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**Facile synthesis of CuSe nanoparticles and high-quality
single-crystal two-dimensional hexagonal nanoplatelets with tunable
near-infrared optical absorption**

Yimin Wu¹, Ilia Korolkov², Xvsheng Qiao¹, Xianghua Zhang², Jun Wan¹, Xianping
Fan^{1*}

*¹State Key Laboratory of Silicon Materials, School of Materials Science and
Engineering, Zhejiang University, Hangzhou 310027, P.R. China*

*²Laboratory of Glasses and Ceramics, Institute of Chemistry, CNRS-Université de
Rennes I, campus de Beaulieu, 35042 Rennes cedex, France*

Abstract

A rapid injection approach is used to synthesize the copper selenide nanoparticles and two-dimensional single crystal nanoplates. This technique excludes the use of toxic or expensive materials, increasing the availability of two-dimensional binary chalcogenide semiconductors. The structure of the nanocrystals has been studied and the possible formation mechanism of the nanoplates has been proposed. The optical absorption showed that the nanoplates demonstrated wide and tuneable absorption band in the visible and near infrared region. These nanoplates could be interesting for converting solar energy and for nanophotonic devices operating in the near infrared.

Keywords: copper selenide; nanoparticles and nanoplates; rapid injection approach;
optical absorption

1. Introduction

Recently, extensive attention has been paid to the preparation and characterization of metal-selenides mostly due to their unique electronic properties such as high concentration and mobility of electrons and temperature tunable band-gap [1-6]. These properties are of crucial importance for the design of nanoscale electronic components operating in near infrared [7, 8]. Among others, copper selenides (CS) is a particularly interesting class of materials due to its ability to form various stoichiometric and nonstoichiometric compounds. For instance, Riha et al. showed the possibility of tuning the electronic structure thanks to the controllable surface oxidation of Cu_2Se (copper rich) nanoparticles, which allows a transition from Cu_2Se monoclinic crystal cell to $\text{Cu}_{1.8}\text{Se}$ cubic cell [9]. A detail description of the Cu_2Se crystal structure can be found elsewhere [10, 11]. At the same time, CuSe_2 (copper poor) compounds were studied as a possible anion conductors due to the dominant chalcogen character at the Fermi level and consequent absence of electronic correlation inherent in copper rich compounds [12]. Between copper rich and copper poor compounds, a variety of stable and metastable phases such as Cu_7Se_4 , Cu_3Se_2 , CuSe exist in different crystallographic forms: orthorhombic, cubic, tetragonal, hexagonal etc [13]. It has been reported that copper selenides are p-type semiconductors whose thermal stability and band gap strongly depend on the stoichiometry and phase [14, 15]. The tunability of the electronic properties upon the stoichiometry opens a vast field of possible applications such as solar cells, optical filters, nanoswitches, thermoelectric and photoelectric energy convertors,

superconductors [16-20].

Many attempts to prepare metal selenides nanomaterials in different stoichiometries and morphologies have been reported. The solution-phase synthetic method for CuSe was successfully utilized to obtain hexagonal nanoplates [21]. Synthesis route involving thermal decomposition of $\text{Cu}(\text{Se}=\text{CNEt}_2)_2$ in refluxing 4-ethylpyridine solutions has also been described [22]. Platelet shaped nanostructures of CuSe have been also synthesized through solution phase reaction [23, 24]. The surfactant-thermal method for synthesis of metal chalcogenides attracted also an attention. The surfactant media could serve as a cheaper and multifunctional analogue of the ionic liquids, demonstrating suitability for the obtaining of metal-chalcogenide quantum dots, quantum wires, nanoplates and bulk crystals in a wide variety of stoichiometries altering synthesis time and surfactant solvent [25-28]. This method has demonstrated its efficiency also for synthesis of complex quaternary two-dimensional chalcogenides for photocatalytic and photovoltaic applications [29, 30]. However, the above mentioned and widely used methods are either toxic or complicated, time-consuming or energy inefficient. In this work, we report a new rapid-injection approach to prepare CuSe nanoplates with high quality single-crystal and two dimensional nanostructure. The mechanism of forming two-dimensional structure from nanoparticles will be proposed. To the best of our knowledge, this is the first report of this particular synthesis route for CuSe nanoplates which match the primitive hexagonal phase. This study opens a new way for energy-efficient, environment friendly and low cost controllable synthesis of binary chalcogenides.

