Recent Advances in Zinc-based Colloidal Semiconductor Nanocrystals for Photoelectronic Energy Conversion

Dechao Chen, [a] Aixiang Wang*[b], Mark A. Buntine [a] and Guohua Jia*[a]
Abstract: Colloidal semiconductor nanocrystals (NCs), especially cadmium (Cd)- and lead (Pb)-based ones, have been proved to be the promising materials for photoelectronic energy conversion applications. However, the high toxicity and cost of these materials restrict their widespread use. Zinc (Zn)-based colloidal semiconductor NCs are non/toxic and environmental friendly materials, manifesting stimulating optical and electronic properties with relevance to a broad scope of applications from light emitting diodes (LEDs), sensors, photocatalysis and more. In this review, we elaborate the shape control of Zn-based colloidal semiconductor NCs achieved by a variety of wet-chemical synthetic approaches. Moreover, the formation of core-shell, doping and hybrid structures based on Zn-based colloidal semiconductor NCs allow for the optimization of their functionalities, which underpin stimulating photoelectronic energy conversion applications in quantum dots LEDs (QLEDs), photodetectors and photocatalysis. Zn-based colloidal semiconductor NCs that combine the green chemistry with sustainable developments possess a bright future.

1. Introduction

Colloidal semiconductor NCs, also termed quantum dots (QDs), are tiny crystals made of semiconductor materials with dimensions being comparable to their exciton Bohr radius. Presently, Cd- and Pb-based semiconductor NCs are well developed in terms of both fundamental science and practical applications due to their facile synthetic accessibility and intriguing properties. However, Cd and Pb are heavy metals. The high toxicity of Cd- and Pb based QDs and legistory regulations are the major obstacles for their widespread use. As a result, zinc-based QDs have been considered as the potential alternatives to the traditional heavy metal-based QDs.

The compounds of zinc-based colloidal semiconductor NCs typically contain II–VI group (e.g. ZnSe, ZnS and ZnTe) and II–V group QDs (e.g. ZnS
2 and ZnAs2). Being analogous to the heavy metal-based QDs, the band gap of zinc-based colloidal semiconductor NCs covers a wide spectral range spanning from ultraviolet to near-infrared. Meanwhile, many intriguing optical and electrochemical properties of Zn-based QDs are emerging. Furthermore, according to the band structure alignment, tailoring the dimensions of NC themselves in conjunction with the combination of semiconductor NCs with other materials such as metals, can manipulate the quantum confinement of excitons and induce efficient charge separation to meet the specific requirements in diverse applications. In consideration of energy application based on Zn-based QDs, they offer an environmental benign and low cost platform by using non/toxic and earth abundant materials, to exploit many stimulating technological applications in optoelectronics, catalysis, sensors, detector, biomedicine and more.

In this Review, firstly we overview the development of zinc-based colloidal binary semiconductor NCs (ZnSe, ZnS, ZnTe, ZnS
2 and ZnAs2). Then we elaborate structural engineering of Zn-based QDs in terms of core-shell, doping and hybrid, followed by a discussion on their stimulating properties. Thirdly, the recent advances in energy conversion applications of Zn-based QDs in light-emitting diode (LED), photoelectrochemical reactions and photocatalysis are summarized and highlighted. Finally, future perspectives in this stimulating research field from fundamental studies to the emerging applications have been proposed.

2. Tailoring Band Gap through Quantum Confinement Effects

The band gap of bulk zinc chalcogenides ranging from 2.39 eV to 3.61 eV falls in blue and green spectral ranges. In particular, the size control of single content zinc chalcogenide NCs provides an approach to tune their band gap. As shown in Fig. 1, the band gap energies of zinc chalcogenide NCs can cover almost the entire violet-blue and blue spectral ranges. Their
band gaps can be further expanded through the size tuning of zinc chalcogenide NCs, as depicted by gaps between the conduction band and predicted energies (red bars in Figure 1). Beyond the size control, the control in morphology shows the potential in tailoring their unique physical properties. Furthermore, other strategies such as compositing core/shell, alloying and doping structures are often used to improve the fluorescence quantum yields, conductivity and stability. As the lighting in the violet-blue and blue spectral ranges is highly demand, zinc-based chalcogenides are potential candidates for next-generation environmental friendly lighting industries.

![Figure 1. Electronic energy levels of bulk zinc chalcogenide (green bar) and its adjustable band gap (red bar).](image)

**3. Synthetic Methodology**

The synthetic strategies of Zn-based QDs include almost all of the general colloidal synthetic approaches for colloidal NCs such as heating-up (HU) method, hot-injection (HI) method and cation exchange (CE) reaction. Those basic synthetic methods are based on various growth mechanisms.

A heating-up method is a thermal decomposition process which combines the nucleation and growth stages in a same reaction. For example, in a typical synthesis of this method for zinc chalcogenide NCs, zinc diethylthiocarbamate (Zn(ddtc)_2) and zinc dibutyldithiocarbamate (Zn(dbdc)_2) act as the single source precursors and the surfactant/reaction medium, respectively, leading the formation of nearly monodisperse ZnS.\[10\]\[11\] By the modification of the passivating surface ligands, the growth of zinc-based NCs can be control via a variety of growth mechanisms including epitaxial growth, ripening, oriented attachment and lead to the formation of nanostructures with diverse dimensionalities.\[12\]\[13\]\[14\]\[16\] Until now, the heat-up method can be adopted into the syntheses of almost all types of Zn-based one dimensional (1D) and two dimensional (2D) nanostructures (Table 1).\[16\]

Besides the HU method, the HI method is also a powerful synthetic approach for zinc-based NCs. In a typical synthesis, zinc precursors or anion precursors are injected into the stock solution of another precursor. Hot-injection of precursors can increase the supersaturation of the solution, thus overcome the energy barrier that required for the nucleation. The nucleation of zero-dimensional (0D) NCs can be used as the seeds for further growth of the NCs. Zinc precursors such as zinc stearate (ZnSt) and diethylzinc (ZnEt_2) are widely used in the reactions with sulfur or selenium precursors (Table 1).\[17\]\[18\] Until now, most Zn-based nanostructures can be synthesized through the HI method by the control of activity of both precursors and solvents.

Cd-based CdSe/CdS core/shell nanorods can be readily prepared by a seeded growth method.\[19\] However, this synthetic approach does not work for Zn-based NCs because Zn-based NCs may not be compatible with anisotropic growth under similar synthetic conditions. The CE method provides an accessible approach in compositing desirable nanostructures which is hard to be directly synthesized using conventional synthetic methods. A representative example is the formation of blue-emitting ZnSe/ZnS core/shell nanorods through sequential cation exchange, in which CdSe/CdS nanorods firstly convert into Cu_2Se/CuS nanorods, followed by the substitution of Cu^2+ ions in the crystal lattices by Zn^2+ ions that produces the final products of ZnSe/ZnS nanorods.\[20\]

By optimizing the synthetic conditions, the control of size, shape and structure of Zn-based NCs can be achieved and further used in diverse energy conversion applications.

