Conversion efficiency of strained wurtzite $In_xGa_{1-x}N$/$ZnSnN_2$ core/shell quantum dot solar cells under external electric field*

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In this study, the conversion efficiency (*CE*), open-circuit voltage (V_{OC}) and short-circuit current density (J_{SC}) of wurtzite $In_xGa_{1-x}N/ZnSnN_2$ core/shell quantum dot (QD) solar cells are studied by using the detailed balance model. The effects of strain and external electric field have been considered. The results show that with the increase of the core size, the V_{OC} increases, while the J_{SC} and *CE* decrease. With the increase of shell size or In content, the V_{OC} decreases, while the J_{SC} and *CE* increase. In addition, our calculations show that the band gap of QD increases due to strain, which leads to an increase of the V_{OC}, but decreases of the *CE* and J_{SC}. By contrast, the situation is opposite under the effect of external electric field.

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Solar energy is a clean and non-polluting renewable energy source. Its efficient development and utilization is a key measure to solve the current energy and environmental problems. Converting solar energy to electricity using solar cells is one of the important ways to utilize solar energy. In recent years, with the continuous advancement of photovoltaic technology, there are more and more types of solar cells, which can be mainly divided into crystalline silicon solar cells, silicon thin-film solar cells, organic polymer solar cells, quantum dot (QD) solar cells, etc[1]. Because the electron is confined in three-dimensional QDs, it will exhibit unique quantum size effects, macroscopic quantum tunneling effects, and surface effects, etc[2]. Compared with traditional solar cells, QD solar cells are not only low-cost to produce, but also have high solar absorption coefficient[3]. In 1961, Shockley and Queisser calculated the upper limit of the conversion efficiency (*CE*) of a single-junction solar cell with an energy gap of 1.1 eV using the detailed balance model, and found its *CE* is about 33%. After that, this model is widely used to calculate the efficiency of solar cells, including the QD solar cells[4]. Later, JIANG et al[5] theoretically and experimentally proved that the piezoelectric effect can modulate quantum photovoltaic devices, thus indicating that the electric field has a modulating effect on the performance of solar cells. LU et al[6] investigated the effect of external electric field on semiconductor structure and charge transport to provide some theoretical strategies for improving charge mobility.

In nanoscale semiconductor materials, strain has been found to have a significant effect on the band structure and optical properties of QD, and it has an effect on the photogenerated carriers[7]. For example, LI et al[8] found that the band gap and mechanical properties of monolayer $HfSe_2$ can be effectively controlled by biaxial strain and charge doping. WU et al[9] showed that biaxial strain and external electric field can change the band gap of $MoSi_2N_4$ and WSi_2N_4 semiconductor materials. Since the *CE* is closely related to the band gap of the system, it is very meaningful to consider the strain and external electric field in the study of the *CE* of QD solar cells.

In recent years, Zn-IV-N, such as $ZnSnN_2$ and $ZnGeN_2$, have been considered as promising materials for solar cell applications. As a new type of ternary compound semiconductor material, $ZnSnN_2$ has many advantages, such as large band gap, large reserves, perfect recycling system, low material cost, non-toxicity and high absorption coefficient[10,11]. Moreover, the lattice constant of $ZnSnN_2$ is between those of GaN and InN, which can match the lattice constant of $In_xGa_{1-x}N$. These In-containing QDs are like three-dimensional traps, trapping the electrons and holes in QD, and the degree of spatial confinement of electrons and holes is strengthened, thereby improving the luminous efficiency of optical devices with $ZnSnN_2$ as the active layer[12]. In summary, to the best of our knowledge, few studies have considered the influence of strain and electric field on the

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properties of QD solar cell, especially for the $ZnSnN_2$ materials.

In this paper, the wurtzite $In_xGa_{1-x}N/ZnSnN_2$ spherical QD is taken as the research object, the relationships between the CE, V_{OC} and J_{SC} of solar cells with the structure of QD and In content are theoretically studied by using the detailed balance model, and the effects of uniaxial and biaxial strain and external electric field on QD solar cells are also considered.

In this study, we choose $In_xGa_{1-x}N/ZnSnN_2$ core/shell spherical QD for the numerical calculation, as shown in Fig.1, where the core material is $In_xGa_{1-x}N$ with a large band gap, the shell material is $ZnSnN_2$ with a small band gap, R_c is the core radius, and R_s is the shell radius.

