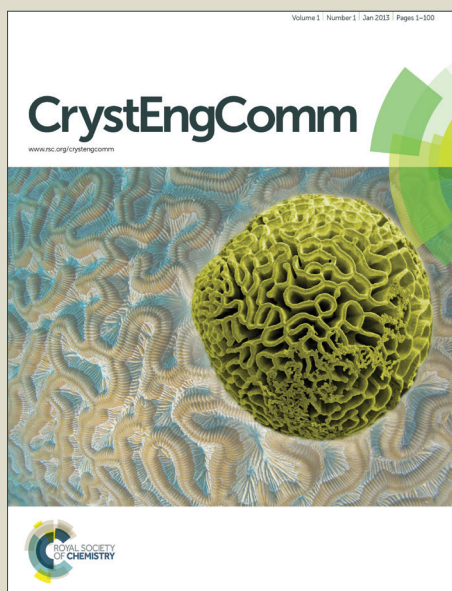


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## ARTICLE

# Synthesis of $\text{Cu}_{2-x}\text{S}$ Nanocrystals Induced by Foreign Metal Ions: Phase and Morphology Transformation and Localized Surface Plasmon Resonance

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High-quality rhombohedral digenite ( $\text{Cu}_{1.8}\text{S}$ ) nanocrystals (NCs) were synthesized using a facile one-pot approach, in which the foreign metal ions ( $\text{Zn}^{2+}$  and  $\text{Cd}^{2+}$ ) were added to drive a transformation in the phase and morphology of the as-obtained  $\text{Cu}_{2-x}\text{S}$  NCs. During this process, the as-obtained products could transform from monoclinic djurleite ( $\text{Cu}_{1.94}\text{S}$ ) NCs to rhombohedral  $\text{Cu}_{1.8}\text{S}$  NCs in the presence of  $\text{Zn}^{2+}$  and  $\text{Cd}^{2+}$  ions by extending the reaction time and increasing the reaction temperature, which could provide sufficient energy to overcome activation energy barriers. Moreover, we further studied the evolution of the plasmonic properties of the as-obtained  $\text{Cu}_{2-x}\text{S}$  NCs, and the near-infrared (NIR) localized surface plasmon resonance (LSPR) absorption wavelength could be tuned by varying the amount of  $\text{Zn}^{2+}$  and  $\text{Cd}^{2+}$  ions added into the reaction system, which was in close associated with the change of copper deficiencies and free hole densities induced by the foreign metal ions.

## 1. Introduction

The LSPR absorbance has often been observed in noble metal NCs due to their high charge carrier density, which result in surface-enhanced Raman scattering (SERS) and enhanced photovoltaic performances.<sup>1-4</sup> Very recently, LSPR effects have also been observed in colloidal  $\text{Cu}_{2-x}\text{E}$  ( $\text{E}=\text{S}$ ,  $\text{Se}$  and  $\text{Te}$ ) NCs due to the copper deficiencies, which have exhibited well-defined plasmonic absorption in the near-infrared (NIR) region, and have potential applications in photothermal therapy.<sup>5-16</sup> Previous reports have demonstrated that the NIR plasmonic absorption wavelength can be affected by the Cu-defect density, which can be modulated by controlling their size, geometry, composition and surface ligands.<sup>5-10</sup> For example, Luther et al have systematically studied the size-dependent NIR LSPR behavior of  $\text{Cu}_{2-x}\text{S}$  NCs, and the effects of the dielectric constant of the surrounding medium on the LSPR absorption wavelength.<sup>5</sup> Besides, Tao's group have demonstrated that the anisotropic  $\text{Cu}_{2-x}\text{S}$  nanodisks display shape-dependent LSPR behaviors which possess two distinct absorption peaks due to in-plane and out-of-plane dipolar resonances, and the LSPR can be tuned by changing the aspect ratios of nanodisks.<sup>6, 14</sup> Furthermore, an alternative approach that the introduction of oxidizing and reducing agents into plasmonic NCs has been exploited to tune the LSPR wavelength, in which the free carrier density is increased through the oxidation of stoichiometric copper chalcogenides NCs into non-stoichiometric NCs.<sup>11-13</sup> Upon oxygen oxidation, phase

transformation could take place during the reduction process through the addition of Cu(I) complex.<sup>12</sup> However, to the best of our knowledge, the study on the effects of foreign metal ions on the LSPR behavior of the  $\text{Cu}_{2-x}\text{S}$  NCs has rarely been reported, in which the crystal phase and morphology can be transformed by the foreign metal ions.