**Table 1. Typical synthetic approaches of Zn-based NCs. (N/A: nor reported or not existence)**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Metal Precursor</th>
<th>Anion Precursor</th>
<th>Method</th>
<th>Morphology</th>
<th>Emission Range</th>
<th>Quantum Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 D Structures</td>
<td>ZnSe NCs[17]</td>
<td>ZnEt_2</td>
<td>Se-TOP</td>
<td>Injection</td>
<td>Dots</td>
<td>365-410nm</td>
</tr>
</tbody>
</table>


<table>
<thead>
<tr>
<th>Material</th>
<th>Precursors</th>
<th>Reaction</th>
<th>Product Form</th>
<th>Emission Range</th>
<th>Intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnSe NCs</td>
<td>Zn(Si)₂</td>
<td>Se</td>
<td>Injection</td>
<td>Dots</td>
<td>365-430 nm</td>
</tr>
<tr>
<td>ZnSe NCs</td>
<td>ZnCl₂</td>
<td>N/A</td>
<td>Cation</td>
<td>Spherical NCs</td>
<td>N/A</td>
</tr>
<tr>
<td>ZnS NCs</td>
<td>ZnEt₂</td>
<td>S</td>
<td>Injection</td>
<td>Dots</td>
<td>335 nm, 350 nm</td>
</tr>
<tr>
<td>ZnS QDs</td>
<td>Zn(NO₃)₂</td>
<td>Na₂S</td>
<td>Injection</td>
<td>Dots</td>
<td>440 nm</td>
</tr>
<tr>
<td>ZnTe quasi-Spheres</td>
<td>ZnAc₂</td>
<td>Te-TOP</td>
<td>Injection</td>
<td>Quasi-spheres</td>
<td>N/A</td>
</tr>
<tr>
<td>Zn₃P₂ nanoparticles</td>
<td>Zn(OEt)₂ or Zn(CHMeCH₂NMe₂)₂</td>
<td>P(SiMe₃)₃</td>
<td>Heat up</td>
<td>1.5-2.5 nm dots</td>
<td>N/A</td>
</tr>
<tr>
<td>Zn₃P₂ QDs</td>
<td>Me₂Zn</td>
<td>HPBu₂</td>
<td>Injection</td>
<td>3.59-4.32 nm dots</td>
<td>N/A</td>
</tr>
<tr>
<td>Zn₃P₂ QDs</td>
<td>ZnEt₂ and Zn(O₂CR)₂</td>
<td>P(SiMe₃)₃</td>
<td>Injection</td>
<td>2.6-2.9 nm dots</td>
<td>620 nm</td>
</tr>
<tr>
<td>Zn₃P₂ QDs</td>
<td>ZnEt₂</td>
<td>(TMSi)₃P</td>
<td>Injection</td>
<td>3.2-8.8 nm dots</td>
<td>481-545 nm</td>
</tr>
<tr>
<td>Zn₃As₂ QDs</td>
<td>Zn(OA)₂ and ZnEt₂</td>
<td>As(SiMe₃)₂</td>
<td>Injection</td>
<td>2.8 nm dots</td>
<td>642 nm, 939 nm</td>
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</table>

**1D Structures**

<table>
<thead>
<tr>
<th>Material</th>
<th>Precursors</th>
<th>Reaction</th>
<th>Product Form</th>
<th>Emission Range</th>
<th>Intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnSe nanorods and wires</td>
<td>[Zn₄(SPh)₁₀][Me₄N]₂</td>
<td>Se-DPP</td>
<td>Heat up</td>
<td>Rods and wires</td>
<td>390-425 nm</td>
</tr>
<tr>
<td>ZnSe nanorods and wires</td>
<td>Zn(Si)₂</td>
<td>N/A</td>
<td>Attachme</td>
<td>Rods and wires</td>
<td>N/A</td>
</tr>
<tr>
<td>ZnSe nanorods and wires</td>
<td>ZnAc₂</td>
<td>Selenourea</td>
<td>Heat up</td>
<td>Rods and wires</td>
<td>436 nm, 500 nm, 546 nm</td>
</tr>
<tr>
<td>ZnSe NCs</td>
<td>ZnCl₂</td>
<td>N/A</td>
<td>Cation</td>
<td>Rods</td>
<td>N/A</td>
</tr>
<tr>
<td>ZnSe quantum rods and</td>
<td>ZnEt₂</td>
<td>Se</td>
<td>Injection</td>
<td>Rods and Branched NCs</td>
<td>420-450 nm</td>
</tr>
<tr>
<td>branched NCs</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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</table>
### ZnSe nanorod couples

<table>
<thead>
<tr>
<th>Material</th>
<th>Precursor</th>
<th>Reaction</th>
<th>Turbostratic Growth</th>
<th>Product</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnSe, ZnS, ZnTe quantum rods</td>
<td>[31]</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>ZnS nanorods</td>
<td>[32]</td>
<td>Zn(ddtc)$_2$</td>
<td>DDT</td>
<td>Etching</td>
<td>N/A</td>
</tr>
<tr>
<td>ZnS nanorods</td>
<td>[12]</td>
<td>ZnEt$_2$</td>
<td>S</td>
<td>Attachment</td>
<td>N/A</td>
</tr>
<tr>
<td>ZnS nanowires</td>
<td>[10]</td>
<td>Zn(ddtc)$_2$</td>
<td>Zn(ddtc)$_2$</td>
<td>Heat up</td>
<td>Wires</td>
</tr>
<tr>
<td>ZnS nanowires</td>
<td>[11]</td>
<td>Zn(dbdc)$_2$</td>
<td>Zn(dbdc)$_2$</td>
<td>Heat up</td>
<td>Wires</td>
</tr>
<tr>
<td>ZnS nanowires</td>
<td>[33]</td>
<td>Zn(NO$_3$)$_2$</td>
<td>DDT</td>
<td>Injection</td>
<td>Wires</td>
</tr>
<tr>
<td>ZnTe Nanorods</td>
<td>[23]</td>
<td>ZnCl$_2$</td>
<td>Te-TOP</td>
<td>Injection</td>
<td>Rods</td>
</tr>
<tr>
<td>ZnTe Nanorods</td>
<td>[34]</td>
<td>ZnAc$_2$</td>
<td>Te-TOP</td>
<td>Injection</td>
<td>Rods</td>
</tr>
<tr>
<td>ZnTe Nanorods</td>
<td>[35]</td>
<td>Zn(AA)$_2$</td>
<td>NaHTe</td>
<td>Injection</td>
<td>Rods</td>
</tr>
<tr>
<td>ZnTe nanobelts</td>
<td>[36]</td>
<td>Zn(OAc)$_2$</td>
<td>Te-TOP</td>
<td>Heat up</td>
<td>Belts</td>
</tr>
</tbody>
</table>

