



Exploring the Potential of Bismuth Chalcogenide Semiconductors: Synthesis, Properties, and Applications

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Research

Synthesis of semiconductor
nanoparticles:
Applications
Ecotoxicity

- Nanomedicine (cancer treatment)
- Radiation detectors
- Water treatment by photocatalysis

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- **Water treatment by photocatalysis**

Bismuth-based semiconductors

BiSI

$\text{Bi}_{19}\text{S}_{27}\text{I}_3$

Bismuth-based semiconductors

BiSI

Promising candidate:

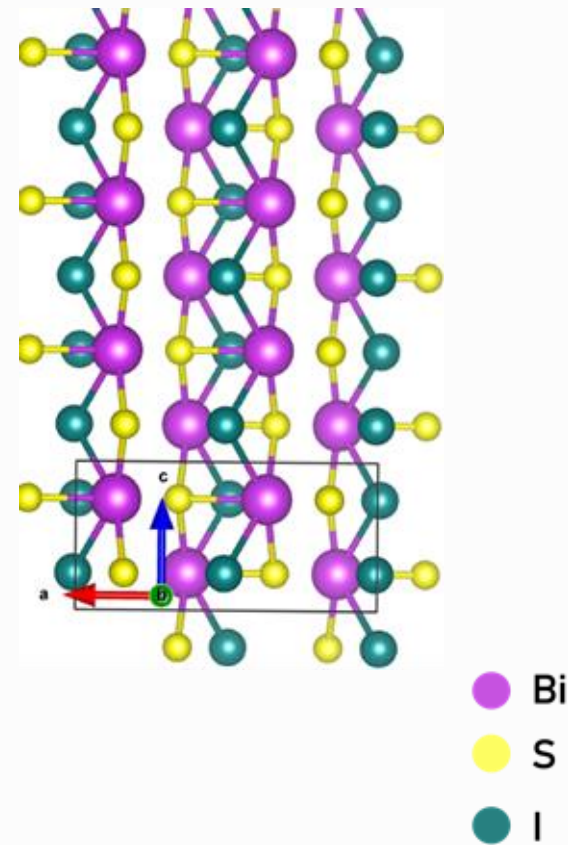
- Photocatalysis
- Photodetection
- Hard radiation detection
- Supercapacitors
- Solar cells

Synthesis

- Presents several challenges in terms of:
 - Phase purity
 - Environmentally friendly methods

BiSI

- Is gaining attention due to:
 - Anisotropic optoelectronic properties
 - Comprising relatively abundant and non-toxic elements



Bismuth-based semiconductors



Promising candidate:

Photocatalysis
Photodetection
Hard radiation detection
Supercapacitors
Solar cells



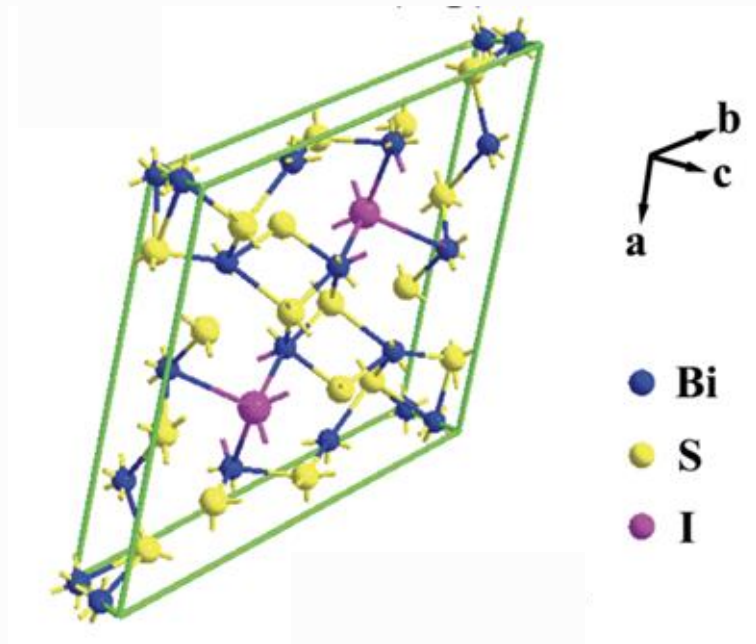
Is gaining attention due to:
Anisotropic optoelectronic
properties
Comprising relatively
abundant and non-toxic
elements

Synthesis

Synthesis and properties are not
thoroughly studied.