It is well known that  $\text{Cu}_{2-x}\text{S}$  ( $x=0\sim 1$ ) is an excellent *p*-type semiconductor, which holds great promise in photothermal therapy, thermoelectronics, CO gas-sensing device, solar cells and Li-ion battery.<sup>17-24</sup> Currently,  $\text{Cu}_{2-x}\text{S}$  has become another research hotspot due to their tunable band gap with varying stoichiometries ranging from Cu-rich  $\text{Cu}_2\text{S}$  (chalcocite) to  $\text{CuS}$  (covellite).<sup>25-30</sup> To date, different synthetic methods have been developed to prepare  $\text{Cu}_{2-x}\text{S}$  NCs, most of which focus on chalcocite, djurleite and covellite nanocrystals.<sup>30-37</sup> Very recently, some attention has been paid to the synthesis of  $\text{Cu}_{1.8}\text{S}$  NCs, but the synthetic methods were mainly focused on the metal-precursor decomposition or hot-injection approach.<sup>11,17</sup> Therefore, it is still challenging to exploit a simple and low-cost approach to prepare high-quality and monodispersed digenite nanocrystals. In our previous work, a facile one-pot heating process was developed to prepare Cu-Zn-S-based NCs and the composition of the products evolves from Cu(I)-doped ZnS NCs to heterostructured NCs consisting of monoclinic  $\text{Cu}_{1.94}\text{S}$  and wurtzite ZnS and even the digenite NCs by controlling the metal precursors ratios.<sup>38</sup> Based on this work, herein, different foreign metal ions ( $\text{Zn}^{2+}$  and  $\text{Cd}^{2+}$ ) were added to drive a transformation in the crystal phase and morphology through a simple one-pot colloidal method. In particular, we

systematically studied the phase and morphology transformation by controlling the reaction temperature, precursor ratios, reaction time and the atomic size of foreign metal ions, and the results indicated that this transformation was dependent on the energy provided by the reaction conditions. Moreover, the LSPR absorption spectra had been employed to study the phase and morphology transformation in the presence of  $\text{Zn}^{2+}$  and  $\text{Cd}^{2+}$ , which could influence the number of copper deficiencies and free holes densities.

## 2. Experimental details

### Materials

Copper acetylacetonate ( $\text{Cu}(\text{acac})_2$ , 97%), zinc acetylacetonate ( $\text{Zn}(\text{acac})_2$ , 97%) and cadmium acetate dihydrate were ( $\text{Cd}(\text{CH}_3\text{COO})_2$ , 99.99%) were purchased from Shanghai Aladdin Reagent Company. 1-Octadecene (ODE, 90%) was purchased from Sigma-Aldrich. 1-dodecanethiol (DDT, 98%) and other solvents such as ethanol and chloroform were commercially available products in analytical grade, which were purchased from Beijing Chemical Reagent, China. All the chemicals were used as received without any further purification.

### Synthesis of Rhombohedral Digenite Nanocrystals

For a typical synthesis of rhombohedral digenite NCs, 9 mmol  $\text{Cu}(\text{acac})_2$  and 1 mmol  $\text{Zn}(\text{acac})_2$  were mixed with 10 mL DDT and 30 mL ODE in a three-neck flask. The reaction mixture was degassed using  $\text{N}_2$  flow under magnetic stirring for about 20 min, and then was heated slowly to 240 °C and kept at this temperature for several time. During the heating process, aliquots were extracted for use in the study of the phase and shape evolution as well as the LSPR response of the resultant products. Afterwards, the reaction mixture was terminated by cooling the reaction mixture down to room temperature naturally after removal of the heating source. The as-obtained colloidal solution was precipitated through addition of excess ethanol and then centrifuged at 6000 rpm for 10 min, and then the supernatant liquid was decanted and the precipitate was collected. To remove residual organic ligands, the precipitate was re-dispersed in chloroform, and then some excess ethanol was added into the solution to re-precipitate the products. The above procedure was repeated three times for purification. Finally, the as-obtained products were dispersed in chloroform or dried in vacuum for further characterization. Besides, the other products were obtained using the above similar procedure under different reaction conditions, such as the reaction temperatures, the precursor ratios, and so on. The different products are denoted as samples A–E, and the detailed experimental conditions are summarized in Table 1.

### Sample Characterizations

Transmission electron microscopy (TEM) observations were taken on a JEM-1400 transmission electron microscope with an acceleration voltage of 100 kV. High-resolution TEM image 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  $\text{Cu K}\alpha$  radiation source ( $\lambda=1.54056 \text{ \AA}$ ). The X-ray photoelectron spectroscopy (XPS) measurement was performed on a VG ESCALAB 220i-XL spectrometer with a 300 W  $\text{Al K}\alpha$  radiation source. All

binding energies for different elements were calibrated with respect to C1s line at 284.8 eV from the contaminant carbon. The atomic ratios were determined by the inductively coupled plasma optical emission spectrometer (ICP-OES) method, which was performed using a Thermo Fisher IRIS Intrepid II XSP. UV-Vis-NIR absorption spectra were performed on a Varian 5000 spectrophotometer. All the measurement was performed at the room temperature.

