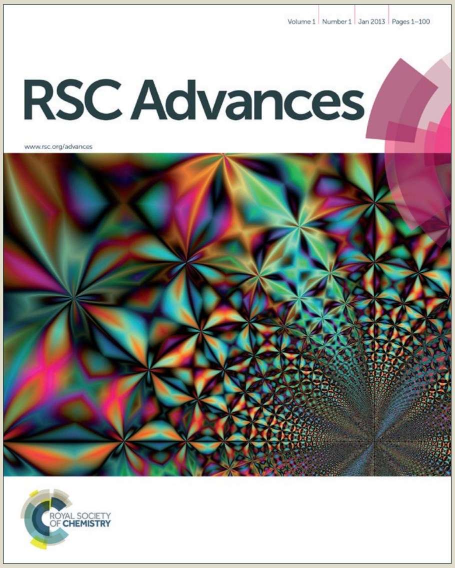
RSC Advances



ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/advances

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

Effect of Sodium Chloride on the Electrochemistry Activity of Electrodeposited CdTe Films with Various Morphologies

Jun Wang[a], Qian Li[b], Yannan Mu[a,c], Xiaoming Zhou[d], Lihua Yang[e], Pin Lv[a], Shi Su[a], Jiasheng Niu[a], Wuyou Fu[a] and Haibin Yang[a,*]

Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
DOI: 10.1039/b000000x

In this paper, cadmium telluride (CdTe) film is successfully synthesized on Ni foils via a simple electrochemical deposition method. Especially, with the sodium chloride (NaCl) being added into electrolyte directly, an interesting morphology evolution from spherical CdTe film to rod-shaped CdTe film, then to clustered CdTe film, and finally to double-layered film is observed with the increase of the NaCl concentration. The products are characterized by the X-ray diffraction (XRD), field-emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM), UV-vis spectroscopy, and photoelectrochemical measurements. It is found that the amount of NaCl played an important role in determining the morphology of CdTe film. The possible growth mechanism is discussed as well. Photoelectrochemical measurements reveal that the morphology of CdTe film can affect their photoelectrical properties greatly, and the uniform CdTe nanorod arrays prepared at 0.05 mol/L NaCl exhibit excellent photoelectrical properties, which is meaningful to the invesitigation of CdTe solar cells. According to the experiments, this simple but effective method can also be extended to the control of the growth of other nanostructures.

1. Introduction

CdTe has been recognized as a very promising material for its use as an absorption layer in solar cell structures,[1] due to its appropriate bandgap, high absorption coefficient, low-cost fabrication technologies.[2-5] It is generally known that controlled synthesis of nanocrystals with specific structures and research into their structure-based properties are important subjects in nanoscience.[6-10] Therefore, a number of synthetic approaches, such as the close space sublimation,[11] thermal evaporation,[12] hydrothermal, solution chemical,[13] template-assisted approaches,[14] and electrochemical deposition,[15] have been developed to synthesize CdTe film with various morphologies, including nanorod,[16] nanowire,[17-18] quantum dot,[19] nanotree,[20] nanotube,[21] and nanoparticle.[22] Among these methods, electrochemical deposition is found to be a suitable method to obtain CdTe with various structures. This method has advantages in a high growth rate, the low temperature, low cost, large scale, and simple operation.[23-24] Particularly, electrochemical deposition is a viable alternative to the traditional preparation methods due to the precise control of the experimental parameters (i.e., potential and current density). For example, it has been proved that the growth of one-dimensional CdTe can be manipulated by adjusting deposition voltage during electrodeposition.[25-26] More importantly, the electrolyte composition is shown to be crucial to tailor morphology and crystalline structure of CdTe nanostructure as well. A common method to change the composition of electrolyte is the utilization of a growth medium containing additives such as cetyltrimethyl ammonium bromide (CTAB), polyvinyl pyrrolidone, and ethylene diamine tetraacetie acid, which can be preferentially adsorbed on specific crystallographic planes, changing the direction and relative rate of crystal growth and resulting in the generation of crystals with different final morphologies.[27-30] Among a variety of organic additives, CTAB is one of the most common organic molecules that have been used as the stabilizer and structure-directing agent to control the nucleation, growth and alignment of crystals. For example, Qian *et al.* have synthesized various CdTe structures by changing the concentration of CTAB in the electrolyte.[31]

In recent years, except for the organic additives, many simple salts, such as NaCl, and potassium chloride, have been widely used as additive to control the crystal growth under an environmentally friendly reaction conditions. Among the various types of simple salts, NaCl has attracted increasing interest because of its widespread industrial use and low price. Besides its role as a supporting electrolyte, other major effects of it have also been found. For example, Zhao and her co-workers have demonstrated that the morphologies of Cu_2O can evolve from dendritic branching to cube-like with the increase of the NaCl concentration, exerting an important impact on their photoelectrochemical properties.[32] The influence of chloride (Cl^-) ions concentration on the morphology of ZnO nanorods has been investigated as well,[33] demonstrating that Cl^- ions can also be considered to be a capping agent due to the adsorption on the ZnO polar face. However, as far as we known, the effect of NaCl on the properties of CdTe film synthesized via electrochemical deposition has not been investigated.

