

Controllable Synthesis of Cu₂S Nanocrystals and Their Assembly into Superlattice

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Supporting Information

Experimental Details:

In a typical synthesis of 8.2 nm **diameter** Cu₂S circular nanocrystals, Cu(NO₃)₂·3H₂O (0.24 g, 0.001 M) was dissolved in deionized water (20 ml) to form a clear blue solution. Then sodium acetate (0.82 g, 0.010M) and acetic acid (0.60 ml) were also introduced into the solution. After keeping stirring for 15 min, the solution was transferred into a Teflon-lined autoclave of 40 ml capacity and dodecanethiol (3 ml) was added finally into the solution. The autoclave was sealed and heated at 200 °C for 6 h. After the autoclave was cooled to room temperature, the product was collected and the water in the autoclave was discarded. Then 20 ml ethanol was introduced and the product was washed and precipitated. The mixture was centrifuged for 5 min at 4800 rpm, and the precipitate was collected.

For hexagonal Cu₂S nanoplates, KCl (1.0 g) was introduced into the Cu(NO₃)₂ solution, without sodium acetate and acetic acid.

For elongated nanocrystals, only 0.12g Cu(NO₃)₂·3H₂O was dissolved in deionized water (20ml) and neither sodium acetate nor KCl was added. After keeping stirring for 15 min, the solution was transferred into a Teflon-lined autoclave of 40 ml capacity. Then toluene (5 ml) and dodecanethiol (0.5 ml) were added into the solution. The autoclave was sealed and heated at 200 °C for 20 h. After the autoclave was cooled to room temperature, the product was treatment as **previously** described.

The Cu₂S nanocrystals and assemblies were determined by using transmission electron microscopy (TEM, JEOL JEM 1200EX working at 100 kV) and high-**resolution** transmission electron microscopy (HRTEM, FEI Tecnai G2 F20 S-Twin working at 200 kV). The phases of the products were determined by XRD on a Bruker D8 Advance X-ray powder diffractometer with Cu K α radiation ($\lambda=1.5418$ Å).