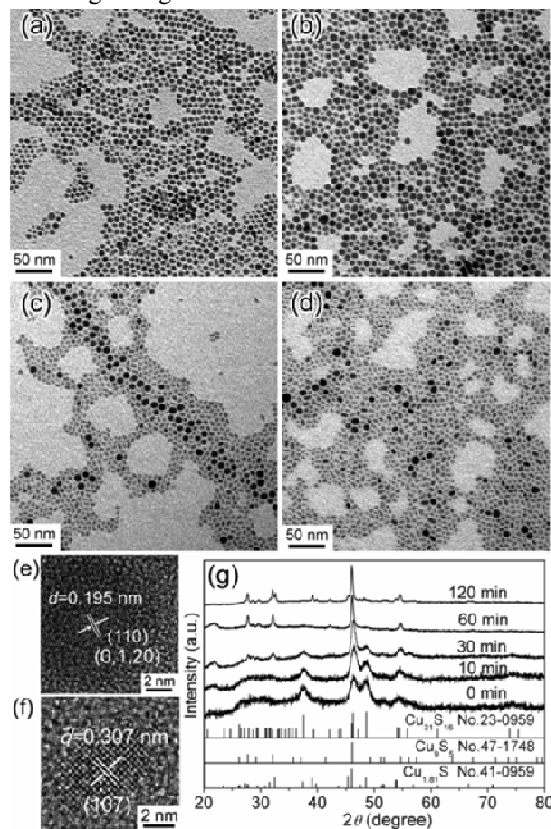
**Table 1.** Detailed experimental conditions for synthesis of different products and the corresponding results

| samples | metal precursors                                                                   | reaction temp (°C) | crystal phase                                                                       |
|---------|------------------------------------------------------------------------------------|--------------------|-------------------------------------------------------------------------------------|
| A       | 9 mmol $\text{Cu}(\text{acac})_2$ +<br>1 mmol $\text{Zn}(\text{acac})_2$           | 220                | monoclinic $\text{Cu}_{1.94}\text{S}$ and<br>rhombohedral $\text{Cu}_{1.8}\text{S}$ |
| B       | 9 mmol $\text{Cu}(\text{acac})_2$ +<br>1 mmol $\text{Zn}(\text{acac})_2$           | 240                | rhombohedral $\text{Cu}_{1.8}\text{S}$<br>and tetragonal $\text{Cu}_{1.81}\text{S}$ |
| C       | 9 mmol $\text{Cu}(\text{acac})_2$ +<br>1 mmol $\text{Zn}(\text{acac})_2$           | 260                | rhombohedral $\text{Cu}_{1.8}\text{S}$                                              |
| D       | 9 mmol $\text{Cu}(\text{acac})_2$ +<br>1.5 mmol $\text{Zn}(\text{acac})_2$         | 240                | rhombohedral $\text{Cu}_{1.8}\text{S}$                                              |
| E       | 9 mmol $\text{Cu}(\text{acac})_2$ +<br>1 mmol $\text{Cd}(\text{CH}_3\text{COO})_2$ | 240                | monoclinic $\text{Cu}_{1.94}\text{S}$ and<br>rhombohedral $\text{Cu}_{1.8}\text{S}$ |

## 3. RESULTS AND DISCUSSION

In general, monoclinic  $\text{Cu}_{1.94}\text{S}$  NCs have often been obtained using DDT as sulfur sources at a relatively high temperature, and the morphology can be controlled by varying the reaction parameters.<sup>34, 39</sup> In our previous work, we attempted to prepare  $\text{Cu}_{1.94}\text{S}$ -ZnS heterostructured NCs with small “head” while all other parameters were kept the same except the Zn/Cu precursor ratio was reduced to 1:9, unfortunately, no any heterostructured NCs were obtained and some monodispersed rice-shaped digenite NCs were produced.<sup>38</sup> To further study the influence of the foreign ions incorporating into the reaction system, a series of designed experiments have been performed (Table.1). Figs.1a-1d show the low-resolution TEM images of sample B obtained at different reaction time. The products obtained at 0 and 10 min are monodispersed spherical particles with an average diameter of  $6.6\pm0.4$  and  $7.6\pm0.6$  nm (See Fig. S1, ESI†), respectively. As the reaction time is prolonged to 60 and 120 min, some uniform rice-shaped NCs appear and become almost dominant in the products till 120 min, and the nanorices are monodispersed with an average length of  $5.9\pm0.7$  nm (see Fig.S1, ESI†). According to the XRD patterns shown in Fig.1g, all the diffraction peaks of the product obtained at 0 min indicate the formation of monoclinic djurleite ( $\text{Cu}_{1.94}\text{S}$ ) (JCPDS No.23-0959), which is in agreement with previous study.<sup>34</sup> As the reaction time is further prolonged, the diffraction intensity of the peak at  $2\theta=46.4^\circ$  increases but the diffraction intensity of the peaks at  $2\theta=37.6^\circ$  and  $48.6^\circ$  decreases and disappears at 60 min. The well-defined peaks in the XRD pattern of the product obtained at 60 min indicate the formation of pure rhombohedral digenite phase ( $\text{Cu}_{1.8}\text{S}$ ) (JCPDS No. 47-1748), which suggests that the crystal phase of the products can transform from monoclinic  $\text{Cu}_{1.94}\text{S}$  to rhombohedral  $\text{Cu}_{1.8}\text{S}$  phase induced by the presence of  $\text{Zn}^{2+}$  ions in the precursor solution. Moreover, four characteristic diffraction peaks at  $2\theta=27.7^\circ$ ,  $32.1^\circ$ ,  $46.1^\circ$  and  $54.6^\circ$  support the formation of rhombohedral  $\text{Cu}_{1.8}\text{S}$  phase in the XRD pattern of the product obtained at 120 min with some innegligible