Therefore, in this paper, we develop the technology and control the shape of electrodeposited CdTe thin film by firstly adding simple salts (NaCl) as shape-control agents in the reaction solution directly on Ni substrate, because Ni is a promising substrate material for the relatively high work function of 5.1 eV,[34-36] which may imply a smaller barrier height. Moreover, Ni is cheap and suitable for large-scale commercialization. In this paper, we demonstrate that NaCl can change the crystal morphology and the morphology evolves from spherical CdTe film to double-layered film with the increase in the concentration of NaCl. The result demonstrates that NaCl plays an important role in affecting the morphologies of CdTe film. To make clear what kind of ions is the main factor, we chose other salts containing Na^+ ions or Cl^- ions such as KCl and Na_2SO_4 instead of NaCl as additives in the electrochemical process and find that the morphology varies with the concentration of Cl^- ions. The possible growth mechanisms are discussed as well. In addition, the electrochemical experiments are conducted. We find that the rod-shaped CdTe exhibites an improved short circuit current, which may favor its application in solar cells. This simple but effective method is expected to be extended to the synthesis of other nanostructures with controlled morphologies.

2. Experiments

2.1 Deposition of the CdTe film

The electrodeposition of CdTe is carried out in a three electrode electrochemical cell, using the Ni substrate as the cathode, a graphite plate as the counter electrode and a saturated silver/silver chloride (Ag/AgCl) as the reference electrode. The reference electrode is placed far from the counter electrode. The Ni substrates and graphite plate are pretreated with acetone and ethanol in turn and then rinsed thoroughly with deionized water prior to each deposition. For all the experiments presented here, CdTe thin films are electrodeposited at a fixed potential of −0.4 V (vs. Ag |AgCl |KCl(sat)) for 1 h in an acidic electrolytic bath containing 0.001 mol/L $CdSO_4$• 8/3 H_2O, 0.005 mol/L Na_2TeO_3. NaCl (0, 0.05, 0.1 or 1 mol/L) is added into electrolyte, the pH of the electrolytic bath is adjusted to 2 by adding H_2SO_4, and the temperature is maintained at room temperature. After deposition, the films are rinsed with deionized water and dried in air. Finally, the CdTe thin films are annealed at 400 ℃ for 0.5 h under high-purity nitrogen atmosphere, and used for experimental tests.

2.2 Characterization

The crystal phases of the as-prepared films are characterized by a Rigaku D/max-2500 X-ray diffractometer (XRD) with Cu Kα radiation (λ = 1.5418 Å), in the scanning range between 20° and 80°. The morphologies and lattice structures of the as-prepared films are examined with the field-emission scanning electron microscopy (FESEM) (JEOL JSM–6700F), transmission electron microscopy (TEM), and energy dispersive x-ray spectroscopy (EDS). The optical absorption spectra of the as-prepared products are recorded in the range from 300 to 900 nm by UV-3150 double-beam spectrophotometer at room temperature. Photoelectrochemical measurements are conducted via an electrochemical workstation (CH Instruments model CHI601C) in a typical three electrode system. The As-synthesized CdTe, Pt wire and Ag/AgCl are used as the working electrode, the counter electrode and the reference electrode, respectively. A mixture of 0.25 mol/L Na_2S and 0.35 mol/L Na_2SO_3 aqueous solution has been used as the electrolyte. The Photocurrent–voltage curve is measured under a xenon lamp with power of 500 W and intensity of 100 mW/ cm^2.

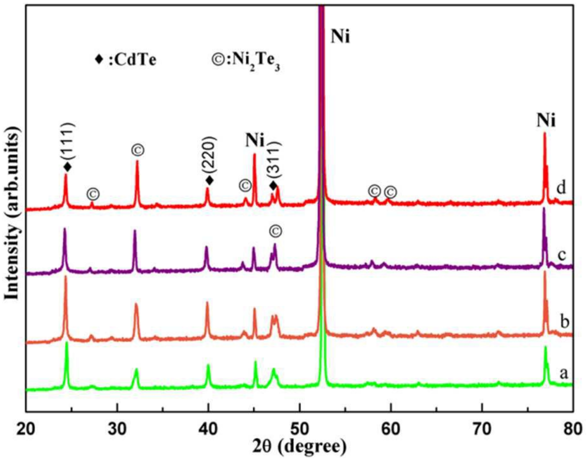


Fig. 2 XRD patterns of CdTe films synthesized at various NaCl concentrations: (a) 0, (b) 0.05 mol/L, (c) 0.1 mol/L, and (d) 1 mol/L.

