Preparation of AgInS₂ nanocrystals and their application as sensitizers for TiO₂ nanorod array photoelectrodes

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Abstract. This paper reports the controlled synthesis of AgInS₂ nanocrystals and their application as sensitizers for TiO₂ nanorod array photoelectrode. The analytical results of high resolution transmission electron microscope (TEM) and laser particle analyzer show that the as–prepared AgInS₂ nanoparticles are highly crystallized with an average diameter of 16.67 nm. The results of ultraviolet (UV)–visible absorption spectra indicate that the as–prepared AgInS₂ nanoparticles have strong absorption in the spectral range of 300 nm–700 nm. The photovoltaic detectable results of TiO₂ nanorod array photoelectrode sensitized by AgInS₂ nanocrystals reveal that the composite films red shift to visible light range with high photovoltaic conversion efficiency of 2.076%, which is 3 times higher than that of bare TiO₂ photoelectrodes.

1. Introduction

In recent years, the controllable synthesis of nanostructural materials remains a research topic of great interest due to their unique chemical and physical properties and potential applications in various areas such as energy storage, luminescence and photoelectricity [1-3]. Metal sulfide nanostructural materials have attracted more and more researchers’ attention due to their excellent luminescence and photoelectricity properties [4], for example, the excellent photoluminescence property of ZnS [5], the potential application of Cu₂S and CdS in photovoltaic fields [6, 7], and the appropriate band-gap of In₂S₃ and Bi₂S₃ [8-10]. Ternary metal sulfide semiconductors, alternatives for appropriate band–gap energies, have been the focus of much recent research because of their unique optical properties and electrical properties as well as their potential applications in linear and nonlinear optical devices and solar cells [11-14]. CuInS₂ with band gap energy of 1.50 eV and absorption coefficient 1.0×10⁵ cm⁻¹, is considered to be ideal in solar cells [15-20]. However, few studies have been conducted on the photovoltaic characteristics of AgInS₂ so far, though its band gap energy is only 1.8 eV [21] and suitable for photovoltaic application. Yet, most researchers keep their eyes on the photocatalytic and luminescent properties. Tsuji and his coworkers reported photocatalytic characteristics of AgInS₂ and ZnS composite materials [22], Torimoto and his partners studied their color–adjustable luminophore...
Hamanaka and his coworkers only studied the photoluminescence properties of AgInS$_2$ quantum dots [24], while ignored their photovoltaic characteristic; Cheng and his partners used AgInS$_2$ crystals as sensitizers on TiO$_2$ thin film solar cell, but only 0.05% low energy conversion efficiency was achieved [25].

In this paper, a high energy conversion efficiency of AgInS$_2$ nanocrystals as sensitizers is achieved and a systematic study of their photovoltaic application on TiO$_2$ nanorod arrays is discussed. The study results show that AgInS$_2$ nanocrystals are appropriate sensitizers.

2. Experimental

2.1. Chemicals

Indium (III) chloride tetrahydrate (InCl$_3$·4H$_2$O), titanium tetrachloride (TiCl$_4$) and thiourea were purchased from Shanghai Chemical Reagent Corporation; thioglycolic acid, silver nitrate (AgNO$_3$), iodine, potassium iodide, hydrochloric acid, methanol anhydrous, ethanol absolute, hexane and acetonitrile were all obtained from Tianjin Chemical Reagent Corporation; Cetylamine (Chengdu) was purchased and used as–received.

2.2. Synthesis of AgInS$_2$ nanocrystals

Typical synthesis of AgInS$_2$ nanocrystals was shown as follows: AgNO$_3$ (1.0 mmol), InCl$_3$·4H$_2$O (1.0 mmol) and thiourea (2.0 mmol) were added to 20 mL cetylamine in a 50 mL three–necked bottle at 120°C under the protection of N$_2$. After reaction for 5 minutes for nucleation, the system was subsequently heated to 180°C and the reaction continued for 60 minutes under N$_2$ flow. Cooling naturally, the nanocrystals were separated by adding 100 mL absolute ethanol. The nanocrystals were washed by excess absolute ethanol for two more times and dispersed in a methanol solution of thioglycolic acid (120 mM) and tetramethylammonium hydroxide (150 mM) to exchange cetylamine molecules which were adsorbent on the surface of nanocrystals for 60 minutes to activate the optical activity. After being precipitated with an ethyl acetate–hexane (1/4, v/v) solution, the as–prepared samples were redispersed in methanol.

