

Study on synthesis and photoelectric properties of AgInS₂ quantum dots

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AgInS₂ Quantum dots (AIS QDs) have high quantum yield and catalytic performance, which is promising materials in photo-catalytic and optoelectronic fields. In the paper, it adopted a simple and non-toxic method to synthesize AIS QDs. The effect of reaction temperature on the growth mechanism, optical and physical properties of AIS had been extensively investigated by using L-cysteine as the sulfur source, and their application in catalytic hydrogen production was also studied. The results demonstrated that the fluorescence properties will be quenched with the increase of temperature, indicating that the separation speed of electron hole pairs of samples obtained at higher temperature was faster. Meantime, the electron transport capacity and the photocurrent had also improved with the increase of reaction temperature. Finally, the sample obtained at 100 °C had higher hydrogen production rate.

Keywords: AgInS₂; Quantum dots; Optical properties; Photocatalytic hydrogen production.

INTRODUCTION

With the development of measurement and characterization technology, nanoscience and nanotechnology had become a highly interdisciplinary research field¹. QDs had a quantum confinement effect because of their small size (< 10 nm), which was not only equipped with excellent optical and electronic properties, but also had high specific surface area, electrocatalytic activity, and electron transport properties². QDs had been widely used in various fields, such as fluorescence imaging, biosensor, and electrocatalytic^{3–4}. At present, the synthesis of binary QDs based on II-VI and IV-VI materials had been widely investigated. However, QDs based on II-VI and IV-VI materials application in the biological field were limited due to their high toxicity^{5–6}. Unlike binary quantum, ternary QDs were a wider visible light absorption range, low band gap energy value, a lot of crystallographic defects, and ease of formation of n/p carriers, which made them have broader application prospects in the fields of biology and optoelectronics⁷. Among them, ternary quantum dots (such as CuInS₂, AgInS₂) provided more possibilities for their applications by using I (Cu, Ag) and III (Al, Ga, In, Ti) family metals to replace the toxic cations of II-VI and IV-VI quantum dots^{8–9}, thus attracting increasing attention from scholars.

The synthesis methods of ternary quantum dots mainly included solid, hydrothermal method, hot injection method and decomposition of single-source precursors, and so on. For instance, Song et al.¹¹ synthesized AgIn₅S₈ with higher crystallinity and fewer defects through a facile hydrothermal route and found AgIn₅S₈ exhibited excellent photocatalytic activity for H₂ production by promoting the charge separation and transfer processes. Sousa et al.¹² synthesized AgIn₅S₈ using electrochemical method, which demonstrated high photoluminescence properties and redshifted with the gradual increase of Ag⁺/In³⁺. AgInS₂ is quite extensive in this kind of QDs. Torimoto et al.¹³ used thermal decomposition to obtain ZnS-AgInS₂ without highly toxic elements. Tang et al.¹⁴ obtained Zn-AgInS₂ nanocrystals by a simple solution method which provided a reference for I-III-VI-based semiconductors. In addition, AgInS₂ also had a wide range of applications. Luo et al.¹⁵ carried out a series of experiments on

AgInS₂ complexes with highly active in photocatalytic processes. Kameyama et al.¹⁶ also studied the application of ZnS-AgInS₂ for photocatalytic hydrogen production. Lan et al.¹⁷ represented one-pot synthesis of direct Z-scheme AgInS₂/AgIn₅S₈ QDs heterojunction, which was employed for photocatalytic reduction of aqueous Cr⁶⁺. Kurshanov et al.¹⁸ synthesized colloidal ternary quantum dots of AgInS₂ and AgInS₂/ZnS in water in the presence of mercapto alkyl carboxylic acid.

In this study, AIS QDs were synthesized through an environmentally friendly and reliable hydrothermal method. The morphology and composition of the samples synthesized at different temperatures were analysed, and the formation mechanism was deduced. Finally, the electrochemical and catalytic hydrogen production tests were characterized to explore the influence of experimental temperature on the catalytic performance of the material. The results showed that temperature had an important influence on the formation and properties of AIS QDs.

