Tunable near-infrared localized surface plasmon resonances of heterostructured Cu$_{1.94}$S-ZnS nanocrystals

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Abstract: Strong near-infrared (NIR) localized surface plasmon resonances (LSPRs) have been observed in spherical Cu$_{1.94}$S nanocrystals and matchstick-like Cu$_{1.94}$S-ZnS heterostructured nanocrystals, which have been synthesized using a simple one-pot approach without any injection and pre-synthesis of metal precursors. The LSPRs peak of the Cu$_{1.94}$S nanocrystals could be tuned from 1680 nm to 1375 nm by heterogrowth of ZnS onto the Cu$_{1.94}$S nanocrystals due to the increase of free carriers (holes). The LSPRs absorbance can be optimized to 1322 nm by prolonging the growth time of the heterostructured nanocrystals, which may be used as a light absorbing agent for photothermal therapy.

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OCIS codes: (240.6680) Surface plasmons; (300.1030) Absorption; (160.4236) Nanomaterials; (300.6490) Spectroscopy, surface.

References and links


1. Introduction

Semiconductor nanocrystals have attracted much attention due to their tunable size- and shape-dependent physical and chemical properties, as well as their wide potential applications in light-emitting diodes, photovoltaic cells, biological labels and so on [1–6]. To meet the growing demand of applications in optoelectronic devices and biological technology, enormous efforts have been devoted to developing various methods for synthesis of different types of semiconductor nanocrystals, in which wet-chemical methods are commonly used [7–10]. In the past few years, copper-based chalcogenide nanocrystals have been extensively studied due to their potential applications from light-emitting devices to photothermal therapy [11–15]. In particular, these nanocrystals are less toxic, economic and have unique crystal phase and electrical properties. In general, they are p-type semiconductor with bulk band-gap energies of 1.0–1.5 eV, which match well with the solar spectrum at the earth’s surface [12]. Since Gao et al demonstrated that Cu_{1-x}S nanocrystals could serve as catalysts for synthesis of different-sized semiconductor heterostructured nanocrystals, various Cu_{1-x}S-based chalcogenide semiconductor heterostructured nanocrystals have been reported using a colloidal chemical approach, such as hexagonal-prismatic Cu_{1-x}S-ZnS, disk-shaped Cu_{1-x}S-CdS and so on [16–18]. These semiconductor heterostructured nanocrystals provide an
effective mean to endow them with diverse functionalities or unique properties in a single nanostructure.

Typically, localized surface plasmon resonances (LSPRs) have been studied on noble-metal nanocrystals with different shapes and size, which often results in surface-enhanced Raman scattering (SERS) and enhanced photovoltaic performances [19, 20]. Very recently, NIR LSPRs absorbance has been observed in some heavily-doped semiconductor nanocrystals, such as Cu$_{2-x}$E(E = S, Se) and tin oxide [21–24]. In 2011, Luther et al reported the size-dependent NIR absorbance of Cu$_{2-x}$S nanocrystals experimentally and theoretically, which could be attributed to plasmon resonance of free holes in vacancy-doped semiconductor nanocrystals [21]. In 2012, Manthiram et al observed strong and tunable LSPRs absorbance from metallic phases of tungsten oxide nanocrystals due to the unique character of the outer-$d$ valence electrons [24]. In 2013, Swihart et al demonstrated that the NIR plasmonic absorbance could be tuned by varying the amount of the surfactant which had an important effect on the number of free carriers of the nanocrystals [12]. Lately, there are few reports on the tunable LSPRs absorbance by constructing Cu$_{1.94}$S-based heterostructured nanocrystals reported by the same group [25, 26]. However, there exists a contradiction in the LSPR shift of the heterostructured nanocrystals as compared to that of pure Cu$_{1.94}$S nanocrystals. The authors attributed the blue-shift of the sandwich-like Cu$_{1.94}$S-ZnS-Cu$_{1.94}$S heterostructured nanocrystals to the enhanced polarized electric field [25], but in the other work, they ascribed the red-shift of Cu$_{1.94}$S-ZnS dimeric nanoheterostructures to the change in capacitance value due to the change of ZnS length [26]. Therefore, it is necessary to study the LSPRs behavior of heterostructured nanocrystals by changing the ZnS length, which may be useful to clarify the reason of LSPRs shift.