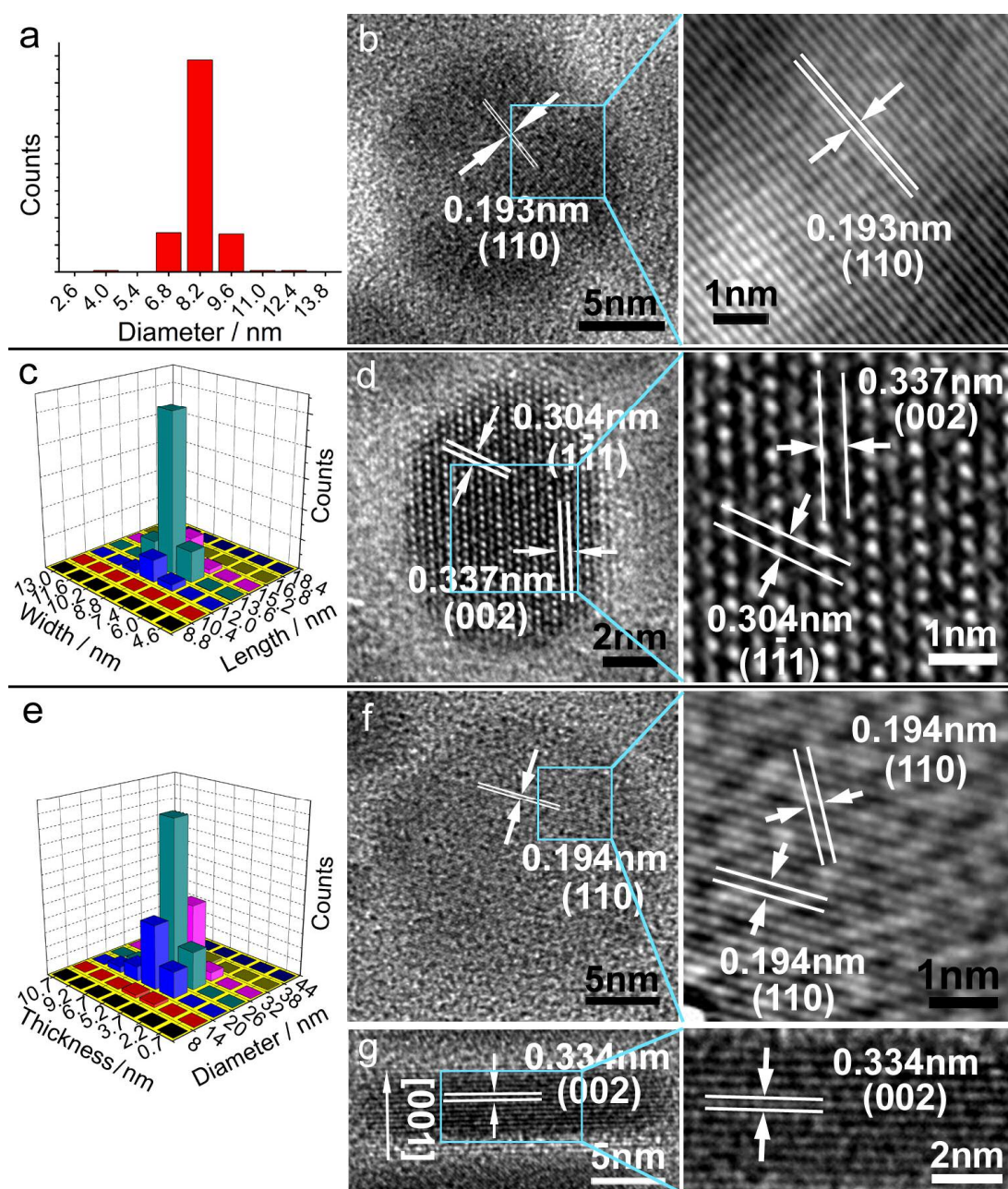


Figure S1. The enlarged size distribution patterns, HRTEM images and the magnified HRTEM images. (a) size distribution of the circular Cu₂S nanocrystals. (b) HRTEM and magnified HRTEM images of a circular Cu₂S nanocrystal. (c) size distribution of the elongated Cu₂S nanocrystals. (d) HRTEM and magnified HRTEM images of an elongated Cu₂S nanocrystal. (e) size distribution of the hexagonal Cu₂S nanoplates. (f) HRTEM and magnified HRTEM images of a face-down hexagonal Cu₂S nanoplate. (g) HRTEM and magnified HRTEM images of a stand-up hexagonal Cu₂S nanoplate.

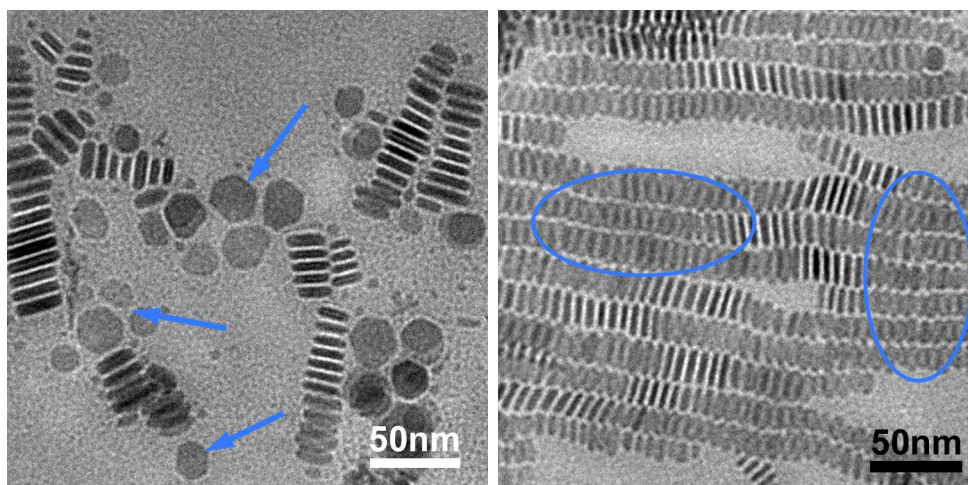


Figure S2. The TEM images show the face-down nanoplates (point out by arrows in the left figure) and the overlap of the nanoplates (the circled regions in the right figure), respectively.