EXPERIMENTAL

Materials

Indium nitrate tetrahydrate (In(NO₃)₃ · 4H₂O, technical grade, 99.9%), silver acetate (CH₃COOAg, 99.5%), and L-cysteine (C₃H₇NO₂S, 98.5%) were purchased from Sinopharm Chemical Reagent Co, Ltd (SCRC). All the chemicals were used without further purification.

Synthesis of AIS QDs

Firstly, 1 mmol CH₃COOAg, 4 mmol In(NO₃)₃, and 4 mmol L-cysteine were successively added to deionized water and stirred evenly. Then, the above reaction solution was moved to the Teflon-lined stainless autoclave (50 mL). The autoclave was placed in the drying oven, and maintained at 90 °C, 100 °C and 120 °C within a certain reaction time, respectively. After that, it was cooled to room temperature and removed the excess impurities with ethanol.

Characterization

X-ray diffraction (XRD) patterns were recorded with a Rigaku Ultima IV diffractometer operating with Cu

K α radiation. The SEM specimens were prepared by sonicating the products in absolute ethanol, and the morphology was characterized by Zeiss sigma 300 scanning electron microscope. Transmission electron microscopy (TEM) images were acquired using FEI Tecnai G2 F20 attached with energy-dispersive X-ray spectrum (EDS). Fourier transform infrared (FTIR) was operated by Nicolet IS 10. X-ray photoelectron spectroscopy (XPS) was acquired by Thermo Kalpha. The fluorescence properties and photoluminescence (PL) spectra were tested by F97Pro spectrophotometer. The absorption properties were acquired by UV-3600. Photocatalytic hydrogen production was tested by the Photocatalytic reaction system (PerfectLight, Labsolar-IIIAG). First, photocatalyst (50 mg) was dispersed in methanol (5 mL) and deionized water (45 mL). Then, the resulting mixture was degassed to completely remove air to about -0.1 MPa. Ar was used as the carrier gas in H₂ production. A 300 W Xenon lamp with a filter ($\lambda > 420$ nm) was used as the light source. The amount of H₂ was quantitatively analysed by a GC9200 gas chromatograph. Photoelectrochemical properties were tested using a CHI760E workstation in 0.5 M Na₂SO₄, where Pt plate was used as the counter electrode, and Ag/AgCl in saturated KCl was used as the reference electrode, and the prepared films with an area of 0.8 cm² were used as the working electrode. Full band spectrum was used as the illumination source with 300 W xenon lamp.

RESULTS AND DISCUSSION

Fig. 1 showed three samples with experimental temperatures of 90 °C, 100 °C and 120 °C for 4 h, which were labeled 1#, 2#, and 3#, respectively. It can be seen from the XRD pattern that the diffraction peaks become obvious with the increase of temperature, which indicated that higher temperature was more conducive to the crystallization of samples. The materials synthesized at 90 °C and 100 °C were composites composed of Ag, In, S and L-cysteine. The sample obtained at 120 °C showed the characteristic peaks at $2\theta = 24.95^\circ$, 26.55° , 28.34° , 43.66° , 44.50° , 48.03° and 52.60° , which corresponded to (120), (002), (121), (040), (320), (123), and (322) crystal planes of AIS (PDF No. 01-089-5020). Besides, the wider peak width indicated that sample 3 has a small size. L-cys has symmetric and asymmetric stretching vibrations with -CH₂ groups located at 3180

