Size dependent photoelectrochemical performance of eco-friendly CuInS₂ quantum dots

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Abstract. Colloidal quantum dots (QDs) are considered as new energy materials with great potential, especially environmentally friendly QDs that do not contain heavy metals. Compared with heavy metal QDs, non-toxic QDs still suffer low performance in photovoltaic (PV) as well as photoelectrochemical (PEC) applications. The fabrication of high-performance PV devices from environmentally friendly QDs has become the focus of researchers. Before moving to experiments, the theoretical aspect is a very good way to deeply understand the charge carrier dynamics inside the QDs, which can provide possible solutions to improve the PEC performance of the QDs based photoelectrodes. Here, we report the successful synthesis of eco-friendly CuInS₂ (CIS) QDs with variable particle size. Through time-domain PL spectroscopy, we found that the photoluminescence (PL) lifetime gradually decreased from 273.2 ns to 172.9 ns as the size of CIS QDs increased. By theoretical calculations we also studied the dynamics of electrons and holes. The theoretical studies revealed that as the size of CIS QDs increases, the wave functions of the overlap between the electron and impurity hole increases leading to the decreased PL lifetime.

1. Introduction

Energy restricts the development of society. Traditional fossil fuels have become a major problem for social development due to low energy density and high pollution. In order to alleviate the social problems caused by such factors, people are eagerly looking forward to the establishment of emerging technologies for the development and utilization of green and pollution-free renewable energy. For the time being, renewable energy mainly includes solar energy, wind energy and hydropower are regarded as the basis for achieving green and sustainable development. Among them, solar energy is inexhaustible, green and pollution-free. In this perspective, high-efficiency, low-cost quantum dots (QDs) sensitized solar cells (QDSCs) represent a promising approach that can deal well with future energy demands[1-3]. As a promising photoelectric device material, colloidal semiconductor QDs have been widely investigated in various applications including photoelectrochemical (PEC) cells, luminescent solar concentrators (LSCs), solar-driven QDs-sensitized solar cells (QDSCs) [4, 5].

At this stage, people are widely concerned about CuInS₂ (CIS), AgInS₂ (AIS) and other environmentally friendly quantum dots, mainly because they do not contain toxic heavy metals such as Pb, Cd, etc. CIS QDs have many advantages: (i) Direct optical band gap (1.5 eV), can be well applied to optoelectronic devices; (ii) Wide fluorescence spectrum, large Stokes shift; (iii) Large absorption coefficient and wide absorption spectrum; (iv) Environmentally friendly, simple and stable synthetic process.
Here, we have successfully synthesized CIS QDs of different sizes with tetragonal chalcopyrite crystal structure, and studied its time-domain photoluminescence (PL) spectrum, obtained the change rule of PL lifetime, and a better understanding of the internal carrier dynamics through theoretical calculations.

2. Experimental and theoretical simulation

2.1. Synthesis of CuInS\textsubscript{2} CQDs
We synthesize CIS QDs via a one-pot synthesis scheme using the efficient method reported by Liang Li et al.[6]. Typically, indium acetate (1 mmol, 0.292g), copper (I) iodide (1 mmol, 0.190g) and 1-dodecanethiol (DDT, 5 mL) are loaded in a three-neck flask. The mixture is purged by N\textsubscript{2} at room temperature for at least 30 min. The temperature is then increased to 120 ℃ with purging. The reaction system was degassed for 30 min at 120 ℃ until the solution turned clear and transparent. Next, raised the temperature to 230 ℃. In order to get CIS QDs of different sizes, the reaction time and temperatures can be controlled. When the temperature reached 215 ℃, the reaction was quenched with cold water quickly. This sample was named as S0. Following the same method, we quenched the reaction at the temperature of 220 ℃ and 225 ℃ to get bigger sizes of CIS QDs and named them as S1 and S2. Here we have grown three sets of QDs of different sizes, ranging from small to large, named S0, S1, S2.

2.2. Theoretical Method
We solve the stationary Schrödinger equation for the electrons and holes in potential wells defined with information about the bulk material of CIS, using commercial software of COMSOL. These potential wells for electrons and holes were approximated attending to the conduction band minimum (CBM) and valence band maximum (VBM) of the corresponding bulk materials. The position function of the electron potential was approximated by the lowest unoccupied molecular orbital of the bulk materials and the position function of the hole potential was approximated by the highest occupied molecular orbital of the bulk materials. We respectively used \( m_e=0.16m_0 \) and \( m_h=0.85m_0 \) as the bulk values for the effective masses of electrons \( (m_e) \) and holes \( (m_h) \) for CuInS\textsubscript{2}, where \( m_0 \) is the electron mass at rest in vacuum[7, 8]. For CuInS\textsubscript{2} the levels are \(-4.39\text{eV}\) and \(-5.92\text{eV}\) and the bandgaps was \( 1.53\text{eV}\)[9-13]. In the simulation phase, in order to reduce the complexity of the calculation that we ignored the interaction between electrons and holes. The wave functions were calculated according to the effective mass Schrodinger equation. Use the appropriate boundary conditions at the interface to solve the equation and normalize the wave function as follow:

\[ \int |\psi|^2 dV = 1. \] 

