Supporting Information

Tuning and Locking the Localized Surface Plasmon Resonances of CuS (Covellite) Nanocrystals by an Amorphous CuPdₓS Shell

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1. TEM images, optical spectra and XRD patterns of the sample collected by exposing CuS NCs to Pd\textsuperscript{2+} in the absence of AA

**Figure S1.** TEM images from the CuS nanocrystals (NCs) as-synthesized (a) and after exposure to Pd\textsuperscript{2+} ions at room temperature (RT) in the absence of ascorbic acid (AA) (b). The scale bar is 20 nm. Corresponding optical spectra (c) and XRD patterns (d) from the two samples shown in panels a-b. The precursor Pd:Cu molar ratio in the reaction is 1:1.
2. Results of various core-shell nanoparticles collected at different time by reacting CuS NCs with Pd\(^{2+}\) cations at RT in the presence of AA

Figure S2. Evolution of morphologies (a-g), XRD patterns (h), and optical spectra (i) of the CuS NCs and various CuS@CuPd\(_x\)S core-shell nanostructures collected at different time by the reaction of CuS with Pd\(^{2+}\) cations at RT in the presence of AA. The scale bars in panels a-g are 20 nm.
**Figure S3.** Size distribution histograms of CuS (a), and CuS@CuPdS core-shell nanostructures collected by reacting CuS with Pd$^{2+}$ cations for 4 h (b) and 24 h (c), respectively. The size is calculated from the representative TEM images. The average diameter of these samples from a to c are 19.2 ± 0.9 nm, 19.4 ± 1.0 nm, and 19.4± 1.0 nm, respectively.

**Figure S4.** Raman spectra of the NPs obtained by reacting covellite CuS with Pd$^{2+}$ cations at RT for 1 h (a), 4 h (b) and 24 h (c), respectively, and the corresponding samples annealed at 100 °C for 1 h (d-f).
Figure S5. High resolution XPS of Cu 2p, Pd 3d, and S 2p from the as-synthesized covellite NCs and the core-shell samples collected at different time of reaction with Pd$^{2+}$ cations.

Figure S6. False color representative HRTEM images from [001] oriented core-shell nanostructures collected at different time of the reaction of CuS with Pd$^{2+}$ at RT in the presence of AA (as in Figure 2 of the manuscript). The images here are filtered on the {110} reflections (Bragg filtering), to better visualize the growing amorphous shell (with dominant green color in the images) and the size reduction of the covellite core (scale bar is 5 nm). A similar filter cannot be applied to side views due to the weak (00l) reflections.
Figure S2 provides the results of the as-synthesized CuS (covellite) nanocrystals (NCs) and various CuS@CuPdₓS core-shell nanostructures with different shell thicknesses achieved at different time of reaction with Pd²⁺ cations at RT in the presence of AA. The experimental XRD peaks at 2θ=27.68°, 29.28°, 31.79°, 32.85°, and 47.94° are indexed with the diffraction planes (101), (102), (103), (006) and (110) of covellite CuS, respectively (Figure S2h, bottom). The phase evolution from the initial covellite phase to amorphous-like structure as a function of the reaction time is evidenced by XRD characterization (Figure S2h). The most important clue comes from the absence of the initial diffraction peaks at 24 h of reaction time and from the presence of a broad and weak peak at 2θ around 29°. The feature and indexing of this abroad peak is consistent with the amorphous Cu-Pd-S nanostructure recently reported by Wang et al.¹ In their work, a new broad XRD peak emerged in the range of 20-50° and was indexed to an amorphous structure. The change in the relative intensities of the various peaks as the reaction proceeds might indicate different amorphization speeds along different directions. For example, one can see that, at 2 h and 4 h of reaction, the relative intensity of the diffraction peak at 31.8° (indexed to the (103) planes) has decayed faster than that of the peak at 47.9° (indexed to the (110) planes). On the other hand, we cannot rule out the possibility that some XRD peaks are more intense than others due to preferential orientation effects. The evolution of XRD patterns over the reaction time is well consistent with the HRTEM characterization (see details of the main text). The damping and red-shift of the NIR plasmon absorption observed in Figure S2i are due to the increasing shell thickness of CuPdₓS as the reaction proceeds.