diffraction peaks ascribed to tetragonal  $\text{Cu}_{1.81}\text{S}$  phase (JCPDS No. 41-0959). As a matter of fact, the  $\text{Cu}_{1.81}\text{S}$  phase also belongs to digenite phase in the Cu-S natural minerals. It is worthy to point out that the tetragonal  $\text{Cu}_{1.81}\text{S}$  phase is unstable, which can transform to rhombohedral  $\text{Cu}_{1.8}\text{S}$  phase after a few days under ambient conditions (shown in Fig.S2b, ESI†). By contrast, there is no any change in the XRD pattern of the product obtained at 60 min between the day of synthesis and the 90 days after synthesis (see Fig.S2a, ESI†). Based on the above experimental results (shown in Fig.1c), the nanospheres and nanorices coexist in the product obtained at 60 min. To further distinguish the two different shaped NCs, the corresponding HRTEM images are given in Figs.1e-f, respectively. Clear lattice spacings of 0.195 nm and 0.307 nm are observed in the HRTEM images of the nanospheres and nanorices, which can be ascribed to the (110)/(0,1,20) and (107) planes of rhombohedral  $\text{Cu}_{1.8}\text{S}$  phase, respectively. This result also suggests high crystallinity of the as-obtained products, which is in good agreement with the XRD results.



**Fig.1** TEM images of sample B obtained at different reaction time: (a) 0 min, (b) 10 min, (c) 60 min and (d) 120 min, and (e, f) HRTEM image of the spherical and rice-shaped NCs from (c), (g) XRD patterns of Sample B for different reaction time, and the vertical bars indicate the standard diffraction peaks of monoclinic  $\text{Cu}_{1.94}\text{S}$  (JCPDS card 23-0959), rhombohedral  $\text{Cu}_{1.8}\text{S}$  (JCPDS card 47-1748) and tetragonal  $\text{Cu}_{1.81}\text{S}$  (JCPDS card 41-0959).

Further evidence for determining the composition and phase of  $\text{Cu}_{2-x}\text{S}$  NCs comes from the LSPR results. Fig.2a shows the evolution of the UV-Vis-NIR absorption spectra of sample B. All the products collected at different reaction time exhibit a well-defined but broad NIR absorption band in the region from 900 to 1800 nm, which results from the LSPR effect of the non-stoichiometric copper sulfide NCs with some Cu-deficiencies.<sup>11</sup> In accompany with the phase transformation from monoclinic  $\text{Cu}_{1.94}\text{S}$  phase to rhombohedral  $\text{Cu}_{1.8}\text{S}$  phase, the plasmonic

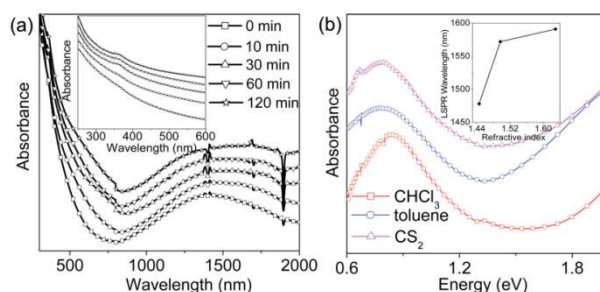
absorption band exhibits a red-shift from 1469 nm (0 min) to 1653 nm (120 min). Previous reports have shown that the plasmon absorbance shifts to lower wavelength with an increase of  $x$  in  $\text{Cu}_{2-x}\text{S}$  due to the increasing number of free carriers.<sup>29,40</sup> In this case, the red-shift and lowering in intensity of NIR LSPR absorption band can be attributed to the decrease of free carrier density, which may arise from the occupation of Cu-related vacant sites by  $\text{Zn}^{2+}$  ions to reduce Cu deficiencies. By fitting the NIR absorption band to a Gaussian function, thus the holes carrier density can be calculated according to Mie-Drude theory, the LSPRs frequency ( $\omega_{\text{sp}}$ ) can be expressed as follows:<sup>5</sup>

$$\omega_{\text{sp}} = \sqrt{\frac{\omega_{\text{p}}^2}{1 + 2\varepsilon_{\text{m}}} - \gamma^2}$$

