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ABSTRACT

The solvothermal method is used to prepare CuInSe\textsubscript{2} quantum dots (QDs). This method mainly uses ethanolamine as a solvent with CuCl\textsubscript{2}⋅2H\textsubscript{2}O, InCl\textsubscript{3}⋅4H\textsubscript{2}O, and selenium powder used as raw materials. The powder morphology, phase, and light absorption characteristics of different reaction temperatures and times were characterized in this work. Other characterization methods were used to optimize the CuInSe\textsubscript{2}QDs. It was substantiated that the optimum reaction condition is at 180°C for 20 h, the proportion of Cu, In, and Se is 1:2:1, the particle size is 10 nm, and the emission peak is at 800 nm. Furthermore, the CuInSe\textsubscript{2}QDs with the best performance were adsorbed on the TiO\textsubscript{2} film, and it was concluded that TiO\textsubscript{2} could be successfully decorated via the CuInSe\textsubscript{2}QDs, and the absorption band edge was enlarged to enhance the light absorption performance.

I. INTRODUCTION

Increasing the photoelectric conversion efficiency of QD sensitized solar cells is mainly manifested in the following two aspects: one is to increase the absorption range of the photoanode and to enhance the absorption intensity of the photoanode; the second is to accelerate the electron mobility. In these two efficiency-enhancing schemes, the selection of sensitizers plays an important role. QDs, such as CdS, CdSe, PbS, and CuInS\textsubscript{2}, were selected as candidates for high conversion efficiency solar cells due to their unique physical properties: tunable size of the absorption edge, ultra-fast electron transfer, and multi-exciton generation provide good conditions for light absorption throughout the solar spectral region. As a chalcogen compound, ternary CuInSe\textsubscript{2} (CISe) is considered to be a good direct bandgap semiconductor material. It not only has the advantages of high light absorption coefficient and good photoelectric conversion efficiency, but also has stable performance and simple preparation method, which has attracted the attention of photovoltaic researchers at home and abroad. As a material of the light absorbing layer alone, the prepared thin film solar cell has become one of the most promising solar cells. Compared with the vacuum method, the solvothermal method is the most advantageous solution in the non-vacuum process. The preparation process is simple and easy to control, and the preparation results are close to the ideal stoichiometric ratio.

In this work, the reducing properties of ethanolamine were utilized. Chalcopyrite CISeQDs were prepared via the solvothermal method and the diffraction peaks were found at 26.6°, 44.23°, and 52.39° by XRD analysis, which can be indexed to the (112), (220), and (312) crystal planes, respectively. It proves the synthesis of CISe phases. In the experiment, the reaction temperature and time were controlled to tune the phase and composition of the product. EDX showed that the impurity phase obtained was less when the conditions were 180°C 22 h. TEM analysis also showed that the morphology of QDs was better at 180°C 22 h with a regular spherical shape and an average particle size of about 7 nm can be observed clearly. Combined with the PL spectrum, we finally determined that 180°C 22 h is the optimal reaction condition, and the absorption peak is redshifted. The bandgap is 1.58 eV. After that, we allowed adsorption of CISeQDs on the TiO\textsubscript{2} film and compared the light absorption characteristics of TiO\textsubscript{2} when TiO\textsubscript{2} was not decorated by CISeQDs. It was found that CISeQDs were successfully
adsorbed by TiO$_2$, the absorption band edge was enlarged, and the light absorption intensity was enhanced.

II. EXPERIMENT

A. Preparation process of CISe quantum dots

0.5 mmol of CuCl$_2$·2H$_2$O, InCl$_3$·4H$_2$O, and selenium powder were dissolved in 40 ml ethanolamine according to the raw material ratio of 1:2:1, and the mixture was placed on a magnetic stirrer and stirred. After being dissolved, the sample was transferred into an autoclave and hydrothermally treated at 180 °C for 22 h. After cooling, remove and get the black solution, the products ethanol were washed and centrifuged with an ethanol solution. Subsequently, the precipitate was dried in a vacuum oven at 60 °C for 4 h to finally obtain CISeQD powder. First, changing the reaction temperature in the range of 160–200 °C under the constant reaction time, the optimum reaction temperature was determined. Then, while controlling the optimum temperature, the reaction time was adjusted in the range of 18–24 h to ensure the best performance of the obtained quantum dots.