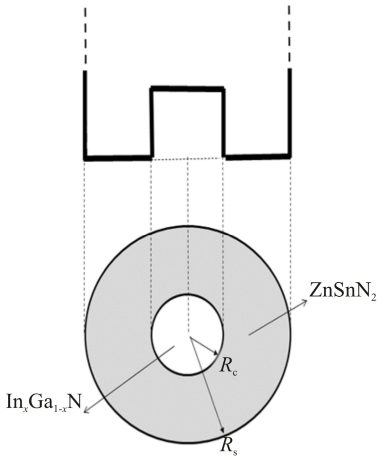


Fig.1 Schematic diagram of $In_xGa_{1-x}N/ZnSnN_2$ core/shell spherical QD

In the effective mass approximation, the Hamiltonian for electrons (holes) in a spherical QD under the influence of electric field is given by

$$H_{e,h}=-\frac{\hbar^2}{2m_{e,h}}\nabla^2+V_{e,h}(r)\pm eFr\cos\theta, \tag{1}$$

where F is the external electric field along the z-axis, e is the absolute value of the electron charge, the sign + (−) is for the electron (hole), and the effective mass is given by

$$m_{e,h}=\begin{cases}m^c_{e,h}, & r<R_c\\ m^s_{e,h}, & R_c\le r\le R_s\end{cases}, \tag{2}$$

where $m^c_{e,h}$ and $m^s_{e,h}$ are the electron (hole) effective masses of $In_xGa_{1-x}N$ and $ZnSnN_2$, respectively. The confining potential $V_{e,h}(r)$ is given by

$$V_{e,h}(r)=\begin{cases}V_{e,h}, & r\le R_c\\ 0, & R_c\le r\le R_s\\ \infty, & r\ge R_s\end{cases}, \tag{3}$$

where the confining potential V_e (V_h) of electrons (holes) is

$$V_e=0.6\left(E^c_g-E^s_g\right), \tag{4}$$

$$V_h=0.4\left(E^c_g-E^s_g\right), \tag{5}$$

where E^c_g and E^s_g are the bandgap energy of $In_xGa_{1-x}N$ and $ZnSnN_2$, respectively.

Because no analytical solution exists for Eq.(1), we use the variational method. The corresponding trial wave function with variational parameter λ is

$$\Phi_{e,h}(r)=\varphi_{e,h}(r)e^{-\lambda r\cos\theta}, \tag{6}$$

with

$$\varphi_{e,h}(r)=\begin{cases}\dfrac{A^c_{e,h}\sinh\left[K^c_{e,h}r\right]}{r}, & r\le R_c\\ \dfrac{A^s_{e,h}\sin\left[K^s_{e,h}(r-R_s)\right]}{r}, & R_c\le r\le R_s\\ 0, & r\ge R_s\end{cases}, \tag{7}$$

where $K^c_{e,h}=\sqrt{\dfrac{2m^c_{e,h}(V_{e,h}-E_{e,h})}{\hbar^2}}$, $K^s_{e,h}=\sqrt{\dfrac{2m^s_{e,h}(V_{e,h}-E_{e,h})}{\hbar^2}}$, $A^c_{e,h}$ and $A^s_{e,h}$ are normalization coefficients, which can be obtained from the normalization condition and the continuity condition of the wave function:

$$\int_0^{R_s}\left|\varphi_{e,h}(r)\right|^2 4\pi r^2 dr=1, \tag{8}$$

$$\varphi^c_{e,h}(r)\big|_{r=R_c}=\varphi^s_{e,h}(r)\big|_{r=R_s}. \tag{9}$$

The electron (hole) ground-state energy $E_{e,h}$ in the absence of an external electric field is obtained from the probability current density continuum condition as

$$\frac{1}{m^c_{e,h}}\frac{d\varphi^c_{e,h}(r)}{dr}\bigg|_{r=R_c}=\frac{1}{m^s_{e,h}}\frac{d\varphi^s_{e,h}(r)}{dr}\bigg|_{r=R_s}. \tag{10}$$

The electron (hole) ground-state energy $E_{e,h}$ under the external electric field is

$$E_{e,h}=\min_{\lambda}\frac{\left\langle\Phi_{e,h}(r)\middle|H\middle|\Phi_{e,h}(r)\right\rangle}{\left\langle\Phi_{e,h}(r)\middle|\Phi_{e,h}(r)\right\rangle}. \tag{11}$$

