount on TiO_2 film electrode. High pH value in QD solution favors the dispersibility of QD, and consequently benefits the QD loading. High QD loading means more incident photons can be harvested and higher photocurrent and PCE are expected in the resulting cell devices. To confirm this, the corresponding photovoltaic performance of the resultant solar cells was investigated below.
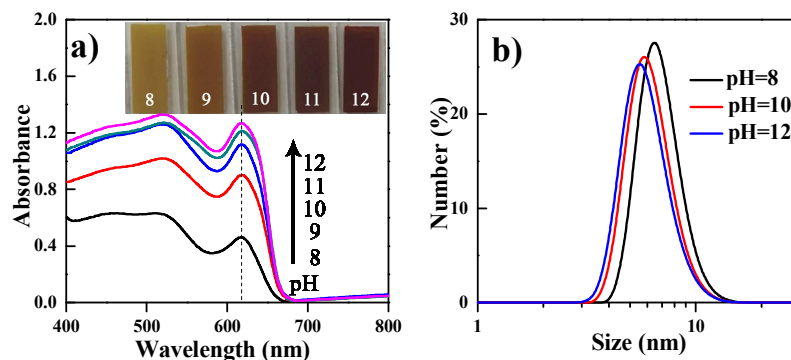
Fig. 1 (a) Absorption spectra of CdSe QD-sensitized TiO_2 films under different pH conditions. Inset: photographs of corresponding TiO_2 films. (b) Dynamic light scattering graphs of three pH values based CdSe QDs aqueous solution

After the saturation of QD sensitization, regenerated Sandwich-type QDSCs were assembled with use of the sensitized film electrode as photoanode, Cu_2S/brass as counter electrode, and S_n^{2-}/S^{2-} aqueous solution as electrolyte media. The *J-V* curves of five champion QDSCs corresponding to photoanode deposition under different pH conditions as discussed above were measured under the illumination of AM 1.5G solar simulator at the intensity of one full sun (100 mW/cm^2), and the results are presented in Fig. 2a and the corresponding average photovoltaic parameters are summarized in Table 1 and details for each cell are listed in Table S1 of ESI.† Both the average open-circuit voltage (V_{oc}) and fill factor (FF) show no significant difference among five cells, while the average short-circuit density (J_{sc}) have a significant enhancement from 5.26 to 15.30 mA/cm^2 with the increase of pH value in QD solution as expected. The ratio of J_{sc} of each pH based QDSCs device is 1 : 2.26: 2.67 : 2.82 : 2.91 from pH 8 to 12, which is highly consistent with the ratio of absorbance corresponding to sensitized photoanodes under different pH conditions. Benefited from the higher J_{sc}, the cell corresponding to QD deposition at pH 12 exhibits the best PCE of 6.03 with V_{oc} of 0.614 V, J_{sc} of 15.30 mA/cm^2 and FF of 0.642.

Table 1 The average photovoltaic performance of solar cells based on different pH of CdSe QD aqueous solutions

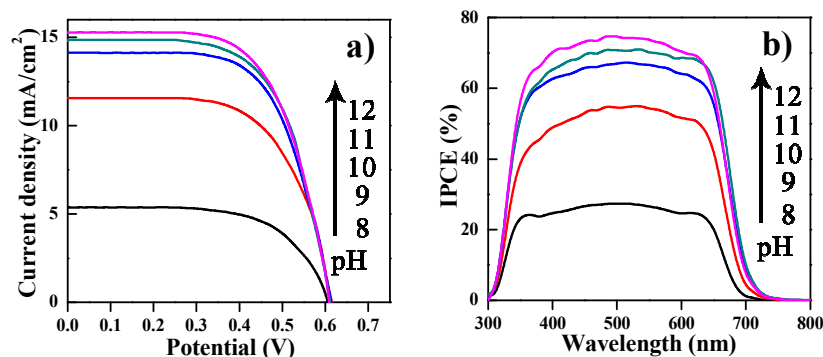| pH	V_{oc} (V)	J_{sc} (mA/cm^2)	FF	PCE (%)
8	0.613	5.26	0.653	2.14±0.07
9	0.614	11.90	0.643	4.70±0.10
10	0.611	14.04	0.640	5.49±0.11
11	0.610	14.85	0.645	5.83±0.06
12	0.614	15.30	0.642	6.03±0.09