Stoichiometry

More than one way of
writing it:
 $\text{Bi}(\text{Bi}_2\text{S}_3)_9\text{I}_3$ or $\text{Bi}_{13}\text{S}_{18}\text{I}_2$



Synthesis – BiSI

Pure and a composite

BiSI

SOLUTION SYNTHESIS



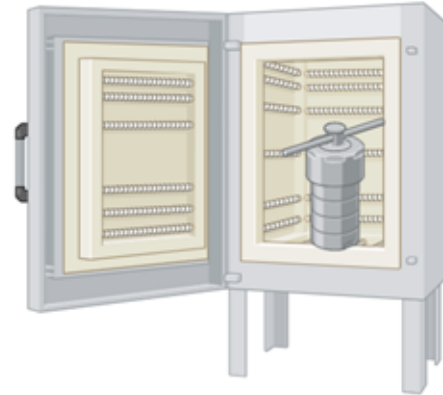
Medium
Mono ethylene glycol
(MEG)

Precursors
 Bi_2S_3 , I_2

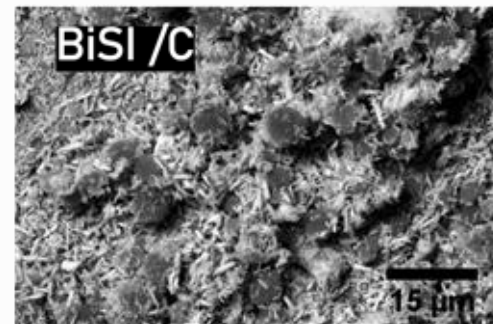
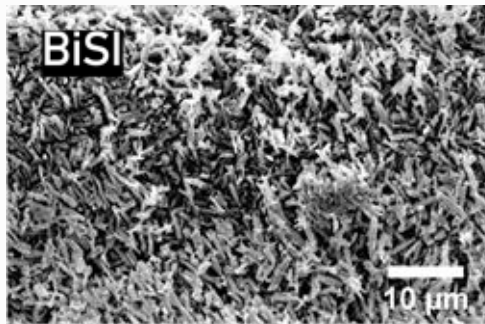
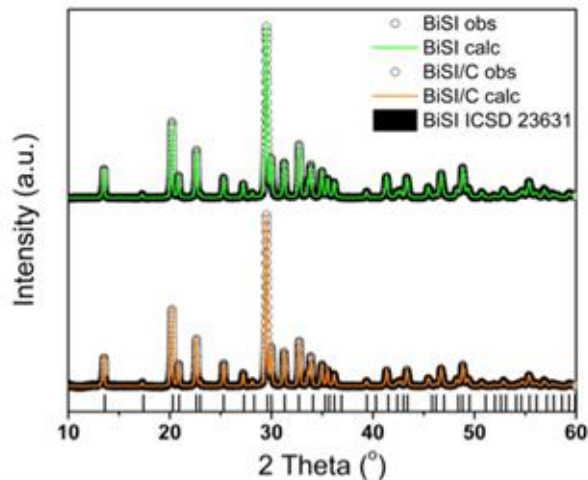
Temperature
 180°C

BiSI/C

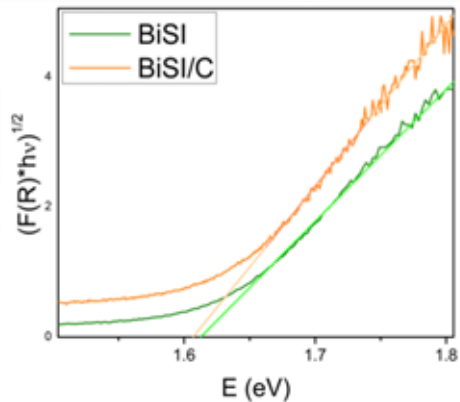
SOLVOTHERMAL SYNTHESIS



Characterization



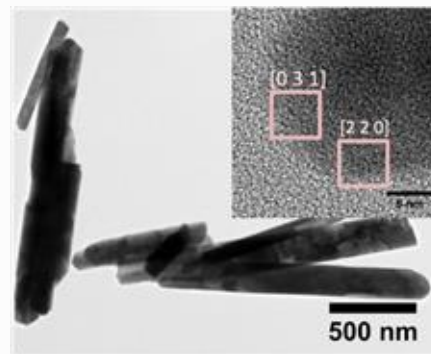
SEM images show BiSI nanorods in both cases, but also carbon round particles in the solvothermal synthesis.



E_g BiSI: 1.61 eV

E_g BiSI/C: 1.61 eV

BiSI and BiSI/C have the same indirect band gap



TEM images of nanorods found in samples from BiSI and BiSI/C. HR-TEM shows planes corresponding to BiSI.