The TEM images (Figure S2a-g) and size distribution histogram (Figure S3) reveal that the resulting nanoparticles (NPs) preserve their overall shape and size, although the amorphous CuPdₓS shell increases in size and concomitantly the covellite core becomes smaller as the reaction proceeds. Figure S6 evidences the reduction of the CuS core size upon reaction with Pd²⁺ by Bragg filtering the covellite reflections from [001] orientations, to enhance the contrast in Figure 2 of the manuscript.

Figure S4 compares the Raman spectra of the CuS@CuPdₓS core-shell nanostructure and the corresponding samples annealed at 100 °C for 1 h. The evolution of the Raman spectra from panel a) to c) indicates that the S-S bond is partly broken upon the Pd incorporation. The broad peak ranging 220-400 cm⁻¹ is due to the overlapping Cu-S, poor Pd-S and Si-Si (from the substrate for Raman test) vibrational bonds, as discussed in the manuscript. After annealing
under N\textsubscript{2} atmosphere for 1 h, one could observe Raman peaks at 265, 323, 346, 386 and 451 cm\textsuperscript{-1} (Figure S4e). The peak at 265 cm\textsuperscript{-1} and 451 cm\textsuperscript{-1} are due to Cu-S and S-S mode, respectively, while other three peaks at 323, 346 and 386 cm\textsuperscript{-1} match well with the Raman mode from Pd-S.\textsuperscript{2-3} Similar observation is shown in the annealed 24 h sample except that the S-S mode vanishes completely and the Cu-S mode shifts to around 295 cm\textsuperscript{-1} (Figure S4f). The prominent shift of Cu-S mode from 264 cm\textsuperscript{-1} to 298 cm\textsuperscript{-1} indicates a drastic change in the bond length and force field at which they oscillate in the alloyed CuPd\textsubscript{x}S system.

\textbf{Table S1.} \textit{Final composition of the representative samples collected at different time of reaction of CuS with Pd\textsuperscript{2+} cations at RT in the presence of AA (found by EDS and XPS analyses).}

| Reaction time (hours) | EDS       | XPS       |
|-----------------------|-----------|-----------|
| 1 h                   | Cu\textsubscript{1.01}Pd\textsubscript{0.21}S | Cu\textsubscript{1.3}Pd\textsubscript{0.2}S |
| 4 h                   | Cu\textsubscript{1.0}Pd\textsubscript{0.33}S | Cu\textsubscript{1.2}Pd\textsubscript{0.4}S |
| 24 h                  | Cu\textsubscript{1.04}Pd\textsubscript{0.64}S | Cu\textsubscript{1.2}Pd\textsubscript{0.5}S |
3. TEM images and optical spectra of CuS@CuPd₃S core-shell nanostructures collected by reacting CuS with different amounts of Pd²⁺ cations at RT

Figure S7. (a-e) TEM images of the CuS and CuS@CuPd₃S core-shell nanostructure achieved with different precursor Pd:Cu molar ratios: (a) 2:10, (b) 3:10, (c) 4:10, (d) 6:10 and (e) 10:10, at RT in the presence of AA. The scale bar is 20 nm. (f) Optical spectra of the corresponding NPs dispersed in toluene.
4. TEM images, optical spectra and XRD patterns of the samples collected at different temperatures by reacting CuS NCs with Pd$^{2+}$ cations

Figure S8. (a-c) TEM images of the nanostructures obtained by reacting CuS NCs with Pd$^{2+}$ at RT (a), at 50 °C (b), and at 80 °C (c). The reaction time is 4 h for all cases. The scale bar is 20 nm. (d-e) HRTEM images from single NCs collected at 80 °C. Optical spectra (f), and XRD patterns (g) of the corresponding samples.