Where  $\varepsilon_{\text{m}}$  represents the dielectric constant of the solvent (for chloroform,  $\varepsilon_{\text{m}}=4.8$  at 20 °C),  $\omega_{\text{p}}$  is the bulk plasmon frequency and  $\gamma$  is the linewidth of the plasmon resonance band. We take the propduct obtained at 0 min as an example, the LSPR frequency ( $\omega_{\text{sp}}$ ) is 0.85 eV and the linewidth of the LSPR band ( $\gamma$ ) is 0.17 eV, which was determined by fitting the NIR absorption band to a Gaussian function. As a result,  $\omega_{\text{p}}$  is estimated to be about 2.82 eV. The relationship between the carrier density ( $N_{\text{h}}$ ) and the bulk plasmon frequency ( $\omega_{\text{p}}$ ) can be expressed by using the following equation:<sup>5</sup>

$$\omega_{\text{p}} = \sqrt{\frac{N_{\text{h}}e^2}{\varepsilon_0 m_{\text{h}}}}$$

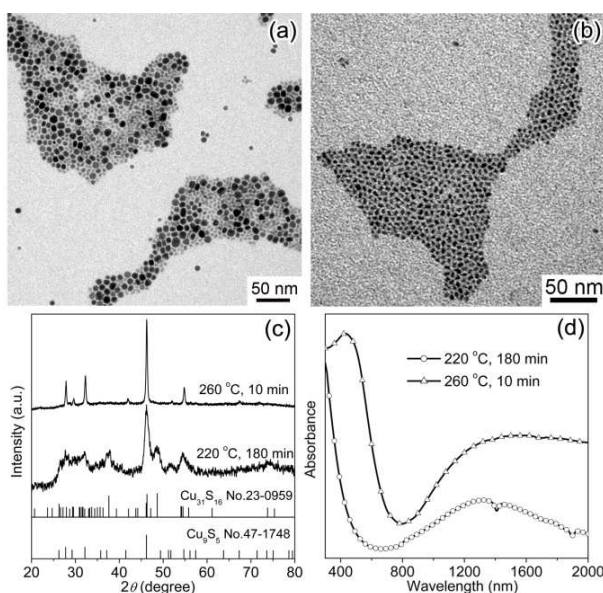
where  $e$  is the electron charge,  $\varepsilon_0$  is free space permittivity and  $m_{\text{h}}$  is the hole effective mass (approximated as 0.8  $m_0$ , where  $m_0$  is electron mass). From the above equation,  $N_{\text{h}}$  is estimated to be  $4.68 \times 10^{21} \text{ cm}^{-3}$ , which is of the same order of magnitude as the value of copper chalcogenide films reported previously.<sup>5</sup> Similarly, the holes carrier density of other products obtained at different reaction time is calculated to be  $4.0\text{-}4.4 \times 10^{21} \text{ cm}^{-3}$ , and the important parameters, such as LSPR frequency ( $\omega_{\text{sp}}$ ), the bulk plasmon frequency ( $\omega_{\text{p}}$ ) and the carrier density ( $N_{\text{h}}$ ) are



**Fig.2** (a) NIR LSPR absorption spectra of sample B for different reaction time, and the inset shows the UV-Vis absorption spectra in the region of 250-600 nm; (b) LSPR absorption spectra of sample B obtained at 30 min dispersed in three different solvents, and the inset shows the LSPR maximum with increasing solvent refractive index.

summarized in Table.S1†, which further interprets the plasmonic behavior of the products obtained at different reaction time. The holes carrier density shows a strong dependence on the Zn/Cu atomic ratio, which can be determined by the ICP-OES results (Fig.S3, ESI†). Based on the aforementioned results, the fitting LSPR absorption spectra on the energy scale are given in Fig.S4†, and the linewidth of the LSPR absorbance band is broader with the increasing

reaction time, which may arise from the composition distribution and surface scattering of free carriers of the nanoparticles due to smaller size and morphology change.<sup>11, 41</sup> Except the LSPR absorbance in the NIR region, it is worthy to mention that the absorbance in the region of 300-400 nm becomes more evident with the reaction time increasing from 0 to 120 min (inset of Fig.2a), which may be attributed to the photonic transition between the Zn-related energy level and the valence band of the host NCs. The dependence of the NIR plasmon absorbance upon the refractive index of the solvents is given in Fig.2b to demonstrate the LSPR behavior of sample B. It can be seen that the NIR plasmon absorbance shows an obvious red-shift with increasing refractive index, as expected for LSPR absorbance.<sup>5, 42</sup> Compared those experimental results obtained above to the pure  $\text{Cu}_{1.94}\text{S}$  NCs synthesized in the same reaction condition (Fig.S5, ESI†), it is evident that  $\text{Zn}^{2+}$  ions play a crucial role in the phase and morphology transformation of the as-obtained products. Herein, the DDT was used not only as the sulfur source but also as the surfactant, which could form chemical bonds to both host NCs and impurity atoms in the solution. Moreover, if the reaction temperature is high enough, the  $\text{Cu}^+$  could act as “fluid”, flowing through the lattice of the  $\text{Cu}_{2-x}\text{S}$  NCs.<sup>34</sup> As a result, when a small quantity of  $\text{Zn}^{2+}$  ions were present in the precursor solution, the  $\text{Zn}^{2+}$  ions could diffuse into the  $\text{Cu}_{2-x}\text{S}$  NCs, which resulted in the transformation in both of the phase and morphology.