### 2D Structures

<table>
<thead>
<tr>
<th>Material</th>
<th>Precursor</th>
<th>Reaction</th>
<th>Turbostratic Growth</th>
<th>Product</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnSe nanosheets</td>
<td>[37]</td>
<td>Zn(NO$_3$)$_2$</td>
<td>Se</td>
<td>Heat up</td>
<td>Sheets</td>
</tr>
<tr>
<td>ZnS nanoplatelets</td>
<td>[38]</td>
<td>Zn-dedtc</td>
<td>Zn-dedtc</td>
<td>Heat up</td>
<td>Platelets</td>
</tr>
<tr>
<td>ZnSe and ZnS quantum platelets</td>
<td></td>
<td>Zn(OAc)$_2$</td>
<td>Selenourea or thioacetamide</td>
<td>Injection</td>
<td>Platelets</td>
</tr>
</tbody>
</table>

### 3D Structures

<table>
<thead>
<tr>
<th>Material</th>
<th>Precursor</th>
<th>Reaction</th>
<th>Turbostratic Growth</th>
<th>Product</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnSe nanoflowers</td>
<td>[40]</td>
<td>Zn(St)$_2$</td>
<td>Se-TBP</td>
<td>Injection</td>
<td>Nanoflowers</td>
</tr>
<tr>
<td>ZnTe nanoclusters</td>
<td>[41]</td>
<td>ZnCl$_2$</td>
<td>Te-TOP</td>
<td>Injection</td>
<td>Platelets</td>
</tr>
<tr>
<td>ZnTe nanoflowers</td>
<td>[42]</td>
<td>Zn(St)$_2$</td>
<td>Te-TOP or Te-TBP</td>
<td>Injection</td>
<td>Nanoflowers</td>
</tr>
<tr>
<td>ZnTe Tetrahedrons</td>
<td>[23]</td>
<td>ZnCl$_2$</td>
<td>Te-TOP</td>
<td>Injection</td>
<td>Tetrahedrons</td>
</tr>
</tbody>
</table>
4. Types of Zn-based semiconductor NCs

Zn-based colloidal semiconductor NCs can be divided into two main categories. The most extensively studied ones in terms of materials synthesis and energy conversion-related applications are zinc chalcogenide semiconductor NCs, including zinc selenide (ZnSe), zinc sulfide (ZnS) and zinc telluride (ZnTe). Another type of Zn-based colloidal semiconductor NCs, which are rarely reported, is zinc oxypnictide such as zinc phosphide (Zn3P2) and zinc arsenide (Zn3As2). In this section, we review the fundamental aspects of Zn-based colloidal semiconductor NCs and elaborate their stimulating optical and electronic properties.

4.1 ZnSe

ZnSe is the most basic and well-developed zinc chalcogenide semiconductor NCs with a wide direct band gap manifesting emission from ultraviolet to visible spectral ranges (325 nm-460 nm). By the control and modification of colloidal chemical synthetic methods, the particles size tuning ranging from 1.7 to 12 nm can be achieved, and the band gap energies can be tuned from the bulk band gap of 2.7 eV (460 nm) to 3.8 eV (326 nm), covering a large proportion of the near ultraviolet and blue spectral ranges (Fig. 1c). ZnSe QDs exhibit a rich phase diagram with both hexagonal and cubic crystal structures. The optical properties can be tailored by precisely tune the band gap and phase.

Colloidal ZnSe NCs have been readily synthesized through a variety of methods including the HI method and HU method. The HI method was firstly introduced to prepare nearly monodisperse ZnSe spherical nanoparticles with narrow emission line widths. In contrast, 1D ZnSe nanowires and nanorods can be obtained through an oriented attachment mechanism and HU method. Ostwald ripening and self-assembly from magic-sized clusters (Fig. 2a-c). ZnSe nanoparticles with other morphology such as polypods can be obtained by adjusting the amount of precursors and temperature, as shown in Fig. 2f. Beyond the traditional 1D structure, Jia et al. reported a unique structure of ZnSe nanorod couples which can confine the band edge states to small short edges of the ZnSe structure (Fig. 2d). ZnSe nanosheets was introduced by HU method in which the 2D ZnSe structures were formed via the oriented attachment process (Fig. 2e). Another report by Buhr et al. demonstrated that ZnSe nanoplates can be prepared from (ZnSe)15(n-butylamine)13 nanoclusters. Other than the direct synthetic methods, cubic ZnSe and wurtzite ZnSe spherical nanoparticles as well as wurtzite ZnSe nanorods were synthesized via a sequential cation exchange method starting from cadmium-based nanoparticles.

4.2 ZnS

ZnS has a direct wide bulk band gap of 3.54 eV for the cubic phase and 3.91 eV for the hexagonal phase with high transmittance in the visible range. The large exciton binding energy of 40 meV and the small Bohr radius of 2.4 nm make ZnS a significant semiconductor material in photonic and optoelectronic applications.

Generally, due to the large band gap of ZnS, it's hard to find a suitable semiconductor as the shell material to constitute the core/shell structure in order to achieve strong luminescence with high quantum efficiency by confining the electrons and holes into the core of ZnS. In 2007, there is a report about the highly blue-emissive 3-mercaptopropionic acid (MPA) capped ZnS QDs with a quantum yield of 31%. The blue photoluminescence (PL) in the range from 415 nm to 440 nm is far from the band gap energy of the bulk ZnS (3.54 eV) and thus it can be attributed to the trap state emission. Later on, 1D ZnS nanorods and nanowires had been prepared in the presence of octadecylamine. Another parallel work reports the synthesis of nanowires and nanodots with high crystallinity by the use of single source precursor of Zn(dbdc)2. Compare to bulk ZnS, ZnS nanodots and nanowires show a blue shift of 17-25 nm in the absorption spectra, and the emission falls in 354-358 nm. Furthermore, the wurtzite ZnS nanowires prepared using a similar synthetic method exhibited a strong ultraviolet emission band centered at 337 nm without any trap state emission.

