Colloidal semiconductor quantum dots; syntheses, properties and applications

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The solution synthesis of colloidal semiconductor quantum dots (QDs), such as CdSe QDs, has developed tremendously in the last two decades. Such QDs exhibit excellent optical properties, such as size dependent optical gaps and efficient carrier multiplication, because of the quantum confinement effect. Colloidal QDs have potential in various optical and optoelectronic devices, such as light emitting devices, solar cells and wavelength converters for displays. The use of toxic cadmium materials in light emitting devices and wavelength converters is currently unavoidable for achieving full color visible emission. Less toxic alternatives are required. Safe facile procedures for synthesizing narrow gap arsenide QDs are also required for QD-solar cells, which exploit low threshold energies of carrier multiplication. This article reviews recent advances in the synthesis and properties of colloidal QDs. Their applications are reviewed in terms of cadmium-free QD-phosphors, and safe and facile syntheses of arsenide QDs for solar cells. Our group’s research on the synthesis of the ternary chalcopyrite I-III-VI$_2$ semiconductors, ZnO and InAs QDs, and fabrication of electroluminescent devices using ZnO QDs is discussed.

Key-words : Colloidal quantum dots, Solution synthesis, Phosphors, Photoluminescence, Electroluminescence, Quantum dot solar cells

1. Introduction

Semiconductor nanocrystals or quantum dots (QDs) exhibit interesting optical properties due to their quantum size effects, and are expected to be used in various optoelectronic devices. One of their most attractive features is their size-dependent light emission resulting from exciton recombination, shown in Fig. 1. QDs are commonly synthesized in hot organic solvents with surfactants, known as the hot-injection method. This technique was first reported by Murray et al. to synthesize colloidal CdSe and CdTe QDs. Many procedures for synthesizing various II-VI and III-V semiconductor QDs have since been developed. The emission intensity and efficiency of colloidal QDs can be significantly improved by coating the QD core with a shell, yielding core/shell nanostructures. This passivates surface states acting as non-radiative recombination centers. Photoluminescence quantum yields (PLQYs) of $>80\%$ have been achieved for CdSe/ZnS core/shell QDs. Colloidal QDs are now widely commercially available, and are used as phosphors in commercial displays. The use of toxic cadmium compounds such as CdTe, CdSe or CdS is currently unavoidable for achieving full color visible emission. Less toxic alternative materials are highly desirable.

Carrier multiplication in QDs including multiple exciton generation (MEG) has received much recent attention. Figure 2(a) illustrates MEG, in which a single absorbed photon generates two or more electron–hole (exciton) pairs. This process allows a material to surpass the theoretical Shockley-Queisser limit for single-junction solar cells. For this purpose, PbSe QDs and their nanostructured films have been extensively studied.
studied, because their optical gap \( E_g(\text{QD}) \) is adjustable from 0.5 to 1.0 eV, and because the synthesis of high-quality colloidal PbSe QDs is well established.\(^{28)}\) The threshold photon energy of carrier multiplication is an important consideration. InAs QDs have a threshold energy of \( \sim 3E_g(\text{QD}) \),\(^{21,32)} \) which is preferable over that of PbSe QDs \( \sim 3E_g(\text{QD}) \).\(^{23,24)} \) InAs QDs are generally synthesized from tris(trimethylsilyl)arsine, which is highly pyrophoric and forms toxic and explosive arsine gas upon reaction with air or water.\(^{33,34)} \) A safe and facile procedure for preparing InAs QDs is required to promote the development of InAs QD-containing solar cells.

This review covers recent advances in the synthesis and properties of colloidal QDs. The application of cadmium-free QD-phosphors, and the safe and facile synthesis of arsenide QDs for solar cells are discussed. Our group’s research on the synthesis of the ternary chalcopyrite I-III-VI\(_2\) semiconductors, ZnO and InAs QDs, and the fabrication of electroluminescent (EL) devices using ZnO QDs is also discussed.

2. Cadmium-free visible QD phosphors

Chalcopyrite-type I-III-VI\(_2\) semiconductors are alternatives to Cd-based QD phosphors for visible light emission, because of their low toxicity and various band gaps of bulk materials, which are summarized in Table 1. Ternary compounds are generally more difficult to synthesize than binary compounds, because the reaction of two metallic cations must be balanced. The first reported synthesis of CuInS\(_2\) QDs exhibiting photoluminescent (PL) emission used the single-source precursor (PPh\(_3\))\(_2\)CuIn(Se\(_2\))\(_3\) to achieve the desired stoichiometry.\(^{35,36)} \) However, exciton recombination could not be achieved in the resulting QDs, and PL emission was related to deep defect levels. Therefore, it was difficult to experimentally determine their size-dependent optical properties. In this case, theoretical calculations can be powerful. The theoretical calculation of the size-dependent optical gaps of I-III-VI\(_2\) semiconductors is first briefly discussed, and the development of synthesizing I-III-VI\(_2\) QDs is subsequently described.