Synthesis mechanism

Self-sacrificing template process

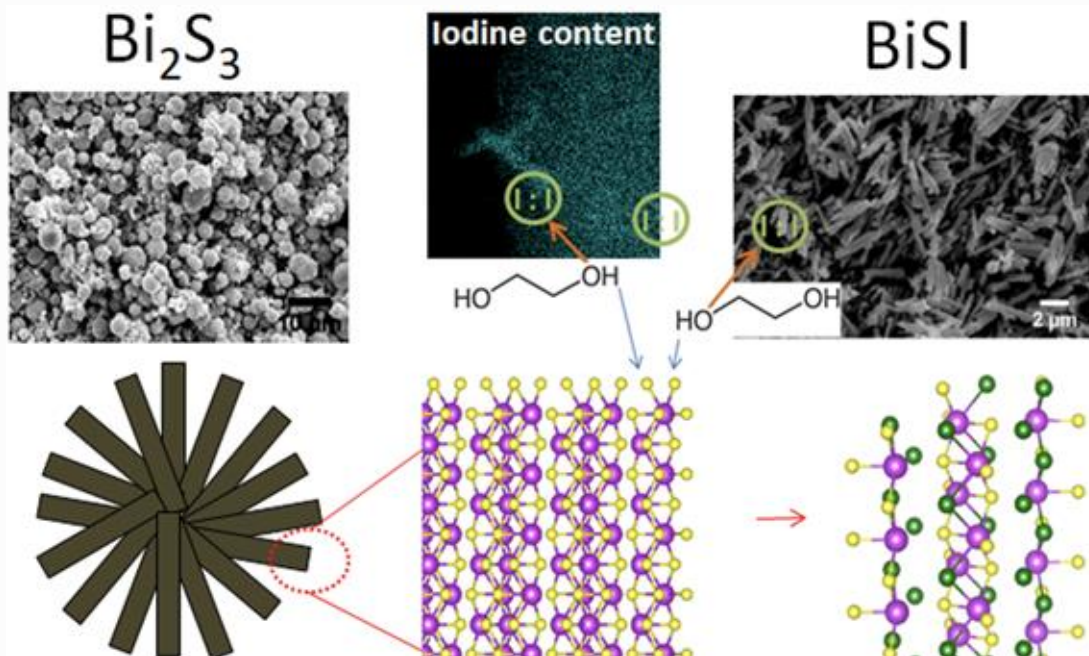
Inorganic Chemistry

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Article

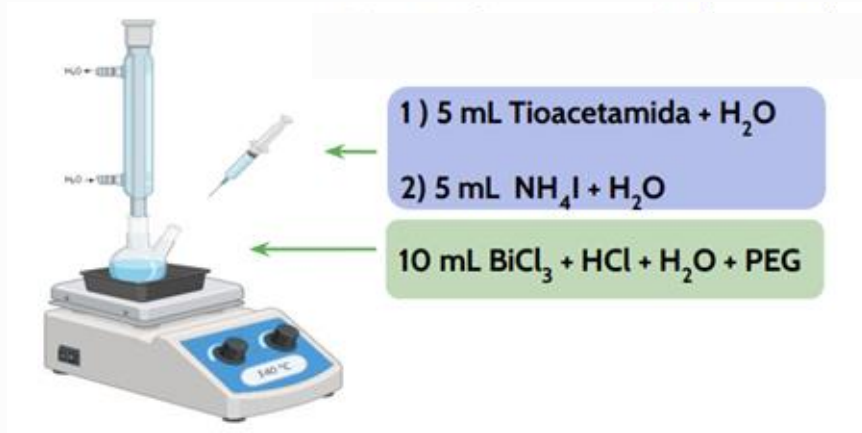
Understanding the Crystal Growth of Bismuth Chalcogenide Nanorods through a Self-Sacrificing Template Process: A Comprehensive Study

Maia Mombrú Frutos,* Carolina Grosso, Álvaro Olivera, Heinkel Bentos Pereira, Laura Fornaro, and Ivana Aguiar



