Supporting Information

10-Fold Quantum Yield Improvement of Ag$_2$S Nanoparticles by Fine Compositional Tuning

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This supplementary information includes the following sections:

S1. Chemical conditions for the NPs production
S2. XRD characterization of the synthesized NPs
S3. XPS, XANES and Fourier transform EXAFS of the NPs
S5. PLQY measurements
S4. Dose dependent experiment and performance comparison between optimized NPs and commercially available NPs
Section 1. The chemical conditions of the nanoparticles S1.

Table S1 shows the chemical conditions used to synthesize the NPs. In this table the amount of dodecanethiol and oleylamine are given as a molar fraction.

Table S1. Solvent mixtures used in each synthesis. In all the experiments the amount of precursor Ag(DDTC) was kept constant at 25 mg (0.1 mmol).

<table>
<thead>
<tr>
<th>Synthesis name</th>
<th>Solvent mole fraction ($\chi_{DDT}$)</th>
<th>mmol DDT</th>
<th>mmol OLA</th>
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<tbody>
<tr>
<td>A</td>
<td>0</td>
<td>0.0</td>
<td>15.2</td>
</tr>
<tr>
<td>B</td>
<td>0.15</td>
<td>2.4</td>
<td>13.7</td>
</tr>
<tr>
<td>C</td>
<td>0.30</td>
<td>5.2</td>
<td>11.4</td>
</tr>
<tr>
<td>D</td>
<td>0.60</td>
<td>10.4</td>
<td>7.6</td>
</tr>
<tr>
<td>E</td>
<td>0.9</td>
<td>18.8</td>
<td>1.5</td>
</tr>
<tr>
<td>F</td>
<td>1</td>
<td>20.9</td>
<td>0</td>
</tr>
</tbody>
</table>

As a result of the synthetic conditions, pretty monodisperse NPs are obtained. These NPs have sizes between 5 to 12 nm, depending on the solvent composition. The Figure S1A depicts a TEM image of a typical NPs synthesis using the conditions namely as F. Figure S1B, shows the EDS elemental mapping of these NPs.
Figure S1 A) TEM image of Ag$_2$S nanoparticles synthesized under conditions namely as F. B) EDS elemental mapping of the previously showed Ag$_2$S nanoparticles merged with the STEM micrograph.

![Image of TEM and EDS mapping]

Figure S2. Mean size of the Ag$_2$S/Ag nanoparticles (green) and the Ag cores (red) as a function of the DDT/OLA ratio.

![Graph showing size vs DDT ratio]

S2. XRD characterization of the synthesized NPs
Figure S3. XRD patterns of Ag\textsubscript{2}S/Ag nanoparticles synthesized using different ratios between DDT/OLA, Ag\textsubscript{2}S-1 black, Ag\textsubscript{2}S-0.60 blue, Ag\textsubscript{2}S-0.15 pink, Ag\textsubscript{2}S-0.9 orange, Ag\textsubscript{2}S-0.3 green, Ag\textsubscript{2}S-0 cyan. The reflection attributed to cubic phase of Ag are highlighted in red.

The XRD pattern of the different NPs is given in Figure S3. In this Figure, we can observe the presence of several reflections at 2theta = 28.97, 31.49, 33.57, 34.48, 34.83 or 36.9 degrees that can be assigned to monoclinic Ag\textsubscript{2}S (JCPDS card No. 14-0072; lattice constants: a = 4.229 Å, b = 6.931 Å, c = 7.862 Å). In addition, we can observe some tiny reflections at 2theta = 38.15 and 44.18 degree that can be assigned to the cubic metallic Ag (JCPDS card No. 04-0783; lattice constants: a = 4.0862 Å). This result would indicate the presence of a metallic Ag phase in the Ag\textsubscript{2}S samples.

S3. XPS, XANES and Fourier transform EXAFS of the NPs

Wide scan survey spectra of the NPs show the presence of Ag 3d (366.5 eV, 373 eV) and S 2p (161 eV, 162.2 eV) doublets as well as C 1s (285 eV), O 1s (532 eV) is shown in Figure S4A. High-resolution scans of Ag 3d core-level spectra of the different samples are shown in Figure S4B. The Ag 3d binding energy spectra of the different samples were deconvoluted and fitted with two silver doublets following the method previously published by Surojit Prae et al. (Langmuir 2017, 33, 13, 3178-3186) and Shripathi et al. ACS Appl. Energy Mater. 2019, 2, 6383−6394. The Ag\textsuperscript{+} binding energy of the peaks centred at 372.2 eV (3d3/2) and 366.6 eV(3d5/2) could be attributed with the Ag\textsubscript{2}S, whereas those peaks at 373.6 eV (3d3/2) and 367.5 eV (3d5/2) could be related with Ag0, see Figure S4B.
With the aim of completing the structural characterization of the synthesized NPs, we have performed X-ray absorption near edge structure (XANES) for the Ag K-edge spectra of Ag$_2$S NPs. XANE is a technique that can be used to determine the oxidation state of the atoms that constitute the samples. Using this technique, we have analysed the NPs namely Ag$_2$S-0 and Ag$_2$S-0.60 and that correspond with Ag$_2$S NPs that exhibit the lowest and the highest absolute QY respectively.