The reaction of CuS NCs with Pd$^{2+}$ ions at higher temperature of 50 °C and 80 °C leads to the formation of majority of alloyed CuPd$_x$S nanoplates as well as a minority of smaller (relative to the alloyed amorphous CuPd$_x$S nanoplates) Pd-like NPs containing very small amount of S and Cu (Figure S8b-e). The results indicate that higher temperature facilitates the Pd$^{2+}$ incorporation and thus the conversion from covellite NCs to amorphous alloyed ones.
5. Calculation based on density functional theory

**Geometry structure relaxation.** We have fully relaxed models using the density functional theory (DFT)-based *Vienna Ab Initio Simulation Package* (VASP). We used the projector augmented wave (PAW) method with the Perdew-Burke-Ernzerhof (PBE) potential for exchange correlation functional together within the generalized gradient approximation (GGA). For the electronic relaxation, a high energy cutoff of 600 eV is used with the electronic convergence criterion set at $10^{-4}$ eV. For ionic relaxation, we set the force convergence criteria to be $10^{-2}$ eV/Å. The 7×7×7 Monkhorst-Pack grids of k points are selected for these models.

**Results and discussion.** We first start the calculation by using one cell. The unit cell containing 6 Cu atoms and 6 S atoms is used as the basic cell. From the energetic viewpoint, we choose two different interstitial sites for the location of a Pd atom marked with Pd1 (Figure S9b) and Pd2 (Figure S9c), respectively, and two substituted states of Pd atom by replacing Cu lattices which are labeled as Pd3 (Figure S9d) and Pd4 (Figure S9e), respectively. The stoichiometry of the above-mentioned four states could be described as (a) CuSPd$_{0.167}$, (b) CuSPd$_{0.167}$, (c) Cu$_{0.833}$SPd$_{0.167}$ and (d) Cu$_{0.833}$SPd$_{0.167}$, respectively.

![Figure S9](image)

*Figure S9.* (a) Pure CuS model; (b)-(c) Interstitial doped sites of Pd1 and Pd2. (d)-(e) substituted sites of Pd3 and Pd4. Cu, S, and Pd atoms are marked by red, yellow and blue balls, respectively.
The formation energy for the interstitial Pd is calculated as follows:
\[ E_f = E(\text{Pd}, \text{CuS}) - E(\text{CuS}) - x \times E(\text{Pd}). \]

The substitution energy of Pd is defined as:
\[ E_s = E(\text{Pd}_{x} \text{Cu}_{1-x} \text{S}) - E(\text{CuS}) + E(\text{Cu}) - E(\text{Pd}). \]

Here, \( E(\text{Pd}, \text{CuS}) \), \( E(\text{Pd}_{x} \text{Cu}_{1-x} \text{S}) \), and \( E(\text{CuS}) \) are the total energies of the Pd-doped CuS and pure CuS; both \( E(\text{Cu}) \) and \( E(\text{Pd}) \) are the energies of individual Cu and Pd atoms, respectively.

Based on the above definition, the formation energies of intercalation and substitution are reported in Table S2, which indicates the stabilization of the system. Clearly, the formation energy is negative only at first site as the interstitial doped state, indicating that the interstitial doping Pd between S-S layers of covellite CuS occurs more likely with respect to the substitution state.

**Figure S10.** (a) Relaxed pure covellite CuS and (b) relaxed Cu-S-Pd\(_{0.167}@1\) with interstitial Pd between S-S layers.
Figure S10 shows the relaxed unit cells of pure CuS and CuSPd_{0.167}@1, and Table S3 reports the relaxation results of the unit cell lattice. The interstitial site of Pd atom between the S-S layers induced the cell distortion, with a total expansion of the cell along axis \(a\), \(b\), and \(c\) of 2.19%, 2.19% and 7.42%, respectively. Concomitantly, the S-S bonds break and the angles of Cu-S-Cu and S-Cu-S change, which consequently breaks the symmetry of S lattices along the direction of axis \(a\) and \(b\) (Figure S10b).