The strain dependent energy gaps of InN, GaN, $ZnSnN_2$ and $In_xGa_{1-x}N$ are[13,14]

$$E_g^{InN^*}=E_g^{InN}+2a_2^{InN}\varepsilon_{xx}^{InGaN}+a_1^{InN}\varepsilon_{zz}^{InGaN}, \tag{12}$$

$$E_g^{GaN^*}=E_g^{GaN}+2a_2^{GaN}\varepsilon_{xx}^{InGaN}+a_1^{GaN}\varepsilon_{zz}^{InGaN}, \tag{13}$$

$$E_g^{ZnSnN_2^*}=2(a_2^{ZnSnN_2}+b_2^{ZnSnN_2})\varepsilon_{xx}^{ZnSnN_2}+(a_1^{ZnSnN_2}+b_1^{ZnSnN_2})\varepsilon_{zz}^{ZnSnN_2}+E_g^{ZnSnN_2}, \tag{14}$$

$$E_g^{InGaN^*}=xE_g^{InN^*}+(1-x)E_g^{GaN^*}, \tag{15}$$

where a_1^i, a_2^i, b_1^i and b_2^i are the deformation potentials for the material i.

In the well and barriers, the biaxial lattice mismatch induced strains are given as[13,14]

$$\varepsilon_{xx}^i=\varepsilon_{yy}^i=\frac{a_{ep}-a_i}{a_i}, \tag{16}$$

$$\frac{\varepsilon_{zz}^i}{\varepsilon_{xx}^i}=\frac{C_{11}^i+C_{12}^i-2C_{13}^i}{C_{33}^i-C_{13}^i}, \tag{17}$$

where a_i is the lattice constant, and C_{11}^i, C_{12}^i, C_{13}^i and C_{33}^i are the elastic constants. a_{ep} represents the equilibrium lattice constant for the strained layer, which is given by[13,14]

$$a_{ep}=\frac{a_w R_c+a_b(R_c-R_s)}{2R_c+R_s}. \tag{18}$$

Generally speaking, the *CE* of a solar cell is[15]

$$\eta=\frac{V_{OC}\times J_{SC}\times FF}{P_{in}}, \tag{19}$$

where *FF* is the fill factor, which is taken as 1 in this study, $P_{in}=\sigma T_s^4$ is the incident power from the sun[16], T_s=5 672 K is the solar temperature, σ=5.67×10^{-8} Wm^{-2}K^{-4} is the Stefan-Boltzmann constant, and J_{SC} and V_{OC} are the short-circuit current density and open circuit voltage, which can be derived from[16,17]

$$J_{SC}=q\int_{E_g}^{\infty}\frac{f_w\times(2\pi/c^2h^3)\times E^2}{\exp(E/kT_s)-1}\mathrm{d}E, \tag{20}$$

$$V_{OC}=kT_c\ln\left(J_{SC}/J_0+1\right)/q. \tag{21}$$

In the above formula, E is the energy of the photon, q is the elementary charge, c is the speed of light in vacuum, h is Planck's constant, k is Boltzmann's constant, and $f_w=\sin^2\varphi_s$, where φ_s is the sun exposure angle, which is taken as 0.266°[17]. $J_0=qQ_c$, where Q_c is the photon flux and has the form of

$$Q_c=\sin^2\theta\int_{E_g}^{\infty}E^2/\left(\exp(E/kT_c)-1\right)\mathrm{d}E, \tag{22}$$

where θ is the emitted composite radiation angle of the solar cell, which is taken as 90° here. T_c=300 K is the solar cell temperature. E_g is the band gap of the QD, and given by

$$E_g=E_e+E_h+E_g^s, \tag{23}$$

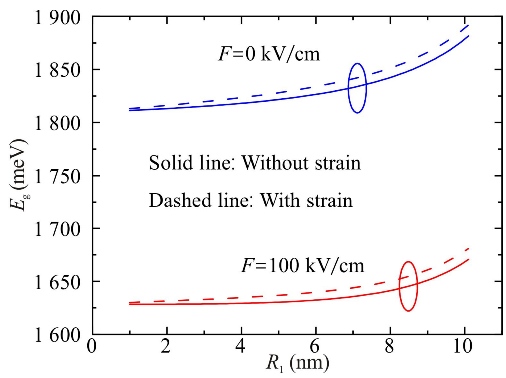
where E_e and E_h are the ground-state energies of electrons and holes, respectively.