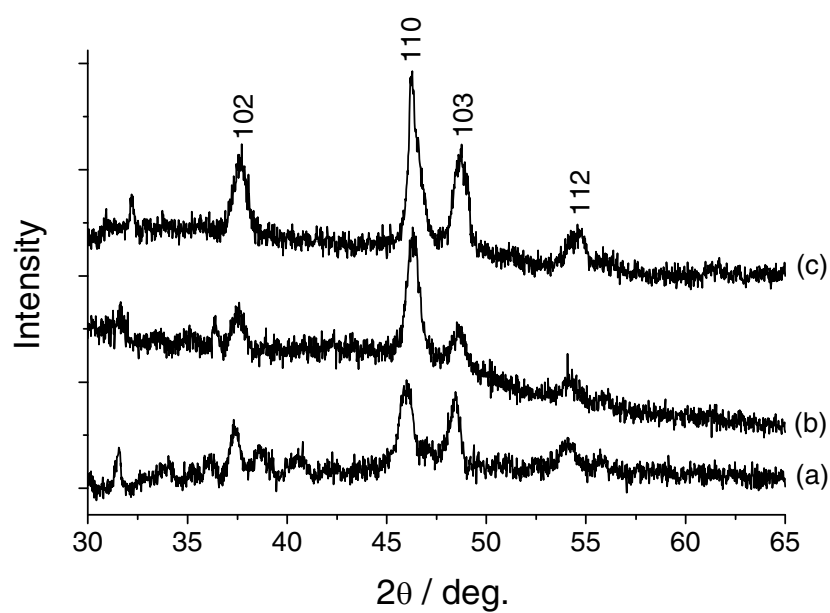


Figure S3. XRD patterns of the as-obtained nanocrystals. (a) circular nanocrystals; (b) elongated nanocrystals; (c) hexagonal nanoplates. All the peaks can be indexed as hexagonal Cu_2S structure (JCPDS card No.84-0208).

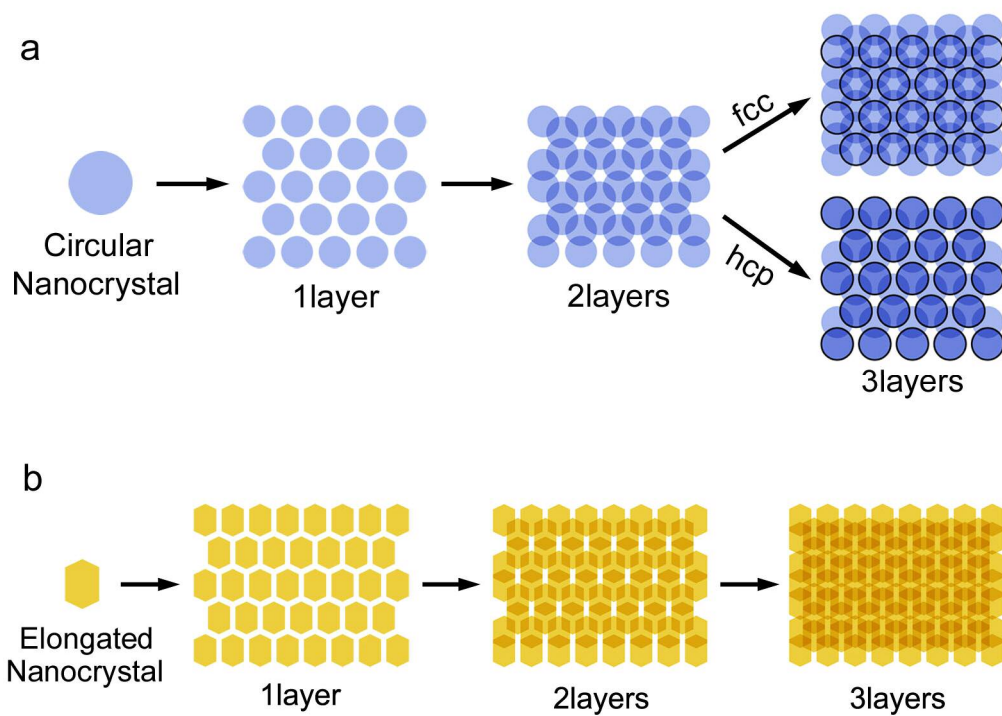


Figure S4. Schemes of the stacking of Cu_2S nanocrystals: (a) circular nanocrystal as building blocks. (b) elongated nanocrystal as building blocks.

