Near-Infrared Photoluminescent Ag 2 S Quantum Dots from a Single Source Precursor

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Near-Infrared Photoluminescent Ag_2S Quantum Dots from a Single Source Precursor

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Colloidal semiconductor nanocrystals [or quantum dots (QDs)] have been widely used in biolabeling and bioimaging because of their advantageous optical properties compared with organic fluorophores in terms of fluorescence intensity, photostability, and chemical stability.[1] The most popular QDs currently used are CdSe@ZnS core−shell QDs, which offer appealing optical properties in the range of the visible spectrum from 400 to 700 nm.[1c] However, the autofluorescence of living tissues, which blocks the visible emission from the CdSe@ZnS QDs and makes imaging ambiguous, precludes the utilization of visible-emission QDs for most in vivo bioimaging.[1c−f]

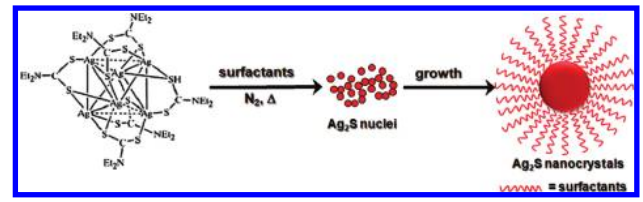
Near-infrared (NIR) light solves the autofluorescence problem by reducing the fluorescence background, making NIR QDs a promising candidate for biomedical imaging in living tissues.[2−5] To date, various kinds of NIR QDs, such as CdTeSe, CdHgTe, CdHgTe/ZnS, CdTe/CdSe, ZnTe/CdSe, PbS, etc., have been successfully synthesized, and exciting progress has been achieved in regard to in vivo biomedical applications.[2] However, the toxicity of NIR QDs has not yet been fully examined and has been a big concern since the NIR QDs were loaded in living bodies.[5] In their elemental forms, cadmium, mercury, lead, tellurium, and selenium have known acute and chronic toxicities.[1f] Therefore, it is desirable to have new kinds of NIR QDs that possess the unique optical window for tissue penetration but low or no toxicity for living bodies.[2−5]

Monoclinic α-Ag_2S, which has a bulk band gap of 1.1 eV and a relatively large absorption coefficient, has been used in photoconductors, photovoltaic cells, IR detectors, etc.[6a−e] In addition, Ag_2S is reported to have negligible toxicity in organisms.[6f] Therefore, the appropriate narrow band gap and low toxicity of Ag_2S QDs render them excellent NIR QDs. To date, different methods have been developed for Ag_2S nanocrystal synthesis.[6b−e] However, to the best of our knowledge, there is no report addressing the NIR emission of Ag_2S nanocrystals.

In this communication, we report our strategy for obtaining single-crystalline, monodisperse Ag_2S QDs with a size of ∼10 nm using a single source precursor (SSP) of Ag(DDTC) [$(C_2H_5)_2NCS_2Ag$]. The as-obtained Ag_2S QDs are the first observed to present NIR emission at 1058 nm.

Scheme 1 illustrates our strategy for preparation of Ag_2S QDs from a SSP of Ag(DDTC). Typically, a slurry containing 0.1 mmol of Ag(DDTC) hydrate (Table S1 and Figure S1 in the Supporting Information), 10 mmol of oleic acid (OA), 10 mmol of octadecylamine (ODA), and 20 mmol of 1-octadecane (ODE) in a three-necked flask (100 mL) was heated to 100 °C to remove water and oxygen, thus forming a homogeneous brown solution. The resulting mixture was heated to 200 °C under N_2 and kept at that temperature for 30 min, affording a dark colloidal solution. After this solution was air-cooled, the nanocrystals were precipitated with excess ethanol and then washed with ethanol and dried in air at 60 °C. The as-prepared products could be easily dispersed in apolar organic solvents (e.g., cyclohexane).