Fig. 2 (a) *J-V* curves and (b) IPCE curves of CdSe QDSCs prepared with different pH in the absence of free ligands.

The generation of higher photocurrent under high pH value is further verified by the incident-photo-to-carrier conversion efficiency (IPCE) spectra of five pH based QDSCs as shown in Fig. 2b. The curves of IPCE show an identical spectral profile and photoresponse range for five different cell devices. Consistent with the trend of absorbance, the highest IPCE value for each QDSCs increases from 27.42 to 74.65 % with the increase of pH, which can be explained by the superior light-harvesting efficiency as more loading amount of QD sensitizers at the condition of high pH value.

Influence of free ligand in QDs aqueous solution under pH 12.0

The above results indicate that the QD dispersity has a heavy effect on the amount of QD loading. Previous reports on colloidal QD solutions tell us that the presence of free capping ligands can improve remarkably the dispersibility of QD solutions.[51-53] The instability of the

QDs dispersion is mainly caused by the ligands desorption from the surface of QD. In the presence of free ligand in QD solution, free ligand combined with QD and kept the nanocrystals stable in solution for a longer period of time. Therefore, the effect of the free ligand MPA in the QD solution was studied. In this experiment, the effect of the concentration of free ligand MPA in the QD solution with the pH of 12 was investigated. Our experimental results indicate that stable QD aqueous solutions can be obtained with the free ligand MPA in the concentration range of 0-0.3 M. Therefore, the investigated MPA concentration range was set at 0-0.3 M. Similar to the above experiment, except for the concentration of MPA, all the other experimental variables are the same. To each QD aqueous solutions with different MPA concentration (0, 0.05, 0.1, 0.3 M), 3 pieces of TiO_2 film electrodes from the same batch are immersed and the relative loading amount was characterized by absorption spectra of the sensitized film electrode, which is shown in Fig. 3a. The saturation adsorption time of CdSe QDs onto TiO_2 electrode is 2 h and the absorbance can not be enhanced by extending the deposition time, and the curves of time evolution of the absorption spectra at the first absorption peak of the corresponding samples were shown in Fig. S2b of ESI. † All the absorption spectra have the similar profile but with different absorption intensity. The intensity of the absorption peak follows the sequence of 0.3 M ≈ 0.1 M ＞ 0.05 M＞ 0 M with normalize ratio of 1 : 1 : 0.95 : 0.87. This result is also verified by the coloration of corresponding photograph of sensitized film electrode shown in the inset of Fig. 3a. This result clearly indicates that with the presence of free ligand in QD solution (herein the proper concentration in the range of 0.1-0.3 M), the amount of QD loading can be enhanced by ~10%. In order to further determine the enhancement of QD loading is ascribed to the improvement of QD dispersibility in solution, DLS measurement was also carried out for QD solution with presence of different concentrations MPA and the results are shown in Fig. 3b. It is found that the average hydrodynamic diameter of QD in solution with different MPA concentrations follows the sequence of 0.3 M ≈ 0.1 M < 0.05 M < 0 M. Clearly, the presence of free ligand MPA in QD dispersion favors the reduction of hydrodynamic diameter of QD, and this brings forward to higher QD loading in the film electrode. Therefore, we can conclude that the enhancement of QD loading is benefitted from the improvement of QD dispersibility. The -S-Cd bond between capping ligand MPA and the surface of QD is not

