Electronic Supplementary Information on

Towards the Liquid Phase Exfoliation of Bismuth Iodide

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Experimental details

General

Unless otherwise indicated, all steps were performed under inert conditions using a Schlenk line, glove box and pre-dried glassware. Solvents were obtained from commercial sources and dried by standing over activated 3 Å (alcohols) or 4 Å (aromatic solvents) mole sieve (about 10-20 Vol-%) for 12 h and subsequent distillation onto another portion of activated mole sieve.

BiI_3 was prepared from stoichiometric amounts of the elements at 180°C. The raw material was recrystallized under solvothermal conditions from aqueous hydriodic acid (20 w-%) at 160°C, washed with water, ethanol and diethyl ether and stored under inert conditions afterwards. This treatment removes traces of unreacted starting material and BiOI.

Powder Diffraction

Measurements were performed on a *STADI MP* (*STOE Darmstadt*) powder diffractometer in transmission geometry, with Cu$K\alpha_1$ radiation (λ= 1.54056 Å) at room temperature.

Exfoliation method

25 mg of BiI_3 were sonicated with 8 mL of the respective solvent for 60 min. The resulting suspension was centrifuged for 90 min at 500 rpm and the supernatant used for all further measurements. Ethanol and isopropanol were tested both dried and used as received, but toluene and chlorobenzene were only used dried.

It is noteworthy that the literature procedures that the use of “wet” solvent aimed to replicate did not include a centrifugation step.[1]

Spectroscopic Characterization

The optical absorption in the range of 800-200 nm of the solutions/suspensions obtained during exfoliation were measured using a *Varian Cary 5000* UV/Vis/NIR spectrometer.

Solid BiI_3 powder was measured on the same spectrometer using a Praying Mantis accessory (Harrick). To allow for an easier comparison with data obtained from measurements in solution/suspension, raw data was transformed from %Reflectance R to Absorbance A according to $A = \log(1/R)$.[2]

TEM Investigations

The BiI_3 suspension in chlorobenzene was drop-cast onto carbon TEM grids. The samples were dried under vacuum and kept under Argon atmosphere afterwards.

The samples were transferred into the TEM minimizing the duration of exposure to ambient air. High angle annular dark field (HAADF) images were acquired in a double C_S corrected JEOL JEM 2200FS operating at 200 kV. Supplementary transmission electron diffraction patterns were acquired in a JEOL JEM 3010 operating at 300 kV.

Additional Figures

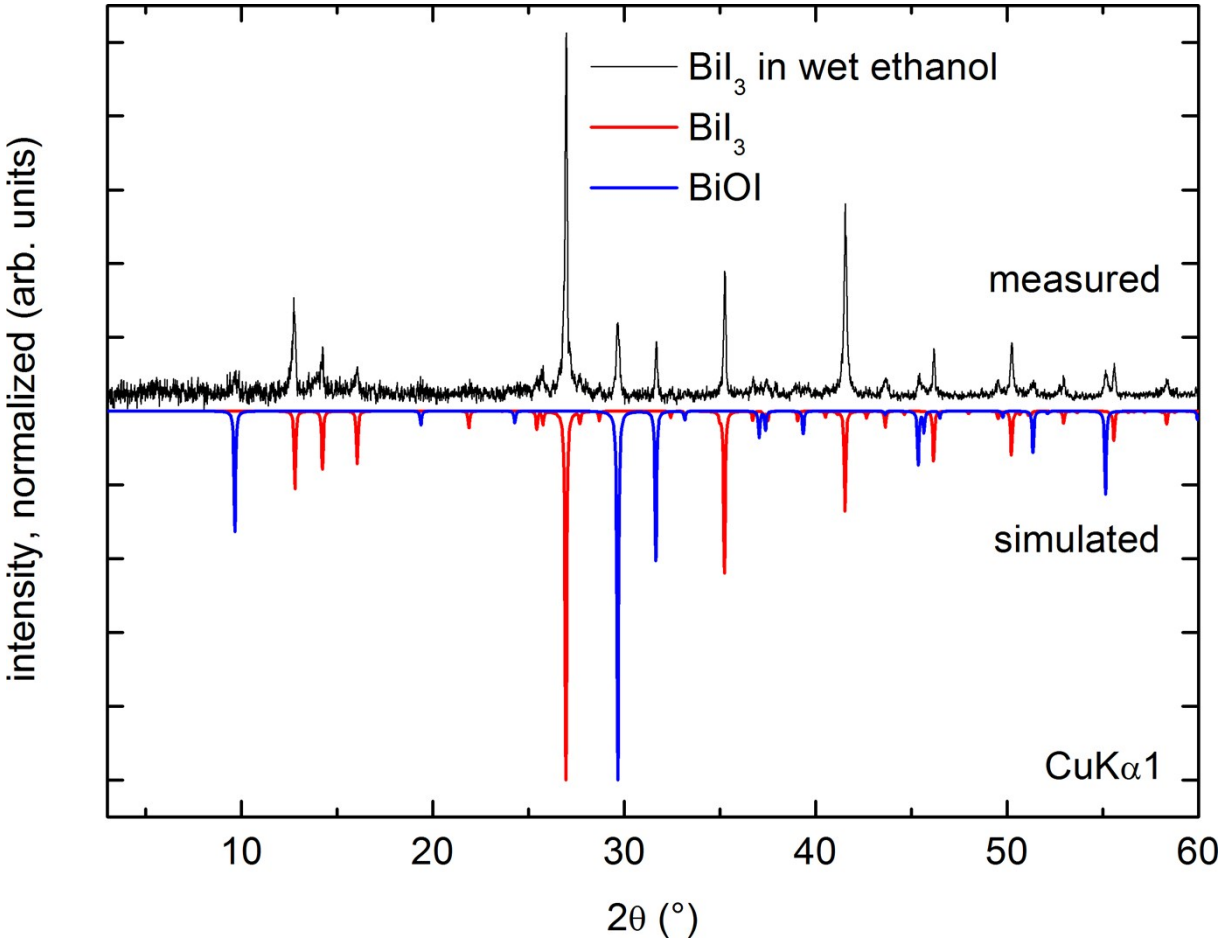

Figure S1. Powder diffractogram of a BiI_3 sample suspended in ethanol under aerobic conditions showing the formation of significant amounts of the hydrolysis product BiOI.

References

1 (a) H. Li and J. Jiao, *Chem. Mater.*, 2008, **20**, 3770; (b) H. Li, J. M. Green and J. Jiao, *J. Phys. Chem. C*, 2008, **112**, 15140; (c) K. Moorthy Boopathi, S. Raman, R. Mohanraman, F.-C. Chou, Y.-Y. Chen, C.-H. Lee, F.-C. Chang and C.-W. Chu, *Sol. Energ. Mat. Sol. Cells*, 2014, **121**, 35.

2 S. I. Boldish and W. B. White, *Am. Mineral.*, 1998, **83**, 865.