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Advances in Colloidal I-III-VI₂-Based Semiconductor Quantum Dots toward Tailorable Photofunctional Materials

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ABSTRACT

Group I-III-VI₂ semiconductor-based quantum dots, such as AgInS₂, CuInS₂ and their solid solution with ZnS, have recently been reported to show intense photoluminescence, the wavelength of which is tunable in a wide range from visible to near-infrared (NIR) light regions by controlling their chemical composition and/or size. Due to their low toxicity and tunable optical properties, these multinary semiconductor quantum dots (QDs) have been intensively developed as alternative materials to conventional Cd- and Pb-based QDs for applications to photoluminescent devices, photocatalysts, quantum dot solar cells, and biological imaging materials. In this review, the recent progress in the photofunctionality of I-III-VI₂-based semiconductor QDs prepared by the colloidal method is outlined with focus on two advances: (1) extension of the photoluminescence wavelength to NIR light for in vivo biological imaging and (2) improvement of photoenergy conversion properties by nanostructure control of QDs.

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1. Introduction

The preparation and application of low-toxic semiconductor nanocrystals of so-called quantum dots (QDs) chemically synthesized in solution have recently become one of the mainstreams of colloidal chemistry. Conventional QDs such as CdSe, CdTe and PbSe have (1) a wide absorption band, (2) a high photoluminescence quantum yield (PL QY), and (3) a controllable energy gap (E_g) by the quantum size effect.^{1,2} Due to these attractive optical properties, QDs have become key materials for optical and optoelectronic applications such as biological markers,^{3–6} light emitting devices,^{7,8} and solar cells.^{9,10} However, one of the biggest problems of CdSe and PbSe, which are the most well-developed semiconductor QDs, is that they contain highly toxic elements and therefore have limitations for commercial QD-based applications.

To overcome this disadvantage, efforts have been focused on the preparation of multinary semiconductor QDs consisting of a group I-III-VI₂ semiconductor and their solid solution, such as CuInS₂,^{11–14} AgInS₂,^{15–17} CuInS₂-CuGaS₂,^{12,18} and ZnS-AgInS₂.^{19–23} These low-toxic semiconductor QDs having a direct band gap and a large absorption coefficient have been extensively studied as luminescent and absorbing materials over the past two decades. Due to many efforts worldwide, these multinary QDs have been developed to show sufficiently strong emission (PL QY > 80%) in visible and the near-infrared (NIR) light regions. Unlike conventional binary QDs, the E_g of I-III-VI₂-based multinary QDs can be conveniently altered by changing the particle size as well as their chemical composition. Group I-III-VI₂ semiconductors can easily form a solid solution with a group II-VI semiconductor having a similar crystal structure, and the particle composition greatly influences the E_g of QDs. A typical example of ZnS-AgInS₂ QDs is shown in Fig. 1a. Since this composition control does not require tight control of the size and reaction conditions during the synthesis procedure, it is a more feasible method for obtaining the desired PL wavelength.

The author and co-workers have developed I-III-VI₂-based semiconductor QDs of ZnS-AgInS₂ (ZAIS) solid solution with

Figure 1. (a) Schematic illustration of the flexibly-controllable electronic energy structure of a solid solution semiconductor quantum dot. Absorption (b) and PL spectra (c) of ZAIS QDs with an average diameter of ca. 5.5 nm in chloroform. Reprinted with permission from Ref. 25.

good PL properties and have been working on the control of their PL wavelength in the visible wavelength region by tuning in their size and chemical composition of the solid solution (Fig. 1b

and c).^{19,20,24,25} Furthermore, we have found that ZAIS QDs precisely synthesized in this manner are useful not only as light-emitting materials but also as energy conversion materials such as photocatalysts²⁵ and sensitizers in solar cells.^{26,27} However, further improvements in the optical and photoelectrochemical properties are needed to replace high-quality conventional QDs with these multinary QDs. Recent advances in I-III-VI₂-based semiconductor QDs and their solid solutions for photoluminescence and photoelectrochemical applications are presented in this review article. Two topics are focused on. The first topic is extension of the responsive wavelength to the NIR light region in I-III-VI₂-based QDs for in vivo biological imaging. The second topic is improvement of the light energy conversion properties by nanostructure control of the QDs.

