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Full Length Article

Photostable fluorescent Near-infrared colloidal Mn-doped CuInSe/ZnS quantum dots for cancer-bacteria dual imaging

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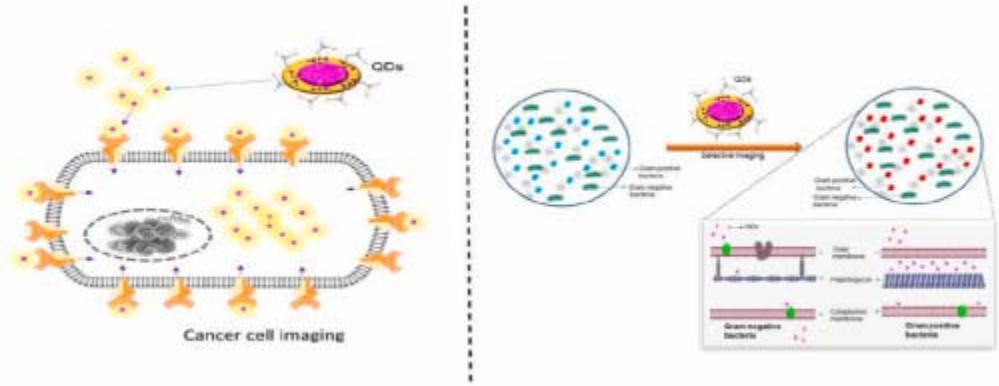
Highlights

- •
  Synthesis of NIR emitting colloidal Mn-doped CuInSe/ZnS quantum dots (QDs).
- •
  Low toxicity from Mn-doped CuInSe/ZnS QDs against mouse colon carcinoma cells.
- •
  Selective QDs for screening Gram-positive bacteria from Gram-negative bacteria.
- •
  Effective Mn-doped CuInSe/ZnS QDs for targeting prostate cancer cells.

Abstract

Near-infrared quantum dots (NIR QDs) with tunable fluorescence emission are promising materials for bioimaging applications. However, they face several challenges, including low photostability, reduced brightness, and poor fluorescence emission. Herein, we report the synthesis of NIR emitting colloidal Mn-doped CuInSe/ZnS QDs synthesised via the hydrothermal method in a commercial pressure cooker. These fluorescent materials had a peak corresponding to photoluminescence maxima at 765 nm and had good photostability. The *in vitro* analysis showed that the as-synthesised QDs displayed good cell viability against mouse colon carcinoma (C26) cells. They selectively screened Gram-positive bacteria from Gram-negative bacteria and effectively targeted prostate cancer cells compared to normal cells. Thus, they can be used for cancer-bacteria dual-imaging in the biomedical field.

Graphical abstract



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Introduction

The noninvasive imaging of living cells is critical for diagnosing and curing several chronic diseases, including cancer [1,2]. However, limitations of imaging modality such as insufficient sensitivity or low spatial resolution are still a dilemma in clinical application. Thus, integrating different imaging techniques into one material will be advantageous for the efficacy of clinical imaging diagnosis [3]. During the last couple of decades, the research on biomedicine is focused on the photoluminescence characteristics of organic fluorophores, due to their ability to be employed in advanced bioimaging. However, they face several challenges including photobleaching and poor stability [4]. Quantum dots (QDs) have gained a lot of attention in this context due to a myriad of attractive physicochemical properties. Whereas fluorescent tagging of cells with organic fluorophores suffers from their narrow excitation wavelengths, QDs have a wide excitation range from UV to red light. Another drawback of organic fluorophores is their wide emission spectra, which confines the number of fluorescent probes that can be concurrently resolved. QDs on the contrary have tunable emission spectra and hence can resolve emission from multiple QDs. Compared to organic fluorophores, QDs are resistant to metabolic and chemical degradation with a very high threshold for photobleaching [5]. Lastly, organic fluorophores require tailored chemistry for biomolecule conjugation, whereas QDs adopt a common method for conjugating biomolecules [6]. Thus, the inimitable optical properties of QDs, such as large molar extinction coefficients, tunable emission based on size, high photostability and high quantum yields make them better candidates than organic fluorophores. However, the main issues encountered in designing ideal QDs for biological applications are synthesizing luminescent hydrophilic QDs with tunable surface chemistry for different biological applications; developing strategies to specifically label cells and biomolecules and establishing that QDs do not impact normal physiology. Owing to their minimum biological autofluorescence and greater tissue penetration, near-infrared (NIR) fluorescent QDs are employed for high-sensitivity and high-resolution bioimaging in the NIR wavelength window in the range of 700–900 nm. NIR-emitting QDs are not that explored due to complex synthesis routes and post-treatment operations [7]. The epitaxial shell growth method was used to prepare water-dispersible NIR QDs in 2010 [8]. Recently microwave irradiation was adopted to synthesise NIR-emitting CdTe QDs