Tab.1 Parameters of materials used in the calculations[18-25]

Parameter	$ZnSnN_2$	InN	GaN
E_g (eV)	1.8	1.994	3.5
m_e (m_0)	0.17	0.12	0.20
m_h (m_0)	2.0	0.27	1.1
a_1 (eV)	−3.5	−3.5	−4.1
a_2 (eV)	−3.5	−3.5	−8.9
b_1 (eV)	−8.8		
b_2 (eV)	4.4		
a (Å)	3.3	3.5	3.2
C_{11} (GPa)	272	223	390
C_{13} (GPa)	128	115	145
C_{31} (GPa)	100	92	106
C_{33} (GPa)	306	224	398

It can be seen from Fig.2(a) that the QD band gap increases monotonically with the increasing core size, and the variation becomes more and more obvious due to the influence of the quantum confinement effect. Because the strain increases the barrier height and increases the energy of electrons and holes, the band gap with strain is higher than that without strain (the maximum energy difference is 11.13 meV). It can also be seen that the band gap with electric field is significantly smaller than that without electric field. It can be seen from Fig.2(b) and (c) that the V_{OC} increases monotonically with the increase of the core size, and it is increased by the strain but decreased significantly by the electric field. For the J_{SC}, because the QD band gap increases with the increasing core size, the photon absorption is weakened and the J_{SC} is reduced. In addition, because the strain increases but electric field decreases the energy gap (see Fig.2(a)), the J_{SC} is decreased with strain but increased significantly with electric field. It can be seen from Fig.2(d) that the *CE* decreases with the increase of the core radius due to the increasing band gap, so that the photon absorption decreases and the *CE* decreases. The *CE* with the strain is significantly lower than that without the strain due to the larger band gap of the QD caused by the strain. In addition, compared with the case without electric field, the *CE* can be increased by up to 15% under the influence of the electric field. The above results show that the electric field is a powerful means to improve the solar cell performance.

Fig.3(a) shows the QD band gap as a function of the shell size R_2. It can be seen that the QD band gap decreases with increasing shell radius due to the fact that the influence of the outermost infinite barrier is weakened with the increasing shell size, and thus the quantum confinement effect decreases, i.e., the electron and hole energy levels decrease. We also observe that the band gap under the electric field is much lower than that without the electric field, and the difference between the two rapidly increases with the increasing shell size. It can be seen from Fig.3(b) and (c) that V_{OC} decreases but J_{SC} increases monotonically with the increase of shell size. Furthermore, we again find that the V_{OC} is increased but the J_{SC} is decreased by the strain. In addition, the electric field reduces V_{OC} but increases J_{SC}, and the effect of the electric field increases rapidly with the QD shell



(a)

