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REVIEW ARTICLE

Recent advances in the use of near-infrared quantum dots as optical probes for bioanalytical, imaging and solar cell application

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Abstract Near-infrared quantum dots (NIR QDs) represent a powerful material and diagnostic tool owing to their long emission wavelength which extends into the near-infrared region where permeation depths are much larger and where the intrinsic absorbance and autofluorescence of tissue is much smaller compared to shortwave emitting QDs. We are reviewing here recent (2008–2013) methods for the preparation of NIR QDs, their (bio)chemical modifications, and their applications. The article is subdivided into the following sections: (a) Synthesis of NIR QDs; (b) modification of NIR QDs and probe preparation; (c) applications of NIR QDs (with subsections on fluorescence quenching and fluorescence enhancement-based bioanalytical detection, on fluorescence bioimaging, on uses in photovoltaic cells and solar cells, and on molecular detection based on electrogenerated chemiluminescence). We finally make conclusions and discuss current challenges, trends, and future applications. The review contains 119 references.

Keywords Near-infrared quantum dots · Bioanalytical application · review

Introduction

Recent developments in nano-biotechnology have paved the way for dramatic exploration of novel advanced materials into the application of bioanalytical chemistry. Quantum dots (QDs) are one class of these new emerging nano-materials and have attracted more and more attention by analytical chemists and biologists owing to their unique electronic, optical and magnetic properties, such as broad excitation spectra, size tunable fluorescence emission, large Stoke's shift, muti-color fluorescence with a single wavelength light source excitation and high resistance to photobleaching [1–3]. However, in the past few periods, researchers are devoting enormous efforts on visible quantum dots, which is because most emitting spectra of fluorescent labels are in the visible region [4–6]. For these applications, visible quantum dots have shown their obvious advantages over fluorescent organic dyes in many aspects. First, quantum dots have good aqueous and colloid stability. Second, quantum dots have narrower half peak widths than other fluorescent dyes which can minimize the spectra overlap when used in multiple analytes detection. Third, quantum dots have higher fluorescence quantum yield than organic dyes which makes quantum dots much brighter for long term exposure under excitation light. Despite visible quantum dots have such obvious advantages in analytical applications, there still exist some problems when using visible quantum dots. For example, their emission wavelengths in visible region have limited their utilization especially in fluorescence imaging for medical diagnosis, which may due to the weak penetration ability of visible quantum dots. To circumvent this issue, researchers try to prepare longer wavelength emission quantum dots. Fortunately, quantum dots can be systematically tuned to emit in different wavelengths ranging from visible to near infrared by regulating their particle size, shape and composition [7]. Near infrared quantum dots (NIR QDs) have emerging by this preparation strategy and has becoming a powerful tool in medical diagnosis and bioanalytical application [8–10]. Since the emission wavelength of NIR QDs can be easily regulated by the preparation method [11] (Fig. 1), to date, various NIR QDs have been synthesized including CdTe, CdHgTe, HgTe, InP, PbS, PbSe, PbTe, Ag_2S, AgSe and so on [12–19].

NIR QDs not only retain all of the advantages of visible quantum dots, but also have their own unique optical features

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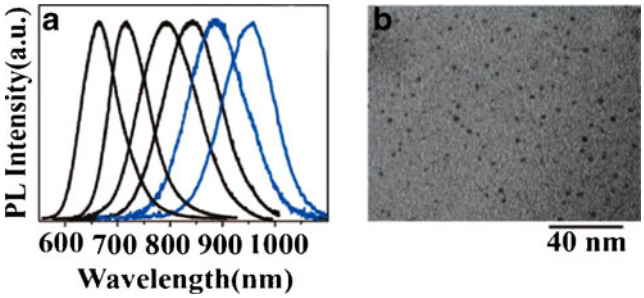

Fig. 1 **a** Fluorescence spectrum of NIR QDs. **b** Transmission electron microscopy of NIR QDs. (Reprinted with permission from ref. 11. Copyright 2008 ACS)

[20–22]. As is well known that the emission wavelengths of the quantum dots are increased with the enhancement of quantum dots particle sizes, NIR QDs have larger particle sizes than the visible quantum dots as well as more colloid stability in aqueous solution. More importantly, NIR QDs have stronger penetration ability when utilized in tumor targeting imaging, which can effectively avoid the absorbance and auto fluorescence from the tissues. This is key factor why NIR QDs have become the workhouse for biological fluorescence labeling and imaging, which has broadly enlarged the quantum dots' utilization for bioanalytical chemistry. In this review, we will systematically discuss some basic and widely used NIR QDs' preparation methods, modifications and applications in bioanalytical chemistry.