strong enough, and the dissociation and re-coordination of the ligand in QD dispersion is a dynamic process. With the detachment of MPA from QD, agglomeration of QDs would occur. While, with the presence of free MPA, the dissociation of the ligand from QD surface would be hindered, and therefore the colloidal stability and dispersibility of QD is improved.
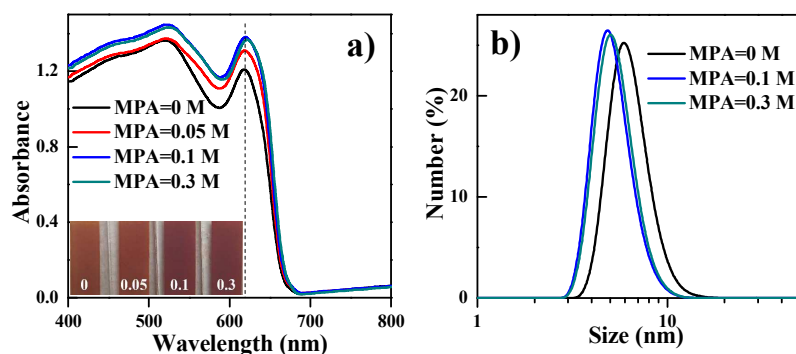

Fig. 3 (a) Absorption spectra of CdSe-sensitized TiO_2 films under different concentration of free MPA conditions. Inset: photographs of corresponding TiO_2 films. (b) Dynamic light scattering graphs of three free MPA concentrations based CdSe aqueous solution.

Similarly, photovoltaic performance of the cell devices derived from the photoanode deposited under different free ligand concentrations were measured under standard conditions. The *J-V* curves for champion cells are shown in Fig. 4a, the average performance from 5 samples in parallel are listed in Table 2, and the photovoltaic parameters for each cell are available in Table S2 of ESI.† As found in Table 2, cell devices corresponding to photoanodes with higher QD loading under the condition of free MPA concentration of 0.1 to 0.3 M have higher PCE in comparison with cells of lower QD loading under the absence of MPA. The higher PCE is derived from the higher J_{sc} (15.87, 15. 91 *vs.* 15.63, 15.21 mA/cm^2), while the V_{oc} and FF keep nearly constant for all cell devices. IPCE results as shown in Fig. 4b give the same observation. Cell device corresponding to absence of free MPA and 0.05 M MPA give lower IPCE value in comparison with cell devices corresponding to 0.1-0.3 M MPA. Both the optical and photovoltaic results indicate that the presence of free MPA with concentration in the range of 0.1-0.3 M in CdSe QD solution favors the loading of QD on TiO_2 film electrode, and consequently benefits the performance of the resulting cell devices.

Table 2 Average photovoltaic performance of solar cells based on different concentrations of free MPA ligand

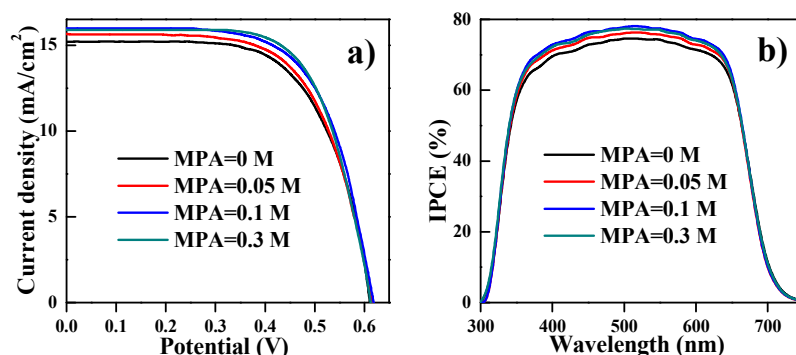| MPA (M)	V_{oc} (V)	J_{sc} (mA/cm^2)	FF	PCE (%)
0	0.612	15.21	0.642	5.96±0.06
0.05	0.618	15.63	0.649	6.27±0.06
0.1	0.618	15.91	0.660	6.49±0.07
0.3	0.617	15.87	0.661	6.48±0.08