Herein, a simple one-pot colloidal chemical approach has been adopted to prepare spherical Cu$_{1.94}$S nanocrystals and matchstick-like Cu$_{1.94}$S-ZnS nanocrystals. A strong but broad NIR LSPR absorbance has been observed in Cu$_{1.94}$S nanospheres. Moreover, the NIR plasmonic absorption peak shifts to shorter wavelength by heterogrowth of ZnS “stick” onto Cu$_{1.94}$S “head”, and the LSPRs wavelength can be optimized at 1322 nm by changing the reaction time, which falls within the spectral range of the therapeutic window, indicating potential applications in photothermal therapy.

2. Experimental section

Spherical Cu$_{1.94}$S nanocrystals and matchstick-like Cu$_{1.94}$S-ZnS heterostructured nanocrystals were synthesized according to our previous report [15]. Typically, Cu$_{1.94}$S nanocrystals were synthesized by direct heating 5 mmol of copper(II) acetylacetonate (Cu(acac)$_2$) in the mixture of 5 mL of 1-dodecanethiol (DDT) and 15 mL of 1-octadecene (ODE) at 240 °C. In similar, Cu$_{1.94}$S-ZnS heterostructured nanocrystals were obtained by using 3.5 mmol of Cu(acac)$_2$ and 1.5 mmol of zinc acetylacetonate (Zn(acac)$_2$) in the same reaction system at 240 °C, which avoids the injection of Cu$_{1.94}$S precursors. The as-obtained products were purified by three repeated actions of dissolving the precipitate in chloroform and then reprecipitating by adding excess ethanol.

Transmission electron microscopy (TEM) observations were taken on a JEM-1400 transmission electron microscope with an acceleration voltage of 100 kV. High-resolution TEM images were taken on a JEM-2010 at an acceleration voltage of 200 kV. The X-ray diffraction (XRD) patterns were recorded on a Bruker D8 Advance diffractometer using a Cu Kα radiation source ($\lambda$ = 1.54056 Å). UV-Vis-NIR absorption spectra were performed on a Varian 5000 spectrophotometer. All the measurement was performed at the room temperature.

3. Results and discussions

The XRD patterns of Cu$_{1.94}$S nanocrystals are shown in Fig. 1, and it can be seen that all the diffraction peaks can be indexed to monoclinic Cu$_{1.94}$S phase (JCPDS no.23-0959), which possesses a cationic deficiency structure [16]. Figure 2 shows the TEM image and size
distribution histograms of Cu$_{1.94}$S nanocrystals. As shown in Fig. 2(a), the as-obtained product is spherical in shape and the dispersion is very uniform. It can be seen in Fig. 2(b) that the average diameter is estimated to be 7.9 ± 0.8 nm by measuring 100 particles.

![Fig. 1: XRD patterns of Cu$_{1.94}$S nanocrystals](image)

**Fig. 1.** XRD patterns of Cu$_{1.94}$S nanocrystals, and the bottom lines are the standard diffraction lines of monoclinic Cu$_{1.94}$S (JCPDS. No 23-0959).

![Fig. 2: TEM image and size distribution histogram](image)