Synthesis of near infrared quantum dots

NIR QDs preparation method has been divided into two major strategies as visible quantum dots preparation method: organometallic route and aqueous synthesis approaches [23, 24]. Considerable efforts have been devoted to the preparation of NIR QDs to obtain good quality ones for biological use. NIR QDs with diverse composites have different reaction conditions, such as control of temperature, hot injection time, precursor reagents and exchange ligands, etc. [25]. It is intelligible to introduce these preparation methods in the listed categories. The first type of NIR QDs is the II–VI type quantum dots, which is the largest group of the quantum dots' family [26–28]. The typical ones are CdSe quantum dots and CdTe quantum dots, which are easily prepared to monodisperse nanoparticles and represent bright fluorescence luminescence. However, visible CdSe quantum dots and CdTe quantum dots are more available than near infrared ones. Therefore, exploration of simple and convenient near infrared CdSe quantum dots and CdTe quantum dots preparation methods are urgently desirable [29, 30]. On the other hand, ZnX and HgX (X refers to sulfur, selenium, tellurium) quantum dots can be prepared relative easily to emit near infrared fluorescence, which is due to the effective increase of the bandgap by the mercury chalcogenide [31–33]. For instance, HgTe quantum dots have an inverted band structure and thus an effectively negative band gap of around 0.15 eV at 295 K. However, mercury chalcogenide may cause potential environmental problem and more environmental friendly quantum dots have been explored by researchers nowadays. The second type of quantum dots is IV–VI group, for example, PbX (X refers to S, Se, Te) [17, 34, 35]. Among them, PbS is the most popular one due to the small bulk band gap (0.41 eV at 300 K) and relative large exciton Bohr radius, which allows quantum confinement in relatively large-sized quantum dots together with their tunable near infrared emission. More importantly, PbS quantum dots are lower toxic and more environmental friendly and can be produced with inexpensive and relatively safe synthetic precursors compared to the Cd and Hg based quantum dots [36]. Accordingly, the first synthesis of colloidal PbS quantum dots was reported in 2003 with a hot-injection organometallic approach by Scholes' group [37]. Recently, a lot of research groups have prepared PbS quantum dots via new organometallic approach and aqueous methods. For instance, Hyun et al. and Gu et al. groups have succeeded in synthesizing near infrared PbS quantum dots with large band gap greater than 1.24 eV by organometallic method [38, 39]. They also tried to transfer these organic phase PbS quantum dots to aqueous solution to satisfy bioanalytical application requirement. As we all know, the transfer course may inevitably decrease the fluorescence quantum yield. Therefore, intense endeavor has been devoted to search for aqueous method to synthesis high quality PbS quantum dots. Until now, few literatures have reported on aqueous synthesis PbS quantum dots, there is still a long way for exploration. The third type of quantum dots is III–V type quantum dots, InAs and InGa are the two typical ones with this composition [40, 41]. The near infrared InAs quantum dots possess outstanding optical properties as well as significantly lower intrinsic toxicity compared to other NIR QDs containing elements such as cadmium, mercury, or lead. So they have played an important role in biomedical and bioanalytical application. Peng et al. have made great contribution on developing high quality InAs quantum dots by one pot synthesis method [42]. However, compared to II–VI and IV–VI type quantum dots, III–V quantum dots have more challenges to overcome include low emission efficiency, broad spectrum width, poor color control, poor stability and so on [43]. For biomedical labeling, the fluorescence properties such as high quantum yield, long decay time and stability are urgently desirable. Therefore, exploration for newly high quality III–V type quantum dots is an attractive direction in bioanalytical area.