and 2976 cm⁻¹ and O-H, S-H, C-N, C-S, C=O and COO- stretching vibrations bands located at 3428 cm⁻¹, 2552 cm⁻¹, 1062 cm⁻¹, 638 cm⁻¹, 1597 cm⁻¹, 1398 cm⁻¹¹⁹. From Fig. 1b, samples 1 and 2 all showed the symmetric and asymmetric stretching vibrations of the -CH₂ group at 3180 cm⁻¹ and 2976 cm⁻¹ and at 1597 cm⁻¹, 1398 cm⁻¹, 1062 cm⁻¹ appeared C=O, COO-, C-N respectively stretching vibration bands, which validated the presence of carboxylic acid groups in all three samples. Besides, three samples did not show C-H, S-H tensile vibration bands at 2552 cm⁻¹, 638 cm⁻¹. This meant that S-H and C-H bonds were broken and S atom falls off from L-cys to form AIS with Ag and In. Sample 3 did not exhibit asymmetric stretching vibration of the CH₂ group at 2976 cm⁻¹. It showed that the structure of L-cys was more severely damaged with the temperature increased.

Fig. 2 showed the SEM and TEM images of AIS QDs of sample No. 1#, 2# and 3#, which showed a spherical shape. It can be seen from the image that the morphology of the sample had changed significantly. AIS QDs were uniformly dispersed in the matrix of L-cys. For samples No.1# and 2#, the AIS QDs and L-cys complex formed network structure. When the temperature was raised to 120 °C, the matrix of L-cys structure was changed from a loose network to a dense plate structure, which may be due to L-cys structure damage. By observing the TEM image, sample No. 1# was amorphous with homogeneous particle distribution. Sample No. 2# had a dark color area surrounded by a light color, which indicated the complex began to decompose into AIS QDs. For sample No. 3# obtained at 120 °C, there were a large number of small particles about 3 nm, and some large particles, which indicated the complexes consisted of small AIS QDs and large L-cys. In the EDS patterns (Fig. 2d, 2h, and 2l), it can be seen that the peaks of Ag and In gradually formed as the temperature increased. In Fig. 2l, when the temperature was 120 °C, the peaks of Ag, In, and S were very obvious and the molar ratio was approximately 1:1:1.5, indicating that high temperature was helpful for the formation of AIS QDs. Based on the above results, when the reaction temperature was low, the structure of L-cys wasn't destroyed, which resulted in a certain agglomeration phenomenon, it can be clearly seen that the samples were a complex composed of Ag-In-L-cys. With the increase of temperature, the structure of L-cys was destroyed and the surface energy of the whole system

