Morphology and optical characterization of semiconducting nanostructures

Author: Ester Carranza Botey

Facultat de Física, Universitat de Barcelona, Diagonal 645, 08028 Barcelona, Spain.*

Advisor: Adriana I. Figueroa

Abstract: Semiconductor nanostructures have an enormous potential for applications in diverse areas of modern technologies due to their versatility and possibility of tuning their properties as desired. In this work, the optoelectronic properties of Bi_2S_3 and Bi_2S_3 -Au nanostructures were correlated with their morphology and hybridization features for samples with different shapes, sizes and Au inclusion. The aim was to find the optimal values of these parameters for enhancing their optical response. This was carried out by characterizing morphologically and optically those nanostructures with TEM imaging, UV-Vis and PL spectroscopies. The results showed that the optical properties depend strictly on the width-to-length ratio and that Au presence enhances light absorption in the infrared range. It was found that the gap energy values of the nanostructures were larger than that of bulk Bi_2S_3 .

I. INTRODUCTION

Semiconductors have proven to be of great use in many areas, such as biomedicine, electronics, and optics. Due to recent scientific breakthroughs in the nanoscale field, nanostructured materials are a tremendous opportunity to revolutionize countless applications, such as contrast enhancement in imaging techniques, drug delivery, nanoelectronics and further more. This advanced nanotechnology is of key interest due to its multifunctionality and versatility since the performance of nanoobjects strictly depends on their morphology and chemical composition [1]. In particular, Bi_2S_3 stands out for its optoelectronic properties. It presents a band gap energy of about 1.3 eV so that it absorbs in the visible light and infrared ranges, which is convenient for biomedical applications, as X-ray imaging and photothermal therapy [2][3]. Hence, it is an attractive candidate as a nanoobject chemical compound. Additionally, it has been demonstrated that the inclusion of gold in semiconducting nanostructures improves the optical absorption [4]. On top of that, the use of different synthesis processes allows for obtaining a wide variety of sizes and geometries of nanostructures, such as nanoneedles (NN), nanorods (NR), nanospheres (NS), among many more. Optimization and tunability of the most suitable parameters for a specific application, promote the creation of nanotechnology à la carte with a whole world of possibilities.

This project aims at characterizing the morphology and optical properties of Bi_2S_3 and hybrid Bi_2S_3 -Au nanostructures experimentally. This way, it is possible to establish correlations between their optoelectronic response with their morphology and hybridization features, so that optimization of the latter two is performed. Therefore, these optical properties can be enhanced for applications ranging from biomedicine to optoelectronic devices in new technologies.

II. EXPERIMENTAL

A. Bi_2S_3 and Bi_2S_3 -Au synthesis

Seven samples with different morphology, with and without Au inclusions, were prepared from optimized protocols, as extensively described in [2][4], based on hot injection of Bi₂S₃. During the synthesis, the temperature of the sulfide injection controls the shape, size, and crystallinity of the nanostructures. A step of gold injection was added for the hybrid Bi₂S₃-Au samples, so that a series of sister samples, with and without gold, is obtained. Tables I and II list the most relevant parameters that describe the characteristics of the samples in terms of their length (L), width (W), and width-to-length (W:L) ratio, as well as bismuth-to-gold (Bi:Au) ratio in the case of hybrid structures.

B. Characterization methods

Imaging techniques and optical methods were used to characterize the Bi_2S_3 and hybrid Bi_2S_3 -Au samples, namely:

Transmission electron microscopy (TEM). The morphology of the nanostructures was characterized from images obtained by a JEOL 1010 electron microscope operating at 80 kV.

Ultraviolet-visible (UV-vis) spectroscopy. The optical absorbance and transmittance of the samples were characterized using a Specord 205 spectrometer with a wavelength range between 300 and 1100 nm and a spectral resolution of 1 nm. Measurements were performed at room temperature.

Photoluminescence (PL). The optical transmittance and reflectance spectra of the nanostructures were also obtained using a integrating sphere (Bentham PV300 EQE) system, with monochromatic light from a Xe and quartz halogen dual lamp source, collected with a InGaAs photodetector. Measurements were performed at room temperature.