For the circular nanocrystal assembly, it starts with a close-packed layer, and the second layer fits into the voids on the first-layer crystals. For the third layer (marked by black border in the right of Figure S4a), there are two ways. Each third-layer nanocrystal fits into a void that is directly over a void in the first layer (fcc type) or directly over the first-layer nanocrystal (hcp type).

For the elongated nanocrystal assembly, it can also start with a close-packed layer. Because of the anisotropic morphology of elongated nanocrystal, this type of close-packed layer has lower symmetry than the layer building up by circular nanocrystals. Another layer can also fit into the voids between the lower-layer nanocrystals and finally construct a multi-layer superstructure.

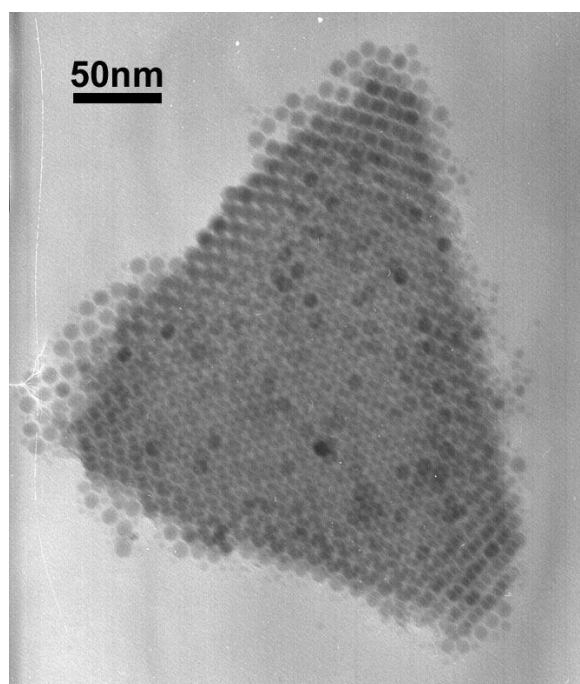


Figure S5. TEM image of a faceted fcc Cu₂S superlattice. It displays the (111) projection of fcc-type faceted superlattice and results in a triangular morphology.

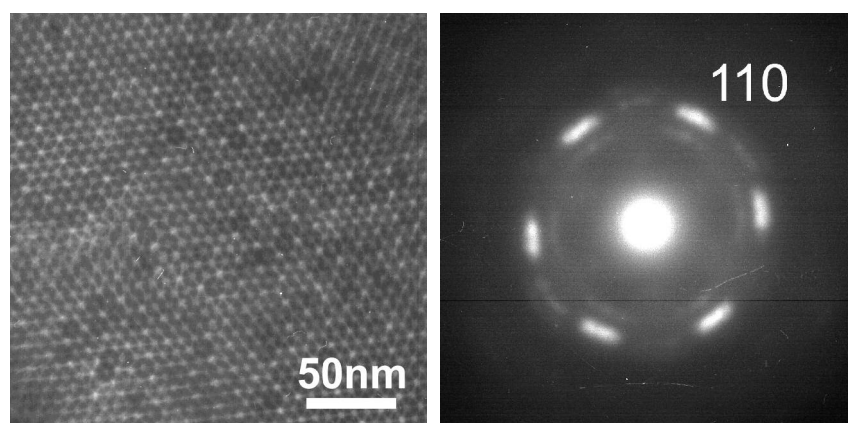


Figure S6. TEM image of fcc circular Cu₂S nanocrystal superlattice and its corresponding SAED pattern. It displays six symmetrical arcs, which indicate that the building block nanocrystals have a preferred orientation. The nanocrystals are oriented along [001].

