Crystal growth of quantum dot phosphors and their application to photoelectric conversion device*

Junki NAGAKUBO*1, Seungjun OH*1, Tsutomu NISHIHASHI*1 and Hirohiko MURAKAMI*1

*1 Future Technology Research Laboratory, ULVAC, Inc., 5-9-6 Tohkohdai, Tsukuba, Ibaraki, 300-2635, Japan

In order to obtain semiconductor quantum dots with superior opto-electronic performance, several technologies are required including epitaxial growth, fine particle size control, and ligand control. We have synthesized quantum dot phosphors via these technologies. The quantum dot phosphors showed better color purity (full width at half maximum: 45.0 nm, chromaticity coordinates: 0.177, 0.688) than conventional phosphors such as β-SiAlON. A photoelectric converter using these quantum dots has been fabricated, which shows 16.7% of external quantum efficiency at 850 nm of infrared light. The result indicates a possibility of developing superior infrared image sensor than conventional organic CMOS image sensors.

1. Introduction

Quantum dots are defined as electrons in a quantum state where they are confined in three dimensions and their degree of positional freedom is restricted. Typically, they take the form of semiconductor nanocrystals. As the crystal size become larger, the energy gap become narrow due to the quantum size effect[1)]. The crystal size is controlled as large as the exciton Bohr radius of the semiconductor, the exciton binding energy increases due to the quantum confinement effect, which inhibits the thermal relaxation of excitons. It has also been reported that the quantum confinement leads to level discretization and the density of states can be expressed like a delta-function.

These theories mean that when quantum dots are used as phosphors, although they have the same composition and crystalline structure, they can show different fluorescence wavelengths with different grain sizes. In addition, the transition between the discretized levels can provide a sharp fluorescence spectrum.

It has been reported that the CdSe-ZnS core-shell quantum dots whose crystals were grown in a solution have an emission full width at half maximum(FWHM) of 35 nm or less, emission wavelength can be tunable between blue and red with the quantum size effect, and an extremely high fluorescence quantum yield (>90%). It has demonstrated that semiconductor nanocrystals having a low density of defects can be obtained even when the crystals are grown in a solution[3)]. However, cadmium is included in the composition, the crystals does not comply with RoHS2. Alternate materials that do not contain cadmium but have excellent emission properties are required.

A back light of conventional liquid crystal displays (LCDs) consist of blue light emitting diodes and green and red phosphors, and these phosphors have relatively broad fluorescence spectra. Therefore, a color filter is used to go through specific wavelengths, thereby dividing white light into red, green, and blue. The color space range of liquid crystal displays can be widened by absorbing an extra light with the color filter and go throgh further narrowing emission spectra, but the light intensity decreases depending on the amount of absorbed light. This means that there is a trade-off relationship between the color space and power consumption.

To resolve this issue, quantum dot phosphers are considered as alternatives for green and red phosphors. They have already been adopted for Amazon's tablets and Samsung' s displays. The quantum dot phosphers applying for lighting and DC light emitting-type devices are also being developed, and the markets are expected to expand.

The following four technical fields are important to control the properties of quantum dots:

(1) Core/Shell Epitaxial crystal growth without defects
(2) Narrow grain size distribution
(3) Controlled particle dispersion
(4) Support or printing technique

This article reports on our development examples on the above four items, the properties of quantum dot phosphors, and the application of quantum dots to photoelectric conversion devices.

2. Preparation of semiconductor quantum dot phosphors

2.1 Semiconductor nanocrystal growth

The advancement of semiconductor crystal growth technique brought some reports that they can be grown epitaxially even at a low temperature of around 300℃. The crystal growth model has been suggested in which the

---

* Presented at the 16th JSAP (The Japan Society of Applied Physics) Spring Meeting, held at March 18, 2014.

crystal nuclei are formed rapidly by non-equilibrium decomposition of the metal-organic complex, then the metal elements on the surface are bound with their counter ions and organic ligands in equilibrium, and grow the crystals gradually by comsumption of raw materials4). Therefore, it can be expected that compared with conventional physical crystal growth methods, better crystals can be grown at lower temperatures.