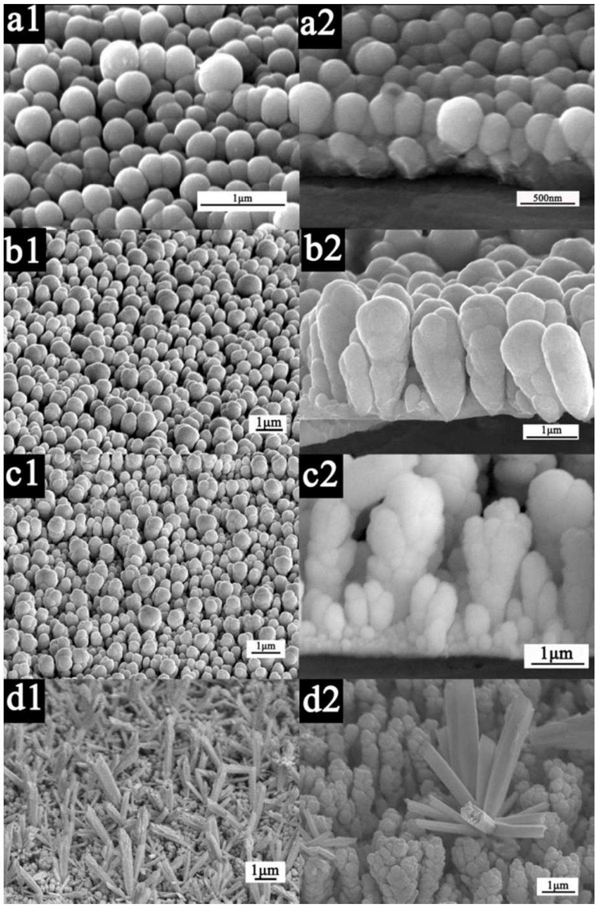


Fig. 3 Top view (a1, b1, c1, d1) and side views (a2, b2, c2, d2) of FESEM images of the CdTe films synthesized at various NaCl concentrations: (a1, a2) 0, (b1, b2) 0.05 mol/L, (c1, c2) 0.1 mol/L, (d1, d2) 1 mol/L.

3. Results and discussion

3.1 Synthesis of the CdTe film

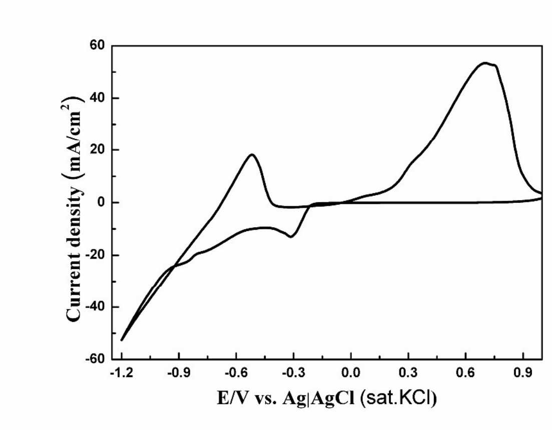


Fig.1. Cyclic voltammogram of 0.001 mol/L $CdSO_4$• 8/3 H_2O + 0.005 mol/L Na_2TeO_3 + 0.05 mol/L NaCl at room temperature, pH = 2 and scan rate = 100 mV/s.

To investigate the synthesis of the CdTe film, a cyclic voltammetry test is performed in an aqueous bath of 0.001 mol/L $CdSO_4$• 8/3 H_2O, 0.005 mol/L Na_2TeO_3 and 0.05 mol/L NaCl, as shown in Fig. 1. The potentials are changed between +1 V and -1 V (vs. Ag |AgCl |KCl(sat)) at a scan rate of 100 mV/s. The electrochemical reaction process can be simply expressed by the following equations:[37,38]

$$TeO_3^{2-} + 6H^+ + 4e \rightarrow Te + 3H_2O \qquad (1)$$

$$Te + 2e \rightarrow Te^{2-} \qquad (2)$$

$$Te + Cd^{2+} + 2e \rightarrow CdTe \qquad (3)$$

When the potential is scanned to negative potential direction, a visible little black film appears on Ni substrate at a potential about -0.2 V in the experiment, which indicates that the TeO_3^{2-} has been reduced to elemental Te and the chemical reaction process is described in Eq. (1). One small cathodic peak is observed at –0.3 V. The chemical reaction process is represented by Eq. (2). Another large anodic peak is observed at –0.8 V, corresponding to the following equation:

$$Cd^{2+} + 2e \rightarrow Cd \qquad (4)$$

We can't determine the exact value of the CdTe film deposition potential, but it indeed provides us a reference. It can be seen from Fig. 1 that if the deposition potential is closer to –0.2 V, the TeO_3^{2-} will not be reduced to Te^{2-} to react with Cd^{2+}, and if the potential becomes more negative, elemental Cd will be deposited on the Ni substrate. For this reason, the deposition potential limit is moved from –0.25 V to –0.8 V so as to avoid the appearance of elemental Cd or Te. Therefore, in the experiment, the deposition of CdTe on Ni substrates may be formed at a fixed potential of -0.4 V to promote the one-step reaction, as shown in Eq. (3).

3.2 Structure of the CdTe film

The crystal structures of CdTe thin films electrodeposited using NaCl with different concentrations are investigated by XRD, as shown in Fig. 2. It can be seen in Fig. 2(a-d), besides the Ni-substrate and Ni_2Te_3 peaks generated by the reaction between CdTe and Ni, the diffraction peaks at 2θ values for 23.98°, 39.70° and 49.90° demonstrate crystalline planes (111), (220) and (311) of zinc-blende CdTe (JCPDS File No. 75-2086). No characteristic peaks of other impurity phases such as CdO are presented. Noticeably, with the increase of the NaCl concentration, the intensity of CdTe (111) peak initially increases, and then decreases, which indicates that the amount of NaCl has to be controlled so as to obtain well crystallized CdTe phase. In addition, we confirm that all as-prepared films have the same structures indicating that the change of NaCl concentrations does not significantly affect the structure of CdTe films.