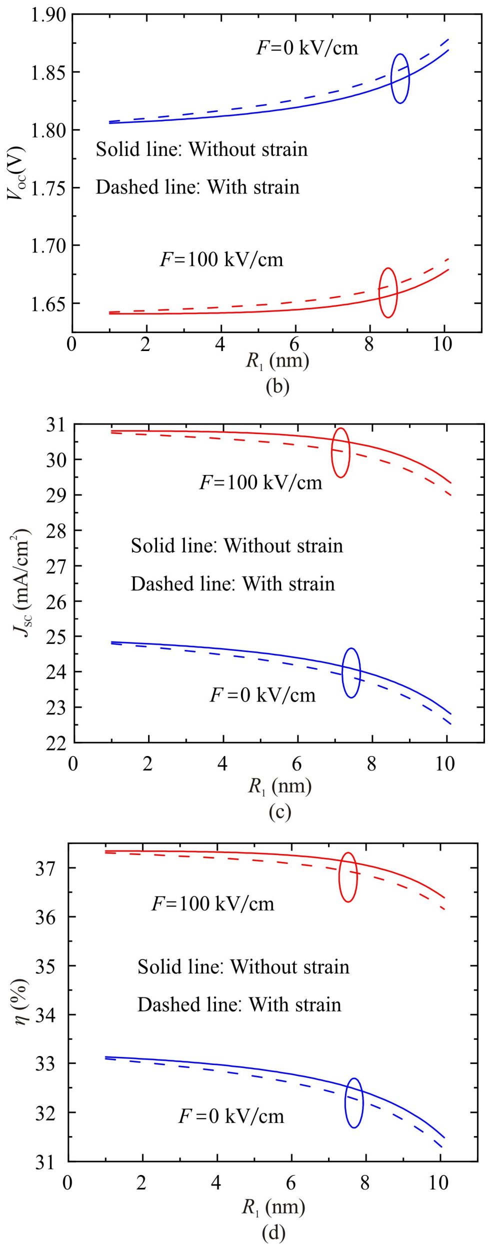


Fig.2 The QD (a) band gap, (b) V_{OC}, (c) J_{SC}, and (d) η as a function of QD core size R_1 with and without strain for In content x=0.3, QD shell size R_2=15 nm, and external electric field F=0, 100 kV/cm

size. Fig.3(d) shows the *CE* of the solar cell with or without electric field and strain as a function of the shell radius R_2. It can be seen that with the increase of the shell radius, the band gap of the QD decreases and the absorption of photons increases, so the *CE* increases accordingly. In addition, we observed a maximum increase of about 15.7% in *CE* under electric field, but it is slightly decreased by the strain.

Fig.4(a) shows the variation of the band gap of QD with the In content. From Fig.4(a), it is found that the In content has little effect on the band gap without the strain effect. However, when the strain is considered, the band gap decreases significantly with increasing In content. Fig.4(b) and (c) show the variations of the V_{OC} and the J_{SC} with the In content. It can be seen that under the influence of strain, V_{OC} decreases but J_{SC} increases with

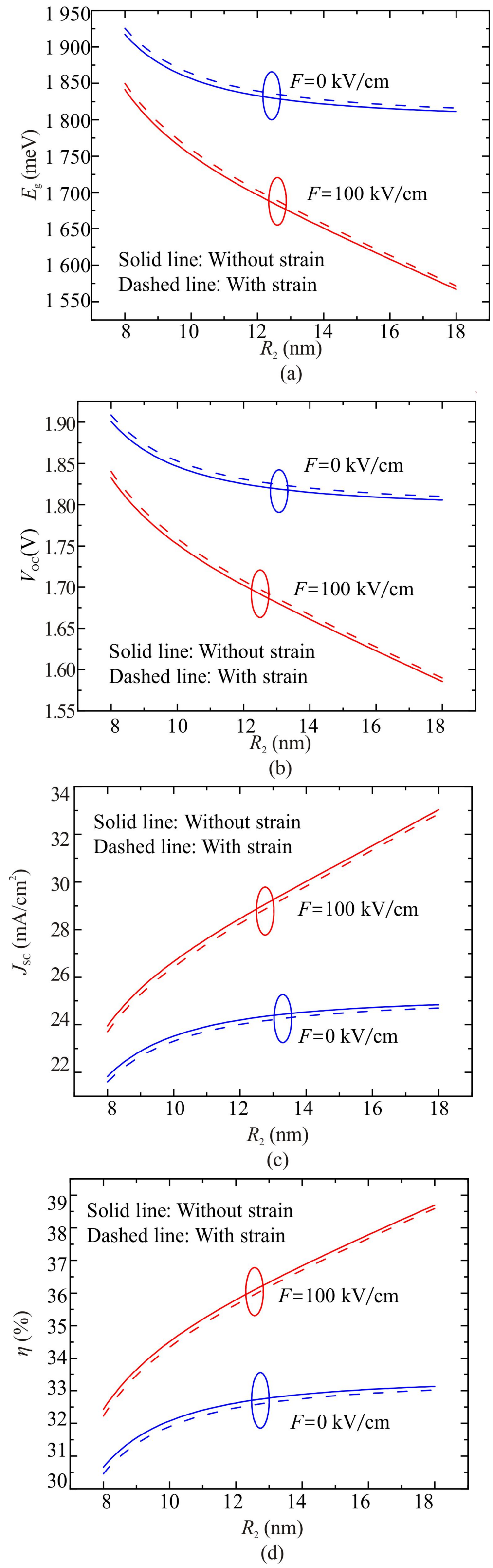
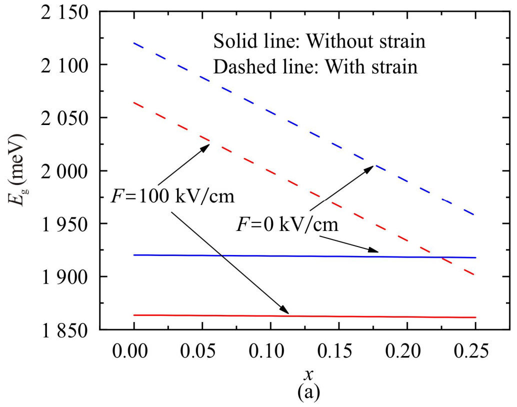