Fig. 4 (a) The *J-V* curves and (b) resulted IPCE curves of QDSCs prepared under different concentrations of free MPA ligand

Influence of pH value in the presence of 0.1 M free ligand

In the above experiment, the effect of pH was studied in the absence of free ligand. While, the presence of free ligand has also a significant influence on the QD loading. Therefore, the experiment of the influence of pH value in the presence of 0.1 M free MPA was designed and employed. Similar to above experiments, except the pH, all the other experimental variables are the same. To each CdSe aqueous solution with presence of 0.1 M free MPA but with different pH (8, 9, 10, 11, 12), TiO$_2$ film electrodes were immersed for 2 h and then absorption spectra of the sensitized film electrodes were measured and shown in Fig. 5a. Different from the case of absence of free MPA, wherein the pH in QD solutions has a remarkable influence on the QD loading, herein the pH has almost no effect on the QD loading with nearly identical absorption peak intensity in the absorption spectra. The *J-V* curves for champion cells are shown in Fig. 5b, the average performance from 5 samples in

parallel are listed in Table 3, and the photovoltaic parameter for each cell are available in Table S3 of ESI.† Correspondingly, *J-V* measurement results from all the five groups of cells show also the same performance for the champion cells in each group of cells. These experiment results suggested that with the presence of 0.1 M free MPA in the QD solution, the loading amount of QDs on TiO_2 film electrode is insensitive to the pH of QD solution, and the appropriate pH value range can be expanded to a wide range of 8-12. This brings forward the high reproducibity for the CLIS deposition approach.
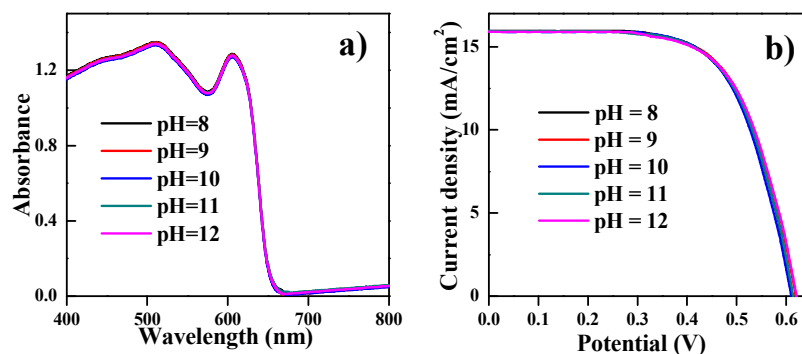

Fig. 5 (a) UV-vis absorption spectra of CdSe QD-sensitized films which contains only transparent layer prepared under different pH value with 0.1 M free MPA ligands, (b) the *J-V* curves of five pH based CdSe-sensitized QDSCs.

Table 3 Average photovoltaic performance of CdSe QDSCs based on different pH values with the presence of 0.1 M free MPA ligand

pH	V_{oc} (V)	J_{sc} (mA/cm^2)	FF	PCE (%)
8	0.617	15.96	0.652	6.43±0.07
9	0.618	15.93	0.655	6.45±0.05
10	0.619	15.93	0.658	6.49±0.06
11	0.618	15.91	0.655	6.45±0.03
12	0.617	15.94	0.656	6.46±0.07

Influence of deposition temperature and QD concentration

In the above experiments, the optimum pH value and the concentration free MPA in CdSe QD solution have been ascertained. Herein, the effect of other variables, such as the

