Electronic Supplementary Material (ESI) for Nanoscale.
This journal is © The Royal Society of Chemistry 2023

Supporting Information

Reactive Sputtering onto an Ionic Liquid, A New Synthesis Route of Bismuth-Based Nanoparticles

Sara Ibrahim, Vitalios Ntomprougkidis, Mathias Goutte, Guillaume Monier, Mounir Traïkia, Jean-Michel Andanson, Pierre Bonnet, Angelique Bousquet *

Synthesis of bismuth-based nanoparticles

Preparation of grids for TEM and HR-TEM:

A drop of IL-containing NPs is placed on a TEM grid without washing or diluting. A lint-free absorbent paper is used to absorb a large amount of the liquid. Then, the excess is sponged without breaking down the grid film. The remaining small quantity of IL, which can withstand the vacuum, still has a slight effect on the measurements.

Extraction of NPs from IL:

The NPs dispersion into IL, diluted with ethanol, are ultracentrifuged for 30 min. Then the surnageant was carefully removed and ethanol was added again, before a second step of ultracentrifugation for 15 min. Several steps are then performed to collect NPs dispersed into ethanol. This dispersion can then be put of various supports for material characterization. The ethanol will evaporate, leaving only the NPs.

Sputtering Bismuth target in Ar plasma

The EDS data obtained simultaneously clearly confirm that the imaged nanoparticles are Bi-based compounds (**Figure S.1**). The presence of C, N, O, F and S atoms is due to the presence of a persistent layer of IL.

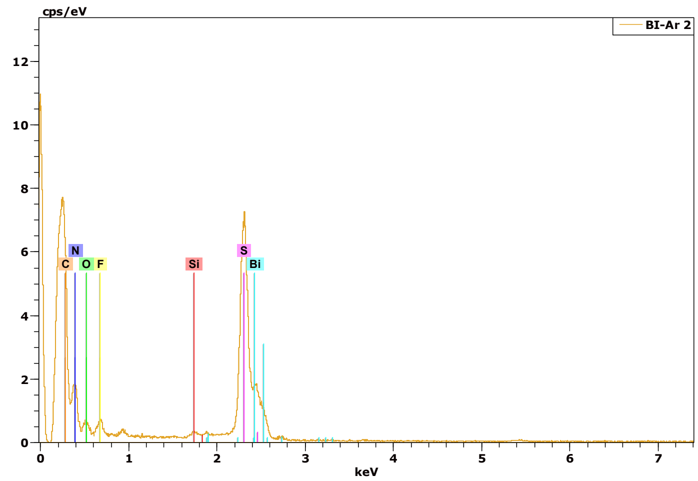

FIGURE S.1: EDS spectrum obtained on the NPS sputtered with Ar plasma onto the IL.

The XPS spectra of C 1s and O 1s are plotted on Figure S2 for NPs synthesis in pure argon plasma. To better distinghuish contributions from Bi-based compound and IL, the XPS spectra was also recorded for metallic powder dispersed into IL and then extracted from it by the same protocol than for NPs.

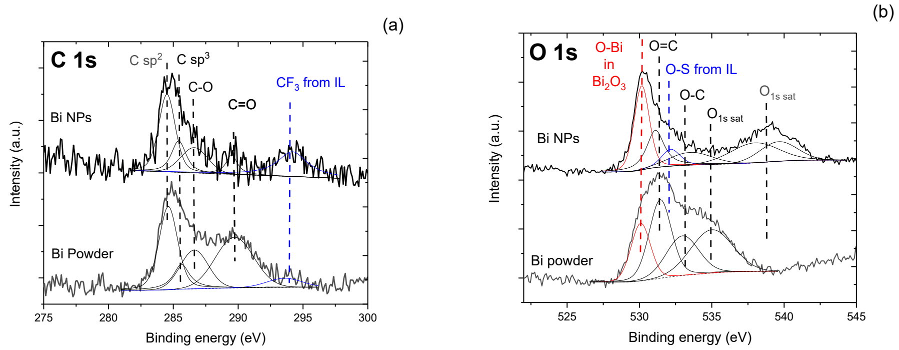

FIGURE S.2: (a) C 1s and (b) O 1s XPS spectra for NPs produced in pure Ar plasma compared to metallic powder.