2.1 Theoretical calculation of size dependent optical gap of I-III-VI\(_2\) QDs

The size dependent optical gap and emission energy are important considerations when synthesizing I-III-VI\(_2\) semiconductors. They are frequently evaluated theoretically using the effective mass approximation, which is expressed by:\(^{37,38)}

\[
E_g(\text{QD}) = E_g(\text{bulk}) + \frac{2\hbar^2\pi^2}{d^2} \left[ \frac{1}{m_{e^*}} + \frac{1}{m_{h^*}} \right]
\]

The effective mass approximation overestimates the quantum size effect, as shown by the blue line in Fig. 3(b). This is because the approximation assumes an infinite-depth quantum well. An effective mass approximation calculated using a finite-depth well can overcome this.\(^{39-41)} \) The electron and hole are considered as independent particles of effective mass \( m_{e^*} \) and \( m_{h^*} \) inside the spherical QDs, respectively, but of mass \( m_0 \) outside the QDs, where \( m_0 \) is the free electron mass. The confining potentials of the electrons and holes are finite values. This method excellently reproduces the size dependent optical band gap of the QDs, as indicated by the red line in Fig. 3(b).

The Schrödinger equation for a particle of mass \( m \) in a potential \( V(r) \) is expressed as:

\[
\left[ \frac{\hbar^2}{2m} \nabla^2 + V(r) \right] \psi(r) = E\psi(r)
\]
The centrally symmetric $V(r)$ represented according to Eq. (3) is adopted as the $V(r)$:

$$V(r) = \begin{cases} 0, & r < r_0 \\ V_0, & r > r_0 \end{cases}$$

where $r_0$ is the radius of the spherical QDs. The potential $V_0$ is obtained from:

$$2V_0 = V_{0e} + V_{0h} = \Delta E_{\text{LUMO-HOMO}} - E_g(\text{bulk})$$

where the confining potentials for the electrons ($V_{0e}$) and holes ($V_{0h}$) are assumed to be the same for simplicity [Fig. 3(a)]. This assumption has been shown to be valid for various materials.\(^{39,40}\)

$\Delta E_{\text{LUMO-HOMO}}$ is the energy gap between the lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO) of the capping surfactant. The method excellently reproduces the size dependent optical gap of the QDs $E_g(\text{QD})$, as indicated by the red line in Fig. 3(b). Details of the calculation have been described previously.\(^{40}\)

Figure 4(a) shows the size dependent optical gap calculated by the finite-depth well effective mass approximation, for various I-III-VI\(_2\) semiconductors capped with oleyamine ($\Delta E_{\text{LUMO-HOMO}} = 4.430 \text{ eV}$; this value was experimentally determined based the optical absorption spectrum), using $m^*_e$ and $m^*_h$ values sourced from the literature.\(^{41}\) Figure 4(b) shows the coverage of the visible spectrum by these I-III-VI\(_2\) QDs of diameters of 2–5 nm. No single material covers the entire visible spectrum, however red, green and blue phosphors can theoretically be achieved using two or three materials. Thus, I-III-VI\(_2\) QDs can theoretically be used as visible phosphors.

2.2 CuInS\(_2\) QDs

In 2004, Castro et al. reported the synthesis of CuInS\(_2\) from the single-source precursor (PPh\(_3\))\(_2\)CuIn(SEt)\(_4\). This was the first reported observation of size-dependent PL emission from CuInS\(_2\) QDs.\(^{36}\) The emission resulted from electron–hole recombination via a defect level, so appeared in the near-infrared region because of the large Stokes shift.