14

temperature for the deposition process and the concentration of QD in solution, on the QD loading were also exploited. In the temperature experiments, QD solution with pH of 10.0, 0.1 M of free MPA was stored in a fridge with temperature of 5 ^{o}C, or in an oven with temperature of 25, or 50 ^{o}C, respectively. It is noted that, the container for QD solution is closed in the whole deposition process to avoid the evaporation of solvent. Experimental results indicate that the period for reaching the saturation loading amount is extended to about 4 h when the solution temperature is lowered to 5 ^{o}C, while only 1.0 h is needed to reach the saturation loading amount when the solution temperature is raised to 50 ^{o}C. This observation is reasonable since the both diffusion rate of QD and the coordination reaction rate for the terminal carboxyl and TiO_2 are temperature-dependent. However the absorption spectra for the sensitized film electrodes under different deposition temperatures, as shown in Fig. S3 of ESI,† gives a nearly identical peak intensity corresponding to the equal amount for QD loading. Furthermore, the photovoltaic measurement results indicate that all the cell devices corresponding to different deposition temperatures show nearly the same performance as listed in Table 4 and Table S4 of ESI.† Hence we can conclude that the deposition temperature can influence the deposition rate, but has no observable effect on the loading amount and on the performance of the resultant cell devices. Therefore, from the view of convenience, the room temperature of 25 ^{o}C is suggested to adopt in the CLIS.

Table 4 The average photovoltaic performance of CdSe QDSCs based on different QD deposition temperatures, and concentrations of CdSe QD solution.

		V_{oc} (V)	J_{sc} (mA/cm^2)	FF	PCE (%)
Temperature (^{o}C)	5	0.619	15.93	0.649	6.41±0.06
	25	0.615	15.91	0.650	6.41±0.09
	50	0.615	15.92	0.654	6.40±0.08
Concentration (μM)	3.6	0.618	15.87	0.658	6.45±0.10
	1.8	0.616	15.94	0.658	6.46±0.05
	0.72	0.617	15.94	0.654	6.43±0.06
	0. 36	0.616	15.83	0.656	6.40±0.10

15

Meanwhile, the influence of QD solution concentration was also studied. The investigated QD concentrations were: 3.6 μM, 1.8 μM, 0.72 μM, and 0.36 μM, which corresponds to absorbance at excitonic peak of 2.0, 1.0, 0.4, and 0.2, respectively. Similar to the influence of temperature, with the decrease of QD concentration, the saturation deposition time was extended to about 24 h corresponding to QD concentration of 0.36 μM from the 2 h corresponding to QD concentration of 3.6 μM. However, from the absorption spectra of four concentrations based CdSe-sensitized TiO_2 electrode films shown in Fig. S3 of ESI,† the maximum loading amount for QD on TiO_2 film electrode is nearly insensitive on the QD concentration. Correspondingly, the photovoltaic performances for the resulting cell devices are also insensitive to the QD concentration during the CLIS process for QD uploading on TiO_2 electrode, as can be seen from Table 4 and Table S5 of ESI.† Therefore, the concentration of QD solution has no significant effect on the amount of QD loading, and on the performance of the resultant cell devices. For purpose of time saving, the concentration of QDs at 3.6 μM was selected in the CLIS process.

4. Conclusion

The influence of experimental parameters during the CLIS process, including pH value, free ligand MPA, temperature and concentration of QD solution on the amount of QD loading on TiO_2 film electrode and on the photovoltaic performance of the resulting cell devices have been systematically investigated and optimized. The experimental results show that the adsorption temperature and concentration of QD have nearly no effects, while pH value and the presence of free ligands MPA have heavy influences. The optimum conditions for the CLIS process are that the QD aqueous solutions contain 0.1-0.3 M free MPA with pH in the range of 8-12. Under the optimum deposition condition, CdSe based QDSC with average PCE of 6.49% under 1 full sun intensity can be obtained with high reproducibility. It is expected that this work could provide a guide to effective deposition of QDs for high efficiency QDSCs with high reproducibility.

