

Supporting Information

Bismuthene Nanosheets produced by Ionic Liquid Assisted Grinding Exfoliation and their Use for Oxygen Reduction Reaction

Manila Ozhukil Valappil,^{ab,e} Abhijit Ganguly,^{ae} John Benson,^c Vijayamohanan K Pillai,^d Subbiah Alwarappan^b and Pagona Papakonstantinou^{*a}

^a*Engineering Research Institute, School of Engineering, Ulster University, Newtownabbey BT37 0QB, United Kingdom*

^b*Electrodics and Electrocatalysis Division, CSIR-Central Electrochemical Research Institute, Karaikudi, Tamil Nadu, India-630003*

^c*2-DTech Ltd, Core Technology Facility, 46 Grafton St, Manchester M13 9NT, United Kingdom*

^d*Department of Chemistry, Indian Institute of Science Education and Research, Tirupati, India.*

^{*}Corresponding author: p.papakonstinou@ulster.ac.uk

^eFirst 2 authors have contributed equally

Statistical analysis of Morphological (FESEM) study

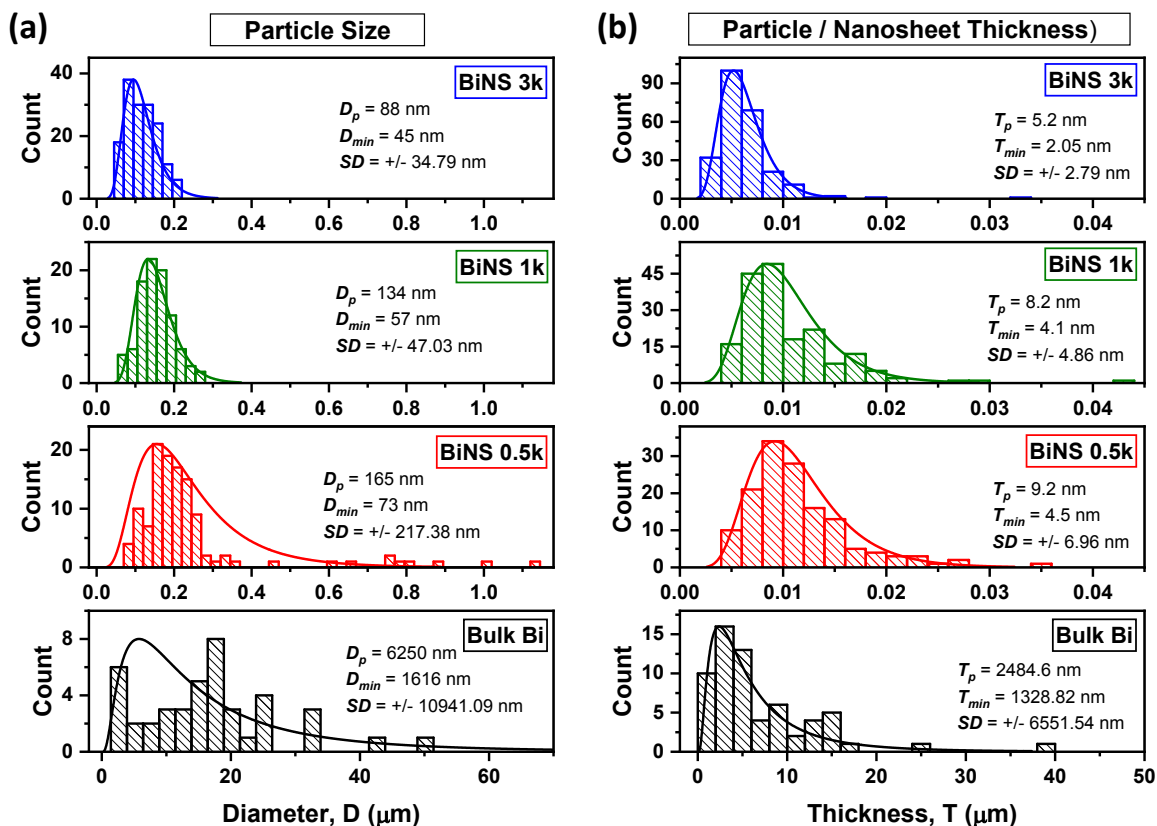


Fig. S1 Statistical analysis of FESEM images for bismuthene nanosheets (BiNS) illustrating (a) particle size histograms and (b) nanosheet thickness histograms. D_p and T_p represent the peak values of diameter and thickness distribution; while D_{min} and T_{min} are the respective minimum values measured. SD : standard deviation of the data values. Statistical analysis has been performed on at least 3 independent images for each sample. For comparison, histograms of (a) particle size and (b) particle thickness of bulk Bi powder were shown at the bottom.