To have a further investigation on the charges and bonds of the doping CuSPd_{0.167}@1 system, we calculate the Hirshfeld charges and Mulliken bond populations by using CASTEP (Tables S4 and S5). One can see from Table S4 that the Hirshfeld charges of S3 and S4 change from -0.10 e to -0.24 e before and after Pd incorporation, and the charge of Pd is 0.28 e. The charges on S1, S2, S3, S4 atoms in the initial cell are quite different with those after the Pd doping, indicating the breaking periodicity of S-S layers along the \(c\) axis.

No S3-S4 bond exists in CuSPd_{0.167}@1 due to the breaking S-S layers upon inserting the Pd atom. The negative values in the population means the pseudo bonds between Cu and Pd atoms. After the insertion, Pd bonds with S3 and S4 atoms, which weakens the bonds between S3-Cu3 and S4-Cu4.

Table S2. The calculated Pd formation energy and substitute energy at different sites (eV).

|                | CuSPd_{0.167}@1 | CuSPd_{0.167}@2 | Cu_{0.833}SPd_{0.167}@3 | Cu_{0.833}SPd_{0.167}@4 |
|----------------|-----------------|-----------------|--------------------------|--------------------------|
|                | -0.01962335     | 0.61224334      | 0.60453139               | 0.0907393                |
**Table S3.** The lattice of the unit cell for pure CuS and CuSPd_{0.167}@1.

|          | CuS       | CuSPd_{0.167}@1 | Expansion upon Pd incorporation (%) |
|----------|-----------|-----------------|-------------------------------------|
| Axis: a (Å) | 3.81041   | 3.89384         | 2.19                                |
| Axis: b (Å) | 3.81041   | 3.89384         | 2.19                                |
| Axis: c (Å) | 16.4968   | 17.7205         | 7.42                                |
| Angle: α   | 90        | 87.8690         |                                     |
| Angle: β   | 90        | 92.1310         |                                     |
| Angle: γ   | 120       | 124.666         |                                     |

**Table S4.** The Hirshfeld charges for CuS and CuSPd_{0.167}@1.

| Species | Ion | CuS          | CuSPd_{0.167}@1 | Species | Ion | CuSPd_{0.167}@1 |
|---------|-----|--------------|-----------------|---------|-----|-----------------|
| S       | 1   | -0.10        |                 | S       | 1   | -0.09           |
| S       | 2   | -0.10        |                 | S       | 2   | -0.09           |
| S       | 3   | -0.10        |                 | S       | 3   | -0.24           |
| S       | 4   | -0.10        |                 | S       | 4   | -0.24           |
| S       | 5   | -0.25        |                 | S       | 5   | -0.25           |
| S       | 6   | -0.25        |                 | S       | 6   | -0.25           |
| Cu      | 1   | 0.15         |                 | Cu      | 1   | 0.16            |
| Cu      | 2   | 0.15         |                 | Cu      | 2   | 0.16            |
| Cu      | 3   | 0.15         |                 | Cu      | 3   | 0.14            |
| Cu      | 4   | 0.15         |                 | Cu      | 4   | 0.14            |
| Cu      | 5   | 0.14         |                 | Cu      | 5   | 0.15            |
| Cu      | 6   | 0.14         |                 | Cu      | 6   | 0.15            |
| Pd      | 1   | 0.28         |                 |         |     |                 |
We further performed the simulation by using $2 \times 1 \times 1$ supercell of covellite CuS, in which we put 4 Pd atoms (i.e. with final composition of $\text{Cu}_{12}\text{S}_{12}\text{Pd}_4$) at three different interstitial positions. The initial three models and the structures after relaxation are depicted in Figure S11. It is interesting that the final stable structures upon relaxation are almost the same in cases of a) and c) in Figure