2.3. Preparation of AgInS$_2$ nanocrystal sensitive solar cell

TiO$_2$ nanorod arrays were prepared on fluorine doped tin dioxide (FTO) substrates (20×20 mm) by hydrothermal route and the process was similar to the literature [26]. In order to attach the linker molecules to the TiO$_2$ surface, TiO$_2$ nanorod array film was immersed in acetonitrile solution of thioglycolic acid (1.2 M) and sulfuric acid (0.15 M) for 12 h. After that, spin–coating method was used for sensitized TiO$_2$ nanorod arrays by AgInS$_2$ nanocrystals for 2 times, 5 times and 10 times (1000 R/min), respectively. Then, I$_2$/KI solution with a definite concentration was used as the electrolyte, and transparent platinum glass electrode as the cathode to prepare AgInS$_2$ nanocrystal sensitive solar cell.

2.4. Characterization

High resolution transmission electron microscope (HRTEM, Hitach H–7500, Japan) was used to study the microstructure of the AgInS$_2$ nanocrystals, and the average diameter of the AgInS$_2$ nanocrystals was studied by laser particle size analyzer (Zetasizer Nano 3600). Scanning electron microscope (FESEM, JSM–6701F, Japan) was utilized to study the microstructure of the thin films. The crystal structure measurements of the samples were performed by power X–ray diffraction (XRD, Rigaku D/MAX–2500, Japan) using Cu K$_\alpha$ radiation ($\lambda=0.15418$ nm) at the scanning speed of 1.2/’min. UV–vis absorption spectra were recorded using a LabTech (China) spectrophotometer within the wavelength range of 300–1000 nm. The photovoltaic conversion efficiency of the sensitized TiO$_2$ arrays was studied by solar simulator of CELL–S500 (China).
3. Results and discussions

Figure 1 shows the morphology and structure characterization of TiO$_2$ nanorod array film. Figure 1a shows the general SEM image of TiO$_2$ nanorod arrays, and it can be seen that they are uniform on FTO from the inset of which the thickness is observed to be 1.0 µm. Seen from the TEM image (figure 1b), the average diameter of the nanorods is about 120 nm. Figure 1c reveals the clear lattice fringes of TiO$_2$ with an interplanar distance of about 0.323 nm, which is a typical characteristic fringe spacing of the (110) plane of rutile, showing that the TiO$_2$ nanorods grow along the (001) plane.

Figure 1d displays the XRD patterns of TiO$_2$ nanorod arrays. All the diffraction peaks agree well with the tetragonal rutile phase (SG, P42/mmm; JCPDS No. 88–1175, a = b = 0.4517 nm and c = 0.2940 nm). Compared with the powder diffraction pattern, the (002) diffraction peak is significantly enhanced, and some diffraction peaks including (110), (111), and (211) are absent, which indicates that the nanorod arrays are highly oriented with respect to the substrate surface and the TiO$_2$ nanorods grow in the (001) direction with the growth axis parallel to the substrate surface. Moreover, these conclusions are also confirmed by HRTEM measurement.

Figure 2 shows characterization of AgInS$_2$ nanocrystals. Figure 2a displays the TEM image of monodispersed AgInS$_2$ nanocrystals with the average size range of 7–20 nm, which coincides with the characterization result of the laser particle size analyzer as shown in figure 2d where the average diameter is observed to be 16.67 nm. From the HRTEM image (figure 2b), it can be seen that these nanoparticles are well crystallized, and the inset of figure 3b reveals clear lattice fringes with an interplanar distance of about 0.356 nm which is a characteristic fringe spacing of the orthorhombic AgInS$_2$ crystal phase in the (120) crystal plane. The average particle size of the AgInS$_2$ nanocrystals is calculated to be about 16.5 nm according to Scherrer Equation which also matches the results of the
TEM and the laser particle size analyzer very well.

Figure 2. Characterization of AgInS$_2$ nanocrystals: (a) TEM image; (b) HRTEM image; (c) XRD pattern; (d) size distribution chart by number.

Figure 3. UV–vis absorption spectra of AgInS$_2$ nanocrystals.

The crystal structure of the as–synthesized products is examined by XRD. Figure 2c shows the XRD patterns of AgInS$_2$ nanocrystals, from which it can be seen that all the diffraction peaks can be assigned to the orthorhombic–phase AgInS$_2$, and this result has been also proven by the HRTEM (figure 2b).

The UV–vis absorption spectrum of AgInS$_2$ nanocrystals is shown in figure 3. It shows a wide absorption in the spectral range of 300 nm to 700 nm, and the wavelength of the absorption edge can be clearly identified at around 700 nm (corresponding to $E_g$ of 1.8 eV). Since the $E_g$ of AgInS$_2$ is reported to be 1.8 eV within the band energy range of 0.9–1.9 eV in which most of the solar energy can be absorbed, it can be one of the best solar cell sensitizers.