[8]. However, cadmium-based QDs released toxic ions under UV irradiation. Still, considerable research needs to be done to synthesise water-dispersible QDs for extending their biomedical applications. Several transition metals, such as copper, manganese, etc., have been used to modify pure QDs to produce materials with both fluorescence and magnetic imaging properties [[9], [10], [11]]. However, most of these syntheses have been via the organic synthetic route and usually involve toxic binary-based QDs, thus, limiting their biological applications [12,13]. Li and coworkers reported that production of doped-quantum dots or alloyed ternary quantum dots enhanced the optical properties as well as the relaxivity of the ternary and quaternary QDs [14]. Gadolinium doping has been reported to increase the Longitudinal relaxation rate of the AgInS2/ZnS QDs to 1.7 times higher than the normal relaxation time of the commercially available contrast agents, thus doping can provide properties that makes QDs ideal dual-imaging bio-nanoprobes [15]. Herein, we synthesised water-soluble Near-infrared QDs (NIR-QDs) using hydrothermal techniques. We then doped these QDs with magnetic material to modify their properties for future dual imaging applications. There are trillions of bacteria in the human body. Some of them are friendly, while others cause serious infections and diseases [16]. Bacterial and cancer therapies have been managed independently in cancer patients. Thus, the development of multifunctional nanoplatforms for imaging both pathogenic bacteria and cancerous tissues will enable clinicians to analyze the intricacy of the disease and choose a better way to avert the spread of cancer [[17], [18], [19], [20]]. This can also put an end to drug resistance developed in such patients due to their recurrent use. In contributing to the development of multifunctional nanoplatforms for imaging both pathogenic bacteria and cancerous tissues, we herein report the synthesis of water-soluble manganese-doped CuInSe/ZnS NIR QDs as a probe for cancer-bacterial dual imaging. The as-synthesised Mn-doped QDs emitted in the red region with good medium stability exhibited selective screening properties to distinguish Gram-positive and Gram-negative microbiota.

Section snippets

Materials

Manganese chloride ($MnCl_2$), copper chloride ($CuCl_2$), indium nitrate ($In(C_2H_3O_2)_3$), sodium selenite (Na_2SeO_3), thioglycolic acid (TGA), sodium borohydride ($NaBH_4$), tri-sodium citrate (CT), zinc acetate dihydrate ($Zn_4H_6O_4$), ammonium hydroxide (NH_4OH), Dulbecco's Modified Eagle's Medium (DMEM) and phosphate-buffered saline (PBS) were bought from Sigma Aldrich and used as received**.** Streptomycin and Penicillin were obtained from Life Technologies. Tryptone Soy Broth (TSB) was procured from Oxoid.

Physicochemical characterization

Highly fluorescent cadmium-free Mn-doped CuInSe/ZnS QDs were prepared hydrothermally in a pressure cooker and were stable for more than 6 months without any aggregation. As shown in Fig. 1a, the optical properties of Mn-doped QDs exhibited the characteristic luminescence absorption peak at 765 nm with FWHM of 155 nm and fluorescence quantum yield (QY) of 22% with improvement of 2% compared to the recently reported QY for MnCuInSe/ZnS synthesised at the same temperature by Irmania et al., 2022 [

Conclusion

In summary, highly fluorescent, photostable, water-soluble, NIR-emitting Mn-doped CuInSe/ZnS QDs were prepared hydrothermally in a pressure cooker. Their photoluminescence spectrum was around 765 nm. The MTT assays showed that the as-synthesised QDs were highly biocompatible with C26 cells. The QDs could selectively screen Gram-positive bacteria from Gram-negative bacteria. The QDs uptake was higher in prostate cancer cells compared to normal cells due to the enhanced permeability and retention

Authors contribution

Conceptualization, O.S.O. and N.N.; methodology, V.N., N.N., A.R.G. and R.B.; software, V.N., T.C.L., N.N., A.R.G. and R.B.; validation, O.S.O., S.P., N.N., A.R.G. and R.B.; formal analysis, V.N., S.P., O.A.A. and R.M.; investigation, V.N., S.P., N.N., A.R.G. and R.B.; resources, O.S.O. and T.K.; data curation, V.N. and T.C.L.; writing—original draft preparation, V.N., N.N., S.P. and O.S.O.; writing—review and editing, O.S.O., S.P., and K.V.; visualization, V.N., O.A.A. and R.M.; supervision,

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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