**Table S5.** The Mulliken bond populations and bond length for CuS and CuSPd$_{0.167}@1$. 

| Bond   | Population | Length (Å) | Bond   | Population | Length (Å) |
|--------|------------|------------|--------|------------|------------|
| S3--S4 | 0.38       | 2.11126    | S1--S2 | 0.37       | 2.11288    |
| S1--S2 | 0.38       | 2.11126    | S1--Cu1| 1.37       | 2.30482    |
| S2--Cu2| 1.38       | 2.31177    | S2--Cu2| 1.37       | 2.30482    |
| S3--Cu3| 1.38       | 2.31177    | S3--Cu3| 1.24       | 2.25326    |
| S4--Cu4| 1.38       | 2.31177    | S4--Cu4| 1.24       | 2.25326    |
| S5--Cu1| 0.20       | 2.35825    | S5--Cu1| 0.26       | 2.33107    |
| S5--Cu4| 0.20       | 2.35825    | S5--Cu4| 0.13       | 2.34393    |
| S5--Cu6| 1.48       | 2.19994    | S5--Cu6| 1.46       | 2.20775    |
| S6--Cu2| 0.20       | 2.35825    | S6--Cu2| 0.26       | 2.33107    |
| S6--Cu3| 0.20       | 2.35825    | S6--Cu3| 0.13       | 2.34393    |
| S6--Cu5| 1.48       | 2.19994    | S6--Cu5| 1.46       | 2.20775    |

|        |            |            | S4--Pd1| 0.41       | 2.40750    |
|        |            |            | S3--Pd1| 0.41       | 2.40750    |

Cu4--Pd1  -0.79  2.75296  
Cu3--Pd1  -0.80  2.75296  
Cu3--Cu5  -0.29  2.85910  
Cu4--Cu6  -0.29  2.85910
S11, although the starting doping sites are different. In both cases, the final Pd atoms are stable between S-S layers and thus break S-S bonds.

Table S6 provides the formation energies at different sites mentioned above. The formation energy for Cu$_{12}$S$_{12}$Pd$_4$@2 (Figure S11b) is much higher than those of other tow cases (Figure S11a,c), which further indicates that Pd inserting between S-S layers is more energetically favorable than other sites.

After relaxation, the values of the cell lattices for pure CuS and Cu$_{12}$S$_{12}$Pd$_4$@1 are listed in Table S7, and the relaxed supercells are shown in Figure S12. Clearly, the doping Pd between S-S layers induces the cell distortion, with a total expansion of the cell along axis c of 11.99%. Furthermore, the S-S bonds break and the angles of Cu-S-Cu and S-Cu-S change upon the insertion of Pd atoms (Figure S12b), which is in agreement with the calculation using one cell.

**Figure S11.** Different interstitial doping sites labeled as (a) Cu$_{12}$S$_{12}$Pd$_4$@1, (b) Cu$_{12}$S$_{12}$Pd$_4$@2 and (c) Cu$_{12}$S$_{12}$Pd$_4$@3, respectively.
**Figure S12.** (a) Relaxed pure CuS and (b) relaxed Cu_{12}S_{12}Pd_{4}@1

**Table S6.** The calculated Pd formation energy at different sites shown in Figure S11.

| Sites       | Cu_{12}S_{12}Pd_{4}@1 | Cu_{12}S_{12}Pd_{4}@2 | Cu_{12}S_{12}Pd_{4}@3 |
|-------------|-----------------------|-----------------------|-----------------------|
| Pd formation energy (eV) | 0.28865836            | 2.55904077            | 0.28944345            |