Obtaining better crystals with the scheme requires purer metal and counter ion precursors, selection of raw materials and prediction of their reactions, and crystal growth atmosphere control. ULVAC, Inc. has been selling distillation and purification systems for solutions and semiconductor material deposition systems, has accumulated dispersion technology through the sale of metal nanoparticle inks. We have been developing the fundamental synthesis process of semiconductor quantum dots with these technologies. The following reports show the properties of quantum dot phosphors revealed in the course of the development.

2.2 Fluorescence properties of core-shell quantum dot phosphors

Core-shell quantum dot phosphors are being considered for use in lights and lasers, including wavelength conversion materials for liquid crystal displays. In particular, in order to meet the BT.2020 standard, which is the standard for Ultra High Definition Television (UHDTV), green wavelength conversion materials with a narrower fluorescence spectrum half-width than existing phosphors and commercially available quantum dots are required. We have succeeded in synthesizing CdS/ZnS quantum dots, which emit blue fluorescent light, InP/GaP/ZnS quantum dots, which emit green fluorescent light, and InP/ZnS quantum dots, which emit red fluorescent light. Other quantum dots can be prepared but this article focuses on the fluorescence properties of these representative quantum dots that emit blue, green, and red fluorescent lights.

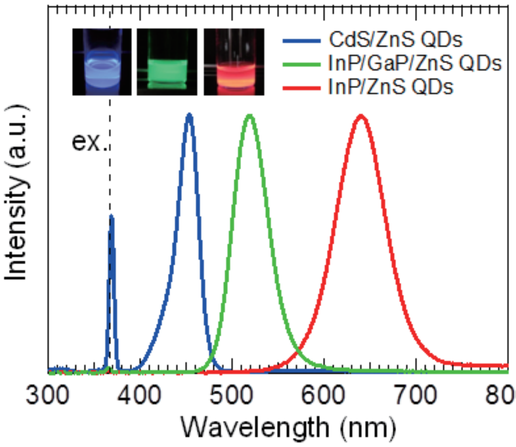

Figure 1 Normalized emission spectra of blue CdS/ZnS quantum dots, green InP/GaP/ZnS quantum dots and red InP/ZnS quantum dots.

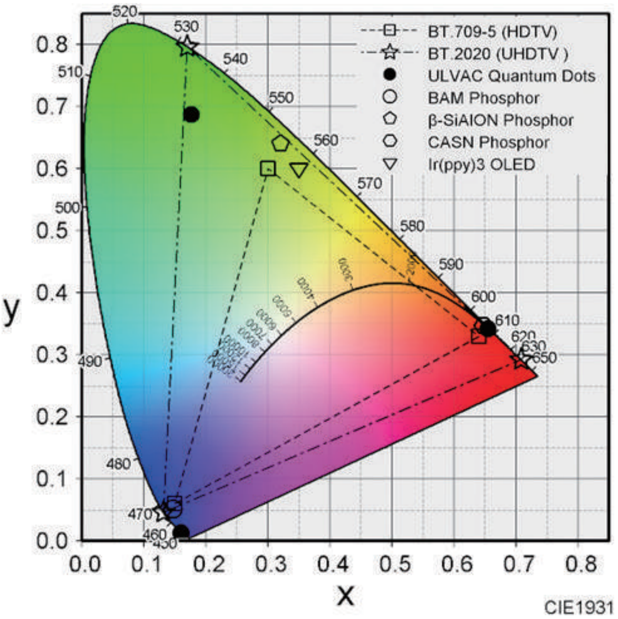

Figure 2 CIE chromaticity coordinates of phosphors and quantum dots.

Figure 1 shows the fluorescence spectra of the prepared CdS/ZnS, InP/GaP/ZnS, and InP/ZnS core-shell quantum dots, Figure 2 shows the CIE chromaticity diagram obtained from the spectra, and Table 1 shows a summary of the fluorescence properties using 365-nm ultraviolet light as an excitation light source.