Synthesis – $\text{Bi}_{19}\text{S}_{27}\text{I}_3$

Gren method



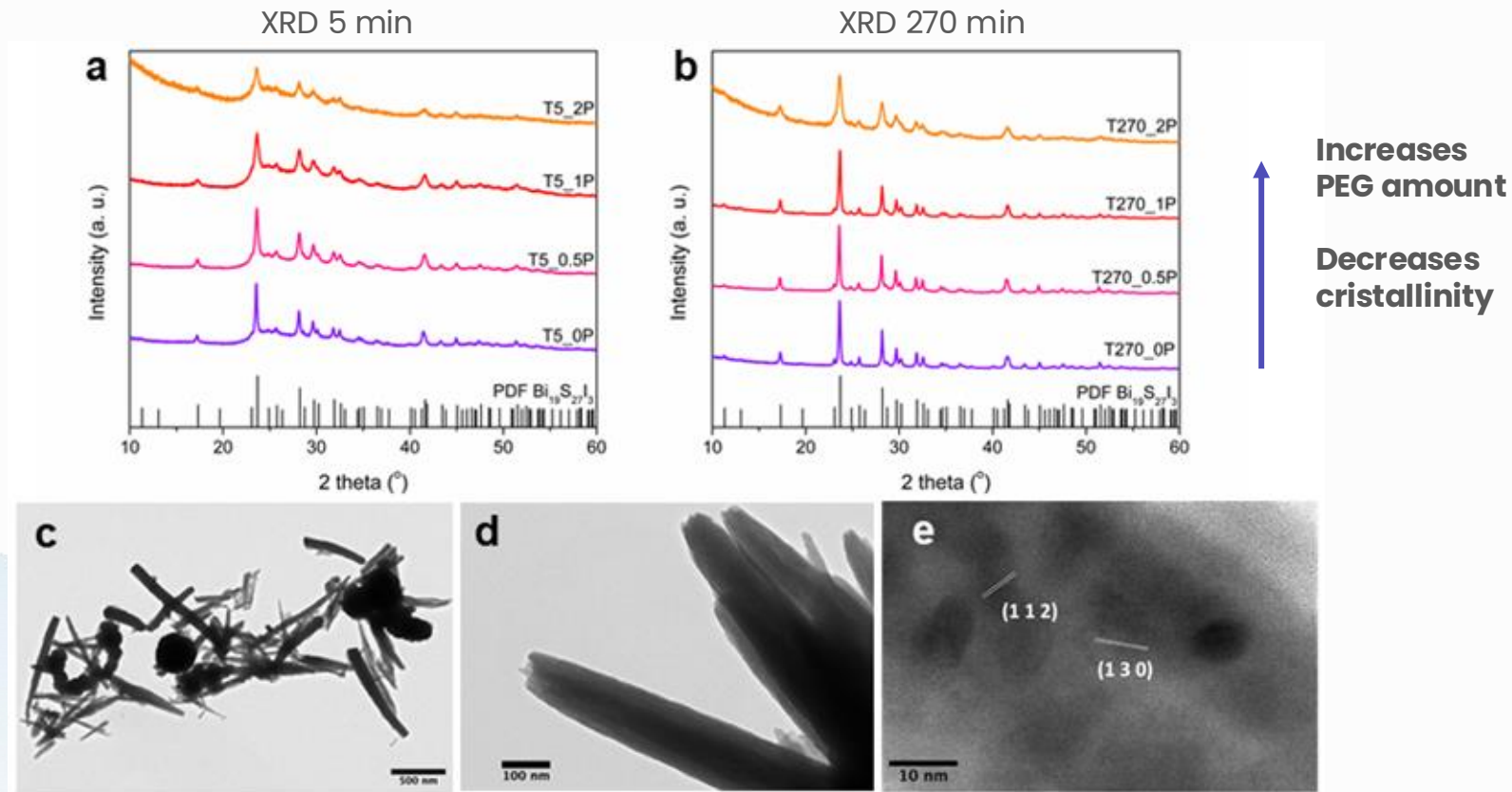
Hot injection method

Water as solvent

PEG as capping agent

Variations: time and PEG amount

Results



Two morphologies: nanorolls and rounded nanoparticles

Results

Journal of
Materials Chemistry C



PAPER

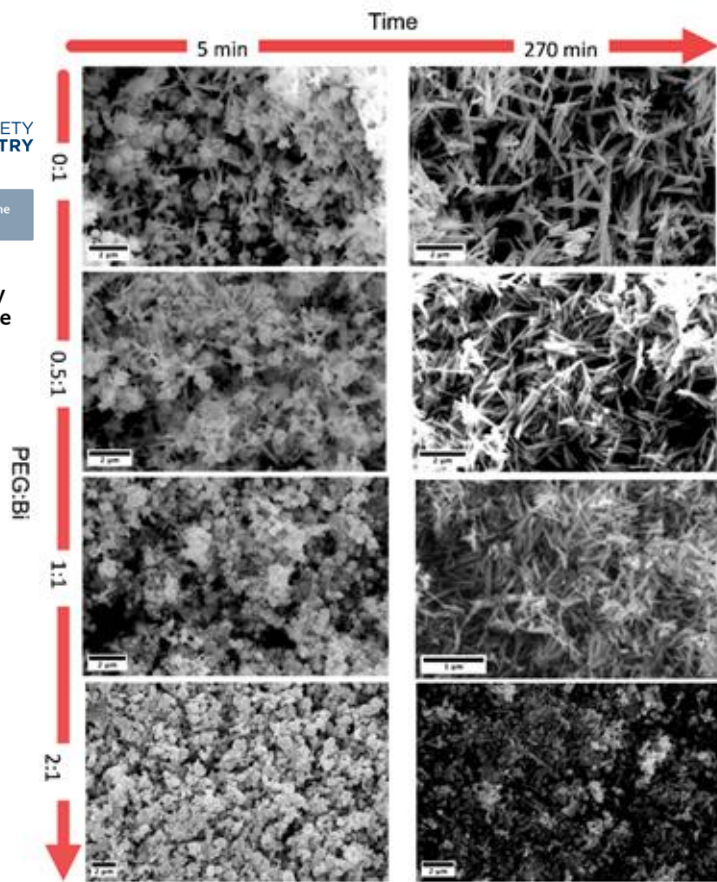
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Green solution synthesis of $\text{Bi}_{19}\text{S}_{27}\text{I}_3$ nanostructures – engineering their morphology through polyethylene glycol and their use in the photocatalytic reduction of $\text{Cr}(\text{VI})^\dagger$