**Table S7.** The lattice parameters of the unit cell for pure CuS and Cu_{12}S_{12}Pd_{4}@1

|                  | CuS      | Cu_{12}S_{12}Pd_{4}@1 |
|------------------|----------|-----------------------|
| Axis:  a (Å)     | 7.6208   | 7.62256               |
| Axis:  b (Å)     | 3.81041  | 3.81117               |
| Axis:  c (Å)     | 16.4968  | 18.47463              |
| Angle:  α        | 90       | 90.03001              |
| Angle:  β        | 90       | 89.83466              |
| Angle:  γ        | 120      | 119.98273             |
6. Theoretical framework and simulation of plasmon absorbance

Volume particle

\[ V = \frac{4}{3} \cdot \pi \cdot \left( \frac{d_{\text{core-shell}}}{2} \right)^2 \cdot \left( \frac{h_{\text{core-shell}}}{2} \right) \]

aspect ratio: diameter/height

\[ r = \frac{d}{h} \]

\[ e = \sqrt{1 - \frac{1}{r^2}} \]

\[ g = \sqrt{\frac{(1 - e^2)}{e^2}} \]

Depolarization factors for oblate with \( L_a < L_b = L_c \)

\[ L_b = \left( \frac{g}{2e^2} \right) \cdot \left( \frac{\pi}{2} - \tan^{-1} g \right) - \frac{g^2}{2} \]

\[ L_a = \frac{(1 - L_b)}{2} \]

Polarizability

\[ \alpha = \varepsilon_0 \cdot V \cdot \frac{1}{3} \left[ \frac{\varepsilon_p - \varepsilon_H}{3L_a(\varepsilon_p - \varepsilon_H) + 3\varepsilon_H} \right] + \frac{2}{3} \left[ \frac{\varepsilon_p - \varepsilon_H}{3L_b(\varepsilon_p - \varepsilon_H) + 3\varepsilon_H} \right] \]

Fraction of the particle occupied by inner ellipsoid: core

\[ f = \frac{\left( \frac{d_{\text{core-shell}}}{2} \right)^2 \cdot \left( \frac{h_{\text{core-shell}}}{2} \right)}{\left( \frac{d_{\text{core}}}{2} \right)^2 \cdot \left( \frac{h_{\text{core}}}{2} \right)} \]
Polarizability for core shell oblate:

\[ \alpha = \varepsilon_0 \cdot V \]

\[
\frac{1}{3} \left( \frac{(\varepsilon_{\text{shell}} - \varepsilon_H) \cdot (\varepsilon_{\text{shell}} + (\varepsilon_p - \varepsilon_{\text{shell}}) \cdot (L_{a,\text{shell}} - f \cdot L_a) + f \cdot \varepsilon_{\text{shell}} \cdot (\varepsilon_p - \varepsilon_{\text{shell}}))}{(\varepsilon_{\text{shell}} + (\varepsilon_p - \varepsilon_{\text{shell}}) \cdot (L_{a,\text{shell}} - f \cdot L_a)) \cdot (\varepsilon_H + (\varepsilon_{\text{shell}} - \varepsilon_H) \cdot L_a) + f \cdot L_a \cdot \varepsilon_{\text{shell}} \cdot (\varepsilon_p - \varepsilon_{\text{shell}})} \right) \\
+ \frac{2}{3} \left( \frac{(\varepsilon_{\text{shell}} - \varepsilon_H) \cdot (\varepsilon_{\text{shell}} + (\varepsilon_p - \varepsilon_{\text{shell}}) \cdot (L_{b,\text{shell}} - f \cdot L_b) + f \cdot \varepsilon_{\text{shell}} \cdot (\varepsilon_p - \varepsilon_{\text{shell}}))}{(\varepsilon_{\text{shell}} + (\varepsilon_p - \varepsilon_{\text{shell}}) \cdot (L_{b,\text{shell}} - f \cdot L_b)) \cdot (\varepsilon_H + (\varepsilon_{\text{shell}} - \varepsilon_H) \cdot L_b) + f \cdot L_b \cdot \varepsilon_{\text{shell}} \cdot (\varepsilon_p - \varepsilon_{\text{shell}})} \right)
\]

\[ C_{\text{ext}} = 2\pi \cdot \lambda \cdot \sqrt{\varepsilon_H} \cdot \text{Im}(\alpha) \]

**Figure S13.** Comparison of experiment and theory by applying the Mie-Gans theory and the Drude model to simulate the optical spectra of our CuS NCs of 5.5×19.5 nm (height × diameter) dimensions.
Figure S14. Shift of the LSPR with increasing the refractive index of the shell layer, for different shell thicknesses. The legends give the core sizes (height × diameter).