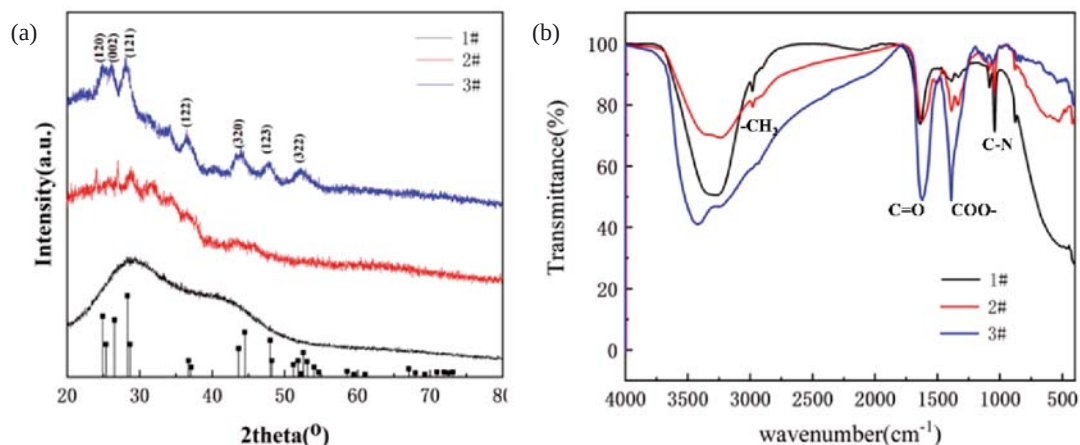


Figure 1. (a) XRD pattern and (b) FTIR spectra of the samples No. 1#, 2# and 3#

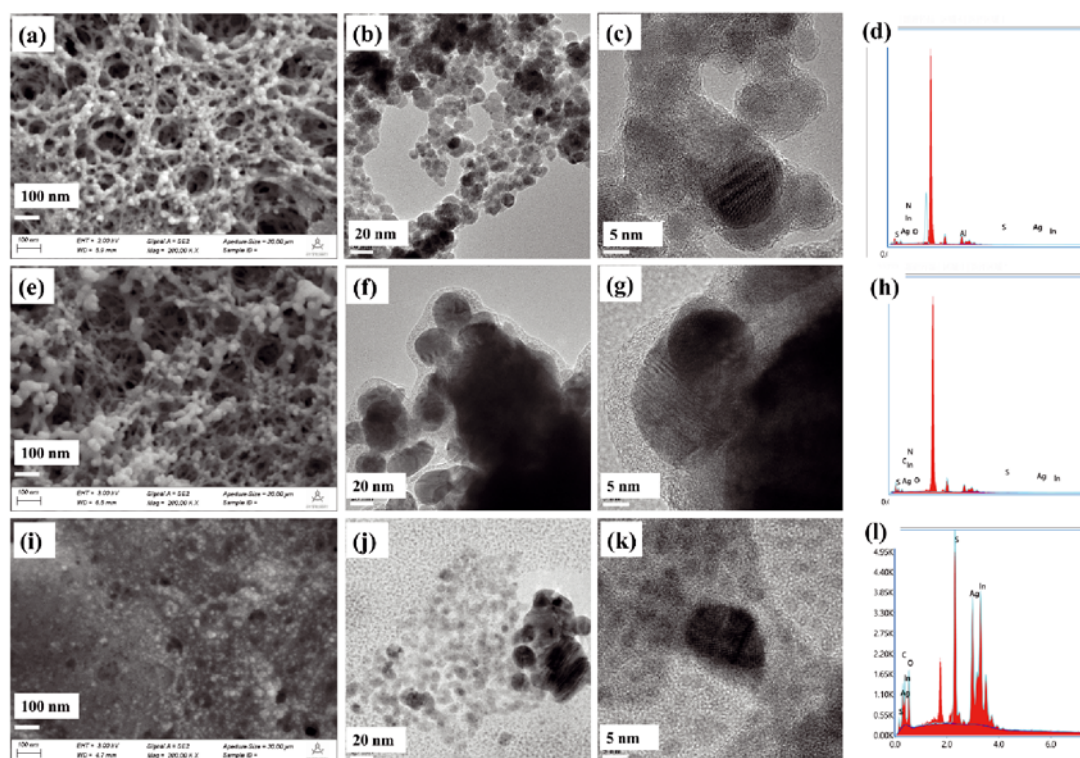


Figure 2. (a, e, i) SEM patterns, (b, c, f, g, j, k) TEM patterns) and (d, h, l) EDS patterns; a–c, d–h, and i–l were synthesized at 90 °C, 100 °C, and 120 °C, respectively

reduced, which meant that the Ag-In-L-cys complexes started to be destroyed and decomposed into AIS QDs. Meantime, L-cys as a coating agent was able to separate the QDs and then prevented their agglomeration. Thus, AIS quantum dots with uniform dispersion were formed.

Fig. 3 showed the X-ray photoelectron spectroscopy information (XPS) of the sample at 120 °C, which can be used to study the element valence states of AIS. Fig. 3a showed that AIS was composed of Ag, In, S, C, N and O. Among them, O, C and N may come from L-cysteine or air. Fig. 3b showed that the binding energies of Ag

$3d^{3/2}$ and Ag $3d^{5/2}$ orbitals were 374.1 eV and 368.1 eV, respectively, indicating that the type of Ag was Ag^+ . Fig. 3c showed that the binding energies of In $3d^{3/2}$ and In $3d^{5/2}$ orbits were 452.4 eV and 444.8 eV, which indicated that the type of In was In^{3+} . Fig. 3d showed that the binding energies of S $2p^{1/2}$ and S $2p^{3/2}$ were 162.8 eV and 161.7 eV, respectively, which was assigned to the S^{2-} binding energy spectrum in turn. The above results further proved the production of $AgInS_2$.