^{*}Electronic address: ecarrabo10@alumnes.ub.edu

III. RESULTS AND DISCUSSION

A. Morphological characterization

TEM images of Bi_2S_3 and hybrid Bi_2S_3 -Au samples are shown in Figs. 1 and 2, respectively. In order to quantitatively characterize the morphology of the nanostructures, these images were digitally processed using the ImageJ software [5]. The length (L) and width (W) values of about 100 nanoobjects were analyzed for each sample, and the histograms obtained for the distribution of L and W in each case were fitted to log-normal distributions using the following expression

$$f(x) = \frac{1}{x\sigma\sqrt{2\pi}}e^{-\frac{1}{2}\left(\frac{\ln(x-\mu)}{\sigma}\right)^2} \tag{1}$$

where x corresponds to the fitted parameter (W or L), σ is the standard deviation and μ is the mean value. With this procedure, it is possible to examine the uniformity of the samples in terms of size.



FIG. 1: TEM images for the series of Bi_2S_3 NRs: (a) NR2 and (b) NR3. The corresponding W:L ratio is included.

TABLE I: Structural parameters for the Bi_2S_3 samples as obtained by TEM. Length (L), width (W) and W:L ratio.

Name	L (nm)	W (nm)	W:L ratio
NR1	88 ± 32	6.5 ± 2.5	1:14
NR2	38 ± 19	6 ± 4	1:6
NR3	31 ± 18	12 ± 7	2:5

TABLE II: Structural parameters for the hybrid Bi_2S_3 -Au samples, as obtained by TEM. Length (L), width (W), width-to-length (W:L) and bismuth-to-gold (Bi:Au) ratios.

Name	L (nm)	W (nm)	W:L ratio	Bi:Au ratio
NR1h	80 ± 21	8 ± 2	1:10	5:3
NR2h	45 ± 5	7 ± 2	1:6	5:2
NR3h	32 ± 7	12 ± 3	2:5	5:2

Figure 1 and Table I show that the non-hybrid samples present a morphology and average size values similar to those reported in [2]. TEM images in Fig. 2 show that Au NPs are embedded in the NRs for all hybrid Bi₂S₃-Au samples. The most notable difference is that the sample NR1h has such embedding mainly along its length, while



FIG. 2: TEM images for the series of hybrid Bi_2S_3 -Au samples: (a) NR1h, (b) NR2h and (c) NR3h. The W:L and the bismuth-to-gold (Bi:Au) ratios are included for each sample.

the other two nanostructures have gold throughout both of their dimensions. This is a consequence of the W:Lratio of the former, since the sample NR1h has the most elongated geometry. A plausible interpretation is that Au NPs tend to embed along the less confined dimension.

For the hybrid samples listed in Table II, the length and width averages vary considerably from their respective gold-free sister ones. This could be explained by the Au inclusion and the statistics analysis performed.

B. Optical characterization

1. Ultraviolet-visible (UV-vis) spectroscopy

Results of the UV-vis absorbance spectra for the Bi₂S₃ and hybrid Bi₂S₃-Au samples are displayed in Figs. 3 and 4. The shape of the curves of both types of samples is similar, showing first a bump, followed by a linear zone that ends in a continuous decay. Fig. 3 depicts a comparison of the optical absorption properties for two Bi₂S₃ nanostructures with similar W:L, with and without Au inclusions. It shows that the Bi_2S_3 samples absorb more than the hybrid ones for shorter wavelengths, while the Bi₂S₃-Au nanostructures show higher absorbance as the wavelength increases. That is, the absorbance of samples without Au decays more steeply, so that it becomes practically zero for long wavelengths (above ~ 800 nm and ~ 700 nm, for W:L ratios of 1:14 and 1:6, respectively). Therefore, the inclusion of Au suggests an improvement of optical absorption towards the infrared range. The absorption shoulder (turning point in the curves) occurs around 400 nm for samples with W:L ratio 1:6 and around 600 nm for those with W:L ratio of around 1:10. Hence, in both cases it is blue-shifted compared to Bi_2S_3 in bulk form (around 950 nm) [6].

Figures 4(a) and 4(b) show the comparison of the ab-

Treball de Fi de Grau



FIG. 3: UV-vis absorbance spectra for the series of Bi_2S_3 NRs, with and without Au inclusions, with W:L ratios of around (a) 1:10 and (b) 1:6, included in the legend.