3.3 Morphology of the CdTe film

Fig.3 shows the FESEM images of CdTe film obtained under different reaction conditions in order to investigate the microstructure of various CdTe films grown in our study. When no NaCl is added, films are mainly composed of spherical particles with diameters in the range of 200 nm, as which can be seen in Fig. 3(a1) and (a2). In contrast, the products prepared with 0.05 mol/L NaCl show the rod-shaped morphology. Both the length and the diameter of the CdTe particles increase significantly, single CdTe nanorod with diameter of 500 nm and length of 1.5 μm is formed on Ni substrate. However the products synthesized with the assistance of 0.1 mol/L NaCl exhibit clustered morphology. The diameter of the products decreases, and the length of CdTe crystals remains the same as the one in Fig. 3(b1) and (b2). As the concentration of NaCl increases to 1 mol/L, the products are changed into double-layered structures, which consist of clustered structure and flower-like structure as the underlayer and overlayer, respectively.

Besides the FESEM, the as-prepared films are further investigated with TEM, as shown in Fig. 4. From the TEM, we can see the morphology of CdTe particles more clearly, which dramatically changes from spherical shape to double-layered shape with increase in the concentration of NaCl. The TEM images show similar morphology evolution of the CdTe with the increasing NaCl concentration, indicating that NaCl plays a very important role in the formation of the CdTe, which is in good agreement with the FESEM results (Fig. 3). Notably, the typical morphology of double-layered structure is also evaluated by EDS, as shown in Fig. 4(d1) and (d2). The elemental composition analysis of the clustered structure from EDS in Fig. 4(d1) shows that Cd and Te are the dominant elements, and the ratio of Cd : Te was found 1 : 1.4, confirming that the composition of this structure is CdTe. The composition of the rod-like structure is also identified (Fig. 4(d2)). Only the Te peaks are visible in the EDS spectrum, indicating that composition of this structure is Te. It reveals that the hierarchical architecture is constructed with two parts: one is Te flower on the top and the other is clustered CdTe array at the bottom. What's more, these results demonstrate that high-density rod-like CdTe array vertically aligned in a large area can be obtained by appropriately adding NaCl in electrolyte, and the amount of NaCl plays an important role in the formation of different morphologies of CdTe thin films. However, the interaction mechanism between CdTe and NaCl is complicated and nearly no further works in this aspect has been carried out.

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

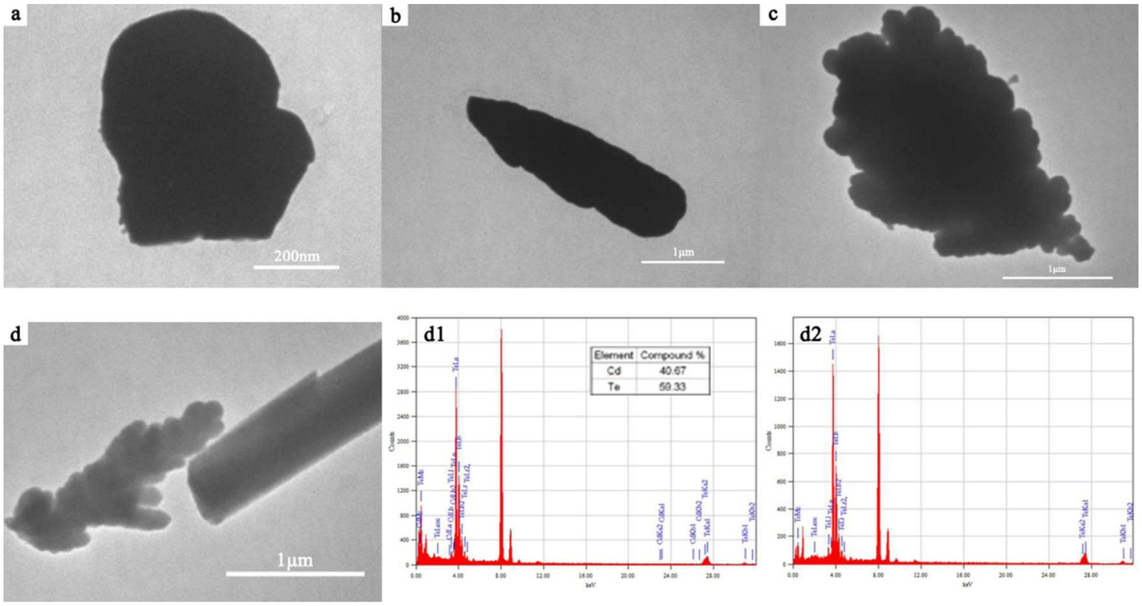


Fig.4 TEM images of the CdTe films deposited from electrolyte containing different concentration: (a) 0, (b) 0.05 mol/L, (c) 0.1 mol/L, (d) 1 mol/L. EDS spectrum taken from (d1) the clustered structure, and (d2) the rod-like structure of the double layer structure in Fig.4d.