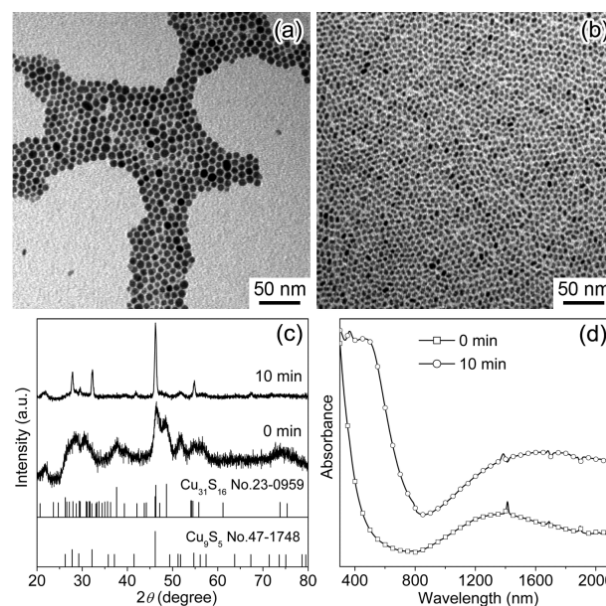


**Fig.3** TEM images the products obtained under different reaction temperature: (a) 220 °C (180 min); (b) 260 °C (10 min); (c) the corresponding XRD patterns together with the standard lines at the bottom; (d) LSPR absorption spectra of the products dispersed in chloroform.

To determine the effects of reaction temperature on the phase and morphology transformation and the growth of digenite NCs, various control experiments were performed. Fig.3 shows the TEM images, XRD patterns and LSPR spectra of the products obtained at different reaction temperatures. It is well known that the reaction temperature is an important factor for controllable synthesis of colloidal inorganic NCs.<sup>43-46</sup> As shown in Figs.3a-b, the vast majority of sample A is large-sized quasi-spherical NCs even if the reaction time is prolonged to 180 min when the reaction temperature is decreased to 220 °C. In stark contrast, all the products exhibit a rice shape in the sample C

obtained at only 10 min. The corresponding XRD patterns shown in Fig.3c demonstrate that the sample A obtained at 180 min is composed of monoclinic  $\text{Cu}_{1.94}\text{S}$  phase and rhombohedral  $\text{Cu}_{1.8}\text{S}$  phase, but all the diffraction peaks of sample C match well with that of rhombohedral  $\text{Cu}_{1.8}\text{S}$  phase (JCPDS No. 47-1748). Obviously, higher reaction temperature is in favor of phase and morphology transformation, which is governed by the thermodynamics growth process. As shown in Fig 3d, the LSPR peak of sample C at 10 min red-shifts from 1370 nm to 1630 nm as compared to that of sample A at 180 min, which indicates the decrease of the free holes density in sample C. Moreover, a significant absorption band in the region of 400-500 nm is observed in the sample C. These results suggest that higher temperature can accelerate the fluidity of the  $\text{Cu}^+$ , which makes the  $\text{Zn}^{2+}$ -related diffusion become more quickly, leading to the transition in both of phase and morphology in advance.

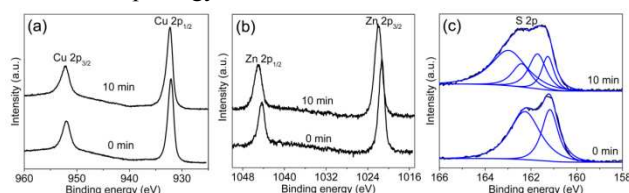
Apart from the reaction temperature, the  $\text{Zn}^{2+}$  concentration in the precursor solution has a strong influence on the phase and morphology transformation of the products. Figs.4a-b show the TEM images of sample D with the Zn/Cu precursor molar ratio of 1:6, and the morphology of the as-obtained products transforms from nanospheres completely when the reaction time is increased from 0 to 10 min. Accordingly, the XRD pattern of sample D at 10 min can be indexed as rhombohedral  $\text{Cu}_{1.8}\text{S}$  phase (shown in Fig.4c). Similar to the LSPR result of the products obtained at different reaction temperatures, the NIR plasmonic absorption bands of sample D shown in Fig.4d exhibit a red-shift from 1416 nm to 1752 nm as the reaction time is increased from 0 to 10 min, and an absorption band in the region of 400-500 nm is also observed in sample D obtained at 10 min.



**Fig.4** TEM images of sample D obtained at (a) 0 min and (b) 10 min, and (c) XRD patterns, (d) NIR LSPR absorption spectra of sample D obtained at 0 min and 10 min.