Maia Mombrú-Frutos,^a Martina Viera,^{ab} Carolina Grosso,^a
Mauricio Rodríguez Chialanza,^c Laura Fornaro,^b
María Eugenia Pérez Barthaburu,^{a*} and Ivana Aguiar^{b,*}

Cite this: DOI: 10.1039/d4tc01480d

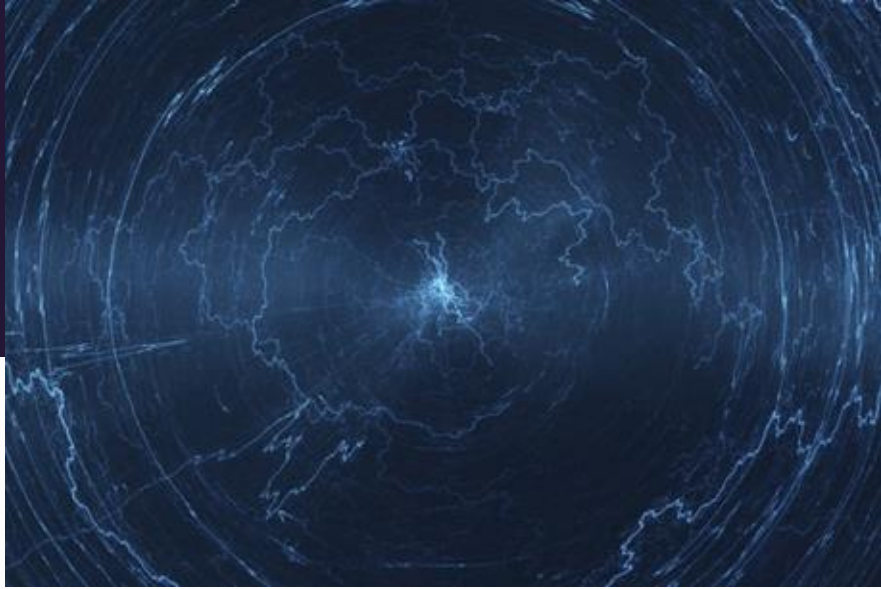


With time 5 min the samples are formed by nanorolls and round nanoparticles

With time 270 min the samples only have nanorolls



Round nanoparticles dissolve with time



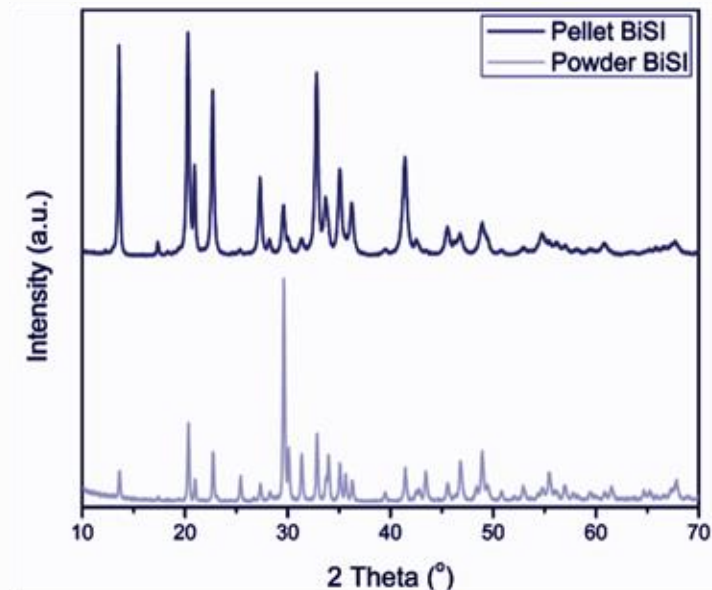
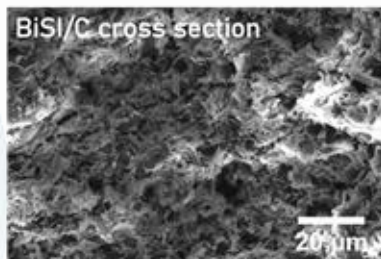
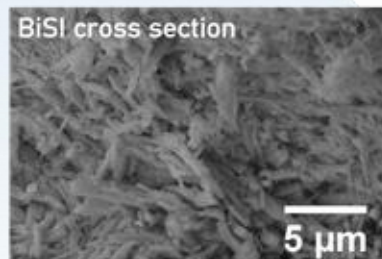