FIG. 4: UV-vis absorbance spectra for all Bi_2S_3 and Bi_2S_3 -Au samples, grouped as (a) samples without Au and (b) samples with Au inclusions. The respective W:L ratio is included in the legend as reference. The curves for the NR2 and NR2h nanostructures have been rescaled according to their concentration to ensure a proper comparison between the samples.

sorbance response of all Bi_2S_3 samples, grouped as samples without Au and with Au inclusions, respectively. Given that samples NR2 and NR2h had half the concentration of the rest, their absorbance curves were rescaled

to the concentration. The absorbance, A is defined as

$$A(\lambda) = \varepsilon(\lambda)lc \tag{2}$$

where ε , l, and c are the extinction coefficient, the thickness, and the concentration, respectively. Thus, A and c were assumed to be proportional for the same sample, so the estimated absorbance for twice the concentration would also be twice as high. This way, the qualitative comparison between samples is more accurate.

For non-hybrid nanoobjects, sample NR1, which corresponds to the most elongated geometry, shows the highest absorbance for the whole spectrum. This suggests that lower confinement in the length direction results in higher absorption, so the NR1 geometry resulted to be optimal for the optical response. The NR2 and NS1 nanostructures, corresponding to shorter NRs and nanospheres, respectively, show absorbance spectra similar to each other, but lower than the case of NR1.

Hybrid NRs with more elongated geometries, i.e. sample NR1h, also show the highest absorbance for these kind of samples. In Fig. 4(b), it observed that nanostructures with this morphology are the ones that absorb the most in the infrared range. The Bi:Au ratio could explain this phenomenon, as it is slightly higher for this sample, being 5:3 instead of 5:2 for NR2h and NR3h. This way, the enhancement of infrared light absorption is better appreciated.

2. Photoluminescence (PL)

Results for the transmittance spectra, as measured in PL for all samples, are plotted in Fig. 5. These plots



FIG. 5: PL transmittance spectra for the Bi_2S_3 and Bi_2S_3 -Au samples with W:L ratios of around (a) 1:10 and (b) 1:6, included in the legend.

Treball de Fi de Grau

show that the transmittance of the non-hybrid samples increases and reaches saturation for shorter wavelengths than for the hybrid ones. Therefore, the inclusion of Au delays the wavelength from which the sample transmits. In other words, it increases the spectral range in which the nanostructure absorbs.

Figures 6 and 7 show the absorbance, transmittance and reflectance of Bi_2S_3 and Bi_2S_3 -Au samples, respectively. The shape of the curves is similar for all the samples analyzed. They show that absorbance decays, transmittance increases, and reflectance generally remains constant with wavelength. Transmittance of the hybrid NRs does not reach saturation due to an instrumental limitation since the PL equipment employed could not reach longer wavelengths. Future projects should consider a broader spectral range using another optical method to better characterize the transmittance of Bi_2S_3 -Au nanostructures.

The intersection between the absorbance and transmittance curves can be considered an accurate estimate of the wavelength at which the sample starts to transmit, which should be as high as possible so that it absorbs



FIG. 6: PL transmittance (T), reflectance (R), and absorbance (A) spectra for the series of non-hybrid samples (a) NR1, (b) NR2 and (c) NS1, with their respective W:L ratio.



FIG. 7: PL transmittance (T), reflectance (R), and absorbance (A) spectra for the hybrid samples (a) NR1h and (b) NR2h. The respective W:L ratio is included as reference.

light over a broader spectral range. The NS1 nanostructures show a longer wavelength for the intersection, followed by the samples NR1 and NR2, in that order. These results suggest that a geometry with three confined dimensions, i.e., the spherical one, is more optimal for retarding the absorbance for non-hybrid samples.

Relevant optoelectronic parameters of the nanostructures, such as their band gap energy $E_{\text{band gap}}$, can be extracted from the graphical representation of the absorbance curves in a Tauc plot. This kind of graph represents the square of $\alpha dh\nu$, where α is the absorption coefficient, d is the sample thickness and $h\nu$ is the inci-



FIG. 8: Tauc plot of the square of $\alpha dh\nu$, where α is the absorption coefficient, d is the sample thickness and $h\nu$ is the incident photon energy, as a function of the latter parameter. The sample name and their respective W:L ratio are included.

Treball de Fi de Grau

dent photon energy, as a function of the latter parameter. The absorption coefficient α was calculated as

$$\alpha = -\ln\left(\frac{T}{1-R}\right) \tag{3}$$

where T is the transmittance, and R is the reflectance. Figure 8 displays the Tauc plots obtained for Bi_2S_3 samples without Au. For each curve, the linear region fit at high energies allows for estimation of the $E_{\text{band gap}}$ as the intersection value with the x-axis.

TABLE III: W:L ratio and band gap energy values for the Bi_2S_3 samples, as obtained from the analysis of PL spectra.