To obtain high quality NIR QDs with obvious stability and outstanding optical properties, core/shell type NIR QDs are synthesized for biomedical use [44–46]. Core/shell quantum dots heterostructures can show either type-I or type-II carrier localization, depending on the energy offsets between the core

and the shell materials. In type-I quantum dots both carriers are primarily confined in the same part of the heterostructure, while in type-II core/shell quantum dots electrons and holes are spatially separated. So, type-II core/shell quantum dots have great potential as important near infrared fluorescent probes for biological imaging and diagnostics due to the low fluorescence background and the high penetration capacity [47]. Recently, Kim et al. have successfully obtained type-II CdTe/CdSe quantum dots by means of organic synthesis technique [48]. As for the biological use, quantum dots should be aqueous soluble and dispersed, aqueous synthesis method is desired for preparing type-II NIR QDs. Zhu et al. have developed a one pot type-II CdTe/CdSe quantum dots synthesis method in aqueous medium by employing thiol-capped CdTe quantum dots as a core template and CdCl and Na_2SeSO_3 as shell precursors, respectively [49]. Zhang et al. have developed a single step and non injection method for preparing a series of NIR QDs with different emission wavelengths by simply changing the synthetic recipe with predetermined amounts of reaction reactants [21]. Our group has reported a one-pot aqueous approach for producing highly luminescent near infrared CdTe/CdS core small/shell thick quantum dots. The result demonstrated that the small quantum dots cores were effectively compressed by lattice strain owing to the growing thicker shell, and a transition of band gap offset nanoparticle formed during the well-controlled growth of the shell, allowing largest spectral shifts tuning from the visible to the near infrared spectral region [50].

Although type-II CdTe/CdSe core shell quantum dots have fairly good optical and electrical properties, they present less stability in aqueous solution as Te can be easily oxidized under ambient conditions. However, CdTe quantum dots can form nucleation more quickly than CdSe quantum dots in the first synthesis step. Considering the advantage and disadvantage by Te and Se composition, alloyed ternary NIR QDs have been developed for bioimaging use such as CdTeSe quantum dots to overcome the problem [51]. Recently, Bailey et al. reported the synthesis of near infrared alloyed CdTeSe quantum dots that can solve the stability problem very well [52]. However, the NIR QDs suffered serious fluorescence quantum yield decrease by combination of the two metals for preparation. To obtain high quality alloyed NIR QDs, Chan et al. have developed a systematical method to investigate the effective factors that affect the quality of quantum dots [53]. Under their group's endeavors, they found that precursor concentrations of Te-to-Se and growth time had major impacts on the quantum dots optical properties. By optimizing the experimental conditions, red to near infrared CdS-capped $CdTe_xSe_{1-x}$ alloyed quantum dots have been successfully prepared. Another consideration for preparing the alloyed quantum dots is to reduce the toxicity produced by heavy metal composition such as Cd. Bawendi et al. reported a ternary near infrared $CuInSe_2$ quantum dots preparation method [54]. Afterwards, they extended the same method to synthesis a series of $AgInSe_2$ quantum dots, which has made the ternary quantum dots available as those binary quantum dots [55]. Moreover, the alloyed ternary NIR QDs are without heavy metal composition and low toxic, they will be popular in the biomedicine and bioimaging applications.

Modification of NIR QDs and probe preparation

As in the application of bioimaging and biomedicine, targeting to analyte is very important in the biosensors development. However, quantum dots themselves have not targeting functions. Functionalization is the key point making quantum dots useful in the bioimaging and biomedicine applications [56–59]. To date, modification method of NIR QDs is almost the same with the visible quantum dots' modification method. Generally speaking, the quantum dots' functionalization method can be divided into two steps: surface capping and biomolecular binding. Surface capping can be realized through ligand exchange, polymers coating and hydrophobic interaction, etc. [60–62]. Biomolecular binding can be achieved by covalent binding, thiol binding and electrostatic interaction [63–65]. Considering to rendering quantum dots with functional groups, ligand exchange and polymer coating are proven to be effective. Ligand exchange is a common surface capping strategy for transferring organic phase quantum dots to aqueous soluble ones. For example, CdSeTe/CdS quantum dots with glutathione coating can be synthesized through the method reported by Takashi et al., hydrophobic quantum dots surrounded by trioctylphosphine oxide and hexadecylamine molecules are dispersed in the tetrahydrofuran to exchange by adding excess amount of glutathione, thus glutathione modified CdSeTe/CdS quantum dots will be obtained [66]. However, ligand exchange inevitably may cause fluorescence quantum yield decrease. This is because quantum dots are most often synthesized in the presence of ligand such as trioctylphosphine oxide, which render the nanoparticle surfaces hydrophobic [67]. Amphiphilic polymers can be grafted to quantum dots' surface to make them hydrophilic without serious fluorescence quantum yield losses. Moreover, polymers usually have functional groups which render quantum dots useful in biosensors. Meanwhile, quantum dots with polymers coating can lower their biological toxicity and have potential use in biomedical application [68]. For instance, Zhang et al. reported a molecularly imprinted polymer capsulated CdTe NIR QDs as a sensing material for cytochrome c. The polymer-coated CdTe composites integrate the advantages of the high selectivity of the molecular imprinting and strong fluorescence property of the quantum dots [69]. Other polymer coated quantum dots are also employed as fluorescence resonance energy transfer donors and bioimaging materials [70–72]. The various methods