Dodecanethiol (DDT) plays an important role in controlling the...
morphology of ZnS nanoparticles. For example, the morphology of ZnS nanoparticles can be effectively tuned from nanorod, to nanowires, and spherical dots by changing the amount of DDT.\cite{33} Moreover, Chen et al. recently presented a facile approach to prepare uniform ZnS nanorods from the ZnS nanowires by the etching of DDT.\cite{32} In the aspect of ZnS nanoparticles with a 2D shape, Buhro et al. assembled magic-sized nanoclusters into stacked ZnS nanoplatelets (Fig. 2c).\cite{39} Pradhan et al. observed a phase transformation of ZnS nanoplatelets into wurtzite and zinc blende structures (Fig. 2d).\cite{38}

4.3 ZnTe

ZnTe nanoparticles are less reported in comparison with other zinc chalcogenide NCs such as ZnS and ZnSe because of their difficulty in the synthesis. Zhang et al. first adapted Te-TOP as the tellurium precursor in the synthesis of ZnTe and achieved their shape control of ZnTe nanoparticles as sphere dots, tetrahedrons and nanorods by controlling of the zinc precursors and reaction temperature.\cite{42} Ligand effect in combination with the reaction temperature had also been investigated to optimize the synthetic conditions that are appropriate for the synthesis of ZnTe nanoparticles with diverse shapes including spherical dots, nanorods and nanoflowers (Fig. 3a).\cite{43} To address the issue of instability of ZnTe, aqueous ZnTe spherical dots had been synthesized by thioglycolic acid (TGA) ligand capping.\cite{44} High single-crystalline and uniform ZnTe nanorods with a high quantum yields of 60% and good stability have been obtained through either an oriented attachment mechanism or Ostwald ripening (Fig. 3b).\cite{36} Further-potential applications of oleylamine coated ZnTe nanorods in of LEDs had also been demonstrated in this work.\cite{37} Moreover, the ZnTe nanoclusters play a vital role in the formation of the new emerging structures such as wires, triangle nanoplatelets and rectangular nanoplates (Fig. 3c-f).\cite{41} The spontaneous assembly of 2D ZnTe structures is based on a typical oriented attachment mechanism. Recently, ZnTe nanoclusters have also been used to prepare ZnTe nanoflowers (Fig. 3e).\cite{36}

Figure 2. TEM images of colloidal ZnS nanoparticles with diverse morphologies (a) Nanowires, (b) Nanorods, (c) nanoplatelets, (d) Nanodisks. The panels were adapted with permission from Ref.\cite{11} (Panel a; Copyright 2011 American Chemical Society),\cite{32} (Panel b; Copyright 2018 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim),\cite{39} (Panel c; Copyright 2015 American Chemical Society),\cite{38} (Panel d; Copyright 2014 Nature Publishing Group).

Figure 3. TEM images of colloidal ZnTe nanoparticles with diverse morphologies (a) Spherical dots, (b) nanorods, (c) Nanowires, (d) Triangle plates. (e) Nanoflowers, (f) Rectangular plates. The panels were reorganized with permission from refs \cite{38} (Panel a,b; Copyright 2011 American Chemical Society),\cite{41} (Panel c,d,f; Copyright 2014 American Chemical Society),\cite{36} (Panel d; Copyright 2018 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim).

4.4 ZnP2 and ZnA2

Colloidal zinc oxypnictide semiconductor NCs including ZnP2 and ZnA2 QDs have rarely been studies due to the difficulties in synthesis and unavailability of precursors. There are only a few reports on the synthesis of colloidal ZnP2 and ZnA2 nanoparticles. The developments of synthesis of colloidal zinc oxypnictide nanoparticles with various morphologies and their applications in field of energy conversion are still challenging.

Bulk ZnP2 has a direct band gap around 1.55-1.60 eV and a 1500 cm\(^{-1}\) absorption coefficient with a carrier diffusion length of 5-10 μm.\cite{49,50} The first report of the colloidal synthesis of zinc phosphide nanoparticles can be traced back to 1985 wherein a synthetic approach similar to that of CdS QDs has been reported.\cite{51} O’Brien et al. adapted the metalorganic synthesis of ZnP2 nanoparticles in the trioctylphosphine-trioctylphosphine...
oxide (TOP-TOPO) system and obtained the luminescence of ZnS nanoparticles in the blue and green spectral ranges with a Stokes shift of about 44-180 nm depending on the synthetic temperature.[25] The quantum yield of ZnS nanoparticles is only around 1%.[26] More recently, the ZnS nanoparticles are studied more thoroughly through the investigation of the reaction of two typical precursors of ZnEt$_2$ and P(SiMe$_3$)$_3$ associated with the intermediate state as [EtZnP(SiMe$_3$)$_3$]. Other resource such as PH$_3$ were also reported in the preparation of ZnO@ZnS nanoparticles with an enhanced quantum yield of up to 3%.[54][55]

There is only one report in the literature on the synthesis of colloidal Zn$_{1-x}$S nanoparticles which take advantage of the elevated reactivity of mixed zinc alkyl carboxylate oligomeric precursors such as ZnEt$_2$ and Zn(OA)$_2$.[28] The 3 nm diameter of Zn$_{1-x}$S QDs shows an optical band gap of 2.2 eV.

### 4.5 Alloy

Alloy QDs are ideal structures in overcoming materials issues such as the tendency to form defects, surface trap states and blinking effect of the nanoparticles which are closely relevant to fabricating high-quality nanoparticles. In addition to the band gap tuning of nanoparticles through the size control, alloying of QDs is an alternative approach that could retain the emission with good quantum efficiency and sharp line width. In the following section, we will elaborate two types of alloyed Zn-based nanoparticles with and without Cd ions.

In the Cd-based system, Cd$_x$Zn$_{1-x}$S alloyed QDs show a PL emission from 474 to 391 nm with the quantum efficiency of 25-50%.[56] The luminescence quantum efficiency of alloyed Cd$_x$Zn$_{1-x}$S QDs can be further improved to 70-85% by optimizing the synthetic condition.[57] Cd$_x$Zn$_{1-x}$S alloyed QDs can be also prepared in aqueous solution with a quantum yield of up to 50% which is compared to or even better than most QDs synthesized by the conventional organometallic route (Fig. 4).[58] As shown in Fig. 4a,b, by increasing the ratio of Cd, the emission wavelength trend to red range from blue with fluctuant quantum yield. It's corresponding to the Cd$_x$Zn$_{1-x}$Se alloy QDs structure formed from ZnSe QDs after injection of Cd precursor (Fig. 4c,d). Besides the alloying of the cations in the host of QDs, a broader and tunable emission crossing the entire visible spectral range of 440-850 nm was achieved in quaternary-alloyed QDs such as ZnCdSSe.[59]