Table 1 PL properties of quantum dots made by ULVAC.

Color	Compound	PL peak (nm)	FWHM (nm)	CIE (x, y)
Blue	CdS/ZnS	453.2	28.4	(0.160, 0.013)
Green	InP/GaP/ZnS	519.1	45.0	(0.177, 0.688)
	InP/ZnS	530.4	60.0	(0.274, 0.649)
	InP/ZnS*	521.1	51.3	(0.231, 0.655)
Red	InP/ZnS	640.0	64.1	(0.655, 0.342)

*Synthesis using microreactor

The blue CdS/ZnS quantum dot phosphors have a peak wavelength of 453.2 nm, a FWHM of 28.4 nm. The chromaticity coordinates are (0.160, 0.013). The blue CdS/ZnS quantum dot phosphors have as good a color purity range as $BaMgAl_{10}O_{17}$: Eu^{2+} (BAM) phosphors, which are typical blue phosphors with chromaticity coordinates: (0.147, 0.051)[5], and the FWHM of the fluorescent light obtained from the blue CdS/ZnS quantum dot phosphors is 28.4 nm, which is about half that obtained from BAM, which is 50 nm. The result demonstrated that the blue quantum dot phosphors suitable for an ultraviolet-emitting diode as an excitation source exhibit excellent properties. However, Cd is used to make the blue CdS/ZnS quantum dot phosphors, so there is a need to find an alternate material.

The green InP/GaP/ZnS quantum dot phosphors have a emission peak of 519.1 nm, a FWHM of 45.0 nm, and chromaticity coordinates: (0.177, 0.688). These values show that compared with the chromaticity coordinates of the BT.709-5 standard for high-definition televisions (0.30, 0.60), the green quantum dot phosphors have a better color purity. In addition, compared with $Si_{6-z}Al_zO_zN_{8-z}$: Eu ($0<z<4.2$) (ß-SiAlON) phosphors, which have chromaticity coordinates of (0.32, 0.64)[6], and Tris(2-phenylpyridinato) iridium (III) ($Ir(ppy)_3$) organic semiconductor, which has chromaticity coordinates of (0.35, 0.60)[7], the green InP/GaP/ZnS quantum dot phosphors provide fluorescent light with better color purity. There is a potential that the BT.2020 standard for next-generation super-high definition television (UHDTV) can be applied by the achievement of further narrowing the FWHM.

The InP/ZnS quantum dots, which emit red fluorescent light, have an emission spectrum peak of 640.0 nm, a FWHM of 64.1 nm, and chromaticity coordinates: (0.655, 0.342). These values show that compared with $CaAlSiN_3$: Eu (CASN), which is a typical red phosphor with chromaticity coordinates of (0.647, 0.347)[8], the InP/ZnS quantum dots have a better color purity than the red phospher. If the fluorescence quantum yield and heat resistance of the red quantum dots can be improved, it can be expected that the red quantum dots will be used to improve the color rendering properties of LED lights.

2.3 Grain size distribution control with micro-reactors

In general, semiconductor nanocrystals are grown by the hot injection method. To grow crystals, counter ion precursor is injected swiftly at a certain temperature into the precursor heated in a stirring flask. However, it is known that with this method, it is hardly to avoid a local concentration or temperature distribution. Therefore, the crystals obtained by the method have a certain particle size distribution[4, 9]. Because quantum dots have varying wavelengths in each size, obtaining an emission spectrum with a narrow FWHM requires making the particle size distribution narrower.

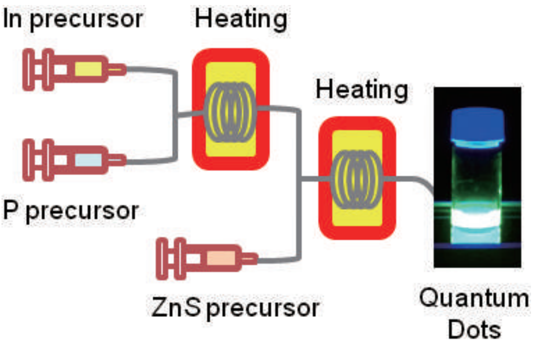

Figure 3 Schematic diagram of the microreactor.