2. Development of Low-toxic Semiconductor QDs for Effective Utilization of NIR Light

Highly-luminescent semiconductor QDs are widely used in biological imaging because of their unique physicochemical properties that can overcome many of the disadvantages of conventional organic fluorescent dyes.^{3–6} These QDs exhibit narrow PL spectra for multicolor imaging, wide absorption for flexible excitation wavelengths, and high stability to excitation light for long time imaging. Since NIR light permeates living tissues (e.g., skin, blood) more efficiently than dose other light such as UV, visible, or IR light, QDs emitting NIR light with a wavelength of 700–1400 nm have attracted much attention for in vivo imaging.²⁸ Although Cd- and Pb-based QDs exhibit the desirable properties described above in the NIR region, concerns remain regarding the use of these highly-toxic heavy metals in biological imaging applications. Therefore, I-III-VI₂-based QDs, such as AgInS₂, AgInSe₂ and CuInS₂, have been developed as materials that exhibit relatively strong PL in the NIR region. For example, Deng et al., successfully prepared highly photoluminescent CuInS₂/ZnS core-shell QDs with a PL peak around 800 nm and showed their good performance as in vitro and in vivo optical imaging probes. These CuInS₂/ZnS QDs with low cytotoxicity were shown to be useful as prove for multicolor biomedical imaging.²⁹

In order to utilize a “second biological window” for in vivo imaging (1000–1350 nm) where optical scattering is reduced compared to that in the case of shallower NIR light (800–1000 nm),^{28,30} the development of new QDs with smaller E_g is necessary. Since AgInTe₂ semiconductors were reported to have a bulk band gap of about 1.0 eV, size-controlled AgInTe₂ QDs are promising as NIR luminescent markers. Although AgInTe₂ nanoparticles of only 11 nm in size showing PL QY as low as 0.06% have been prepared, no AgInTe₂ QDs showing high luminescence have been reported.³¹

2.1 Preparation of multinary QDs and improvement in their NIR-emitting properties

In colloidal synthesis of QDs, the metal and the chalcogenide precursor in the coordinating organic solvent were subjected to heat treatment to initiate the reaction. In the homogeneous nucleation step, the solvent was coordinated on the surface of the generated nucleus to stabilize the surface energy, and a colloidal QD was formed in a solution in which the nanoparticles were uniformly dispersed in the organic solvent after sufficient crystal growth. In the case of AgInTe₂ QDs, the corresponding metal acetate and triethylphosphine telluride as precursors were reacted in 1-dodecane thiol as a solvent by heat treatment under an N₂ atmosphere.³² Anisotropic rod-like particles were obtained at all temperatures between 180 and 300°C, and the diameter and length of the particles increased with increase in reaction temperature (Fig. 2a, b). When the synthesis was carried out at 300°C, the diffraction pattern was in good agreement with the previously reported tetragonal AgInTe₂ in

Figure 2. Representative TEM images of AgInTe₂ QDs prepared at (a) 180°C. (b) Dependence of width (circles) and dependence of length (squares) of AgInTe₂ QDs on temperature in the preparation. (c) Absorption and PL spectra of AgInTe₂ QDs prepared at temperatures of (i) 180°C, (ii) 220°C, (iii) 250°C, (iv) 280°C, and (v) 300°C. The wavelength of excitation light for PL measurement was 700 nm. Reprinted with permission from Ref. 32.

bulk crystals. On the other hand, when the reaction temperature was less than 300°C, a peak that could not be attributed to the reported AgInTe₂ crystal phase was observed. From simulation of the diffraction pattern using analysis software, these diffraction peaks agree well with AgInTe₂ of a hexagonal structure.

When the rod width decreased from 8.2 to 5.5 nm with decrease in the reaction temperature from 300 to 180°C, narrow emission peaks with full width at half maximum (FWHM) of 110–180 meV appeared near the absorption onset wavelength and shifted to a shorter wavelength region (Fig. 2c). It has been reported that typical I-III-VI₂ semiconductor QDs such as AgInS₂, AgInSe₂, and CuInS₂ exhibit broad PL peaks (FWHM of ca. 200–400 meV) due to recombination of donor–acceptor pairs.^{20,33,34} On the other hand, well-developed binary QDs, such as CdTe and PbS, are known to exhibit narrow near-band edge emissions with FWHMs of ca. 50–100 meV.^{35,36} Therefore, it was considered that the PL of the AgInTe₂ QDs showed radiative emission from the electronic state near the band edge state. The maximum PL QY was determined to be 18%, which was more efficient than indocyanine green (PL QY of 14%), a typical organic dye used for current in vivo imaging.³⁷