for quantum dots capping are to improving their stability and fluorescence quantum yield. Hydrophobic interaction is a good choice to this end. For example, our group has developed a method for effectively quantum dots coating by silicate deposition, which allowed quantum dots preserve high fluorescence intensity properties [73]. On the other hand, quantum dots should have good targeting function toward their analytes as the fluorescent contrasting agent. From this point of view, biomolecular binding toward quantum dots is very important for probe development. The most stable binding is the covalent coupling; DNA, enzyme and protein can be coupled to carboxylated quantum dots through covalent bond [74, 75]. With the aim of chemical reagents such as 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide and N-hydroxysulfosuccinimide, the coupling courses are becoming very convenient and time-saving. Protein with mercapto group also can be linked to quantum dots with thiols binding. Another choice for biomolecular linking is electronic interaction; biomolecule with opposite charge to quantum dots may adsorb onto their surface and bind with them by electronic interaction. Quantum dots with ligand modification can also regulate their electronic structures, which is due to the various bonding interactions between quantum dots and ligands. For instance, Whitley et al. have demonstrated a ligand mediate quantum dot electronic structure change mechanism by X-ray absorption spectroscopy [76]. The quantum dots property is regulated by the ligands, by which method both targeting and good quality quantum dots can be obtained.

Applications of near-infrared quantum dots

Fluorescence quenching and enhancement based bioanalytical detection

As visible quantum dots have been widely used in molecular detection based on fluorescence intensity, NIR QDs have also been employed in molecular detection upon their fluorescence by researchers [30, 77, 78]. Zhu' group has made great contributions on biosensors development by NIR QDs. They reported a near-infrared fluorescence sensing strategy for glucose and xanthine based on CdTe quantum dot [49]. The strategy is designed by fluorescence quenching and this biosensor is easy performed with high sensitivity. Compared with the visible quantum dots used in molecular detection, the NIR QDs have shown better performance in developing biosensors as their anti-interference ability is much stronger, especially in complex solutions such as serum, urine etc. Therefore, near-infrared quantum dots are very widely employed as the fluorescence probe for biosensors development [79–83]. On the other hand, fluorescence enhancement is another detection mode for developing biosensors. Su et al. have fabricated a thrombin quantitative determination method by $CuInS_2$ NIR QDs fluorescence enhancement mechanism [84]. The nontoxic $CuInS_2$ NIR QDs based protein biosensor has good performance in application for detecting thrombin in biological blood samples, which may be impossible when employed visible quantum dots (Fig. 2). The NIR QDs based biosensors are more and more widely used in small molecular, DNA, enzyme and protein detection, it has obvious advantages over visible quantum dots in biosensor development [85–87]. More detection methods will be developed by NIR QDs in the near future.

Fluorescence imaging

Due to the excellent optical, electrical and magnetic features of NIR QDs, they have been employed in biological and medical research for a decade, especially in bioimaging application. For example, Gao et al. have developed a kind of NIR QDs based nanoprobe for tumor imaging and obtained good results, as shown in Fig. 3 [88]. NIR QDs based imaging can offer multiple advantages such as deep tissue penetration and high temporal resolution, etc. [89–91]. Before NIR QDs widely used in bioimaging, organic fluorescent dyes are adopted for color contrasting agent in imaging. Unfortunately, organic dyes cannot resist to photobleaching during long time excitation [92]. By contrast, NIR QDs are good candidate for near-infrared bioimaging. To date, many NIR QDs have been employed in imaging use, such as cell imaging, tissue imaging and body imaging, etc.