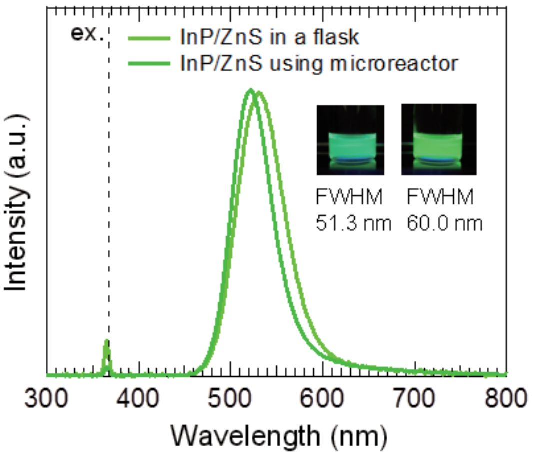

Figure 4 Fluorescence spectra of InP/ZnS quantum dots prepared at different apparatus.

We made an attempt to control the particle size distribution of quantum dots by reducing the concentration and temperature distribution.The process of nucleation with a micro-reactor uses a minute flow path as a reaction field. Figure 3 shows a schematic of the reactor. The reactor is equipped with a micro-mixer with a bore of 0.25 mm, made of SUS316 for mixing raw materials, a cylinder pump for solution transfer, a temperature controller, and a back-pressure regulating valve. When the precursor solution pass through the heater, the core crystal growth time and shell crystal growth time were set to 30 minutes respectively. The reaction conditions and the raw materials are as same as for reactions in flasks. Table 1 and Figure 4 show the fluorescence properties of the quantum dots obtained with this attempt. Compared with the InP/ZnS quantum dots prepared by using a flask, the FWHM was improved from 60.0 nm to 51.3 nm, which suggests that a narrower particle size distribution has been achieved. In addition, the peak wavelength shifted toward the lower wavelength side from 530.4 nm to 521.1 nm. It is indicated the convection distance is restricted to a minute flow path and the raw materials supply rates becomes slow. Furthermore, it was revealed that the chromaticity coordinates of the InP/ZnS quantum dot phosphors synthesized with a flask were (0.274, 0.649), and those synthesized with a micro-reactor were (0.231, 0.655), which means that the InP/ZnS quantum dots synthesized with a micro-reactor emit green fluorescent light with better color purity.

These results suggest that the designed micro-reactor for quantum dots is effective for narrowing the grain size distribution and the narrow emission spectra of quantum dot phosphors.

3. Preparation of quantum dots for photoelectric conversion and their application to devices

3.1 Advantages of quantum dots for photoelectric conversion

It has been reported that quantum dots have been used for the photoelectric conversion layer. Conventionally, a silicon photodiode has been used as the photoelectric converter of an image sensor, but because it is an indirect transition semiconductor, about 3 μm of a film thickness is needed to absorb all incident light. To cut incident light from an large angle, the openings need to be restricted the angle of incident light is 30 to 40 degrees, which leads to reduced device sensitivity[10)].

However, by using direct transition-type quantum dots in the photoelectric converter, higher sensitivity can be expected with a reduced to 0.5 μm of film thickness and an increased incident angle of up to 60 degrees. This will presumably make it possible to mount a high-function circuit (e.g., high speed, wide dynamic range, high saturation) in open space on the silicon board, contributing to the advancement of imaging devices. Because it can be easily distinguished with the discretized levels, the thermal excitation of electrons in the semiconductor from excitation by incident infrared light. There is a potential that infrared imaging devices with a high signal/noise (S/N ratio) can be realized that could not be realized with conventional silicon photodiodes or organic CMOS image sensors. The following reports on the synthesis and ligand exchange of quantum dots suitable for photoelectric conversion in the infrared region and fabrication of photoelectric conversion devices.