To improve PL properties, optimization of the process for synthesis of AgInTe₂ QDs was carried out by changing various reaction conditions such as the precursor concentration and reaction time. The reaction time greatly influenced PL QY of AgInTe₂ QDs. When the reaction time was extended to 180 min from the original 5 min, there was an improvement of PL QY up to 47% without broadening of the PL peak (Fig. 3a, b). Various types of structural defects and thermally induced disorders produce electronic states that act as non-radiative recombination states in the band gap. As the reaction time was increased, these states in AgInTe₂ QDs were probably removed and PL QY was enhanced. However, when the heating time was further extended beyond 180 min, PL QY decreased as shown in Fig. 3b, presumably due to the formation of additional defect sites on the surface of particles. To the best of our knowledge, the maximum value of PL QY obtained with AgInTe₂ QDs (47%) is as high as that of conventional Cd-free or Pb-free QDs as NIR light-emitting materials.³⁸

Although the AgInTe₂ QDs obtained by this method had a hydrophobic surface because long-chain organic ligands were adsorbed on the surface, QDs should be uniformly dispersed in water for use in biological applications. Therefore, the thus-obtained AgInTe₂ QDs were incorporated into liposomes formed by

Figure 3. (a) PL spectra of AgInTe₂ QDs prepared with different heat treatment times at 180°C. The wavelength of excitation light was 700 nm. (b) A plot of PL QYs of AgInTe₂ QDs as a function of heat treatment time. Reprinted with permission from Ref. 38.

Figure 4. (a) In vivo photoluminescence imaging of a mouse after injection of a 50 mm³ portion of liposome-AgInTe₂ QD composites. The concentrations of AgInTe₂ QDs in the dispersions injected were 50 (i), 25 (ii), 12.5 (iii), 6.25 (iv), and 0 nmol (particles) dm⁻³ (v). (b) Time course of PL intensity after the injection of liposome-AgInTe₂ QD composites containing 50 nmol (particles) dm⁻³ AgInTe₂ QDs. Reprinted with permission from Ref. 32.

phospholipids that can be uniformly dispersed in water.³² To explore the potential application of AgInTe₂ QDs for in vivo imaging, the thus-obtained liposome-AgInTe₂ QD composites were injected into the back of a hair-removed C57BL/6 mouse. The obtained PL image was superimposed on a photograph of the mouse as shown in Fig. 4a. NIR PL emitted from the AgInTe₂ QDs was clearly observed and showed a sufficient intensity that was maintained even after 5 hours (Fig. 4b), indicating that AgInTe₂ QDs have a potential as a marker for in vivo imaging.

2.2 PL wavelength control in the NIR region by formation of a solid solution

As described in the previous section, particle size could be changed by controlling the reaction temperature, and the emission wavelength could be also controlled in the range of 1100 nm to

Figure 5. XRD patterns (a) and absorption and PL spectra (b) of ZAITe NCs prepared with various x values. The excitation wavelength was 700 nm. Reprinted with permission from Ref. 38.

1020 nm for AgInTe₂ QDs as shown in Fig. 2c. In order to realize multicolor imaging, it is necessary to achieve a wider range control at the PL wavelength without overlapping in the PL peak. As mentioned in the introduction part, a I-III-VI₂ semiconductor forms a solid solution with a II-VI semiconductor having a similar crystal structure and controls the chemical composition of the solid solution to continuously change E_g . Therefore, we attempted to synthesize ZnTe₂-AgInTe₂ (ZAITe; (AgIn) _{x} Zn_{2(1- x)}Te₂) QDs for PL wavelength control in the NIR light region.³⁸