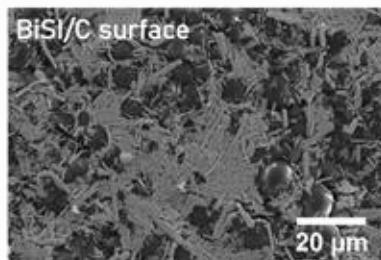
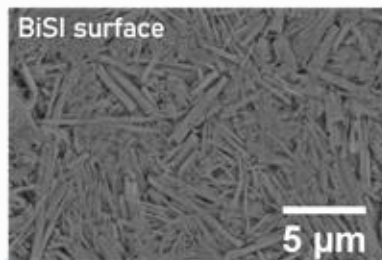
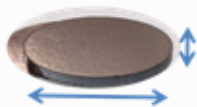
Radiation detectors



Radiation detection with pellets

Pellets fabrication – BiSI

COLD UNIAXIAL PRESS: 9 TON



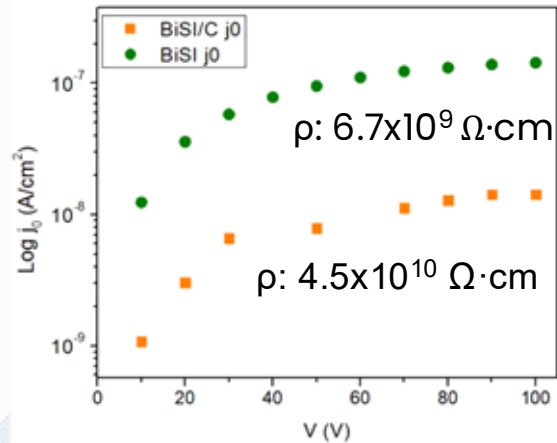
Increase in $(h k 0)$ planes intensities show a slightly preferred orientation of rods parallel to the surface, and this is increased in the pure compound

Radiation detection with pellets

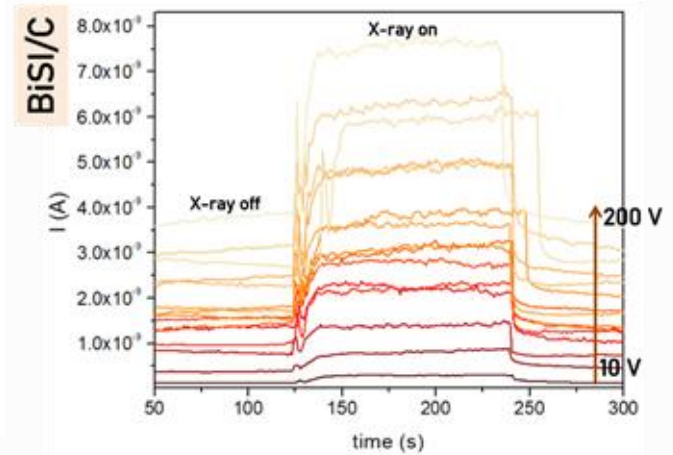
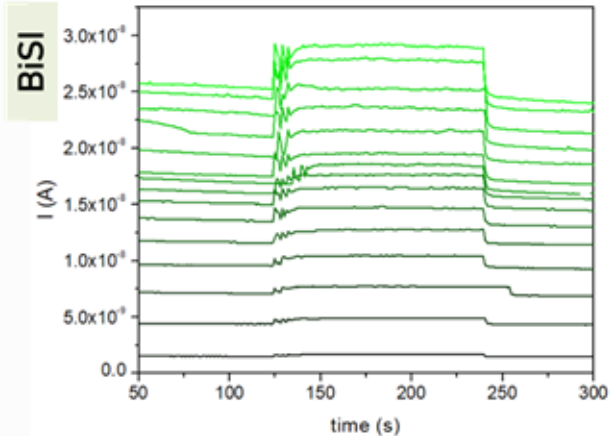
X-ray detection