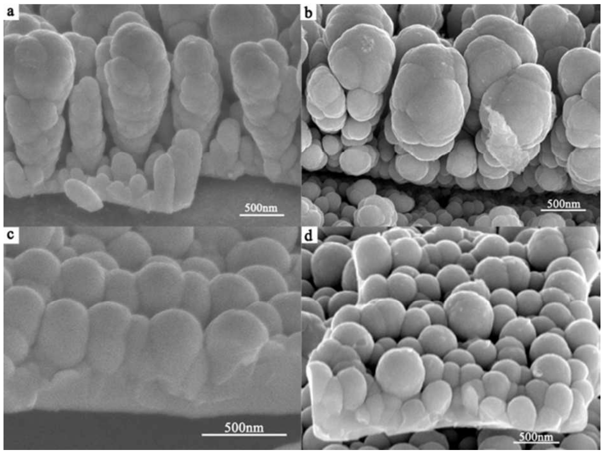


Fig. 5 SEM images of the CdTe films deposited for 1h from electrolyte containing different concentration of Cl^- ions and Na^+ ions: (a) 0.05 mol/l KCl, (b) 0.1 mol/L KCl, (c) 0.05 mol/L Na_2SO_4, (d) 0.1 mol/L Na_2SO_4.

3.4 Possible Formation Mechanism

From the above figures, it can be seen that the morphologies of the final products are greatly dependent on the NaCl concentration. To investigate factors that affect the CdTe crystal morphology in the preparation process, we replace NaCl by other salts such as KCl and Na_2SO_4. The reaction time is also 1 h (Fig. 5) and the concentration of the salt in Fig. 5a, c and Fig. 5b, d is identical with that in Fig. 2b and c, respectively.

When the concentration of KCl salt is low in electrolyte, the rod-like shapes of CdTe films are formed (Fig. 5a), which are similar to that of obtained from electrolyte with small amount of NaCl in Fig. 2(b2). As the concentration of KCl increases, CdTe clustered shapes are obtained (Fig. 5b), which are also similar to the result of obtained films from electrolyte with higher NaCl concentration (Fig. 2(c2)). These results indicate that salts containing Cl^- ions are added into electrolyte instead of NaCl as the capping agents, which can obtain the similar morphology changes. When NaCl is replaced by Na_2SO_4, the morphology of the films obtained do not change much no matter whether at lower concentration (Fig. 5c) or higher concentration (Fig. 5d). Crystals grown in the presence of Na_2SO_4 maintain the similar morphology to that without any additives, which indicates that Na^+ ions do not exert noticeable effect on CdTe crystals. As a result, the morphological changes observed can be reasonably attributed to the effect of Cl^- ions. Similar results have been reported in previous literatures.[39, 40] Based on above results, we believe that the Cl^- ions used in our experiment play a significant role in controlling the morphology of the electrodeposited CdTe films. Moreover, we find that the morphology of the CdTe films depends on the concentration of Cl^- ions in electrolyte. It is well known that NaCl is usually used as a supporting electrolyte to ensure a good conductivity of the aqueous solution. What's more, due to the strong absorption capacity of Cl^-, NaCl may play an additional role in the electrodeposition. Some researchers have reported that the preferential adsorption of molecules and ions in solution to different crystal faces can affect the growth rates along different crystal axes, resulting in the formation of micro- or nano-particles with various shapes. [41] In addition, Cl^- can interact easily with other matters powerfully.[42] On the basis of these theories, the formation mechanisms of the different morphologies of CdTe prepared via the NaCl with different concentrations can be well explained. It may be rationalized by considering that when we prepared the CdTe thin films without using NaCl, the growing speeds of different directions show no obvious difference. Therefore, in order to decrease the energy of the system, the spherical particles with the largest volume and the smallest area form. At a lower NaCl concentration (0.05 mol/L), the upper surface of CdTe seeds deposited on Ni substrate are basically covered by the Cl^-, so consequently, they can be dispersed well, and then grow along a given orientation the (111) direction. In addition, the increasing concentration of Cl^- in the deposition bath can be used to induce the enhanced deposition rate and the formation of nanorod with longer length than the spherical particles.[43] The length of the CdTe nanorods increases with the increasing NaCl concentration, indicating that a proper chloride content (0.05 mol/L) favors the vertical growth of nanorods, as shown in Fig. 3(b1) and (b2).

When we add 0.1 mol/L NaCl into bath solution, the adsorption of Cl^- ions on all the surface of formed CdTe nanoparticles can change the surface energy of different crystal, thus significantly reducing the growth rate of the particals. It can be seen that Cl^- may block the grains growth. As is shown in Fig. 2(c1) and (c2), the grains sizes decrease, and then stay close together, forming clustered morphology finally. Similar phenomena may occur in the electrodeposition of nanocrystalline CdSe and CdS films.[33] In addition, the formation of double-layered structure may be explained as follows. Cl^- ions in the electrolyte also can have a great influence on the Cd and Te content of the CdTe films.[44] The concentration of free Cd^{2+} ion remarkabaly reduced in the electrolyte due to the strong adsorption behaviour of Cl^- and the concentration of the passivated $HTeO_3^-$ ions increases through a reaction involving chlorine, which can account for the deposition of excess Te, the core of the flowers in the deposition process.[45] These aggregated Te would develop bigger as the reaction time prolongs, leading to the formation of flowers. Finally, the double-layered structure is obtained by this electrodeposition method.