Supplementary information of Morphological (FESEM) study

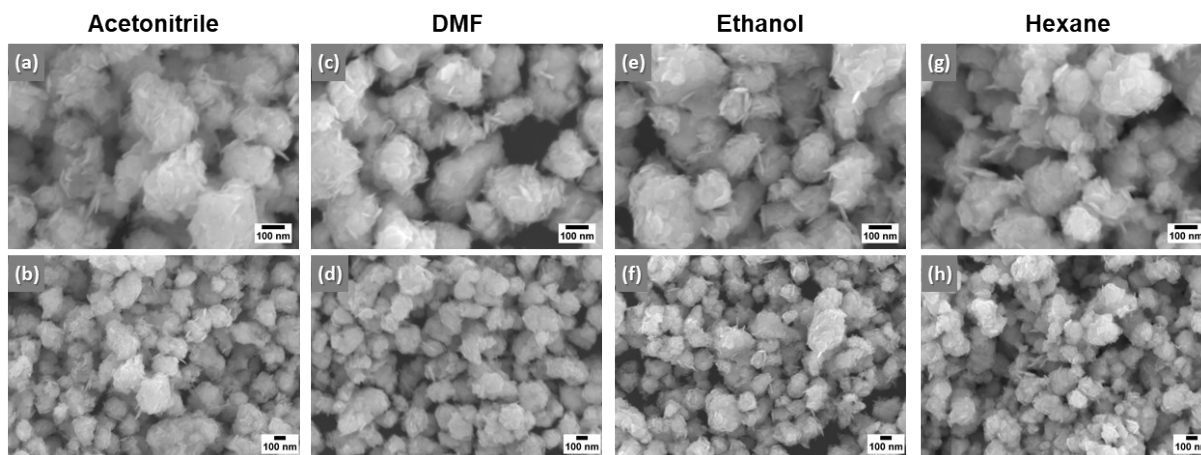


Fig. S2 FESEM images of bismuthene nanosheets (BiNS 1k) dispersed in various solvents: (a-b) Acetonitrile, (c-d) DMF, (e-f) Ethanol, and (g-h) Hexane.

Supplementary information of XPS study

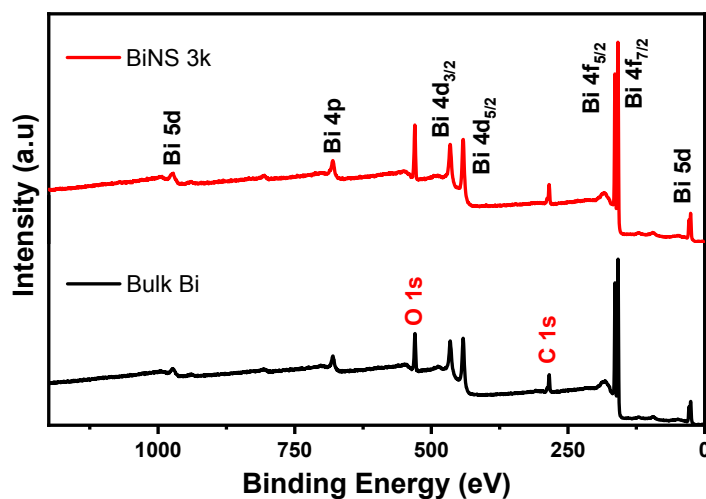


Fig. S3 XPS survey spectra of bulk bismuth and bismuthene nanosheets (BiNS 3k). A C 1s signal originated from adventitious carbon contamination, adsorbed on the sample's surface.

Table S1. Atomic Concentration of Deconvoluted Bi 5d, Bi 4f and O 1s Core Level XPS Signal