Acknowledgements

† Electronic supplementary information (ESI) available: The TEM image and optical properties of the OAm-capped CdSe QDs. The details of photovoltaic performance of each tested solar cell based on different pH values of QDs aqueous solution, different concentrations of free MPA ligands, different pH of QDs solution with free ligands, different deposition temperatures and different concentrations of QDs solution. Temporal evolution of the absorbance at first excitonic absorption peak of CdSe-sensitized TiO_2 films deposition under QD aqueous solution with different pH values and different MPA concentrations. UV-vis absorption spectra of CdSe-sensitized films under different deposition temperatures and concentrations of QD solution

References

1 P. V. Kamat, K. Tvrdy, D. R. Baker and J. G. Radich, *Chem. Rev.*, 2010, **110**, 6664.

2 I. J. Kramer and E. H. Sargent, *Chem. Rev.*, 2014, **114**, 863.

3 J. B. Sambur, T. Novet and B. A. Parkinson, *Science*, 2010, **330**, 63.

4 O. E. Semonin, J. M. Luther, S. Choi, H. Y. Chen, J. Gao, A. J. Nozik and M. C. Beard, *Science*, 2011, **334**, 1530.

5 G. Zhang, S. Finefrock, D. Liang, G. G. Yadav, H. Yang, H. Fang and Y. Wu, *Nanoscale*, 2011, **3**, 2430.

6 Z. Pan, I. Mora-Seró, Q. Shen, H. Zhang, Y. Li, K. Zhao, J. Wang, X. Zhong and J. Bisquert, *J. Am. Chem. Soc.*, 2014, **136**, 9203.

7 K. Zhao, Z. Pan, I. Mora-Seró, E. Canovas, H. Wang, Y. Song, X.-Q. Gong, J. Wang, M. Bonn, J. Bisquert and X. Zhong, *J. Am. Chem. Soc.*, 2015, **137**, 5602.

8 S. Jiao, Q. Shen, I. Mora-Seró, J. Wang, Z. Pan, K. Zhao, Y. Kuga, X. Zhong and J. Bisquert, *ACS Nano*, 2015, **9**, 908.

9 A. Yella, H. W. Lee, H. N. Tsao, C. Yi, A. K. Chandiran, M. K. Nazeeruddin, E. W.G. Diau, C.Y. Yeh, S. M Zakeeruddin and M. Grätzel, *Science*, 2011, **334**,629.

10 S. Mathew, A. Yella, P. Gao, R. Humphry-Baker, B. F. E. Curchod, N. Ashari-Astani, I. Tavernelli, U. Rothlisberger, M. K. Nazeeruddin and M. Grätzel, *Nat. Chem.*, 2014, **6**, 242.

11 R. Wang, K. Hashimoto, A. Fujishima, M. Chikuni, E. Kojuma, A. Kistamure, M. Shimohigoshi and T. Watanabe, *Nature*, 1997, **388**, 431.

12 W.T. Sun, Y. Yu, H. Y. Pan, X. F. Gao, Q. Chen and L. M. Peng, *J. Am. Chem. Soc.*, 2008, **130**, 1124.

13 L. Li, X. Yang, J. Gao, H. Tian, J. Zhao, A. Hagfeldt, and L. Sun, *J. Am. Chem. Soc.*, 2011, **133**, 8458.

14 Q. Zhang, X. Guo, X. Huang, S. Huang, D. Li, Y. Luo, Q. Shen, T. Toyoda and Q. Meng, *Phys. Chem. Chem. Phys.,* 2011, **13**, 4659.

15 X. Huang, S. Huang, Q. Zhang, X. Guo, D. Li, Y. Luo, Q. Shen, T. Toyoda and Q. Meng, *Chem. Commun.,* 2011, **47**, 2664.