A detailed time course study is expected to provide direct evidence for such a speculation. Unfortunately, the experiments show the formation process is formed quickly, which hinders the direct observation of their detailed formation process. However, the exact mechanism for the morphological control of CdTe film by Cl^- is worthy of further investigation.

3.5 UV-vis absorption and photoelectrochemical properties of CdTe film

The comparison of the UV-visible absorption spectra of CdTe films synthesized at different NaCl concentrations is shown in Fig. 6. Light absorption properties of CdTe films with a diversity of morphologies are evaluated using the UV-vis spectrometer from the reflection mode. This property is analyzed on the basis of the Kubelka–Munk equation: $F(R) = k/s = (1 - R)^2/2R$, where k and s are absorption and scattering coefficients, respectively, and R is the reflectance at the front face. F(R) is an indicator of light absorption ability. The y-axis title 'Absorbance' in this Figure corresponds to the F(R) in the equation. It can be seen from the figure that all the synthetic CdTe films have obvious light absorption in the visible region. Comparing the four curves in Fig. 6, it can be found that with the increase of the NaCl concentration, the photoabsorption ability strengthens first and then weakens. Among all of the as-prepared films, the CdTe nanorod appears to have the highest absorptivity in the range of 300 — 900 nm. Several factors may be responsible for the strongest visible light absorption performance of the high density CdTe nanorod arrays. Firstly, the CdTe nanorod has better crystal quality. Secondly, as is shown in Fig. 3(b), the sample with highly uniform morphologies may have significant photoabsorption, and the enhancement of optical absorption can be attributed to an increase of light scattering in the arrays constituted by highly uniform nanorod. In summary, the remarkable photoabsorption capacity of the CdTe nanorod arrays is a direct result of charge carriers generation.

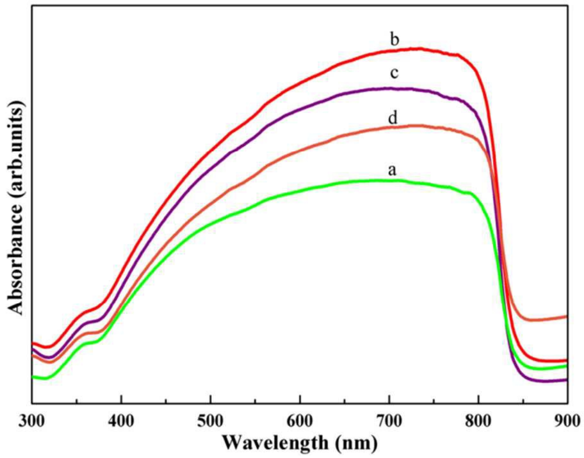


Fig.6 UV-vis absorption spectrum of the as-prepared CdTe films synthesized at various NaCl concentrations: (a) 0, (b) 0.05 mol/L, (c) 0.1 mol/L, and (d) 1 mol/L.

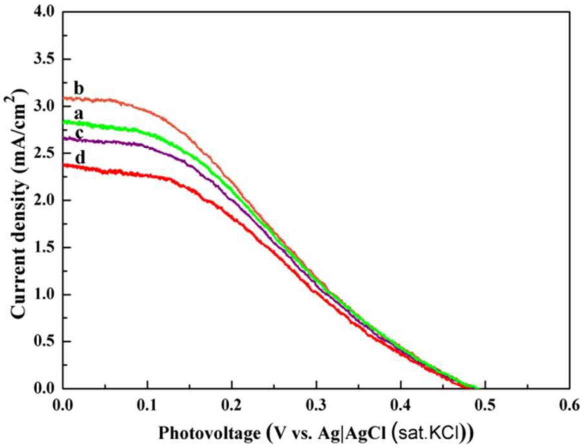


Fig. 7 Photocurrent curve of CdTe films synthesized at various NaCl concentrations: (a) 0, (b) 0.05 mol/L, (c) 0.1 mol/L, and (d) 1 mol/L.

The photovoltaic performance of CdTe films synthesized at various NaCl concentrations irradiated by the visible light is investigated by using a three-electrode photoelectrochemical cell. The typical current density versus voltage (J–V) curves obtained under illumination with the active area of 1 cm^2 as are shown in

Fig. 7. The corresponding photovoltaic performance parameters of these solar cells, including short-circuit current density (J_{sc}) and open-circuit voltage (V_{oc}) are investigated. There is no obvious difference between V_{oc} of all the as-prepared films. However, a remarkable difference in the J_{sc} is observed and it is found with increase in NaCl concentration that the value of J_{sc} increases gradually (from 0 to 0.05 mol/L) at initial stage, and then further increases (from 0.1 mol/L to 1.0 mol/L) leads to the reduction of the J_{sc}. It can be observed that CdTe nanorod exhibits the best photovoltaic performance. Significant improvement of J_{sc} is observed. This phenomenon can be explained as follows: Firstly, the appropriate adding quantity of NaCl can fabricate high-density CdTe nanorod arrays vertically on Ni foils, resulting in high absorption efficiency, thereby generating more photoexcited electrons, which is consistent with the UV-visible absorption spectrum (Fig. 6). Secondly, the vertical array configuration of the rods on substrate ensures a direct pathway for the photogenerated electrons to travel along the longitudinal direction of rods with minimum loss.