![Absorption and fluorescence spectra of ZnSe and Zn$_{1-x}$Cd$_x$Se alloyed QDs with different content ratio of Cd. (b) Absorption and fluorescence spectra of evolution of Zn$_{1-x}$Cd$_x$Se alloyed QDs with time. (c) Quantum yield and emission wavelength of Zn$_{1-x}$Cd$_x$Se alloyed QDs with different content ratio of Cd. (d) Photographs of emission of Zn$_{1-x}$Cd$_x$Se and Zn$_{1-x}$Cd$_x$Se alloyed QDs under UV-Vis light. Reprinted with permission from Ref. Copyright 2007 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.](image-url)
4.6 Core Shell

Core/shell structures allow to grow one or more semiconductor layer(s) to passivate the surface of core and play a vital role in the energy conversion for quantum materials. The band gap of core and shell materials varies from their counterparts of bulk semiconductors due to the quantum confinement effect. Core/shell structures can be engineered based on the conduction and valence band alignments, which allow for the confinement of the electrons and holes partially or completely confined in the core or shell in order to meet the requirements for diverse applications in electronics and photoelectronics. The core/shell structures generally include three types namely type-I, type-II and reverse type-I. In Zn-based core/shell QDs with type-I and type-II configurations are the most intensively investigated structures (Fig. 6). For the type-I structure, band gap of the shell material is larger than that of the core, so that both electrons and holes are confined in the core. Type-II structure shows staggered band alignments so the holes and electrons are partially confined in the core, making them capable in optoelectronic applications. For reversed type-I structure the holes and electrons are localized in the shell.

**Figure 5.** (a) HAADF-STEM image of ZnSe$_{1-x}$S$_x$ alloyed QDs. Reprinted with permission from Ref. [61], Copyright 2012 American Chemical Society. (b) HAADF-STEM image of ZnSe$_{1-x}$S$_x$ alloyed nanorods. (c) Absorption (solid line) and PL spectra (dashed dotted line) of the nanoparticles (from ZnSe nanowires to ZnS$_x$Se$_{1-x}$ alloyed quantum rods). (b,c) are reprinted with permission from Ref. [62], Copyright 2018 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim. (d) TEM image of wurtzite ZnS$_x$Se$_{1-x}$ alloyed nanoplates. Reprinted with permission from Ref. [63], Copyright 2013 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

**Figure 6.** The schematic of band alignments of core/shell materials. Reprinted with permission from Ref. [64], Copyright 2017 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

As discussed previously, ZnSe have a large band gap in the blue spectral range. This makes it an ideal material as the core to fabricate blue emitting core/shell QDs. ZnS has a larger band gap than ZnSe and therefore can acts as the shell material to effectively confine the hole and electron in the ZnSe core, as demonstrated in core/shell ZnSe/ZnS nanoparticles with 0D, 1D and 2D morphologies. The ZnS shell can grow on the ZnSe core by using the precursors of thiourea and zinc acetate in water solution. The obtained ZnSe/ZnS QDs show a blue emission in the range of 390-460 nm with a maximum quantum yield of 65%. The ZnSe/ZnS core/shell nanorods with a maximum quantum yield of 15% can be achieved by a cation exchange method from the CdSe/CdS core/shell nanorods. Recently Ji et al. successfully tailored the ZnSe/ZnS core/shell rods by constructing versatile surface architectures as flat-shell, islands-shell and helical-shell. A quantum yield as high as ~50% can be achieved. The strategy by tailoring the strain at the interface of the core and shell could be expanded to other semiconductor nanoparticles to improve both the quality of shell and the quantum yield. Recently, new types of Zn(Se,Te)/ZnS QDs with tunable emission and narrow emission line width have been prepared. However, the quantum yield of this type of core/shell QDs is very low, which is about 1%. The controllable synthesis of Zn-based core/shell structures with a high quantum yield remains a challenge.

Compare to Zn-based core/shell structures with the type-I configuration, those with a type-II configuration usually adopt CdSe or CdS material for the shell as the cadmium chalcogenides have a good chemical stability and smaller band gap in comparison with that of the core materials. ZnSe/CdS core/shell structures with diverse morphologies including spherical dots and rods have been reported. Zomkov et al. synthesized the ZnSe/CdS core/shell QDs with a quantum yield of 20%. Furthermore, Banin et al. obtained the ZnSe seeded CdS nanorods with a quantum yield of 45%. In comparison with the type-I CdSe/CdS core/shell nanorods, ZnSe/CdS core/shell nanorods with a type-II configuration show a longer fluorescence
lifetime of 105 ns because the electrons are more delocalized into the shell material. As for other type-II core/shell ZnTe/ZnSe nanoparticles, they have a broad emission ranging from 500 nm to 575 nm and a long average fluorescence lifetime of ~77 ns. However, their quantum efficiency is low, i.e. 6%, as the spatial separation reduces the electrons and holes recombination possibilities. In addition, double shell of Zn-based core/shell QDs using the ZnSe as the core material has also been prepared in order to improve quantum efficiency and tailoring the distribution of the charge carriers for type-II core/shell structures. More than double shell, Jia et al recently reported a hetero-ZnS (short arms)-ZnSe (long arms)/ZnS shell nanorod couples with alloyed ZnCdS shell with blue emission. The electron was proved to occupy only ZnSe