B. Fabrication of TiO$_2$/CISe-QD electrodes

The spin coating method is used for TiO$_2$ film preparation. Figure 1 shows that quantum dots are deposited on TiO$_2$ substrates in this way. Certain masses of ethyl cellulose and terpineol were weighed, dissolved in 10 ml of absolute ethanol, and placed on a magnetic stirrer and stirred until no obvious particles in the solution (ethyl cellulose was completely dissolved). 0.8 g of TiO$_2$ was weighed and stirred with a magnetic stirrer for 1 h, and then ultrasonic vibration was performed for 1 h. The stirring and shaking process was repeated until the TiO$_2$ was completely dissolved, the TiO$_2$ slurry was obtained. Later, the dried glass substrate was placed on the homogenizer and the speed of the homogenizer was set. The low speed is 500 r/min for 10 s and the high speed is 1500 r/min for 30 s. The prepared TiO$_2$ slurry was spin-coated on a substrate, followed by drying on a hot plate at 70 °C, and after cooling, the second layer was spin-coated. By analogy, we can get a TiO$_2$ photoanode of different layers by spin coating. TiO$_2$ electrodes were confirmed earlier by Diguna et al. that 11 μm is the optimal thickness. In this experiment, we used a spin-coated two-layer film and the film was then annealed at 500 °C for 30 min.

The thickness was approximately 11 μm. QDs were adsorbed by a functional group modification self-assembly technique. We use 3-mercaptopropionic acid as a method of modifying the functional group. The ratio of 4:33 ethyl cellulose and terpineol with two layers of TiO$_2$ spin-coated film was adjusted by 3-mercaptopropionic acid, and then placed in water-soluble CISeQDs adjusted to pH 10 with NaOH. The adsorption conditions were at room temperature for 2 h.

III. RESULTS AND DISCUSSION

A. Different reaction temperatures

CISeQDs obtained at different reaction temperatures 20 h are characterized in Fig. 2. Consequently, no obvious impurity formation can be observed. The diffraction peaks at 26.6°, 44.23°, and 52.39° correspond to the (112), (220), and (312) crystal planes of CISeQDs, respectively. When the temperature is 160 °C, CISeQDs have been formed with some InSe impurity. The impurity disappears gradually when the temperature is further increased to 180 °C and the peak intensity increases, the half-peak width becomes narrower, and the CISeQDs grow gradually. At a temperature of 190 °C, the CuSe impurity phase begins to be produced. Table I shows the EDX of CIQD QDs with different reaction temperatures. The EDX analysis of CuInSe$_2$ quantum dots shows that the content of Cu and Se increases relatively with the increase of temperature. The impurity phase is due to InSe at low temperature. When the temperature is continuously raised to 180 °C, the atomic ratio of Cu:In:Se is close to 1:1:1. As temperatures continue to rise, the In content is seriously deficient, and the CuSe impurity phase begins to appear. The peaks

![Fig. 1. CulnSe$_2$ quantum dots.](image)
of the (400) and (316) crystal planes measured by XRD are very weak, reflecting that the sample structure is a tetragonal chalcopyrite structure rather than a tetragonal sphalerite structure. Figure 3 shows the PL emission spectra of CuInSe$_2$ quantum dots at different reaction temperatures. The figure displays that the peak intensity does not change much, but the position of the emission peak is different. When the temperature is 160 °C, the center of the emission peak is around 740 nm. As the temperature increases, the particle size of the QDs increases gradually, the components and internal lattice structure will also change, and hence, it gradually moves toward the long wavelength. Combined with the previous XRD and EDAX analyses, the band edge of the best performance obtained at a temperature of 180 °C was approximately 770 nm, and the forbidden bandwidth of the sample was 1.58 eV.\textsuperscript{18,19}

Transmission electron microscopy (TEM) images were obtained using FEITecnaiF20. Figure 4 shows the TEM image of CISeQDs at different reaction temperatures. It can be seen from the figure that when the temperature is 160 °C, the quantum dots are unevenly distributed and have no fixed morphology. With the increasing temperature, the quantum dots begin to grow and appear with a regular spherical shape, and the crystal lattice begins to appear. An irregular shape appears when the temperature is raised further. The main reason may be that a higher temperature will cause the QD crystal structure to change and the agglomeration of QDs begins to appear and becomes more and more obvious. Combined with the above analysis, when the temperature is 180 °C, the obtained QDs have the best performance, and the average particle size is about 7 nm.

**B. Different reaction times**

The XRD pattern of different reaction times can be seen in Fig. 5. When the reaction time is 18 h, the impurity peak is mainly due to CuSe. As the reaction time increases, the impurity peak of InSe weakens gradually until it disappears. At the same time, the intensity of the diffraction peaks of the three strong peaks increases,
and the width of the half peak narrows, which indicates that the CISeQDs grow gradually at this time, and when the time continues to increase, the peak intensity increase is not obvious. Therefore, the best conditions are determined to obtain CISeQDs at a temperature of 180 °C for 22 h. Table II shows the EDX of CuInSe₂ quantum dots with different reaction times; combined with EDX, it was found that it is similar to changing temperature, the influence of time on CISe-QDs makes both of them show a relatively plenty of Cu and Se, while the content of In decreases relatively. At the same time, the atomic ratio of the three elements obtained at a temperature of 180 °C for 22 h is close to 1:1:2, which is the same as that obtained by XRD analysis.