For cell imaging application, Zhang et al. has made some important contributions on developing new near-infrared fluorescent probe. They prepared a Cu doped CdS NIR QDs by a rapid and facile hydrothermal method for Hela cell imaging use and obtain good result [21]. Narendra et al. have fabricated a multi-functional Ni doped NIR QDs for cell targeting and sorting. They believe that the functional NIR QDs will become a potential and powerful tool used in cell imaging [77]. Besides applied in cell imaging, NIR QDs based tumor targeting probe has also many advantages than visible quantum dots based fluorescent probe. First, the biological tissue can emit autofluorescence in blue or green color which

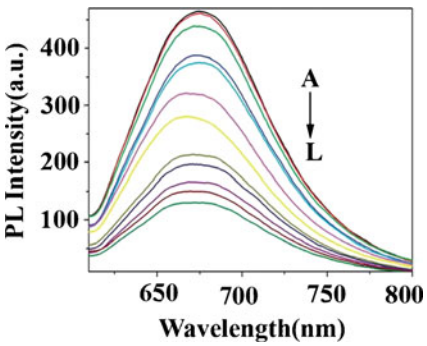

Fig. 2 Fluorescence spectra of NIR QDs based method for thrombin detection. (Reprinted with permission from ref. 84. Copyright 2012 RSC)

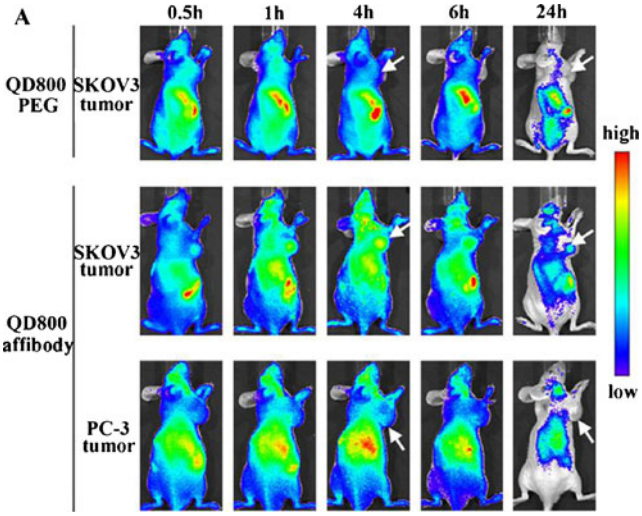

Fig. 3 NIR QDs luminescence photograph in vivo for cancer diagnosis. (Reprinted with permission from ref. 88. Copyright 2009 Wiley)

overlaps with the spectrum of visible quantum dots, whereas the NIR QDs can minimize the tissue autofluorescence in most extent. Second, NIR QDs with stronger penetration ability than visible quantum dots are more suitable for deeper tissue imaging and labeling. The most widely used visible quantum dots are CdSe QDs, but rarely CdSe NIR QDs appeared because the CdSe QDs can only be tuned to 650 nm. Fortunately, CdTe QDs can be tuned from visible to near-infrared spectrum by regulating their sizes. Yong et al. have reported a arginine–glycine–aspartic acid peptide functional CdTe/ZnSe core-shell NIR QDs used for in vivo cancer imaging and targeting [93]. CdTe NIR QDs can be synthesized by simply aqueous solution without the need of hazardous chemical reagents and demanding reaction conditions. The as-prepared CdTe/ZnSe NIR QDs are with small size and suitable for penetrating through biological tissues for cancer imaging. The peptide arginine–glycine–aspartic acid can serve as an antagonist against the growth of vascular endothelial cells and tumors. The probe offered a highly luminescent tool for labeling and imaging pancreatic tumor in live mice. CdTe NIR QDs can be tuned by varying their bandgap to the second biological window 700–1,400 nm spectrum, which can minimize the tissue autofluorescence in biological imaging in most extent [94]. Pang' group has made many significant contributions on NIR QDs' synthesis and application in cancer imaging. For example, they reported a ternary CdSeTe/ZnS NIR QDs and a visible CdSe quantum dots combined as a conjugate for cancer biomarkers in gastric cancer tissues [95].

