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Biocompatible and Highly Luminescent Near-Infrared $CuInS_2/ZnS$ Quantum Dots Embedded Silica Beads for Cancer Cell Imaging

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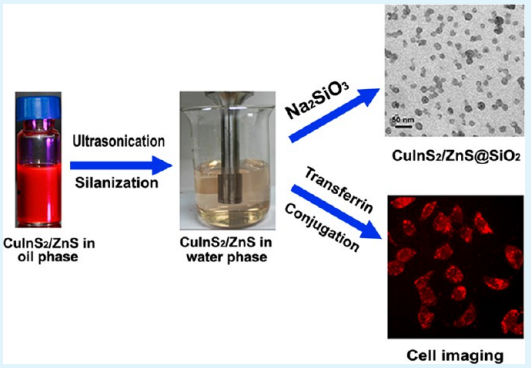
Supporting Information

ABSTRACT: Bright and stable $CuInS_2/ZnS@SiO_2$ nanoparticles with near-infrared (NIR) emission were competently prepared by incorporating the as-prepared hydrophobic $CuInS_2/ZnS$ quantum dots (QDs) directly into lipophilic silane micelles and subsequently an exterior silica shell was formed. The obtained $CuInS_2/ZnS@SiO_2$ nanoparticles homogeneously comprised both single-core and multicore remarkable $CuInS_2/ZnS$ QDs, while the silica shell thickness could be controlled to within 5−10 nm and their overall size was 17−25 nm. Also, the functionalized $CuInS_2/ZnS$ QDs encapsulated in the silica spheres, expedited their bioconjugation with holo-Transferrin (Tf) for further cancer cell imaging. The $CuInS_2/ZnS@SiO_2$ nanoparticles not only showed a dominant NIR band-edge luminescence at 650−720 nm with a quantum yield (QY) between 30 and 50%, without a recognized photoluminescence (PL) red shift, but also exhibited excellent PL and colloidal stability in aqueous media. Impressively, the cytotoxicity studies revealed minor suppression on cell viability under both $CuInS_2/ZnS@SiO_2$ and $CuInS_2/ZnS@SiO_2$@Tf concentrations up to 1 mg/mL. The application in live-cell imaging revealed that the potential of $CuInS_2/ZnS$ QDs as biocompatible, robust, cadmium-free, and brilliant NIR emitters is considered promising for fluorescent labels.



KEYWORDS: *$CuInS_2/ZnS@SiO_2$, NIR QDs, lipophilic silane micelles, cytotoxicity, fluorescent labels, cadmium-free*

1. INTRODUCTION

To date, quantum dots (QDs) have grasped much more attention, in comparison with organic dyes especially in bioimaging fields, because of the enrollment of QDs as a novel class of materials with unique optical and electronic properties, such as remarkable quantum yield (QY), size-tunable photoluminescence (PL), symmetrical and sharp emission peaks, multicolor fluorescence under a single-wavelength excitation source, and high photobleaching resistance.[1,2] Despite all previous motivations that favor the use of QDs for biomedical imaging, until now it remains severely restricted for possible in vivo applications because most available QDs are composed of known toxic elements such as Cd, Hg, Pb, Se, Te, As, etc. Exemplify reports have emphasized the eventual release of heavy elements on the cellular membrane casing biodegradation in the cellular environment and affecting the osmotic equilibrium of the cell, which effectively increases the cytotoxicity effect of these QDs.[3] Therefore, the safety of QD biological labels maintains a major obstacle in their future biomedical exploration.

The I−III−VI_2 QD synthetic research as a rapidly emerging discipline, with intentionally well-controlled structure and multifunctional properties, indicates their potential as novel biolabeling agents.[4,5] At this point, I−III−VI_2 $CuInS_2$ QDs are environmentally friendly and biocompatible because they contain no heavy metal ions. More encouragingly, the narrow band gap of this semiconductor allows their emission to be tunable from a visible to near-infrared (NIR) optical window by tailoring the nanocrystal size. This feature enables $CuInS_2$ QDs to have more sufficient optical penetration in biological tissue from the NIR optical window of 650−900 nm,[6] compared with the traditional II−VI QDs.

Similar to the well-developed II−VI QDs, the I−III−VI_2 QDs with well-controlled shape, size, and composition are commonly synthesized via a thermal decomposition route in organic solvents under elevated temperature.[7,8] Unfortunately, they are incompatible with the physiological environment. Therefore, a phase transfer from oil to water is inevitable to ensure the water solubility of the I−III−VI_2 QDs before further biological applications. Moreover, the fluorescent labels for biomedical imaging should possess several qualities including good photochemical stability, excellent water solubility, and controlled particle size, which should be small enough to avoid possible accumulation in the body and to enhance the transportation ability in cells.[9,10] In the past few years, several techniques such as silica coating,[11] ligand exchange,[12] and amphiphilic polymer encapsulation[13] have been promoted to make hydrophobic nanoparticles water-soluble. Among these

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