Visible emission from CuInS\(_2\)–ZnS QDs was reported in 2006.\(^{43}\) These QDs were also advantageous in that they were synthesized from commercially available CuI, InI\(_3\), and zinc diethyldithiocarbamate {[(C\(_2\)H\(_5\))\(_2\)NCS\(_2\)]\(_2\)Zn}. Figure 5 shows the optical absorption and PL emission spectra of the CuInS\(_2\)–ZnS QDs, where $d$ indicates the average QD diameter. Visible images of the PL emission are shown inset. Blue shifts in absorption and PL emission were observed with decreasing QD size, and the emission wavelength was adjustable from red through to green. This report promoted much activity on the synthesis of I-III-VI\(_2\) QD phosphors, and there have since been many reports of visible emission from I-III-VI\(_2\)-based QDs. The Stokes shift of the emission from CuInS\(_2\)–ZnS QDs is large, e.g. $\sim$500 meV for 2.8-nm-diameter QDs in Fig. 5, so the emission band is usually related to intra-gap defect levels.\(^{44}\) This is not surprising, because the alloying of CuInS\(_2\) with ZnS generates electronic defects, such as zinc at copper sites and zinc at indium sites, which act as donors and acceptors, respectively.

Xie et al. reported the synthesis of CuInS\(_2\) QDs with sizes ranging from 2 to 20 nm, using commercially available air-stable chemicals.\(^{45}\) They adjusted the stoichiometry by controlling the reactivity of the Cu precursor using thiol ligands. The resulting CuInS\(_2\)/ZnS core/shell QDs exhibited visible emission from 500 to 900 nm, dependent on core size, and a PLQY of up to 30%. PLQYs have recently significantly improved. A PLQY of >80% was reported for CuInS\(_2\)/CdS core/shell QDs,\(^{46}\) and approximately 70% of PLQY was attained for AgInS\(_2\) based QDs.\(^{47}\) However, the Stokes shifts of reported CuInS\(_2\) QDs are generally large.\(^{36,45,48-50}\) The exception to this was the PL emission of CuInS\(_2\)/ZnS core/shell QDs with a Stokes shift of $\sim$60 meV.
reported by Nose et al.\textsuperscript{51} This emission was unfortunately very weak, and an intense emission with a large Stokes shift simultaneously appeared. PL emission with a large Stokes shift has been attributed to donor-acceptor pair (DAP) recombination in most previous studies.\textsuperscript{36,45,48}

Hamanaka et al. reported the emission of AgInS\textsubscript{2} QDs,\textsuperscript{52} which was similar to that of CuInS\textsubscript{2} QDs. Emission was attributed to DAP recombination, and the broadened emission feature to electron-phonon interaction based on the configuration coordinate model. The peak energy (\(E_{\text{peak}}\)) of the emission band is given by:

\[ E_{\text{peak}} = E_{\text{ZPL}} - S \omega \]  

(5)

where \(E_{\text{ZPL}}\) is the energy of the zero phonon line, \(S\) is the Huang-Rhys factor representing the average number of emitted phonons and strength of electron-phonon coupling, and \(\omega\) is the frequency of the single phonon mode coupled to the electronic transition. Equation (5) indicates that size dependency in \(E_{\text{peak}}\) arises from the size dependency of the coupling strength \(S\).\textsuperscript{55}

Li et al. observed pronounced bleaching at band-edge spectral energies by transient absorption spectroscopy,\textsuperscript{46} which indicated that emission was related to the quantized levels. Bleaching was dependent on the excitation power, so emission was attributed to the recombinations of electrons in the 1S(e) state and holes in the acceptor level. Li et al. did not identify the species of defects responsible for emission.

We synthesized CuInS\textsubscript{2} QDs exhibiting size-dependent PL emission from commercially available CuI, InBr\textsubscript{3}, and S.\textsuperscript{54} Their size-dependent optical gaps and PL emission energies are shown in Fig. 6, and were analyzed based on the finite-depth well effective mass approximation. PL emission was attributed to the recombinations of electrons in the donor level and holes in the quantized hole state.\textsuperscript{55} Indium atom defects at copper sites or sulfur vacancies were proposed to be defects acting as donors at \(\sim 0.1\text{eV}\) below the conduction band. Bright emission due to exciton recombination from CuInS\textsubscript{2} QDs has not been achieved to date. CuInS\textsubscript{2} QDs were recently used in the active layer of an electroluminescent device.\textsuperscript{56} The large Stokes shift of the defect-related emission suppresses self-absorption, but the broad emission bandwidth had a detrimental effect on color purity. A procedure for synthesizing high-quality defect-free CuInS\textsubscript{2} QDs is required to realize their practical use.