Figure 4 displays the SEM image of TiO$_2$ nanorod arrays sensitized by AgInS$_2$ nanocrystals for different spin–coating cycle times: 2, 5, and 10 times, respectively. The gap in the nanorod arrays is infilled slowly by AgInS$_2$ nanocrystals with the increase of spin–coating cycle times. After spin–coating for 2 times, few AgInS$_2$ nanocrystals can be observed under SEM (figure 4a), but after spin–coating for 10 times, very compact nanocomposite film is obtained, and the nanorod arrays can’t be observed (figure 4c). The optimal spin-coating cycle is 5 times demonstrated by figures 4b and 5a and b, which indicates that they absorb a sufficient number of AgInS$_2$ nanocrystals with TiO$_2$ nanorod arrays being exposed on the surface. Figure 5c shows XRD patterns of the TiO$_2$ nanorod arrays
sensitized by AgInS2 nanocrystals. All the diffraction peaks can be attributed to the tetragonal rutile phase TiO2 and orthorhombic AgInS2 crystals. The peak in (002) plane is weakening compared with figure 1b because it is covered by AgInS2 crystals. The peaks in (121), (040) and (323) crystal planes show that the AgInS2 nanocrystals have no remarkable change.

Figure 4. FESEM images of TiO2 nanorod arrays for different spin–coating times. (a) for 2 times; (b) for for 5 times. (c) for 10 times.

Figure 5. TEM images of TiO2 nanorod arrays sensitized by AgInS2 nanocrystals spin–coating for 5 times. (a) general image; (b) detailed image; (c) XRD pattern.

Figure 6. (a) UV–vis absorption spectra of TiO2 nanorod arrays sensitized by AgInS2 crystals; (b) the photocurrent density–voltage (J–V) curves of the TiO2 solar cells sensitized by AgInS2 nanocrystals for different spin–coating times under AM 1.5 illumination of 100 mW cm–2.
The UV–vis absorption spectra of TiO₂ nanorod arrays sensitized by AgInS₂ nanocrystals are shown in figure 6a. It can be seen that the optical absorption of the TiO₂ nanorod arrays is in the ultraviolet region. However, after being sensitized by AgInS₂ nanocrystals, the absorption edges of the thin films can red shift to the visible region, and the red shift length increases with the sensitized times, indicating that AgInS₂ nanocrystals as the sensitizers for TiO₂ nanorod arrays expand the photoabsorption range.

Figure 6b shows the photocurrent density–voltage (J –V) curves of the solar cells based on the TiO₂ photoelectrodes sensitized by AgInS₂ nanocrystals with an active area of about 0.78 cm² under AM 1.5 illumination of 100 mW cm⁻² for 20 times cycles. The photovoltaic parameters of the solar cells are summarized in table 1. It shows that the solar cell based on bare TiO₂ indicates a short–circuit photocurrent density (Jsc) of 2.474 mA cm⁻², an open–circuit voltage of 501 mV, a fill factor (FF) of 59.5%, and a conversion efficiency of 0.672%. The relatively low efficiency is ascribed to the low density uniform TiO₂ nanorod arrays thin film, which decreases the surface area and the effective quantity of the photo–generated electrons. The relatively high efficiency of thin film can be attributed to the sensitizers AgInS₂ nanocrystals on the surface of TiO₂ nanorods that absorb more solar energy and generate more photo–generated electrons than bare TiO₂ as shown in table 1 (Cell 2 and Cell 3). After being sensitized for 2 times, the energy conversion efficiency is 1.18%, and it almost improves twice up to 2.076% after being sensitized for 5 times and the FF is 70.8% which is the max one of all the values shown in table 1. The decrease of conversion efficiency of Cell 4 is due to a large amount of AgInS₂ nanocrystals being deposited on the TiO₂ film, which agglomerate into chunks and lead to a decrease of quantum efficiency.

### Table 1. Photovoltaic parameters of the TiO₂ solar cells sensitized by AgInS₂ nanocrystals for different spin–coating times: 2 times (TiO₂–2), 5 times (TiO₂–5) and 10 times (TiO₂–10) under AM 1.5 illumination of 100 mW cm⁻².

| Sample | Sensitized times | V oc (mV) | J sc (mA cm⁻²) | FF (%) | η (%) |
|--------|------------------|-----------|----------------|--------|-------|
| Cell 1 | 0                | 501       | 2.474          | 59.5   | 0.672 |
| Cell 2 | 2                | 546       | 3.218          | 67.1   | 0.998 |
| Cell 3 | 5                | 576       | 4.513          | 70.8   | 2.076 |
| Cell 4 | 10               | 525       | 3.013          | 65.4   | 1.180 |

### 4. Conclusion
Orthorhombic AgInS₂ nanocrystals are synthesized by a simple wet chemical route. The results of TEM and laser particle size analyzer show that the diameter of the AgInS₂ nanocrystals is 16.67 nm; and they have strong optical absorption in the spectral range of 300 nm–700 nm. The study results show that AgInS₂ nanocrystals are suitable for use as sensitizers for solar cells. The sensitized results show that the max energy conversion efficiency is 2.076 % after spin–coating for 5 times, and after that the energy conversion efficiency decreases with the increasing the spin–coating times.

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