CdSe/AsS Core−Shell Quantum Dots: Preparation and Two-Photon Fluorescence

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Core−shell semiconductor nanocrystals (Type I) are known to exhibit strongly enhanced fluorescence quantum yield and photostability due to energy confinement as well as passivation of surface trap states by the shell.[1] Applications of such core−shell quantum dots (QDs) span from optoelectronic devices to fluorescent labels in biology and quantum computing.[1c,2] So far, the materials of core−shell nanocrystals (NCs) are limited to II−VI, IV−VI, and III−V groups.[1−3] Their wet synthesis usually involves high-temperature decomposition of organometallic precursors.[1−3] Here, we report the synthesis of a core−shell NC consisting of an arsenic sulfide (AsS, V−VI group) shell and a CdSe core. The growth of the AsS shell took place under mild conditions by a cluster-complex deposition method. The bulk band gap of As_4S_4 ($\sim$2.9 eV)[4] is larger than that of CdSe (1.76 eV), so in principle the wide band gap AsS can passivate and provide energy confinement to the CdSe core and form a type I core−shell system. We found that the synthesized CdSe/AsS core−shell NCs exhibit efficient two-photon upconversion fluoresecence that can be used in infrared (IR) excited cellular labeling.

The mineral Realgar (α-arsenic(II) sulfide) can be dissolved in primary amines to form cluster complexes due to the chelation between the empty *d* orbitals of arsenic and the nitrogen lone pair of amines.[5a] We have recently demonstrated the successful transformation of the AsS/ethylenediamine cluster to an AsS NC in polar protic solvents.[6] Here, the cluster-mediated approach can be further developed for the growth of a crystalline AsS shell on the CdSe NC. The cluster solution of Realgar/butylamine was selected as a precursor for AsS shell growth, and a mixed solvent of chloroform and isopropanol was selected as the reaction media. During the reaction (Scheme S1), the $C_4H_9NH_2$−As−S cluster complex adsorbed on the CdSe NC due to chemical affinity and H-bonding interactions in polar solvents. The addition of isopropanol assists the transformation of the cluster to the crystalline shell because its proton-donation ability dissociates the NH_2−AsS bonds and allows AsS to aggregate.[5,6] With the isopropanol to $CHCl_3$ ratio increase and assistance of thermal prolongation, the AsS cluster gradually crystallizes. The thickness of the AsS shell can be controlled by adjusting the ratio of the cluster precursor to CdSe, as well as the ratio of isopropanol to $CHCl_3$ and reaction time. Finally, hexadecylamine-trioctylphosphine (HDA-TOP) was used to replace the short chain butylamine for the surface passivation of the AsS shell to enhance the quantum yield of the core−shell NC.

A bulk arsenic(II) sulfide crystal consists of subunits made up of four As and four S atoms (As_4S_4) held together by van der Waals forces.[5] The weakly bonded As_4S_4 subunits provide a flexible
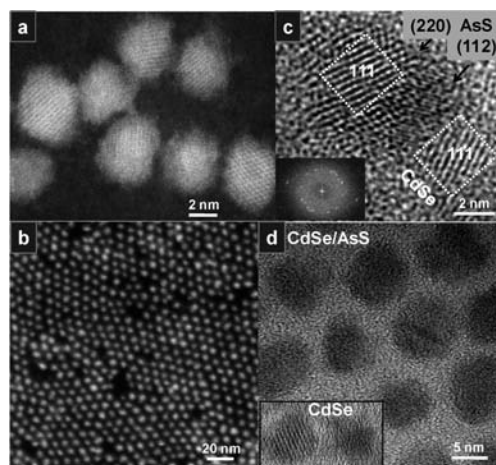