Fig. 4a showed the photoluminescence diagram of the sample at 90 °C, 100 °C, and 120 °C. The sample No. 1#

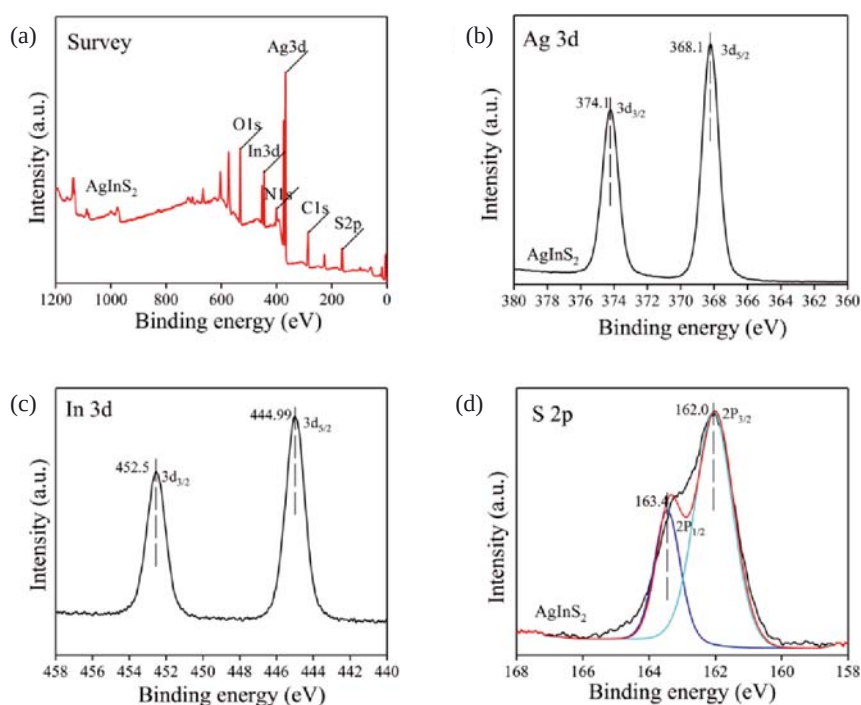


Figure 3. XPS spectrum of sample at 120 °C

showed obvious photoluminescence characteristics, and the emission wavelength was around 620 nm. When the temperatures were 100 °C and 120 °C, it did not show any emission peak. The lack of photoluminescence under the experimental conditions of 100 °C and 120 °C also indicated that the charge separation efficiency may be improved with the increase of the reaction temperature. From Fig. 4b, the band gap of quantum dots changed, which affected the absorption wavelength of the sample due to different crystals⁷. As the heating temperature increased, the absorption edge gradually redshifted and the slope gradually decreased. The bandgap diagram was obtained by converting the formula as shown in Fig. 5d. The reason for the narrowing of the band gap was considered from a microscopic point of view. Due to the increased crystallinity of the quantum dots, the band gap width of the quantum dots was reduced, resulting in a red-shift phenomenon. In addition, each substance had its own special peak, and no other peaks were shown on the absorption diagram, which is used to prove the purity of the samples.

Fig. 5a is the Electrochemical Impedance Spectroscopy (EIS) of samples synthesized at 90 °C, 100 °C and 120 °C. The semicircle in the spectra was caused by the charge

transfer between the sample and the electrolyte, which indicated the impedance of the sample in charge transfer. The smaller the diameter of the semicircle indicated that the sample had a smaller resistance to charge transfer. Thus, the impedance of sample No. 3# was the smallest, which meant it had the fastest rate of electron transfer. Fig. 5b was the curve of transient photocurrent responses. The photocurrent of samples No. 2# and 3# was about 9.05 μA and 13.1 μA , respectively, while the photocurrent of sample No.1 was almost zero. The photocurrent of sample No.2 decreased first and then increased, and remained unchanged after 5 cycles under on/off switching irradiation. The results meant that sample No.2# had high light stability and was reproducible. The photocurrent of sample No.3 can keep up to 64 % after 6 cycles under on/off switching irradiation, indicating that sample had lower light stability and was reproducible. Compare with sample No.2#, the photocurrent of sample No. 3# was higher, but the light stability wasn't high, which indicated that sample No. 3# was easy to agglomerate under light due to the small sample size. The ratio of photocurrent to dark current reached 10^3 for them with very high photosensitive properties. The OER activity of the samples was examined through the