2.3 CuInSe\textsubscript{2} QDs

Allen and Bawendi first reported CuInSe\textsubscript{2}-based QDs exhibiting bright PL emission,\textsuperscript{73} and emission was in the red to near-infrared region. The QD compositions were indium-rich CuIn\textsubscript{x}Se\textsubscript{8} and CuIn\textsubscript{1.5}Se\textsubscript{4}, which significantly deviated from stoichiometric CuInSe\textsubscript{2}. This illustrated the difficult in balancing the reactivity of two metallic cations. The Stokes shift of the PL emission was as large as \(\sim 0.35\text{eV}\), and emission was related to defect levels, similarly to in CuInS\textsubscript{2} QDs. We subsequently synthesized near stoichiometric colloidal CuInSe\textsubscript{2} QDs which exhibited size-dependent PL emission.\textsuperscript{58} The top panel in Fig. 7 shows the optical absorption and PL spectra of these colloidal CuInSe\textsubscript{2} QDs with diameters of 3.8 nm. The Stokes shift (\(\sim 0.14\text{eV}\)) was significantly smaller than that reported by Allen et al. Emission was attributed to the recombinations of electrons in the quantized conduction band and holes at the copper vacancy level. The low PLQY of 2% was improved by surface coating with ZnSe, yielding CuInSe\textsubscript{2}/ZnSe core/shell QDs.\textsuperscript{59} The increased PLQY was due to the passivation of surface states that behaved as non-radiative recombination centers, as described in section 1. The lower two panels in Fig. 7 show the optical absorption and PL spectra of the CuInSe\textsubscript{2}/ZnSe core/shell QDs. The PLQY of the core/shell QDs increased to 16% after ZnSe coating at 250°C, and PL emission was clearly observed with naked eye in the bright room. PLQYs of \(\sim 80\%\) are required for practical application, so further improvement in the syntheses of the CuInSe\textsubscript{2} and/or ZnSe-coating is needed.

CuInSe\textsubscript{2} nanocrystals have potential in printable thin-film solar cells, an excellent review on which was recently published.\textsuperscript{56}
3. ZnO QDs as ultraviolet phosphors and their application in inorganic EL devices

3.1 Synthesis of ZnO QDs

The size-dependent PL emission of QDs is not limited to visible wavelengths. ZnO has received much attention for use in ultraviolet (UV)-sensitive optoelectronic devices, because of its low toxicity, high natural abundance and stability in air. The emission energy of ZnO QDs is tunable in the near UV to UV regions, so ZnO QDs are expected to be applicable in EL devices. Numerous groups have synthesized colloidal ZnO QDs using the hot-injection technique,$^{61-65}$ however the resulting ZnO QDs reportedly exhibited intense defect-related visible emission. No UV emission was often observed, especially for QDs with diameters <5 nm. This is because ensuring a sufficient supply of oxygen is more difficult during reaction in an organic solvent than in aqueous solution. This results in a high oxygen deficiency, and a high concentration of defect levels in the ZnO QDs. Therefore, most ZnO QDs studies have focused on defect-related visible emission.

ZnO QDs with size-dependent UV emission and dispersibility in organic solvents have been synthesized by the two-step one-pot reaction shown in Fig. 8.$^{66}$ The reaction involved the polymerization of zinc monomers to form –Zn–O–Zn– linkages. Specifically, the alkoxide was hydrolyzed by very dilute water in benzylamine, and subsequent dehydration reaction reduced the oxygen vacancies. The surfaces of the resulting QDs were covered with alkoxy and hydroxyl groups and benzylamine. This surface composition is clearly unsuitable for dispersing the QDs in organic solvents, so these surface functional groups were exchanged for oleylamine. The high-purity zinc alkoxide precursor yielded ZnO QDs with size-dependent emission predominantly in the UV region. Figure 9 shows the PL emission spectra of the obtained ZnO QDs, and the insets show HRTEM images of the 4.3-nm-diameter QDs. The UV emission intensity was higher than that of defect-related visible emission, and the UV emission was clearly size dependent. The HRTEM images indicated the excellent dispersibility of the QDs in toluene.

The PLQY for the UV emission of the obtained QDs was <1%. Increasing the emission efficiency remains an important challenge, and fabricating core/shell nanostructures that passivate surface states is a promising approach. The shell material for ZnO QDs should satisfy two criteria: (i) the valence and conduction band offsets should form a type-I quantum well structure; (ii) its crystal structure should be the same as that of ZnO, with a small lattice mismatch. Such a material does not yet exist, except for toxic BeO in binary oxides. However, ternary β-LiGaO$_2$ possessing the wurtzite-derived β-NaFeO$_2$ structure shown in Fig. 10(a) is expected to be suitable.$^{67,68}$ The valence and conduction band offsets between ZnO and β-LiGaO$_2$ are reportedly type I, as shown in Fig. 10(b). Several syntheses of β-LiGaO$_2$ nanocrystals have been developed, but none are applicable for fabricating ZnO/β-LiGaO$_2$ core/shell nanostructures. A procedure for synthesizing ZnO/β-LiGaO$_2$ core/shell nanostructures is still required to achieve high UV emission from ZnO QDs.