2. Experimental

The Cu_xSe nanocrystals (NCs) were produced via a rapid injection approach [30] by reacting $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ with an excess of selenium precursor in the presence of hexadecylamine (HDA). In a typical preparation, 1.5 mmol $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (0.256g, 99.99%, aladdin), 0.3 mmol $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (0.113g, 98%, aladdin), 15 mmol HDA (3.622g, 90%, aladdin) and 30 mL octadecene (ODE, 90%, Aldrich) were introduced inside a three-neck flask and heated to 200 °C under argon flow until all precursors were dissolved. Afterward, the obtained yellowish transparent solution was cooled to 180 °C and maintained under Ar flow for half an hour to remove oxygen, water and other volatile impurities. Then 12 mL ODE-Se (0.8 M) solution was rapidly injected through a syringe. The excess selenium led to the instantaneous formation of nuclei of metal selenides, guarantees the uniformity of grain size and hinders the growth behavior during the grain nucleation. And it could also insure a complete reaction. The mixture was maintained at 180 °C from 0 min up to 60 min. Afterward, the solution was rapidly cooled down to room temperature in air. The generation of Cu_xSe nanocrystallines was evidenced by the color change of the mixture from an initial light orange to eventually deep green color of the solution. To remove the weakly bound HDA, 9 ml of oleic acid (OA, 90%, Aldrich) was added to the mixture during the cooling step at about 70°C [31]. And finally the nanocrystals were isolated and purified using chloroform and isopropanol to complete the standard solvent/nonsolvent precipitation/redispersion procedure and were dried under vacuum at 40°C for about 12 hr.

Transmission electron microscopy (TEM) images were obtained with a Philips CM200 field emission microscope. High resolution transmission electron microscopy (HRTEM) images with selected area electron diffraction (SAED) patterns and Energy Dispersive Spectrometer (EDS) data were obtained with a FEI Tecnai G2 F20 field emission microscope. A Hitachi S-4800 field emission scanning electron microscope was used to observe the morphology. X-ray diffraction (XRD) analysis was carried out on a PANalytical B.V. Empyrean 200895 X-ray diffractometer. UV–VIS absorption spectra were taken with a SHIMADZU UV-3150 spectrophotometer.

3. Results and discussion

Fig.1 shows the XRD patterns of the copper selenides nanoparticles and nanoplates which were synthesized at 180°C for different time with the presence of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$. Wide and relatively weak diffraction peaks can be clearly observed for nanocrystals obtained after less than 10 min synthesis. Moreover their patterns do not accurately correspond to CuSe JCPDS card. This is due to the presence of the big amount of relatively small nanocrystals with slight deviation from the stoichiometry. Extending of the reaction time up to 60 min leads to the enhancement of (006) diffraction peak attributed to hexagonal CuSe. The increase of diffraction intensity in several orders of magnitude and the narrowing of the diffraction peaks indicated a rapid growth of CuSe nanocrystals from smaller aggregates. It is worth mentioning that no XRD peaks of the Se crystals or the other secondary phase were detected.