Figure 1. Electron microscopy images of CdSe/AsS core−shell NCs. (a) HAADF-STEM image of 1−2 layer of AsS-coated CdSe (lower contrast of the edge than the body). (b) Superlattice-like self-assembly of $\sim$4.5 nm NC with a 3.3 nm core (HAADF-STEM image). (c) High resolution TEM image of a single core−shell NC with a $\sim$3 nm CdSe core coated by 4 layers of AsS shell (inset the FFT pattern. (d) Thick AsS shell-coated CdSe (inset plain 5 nm CdSe, for comparison).

interface that can accommodate lattice deformation during the growth of the AsS shell on the CdSe NC. Lattice matching occurs between several faces of the CdSe and β-As_4S_4 (Tables S1 and S2, Supporting Information) crystals. The lattice matching condition between wurtzite phase CdSe and β-As_4S_4 is better than that for the cubic Zinc blende phase. During the growth of the core−shell, the changes in crystal phases with time were probed by powder X-ray diffraction (XRD). As shown in Figure S2, additional XRD peaks associated with the AsS phase emerged. X-ray photoelectron spectroscopy (XPS) provides evidence for the growth of the AsS shell on the CdSe core. As shown in Figure S3, the Se 3*p* peaks of the CdSe core, which are observed at 160.4 and 166.5 eV, become attenuated following the growth of the AsS shell, and this is accompanied by the increase in intensities of the S 2*p* peak at 161.4 eV and As 3*d* peak at 43.3 eV. Both XPS and EDX (energy dispersive X-ray analysis) reveal the trend of increasing atomic ratios of As/Cd and S/Se with increased shell thickness.

High angle annular dark field scanning transmission electron microscopy (HAADF-STEM) in combination with EDX was applied for analyzing the core−shell structure.[7] Figure 1a reveals that the peripheral regions have a lower contrast compared to the core of the NC, which indicates the presence of a low atomic weight material surrounding a high atomic weight core, as would be expected in the case of AsS-coated CdSe. EDX point scanning of a single particle of CdSe/AsS detected four elements of Cd, Se and As, S (Figure S4). Figure 1b demonstrates a superlattice-like
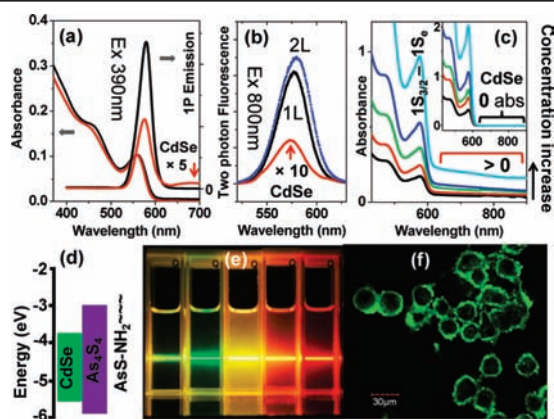
Figure 2. (a-c) Optical properties of CdSe/AsS core−shell NCs compared to bare CdSe NCs. (a) Typical absorption and photoluminescence spectra of CdSe/AsS (black solid lines, ~3.9 nm size) and CdSe (red dash lines, 5 times multiple). (b) Upconversion fluorescence spectra of CdSe/AsS of one layer (1 L) or two layers (2 L) of the AsS shell compared to CdSe (10 times multiple) excited at 800 nm laser. (c) Concentration-dependent absorption spectra of CdSe/AsS in chloroform solutions, compared to bare CdSe (inset). (d) The illustration of electronic energy levels (vs vacuum) of semiconductors As_4S_4 and CdSe and amine-functionalized AsS. (e) The photograph of colorful upconversion fluorescences excited by 800 nm laser shining through the solution containing the core−shell NCs. (f) Two-photon fluorescence labeling (emission at 570 nm excited at 780 nm laser) of HeLa cancer cells after uptaking water-soluble CdSe/AsS QDs for 2 h.

self-assembled array formed by homogeneously sized 4.5 nm particles. Figure 1c shows the HRTEM image of single particle consisting of a 3 nm core coated with a four-layered shell. The increase in the diameter of the CdSe/AsS NC compared to the core-only CdSe NC provides strong evidence of the growth of a thick shell on the wurtzite CdSe core (Figure 1d).