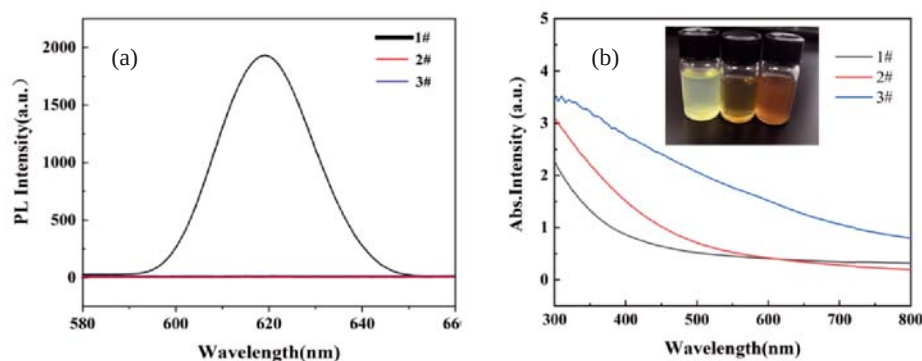


Figure 4. (a) PL spectra of (b) Absorption spectra of the samples No. 1#, 2#, 3#

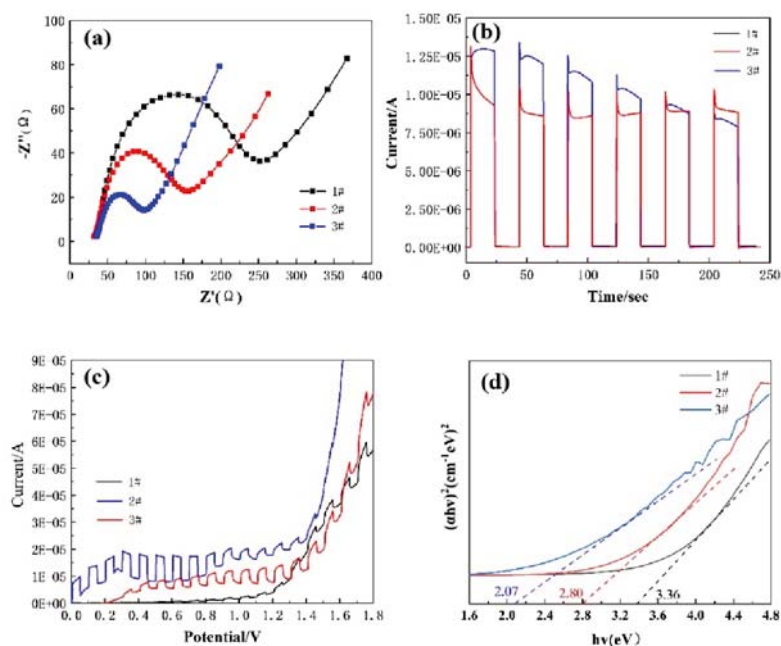


Figure 5. (a) EIS spectra, (b) Transient photocurrent responses, (c) linear sweep voltammetry curves (LSV), and (d) $h\nu$ v.s. $(\alpha h\nu)^2$ curve of samples No. 1#, 2#, and 3#

LSV test. As shown in Fig. 5c, compared with samples No.1# and 2#, sample No. 3# had the lowest starting point of polarization current. Meantime, samples No. 2# and 3# had photosensitive properties with 1.4 V, which showed that they had good catalytic activity and stability. The results showed that the reaction temperature had an important effect on the catalytic activity. Fig. 5d was bandgap spectra of three samples. It can be seen that as the temperature increased, the optical band gap decreased from 3.36 eV to 2.07 eV. Based on XRD and TEM results, the crystallization and particle size were changed with temperature, it can be proved that the results were consistent with the quantum confinement effect²⁰. With the increase of the band gap, the energy of photogenerated carriers was higher, so their migration ability was stronger, which was more conducive to the occurrence of redox reactions.