Interaction of plasma with IL

In the **Figure S.3a**, is plotted the measured UV-visible spectra of IL before and after exposure to Ar, Ar/O_2 and $Ar/O_2/CF_4$ plasmas for 1 hour. In the section 3.1 of the paper, the Δ(absorbance) is plotted, which corresponds to the absorbance for IL after plasma exposure substracted by the absorbance of initial IL. In the **Figure S.3b-c**, the ^{13}C and ^{19}F spectra show no differences after plasma treatment in $Ar/O_2/CF_4$ compared to initial ionic liquid.

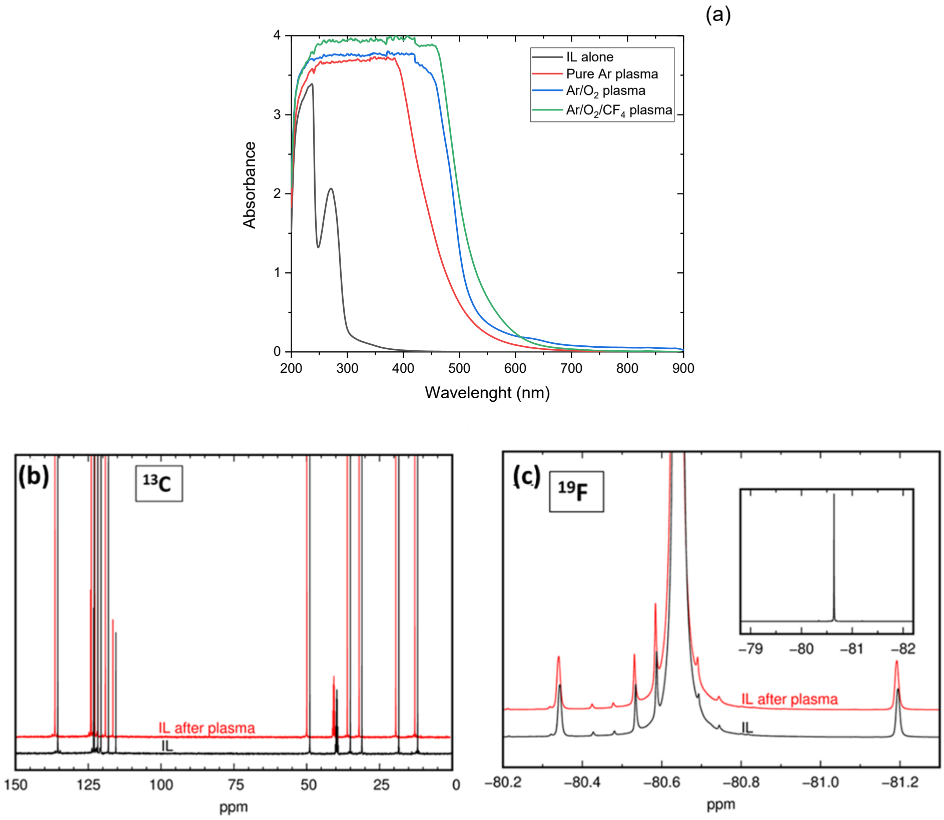

FIGURE S.3: Measured UV-visible spectra (a) for IL before and after exposure to Ar, Ar/O_2 and $Ar/O_2/CF_4$ plasmas for 1 hour and, (b) ^{13}C and (c) ^{19}F spectra of IL before and after plasma treatment in $Ar/O_2/CF_4$.

Sputtering Bismuth target in $Ar/O_2/CF_4$ plasma

In the **Figure S.4**, is plotted the measured UV-visible spectra of IL before and after sputtering in various $Ar/O_2/CF_4$ plasma mixtures. Again, in the section 3.2.2 of the paper, the Δ(absorbance) is plotted.