Figure S15. (a) Simulation of the NP core only with the dimensions (height × diameter) as given in the legend. (b) Simulation of the core-shell structure with varying core size as given in the legend (height × diameter). In both cases the LSPR has been calculated by varying the damping term in the transverse direction only to elucidate the role of additional surface scattering due to the small size of the oblate height.
7. Oxidation on core-shell nanostructure by air exposure

**Figure S16.** The evolution of the NIR plasmon absorbance of various NCs upon oxidation for different time by air exposure: CuS@CuPd$_x$S core-shell nanostructures with different core sizes (h$x$)(a-c) and Cu$_2$S NCs (d). The insets show the TEM images of the corresponding NPs and the legends give the core sizes in height and diameter.

The resulting core-shell heterostructures with locked covellite CuS core exhibit stable NIR plasmon property upon oxidation by air exposure. The maximum blue shift of the NIR plasmon absorbance, which occurred in the sample with thinnest shell thickness (1 h sample, see Tables S8 and S9), is only 41 nm upon oxidation for 31 days (Figure S16a). Thicker shell leads to less blue shift thanks to the protection by the amorphous CuPd$_x$S shell, and no any NIR plasmon absorbance could be developed in a core-shell NPs achieved at 24 h by air exposure for 31 days.
For comparison, we also investigated the evolution of NIR plasmon absorbance upon oxidation of the Cu$_2$S NCs as-synthesized following a procedure reported by us,$^4$ which confirm a gradual development of the NIR plasmon absorbance and prominent blue shift up to around 1400 nm after 31 days of oxidation by air exposure (Figure S16d).
8. Oxidation of the CuS@CuPd,S core-shell nanostructure by I₂

We noticed that the core-shell NPs show slight red shift of NIR plasmon resonance upon oxidation in the presence of I₂ (Figure S17a-c). Thicker shell leads to less shift of plasmon absorbance upon oxidation. Furthermore, the fabrication of shell preserves the overall morphologies of the NPs upon oxidation (Figures S18 and S19).

Figure S17. (a-c) The evolution of the NIR plasmon absorbance of the CuS@CuPd,S core-shell nanoparticle dispersion in a cuvette upon the addition of different volumes of iodine solution (pre-dissolved in toluene, 0.05 M). The shell thickness of the NPs increases from a) to c). (d) Optical spectra of iodine dissolved in toluene.
Figure S18. TEM images of two representative core-shell samples (labelled as core-shell-1 and core-shell-2) before and after the oxidation by I₂. The shell in sample core-shell-2 is thicker than that in core-shell-1.
Figure S19. HRTEM images of two representative core-shell samples (labelled as core-shell-1 and core-shell-2) before and after the oxidation by I₂. The shell in sample core-shell-2 is thicker than the one in core-shell-1.
9. Oxidation and reduction of the as-synthesized covellite CuS

**Figure S20.** The evolution of optical spectra of CuS nanoparticles over the amounts of reducing agent DIBAH (a) and oxidation agent I$_2$ (b) added into a cuvette containing 3 mL toluene with CuS NCs. The initial concentration of both I$_2$ and DIBAH is 0.05 M.