NIR QDs have been employed in body imaging in recent decade, as before used in vivo, NIR QDs' toxicity is the most important consideration for cancer imaging. Among those NIR QDs, Ag_2Se nanocrystals are good candidates but less explored ones. Few reports have been involved aqueous synthesis Ag_2Se NIR QDs, only the Heiss group has reported two fluorescent wavelengths 1,030 and 1,250 nm of β-Ag_2Se QDs synthesized in the organic phase, which need to be transferred to aqueous phase for bioimaging [96]. To face this challenge, Pang's group has synthesized high quality Ag_2Se NIR QDs in the aqueous medium for the first time and used in living nude mouse near-infrared imaging. The result demonstrates that the penetration depth of the as-prepared Ag_2Se QDs is at least 1 cm (Fig. 4), which is quite suitable for in vivo near-infrared imaging [97]. However, it is still a big challenge for researchers to prepare high quality NIR QDs for biomedical use because the as-prepared quantum dots not only require good quantum yield and stability, but also need to free of toxicity. Pang's group made a first attempt to synthesize water-soluble carboxylic acid group terminated Ag_2S QDs with tunable emissions in ethylene glycol by a one-step method, and directly injected the Ag_2S QDs with fluorescent emission at 910 nm into the subcutaneous tissue and the abdominal cavity for small animal imaging [98]. After that, Yan et al. have made an outstanding exploration on low toxic NIR QDs' synthesis and applications [99]. They reported a one-pot method by a simple and mild synthetic route without the need for high temperature and inert gas protection for synthesizing bovine serum albumin stabilized Ag_2S QDs in aqueous solution and subsequently bioconjugated with anti-vascular endothelial growth factor for targeting cancer imaging in vivo. The work demonstrates that the functional Ag_2S NIR QDs indeed has lower toxicity when injected into the tumor bearing mouse body for in vivo imaging. $CuInS_2$ QDs are another alternative for decreasing the toxicity when applied in tumor target imaging [100]. Thomas and his co-workers have prepared a new kind of cadmium-free $CuInS_2$/ZnS quantum dots for sentinel lymph node imaging with extremely good results [101].

Besides the single NIR QDs applied in tissue and body imaging, NIR QDs based multiplex mode imaging is more popular due to their more precise location on targets position and diversification [102]. Meanwhile, this kind of imaging mode also puts forward higher requirements to instruments, which should has good distinguishing ability to different

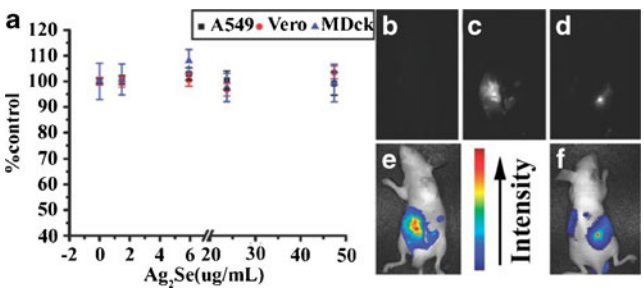

Fig. 4 MTT assay and near-infrared image of a living mouse after injection of Ag_2Se NIR QDs. (Reprinted with permission from ref. 97. Copyright 2011 ACS)

colors of NIR QDs. Fortunately, the NIR QDs signals with narrow half wavelength widths and the different emission color signals can be relatively easily collected. Prasad et al. reported a multi-channel mode for Sentinel Lymph Node mapping and imaging by different color silicon quantum dots from far red to near infrared [103]. The non-toxic silicon quantum dot proved a powerful tool for tumor imaging without any biological toxicity. It is believed that different color NIR QDs based multiplex imaging has a big potential in medical and biological applications.

Photovoltaic and solar cells

Nowadays, NIR QDs have been extensively studied and exploited; many energy conversion devices are developed based on these nanoparticles which have many superior properties, such as higher absorption coefficient than organic dyes, convenient bandgap tunability by size control, efficient charge separation owing to a high intrinsic dipole moment, multiple exciton generation and good stability [18, 104, 105]. Kim et al. have reported HgTe NIR QDs used as the near-infrared photovoltaic cells with very efficient energy transfer ability [106]. The fabrication method is to deposit the multi-layer HgTe quantum dots onto TiO_2, under near-infrared light illumination the cell' energy transfer efficiency can be improved from 0.23 % to 0.84 % which is due to the great absorb ability of HgTe quantum dots. The photovoltaic cell can be used to construct panchromatic and cascade systems to extend the photoresponse in the near-infrared region. Due to the good light harvesting capability, NIR QDs also can be employed to fabricate solar cell. Wang et al. reported a feasible strategy to prepare efficient hybrid solar cells that combine bulk-heterojunction architecture and wide spectral response in ternary photoactive layer [107]. They realize the idea by employing polymer and $CuInS_2$ NIR QDs hybrids for harvesting photons. The $CuInS_2$ NIR QDs give an indelible contribution to the device performance and the related charge generation and transport processes. The results prove that $CuInS_2$ NIR QDs have excellent photoelectric effect and big potential in solar cell fabrication. As the NIR QDs' good properties in fabricating the photovoltaic cell and solar cell, more energy conversion devices based on QDs will be developed to serve for photovoltaic industry vigorous growing.