We can express the wave function of the impurity hole state by using the equation as follow:

\[ \psi_{\text{hole}}(r, r_{\text{impurity}}) = A \exp \left( -\frac{(r-r_{\text{impurity}})^2}{2L_h^2} \right) \] 

In this equation, \( r_{\text{impurity}} \) represents the position of the impurity hole in the CIS QDs; the coefficient \( A \) can be derived from the equation (1); The \( L_h \), scale of the hole, is set to be 0.3 nm (Generally, \( L_h \) is much less than QDs size). The molar ratio of Cu:In in CIS QDs was 1.27:1 calculated from the experimental data. Based on this point, the molar mass and mass density of CIS were employed to calculate the numbers of Cu atoms and In atoms.

3. Results and discussion
The transmission electron microscope (TEM) image of CIS QDs was shown in Figure 1(a), showing clear lattice fringes, which indicate the successful growth of the CIS QDs. Figure 1(b) is the selected area electron diffraction (SAED) pattern. We can clearly see the spotty diffraction pattern of the CIS QDs crystals, which is consistent with the previous reports in the literature[14].
In order to better confirm the successful synthesis of CIS QDs, we further characterized the material with X-ray diffraction (XRD). As shown in Figure 2 that the peaks correspond to the (112), (204)/(220), (116)/(312) planes of tetragonal chalcopyrite crystal structure of CIS (JCPDS file no.85–1575) which intuitively proves that we have successfully synthesized CIS QDs[14].

Then we carried the transient photoluminescence (PL) spectroscopy of three CIS CQDs samples as shown in Figure 3. We performed a three-exponential fit on the original data and calculated the average PL lifetime to be 237.2 ns, 207.2 ns and 172.9 ns for S0, S1 and S2, respectively. The results
revealed that as the size of CIS QDs increases the PL lifetime decreases, and which has never been reported in previous studies.

Figure 3. (a) Transient PL spectroscopy of CIS S0; (b) CIS S1 and (c) CIS S2.

The light emission process in CIS QDs is due to the recombination of electrons and holes in CIS QDs. In order to better understand the behavior of electrons and holes generated in different sized CIS QDs, we calculated the wave functions of electrons and holes in CIS QDs. Our calculations, in Figure 4, show that the electrons and holes are mainly concentrated in the centre of the CIS QDs, and as the size of the CIS QDs increases, the probability of the occurrence of electrons and holes decreases.

Figure 4. Normalized radial distributions functions for the electrons (a) and the holes (b) of CIS QDs.

To qualitatively demonstrate the PL lifetime of the CIS QDs, we calculated the squared overlap integral of the impurity hole as a function of CIS QDs thickness. The squared overlap integral (OI) is given by:

$$OI_{\text{impurity}}(r) = \left| \int \psi_{\text{electron}}(r) \psi_{\text{hole}}(r, r_{\text{impurity}}) dV \right|^2$$

$$= \int \left| \psi_{\text{electron}}(r) \right|^2 dV \int \left| \psi_{\text{hole}}(r, r_{\text{impurity}}) \right|^2 dV$$

(3)
We assumed the interaction between the impurity hole states was so weak that we could ignore it. The lifetime of fluorescence emission should be proportional to the inverse of the squared overlap function. Figure 5 shows the inverse squared overlap integrals of the impurity hole state in CIS QDs as a function of the size of CIS QDs. As shown in the Figure 5, as the size of CIS QDs increase, the tendency of the inverse squared overlap integrals of the impurity hole state was decrease. This trend qualitatively agrees with the measured lifetime, indicating the decrease of PL lifetime in the experimental results due to the increased overlap between electrons and impurity holes.

![Figure 5. The inverse squared overlap integrals of the impurity hole state in CIS QDs as a function of the size of CIS QDs.](image)

4. Conclusion
In summary, we successfully synthesized CIS QDs of different sizes through the one-pot method. Through transient PL spectroscopy, we found that the PL lifetime gradually decreased from 273.2ns to 172.9 ns as the size of CIS QDs increased. For the internal carrier transport characteristics, we theoretically calculated the dynamics of electrons and holes, and found that as the size increases, the probability of electrons and holes occurring is decreasing. As the size of CIS QDs increases, the overlap of the electron and impurity hole wave functions increases which leads to the decrease of PL lifetime. Through experimental analysis and theoretical calculations, we can have a deeper understanding of the photoelectric properties of CIS QDs, which is also an important approach for future research on colloidal QDs based PV applications.

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