Figure 6 shows the TEM images of CISeQDs at different reaction times. When the time is 18 h, the QD imaging is not obvious and does not form a fixed topography. When the time is extended to 20 h, QDs begin to appear with a regular spherical shape, and the crystal lattice begins to appear. With an extended reaction time, the QD growth mechanism is more obvious, and the QD size is about 9 nm. When the reaction time is extended to 24 h, the agglomeration of quantum dots begins to appear and becomes more and more intense. Combined with XRD, the optimal reaction time is 22 h.

A square area is selected from Fig. 7 to obtain Fig. 8. Figure 8(a) represents the high-resolution transmission electron microscopy image of the selected region in Fig. 7, the fast Fourier transform spectra in the selection region are shown in Fig. 8(b), Figure 8(c) shows the Bragg scattering spectra obtained by the fast Fourier transform and Fig. 8(d) represents the initial lattice spacing obtained by performing an inverse Fourier transform on the selected region. From Fig. 8(d), the crystal planes are periodically arranged, and the interplanar spacing D is 0.33 nm. By comparing with the XRD pattern, the corresponding crystal plane is (112), which further illustrates that the crystallization of the obtained quantum dots was excellent.

Figure 9 shows the PL emission spectra of CISeQDs at different reaction times. It can be seen from the figure that the emission peak gradually moves toward the long wavelength direction.
When the temperature is 24 h, the emission peak is about 800 nm. Combined with the analysis of the previous sections, the best performance is obtained at 180 °C for 22 h, the absorption band edge is approximately 790 nm, and the forbidden bandwidth of the sample is 1.56 eV. It can be seen from the results of Figs. 5 and 6.

C. Characteristics of CuInSe$_2$ quantum dots adsorbed by TiO$_2$

For the TiO$_2$ modified by quantum dots, we have analyzed the surface appearance and its absorption characteristics. Figure 10 shows a comparison of scanning electron microscopy (SEM) before and after C1SeQD sensitizers covered the TiO$_2$ film. Picture a shows a TiO$_2$ film prepared before, and picture b shows a photoanode after adsorbing C1SeQDs. Both images are obtained at a magnification of 90k, corresponding to a scale of 500 nm. By comparing the pictures a and b, it can be clearly seen that the original TiO$_2$ film is covered by C1SeQDs. At the same time, the quantum dots fill up the voids of the TiO$_2$ film.

Compared with the simple TiO$_2$ film, the light absorbance of the TiO$_2$/C1Se-QD electrodes was enhanced in the visible region obviously and expanded to the near-infrared light region. Figure 11 shows that the absorption range is increased, and a shoulder of the strongest absorption peak appears between 300 nm and 400 nm.

When the CISeQDs were adsorbed, the absorption band edge extended to 800 nm, which was consistent with the CISeQD absorption results obtained earlier. It can be sure that the TiO$_2$ film not only successfully adsorbed CISeQDs, but also expanded the absorption band edge, enhanced the light absorption intensity, and completed the experimental expectation.
IV. CONCLUSIONS

The solvothermal method was successfully used to prepare CuInSe_{2} quantum dots. In addition, the TiO_{2} film prepared by the spin coating method successfully adsorbed quantum dots to obtain photoanodes of quantum dot sensitized solar cells. The prepared samples were analyzed by XRD, EDAX, TEM, SEM, UV–Vis spectra, PL emission spectroscopy, etc., to test the prepared quantum dots and its photoanodes. The optimal reaction conditions of CuInSe_{2} quantum dots prepared by controlling the reaction time, temperature, and the Cu:In:Se raw material ratio of 1:2:1 quantum dots were certified. Optimal QDs were obtained at 180 °C for 22 h with the closest stoichiometric ratio, and the bandgap and emission spectrum of CISQDs can be controlled by modulating the size. The TiO_{2} film was prepared by the spin coating method. By adjusting different ratios of ethyl cellulose and terpineol, the TiO_{2} film with the number of spin coating times of secondary was produced. The experimental results are in line with expectations with a thickness of 11.4 μm. The experiment used the self-assembly method to adsorb CuInSe_{2} quantum dots. It was finally found that the absorption band edge was enlarged and the light absorption intensity was enhanced.

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