Fig.2 shows the TEM images of the copper selenides nanoparticles and

nanoplates which were synthesized at 180°C for different time with the presence of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$. The average size of the spherical nanocrystals increased from 10 nm to about 30 nm after 10 min synthesis. These spherical nanocrystals were eventually transformed to regular-shape triangular and hexagonal nanoplates after 60 min synthesis. Inserts in fig.2 a and b show the measured size distribution confirming that 10 min synthesis was enough to obtain quasi-spherical CuSe nanocrystals with narrow size distribution. HRTEM images (Fig.2 d, e) show that the typical lattice spacing of the CuSe nanoparticles and nanoplates is 3.56 Å, which is in good agreement with the standard value for (220) plane of CuSe hexagonal phase. The SAED pattern (insert of fig.2c) demonstrates ordered diffraction spots which could be attributed to the primitive hexagonal structure of copper selenide with the zone axis along the (006) plane direction. This indicates that the nanoplates were well crystallized and have a single-crystal nature. Fig.2f shows the SEM image of the copper selenides nanoplates which were synthesized at 180°C for 60 min. The regular hexagonal and triangle plates with about 50 nm thickness could be observed.

Fig.3 shows energy dispersive spectroscopy (EDS) of the copper selenides nanoparticles and nanoplates which were synthesized at 180°C for different time with the presence of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, which indicated the absence of Al inside the nanoparticles. The presence of Al^{3+} tends to attract not only Cl^- but also negatively charged selenium ions that lead to the slower growth of CuSe nanoplates. From EDS results, it can be estimated that the Cu/Se ratio of the nanoparticles which were synthesized at 180°C for 0 min was 50/50. The nanoparticles which were synthesized

at 180°C for 10 min show slight deviation from the stoichiometry (47/53). A significant Se excess with a ratio of 37/63 could be observed for the copper selenides nanoplates which were synthesized at 180°C for 60 min. However, XRD result (Fig.1) shows that only CuSe hexagonal phase was formed in the nanoplates which were synthesized at 180°C for 60 min, which indicated that nanoplates followed CuSe hexagonal phase even in case of Se-excess.

Copper selenide is a well-known p-type semiconductor possessing a direct band gap with E_g depending on the stoichiometry and varying from 1.0 eV to 2.0 eV. [13] According to Chen et al. [8], the Cu vacancies (V_{Cu}) created a shallow acceptor level close to the valence band. This self-doping effect was responsible for p-type conductivity of CuSe. For the elucidation of the electronic properties, UV-VIS-NIR absorption spectra were recorded. Since copper selenide is a direct band semiconductor the optical absorption data could be calculated from diffuse reflectance data using Kubelka–Munk equations: $F(R)=\alpha/\Lambda=(1-R)^2/(2R)$, where R is the reflectance, α and Λ are the absorption and scattering coefficients, respectively [32]. Fig.4 shows the plots of $[F(R)hv]^2$ versus energy ($h\nu$) for the copper selenides nanoparticles and nanoplates which were synthesized at 180°C for different time. It was estimated E_g is 1.29eV for 0 min, 1.18eV for 10 min and 1.52eV for 60 min. The red shift for nanocrystals obtained after 10 min reaction can be explained from the point of view of quantum confinement, since the size of 0 min synthesized nanocrystals was about 10 nm, the same order of magnitude as the De Broglie wavelength of a free electron. Therefore the quantum confinement effect can be

significant to increase the band gap width of nanocrystals, compared to a bulk material. Increase of nanocrystal size reduces the influence of quantum confinement on the electronic structure. However this does not explain the strong blue shift for the 60 min synthesized nanocrystals. In fact, in the above mentioned EDS pattern (Fig.3), one can see that 60 min synthesized nanocrystals possess an excess of Se, which can lead to the formation of Se_{Cu} type of defects. The increase of the electronegative element (Se) in a CuSe crystal cell in its turn causes significant widening of the band gap. This result provides a possibility of controlling the E_g simply by controlling the synthesized time.