The oxidation state of Ag was analysed by linear combination fitting procedure. The Figure S5A and B represent the XANE spectra of the Ag$_2$S-0 and Ag$_2$S-0.6 samples (open circles) together with the spectra of the Ag (orange line) and Ag$_2$S (green line) used as references. The results show that in both cases that the synthesized NPs are constituted by a predominant phase of Ag$_2$S with a ratio close to 0.75 and a metallic Ag phase with a ratio around 0.25.
Figure S5. A) XANES spectra of Ag\(_2\)S-0 (open circles), Ag\(_2\)S reference (green line) and Ag foil reference (orange line) B) XANES spectra of Ag\(_2\)S-06 (open circles), Ag\(_2\)S reference (green line) and Ag foil reference (orange line). The red line shows the result of the linear combination fitting procedure.

Further, we have performed Fourier transform EXAFS of both types of NPs, as seen in Figure S6. These analyses provide information about the distances of the Ag atoms in the sample and can be used to describe the environment around the Ag atoms.

Figure S6. Fourier transform of Ag K-edge EXAFS for A) Ag\(_2\)S used as reference (red squares), Ag foil used as reference (orange squares) and Ag\(_2\)S-0 sample (blue squares) B)
Ag$_2$S used as reference (red circles), Ag foil used as reference (orange circles) and Ag$_2$S-06 sample (blue circles)

As one can observe, NPs Ag$_2$S-0 (Figure S6A) and Ag$_2$S-06 (Figure S6B) exhibit two main peaks, one located at 2 Å, which matches perfectly with the Ag-S distance in Ag$_2$S phase and a second peak at 2.8 Å, which is characteristic of Ag-Ag distance in metallic Ag phase.

In summary, these results (XRD, XANE and EXAFS) would indicate the presence of a metallic Ag phase within the synthesized Ag$_2$S NPs. Furthermore, we could conclude that although these samples present very different quantum yields the amount of metallic Ag phase is similar in both samples. That would be indicative of the negligible influence of the metallic Ag phase in the overall optical properties of these nanoparticles.

S5. PLQY measurements

The absolute PLQYs of the samples were measured using the same method as the published in Opt Exp 20, 106, A879-A887 (2012). For that, we used a calibrated spectrofluorometer (Edinburgh Instruments, FLS920) equipped with an integrating sphere (Jobin-Yvon). The spectrometer is coupled with a liquid nitrogen cooled NIR photon multiplier tube (PMT; Hamamatsu, R-5587), that was used to measure the excitation and emission. As excitation source we used a Xenon lamp (800nm), (monochromator excitation slits: $\Delta \lambda = 12$nm, emission slit: $\Delta \lambda = 12$nm). The Table S2 depicts the sample name of each measurements. Figure S8 shows an optical image of each samples. The absorption of each sample at the excitation wavelength (exc. 800 nm) was measured in an integration sphere. The signal intensity of the straight light in the absence and the presence of each sample is plotted in Figure S7, while the emission of the NPs after excitation at 800 nm is represented in the Figure S8. The PLQY of these samples was inferred by applying the following equation:

$$PLQY = \frac{\text{No. of Photons Emitted}}{\text{No. of Photons Absorbed}}$$

where the integral of the photons emitted at shorter wavelengths is divided by the total number of excitation photons absorbed in relation to a non-luminescent reference.
The result of the PLQY is showed in the Table S3.

<table>
<thead>
<tr>
<th>Sample</th>
<th>PLQY (%)</th>
<th>Absorption (%)</th>
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</thead>
<tbody>
<tr>
<td>H1</td>
<td>0</td>
<td>70.47</td>
</tr>
<tr>
<td>H2</td>
<td>0.36648</td>
<td>68.38</td>
</tr>
<tr>
<td>H3</td>
<td>1.93267</td>
<td>67.27</td>
</tr>
<tr>
<td>H4</td>
<td>2.31753</td>
<td>66.34</td>
</tr>
<tr>
<td>H5</td>
<td>0.44572</td>
<td>67.31</td>
</tr>
<tr>
<td>H6</td>
<td>0.11854</td>
<td>65.45</td>
</tr>
</tbody>
</table>

S4. Dose dependent experiment and performance comparison between optimized NPs and commercially available NPs.

To demonstrate the superior performance of the optimized NPs, we have designed an experiment in which quartz cuvettes are filled with different solutions of optimized and commercial NPs in phosphate buffer saline (PBS). On top of the cuvette, we placed a piece of a biological tissue (chicke breast) cut in such a way that resemble a right triangle, to simulate the contribution of a living tissue, see Figure S9A. Upon illuminating with a CW laser at 800 nm at a power density of 45 mW/cm², the PL emission of each sample was taken with a Peltier cooled InGaAs camera (Xeva 320 from Xenics). The InGaAs detector was cooled down to -40 °C and two long-pass filters (FEL850 from Thorlabs) were used to remove the background signal generated by the scattered laser radiation. From these images, (Figure S11B) one can observe the superior performance of the optimized NPs when they are compared with the commercially available NPs.
under the same experimental conditions. In a more systematic way, when we measure the PL intensity obtained from these samples, we can determine that the PL emission of the optimized NPs is at least 10 fold higher than the one obtained from the commercial NPs, see Figure S11C. These results are in agreement with the PL lifetime measurements carried out for the commercial and optimized NPs and that give values of 45 ns and 395 ns respectively and which are directly related with QY of the NPs.

**Figure S9.** A) optical image of a cuvette with a piece of tissue on top. B) PL NIR images of cuvettes having different concentrations of commercial Ag2S or optimized Ag2S nanoparticles. C) PL intensities obtained after integrating the PL NIR images of each sample at different concentration. The PL NIR images were obtained upon illumination the samples with a CW laser working at 800 nm and at a power intensity of 45 mW/cm² and an acquisition time of 0.01s.