**Fig. 2.** (a) TEM image and (b) size distribution histogram of Cu$_{1.94}$S nanocrystals.

Figure 3 shows the XRD pattern of heterostructured Cu$_{1.94}$S-ZnS nanocrystals. Based on the XRD pattern, it can be seen that the as-obtained sample is made up of monoclinic Cu$_{1.94}$S (JCPDS No. 23-0959) and wurtzite ZnS (JCPDS No. 79-2204), and no other impurities are detected, indicating that the heterostructured nanocrystals is undoubtedly constructed by Cu$_{1.94}$S and ZnS nanocrystals. To further demonstrate the formation of Cu$_{1.94}$S-ZnS nanocrystals, TEM techniques have been employed to characterize the morphology of the as-obtained products. Typical TEM images of the Cu$_{1.94}$S-ZnS nanocrystals obtained at 120, 180 and 270 min are given in Figs. 4(a)-4(c), respectively. It can be seen that all the products exhibit matchstick-like shape, which is comprised of spherical “head” and slightly thinner “stick”. Moreover, some isolated spherical Cu$_{1.94}$S nanocrystals are still present in the TEM image, which suggests that there is not enough amount of ZnS growth onto the Cu$_{1.94}$S nanocrystals. To further identify the composition of the as-obtained products, a typical high-resolution TEM image of the matchstick-like heterostructured nanocrystals is given in Fig. 4(d), some obvious lattice fringes with a spacing of 0.333 nm can be observed in the “head” part, which is indexed as the (800) plane. On the other hand, the lattice fringes with an interplanar distance of 0.310 nm can be observed in the “stick” of the product, corresponding to (002) plane, which can be identified as the c axis of wurtzite ZnS. Additionally, the lattice fringes with a spacing of 0.191 nm are also observed in the “stick”, corresponding to (110)
plane, which is vertical with the (002) plane. This result further confirms the formation of matchstick-like Cu$_{1.94}$S-ZnS nanocrystals with the Cu$_{1.94}$S “head” and ZnS “stick”. By measuring 100 particles obtained at different reaction time, the relationship between the “head” width or “stick” length and the reaction time is given in Fig. 4(e), it can be seen that the width of the “head” is almost unchanged but the length of the “stick” increases with the reaction time prolonging. It is worth noting that the width of the “head” is kept at about 8 nm, which is similar to the diameter of pure Cu$_{1.94}$S nanospheres.

![XRD patterns of Cu$_{1.94}$S-ZnS heterostructured nanocrystals with the standard lines of monoclinic Cu$_{1.94}$S (JCPDS no. 23-0959) and wurtzite ZnS (JCPDS no. 79-2204) at the bottom.](image1)

Fig. 3. XRD patterns of Cu$_{1.94}$S-ZnS heterostructured nanocrystals with the standard lines of monoclinic Cu$_{1.94}$S (JCPDS no. 23-0959) and wurtzite ZnS (JCPDS no. 79-2204) at the bottom.

![Typical TEM images of the Cu$_{1.94}$S-ZnS nanocrystals obtained at different reaction time: (a) 120 min; (b) 180 min; (c) 270 min; (d) A typical HRTEM image; (e) Size evolution of the “head” and “stick” of the matchstick-like as a function of reaction time.](image2)

Fig. 4. Typical TEM images of the Cu$_{1.94}$S-ZnS nanocrystals obtained at different reaction time: (a) 120 min; (b) 180 min; (c) 270 min; (d) A typical HRTEM image; (e) Size evolution of the “head” and “stick” of the matchstick-like as a function of reaction time.
LSPRs behavior has often been reported in Cu_{2-x}S and Cu_{2-x}Se nanocrystals, which arises from the $p$-type free charge carriers (holes) in the nanocrystals [21, 22]. These charge carriers are generated from copper vacancies, which is associated with the nonstoichiometric composition of the nanocrystals. As mentioned above, the Cu_{1.94}S nanocrystals have been demonstrated to possess a cationic deficiency structure. UV-Vis-NIR absorption spectroscopy has been employed to study the LSPRs behavior of our product. Figure 5 shows the absorption spectra of Cu_{1.94}S and Cu_{1.94}S-ZnS nanocrystals obtained at 180 min dispersed in chloroform. An obvious strong NIR absorption peak at 1680 nm is observed in Cu_{1.94}S nanocrystals, which can be ascribed to the LSPRs absorbance of nonstoichiometric Cu_{1.94}S due to copper deficiencies [21]. Interestingly, the NIR LSPRs peak shifts from 1680 nm to 1375 nm with epitaxial growth of ZnS nanocrystals onto the Cu_{1.94}S nanocrystals. Moreover, the absorption spectra of both the samples on the energy scale shown in the inset of Fig. 5 indicates that the absorption region in our work is distinguished by remarkable well-defined peaks, characteristic of LSPR modes [21]. As stated by Alivisatos et al. that the LSPRs absorbance can be tuned by changing the particle size [21]. According to the TEM results and the size evolution of heterostructured nanocrystals as a function of reaction time shown in Fig. 5, the diameter of the “head” of the heterostructured nanocrystals is similar to that of the Cu_{1.94}S nanocrystals, which rules out the effects of particle size on the LSPRs absorbance. Therefore, the incorporation of wurtzite ZnS into the heterostructured nanocrystals plays an important role in the blue-shift of LSPRs peaks of Cu_{1.94}S nanocrystals.