Dark current density vs applied voltage



Response to X-rays (~ 20 mGy/s) with applied voltage

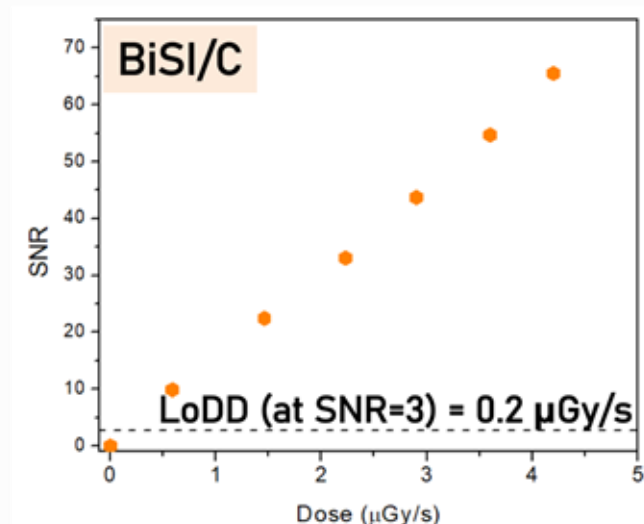
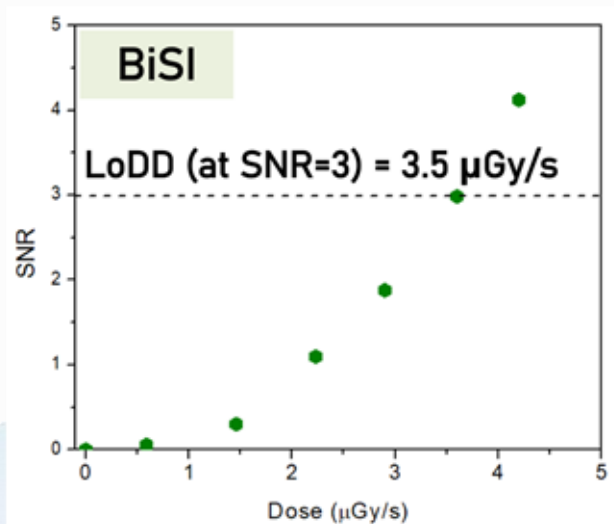


The higher resistivity of BiSI/C nanocomposite results in a lower background noise and a better response to radiation either for an increasing voltage bias or dose rate.



Radiation detection with pellets

X-ray detection



Carbon particles in the nanocomposite
BiSI/C allow for a more robust device
capable of detecting lower doses than pure
BiSI