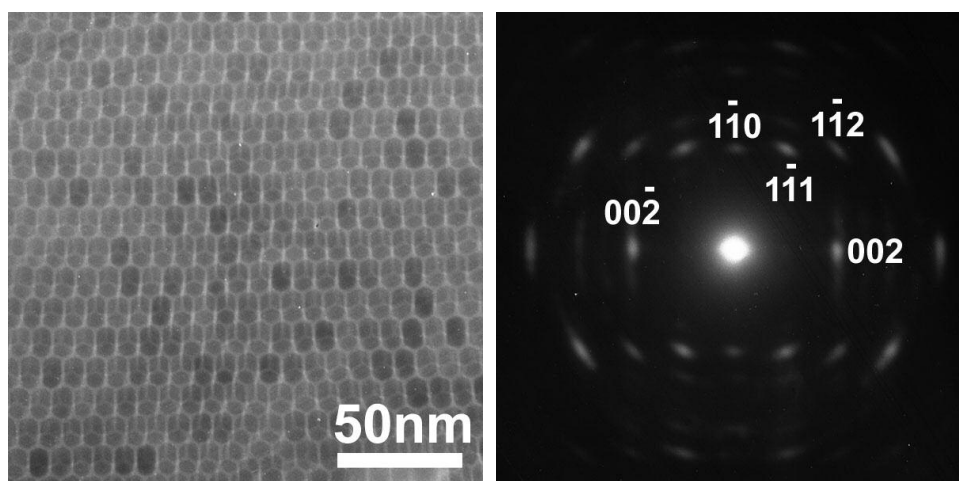


Figure S7. TEM image of elongated Cu₂S nanocrystal superlattice and its corresponding SAED pattern. It indicates that the building block nanocrystals have a **preferred** orientation. The nanocrystals are oriented along $[110]$, which are different from the circular nanocrystals assemblies.

S8 The dipole moment of the Cu₂S nanocrystals

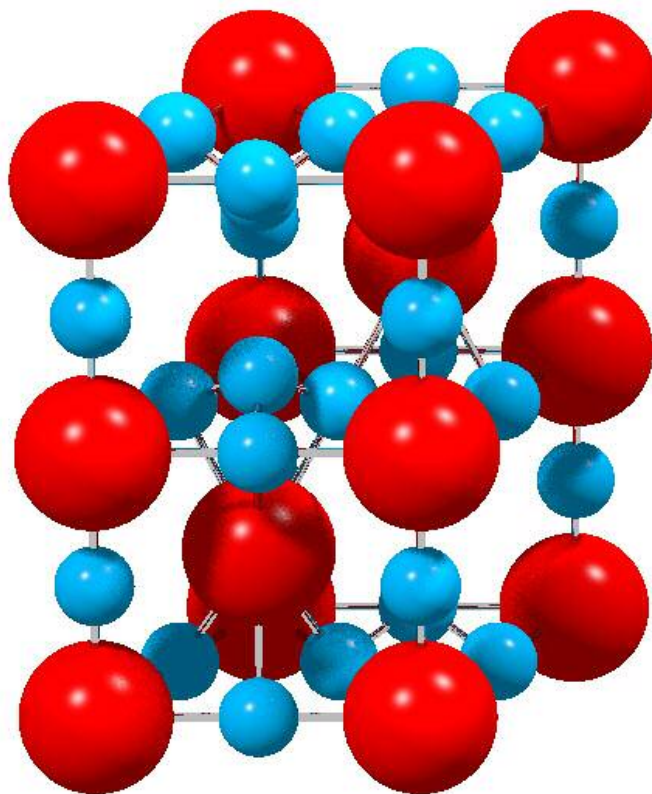


Figure S8-1. The scheme of the crystal structure of hexagonal Cu₂S.¹ In a unit cell, there are 4 S atoms and 12 sites for copper atoms. However, only 8 copper atoms in a cell thus the occupancies of the sites are not 100%.