16 P. K. Santra and P. V. Kamat, *J. Am. Chem. Soc.*, 2012, **134**, 2508.

17 J. W. Lee, J. D. Hong and N. G. Park, *Chem. Commun.,* 2013, **49**, 6448.

18 C. Lévy-Clément, R. Tena-Zaera, M. A. Ryan, A. Katty, G. Hodes, *Adv. Mater.*, 2005, **17**, 1512.

19 A. Zaban, O. I. Micic, B. A. Gregg and A. J. Nozik, *Langmuir* , 1998, **14**, 3153.

20 S. Giménez, I. Mora-Seró, L. Macor, N. Guijarro, T. Lana-Villarreal, R. Gómez, L. J. Diguna, Q. Shen, T. Toyoda and J. Bisquert, *Nanotechnology*, 2009, **20**, 295204.

21 N. Guijarro, T. Lana-Villarreal, I. Mora-Seró, J. Bisquert and R. Gómez, *J. Phys. Chem. C*, 2009, **113***, 4208.

22 N. J. Smith, K. J. Emmett and S. J. Rosenthal, *Appl. Phys. Lett.*, 2008, **93**, 043504.

23 P. K. Santra and P. V. Kamat, *J. Am. Chem. Soc.*, 2013, **135**, 877.

24 N. P. Benehkohal, V. González-Pedro, P. P. Boix, S. Chavhan, R. Tena-Zaera, G. P. Demopoulos, I. Mora-Seró, *J. Phys. Chem. C*, 2012, **116**, 16391.

25 A. Kongkanand, K. Tvrdy, K. Takechi, M. Kuno and P. V. Kamat, *J. Am. Chem. Soc.*, 2008, **130**, 4007.

26 H. Zhang, K. Cheng, Y. M. Hou, Z. Fang, Z. X. Pan, W. J. Wu, J. L. Hua and X. H. Zhong, *Chem. Commun.,* 2012, **48**, 11235.

27 Z. Ning, H. Tian, C. Yuan, Y. Fu, H. Qin , L. Sun and H. Ågren, *Chem. Commun.*, 2011, **47**, 1536.

28 D. F. Watson, *J. Phys. Chem. Lett*., 2010, **1**, 2299.

29 J. B. Sambur, S. C. Riha, D. Choi and B. A. Parkinson, *Langmuir*, 2010, **26**, 4839.

30 W. Li and X. Zhong, *J. Phys. Chem. Lett.*, 2015, **6**, 796.

31 W. J. Li and X. H. Zhong, *Acta Phys. Sin-Ch. Ed.*, 2015, **64,** 038806.

32 Warren C. W. Chan and S. Nie, *Science*, 1998, **281**, 2016.

33 J. T. Margraf, A. Ruland, V. Sgobba, D. M. Guldi and T. Clark, *Langmuir*, 2013, **29**, 2434.

34 J. Wang, I. Mora-Seró, Z. Pan, K. Zhao, H. Zhang, Y. Feng, G. Yang, X. Zhong and J. Bisquert, *J. Am. Chem. Soc.*, 2013, **135**, 15913.

35 Z. Pan, K. Zhao, J. Wang, H. Zhang, Y. Feng and X. Zhong, *ACS Nano*, 2013, **7**, 5215.

36 K. Zhao, H. Yu, H. Zhang and X. Zhong, *J. Phys. Chem. C*, 2014, **118**, 5683.

37 Z. Pan, H. Zhang, K. Cheng, Y. Hou, J. Hua and X. Zhong, *ACS Nano*, 2012, **6**, 3982.

38 W. Li, Z. Pan and X. Zhong, *J. Mater. Chem. A*,2015, **3**, 1649.

39 J. Chen, D.W. Zhao, J. L. Song, X. W. Sun, W. Q. Deng, X. W. Liu and W. Lei, *Electrochem. Commun.*, 2009, **11**, 2265.