### Table 2. Summary of zinc based core shell structures.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Type</th>
<th>Core</th>
<th>Shell</th>
<th>Morphology</th>
<th>Emission range</th>
<th>Quantum yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnSe/ZnS QDs[67][68]</td>
<td>I</td>
<td>ZnSe</td>
<td>ZnS</td>
<td>Dot with shell</td>
<td>390-460 nm</td>
<td>45%, 65%</td>
</tr>
<tr>
<td>ZnSe/ZnS nanoparticles[20]</td>
<td>I</td>
<td>ZnSe</td>
<td>ZnS</td>
<td>Dot in rod</td>
<td>380-440 nm</td>
<td>6-15%</td>
</tr>
<tr>
<td>ZnSe/ZnS nanoplatelets[72]</td>
<td>I</td>
<td>ZnSe</td>
<td>ZnS</td>
<td>Platelet with shell</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>Zn(Te,Se)/ZnS QDs[70]</td>
<td>I</td>
<td>Zn(Te,Se)</td>
<td>ZnS</td>
<td>Alloyed dot with shell</td>
<td>521-559 nm</td>
<td>&lt;1%</td>
</tr>
<tr>
<td>ZnSe/CdSe NCs[73]</td>
<td>Reverse I</td>
<td>ZnSe</td>
<td>CdSe</td>
<td>Dot in dot</td>
<td>418-674 nm</td>
<td>40-85%</td>
</tr>
<tr>
<td>ZnTe/ZnSe QDs[74]</td>
<td>II</td>
<td>ZnTe</td>
<td>ZnSe</td>
<td>Dot in dot</td>
<td>500-575 nm</td>
<td>6%</td>
</tr>
<tr>
<td>ZnTe/CdSe NCs[75]</td>
<td>II</td>
<td>ZnTe</td>
<td>CdSe</td>
<td>Dot in dot</td>
<td>580-880 nm</td>
<td>10-30%</td>
</tr>
<tr>
<td>ZnSe/CdS NCs[71]</td>
<td>II</td>
<td>ZnSe</td>
<td>CdS</td>
<td>Dot in dot</td>
<td>460-630 nm</td>
<td>12-18%</td>
</tr>
<tr>
<td>ZnSe/CdS nanorods[76]</td>
<td>II</td>
<td>ZnSe</td>
<td>CdS</td>
<td>Dot in rod</td>
<td>550-600 nm</td>
<td>26%, 45%</td>
</tr>
<tr>
<td>ZnSe/ZnS/CdS QDs [77]</td>
<td>II</td>
<td>ZnSe</td>
<td>ZnS/CdS</td>
<td>Dot with double shell</td>
<td>~565 nm</td>
<td>6-39%</td>
</tr>
<tr>
<td>ZnSe/CdS/ZnS QDs [78]</td>
<td>II</td>
<td>ZnSe</td>
<td>CdS/ZnS</td>
<td>Dot with double shell</td>
<td>470-630 nm</td>
<td>43-61%</td>
</tr>
<tr>
<td>(Zn,Cd)Te/CdSe nanowires[79]</td>
<td>II</td>
<td>(Zn,Cd)Te</td>
<td>CdSe</td>
<td>Wire with shell</td>
<td>530-760 nm</td>
<td>20-60%</td>
</tr>
</tbody>
</table>
states, while the hole occupies a ZnS-ZnS state. Over-coating ZnCdS layer of the nanorod couples eliminates the surface traps and improves the quantum efficiency.\[^{[80]}\] The emission of ZnSe/CdSe core/shell QDs with a type II configuration can be precisely tuned from violet to red by depositing a CdSe shell with difference thickness on the ZnSe core.\[^{[73]}\] In the CdSe/ZnSe core/shell QDs, the increase of the shell thickness of ZnSe leads to a continuous transition from type-I to type-II and then back to type I structures.\[^{[81]}\]

### 4.7 Doping

Doping is another powerful strategy to tune the band gap through creating electronic energy levels. Generally, doping transition metal ions into the lattice of semiconductors allows for lower energy light emission without changing the band gap of the host semiconductor, leading to a large Stokes shift in comparison to the band gap of the host QDs. The doping of Zn-based semiconductor NCs have been extensively investigated because of the weak emission of nanoparticles and large band gap.

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**Figure 7.** Illustrations and corresponding PL of different doping states. (a) Doping process along with host precursors, (b) Doping process before the nucleation of host, (c) Doping process during the shell growth of host. Reprinted with permission from Ref.\[^{[82]}\], Copyright 2011 American Chemical Society.

Doping of semiconductor NCs is typically involving two transition metal ions such as Mn and Cu and the doping strategy can vary, as shown in Fig. 7.\[^{[82]}\] In the nucleation-doping (Fig. 7a), Mn was doped in ZnSe QDs with Mn and Zn precursors prepared at the same time.\[^{[83]}\] The emission peak of Mn-ZnSe QDs keeps as the same at wavelength of 580 nm but the emission intensity becomes stronger as the dopant concentration of Mn increases. Those evidences indicate the high efficient energy transfer from the host of ZnSe QDs to the Mn dopants. For the growth-doping, Cu was doped on the surface of ZnSe particles and a further ZnSe shell grew on the Cu-ZnSe particles (Fig. 7b).\[^{[84]}\] This strategy can form a well complete encapsulation for the dopant cations and the emission wavelength can be tuned by changing the size of host QDs. The QY of Mn-ZnSe QDs was increased to 50% though growth-doping method. Beyond that, the shell could be expanded to a heterogeneous shell. As shown in Fig. 7c, Mn was doped in ZnS shell to form the core/shell doping structures.\[^{[85]}\] The energy transfer between core/shell nanoparticles and Mn dopants can be switched depending on the level of the doping concentration.

---

**Figure 8.** UV-Vis absorption and PL spectra of (a) Mn doped ZnSe/ZnS core/shell nanowires and (b) Mn doped ZnSe/CdS/ZnS core shell nanowires. The optical image of (c) Mn doped ZnSe/ZnS core shell nanowires and (d) Mn doped ZnSe/CdS/ZnS core shell nanowires. Reprinted with permission from Ref.\[^{[86]}\], Copyright 2017 American Chemical Society.

Mn\(^2+\) has also been doped into 1D Zn-based NPs to improve their luminescence such as in Mn-ZnSe nanowires.\[^{[87]}\] Mn-ZnS nanorods,\[^{[88]}\] Mn-ZnSe nanorods\[^{[89]}\] Those doped nanostructures exhibit enhanced fluorescence and controlled electronic and magnetic properties.\[^{[90]}\][\[^{[91]}\]] Compared with Mn doped type-I ZnSe/ZnS core shell nanowires (Fig. 8a,c), Mn doped quasi type II/type I ZnSe/CdS/ZnS double shell nanowires showed shell thickness-dependent emission wavelength and quantum yields (Fig. 8b,d).\[^{[86]}\]

### 4.8 Hybrid

The hybrid structures combine the Zn-based semiconductor NCs with other materials such as noble metal particles or other semiconductor materials to form hetero-nanostructures manifesting synergistic properties. The growth methods for such hetero-nanostructures usually contain surface growth, surface growth and diffusion, simultaneous nucleation and growth of both components and replacement of a sacrificial domain.\[^{[92]}\]
Noble metal particles can be specifically deposited on a certain location on 1D zinc chalcogenide nanorods. Yu et al. presented a novel hybrid structure which uses ZnS as main rods, and integrated Au, CdS or CuS to expand the absorption range from UV, visible to NIR, as shown in Fig. 9a,b,[103,104] Moreover, except for the composition control, noble metal nanoparticles can also selective grow on the tips of 1-D zinc chalcogenide NCs, as shown in Au-ZnS[95,96] (Fig. 9c) and Pt-ZnSe[97] (Fig. 9d). On the other hand, zinc component can be modified onto other host as tips. Banin et al. reported the heavy-metal free type-II ZnTe/ZnSe nanodumbbells with fluorescence tunable from 480 nm to 585 nm by changing the size of the ZnSe tips.[98] As illustrated in Fig. 9e,f, ZnSe particles can grow on one of the end facets of CdS nanorods and the Au particles grow on the other end, whereas in another study ZnSe particles have been deposited on both end facets of CdS nanorods.[99,100,101] All of those semiconductor nano-dumbbells showed efficient charge separation due to the type-II configuration of the hybrid structures. Similarly, ZnSe tips could also be grow on the edges of CdSe nanoplates to form 2D hybrid structures.[102]