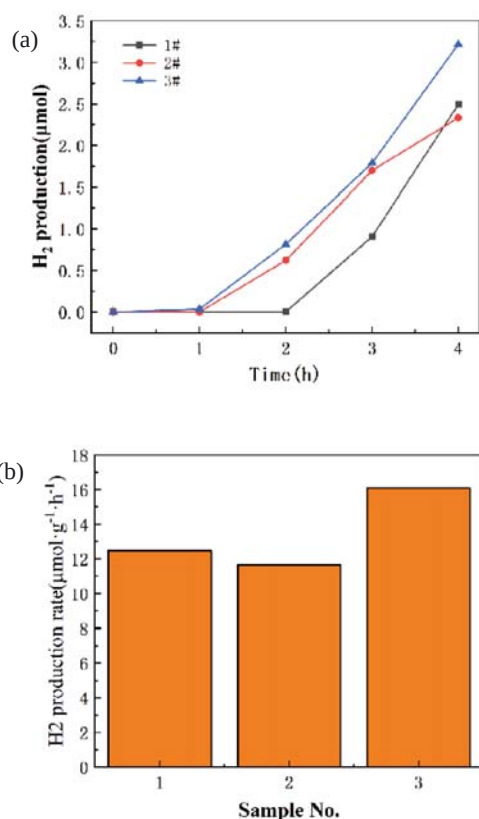


Figure 6. (a) Photocatalytic H₂ production, (b) H₂ production rate of samples No. 1#, 2#, and 3#

Fig. 6 showed photocatalytic performance of AIS QDs for H₂ production. Sample No. 3# had a higher hydrogen yield than the other two samples. It can be seen from Fig. 6a that samples No. 2# and 3# gradually generated hydrogen gas after 1 h, but sample No. 1# started to generate hydrogen gas after 2 hours. The hydrogen production rate of sample No. 2# was reduced after 3 h, which may be that the 2# had poor stability and the low crystallinity of the sample. In addition, AIS QDs obtained at 120 °C had the highest hydrogen generation rate, this result was consistent with the result of the above EIS electrochemical test. With the gradual formation of AIS QDs, the efficiency of hydrogen production increased. Based on the above results, crystallinity and particle size

played an important role in the efficiency and stability of hydrogen production.

CONCLUSIONS

In this paper, AIS QDs were synthesized by a one-step hydrothermal method, and the experimental process was simple, safe and easy to synthesize. AIS QDs gradually formed with the temperature increased, and the samples obtained at 120 °C were proved to be AIS QDs. The high temperature can effectively promote the crystallization of particles. By XPS testing, the samples obtained at 120 °C was proved to be AIS. Meantime, through XRD, SEM, TEM, XPS and FTIR analysis, the samples were a complex composed of Ag-In-L-cys when the reaction temperature was low, and then the Ag-In-L-cys complexes started to destroyed and decomposed into AIS QDs with an increase of temperature. In the process, L-cys as a coating agent was able to separate the QDs and then prevented their agglomeration. In addition, the impedance and the electron hole recombination rate in charge transfer will decrease with the increase of temperature. Due to the influence of crystallization and particle size, the band gap decreased from 3.36 eV to 2.07 eV with the increase of temperature. By the photocatalytic test, it was found that AIS QDs obtained at 120 °C exhibited the highest catalytic hydrogen production efficiency. It can be concluded that temperature played a very important role in the formation of AIS QDs and their hydrogen production efficiency.

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