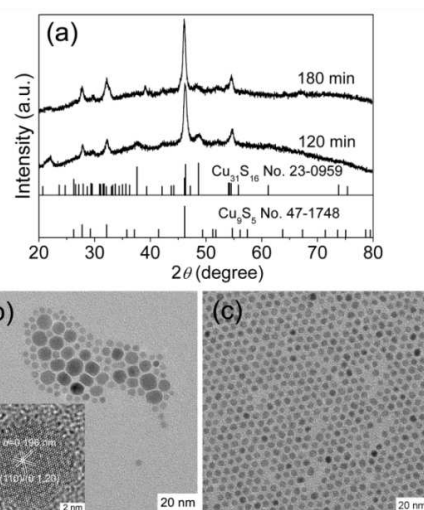
To further determine the composition and the actual Zn/Cu atomic ratio of sample D obtained at different reaction time, the corresponding XPS spectra were measured, and the corresponding result is depicted in Fig.5. The Cu  $2p_{3/2}$  and Cu  $2p_{1/2}$  peaks are symmetric and narrow (Fig.5a), and the satellite peaks related with Cu(II) have not been observed, which is

indicative of monovalent copper.<sup>30</sup> The XPS spectra of Zn 2p are composed of two peaks assigning to Zn 2p<sub>3/2</sub> and Zn 2p<sub>1/2</sub> (Fig.5b), respectively. A slightly shift of Cu 2p<sub>3/2</sub> and Zn 2p<sub>3/2</sub> towards high binding energy with the increasing reaction time, indicating the change of the coordination conditions for Zn<sup>2+</sup> and Cu<sup>+</sup>. According to the previous reports, the shift of Cu 2p<sub>3/2</sub> can be attributed to the formation of digenite phase, and the shift of Zn 2p<sub>3/2</sub> is related with the coordination of Zn<sup>2+</sup> with S<sup>2-</sup>.<sup>40, 47</sup> As shown in Fig.5c, the S 2p peak of sample D obtained at 0 min can be fitted into two doublets centered at 161.2 and 162.3 eV, corresponding to the sulfides and the DDT bound to Cu, respectively.<sup>48</sup> As for the sample D obtained at 10 min, the XPS peak can be fitted into multiple peaks, suggesting a greater variety of sulfur species due to the formation of digenite phase.<sup>40</sup> The atomic ratio of Zn:Cu determined by the XPS result indicates that the Zn:Cu atomic ratio increases from 0.26:1 to 0.36:1 with the reaction time increasing from 0 to 10 min. The aforementioned results indicate that higher Zn<sup>2+</sup> concentration in the precursor solution is also beneficial to the phase and morphology transformation.



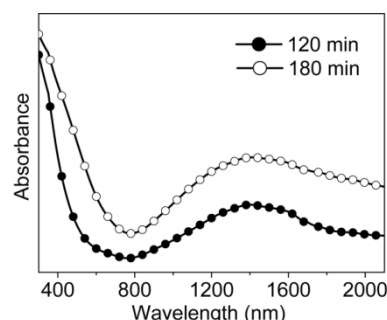
**Fig.5** XPS spectra of sample D obtained at 0 min and 10 min: (a) Cu 2p, (b) Zn 2p, (c) S 2p.

It is notable that the phase and morphology transformation still takes place when larger metal ions such as Cd<sup>2+</sup> are used to replace Zn<sup>2+</sup> ions in the reaction system. Fig.6 shows the XRD patterns and TEM images of sample E obtained at 120 min and 180 min. The XRD patterns shown in Fig.6a indicate that the rhombohedral Cu<sub>1.8</sub>S phase is dominant with some innegligible diffraction peaks ascribed to monoclinic djurleite NCs. The corresponding TEM images are displayed in Figs.6b and 6c, and the large-sized quasi-spherical nanoparticles and small-sized nanospheres coexist in the product obtained at 120 min. To distinguish the composition of the different-sized particles, the HRTEM image of the large-sized nanoparticles is shown in the inset of Fig.6b. The as-obtained products are single-crystalline with a clear lattice plane spacing of 0.196 nm, which matches well with the (110) or (0,1,20) lattice distance of rhombohedral Cu<sub>1.8</sub>S phase. The products obtained at 180 min (see Fig.6c) exhibit a spherical shape with a mean diameter of 5.0±0.4 nm (Fig.S6, ESI†). As compared to sample B, the phase and morphology transformation of sample E needs longer time, which indicates that more energy is required to overcome larger activation barrier for Cd<sup>2+</sup>-related diffusion. The difference between the atomic size of Cu<sup>+</sup> and Cd<sup>2+</sup> is larger than that of Zn<sup>2+</sup> and Cu<sup>+</sup>, which makes the diffusion of Cd<sup>2+</sup> become more difficult, thus the incorporation amount of Cd<sup>2+</sup> ions become relatively low. The XPS spectra of sample E (Fig.S7, ESI†) confirm the presence of Cu, S and Cd elements. To further demonstrate the incorporation of Cd<sup>2+</sup> ions into Cu<sub>1.94</sub>S lattice, the energy dispersive X-ray (EDX) and element mapping analysis inside a scanning electron microscope (SEM) also indicate the presence of Cd, Cu and S elements in our products (Fig.S8, ESI†), and the atomic ratio of Cu to Cd is 28:1. This result indicates that the small amount of Cd<sup>2+</sup> plays an important role in the phase and morphology transformation.