Name	W:L ratio	$E_{\rm bandgap}$ (eV)
NR1	1:14	2.4 ± 0.1
NR2	1:6	2.4 ± 0.1
NS1	-	2.1 ± 0.1

Table III lists the $E_{\text{band gap}}$ values obtained for the nanostructures. These values differ considerably from the gap energy value of bulk Bi₂S₃ ($E_{\text{band gap}} \approx 1.3 \text{ eV}$) [7]. As expected, the energy gaps for these nanostructures are larger [2], as their dimensions give rise to quantum confinement effects. The samples NR1 and NR2 are the ones with higher values, which means that they absorb from a higher incident frequency. In other words, compared to the NS1 spheres, they absorb more light below a shorter wavelength. This is consistent with spectra displayed in Fig.6, where it is observed that the sample NS1 absorbs for a broader spectral range. Therefore, the nanostructures with 3-D confinement exhibit a wider and more optimal optical absorption range.

For hybrid nanostructures, the presence of Au makes a quantitative interpretation of the PL data more difficult. Analysis of Tauc plots and similar tools to extract the $E_{\text{band gap}}$ for these kind of samples will be evaluated more rigorously in future works. Instead, a qualitative interpretation of the data shown in Fig. 7 is given as follows. The transmittance of both hybrid samples studied is very similar and starts to increase for a similar wavelength ~ 750 nm, equivalent to a photon energy of around 1.65 eV. If we compare the hybrid NRs with their sister nanostructures without Au and with comparable W:L ratio, it is clear that Au presence effectively delays the increase in transmittance. Hence, its inclusion enhances the absorption, so the latter becomes significant over a broader spectral range. It is worth noting that the curves for samples NR1h, NR2h, and NS1 show an intersection for nearly identical wavelength around $\lambda \approx 760$ nm.

IV. CONCLUSIONS

In this study, the morphology and optoelectronic properties of Bi₂S₃ and Bi₂S₃-Au nanostructures were characterized. In terms of morphology, the most elongated hybrid samples experience the greatest change in length and width with Au inclusion compared to their respective gold-free sister ones. The optical properties of both types of nanostructures show an enhancement of the band gap energy compared to the bulk Bi_2S_3 one. According to UV-vis spectroscopy, the most optimal geometry for optical absorption is the most elongated one. In this work, it corresponds to W:L ratios of 1:14 and 1:10. Additionally, it was found that the hybrid samples show higher absorption in the infrared range. The data obtained by PL shows that hybrid samples and gold-free NSs broaden the spectral range in which they absorb. Therefore, the more significant outcome is that the inclusion of gold in Bi_2S_3 nanostructures enhances optical absorption in the infrared range. Future work is aimed at finding the most optimal Bi₂S₃-Au sample geometry for improving infrared optical absorption while facilitating the embedding of Au nanoparticles.

Acknowledgments

I would like to express my gratitude to my advisor Adriana I. Figueroa for her mentoring, encouragement and dedication, as well as José Ruiz Torres for sharing his knowledge and guiding me throughout this work. I want to acknowledge the collaboration of Magnetic Nanomaterials (GMN) and Micro and Nanotechnology and nanoscopies for Electronic and Electrophotonic Devices (MIND) groups, especially Joshua Diago Forero's help with the PL measurements. Last but not least, I want to thank my family and friends for their huge support.

- Inwati, G. K., et al. "Multifunctional properties of hybrid semiconducting nanomaterials and their applications." Nanoscale Compound Semiconductors and their Optoelectronics Applications. Woodhead Publishing (2022).
- [2] Escoda i Torroella, M., et al. "Selective anisotropic growth of Bi₂S₃ nanoparticles with adjustable optical properties." *Physical Chemistry Chemical Physics* (2022).
- [3] Ajiboye, T. O., and D. C. Onwudiwe. "Bismuth sulfide based compounds: properties, synthesis and applications. Results Chem 3: 100151." (2021).
- [4] Escoda i Torroella, M.. "Tuning the performance of mag-

netic, semiconductor, and multifunctional hybrid nanostructures." Ph.D. thesis, University of Barcelona (2022).

- [5] Abràmoff, Michael D., et al. "Image processing with ImageJ." *Biophotonics international* (2004): 36-42.
- [6] Yu, H., and Wang J. in Proceedings of the 2016 5th International Conference on Advanced Materials and Computer Science. Atlantis Press (2016): 935–938.
- [7] Madelung, O.. Semiconductors: Data Handbook. Springer Science & Business Media (2004): 613–633.