In order to determine the role of Al^{3+} in CuSe nanocrystals growth, the copper selenides nanoparticles and nanoplates were synthesized in the absence of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$. Fig.5 shows the XRD patterns of the copper selenides nanoparticles and nanoplates synthesized at 180°C for different time without the presence of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$. The 0 min synthesized sample corresponds to an unknown phase and consists of a big amount of small crystals. However, obvious (006) diffraction peak corresponding to CuSe hexagonal phase can be observed in the 10 min synthesized sample, which indicated a rapid growth of hexagonal CuSe crystals in the absence of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$. Fig.6 shows the TEM images of the copper selenides nanoparticles and nanoplates synthesized at 180°C for different time without the presence of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$. The 0 min synthesized sample shows the regular spherical nanoparticles with narrow size distribution. These spherical nanoparticles were rapidly transformed to regular-shape triangular and hexagonal CuSe nanoplates only

after 10 min synthesis, which indicated that the absence of Al^{3+} leads to faster growth of CuSe nanoplates.

It was demonstrated that spherical nanoparticles were formed initially and then these particles are progressively aggregated together to form triangular and hexagonal nanoplates. The likely mechanism of nanoplates assembly is proposed in fig.6. Oriented attachment involves spontaneous self-organization including rotation and migration of adjacent particles, thus they share a common crystallographic orientation, followed by joining of these particles at a planar interface [33, 34]. Aggregation of nanocrystals in nanoplates is energetically beneficial since it reduces the overall length of nanocrystal-ligand interface and therefore leads to the reduction of Gibbs energy by removing surface-associated states. As it can be seen from HRTEM image of the intermediate product (Fig.2d), the nanocrystals evidently demonstrate mutual orientation and aggregation according to the oriented attachment mechanism leading to the formation of two-dimensional single crystal nanoplates.

4. Conclusions

The copper selenide nanoparticles and high-quality single-crystal two-dimensional hexagonal nanoplatelets have been synthesized by a rapid injection approach. The possible growth mechanism of the nanoplates is based on the “oriented attachment” nanoparticles. During the synthesis process, Al^{3+} ions in the solution have a significant impact on the growth rate of the nanoplates. It is demonstrated that CuSe band gap can be widely tuned simply by modifying the synthesized time. This gives

the possibility to adjust this important parameter of this interesting semiconductor according to the targeted applications.

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Caption of figures

Fig.1 XRD patterns of the copper selenides nanoparticles and nanoplates synthesized at 180°C for different time with the presence of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$.

Fig.2 TEM images of the copper selenides nanoparticles and nanoplates synthesized at 180°C for (a) 0 min, (b) 10 min, (c) 60 min. (d) HRTEM images of (a), (e) HRTEM images of (c), and (f) SEM images of copper selenide hexagonal nanoplates synthesized at 180°C for 60 min.

Fig.3 Energy dispersive spectroscopy (EDS) of the copper selenides nanoparticles and nanoplates synthesized at 180°C for different time with the presence of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$.

Fig.4 Absorption spectra of the copper selenides nanoparticles and nanoplates synthesized at 180°C for different time.

Fig.5 XRD patterns of the copper selenides nanoparticles and nanoplates synthesized at 180°C for different time without the presence of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$.

Fig.6 TEM images of the copper selenides nanoparticles and nanoplates synthesized at 180°C for (a) 0 min, (b) 10 min, and (c) 60 min without the presence of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$.

Fig.7 Growth mechanism of the copper selenide nanoplates via the “oriented attachment”.