In contrast, the excessive NaCl would cause the aggregation of CdTe and form excessive grain boundaries between CdTe nanoparticles. These grain boundaries can act as potential barrier, enhance the possibilities of the recombination between electrons and holes, and prevent the change transfer, leading to a decrease in the overall efficiency. What's more, the clustered morphology may hinder the diffusion of the electrolyte, which limits the efficiency of charge separation and charge extraction, indicating that this kind of clustered morphology might be detrimental for use in photovoltaic devices. Therefore, the short circuit currents of the clustered CdTe and double-layer film are lower than that of CdTe nanorod arrays. This observation is very similar to the CdTe nanorod arrays reported recently by Sukhada Mishra *et al.*[33]

In summary, it has been observed that the CdTe nanorod arrays has an enhanced short circuit current compared with the products with other shapes, which makes it more suitable for solar energy applications. What's more, as seen from the results of J-V curves, there is still much room for improvement.

Conclusions

This article presented a systematic research on the effect of chloride ions on the morphology of CdTe nanostructures. Spherical CdTe, rod-shaped CdTe, clustered CdTe, and double-layered film have been realized by modulating the concentration of NaCl, suggesting that NaCl can greatly affect CdTe formation. Replacing NaCl by other salts, such as KCl and Na_2SO_4, it is found that Cl^- ions are the main factor that affects the morphology of CdTe crystal. This is a fast, simple and reproducible method which does not require any template and it can be used to synthesize CdTe with various structures. Meanwhile, we also find that the morphology of films has a great influence on photovoltaic performance of the product. Comparing the photoabsorption properties, we can conclude that the rod-shape CdTe films can absorb more light. The short-circuit photocurrent of the rod-shape CdTe films is significantly higher. The higher photocurrent is expected to make the rod-shape CdTe films more suitable for solar energy applications.

Acknowledgements

This work was financially supported by National Natural Science Foundation of China (No. 51272086) and the Technology Development Program of Jilin Province (Grant no. 20100417).

Notes and references

[a] *State Key Laboratory of Superhard Materials, Jilin University, Qianjin Street 2699,Changchun, 130012, People's Republic of China; Fax: +86 431 85168763; Tel: +86 431 85168763; E-mail:yanghb@jlu.edu.cn*
[b] *Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing 100190, China*
[c] *Department of Physics and Chemistry, Heihe University, Heihe 164300, PR China*
[d] *College of Physics, Beihua University, Jilin 132013, PR China*
[e]*College of Electronic Science and Engineering, Jilin University, Chang chun 130012, PR China*

1 B. W. Luo, Y. Deng, Y. Wang, M. Tan, L. L. Cao and W. Zhu, *CrystEngComm*, 2012, **14**, 7922.
2 B. M. Basol, *Solar Cells*, 1988, **23**, 69.
3 A. Shah, P. Torres, R. Tscharner, N. Wyrsch and H. Keppner, *Science*, 1999, **285**, 692.
4 E. I. Parsai, D. Shvydka and J. Kang, *Med. Phys.*, 2010, **37**, 3980.
5 R. L. Yang, D. Z. Wang, L. Wan and D. l. Wang, *RSC Adv.*, 2014, **4**, 22162.
6 B. L. Cushing, V. L. Kolesnichenko and O'Connor, *C. J. Chem. ReV.*, 2004, **104**, 2893.
7 X. G. Peng, *AdV. Mater.*, 2003, **15**, 459.
8 Y. D. Yin and A. P. Alivisatos, *Nature*, 2005, **437**, 664.
9 Y. Xia, B. Gates, Y. Yin and Y. Lu, *AdV. Mater.*, 2000, **12**, 693.
10 Y. Xia, P. Yang, Y. Sun, Y. Wu, B. Mayers, B. Gates, Y. Yin, F. Kim and H. Yan, *AdV. Mater.*, 2003, **15**, 353.
8 Burda, C. Chen, X. B. Narayanan and R. El-Sayed, *M. A. Chem. ReV.*, 2005, **105**, 1025.
9 I. Gur, N. A. Fromer, M. L. Geier and A. P. Alivisatos, *Science*, 2005, **310**, 462.
10 S. J. Jiao, K. J. Zhang, S. S Bai, H. L. Li, S. Y. Gao, H. T. Li, J. Z. Wang, Q. J. Yu, F. Y. Guo and L. C. Zhao, *Electrochimica Acta*, 2013, 111, 64.
11 J. L. Plaza, O. Martı´nez, S. Rubio, V. Hortelanob and E. Die´gueza, *CrystEngComm*, 2013, **15**, 2314.
12 X. Wang, J. Wang and M. J. Zhou, *J. Phys. Chem. C*, 2009, **113**, 16951.
13 Y. M. Sung, W. C. Kwak and T. G. Kim, *CrystEngComm*, 2012, **14**, 389.
14 P. Ramasamy, S. I. Mamum and J. Jang, *CrystEngComm*, 2013, **15**, 2061.
15 S. Ham, B. Choi and N. Myung, *J.Electroanal.Chem*, 2007, **601**, 77.
16 S. Mishra and M. Nath, *Nano Energy*, 2013, **2**, 1207.
17 L. B. Luo, X. L. Huang, M. Z. Wang, C. Xie, C. Y. Wu, J. G. Hu, L. Wang and J. A. Huang, *Small*, 2014, **10**, 2645.
18 L. F. Xi, K. H. Chua,Y. Y Zhao, J. Zhang, Q. H. Xiong and Y. M. Lam, *RSC Adv.*, 2012, **2**, 5243.
19 D. W. Deng, L. Z. Qu and Y. Q. Gu, *RSC Adv.*, 2012, **2**, 11993.
20 B. W. Luo, Y. Deng and Y. Wang, *Appl Surf Sci.*, 2013, **280**, 550.
21 S. Sarkar, S. Saha, S. Paland and P. Sarkar, *RSC Adv.*, 2014, **4**, 14673.
22 A. M. Saad, M. B. Mohamed, K. Abou and T. H. Maram, *Opt. Laser. Technol.*, 2013, **46**, 1.
23 X. H. Li, Iris S. Nandhakumar, T. Gabriel, G. S. Attard, M. L. Markham, D. C. Smith, J. J. Baumberg, K. Govender, P. O'Brienc and D. Smyth-Boylec, *J. Mater. Chem.*, 2006, **16**, 3207.
24 C. H. Chang, H. Jung, Y. Rheem, K. Lee, D. Lim,Y. Jeong, J. Lim and N. V. Myung, *Nanoscale*, 2013, **5**, 1616.
25 S. Y. Yang, J. C. Chou and H.Y. Ueng, *Thin Solid Films*, 2009, **12**, 77.
26 S. Denniso, *J. MATER. CHEM.*, 1995, **5**, 1885.
27 X. H. Ji, X. N. Song, J. Li, Y. B. Bai, W. S. Yang and X. G. Peng, *J. Am. Chem. Soc.*, 2007, **129**, 13939.
28 B. Q. Xie, Y. T. Qian, S. Y. Zhang, S. Q. Fu and W. C. Yu, Eur. *J. Inorg. Chem.*, 2006, **12**, 2454.

