Bi_2O_3 nano-sheets and nanotubes synthesized by discharges in liquid nitrogen

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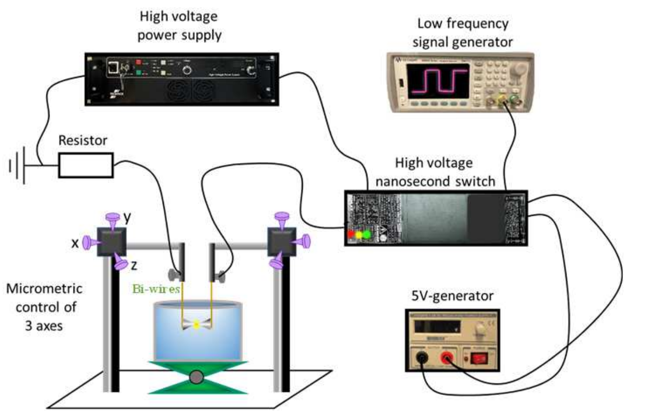
1 – INTRODUCTION

Bismuth oxide has a narrower band gap than TiO_2 [1]. It is an excellent photocatalyst for water photolysis and organic pollutants degradation under visible light. As an important type of layer-structured P-type semiconductor, the photocatalytic behaviour of Bi_2O_3 is pretty different from N-type TiO_2. It is also dependent on the allotropic phase as Bi_2O_3 adopts many polymorphic forms, the most common being monoclinic α-phase, tetragonal β-phase, body-centered cubic γ-phase, and face centered cubic δ-phase.

In this work, we show how it is possible to synthesize easily Bi_2O_3 nanoparticles by nanosecond pulsed discharges in liquid nitrogen. By creating high-voltage (10 kV) discharges between Bismuth electrodes separated by a distance of 100 µm typically, Bismuth nanoparticles are produced with three size distributions. Oxidation occurs in a second step, after nitrogen evaporation. Therefore, a part of the nanoparticles exhibit a core-shell structure if oxidation is incomplete. When the applied voltage is lowered to 4-5 kV, ultra-thin nano-sheets and nanotubes also form. The growth mechanisms of these objects are studied here.

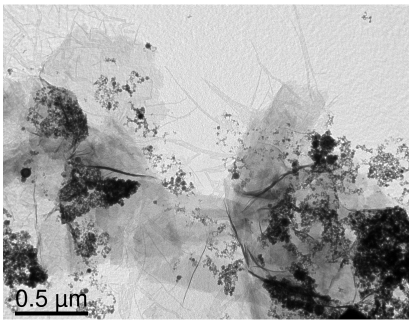
[1] C. H. Ho *et al.* Optics express 21, 11965 (2013)

2 – EXPERIMENTAL SETUP



- Treatment duration: 30 min
- Applied voltage: 4 to 10 kV
- Voltage pulse width: 100 ns
- Discharge frequency: 10 Hz

3 – SYNTHESIZED NANO-OBJECTS



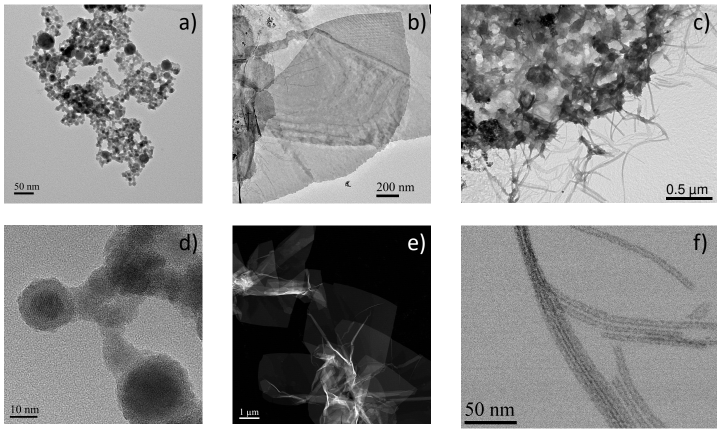
3 distributions of nanoparticles:

- 2-10 nm
- 20-50 nm
- > 100 nm

but also: (only at low voltages 4-5 kV)

- nanosheets (2-3 nm in thickness)
- nanotubes

All nano-objects are metallic bismuth as long as they remain in liquid nitrogen. Once exposed to air, they are oxidized and turn into Bi_2O_3.



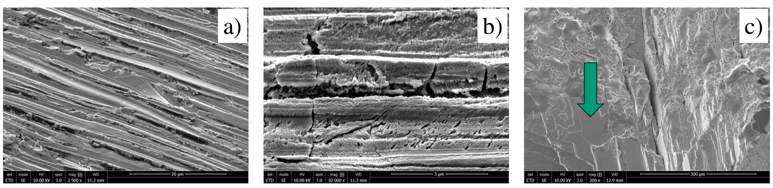
a) Set of nanoparticles showing different size distributions. b) Example of two overlapped Bi_2O_3 nanosheets. c) Bi_2O_3 nanotubes attached to a large cluster of particles. d) Uncomplete air oxidation of a Bi particles, showing a core-shell structure. e) Dark-field image of pleated nanosheets. f) detail of Bi_2O_3 nanotubes showing their hollow structure.

4 – CONDITION FOR NANOSHEET SYNTHESIS

Nanosheets are produced if and only if the applied voltage is low (typically 4-5 kV) and electrodes are chemically etched before treatment.

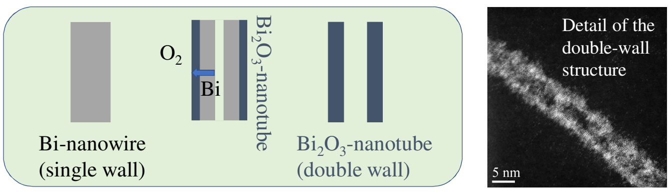
The etching process consists in polishing electrodes with an abrasive paper (800-grit), rinsing the surface with water and immersing the electrodes in Nital reagent for 4 minutes.

This pre-treatment removes crystallographic planes which are easier to etch. Remaining planes are then peeled off by the discharge. The underlying mechanism is still unknown (shock or acoustic waves, current flow, thermal gradients?)



Surface states of Bi pin-electrodes a) before chemical etching, b) after chemical etching and before treatment, c) after chemical etching and after treatment.

Metallic bismuth is probably oxidized when exposed to air. This process transforms Bi-nanowires into Bi_2O_3-nanotubes by Kirkendall effect, bismuth diffusing outward. Indeed, nanotubes are characterized by two-wall filaments (see schematic). Bi_2O_3-nanotubes are always found attached to a cluster of nanoparticles. The way they grow is still unclear and further investigations are needed.



Air oxidation of a Bi-nanowire

5 - CONCLUSION

It is possible to grow different types of bismuth oxide nano-objects by discharges in liquid nitrogen between two bismuth pin-electrodes. The growth of oxide nanosheets is clearly conditioned by the initial state of the electrodes. Chemical etching likely favours crystallographic planes that are harder to etch, leading to their specific erosion by submerged discharges.

Concerning Bi-nanotubes, metallic bismuth is probably oxidized by Kirkendall effect once exposed to air. This process transforms Bi-nanowires into Bi_2O_3-nanotubes. The growth mechanism of these objects remains unclear and further investigations are needed. The allotropic states of these oxides are also under investigation. Several phases are indeed possible on the basis of diffraction patterns obtained by TEM. Other diagnostics like Raman analysis are required to determine the crystallographic states of Bi_2O_3-nano-objects.

Acknowledgements

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