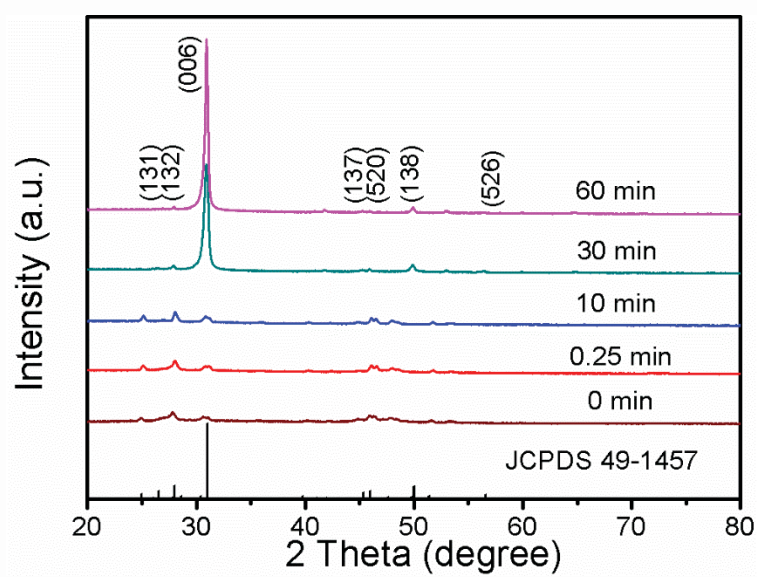


Fig.1

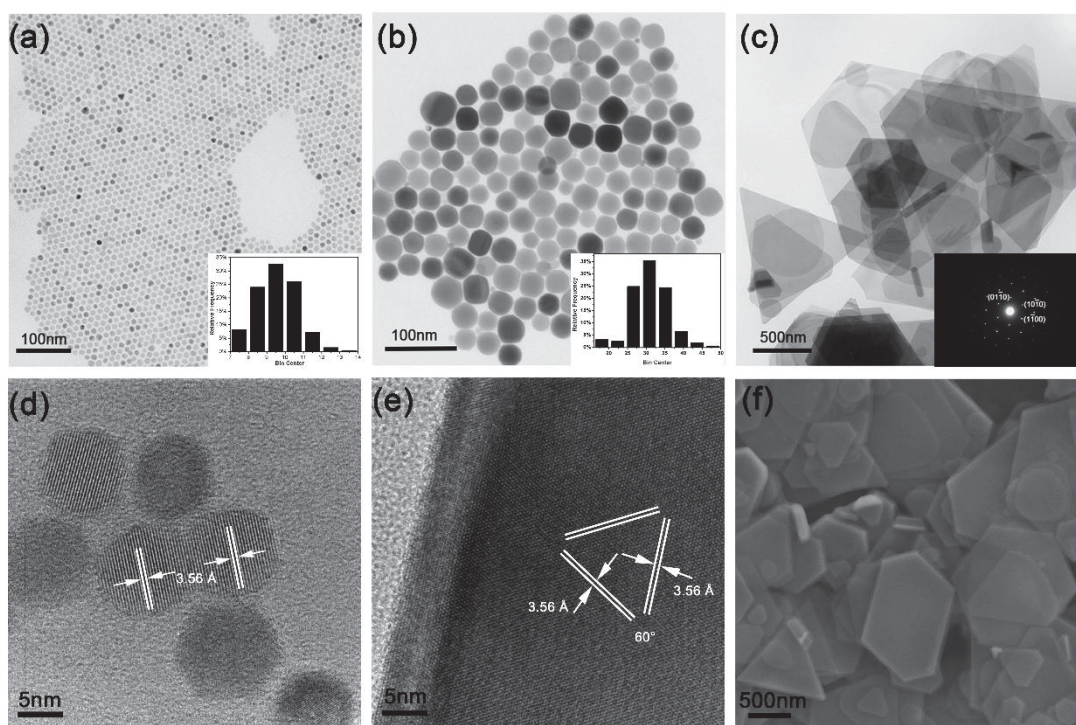


Fig.2

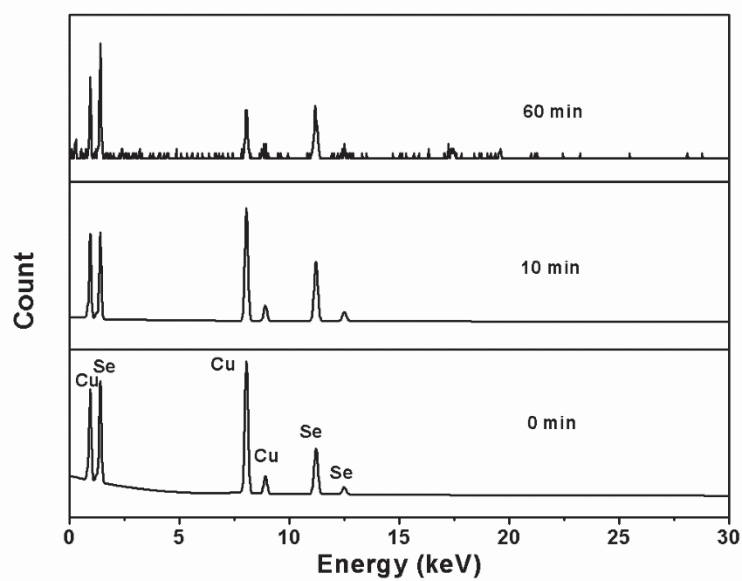


Fig.3

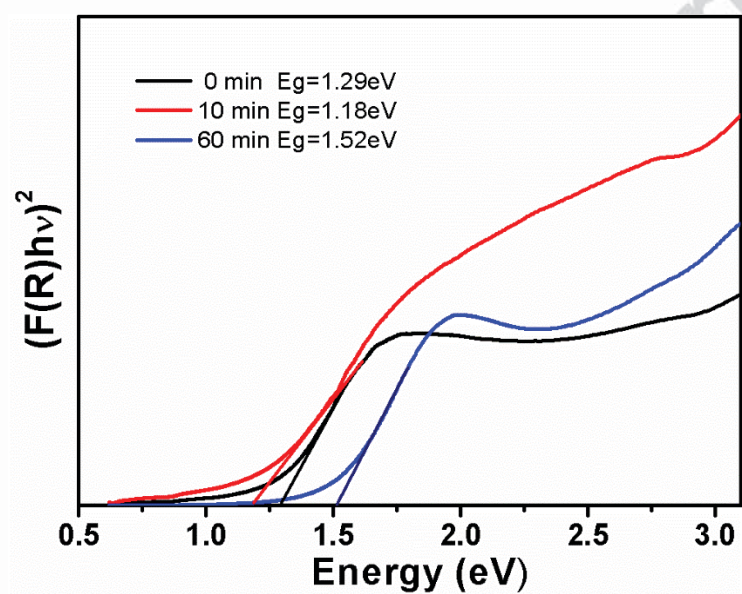


Fig.4

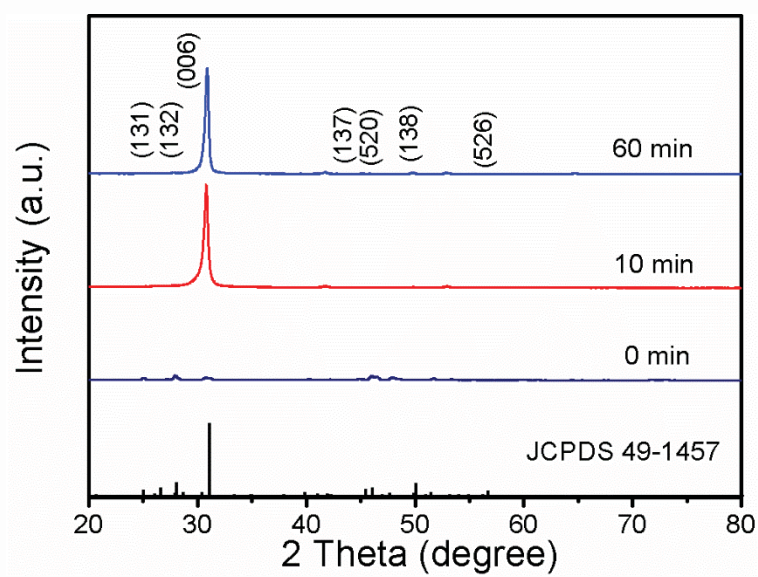


Fig.5

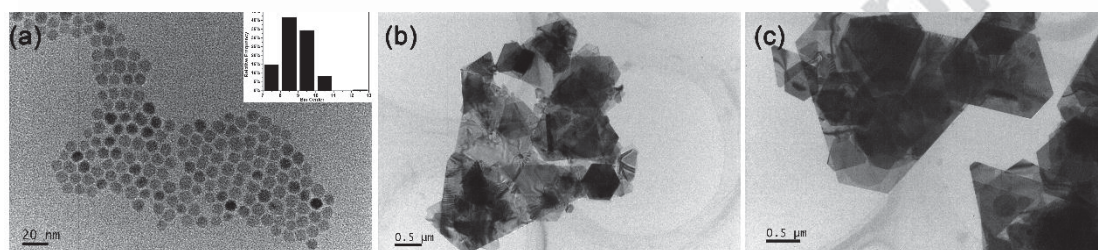


Fig.6