40 F. Bo, C. L. Wang, S. H. Xu, C. F. Zhang, Z. Y. Wang and Y. P. Cui, *J. Phys. D: Appl. Phys.*, 2014, **47**, 305101.

41 S. Xu, C. Wang, H. Zhang, Z. Wang, B. Yang and Y. Cui, *Nanotechnology*, 2011, **22**, 315703.

42 Z. Du, H. Zhang, H. Bao and X. Zhong, *J. Mater. Chem. A*, 2014, **2**, 13033.

43 X. Zhong, Y. Feng and Y. Zhang, *J. Phys. Chem. C*, 2007, **111**, 526.

44 L. Liu and X. Zhong, *Chem. Commun.*, 2012, **48**, 5718.

45 X. G. Peng, L. Manna, W. D. Yang, J. Wickham, E. Scher, A. Kadavanich and A. P. Alivisatos, *Nature*, 2000, **404**, 59.

46 A. N. Jumabekov, F. Deschler, D. Böhm, L. M. Peter, J. Feldmann and T. Bein, *J. Phys. Chem. C*, 2014, **118**, 5142.

47 J. Aldana, N. Lavelle, Y. Wang and X. Peng, *J. Am. Chem. Soc.*, 2005, **127**, 2496.

48 Y. Q. Liang, J. E. Thorne and B. A. Parkinson, *Langmuir*, 2012, **28**, 11072.

49 Y. Zhang, L. Mi, P.-N. Wang, J. Ma and J.-Y. Chen, *Journal of Luminescence*, 2008, **128**, 1948.

50 W. Lin, W. Zou, Z. J. Du, H. Q. Li and C. Zhang, *J Nanopart Res*, 2013, **15**, 1629.

51 M. J. Mulvihill, S. E. Habas, I. Jen-La Plante, J. Wan and T. Mokari, *Chem. Mater.*, 2010, **22**, 5251.

52 J. Aldana, Y. A. Wang and X. Peng, *J. Am. Chem. Soc.*, 2001, **123**, 8844.

53 O. M. Primera-Pedrozo, Z. Arslan, B. Rasulev and J. Leszczynski, *Nanoscale*, 2012, **4**, 1312.

Table of contents

Optimizing the deposition of CdSe colloidal quantum dots on TiO$_2$ film electrode *via* capping ligand induced self-assembly approach

Xinxin Meng, Jun Du, Hua Zhang and Xinhua Zhong*

J_{sc} = 15.91 mA/cm^2
V_{oc} = 0.618 V
FF = 0.660
PCE = 6.49 %
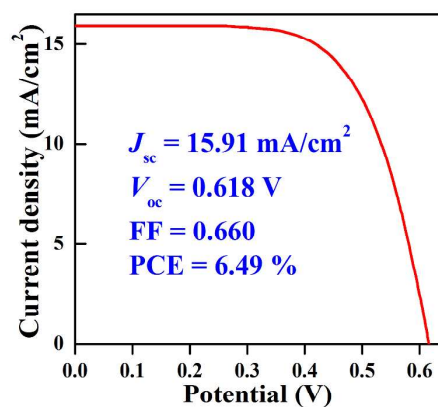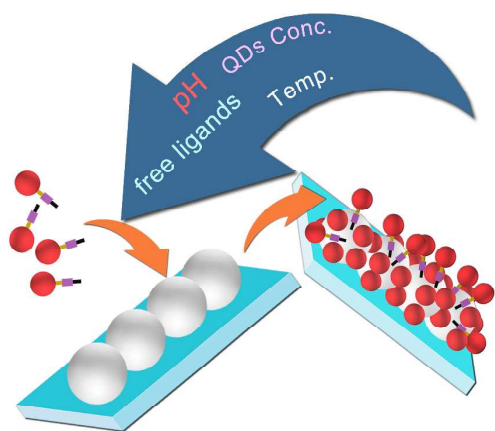
The influences of the experimental parameters in the process of CdSe QD deposition *via* capping ligand-induced self-assembly method on the amount of QD loading and on the performance of the resultant cell devices have been systematically investigated and optimized.