ZAITe QDs with various x values were synthesized by using the optimized synthesis conditions described in the previous section. Rod-like particles of ca. 16 nm in length and ca. 4 nm in width were obtained regardless of the value of x used in the synthesis. When the amount of Zn was increased, that is, when x was decreased, the XRD pattern of the QDs gradually shifted from hexagonal AgInTe₂ to the higher angle side so as to approach hexagonal ZnTe (Fig. 5a). This peak shift according to the x value used in the precursor indicated that the obtained particles were not a mixture but a uniform ZAITe solid solution for which the composition could be controlled by changing the ratio of the precursor. Absorption spectra of the QDs in Fig. 5b show that the absorption onset wavelength of the obtained particles shifted to a shorter wavelength from 1030 nm to 760 nm with a decrease in the value of x . The emission peak wavelength, shown in Fig. 5b, was also shifted to a shorter wavelength. A shoulder of absorption attributable to the exciton peak can be seen in the absorption spectra, and the difference between the wavelength and the emission peak wavelength (Stokes shift) was very small for any particle composition. This indicated that the PL peaks observed in various compositions of ZAITe QDs were near-band-edge emissions. However, when x was decreased to 0.25, strong defect-site emission was observed in the longer wavelength region than the band edge emission peak, suggesting that electronic states were formed as a radiative recombination center between the conduction band and valence band. The PL QY, which was 47% at $x = 1$, also decreased with decrease in x and became 0.36% at $x = 0.25$. These results indicate that radiative and non-radiative recombination states were newly formed when the x value decreased. In order to obtain highly-luminescent ZAITe QDs, it is necessary to remove such a defect state by modifying the synthesis process or introducing a core-shell structure.

Figure 6. Relationship between $R(H_2)$ and average diameter (d_{av}) of ZAIS QDs with various x values. Reprinted with permission from Ref. 25.

3. Improvement of Light Energy Conversion Properties by Nanostructure Control of I-III-VI₂-based Low-toxic Solid Solution QDs

In semiconductor QDs, the quantum size effect increases the E_g , and the potentials at the lower conduction band edge (E_{CB}) and the upper valence band edge (E_{VB}) shift to negative and positive potentials, respectively. This enables enhancement of the high reduction/oxidation driving force for photoenergy conversion systems, such as photocatalysts and solar cells, compared with bulk materials. Furthermore, E_{CB} and E_{VB} of solid solution QDs can be precisely controlled by two parameters, particle size and solid solution composition, at the same time (Fig. 1a), and various efforts have therefore been made to achieve light energy conversion using solid solution QDs.^{24,39} For example, Zhong et al. reported highly efficient CuInSe₂-based multinary QDs-sensitized solar cells.⁴⁰ CuInSe₂ QDs showed a conversion efficiency of 9.5% as a solar cell and showed superior characteristics as a sensitizer from visible light to the NIR region. Meanwhile, electron injection from quantum dots to titanium oxide was optimized by mixing Zn to form a solid solution, and the highest conversion efficiency of 11.6% was recorded in ZnSe–CuInSe₂ QDs.

The authors investigated the influence of the size and composition of ZAIS nanoparticles on their photocatalytic activity for hydrogen evolution reaction using sulfide ion as a hole scavenger.²⁵ Regardless of the composition in ZAIS QDs, the hydrogen evolution rate ($R(H_2)$) increased with decrease in particle size, but $R(H_2)$ decreased when the particles were smaller than about 5 nm (Fig. 6). In the case of semiconductor QDs, surface defect sites, which might be recombination site of photoexcited carriers, increased with decrease in particle size. As a result, the highest photocatalytic activity was obtained when the optimal ZAIS particle composition and particle size, that is, ZAIS particles with sizes of 4.2 to 5.5 nm and E_g of 2.3 to 2.4 eV, were used. However, in order to further improve the photoenergy conversion properties of the solid solution QD, it is not sufficient to merely optimize the electron energy structure shown above.

3.1 Improved photocatalytic activities of ZAIS QDs by formation of anisotropic shape and hetero-interface

It is well known that the physicochemical properties of conventional binary QDs are greatly influenced not only by the particle size but also by their shape, and efficient photoenergy conversion has been achieved by using shape-controlled QDs. For example, Alivisatos et al. reported that conversion efficiencies were greatly improved by using CdSe quantum dot thin-film solar cells grown to a one-dimensional rod shape compared with the conversion efficiencies when using spherical particles as a light absorber.⁴¹ As a photocatalyst, it has been reported that plate-shaped CdS nanoparticles with an exposed {0001} facet showed higher

Figure 7. (a) Typical TEM images of ZAIS QDs with rod, sphere, and rice shapes. (b) Dependence of $R(H_2)$ on x values of ZAIS QDs having various shapes. Reprinted with permission from Ref. 43.

hydrogen generation photocatalytic activity than that of other anisotropically shaped particles.⁴² On the other hand, there has been no study on anisotropic shape control in multinary QDs.