Scheme 1. Synthesis of Ag_2S NIR QDs from a Single Source Precursor of Ag(DDTC)



To achieve the as-expected NIR emission property, the most essential characteristic of the Ag_2S product is to be monoclinic-phase.[6e] Powder X-ray diffraction (X'Pert-Pro MPD) was carried out on the as-formed products. All of the peaks in the XRD patterns (Figure 1) matched those of monoclinic Ag_2S (acanthite type, space group $P2_1/n$), and the calculated lattice constants were $a = 4.226$ Å, $b = 6.928$ Å, and $c = 7.858$ Å (JCPDS 14-0072). In addition, the broadening of the diffraction peaks suggested the nanocrystalline nature of the sample. These results confirmed that we successfully obtained the monoclinic Ag_2S nanocrystals through our SSP method.

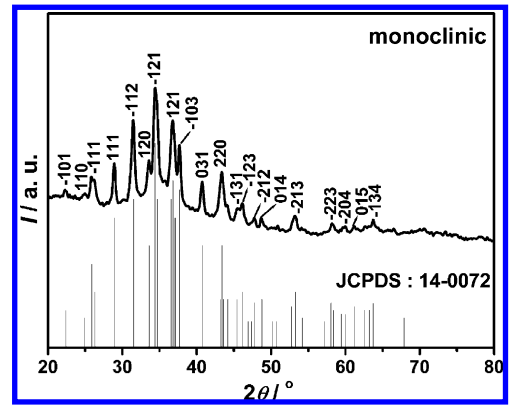


Figure 1. XRD patterns of the as-prepared Ag_2S QDs.

Figure 2a depicts the transmission electron microscopy (TEM, FEI Tecnai F20, accelerating voltage 200 kV) image of Ag_2S QDs. It shows that the as-prepared Ag_2S QDs were monodisperse with a size of 10.2 ± 0.4 nm, as determined by statistical analysis of several hundred nanoparticles. The high-resolution TEM (HRTEM) image (Figure 2b) confirms that the Ag_2S QDs were single-crystalline with an interplane distance of the lattice fringes of ∼0.28 nm, which corresponds to that of the $(\bar{1}12)$ facets of Ag_2S. It is also noted from Figure 2a that the monoclinic Ag_2S QDs are highly dispersed and display a two-dimensional ordered arrangement; this is indicative of the retentivity of capping ligands on the nanocrystal

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surfaces, which can be validated by Fourier transform infrared (FTIR) spectroscopy measurements (Figure S2) as well as by the long-term stability without sedimentation after storage for more than 3 months at room temperature (Figure 3a inset). The X-ray photoelectron spectroscopy (XPS) and energy-dispersive X-ray spectroscopy (EDS) data (Figure S3) verify the formation of the Ag_2S compound (Ag/S atomic ratio = 2.1:1). The core levels of Ag $3d_{5/2}$ and Ag $3d_{3/2}$ in Figure S3b indicate that the Ag ion is univalent in the Ag_2S QDs.[6e,7]

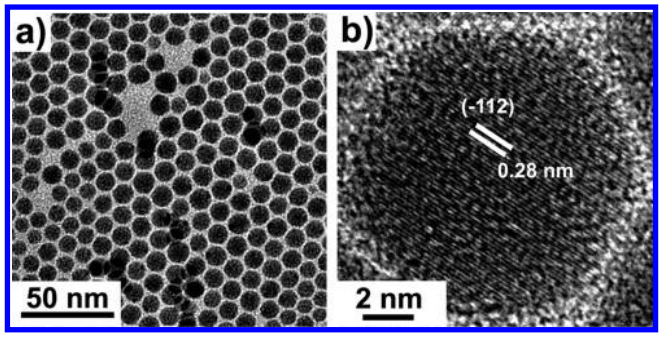

Figure 2. (a) TEM image of Ag_2S QDs. (b) HRTEM image of a single Ag_2S QD.