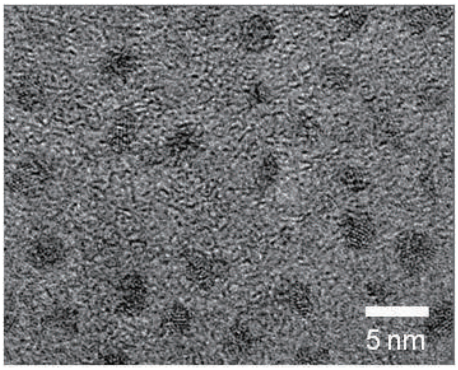

Figure 5　TEM image of Cu-In-Se quantum dots.

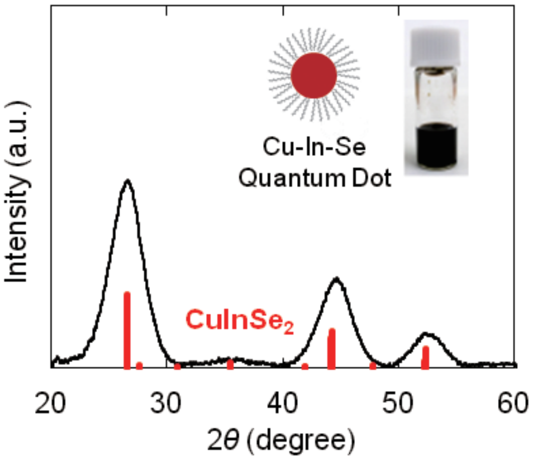

Figure 6　XRD pattern of Cu-In-Se quantum dots.

3.2 Synthesis of Cu-In-Se quantum dots for photoelectric conversion

$CuInSe_2$ is a direct-transition semiconductor that has a chalcopyrite structure and exhibits a band gap of 1.04 eV, and it is a material that complay with RoHS[11)]. The quantum dots were prepared by using the superior semiconductor material.

Figure 5 shows a transmission electron microscope (TEM) image of the Cu-In-Se quantum dots. It shows that nanocrystals of approximately 2 to 3 nm in diameter were formed. It was confirmed that each particles has a lattice pattern and they are monocrystalline because there is no crystal interface in the particle. Figure 6 shows the X-ray diffraction results. The figure shows a diffraction peak, which arise from by the Cu-In-Se chalcopyrite structure, meaning that the intended crystal phase has been obtained.

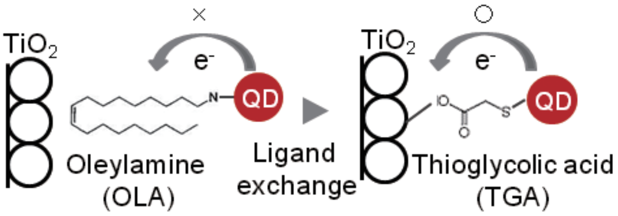

Figure 7 Mechanism of adsorption on TiO_2 film by ligand exchange of quantum dots.

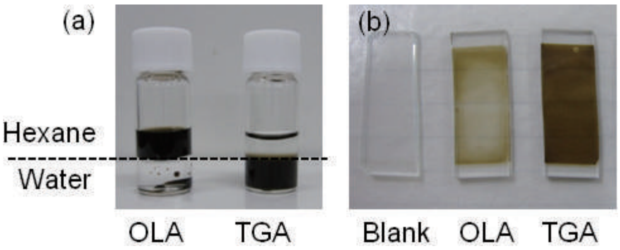

Figure 8 (a) The aqueous phase transfer of quantum dots with Thioglycolic acid (TGA). (b) Adsorption capacity to TiO_2 substrate of ligand-exchanged quantum dots.

3.3 Dispersion control by ligand control and supporting the substrate

In general, to prevent the aggregation of quantum dots, the crystals need to be grown with a long alkyl chain coordinated on the nanocrystal surface. However, because the coordinated molecule has a molecular length of 2 to 3 nm, it may create resistance when the carrier generated in the quantum dot is taken out into an external circuit. Therefore, the ligand was changed to an organic molecule with a shorter chain to reduce the resistance.