The authors succeeded in synthesizing anisotropic ZAIS QDs with rod and rice shapes by slight modification of the method for synthesis of spherical ZAIS QDs (Fig. 7a).⁴³ As photocatalysts, rod-shaped ZAIS QDs (about 4.6×27 nm in size), rice-shaped ZAIS QDs (about 9×16 nm in size) and, spherical ZAIS QDs (about 5.5 nm in size) were used for photocatalytic hydrogen evolution reactions, and then the relationship between shape-dependent $R(H_2)$ and E_g was plotted (Fig. 7b). The photocatalytic activities of spherical particles and rice-shaped particles showed volcanic dependence on E_g , with $R(H_2)$ being the largest values at x value of 0.40 and 0.45, respectively. On the other hand, the rod-shaped ZAIS QDs showed an increase in photocatalytic activity with increase in the value of x , that is, E_g decreased and reached a maximum value at $x = 0.35$. This trend could be explained from the negative potential shift of E_{CB} due to the change in particle composition and the decrease in the number of absorbed photons due to the increase in E_g . With increasing Zn content in the particles, E_{CB} shifted to the negative potential side, the driving force for reduction by photoexcited electrons increased, and then the hydrogen evolution reaction occurred more efficiently. However, when E_g became too large by increasing the Zn content in QDs, the number of photons that could be absorbed by the ZAIS decreased followed by a decrease in $R(H_2)$. Moreover, the optimum photocatalytic activity increased in the order of rice-shaped < spherical-shaped < rod-shaped ZAIS QDs. The difference between the activities of spherical particles and rod-shaped particles was related at least to the lifetime of photogenerated carriers in the particles. The lifetime of photogenerated carriers in rod-shaped particles with maximum photocatalytic activity was 1150 ns, which was sufficiently longer than the lifetime of photogenerated carriers in spherical particles, 602 ns. This increased the reaction probability of photoexcited electrons in rod-shaped ZAIS particles and H^+ in solution.

As a different approach to improve their photoenergy conversion efficiency, the formation of a type-II heterostructure in the nanoparticles is effective for suppressing the recombination of photoexcited carriers. ZAIS QDs with different solid solution

Figure 8. Typical TEM images of purified ZAIS nano-dumbbells (a) and nano-ellipsoids (b) obtained by a size-selective precipitation technique. (c) High-resolution HAADF-STEM image of the interface between the rod part and the ellipsoidal tip part in a ZAIS nano-dumbbell. Reprinted with permission from Ref. 44.

compositions were grown at both ends of the above-mentioned rod-shaped ZAIS QDs to form a type-II electronic energy structure in single dumbbell-shaped particles.⁴⁴ After the reaction, in addition to the dumbbell-shaped particles (Fig. 8a), ellipsoidal ZAIS particles of almost the same sizes deposited on the tips of the dumbbell ZAIS were also produced (Fig. 8b). QDs having different shapes were successfully isolated by the size-selective precipitation technique. Since the ZAIS solid solution composition $((\text{AgIn})_x\text{Zn}_{2(1-x)}\text{S}_2)$ of the obtained particles was $x = 0.92$ for ellipsoidal ZAIS QDs (ZAIS(0.92) ellipsoids) and $x = 0.24$ for rod-shaped ZAIS QDs (ZAIS(0.24) rods), the composition of dumbbell-like particles is presumed to be a combination of them. Here, the dumbbell-shaped particles are denoted as ZAIS($x(\text{tip})/x(\text{rod})/x(\text{tip})$). Therefore, in the above case, dumbbell-shaped particles are shown as ZAIS(0.92/0.24/0.92) dumbbells. The heterointerface between the rod and the ellipsoidal tip in ZAIS(0.92/0.24/0.92) was investigated by HAADF-STEM measurements as shown as Fig. 8c. Even at the interface between the rod and the ellipsoidal tip deposited at the end of the nanorod, continuous lattice fringes were observed throughout the particle without showing grain boundaries inside the particle and ellipsoidal tips were epitaxially grown on both termini of a nanorod.