Molecular detection based on electrogenerated chemiluminescence

Since the electrogenerated chemiluminescence (ECL) from quantum dots was first employed for detection by Bard and co-workers [108], intensive efforts have been devoted to the research for ECL from quantum dots, which is due to the superior advantages of ECL: high signal-to-noise ratio, high sensitivity and selectivity and easily controlled the target detection conditions without interference [109–111]. All above advantages make the ECL from quantum dots use as a platform to develop many analytical methods. Recently, NIR QDs are favored in ECL application as lower background interference in near-infrared window. For instance, our group has studied cathodic electrochemiluminescence from self-designed near-infrared CdTe/CdS/ZnS quantum dots on bare gold electrode in aqueous solution; the NIR QDs have shown good ECL performance under suitable conditions [112]. Notably, compared to fluorescence property, QDs' ECL intensity is relatively weaker and with less stability. During the past decade, ECL emitters were usually metal complex, luminol and oxalic acid, etc. [113–115], few QDs' ECL was reported. However, after great effort on quantum dots' synthesis and modification technology, the ECL from quantum dots is much stronger than before. Fortunately, many signal amplification methods are developed for improving the quantum dots' ECL intensity. For instance, Han et al. have reported a double assisted signal amplification strategy for CdTe/CdS NIR QDs' ECL intensity by gold nanoparticle-graphene nanosheet hybrids and silica nanospheres [116]. Due to the low photoluminescence of NIR QDs and intrinsically low signal-to-noise ratio of the analytical technique, the ECL signal was greatly enhanced and acted as the immunobiosensor' signal molecule for detection of human protein with a satisfied result (Fig. 5). However, in the past, the most ECL studies on quantum dots were used heavy metal composite quantum dots. To develop lower toxic NIR QDs based ECL detection method, Pang' group reported Ag_2Se NIR QDs for ECL detection [117]. Since the ECL intensity was very sensitive upon the

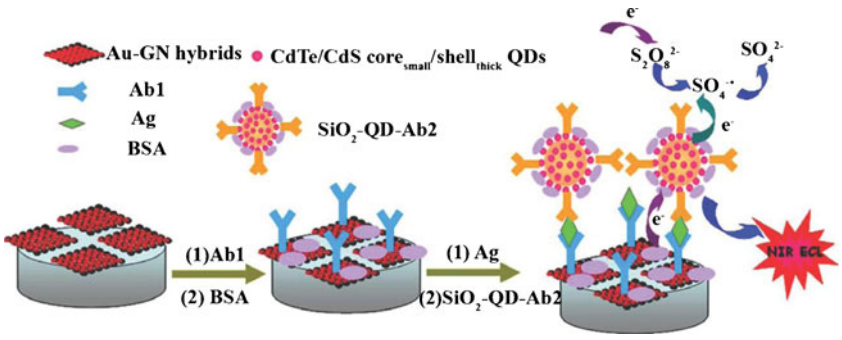

Fig. 5 NIR QDs based immunoassay for electrogenerated chemiluminescence detection of human IgG. (Reprinted with permission from ref. 116. Copyright 2012 ACS)