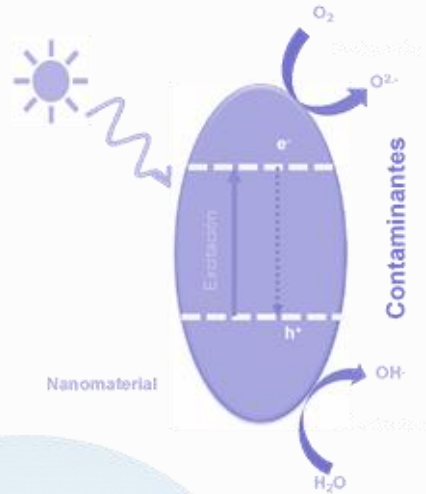


Photocatalysis

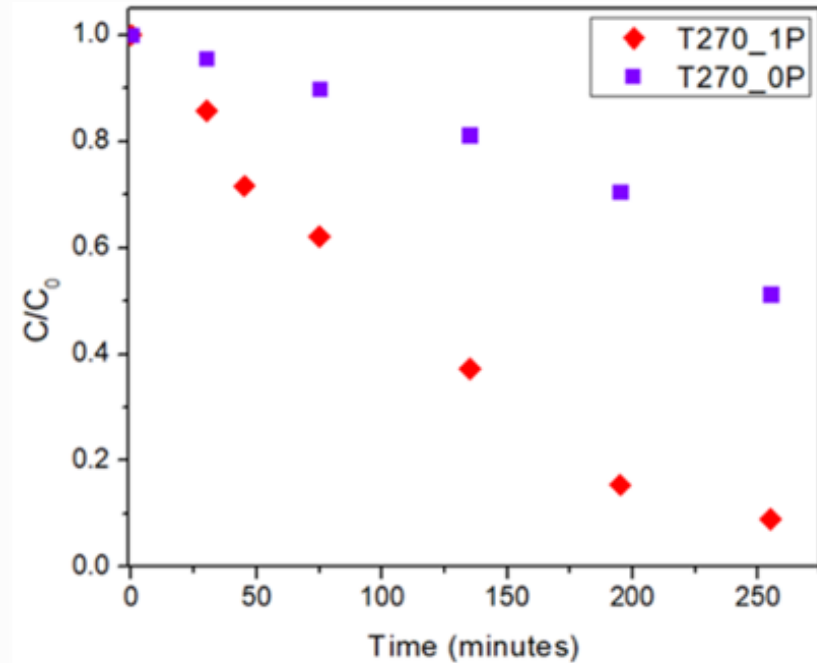


Results – $\text{Bi}_{19}\text{S}_{27}\text{I}_3$

Degradation of Cr(VI) by photocatalysis



**Samples without and with
PEG containing only
nanorolls**



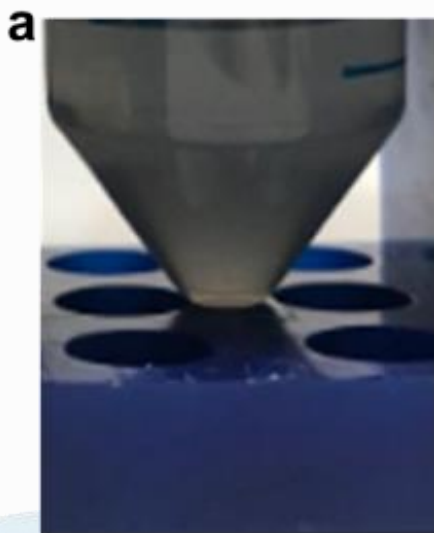
Determination by the diphenylcarbazide method

After 255 min, sample T270_1P achieves 91% of degradation

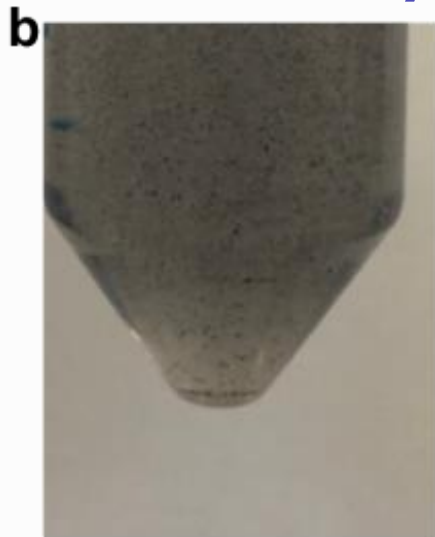


Results

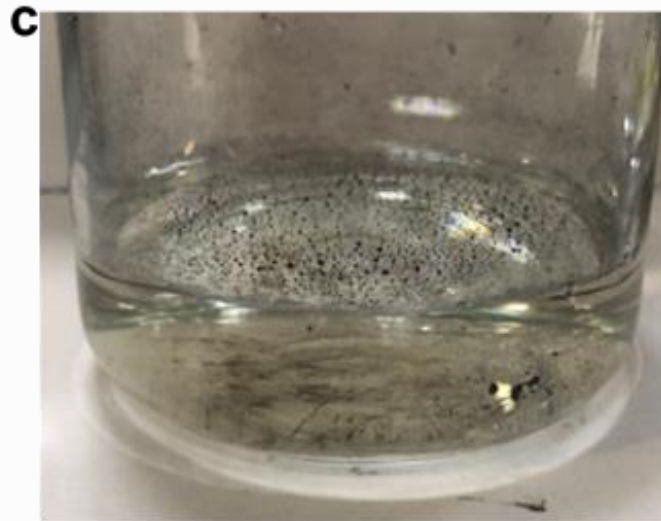
Degradation of Cr(VI) by photocatalysis



Sample T270_IP suspended in Cr(VI) aqueous solution



Sample T270_OP suspended in Cr(VI) aqueous solution



Sample T270_OP in Cr(VI) aqueous solution in the photocatalysis reactor.

PEG-capped nanorolls are better suspended in water

The PEG improves the stabilization of the nanorolls in an aqueous solution, more intimate exchange between the semiconductor nanostructures surface and the Cr(VI)

Conclusions

We present two simple methods for obtaining either pure BiSI phase nanorods or a BiSI-C nanocomposite.

Both materials detect low energy X-rays in a simple sandwich device configuration, but the nanocomposite has a better overall performance.

Conclusions

Green synthesis approach for nanostructures of $\text{Bi}_{19}\text{S}_{27}\text{I}_3$.

We successfully controlled the morphology of the nanostructures by adding PEG as capping agent at different concentrations and varying the reaction time.

The incorporation of PEG enhanced the dispersion of the nanostructures in water, improving the efficiency of $\text{Bi}_{19}\text{S}_{27}\text{I}_3$ nanostructures as a photocatalyst for Cr(VI) reduction.

Our group



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Funding



Collaborators





Thank you!



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