ZAIS(0.39) ellipsoid and ZAIS(0.39/0.24/0.39) dumbbells were also obtained by controlling the solid solution composition. The electronic energy structures of dumbbell-shaped ZAIS QDs were confirmed by measuring photoelectron yield spectroscopy to be quasi-type-II and type-II for ZAIS(0.92/0.24/0.92) and ZAIS(0.39/0.24/0.39), respectively, as shown in Fig. 9a. PL lifetime measurements showed that the dumbbell-shaped particles had a longer PL lifetime than the PL lifetimes of the rod-shaped and ellipsoid-shaped ZAIS QDs. This is evidence that recombination of photogenerated

Figure 9. (a) Schematic illustrations of the electronic energy structures of nano-dumbbells of ZAIS(0.92/0.24/0.92) and ZAIS(0.39/0.24/0.39) estimated from the energy structures of corresponding single-component counterparts. (b, c) Time courses of the amount of H_2 evolution by irradiation to ZAIS nanocrystals. Samples are (i) ZAIS($x/0.24/x$) nano-dumbbells, (ii) ZAIS(x) nano-ellipsoids, (iii) ZAIS(0.24) nanorods, and (iv) mixtures of ZAIS(0.24) nanorods and ZAIS(x) nano-ellipsoids (1:2). The x values of the samples are 0.92 and 0.39 in panels (a) and (b), respectively. Reprinted with permission from Ref. 44.

carriers was suppressed by the formation of a type-II heterointerface in dumbbell-shaped ZAIS QDs.

Photocatalytic hydrogen evolution reactions were carried out using these ZAIS QDs as photocatalysts, and it was found that the amount of hydrogen generated linearly increased with increase in light irradiation time. Regardless of the x value in tip particles, dumbbell-shaped ZAIS QDs showed larger $R(\text{H}_2)$ than that of single ellipsoids or a mixture of ellipsoid-shaped and rod-shaped particles. This is probably because the type-II hetero-structure of dumbbell-shaped particles suppressed the recombination of photogenerated carriers and the number of electrons available for photocatalytic reaction increased. ZAIS(0.32/0.24/0.32) dumbbells exhibited higher photocatalytic activity than that of other ZAIS photocatalysts because, in addition to the formation of a type-II heterointerface, the driving force for the hydrogen evolution reaction was likely to be enlarged by increasing the reduction potential of photoexcited electrons of them with enlarged E_g of tip particles.

3.2 Effective sensitization using I-III-VI₂-based QDs in solar cells

Chemically synthesized QDs are more monodisperse in size than are QDs prepared on a substrate by a physical method, such as PVD or sputtering, and their E_g is also uniform. By using such QDs as a light absorbing layer in a solar cell, highly efficient energy conversion can be expected. Many types of QD-based solar cells have been intensively investigated, and QD-sensitized solar cells (QDSSCs) are a promising low-cost alternative to existing photovoltaic technologies such as crystalline silicon and inorganic thin films.^{45–47} As mentioned above, Zhong et al. recently reported a high conversion efficiency exceeding 11% by using ZnSe–CuInSe₂ solid solution QDs as a sensitizer, and solid solution-based QDSSCs have attracted much attention in recent years.⁴⁰

It was found that ZAIS QDs could be used as a photosensitizer by immobilizing them on a rod-shaped ZnO substrate, but their power conversion efficiency was less than 1%.^{26,27} On the other hand, AgInSe₂ having a bulk E_g 1.25 eV smaller than that of AgInS₂ enabled effective utilization of sunlight. Therefore, we synthesized ZnSe–AgInSe₂ ((AgIn)_xZn_{2(1-x)}Se₂; ZAISE) solid solution QDs as widely E_g -tunable QDs for sensitizers in solar cells.⁴⁸ ZAISE QDs, the average sizes of which were 3.5–6.2 nm, were prepared by reaction of the corresponding metal acetate and selenourea in oleylamine at 250°C. The absorption onset wavelength was blue-shifted from 900 nm to 400 nm by decreasing the x value from 1.0 to 0.25, so the E_g of ZAISE QDs could be varied from the NIR region to the visible region. Photoanodes were prepared by immobilization of ZAISE QDs on a porous TiO₂ thin film electrode using 3-mercaptopropionic acid as a cross-linking agent. Although it was stated above that many defect sites existed on the surface of QDs, in the case of a solar cell, such defect sites became recombination centers, and that the photogenerated carrier was deactivated through this surface defect. This caused a great reduction in the energy conversion efficiency in QDSSCs. In such a case, it has been reported that coating QDs with another semiconductor to form a core-shell structure is effective for removing these defect sites.^{49–51} Therefore, in this case, CdS, one of the most commonly used shell materials, was deposited on ZAISE QDs via successive ionic layer adsorption and reaction (SILAR). Sandwich-type solar cells were prepared by together an aqueous solution containing S²⁻/S_n²⁻ redox species as an electrolyte solution and a Cu₂S electrode as a counter electrode with the thus-prepared photoanode. Figure 10a shows the current-potential curve obtained by simulated solar light (AM 1.5G) irradiation and the action spectrum of J_{SC} . In the absence of surface coating by the CdS layer, there was almost no photocurrent, so it could be seen that the recombination site on the electrode surface was effectively removed by the CdS coating and that formation of core-shell-type heterojunction on the particle surface was necessary for QDSSCs (Fig. 10b).