Table 1 The summary of NIR QDs bioapplications

Application	Material	Targets	Technology	Detection limit	Ref.
Fluorescence detection	CdTe	Glucose Xanthine	Fluorescence quenching	2.7×10^{-6} molL^{-1} 1.8×10^{-6} molL^{-1}	[49]
	$CuInS_2$ /ZnS	Human Interleukin 6	Fluoroimmunoassay	8×10^{-3} ng mL^{-1}	[80]
	$CuInS_2$	Thrombin	Fluorescence enhancement	8.7×10^{-12} molL^{-1}	[84]
	CdSeTe	Hsp70 protein	Immunofluorescence	—	[87]
	HgS	Metal ion	Fluorescence quenching	—	[82]
	CdTe/ZnSe	Cancer biomarker	Fluorescence image		[93]
Fluorescence image	Cu-doped CdS	Hela cell	Fluorescence image	—	[21]
	Ni-doped QDs	Cancer Cell	Cell image and cell sorting	—	[77]
	CdSeTe/ZnS	Cancer biomarker	Spectral imaging	—	[95]
	Ag_2Se	Tumor	Fluorescence imaing	—	[97]
	Ag_2S	Cancer cell	Fluorescence imaing	—	[99]
	CdSeTe/ CdS/ZnS	Tumor marker	ECL	5×10^{-4} pg mL^{-1}	[79]
ECL	CdSeTe/ZnS	Cell	ECL	—	[81]
	CdTe/CdS/ZnS	—	ECL	—	[112]
	CdTe/ZnS	IgG	ECL	87 fg mL^{-1}	123
	HgTe	—	Photovoltaic cells	—	[106]
Photovoltaic cell & solar cell	$CuInS_2$	—	Solar cell		[107]
	PbS	—	Solar cell	—	[105]

ECL refers to electrogenerated chemiluminescence

quantum dots' surface state, the ECL strategy was a good way for studying the surface chemistry of the Ag_2Se NIR QDs. Meanwhile, the NIR QDs based ECL system establishes a sensitive detection platform for dopamine with high signal-to-noise ratio and low background interference. Near-infrared window renders quantum dots a kind of good choice for developing ECL based analytical method. Our group has also synthesized low toxic ZnSe quantum dots for ECL detection method development [118]. To date, few reports on NIR QDs ECL imaging application are appeared [119]. But the NIR QDs for ECL have enormous potential in vivo biological applications; it is believed that the NIR QDs will be widely used in ECL detection as well as the ECL imaging for biomedicine utilization in the near future.

Conclusion and outlook

In summary, NIR QDs are regarded as a good alternative for nanotechnology usage nowadays; Table 1 has listed the above typical applications of the most widely used NIR QDs. It is worth to note that NIR QDs still need to perfect their optical and thermal features to adjust to the increasing demand for bionanotechnology application. Overall, the most urgent problem is the NIR QDs' cytotoxicity. As the most commonly used NIR QDs in bioimaging are usually composed of heavy metal element, it is very difficult to evaluate the exact cytotoxicity of all these NIR QDs to environment and biological tissue. Therefore, it is a challenge to change the traditional NIR QDs synthesis route and prepare lower toxic NIR QDs for biomedical use. Although some efforts have been made to improve the NIR QDs' biocompatibility, such as doping Zn, Ag and Cu to regulate the composite of NIR QDs; different capping materials are also used to insulate the toxic QDs core and reduce toxicity. It is still expected better NIR QDs to satisfy the new medical diagnostic requirements. Another aspect of NIR QDs to be concerned is the photostability, which is one of the advantages of quantum dots. However, as the NIR QDs are usually adopted as the bioimaging contrasting agent, it is demanding to expose to excitation light for long term image, so quantum dots' stability is a most important parameter for the accuracy of the data. Despite many methods have been devoted to improve the stability of NIR QDs, it is still an arduous task to prepare high quality NIR QDs to accommodate the increasing demand of medical use. Notable, the technology for aqueous synthesis NIR QDs is urgently demanded for bioimaging use. Up to now, the aqueous synthesis methods are still relatively less than oil phase synthesis methods, and more difficult to control the condition and quality of quantum dots. As one of the most important nanomaterials, NIR QDs have to develop toward to practical use such as in solar cell applications. However, to date, there is

no practical strategy for the large-scale production of NIR QDs with good quality control. Widely solar cell applications by NIR QDs still need more exploration. Anyway, owing to the superior advantages of NIR QDs, they are becoming more and more popular and widely used in fundamental research in nanotechnology. There is a thriving trend that the emerging new NIR QDs with more stable and lower toxic feature, as well as with more functional groups will play more important role in nanotechnology applications. More important, practical use of NIR QDs for energy transfer is under way in a very near future.

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