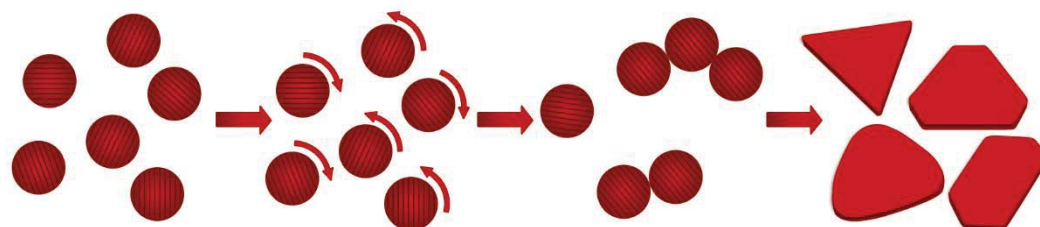
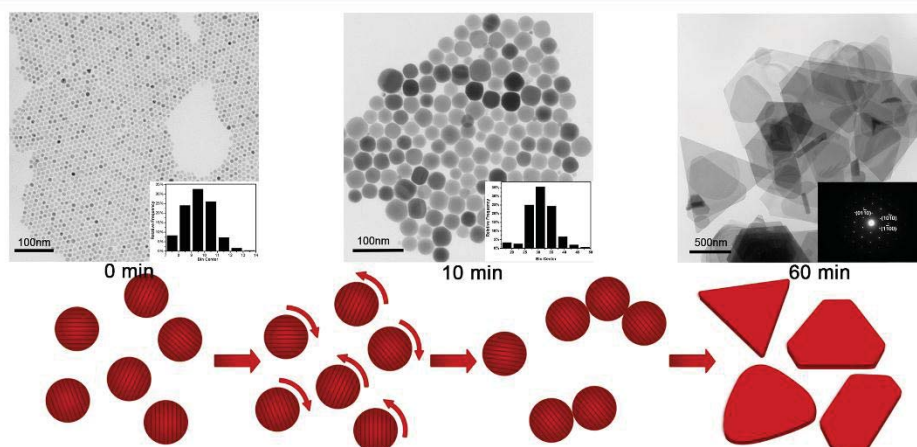


Fig.7

Graphical Abstract



TEM images of the copper selenides nanoparticles and nanoplates synthesized at 180°C for 0 min, 10 min, 60 min. And the growth mechanism of the copper selenide nanoplates via the “oriented attachment”.

Highlights:

- CuSe nanoparticles and nanoplates are synthesized by a rapid injection approach.
- CuSe band gap can be widely tuned simply by modifying the synthesized time.
- Al^{3+} ions have a significant impact on the growth rate of the nanoplates.
- Growth mechanism of the CuSe nanoplates is based on the “oriented attachment”.