**Figure S21.** The optical spectra (a) and XRD patterns (b) of the as-synthesized CuS NCs and DIBAH-treated CuS NCs. The CuS NCs were mixed with DIBAH solution (pre-dissolved in toluene) under stirring at RT and the reaction was kept for 2 h, followed by cleaning and re-dispersing in toluene for optical and XRD characterization.
Figure S22. (a-b) Optical spectra (a) and XRD patterns (b) of the as-synthesized CuS NCs and samples collected by exposing the as-synthesized CuS to I₂ solution for different time. (c-d) TEM images of the as-synthesized CuS (c) and the CuS NPs collected by treatment with I₂ for 1 h (d). Each scale bar is 20 nm.

For comparison, we also investigate the optical stability of CuS NCs upon exposure of the as-synthesized CuS dispersion in a cuvette to different amounts of I₂ and DIBAH (Figure S20), from which we could observe: (i) Slight red shift of NIR plasmon absorbance by exposing covellite CuS to DIBAH (Figure S20a). This is completely different with previously reported change of NIR plasmon properties of Cu₂₋ₓS NPs in the presence of DIBAH, which exhibited significant red shift and damping evolution. (ii) Red shift of plasmon absorbance upon the treatment by I₂ (Figure S20b).
We further scaled up the redox reactions on CuS and collected XRD patterns and TEM images of the representative samples (Figures S21 and S22). No prominent change on crystal phase is observed on the CuS NCs even when the reduction by DIBAH is performed for 2 h (Figure S21b). On the other side, we noticed prominent red shift of NIR plasmon absorbance on the covellite NCs after treatment with I₂ (Figure S22a). The following two reasons cannot be completely excluded to explain the red shift and damping NIR plasmon absorbance of CuS in the presence of I₂: (i) slight aggregation of the NPs, which could be visualized by eye after reaction and cleaning the samples; (ii) slight etching NCs upon the oxidation, as can be seen from TEM observation (Figure S22d). These observations indicate that the as-synthesized covellite CuS NCs are sensitive to the oxidation environment in the presence of I₂.
10. Size and optical spectra of the core-shell nanostructure achieved at different time of reacting covellite CuS with Pd$^{2+}$ cations

![Scheme of the CuS@CuPd$_x$S core-shell nanostructure.](image)

**Figure S23.** Scheme of the CuS@CuPd$_x$S core-shell nanostructure.

**Table S8.** Summary of the parameters of the CuS@CuPd$_x$S core-shell nanostructures as obtained at different reaction time: core size dimensions (h×d), shell thickness ($t_{\text{shell}}$) and experimental plasmon peak position ($\lambda_{\text{exp}}$). The dimensions are calculated based on HRTEM analyses.

| Reaction time (hours) | Core size (h×d) (nm) | $t_{\text{shell}}$ (nm) | $\lambda_{\text{exp}}$ (nm) |
|-----------------------|----------------------|--------------------------|-----------------------------|
| 0 (CuS)               | 5.5×19.5             | 0                        | 1066                        |
| 1 h                   | 4.7×16.2             | 1.7                      | 1290                        |
| 4 h                   | 2.9×13.9             | 2.8                      | 1412                        |
| 24 h                  | 1.1×4.0              | 7.8                      | ×                           |
11. Summary on the NIR plasmon absorbance of the CuS@CuPdₓS core-shell nanostructures upon oxidation by air exposure

Table S9. NIR plasmon absorbance of the representative samples upon oxidation by air exposure. The CuS@CuPdₓS core-shell samples were obtained at 1 h, 4 h, and 24 h, respectively.

| Samples achieved at different time | Initial NIR plasmon peak (nm) | Plasmon peak after 8 days of oxidation (nm) | Plasmon peak after 31 days of oxidation (nm) | Blue shift after 31 days of oxidation (nm) |
|-----------------------------------|-------------------------------|---------------------------------------------|---------------------------------------------|-------------------------------------------|
| 1 h                               | 1290                          | 1259                                        | 1249                                        | 41                                        |
| 4 h                               | 1412                          | 1410                                        | 1411                                        | 1                                         |
| 24 h                              | ×                             | ×                                           | ×                                           | ×                                         |
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