29 Y. Yin , R. M. Rioux, C. K. Erdonmez, S. Hughes and G. A. Somorjai, *Science*, 2004, **304**, 711.

30 Stupp and S. I. Braun, P. V. *Science*, 1997, **277**, 1242.

31 Q. Li, K. L Chi, Y. N. Mu, W. J. Zhang, P. Lv, L.Y. Zhou, H. B. Yang and W. Y. Fu, *CrystEngComm*, 2014, **16**, 5227.

32 W. Y. Zhao, W. Y Fu, H. B. Yang, C. J Tian, M. H. Li, Y. X. Li, L.N. Zhang, Y. M. Sui, X. M. Zhou, H. Chen and G. T. Zou, *CrystEngComm*, 2011, **13**, 2871.

33 H. Y. Yang, Y. S. No, J. Y. Kim and T. W. Kim, *Jpn. J. Appl. Phys.*, 2012, **51**, 06FG13.

34 S. H. Demtsu, D. S. Albin and J. W. Pankow, *Sol. Energy Mater. Sol. Cells.,* 2006, **90**, 2934.

35 C. Rotaru, S. Vatavu, V. Fedorov, M. Kirsch, P. Chetruş, P. Gaşin, M. Ch. Lux-Steiner and M. Rusu, *Thin Solid Films*, 2013, **535**, 241.

36 S. Vatavu, C. Rotaru, V. Fedorov, T.A. Stein, M. Caraman, I. Evtodiev, C. Kelch, M. Kirsch, P. Chetruş, P. Gaşin, M. Ch. Lux-Steiner and M. Rusu, *Thin Solid Films*, 2013, **535**, 244.

37 S.Y. Yang, J.C. Chou and H.Y. Ueng, *Thin Solid Films*, 2010, 518,4197.

38 M.B. Dergacheva, V.N. Statsyuk and L.A. Fogel, *J. Electroanal. Chem.*, 2005, 579, 43.

39 F. Sun, Y. P. Guo, Y. M. Tian, J. D. Zhang, X. T. Lv, M.G. Li,Y. H. Zheng and Z. C. Wang, *J. Cryst. Growth,* 2008, **310**, 318.

40 W. Y. Zhao，C. J. Tian，Z. P. Xie，C. A. Wang and Y. M. Li ，*J. Synt. Cryst*, 2012, **41**, 733.

41 M. J. Siegfried and K. S. Choi, *J. Am. Chem. Soc.,* 2006, **128**, 10356.

42 X. L. Guo, Y. Liao, Q. Zhang and J. Xu, *J. Phys. Chem. B,* 2005, **109**, 13519.

43 Tena-Zaera, R. Katty, A. Bastide, S. Le ´vy-Cle ´ment, C. O'Regan and B. Mun˜oz-Sanjose´, *Thin Solid Films,* 2005, **483**, 372.

44 K. Arai, K. Murase,T. Hirato, and Y. Awakura, J. Electrochem. Soc., 2006, **1532**,121.

45 A. E. Rakhshani , *J. Phys. : Condens. Matter*, 1999, **11**, 9115.