Figure 3a shows the UV−vis−NIR absorption spectrum of as-prepared Ag_2S QDs dispersed in cyclohexane solution. The colloid solution exhibited continuous absorption across the UV−vis−NIR wavelength range (Figure S4). A discernible absorption peak was detected in the NIR window at 920 nm, which is the lowest-energy excitonic absorption peak of Ag_2S QDs. Relative to the band-gap energy of bulk α-Ag_2S (E_g =1.1 eV), the lowest-energy exciton transition peak of Ag_2S QDs exhibits a blue shift, implying that the Ag_2S nanocrystals behave within the quantum-confinement regime.[6e]

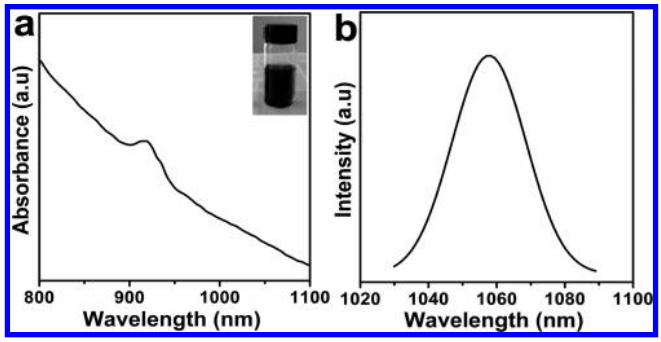

Figure 3. (a) NIR absorption spectrum of as-obtained Ag_2S QDs; the inset is a photograph of Ag_2S dispersed in cyclohexane. (b) NIR fluorescence emission spectrum of Ag_2S QDs at room temperature under λ_{ex} = 785 nm.

Figure 3b depicts the NIR photoluminescence (PL) spectrum of Ag_2S QDs excited with a 785 nm laser diode. The PL spectrum shows a symmetric emission peak centered at 1058 nm with an impressive full width at half-maximum (FWHM) as small as 21 nm, which could be attributed to the narrow size distribution of the Ag_2S QDs. The quantum yield of the as-prepared Ag_2S QDs has not been examined to date because of the difficulty of getting a standard reference. We expect that a core−shell structure similar to that of CdSe@ZnS QDs will improve the quality of the Ag_2S QDs in terms of quantum yield as well as photostability.

In the present synthesis, the combination of different capping ligands and solvents was found to play a key role in obtaining monodisperse Ag_2S QDs. Sole use of OA as the capping ligand and solvent produced soluble but aggregated Ag_2S nanoparticles (Figure S5). Monodisperse Ag_2S QDs were formed in a mixed solvent of OA, ODA, and ODE (Figure 2a). The crystallite size of the as-obtained Ag_2S QDs could be tuned mainly by altering the solution composition. For instance, with 0.1 mmol of Ag(DDTC) as the precursor in 1:1:2 OA/OM/ODE, the reaction at 200 °C for 30 min produced nearly monodisperse Ag_2S nanocrystals with a size of 40.1 ± 5.9 nm (Figure S6a). When the solution composition was changed to 1:1:2 OA/OM/triocytlphosphine oxide, smaller nanocrystals with a size of 21.1 ± 4.4 nm were obtained (Figure S6b). Photoluminescence measurements illustrated that there was no observable NIR emission from the 40.1 and 21.1 nm Ag_2S nanocrystals, demonstrating that these two sizes are beyond the quantum-confinement regime, so no quantum-confinement effect was present in these two Ag_2S nanocrystals.[4,8] Interestingly, our results show that the size and size distribution of as-obtained Ag_2S QDs did not change distinctly with the reaction temperature (180−250 °C) or time (30−60 min) when the reaction composition was kept constant at 1:1:2 OA/ODA/ODE (Figure S7). The narrowing of the size distribution for Ag_2S nanoparticles may be attributed to the temperature-driven "size focusing" process.[9]

In conclusion, we have obtained the first NIR-emission Ag_2S QDs via the pyrolysis of Ag(DDTC) in a mixture of OA, ODA, and ODE. The monodisperse Ag_2S QDs with a size of 10.2 ± 0.4 nm exhibit NIR emission at 1058 nm under 785 nm excitation. The as-obtained Ag_2S QDs may act as new, nontoxic QDs for potential in vivo bioimaging.[1f,5]

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Supporting Information Available: Synthesis details and EA and TGA data for Ag(DDTC); FTIR, EDS, XPS, UV−vis−NIR, and TEM data for the Ag_2S nanocrystals; and a photograph of water-soluble Ag_2S nanocrystals. This material is available free of charge via the Internet at http://pubs.acs.org.

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