3.2 Inorganic UV EL devices activated by ZnO QDs

Most reported QD-activated light-emitting devices emit in the visible region, but UV light emitting devices activated by ZnO QDs have been reported.$^{69-71}$ Toyama et al. reported a light
emitting diode activated by ZnO QDs. UV emission was achieved from the device with the multilayer thin film structure: glass/ITO/pentacene/ZnO/Al. An all-inorganic device is required to achieve a long operating lifetime, so we fabricated a QD-activated all-inorganic EL device for UV emission using ZnO QDs. The inset in Fig. 11 shows the multilayered structure of the EL device. ZnO QDs were deposited from solution, using the liquid-dispersed quantum-dots ion-beam deposition (LIQUID) technique developed by Kobayashi et al. This involved ion-beam deposition, which dissociated surfactants from QD surfaces. Residual organic species in the QD film were lower than in conventional spin-coated films. Figure 11 shows the EL spectrum of the device operated at 170 VAC and 50 kHz, and the PL emission spectrum of the ZnO QDs. The two spectra agreed well. This indicated that EL emission in the UV region originated from the recombination of electrons and holes in quantum confined levels in the ZnO QDs.

4. QDs for solar cells

QD solar cells exploiting MEG have been much studied. Solar cells containing QDs with an \( E_g \) of 0.5–1.0 eV have a theoretical conversion efficiency of >40%, under AM 1.5 conditions. Colloidal PbSe QDs are commonly applied for this purpose, and external quantum efficiencies (conversion of photons into excitons) of >100% have been reported. InAs QDs are alternative materials for QD solar cells, because of their smaller threshold photon energy for MEG as described earlier.

Colloidal InAs QDs with high-quality optical properties and size-dependent PL emission were first reported in 1996 Guzelian et al. InAs QDs were synthesized by the dehalosilylation reaction of InCl \( \text{III} \) and tris(trimethylsilyl)arsine \([\text{As} \left( \text{Si} \left( \text{CH}_3 \right)_3 \right)_3; \text{As(TMS)}_3]\) developed by Wells et al. Twenty years later, this remains the best synthetic route to colloidal InAs QDs; however, \([\text{As(TMS)}_3]\) is highly pyrophoric, and forms toxic and explosive arsine gas upon reaction with air or water. The application of InAs QDs has therefore developed less than that of PbSe QDs.

Wang et al. recently reported a new synthesis route to InAs nanocrystals using triphenylarsine \([\text{As(C}_6\text{H}_5)_3; \text{AsPh}_3]\). AsPh\( _3 \) is more easily handled than As(TMS)\( _3 \). AsPh\( _3 \) is solid, stable at ambient conditions, and its vapor pressure at melting temperature of 60°C is sufficiently low to be safe. The resulting InAs nanocrystals were ~150 nm in diameter, which is much larger than sizes typically exhibiting quantum confinement, and they were also not colloidal.

The reaction developed by Wang et al. has since been modified to form colloidal InAs QDs. AsPh\( _3 \) was reacted with InBr\( _3 \) in oleylamine, with trioctylphosphine oxide as a surfactant. Figure 12 shows the optical absorption spectra of the obtained InAs QDs, with average diameters of 12, 14 and 17 nm. The optical gap range was 0.76–0.72 eV, depending on their size. The crystallinity of the QDs was relatively good, as shown inset in Fig. 12, although they did not exhibit PL emission. Further
improvement of this synthesis is required; however this approach involving AsP₃ is expected to promote research of solar cells containing InAs QDs.

5. Summary

Colloidal QDs are applicable as phosphors in various light emitting devices, and were recently utilized as wavelength converters for blue light-emitting diodes in liquid crystal displays. At the time of writing, Cd-based materials remained the only QDs used in commercial devices. I-III-V₂ and InP QDs are less toxic alternative QD phosphors, and are likely to be used in commercial devices in the near future. Developing QD solar cells has received much recent activity. It will be some time before commercial QD-solar-cell production, however colloidal QDs have a promising future in this area.

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