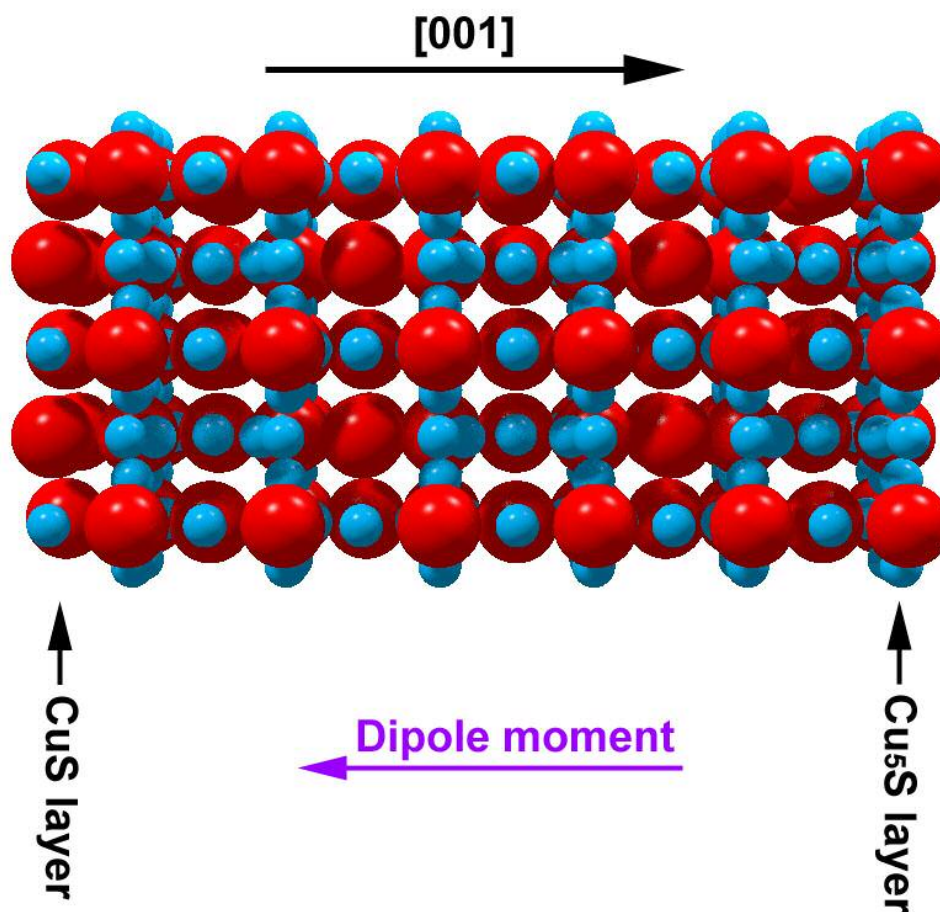


Figure S8-2. The scheme of the crystal structure along the [001] direction, and it is viewed along [100] direction. The hexagonal Cu_2S has a layered structure along the [001] direction, which is the alternation of a copper rich layer ($\text{Cu}/\text{S} = 5/1$) and a sulfur rich layer ($\text{Cu}/\text{S} = 1/1$). To achieve the charge balance, the nanocrystals should be terminated by Cu_5S layer one side and the other side is terminated by CuS layer. **The asymmetry structure has a dipole moment along the [001] direction.²**
The dipole moment make the nanocrystals pack along the [001] direction.