The absorption and visible emissions of the CdSe/AsS NCs can be tuned by controlling the size of the CdSe core (Figure S5).[3a,b] The first absorption peak in the spectra of the CdSe core ranges from 1.78 to 2.75 eV. After coating with the AsS shell, the deep trap emission of bare CdSe is suppressed, as shown in Figure 2a. There is also a small red shift (2−10 nm) of the exciton and photoluminescence (PL) peaks after the shell growth, which can be explained by the partial leakage of the exciton into the shell material.[1,3] The quantum yield of CdSe synthesized in this work has not been optimized and is relatively low (5%, calibrated with Rhodamine 6G). However, after coating it with the AsS shell which was further stabilized by a long carbon chain stabilizer, the one photon fluorescence quantum yield of CdSe/AsS increases to 20−50%. An extended fluorescence lifetime after coating with AsS shell was also observed. For example, the PL of CdSe/AsS (3.9 nm size, emission 2.15 eV) decays biexponentially (2.0 ns + 18.0 ns) with a decay time longer than that for a plain CdSe NC (9.5 ns), which may result from coherency strain effects of mismatched CdSe and As_4S_4.[8]

Effective upconversion fluorescence was observed from the CdSe/AsS core−shell system (Figures 2b,e and S6). The two-photon fluorescence (575 nm) excited by 800 nm light increases by 20 times compared to the core-only system. Figure 2c shows the UV absorption spectra of the CdSe/AsS displayed as a function of increasing concentration of the NCs. Along with the exciton peaks at $1S_{3/2}-1S_e$, the absorption in the 600−900 nm range is seen to increase with the concentration of CdSe/AsS NCs in $CHCl_3$. The near IR absorption is absent from the core-only system of CdSe. These absorptions most likely arise from the vibration modes of AsS-amine (stabilizer) on the surface of the core−shell. UV−visible absorption spectra of the AsS/butylamine cluster complex solution show similar absorption in these regions (Figure S7). The enhanced

absorption in the IR region may be useful for the upconversion. Figure 2e shows the photographs of the colorful fluorescence lines excited by a 800 nm laser shining through five solutions containing CdSe/AsS NCs with different sizes of the CdSe core. It is clear that bright and colorful upconversion fluorescence can be achieved. The quadratic relationship of excitation laser power with the intensity of the upconversion fluorescence proves that the upconversion is two-photon in nature (Figure S6).

The fact that the core−shell NCs exhibited strong two-photon fluorescence suggests its applications in IR-excited bioimaging.[2b,9] The CdSe/AsS NC was rendered water-soluble by coating it with poly(acrylic acid) modified with octadecylamine.[10] The two-photon absorption cross sections of several water-soluble QDs of multiple colors were roughly measured at the excitation wavelength of 800 nm. Our measured values range from 300 to 10 000 Goeppert−Mayer units (GM). Finally, to demonstrate the applicability of these new core−shell NCs for two-photon bioimaging, upconversion fluorescence labeling of HeLa cancer cells that had internalized the CdSe/AsS NCs was successfully obtained using an IR laser (780 nm), as shown in Figure 2f.

In short, we report the synthesis of a new core−shell QD system based on AsS-coated CdSe using a cluster-complex deposition method under mild conditions. These NCs show tunable emissions in the visible band from 450 to 700 nm. The core−shell system shows the characteristics of type I heterointerface: the emission wavelength can be determined by the size of the core, and the quantum yield and longer fluoresence lifetime are markedly improved over the core-only NC. Moreover, upconversion fluorescence imaging of HeLa cancer cells was successfully carried out. The successful synthesis of the AsS/CdSe core−shell NC provides the premise for future investigation of hybrid systems arising from the V−VI group semiconductors.[11]

Supporting Information Available: Experimental procedures and additional characterization. This material is available free of charge via the Internet at http://pubs.acs.org.

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