Figure 7 is a schematic of the ligand exchange. The oleylamine (OLA) coordinated around the quantum dot was successfully replaced by thioglycolic acid (TGA). In addition, it was confirmed that the hydrophobic and hydrophilic properties of the quantum dots can be controlled before and after ligand exchange, and that the dispersion solvent can be changed from an organic solvent to a more environmentally friendly solvent, such as water. By applying this method, quantum dots can be dispersed onto a specific type of polymer or can be confined after dispersed to silica particles, or complexation.

In addition, because the carboxyl of thioglycolic acid (TGA) has the ability to be chemically adsorbed to titanium oxide particles, it is possible to add a function that supports quantum dots to a specific type of carrier. The example in Figure 8 shows that the number of quantum dots adsorbed on the porous titanium oxide film increased after the ligand was changed to thioglycolic acid (TGA). This suggests that the adsorption capacity of quantum dots can be increased by ligand exchange and the carrier transfer resistance on the quantum dot-titanium oxide interface can be decreased at the same time.

3.4 Fabrication and evaluation of quantum dot sensitized solar cells

Figure 9 shows how the quantum dot sensitized solar cell was fabricated. On a glass substrate 0.7-mm thick where a fluorine-doped tin oxide film was deposited until it reached 300 nm, titanium oxide paste with an average

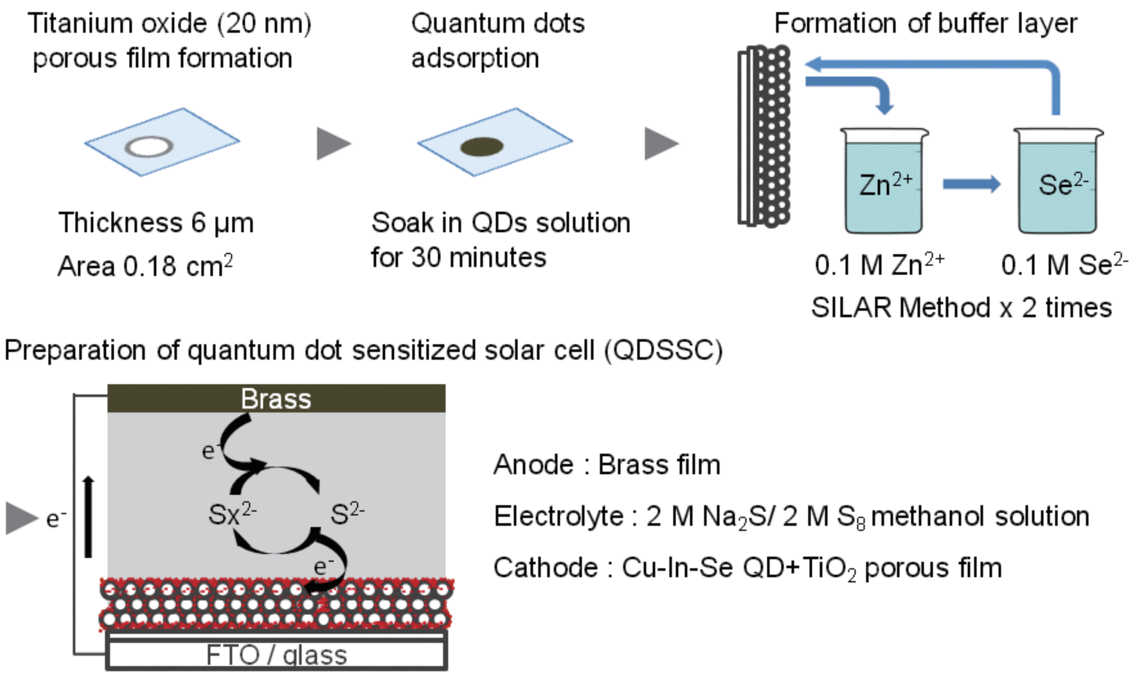

Figure 9 Fabrication process for quantum dot sensitized solar cell.