To further explore the reason for the blue-shift of LSPRs peak of the Cu_{1.94}S-ZnS nanocrystals as compared to that of the Cu_{1.94}S nanocrystals, the absorption spectra of Cu_{1.94}S-ZnS nanocrystals for different growth time are also measured and shown in Fig. 6. As shown in Fig. 6(a), a strong LSPRs peak at 1620 nm is observed at 30 min, which exhibits a slight blue-shift as compared to that of Cu_{1.94}S nanocrystals. Further increasing the growth time to 120 min, the LSPRs peak exhibits a distinct blue-shift over 200 nm. With the growth of Cu_{1.94}S-ZnS nanocrystals proceeding, a consecutive blue-shift takes place, and finally a LSPR peak at 1324 nm is observed at 360 min, which corresponds to a spectral range of the therapeutic windows [26]. As a matter of fact, the consecutive blue-shift of the LSPRs peak is consistent with the increase of the length of ZnS “stick” (Fig. 5(e)). The corresponding absorption spectra on the energy scale are also shown in the inset of Fig. 6(a), and the linewidth of the LSPRs absorbance broadens as the increase of the growth time due to the change of the charge carrier density [21]. Figure 6(b) shows the evolution of the LSPRs peaks as a function of the reaction time of the Cu_{1.94}S-ZnS nanocrystals. It is well known that the free
charge carrier density contributes greatly to the LSPRs peak, and the carrier distribution can be affected by the external electric field [12]. As a matter of fact, II-VI semiconductors possess a strong electric dipole moment along the c-crystallographic axis [27]. Herein, the epitaxial growth of ZnS on the monoclinic Cu_{1.94}S “head” is along c-axis of ZnS, which is confirmed by HRTEM result shown in Fig. 4(d). According to the previous report [27], Cu_{1.94}S “head” should contribute to the electric dipole moment of the heterostructured nanocrystals due to the ferroelectric performance. Besides, the carrier transportation between Cu_{1.94}S and ZnS could enhance the longitudinal electric dipole moment of the heterostructured nanocrystals due to the existence of p-n type heterostructure. Therefore, the ZnS “stick” can provide an external electric field to promote the dissociation of free charge carriers (holes) from the copper vacancies at the top of the Cu_{1.94}S valence band, leading to the increase of free carriers (holes), which results in the blue-shift of LSPRs in the heterostructured Cu_{1.94}S-ZnS nanocrystals as compared to that of Cu_{1.94}S nanocrystals. Furthermore, Alivisatos et al demonstrated that the longitudinal permanent electric dipole moment of wurtzite semiconductor nanocrystals would increase linearly with volume [28]. Herein, the polarized electric field intensifies as the growth of ZnS “stick”, which makes the free charge carriers density of Cu_{1.94}S “head” increase, resulting in a continual blue-shift of LSPR peak as the increase of growth time of the Cu_{1.94}S-ZnS [22, 23].

![Image](image_url)

Fig. 6. (a) UV-Vis-NIR absorption spectra of Cu_{1.94}S-ZnS heterostructured nanocrystals at different reaction time, and the inset shows the absorption spectra on the energy scale; (b) the relationship between the LSPRs peaks and the growth time of Cu_{1.94}S-ZnS heterostructured nanocrystals.

4. Conclusions

In summary, spherical Cu_{1.94}S and matchstick-like Cu_{1.94}S-ZnS heterostructured nanocrystals have been synthesized through a simple one-pot approach without any injection. The Cu_{1.94}S nanocrystals exhibit a strong LSPR peak at 1680 nm due to the existence of copper vacancies. The LSPR peak of the matchstick-like Cu_{1.94}S-ZnS heterostructured nanocrystals can be tuned from 1680 nm to 1322 nm by increasing the length of ZnS stick, which is in close associated with the effects of free charge carrier density due to the formation of polarized electric field. The LSPR peak (1322 nm) matches well with the spectral range of therapeutic window, indicating that the heterostructured nanocrystals may have potential applications in photothermal therapy.

Acknowledgment

This work was partly supported by the National Natural Science Foundation of China (No. 61108063), the National Science Foundation for Distinguished Young Scholars of China (No. 61125505), and the author (A. W) is also grateful to the financial support from Beijing JiaoTong University (2012RC046).