Photoenergy conversion efficiency varied depending on the composition of ZAISE QDs. With a decrease in the x value of ZAISE QDs immobilized on TiO₂ films from 1.0 to 0.5, both J_{SC} and V_{OC} increased, resulting in a remarkable increment of power conversion efficiency. A further decrease of x from 0.5 to 0.25 slightly reduced the values of J_{SC} and V_{OC} . As a result, ZAISE QDs with $x = 0.5$ exhibited optimal photovoltaic performance, J_{SC} of 8.8 mA cm⁻² and PCE of 1.9%. Such volcanic dependence of conversion efficiency was similar to the change of $R(H_2)$ for the ZAIS photocatalyst QDs described above and could be explained in the same manner using increased E_{CB} and a decreased absorption region with increase in E_g of the QDs.

4. Conclusion

In this review, the methodology for preparation, optimization of

Figure 10. (a) Current-voltage curves of QDSSCs prepared with ZAISE immobilized on a TiO₂ electrode before (i) and after (ii–v) surface coating with a CdS thin layer. The samples were prepared with ZAISE particles of $x = 1.0$ (i, ii), 0.75 (iii), 0.5 (iv), and 0.25 (v). (b) Schematic illustration of the mechanism for enhancement with a CdS thin coating layer. Reprinted with permission from Ref. 48.

PL QY, and control of the PL wavelength in the NIR light region for I-III-VI₂-based QDs were described with focus on AgInTe₂. Colloidal AgInTe₂ QDs showed a sufficiently sharp PL peak and high PL QY comparable to that of conventional Pb- or Cd-based QDs, and their PL wavelength was widely controlled in the NIR region by formation of a solid solution with ZnTe. These results indicated that AgInTe₂ and ZnTe–AgInTe₂ QDs had the potential to be an alternative material for conventional QDs containing highly toxic heavy metals in applications with NIR emission including in vivo imaging. The methods introduced here are effective for obtaining a design guideline in the case of synthesizing different I-III-VI₂-based QDs. Furthermore, in these QDs, a method for controlling the nanostructure to improve the efficiency as light energy conversion materials was described. In addition to their size and composition, the hydrogen generation photocatalytic activity of ZAIS QDs could be improved by controlling their shape and introducing a heterojunction interface in the QDs. As shown in this example, nanostructure control was an important factor as it greatly affected photoelectric conversion properties of QDs.

Pb- and Cd-free low-toxic QDs are required for practical applications, but the cost of the elements is often a problem. Since the I-III-VI₂ semiconductor introduced here contains rare metals such as In and Ga, there is a problem of stable supply of raw materials in the future. Against this background, the authors have recently developed QDs of Cu₂ZnSnS₄, which have been attracting much attention as a next-generation solar cell material in bulk crystals, and have investigated their photoelectrochemical properties.^{52,53} Based on multinary semiconductor QDs, we are now trying to develop QDs consisting of cheap and low-toxic elements for advanced generation. For example, we have succeeded in the synthesis and particle size control of Ag₂ZnSnS₄⁵⁴ and Ag₈SnS₆⁵⁵ with a relatively narrow E_g , and showed that they can be used as good photoelectric conversion materials. Since constituent elements became increased and complicated in such multinary QDs, control

of crystal defects is a major problem, and clear PL at room temperature of these novel QDs has therefore not yet been achieved. Dramatic development of colloid synthesis technology is expected to solve these problems in the near future.

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