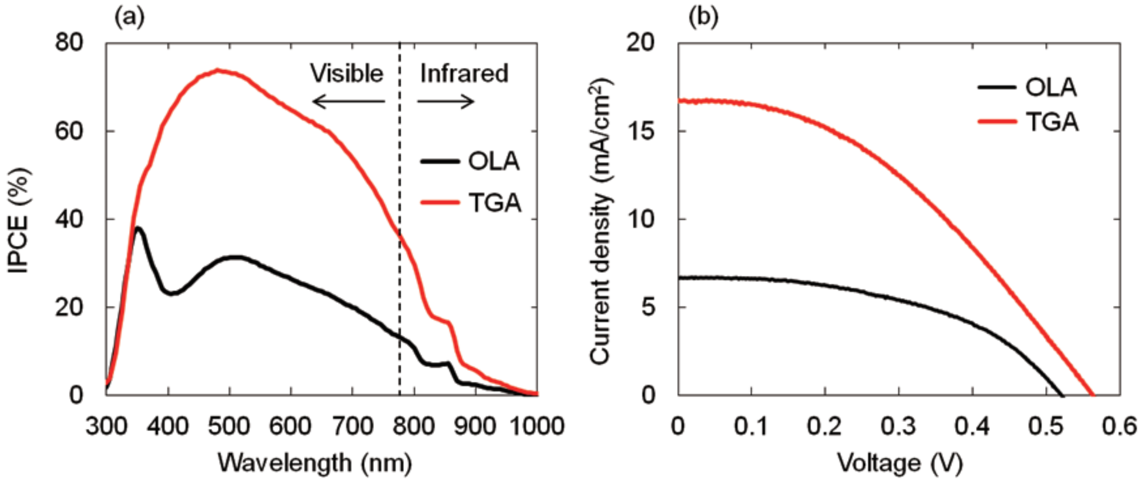

Figure 10 (a) IPCE spectra for the QDSSCs based on the quantum dots. (b) *J-V* curve of the QDSSCs.

Table 2 Properties of the QDSSCs using ligand-exchanged quantum dots.

Ligand	IPCE (%) at 850 nm	J_{SC} (mA/cm^2)	V_{OC} (V)	FF (-)	SCE (%)
OLA	7.2	6.7	0.52	0.49	1.7
TGA	16.7	17.3	0.56	0.40	3.9

grain size of 20 m was applied by the squeegee method, and then calcined in atmosphere at 450℃ for 30 minutes to form a porous titanium oxide film with a thickness of about 6 μm. The prepared substrate was immersed in a Cu-In-Se quantum dot dispersion solution with a concentration of 0.1 mol/L in In-amount equivalent for 30 minutes to form a quantum dot-supported photoelectrode. After that, the ZnSe buffer layer was formed by the SILAR method to prevent the carrier generated from the quantum dots from flowing back to the cathode side and a brass anode electrode was laminated with the prepared photoelectrode with 2 M of sodium polysulfide electrolyte to fabricate a quantum dot sensitized solar cell.

Figure 10 shows the IPCE properties of the fabricated quantum dot sensitized solar cell (QDSSC) and *J-V* comparison, and Table 2 shows the detailed properties. The external quantum dot efficiency with light of 850 nm was improved from 7.2% to 16.7% by changing the ligand from oleylamine (OLA) to thioglycolic acid (TGA). This is presumably because the number of quantum dots adsorbed to the titanium oxide was increased by the ligand exchange of the quantum dots. In addition, the quantum dots exhibit a photoelectrical conversion ability for wavelengths up to 1 μm, and these results demonstrate that the Cu-In-Se quantum dot is effective for photoelectric conversion in the infrared region, which cannot be achieved with organic semiconductors or silicon photodiodes.