Figure 9. (a) Geometric model and HAADF-STEM image of ZnS-(CdS/Au) hybrid. Reprinted with permission from Ref. [93], Copyright 2015 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim. (b) Geometric model and HAADF-STEM image of ZnS-CdS-Cu2S hybrid. Reprinted with permission from Ref. [94], Copyright 2016 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim. (c) TEM image of Pt-tipped ZnSe nanorods. Reprinted with permission from Ref. [95], Copyright 2018 Royal Society of Chemistry. (d) TEM image of Au-tipped ZnS nanorods. Reprinted with permission from Ref. [96], Copyright 2015 Royal Society of Chemistry. (e) TEM image of ZnSe/CdS/Pt hybrid. Reprinted with permission from Ref. [97], Copyright 2011 American Chemical Society. (f) TEM image of ZnSe/CdS/ZnSe Nanobarbells. Reprinted with permission from Ref. [98], Copyright 2010 American Chemical Society. (g) ZnTe/ZnSe nanodumbbells TEM image and its band alignments. Reprinted with permission from Ref. [99], Copyright 2017 American Chemical Society. (h) CdSe/ZnS Dots-on-Plates illustration and its band alignments. Reprinted with permission from Ref. [100], Copyright 2017 American Chemical Society. (i) CdSe/ZnS Dots-on-Plates and its band alignments. Reprinted with permission from Ref. [101], Copyright 2017 American Chemical Society.

In addition, the spherical zinc chalcogenide nanoparticles can be used as the seeds not only for growth of core/shell rods but also for the growth of tetrapods. Cadmium chalcogenide arms can grow on the zinc chalcogenide spherical dots as such a particle with a cubic structure has four dominant (111) facets, such as ZnTe seeded tetrapod-shaped CdSe NCs (Fig. 10a) and ZnTe seeded tetrapod-shaped CdS NCs (Fig. 10b).[103] Typically, the cadmium chalcogenide arms grow on the core of zinc chalcogenide in four directions which are perpendicular to the (111) facet of the core particles.[104] It’s worth noting the nail-shaped rods in Fig. 10f which differ from the core/shell rod using ZnS as seeds are completely under exposure.[105] Other hybrid structures that containing zinc chalcogenide such as ZnSe-CdS nanodots,[106] Zn-Ag-In-S nanorods,[107] Cu2ZnSnS3-Au nanorods,[108] ZnS-CulnS2-Pt nanorods[109] have also been reported.

Figure 10. TEM images of (a) ZnTe seeded tetrapod-shaped CdSe NCs (b) ZnTe seeded tetrapod-shaped CdS NCs, (c) ZnSe seeded tetrapod-shaped CdS NCs, (d) Chess-piece shaped ZnSe/CdSe NCs, (e) and (f) Nail-shaped ZnSe seeded CdSe NCs. Images of a, b were reprinted with permission from Ref. [100], Copyright 2006 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim. Images of c, d, e, f were reprinted with permission from Ref. [109], Copyright 2015 American Chemical Society.

5. Photoelectronic Energy Conversion Applications

The cadmium- or lead-based compounds are toxic and they pose hazards to the environment which restricts their...
widespread uses. In this sense, environmental friendly photoelectric materials are highly demanded. Zn-based compounds have the merits of reduced or non-toxicity, environmental benignity and excellent optical and electronic properties, and have great potential in energy conversion applications such as lighting and displays, photodetectors and photocatalysis.

5.1 Lighting and Displays

Core/shell QDs with high fluorescent quantum efficiency and good stability are ideal materials for lighting and displays applications. The cores passivated by the shell materials can be optically or electrically excited to generate electron and hole pairs which then re-emit photons by the electron and hole recombination, making them useful for QLED devices. Due to its large band gap and high stability, ZnS usually uses as the shell material in the core/shell structures with a type-I configuration, such as CdSe/ZnS. However, an option for heavy-metal free all Zn-based QLEDs may be ZnSe/ZnS core/shell structures.

Typically, the emission of QLEDs using ZnSe/ZnS core/shell materials falls in the violet-blue range which is not good for lighting application. Early reports showed the fabrication of ZnSe/ZnS core/shell structures on QLEDs and achieve a 0.65% quantum efficiency (EQE) and a low current density of 500 mA/cm² with the emission peak at 420 nm. Li et al. improved the ZnSe/ZnS core shell QLEDs with a maximum EQE of 7.83% which is much higher than the best record (1.7%) of their Cd-based counterparts emitting in a similar spectral range (Fig. 11). The current density for ZnSe/ZnS core/shell QLEDs have been promoted to 2856 cd/m² of maximum brightness with a narrow full width at half maximum (FWHM) less than 21 nm.

Figure 11. (a) Schematic of QLEDs device. (b) Energy level of layers. (c) PL spectra of ZnSe/ZnS core shell QDs with octanethiol and S-ODE as S sources, and corresponding EL spectra of QLEDs. (d) EL spectra of QLEDs with different bias voltage. (e) CIE color coordinates of (0.169, 0.023) corresponding to the violet emission spectra in c. Reprinted with permission from Ref.[111], Copyright 2015 Royal Society of Chemistry.

Except for the all zinc-based QLEDs, other nanoparticles such as Cu doped ZnInS/ZnS core/shell QDs with tunable emission from deep red to green have been used in white LEDs. The produced white LEDs show high performances with the colour rendering index up to 96, luminous efficacy of 70-78 lm W⁻¹ and colour temperature of 3800-5760 K.

5.2 Photocurrent Response

Zn-based colloidal QDs are potential candidates for photoelectrochemical application, due to their wide absorption in the UV and visible ranges. Generally, the UV light resource falls in an electromagnetic radiation of the wavelengths ranging from 10 to 400 nm. Meanwhile, zinc chalcogenide QDs can absorb a major part of sunlight spectrum, making it promising candidate for the UV photodetectors. Bulk ZnO and ZnS (in combination with TiO₂) are widely used zinc composites, while the scale of materials is generally beyond the scope of the quantum confinement size. Therefore, more effort is desirable in focusing on the Zn-based colloidal semiconductor NCs to investigate their photoelectrochemical application. To achieve high performance in photoresponsibility, complex structure engineering is an effective approach to gain the absorption and increase the rate for charge recombination (Fig.12), which has also been adopted in recent research.