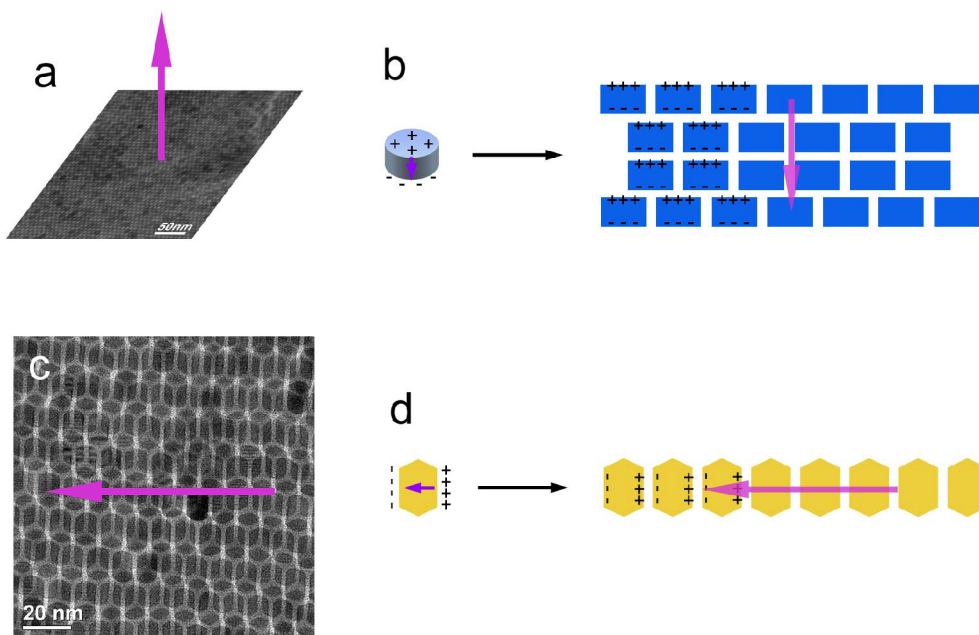


Figure S8-3. The influence of the dipole moments on the stacking of nanocrystals: (a) the orientation of dipole moment in the circular nanocrystals assembly; (b) the scheme of the dipole moment in the circular nanocrystals assembly; (c) the orientation of dipole moment in of elongated nanocrystals assembly; (d) the scheme of the dipole moment in of elongated nanocrystals assembly.

Based on the previous analysis on the structure of the nanocrystals, this figure shows the scheme of the dipole moments in the nanocrystals along $\langle 001 \rangle$ **direction**. This kind of dipole moment is effective in the assembly of Cu_2S nanocrystals.^{3,4}

For circular nanocrystals, the dipole moment is along the vertical direction of hexagonal **close-packed** layers. So they trend to form multilayer structure but single-layer close-packed Cu_2S nanocrystals are rare in the samples. For elongated nanocrystals, the dipole moment **makes the nanocrystals** face-to-face pack and **results in nanocrystal chains**.

S9 The van der Waals interactions in the Cu₂S nanocrystals assemblies

The van der Waals interactions can be classified into two types: one is between the nanocrystals and the other is between the **ligands** capped on the nanocrystals. The van der Waals interactions between nanocrystals can be **calculated with** the expression derive by Hamaker^[5]. The van der Waals interactions between the ligands are generally recognized **a reciprocal of r^6** . Thus it is very sensitive to the distance between the molecules and only **works** when the molecules are very close.

Figure S9 shows the scheme of the ligands capped on the different shape nanocrystals and their conditions in the assemblies. **The closest regions are much larger in the elongated nanocrystal assembly than the ones of the circular nanocrystal assembly, thus it may have stronger interactions.** This result indicates that the shape of the building block nanocrystal is an important factor in the **assembly**. The nanocrystal with anisotropic morphology may enhance the interactions between the nanocrystals and further promote their assembly.

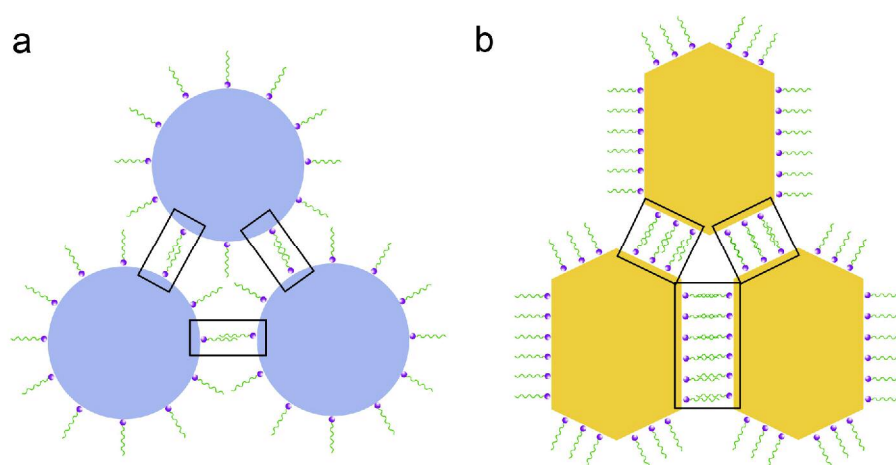


Figure S9 Scheme of the “**closest region**” which has short distance between ligands and results in large van der Waals interactions. These regions are marked by black border. a) circular nanocrystals. b) elongated nanocrystals.

Reference in Supporting Information

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