With regard to the photoelectric conversion efficiency obtained from the *J-V* curve, the conversion efficiency of the quantum dots with oleylamine (OLA) is 1.7% and that with thioglycolic acid (TGA) is 3.9%, showing an improvement in the photoelectric conversion properties. This is because a lot of carriers are generated by increasing with the increased the amount of supported quantum dots, and therefore, the short circuit current density (J_{SC}) was increased from 6.7 mA/cm^2 to 17.3 mA/cm^2. At the same time, the open-end voltage (V_{OC}) was improved from 0.52 V to 0.56 V. This is because the voltage loss decreased with the reduced resistance in the quantum dot-titanium oxide interface. However, the fill factor (FF) decreased from 0.49 to 0.40. Normally, when the current value increases, the internal carrier loss caused mainly by back-flow increases, and therefore, the decrease in the FF is considered reasonable. There is a possibility that uncooling quantum type infrared image sensors and similar devices will be available at lower costs.

4. Conclusion

This article has described the physics, market trends, and current challenges of quantum dots so far. We has already developed the raw material selection, synthesis, and particle size control techniques for semiconductor nanocrystals, and developed quantum dot phosphors having a better color purity than typical wavelength conversion materials used in LCD televisions and lights, such as ß-SiAlON and CASN. In addition, we has realized the process of growing crystals epitaxially in a minute flow path, at a goodyield rate. Furthermore, it has been demonstrated that the InP/GaP/ZnS quantum dots have a great color purity than Ir(ppy)$_3$, which is a representative green organic electroluminance material, and there is a potential that if quantum dot DC light emitting devices can be realized, flexible displays with a much wider color gamut and much lower power consumption than organic EL displays.

The second-half of this article describes the potential of infrared imaging devices using quantum dots, and fabrication and evaluation of photoelectric conversion devices. We have successfully synthesized the Cu-In-Se nanocrystal with excellent photoelectric conversion properties and light stability by applying quantum dot phospher. The article presents changing the organic ligand coordinated at the surface of the crystal and selectively support them on the titanium oxide carrier. The sensitized photoelectric device fabricated using the method enables photoelectric conversion in the infrared region, which cannot be converted with organic dye, indicating a potential for applying to infrared imaging devices used in the quantum dots photoelectric conversion layer.

References

1) A. P. Alivisatos: Science New Series, 271 (1996) 933-937.
2) Garnett W. Bryant: Phys. Rev. B, 37 (1988) 8763.
3) Ki-Heon Lee, Jeong-Hoon Lee, Woo-Seuk Song, Heejoo Ko, Changho Lee, Jong-Hyuk Lee, and Heesun Yang: ACS nano., 7 (2013) 7295.
4) Dickerson, Bryan Douglas: “Organometallic Synthesis Kinetics of CdSe Quantum Dots”, 3 (2005) 41.
5) Jian Chen, Yangai Liu, Lefu Mei, Haikun Liu, Minghao Fang, and Zhaohui Huang: Scientific Reports, 5 (2015) 9673.
6) Naoto Hirosaki, Rong-Jun Xie, and Koji Kimoto, Takashi Sekiguchi, Yoshinobu Yamamoto, Takayuki Suehiro, and Mamoru Mitomo: Applied Physics Letters, 86 (2005) 211905.
7) Cheng-Hsien Yang, Kai-Hung Fang, Chun-Hung Chen and I-Wen Sun: Chem. Commun., 19 (2004) 2233.
8) Xianqing Piao, Ken-ichi Machida, Takashi Horikawa, Hiromasa Hanzawa, Yasuo Shimomura, and Naoto Kijima: Chem. Mater., 19 (2007) 4592.
9) Daniel Franke1, Dr. Daniel K. Harris1, Lisi Xie, Prof. Klavs F. Jensen, and Prof. Moungi G. Bawendi: Angew. Chem. Int. Ed., 54 (2015) 14299.
10) Panasonic Corporation, "Press Release: Panasonic develops 10times Higher Saturation & Highly Functional Global Shutter Technology by controlling of Organic-Photoconductive-Film on CMOS Image Sensor" (February 3, 2016) http://news.panasonic.com/global/press/data/2016/02/en160203-6/en160203-6.html (Last search date：May 12, 2017)
11) W. Hörig, H. Neumann, H. Sobotta: Thin Solid Films, 48 (1978) 67.