Figure 12. (a) Two composites semiconductors (A&B) with combined light absorption of single component A and B. (b) Band gap alignment of two composites semiconductors and its change separation and transportation. Reprinted with permission from Ref.[114]. Copyright 2018 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

1D colloidal zinc chalcogenide nanocrystal-based photodetectors had been reported which have decent photoresponse performance. ZnSe nanowires, ZnSe nanorods and ZnS nanorods show good stability in photoresponse
activities. The ZnSe nanowires exhibited a size-dependent photoresponse in UVA and near-visible radiation.\[115\] As shown in Fig. 12a and b, the ZnSe nanowires with a diameter of 2.1 nm show more than three times of power density than that of ZnSe nanowires with a diameter of 4.5 nm under 365 nm illuminations. When the light is switched to 405 nm, the power density of 4.5 nm diameter ZnSe nanowires surpasses that of ZnSe nanowires with a diameter of 2.1 nm. The results reveal that colloidal zinc chalcogenide nanocrystal-based photodetectors are advantageous in tuning of the band gap to ensure efficient charge carrier transfer and match the window of detection. Similarly, ZnS nanowires exhibit a solar-blind UV photoresponse.\[116\] Recently, the ZnS$_{2/3}$Se$_{1/3}$ quantum rods have been proved to possess an enhanced photoresponse compared with pure ZnSe nanorods and ZnS nanorods.\[32\] The ZnS$_{2/3}$Se$_{1/3}$ quantum rods sensitized photoanode achieves a 90% Faradic efficiency (FE) of the theoretically calculated value as shown in Fig. 13e. The enhancement of the photocurrent density was ascribed to the dominant (100) surface of wurtzite nanorods which was further confirmed by the density functional theory simulations. As for the multicomponent Zn-based colloidal semiconductors NCs, Cu$_2$ZnSnS$_2$/ZnSe (CZTS/ZnSe) core/shell structures show an enhanced charge separation which lead to a fair photoelectrochemical performance.\[117\] ZnS-CdS-Cu$_2$S heteronanorods with the absorption that covers the full spectrum of solar energy from UV to near-infrared were employed in photoelectrochemical water splitting.\[94\] All of those reports on colloidal Zn-based hetero-semiconductors show the consistency in the enhanced photo(electro)catalytic capability. The emerging photoelectrochemical applications of colloidal Zn-based NCs not only show their advantages over the heavy metal-based systems but also challenge the traditional bulk materials.

**Figure 13.** (a) Time response of i-t curves of ZnSe NWs with 2.1 nm, 3.1 nm and 4.5 nm diameter under 365 nm light illumination with a power density of 3.0 mW cm$^{-2}$. (b) ZnSe NWs with 2.1 nm and 4.5 nm diameter under 405 nm light illumination with a power density of 4.0 mW cm$^{-2}$. Images of a, b were reprinted with permission from Ref.\[115\]. Copyright 2017 Royal Society of Chemistry. (c) Time response of i-t curves of ZnSe quantum rods. ZnS quantum rods and ZnS$_{2/3}$Se$_{1/3}$ quantum rods under light ON-OFF cycling. (d) Linear sweep voltammograms under chopped 1 sun light illumination for CZTS before and after deposition of different buffer layers and adsorption of MV. (e) Comparison of the evolved oxygen gases of TiO$_2$ and ZnS$_{2/3}$Se$_{1/3}$-TiO$_2$. Images of c, e were reprinted with permission from Ref.\[32\]. Copyright 2018 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim. Images of d was reprinted with permission from Ref.\[117\]. Copyright 2014 American Chemical Society.

### 5.3 Photocatalysis

Colloidal semiconductor NCs have advantages over their counterparts such as bulk materials as their band gap can be feasibly tuned by changing the size and composition to match the solar spectrum and oxidation/reduction potentials. The enlarged electrochemical potential can enhance the performance in both photocatalysis and photo(electro)catalytic (Fig. 14). On the other hand, Zn-based colloidal NCs can absorb light in the UV range which makes them capable in photocatalysis. Recently, Chen et al. demonstrated that ZnSnS$_x$ alloyed nanorods showed increased oxygen evolution reaction (OER) activity compared with pure ZnSe and ZnS nanorods (Fig. 15a) because the alloyed nanorods have reduced energy barrier.
for oxygen evolution.[12] Following from this work, ZnSe nanorods was applied as the visible light range absorbers for H₂ evolution with performances exceeding those of Cd-based QDs.[118]

Heterostructures contain zinc colloidal NCs and other colloidal semiconductors (e.g. CdS and CuInS₂) and noble metals manifesting synergistic properties are beneficial to their photocatalytic performances. As Zn-based semiconductor NCs may have large band gaps, other materials such as CdS and CuS with small band gaps in visible and near-infrared can be used to expand the capability of heterostructures for harvesting more solar spectrum. Yu et al. reported the remarkable improved hydrogen evolution performance of the type-II ZnS-(CdS/Au) hetero-nanorods for hydrogen evolution(Fig. 15a).[93] Similarly, Cu₃₋ₓS₋ₓZnₓCd₋ₓS hetero-nanorods were proved to have the highest photocatalytic activity for hydrogen production among all the heterostructures with different stoichiometric ratios (Fig. 15c).[120] Besides, hybrid ZnS-CuInS₂ nanorods also show good performances in the hydrogen evolution reaction (HER) using the visible light.[109]

The materials engineering of heterostructures for photocatalysis can be further expanded to other materials. Pt-tipped Zn₀.₃₅Cd₀.₇₅S₄ alloyed nanorods show the higher hydrogen evolution efficiency compared with Pt-ZnSe nanorods or single ZnSe nanorods.[97] Cu₂ZnSn₄S₄-Au nanorods present enhanced catalytic activity than Cu₂ZnSn₄S₄ nanorods alone.[109] These results demonstrate the synergistic effect heterostructures that integrate Zn-based semiconductors with metal particles.[99]

### 6. Summary and Perspectives

In summary, Zn-based colloidal QDs are environmental friendly and cost-effective materials for the energy conversion applications. Although some progresses have been achieved, syntheses in some specific materials such as ZnTe, Zn₂P₂, Zn₃As₂, ZnSe/ZnS and ZnTe/ZnS core/shell structures are still challenging. Better engineering the precursors for the synthesis in combination of the deep understanding of the growth mechanisms are desired and need to be improved. In addition, the performances of Zn-based colloidal QDs in a broad scope of applications need to be further enhanced. Zn-based colloidal QDs already showed their promise in many stimulating applications and are believed to be the stimulating materials in next-generation devices industry.
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Keywords: zinc chalcogenides • colloidal nanoparticles • heavy-metal free • photocatalysis • photoelectrochemical

References


REVIEW


This review elaborates the shape control of Zn-based colloidal semiconductor NCs and functionalities engineering through the formation of core-shell, doping and hybrid structures that underpin their intriguing photoelectronic energy conversion applications in quantum dots QLEDs, photodetectors and photocatalysis.