Fig.3 The QD (a) band gap, (b) V_{OC}, (c) J_{SC}, and (d) η as a function of QD shell size R_2 with and without strain for In content x=0.3, QD core size R_1=4 nm, and external electric field F=0,100 kV/cm

increasing In content. However, both of them without strain have almost no change with In content, which is in agreement with Fig.4(a). Furthermore, we again find that the electric field decreases V_{OC} but increases J_{SC}. Fig.4(d) shows the *CE* of the solar cell as a function of the In content. It can be seen that the *CE* with strain increases with increasing In content. However, the *CE* without strain has almost no change with In content, and thus the difference between the two is decreased. Therefore, how to select materials with matching lattice constants to effectively reduce the influence of strain is an important way to improve the *CE* of solar cells. In addition, the electric field can reduce the QD band gap, thereby improving the photoelectric *CE*.

Fig.5 shows the QD band gap, V_{OC}, J_{SC}, and photoelectric *CE* as a function of electric field. It can be seen that the energy of electrons and holes is reduced due to the electric field and thus the band gap is obviously reduced, so the *CE* increases significantly with the increasing electric field. It is found that when the electric field increases to 200 kV/cm, the *CE* can be increased by a maximum of about 3.5%. Fig.5(b) and (c) show that with the increase of the applied electric field, the V_{OC} decreases significantly, while the J_{SC} increases significantly. The above results again show that the electric field has a significant regulating effect on the photovoltaic properties of solar cells, which can be considered in the development of solar cell devices. In addition, it shows again that the strain increases V_{OC} but decreases J_{SC} and *CE*. It should be pointed out here that in the above study, we only consider the effect of the electric field on the band gap, but do not consider the effect on the recombination of electron-hole pairs. According to theoretical analysis, due to the separation of electrons and holes by the electric field, the corresponding recombination current will be reduced, thus further improving its efficiency.

In conclusion, we have used the detailed balance model to study the *CE*, V_{OC} and J_{SC} of strained core/shell QD solar cell under electric field. The results show that with the increase of the core size, the V_{OC} increases, while the J_{SC} and *CE* decrease. With the increase of shell size and In content, the V_{OC} decreases, while the J_{SC} and *CE* increase. The strain increases the V_{OC}, but decreases the J_{SC} and *CE*. The electric field has a strong modulating effect on the QD solar cell, and can significantly improve the cell performance.



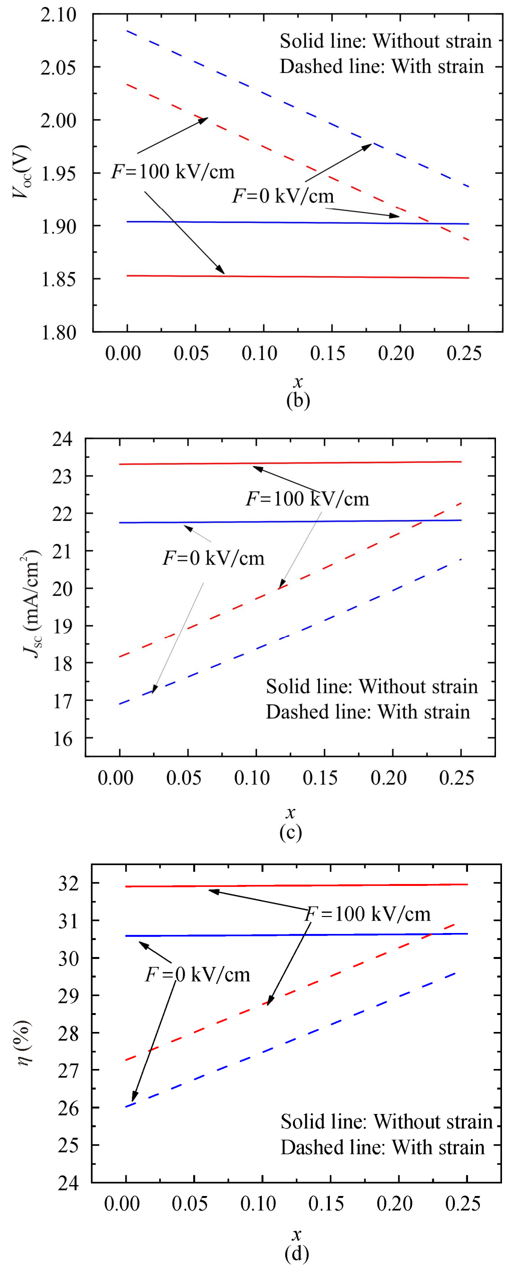
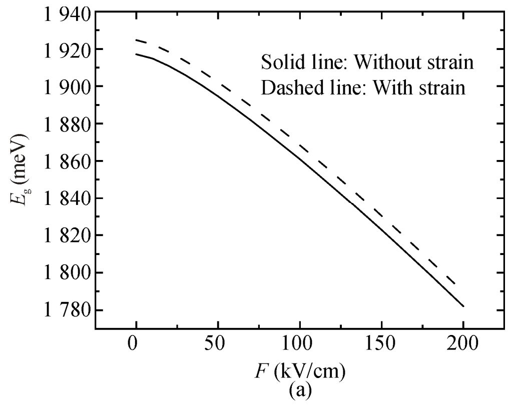