**Fig.6** (a) XRD patterns together with the standard lines and TEM images of sample E obtained at different reaction time: (b) 120 min, inset shows the HRTEM image and (c) 180 min.

Fig.7 displays the LSPR absorption spectra of sample E obtained at 120 and 180 min, and an obvious broad absorption peak is observed in the NIR region, which is similar to that of sample B. In contrast, there is no evident absorption peak in the UV-Vis region, which indicates that no photonic transition takes place between the Cd-related energy level and the valence band of digenite NCs due to the less amount of Cd<sup>2+</sup> diffusion into the NCs. Moreover, a slight red-shift of LSPR peak is observed in the plasmonic absorption spectra of sample E obtained at 180 min, which also arise from the decrease of free holes density in the as-obtained products.



**Fig.7** NIR LSPR absorption spectra of sample E obtained at 120 min and 180 min.

#### 4. CONCLUSIONS

In summary, a simple one-pot heating route was developed to prepare high-quality rhombohedral digenite Cu<sub>1.8</sub>S NCs, which were transformed from monoclinic djurleite Cu<sub>1.94</sub>S in the presence of foreign metal ions (Zn<sup>2+</sup> and Cd<sup>2+</sup>). Accompanying with the phase transformation process, the morphology of the products takes place by extending the reaction time and enhancing the reaction temperature. The phase and morphology transformation induced by the foreign metal ions has also been studied by the LSPR absorption spectra in the NIR region, and the LSPR behavior exhibits a strong dependence on the incorporation amount of foreign metal ions, which bring about the change of free holes density

and the number of copper deficiencies. This approach provides a new pathway to control the phase, morphology and the cationic deficiency of Cu<sub>2-x</sub>S NCs.

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## Notes and references

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## Notes

The authors declare no competing financial interest.

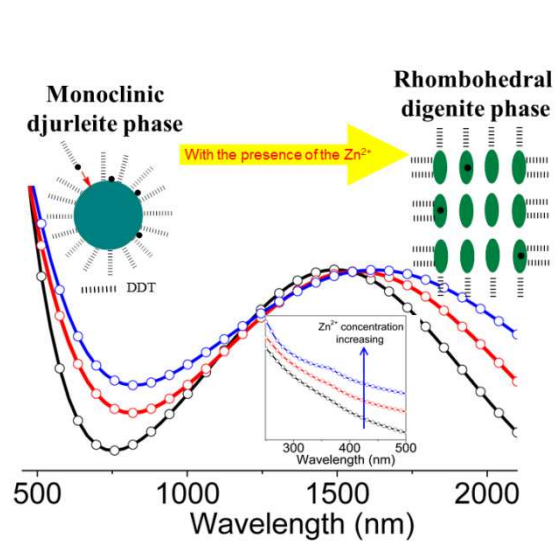
## †Electronic Supplementary Information (ESI)

Size distribution histograms of sample B and E for different reaction time, XRD patterns of sample B for the day of synthesis and after 90 days, ICP data and the relationship between the Zn/Cu atomic and the reaction time of sample B, the fitting NIR LSPR absorption spectra on the energy scale of sample B for different reaction time according to Gaussian function and the XPS spectra and EDX results of sample E. This material is available free of charge via the internet at <http://pub.rsc.org>.

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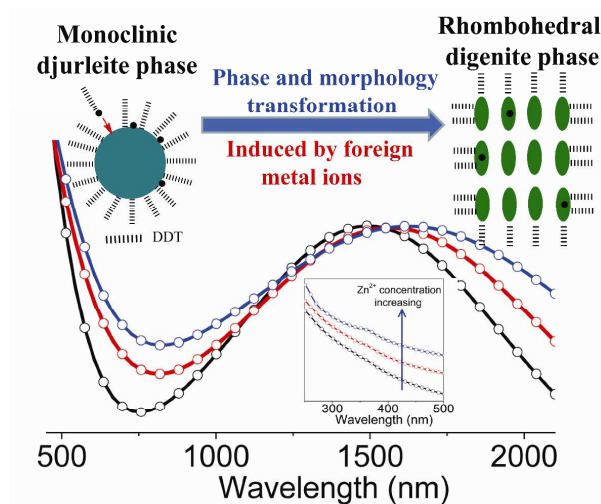
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## Table of Contents



# Synthesis of $\text{Cu}_{2-x}\text{S}$ Nanocrystals Induced by Foreign Metal Ions: Phase and Morphology Transformation and Localized Surface Plasmon Resonance

Haihang Ye, Aiwei Tang, Chunhe Yang, Kai Li, Yanbing Hou and Feng Teng



Phase transformation from monoclinic djurleite phase to rhombohedral digenite phase takes place by addition of different amounts of foreign metal ions, such as  $\text{Zn}^{2+}$  and  $\text{Cd}^{2+}$  into the reaction mixture, in which the morphology is also changed. The LSPR absorption wavelength is dependent on the addition amount of  $\text{Zn}^{2+}$  and  $\text{Cd}^{2+}$  ions.