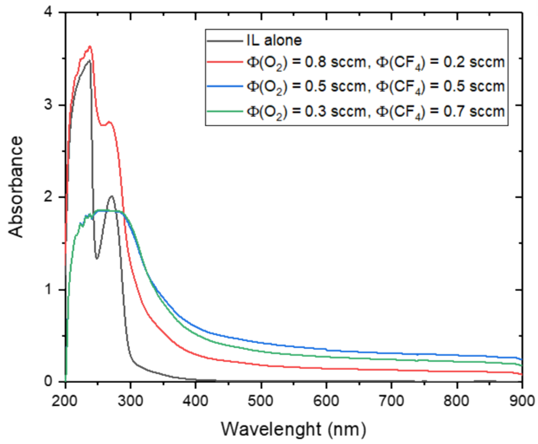

FIGURE S.4: Measured UV-visible spectra for IL before and after Bismuth target sputtering in various $Ar/O_2/CF_4$ plasma mixtures.

Since $BiO_{0.5}F_2$ has a band gap around 4.0 eV, the absorbance in visible range is linked to the presence of Bi metallic domain. In the **Figure S.5**, the the absorbance at 650 nm measured by UV-visible spectroscopy for NPs dispersion into IL and for thin films depositied on quartz indicated the metallic Bi content into both kind of samples obtained in the same conditions (same target applied power, Ar flow rate, O_2 + CF_4 flow rate, pressure) for various O_2 to CF_4 flow rates ratio. For thin films, the metallic domains are observed only for O_2 flow rate below 0.5; whereas absorbance continues to be significantly high for NPs dispersion.

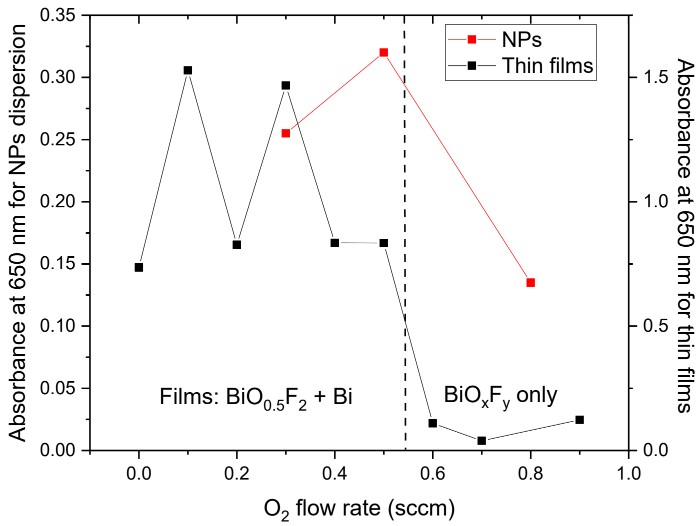

FIGURE S.5: Absorbance at 650 nm for NPs dispersion and for thin films depositied on quartz substrate in the same condition, depending on the O_2 flow rate.

Exposure of a metallic Bismuth film to a Ar/CF_4 plasma

In the **Figure S.6**, the pattern of metallic Bismuth thin film is plotted before and after its direct exposure for one hour to a Ar/CF_4 MW plasma. Before plasma exposure, the referenced diffraction peaks correspond to Bi phase. After, these peaks are drastically reduced and some new ones (indicated with red arrows) appears. The metallic thin film is highly modified by the plasma.

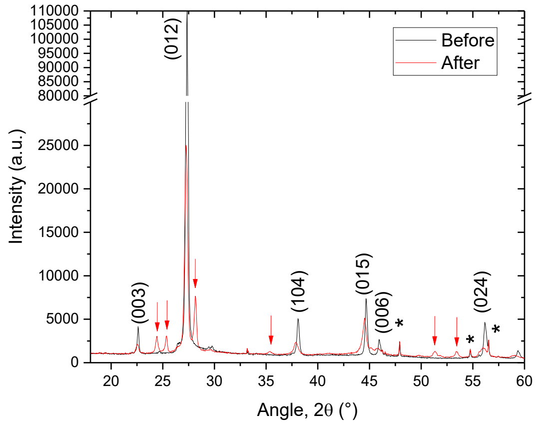

FIGURE S.6: XRD patterns of metallic Bismuth thin film before and after its direct exposure for one hour to a Ar/CF_4 MW plasma. The plane indexes and * refer to Bi phase and Si substrate respectively; while the arrows indicate the presence of a new phase after plasma exposure.