Fig.4 The QD (a) band gap, (b) V_{OC}, (c) J_{SC}, and (d) η as a function of In content x with and without strain for QD core size R_1=4 nm, shell size R_2=7 nm, and external electric field F=0,100 kV/cm



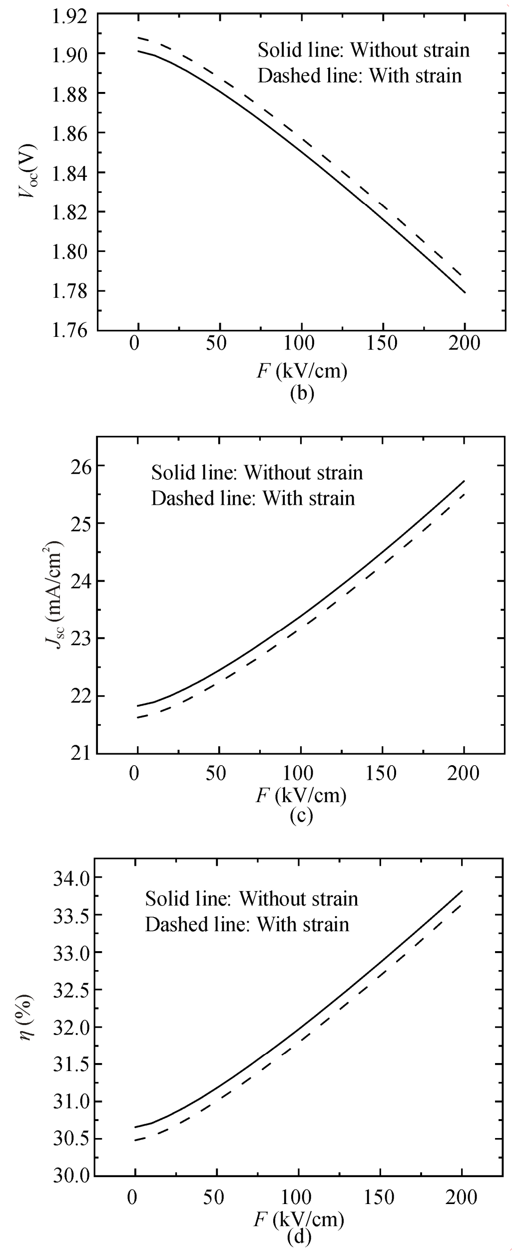


Fig.5 The QD (a) band gap, (b) V_{OC}, (c) J_{SC}, and (d) η as a function of external electric field with and without strain for In content x=0.3, core size R_1=3 nm, and shell size R_2=7 nm

We hope that the current work can help to bring more theory in line with realistic QD solar cells and provide some guidance for the development of QD solar cells, for example, how to choose the size of the device to improve the *CE* of solar cells.

Statements and Declarations

The authors declare that there are no conflicts of interest related to this article.

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