	Peak	Bulk Bi		BiNS 3k	
		Position (eV)	Atomic%	Position (eV)	Atomic%
Bi 5d	5d _{5/2}	25.81 ± 0.02	48.91 ± 0.06	25.73 ± 0.01	52.84 ± 0.04
	BiOx _{5/2}	26.14 ± 0.12	10.67 ± 0.13	26.25 ± 0.1	6.3 ± 0.12
	5d _{3/2}	28.83 ± 0.04	39.86 ± 0.1	28.75 ± 0.01	40.86 ± 0.02
	BiOx _{3/2}	30.09 ± 0.96	0.56 ± 0.12	—	—
Bi 4f	4f _{7/2}	158.82 ± 0.02	56.9 ± 0.03	158.77 ± 0.12	56.89 ± 0.02
	4f _{5/2}	164.13 ± 0.1	43.1 ± 0.12	164.08 ± 0.12	43.11 ± 0.02
O 1s	Bi—O	529.41 ± 0.42	32.91 ± 0.31	529.49 ± 0.33	28.94 ± 0.22
	—OH	530.65 ± 0.21	67.09 ± 0.2	530.65 ± 0.2	55.57 ± 0.12
	=O	—	—	531.65 ± 0.32	15.48 ± 0.35

BiOx_{5/2} : Oxide peak adjacent to Bi 5d_{5/2}

BiOx_{3/2} : Oxide peak adjacent to Bi 5d_{3/2}

Bi—O : C atoms directly bonded to oxygen

—OH : Singly bonded Oxygen functional groups

=O : Doubly bonded Oxygen functional groups

Supplementary information of Raman spectroscopic study

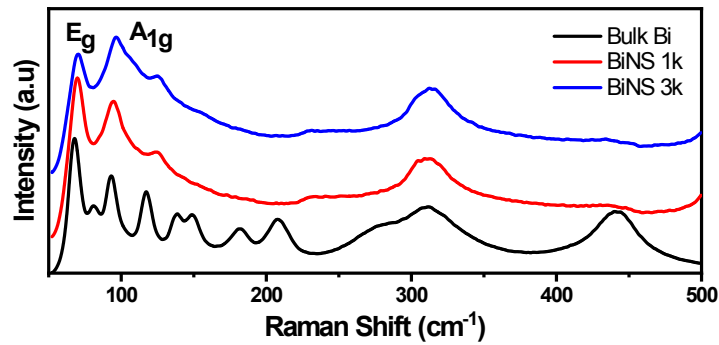


Fig. S4 Full-range Raman spectra of bulk bismuth and bismuthene nanosheets (BiNS).

Table S2. Numerical Analysis of Raman Spectroscopic Data

	E _g mode		A _{1g} mode		Intensity Ratio I _{Eg} / I _{A1g}
	Position (cm ⁻¹)	FWHM (cm ⁻¹)	Position (cm ⁻¹)	FWHM (cm ⁻¹)	
Bulk Bi	67.88 ± 0.12	7.98 ± 0.13	92.99 ± 0.21	6.82 ± 0.91	2.39 ± 0.09
BiNS 1k	69.74 ± 0.15	10.18 ± 0.26	94.64 ± 0.28	11.87 ± 1.04	1.64 ± 0.08
BiNS 3k	71.04 ± 0.19	10.74 ± 0.28	96.25 ± 0.26	15.77 ± 1.23	1.18 ± 0.1

Supplementary information of XRD study

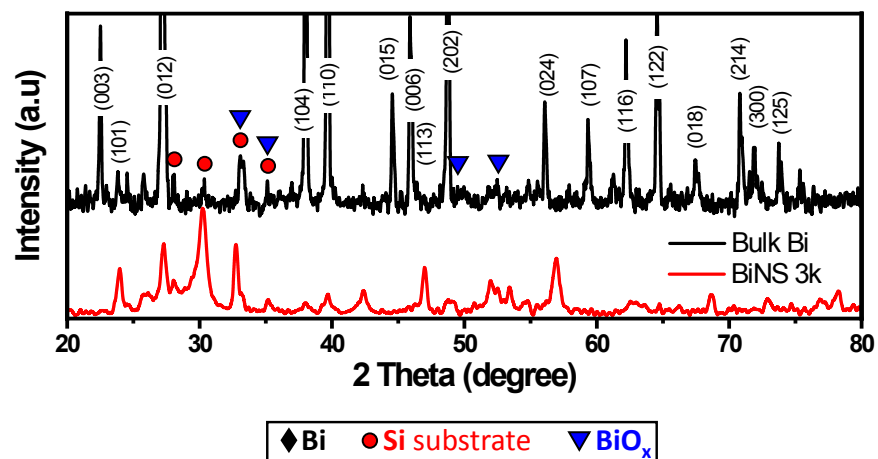


Fig. S5 The upper panel presents the XRD pattern of bulk Bismuth, magnifying the low intensity signals. For comparison, the XRD pattern of BiNS 3k is presented in the bottom panel.

Supplementary information of ORR study

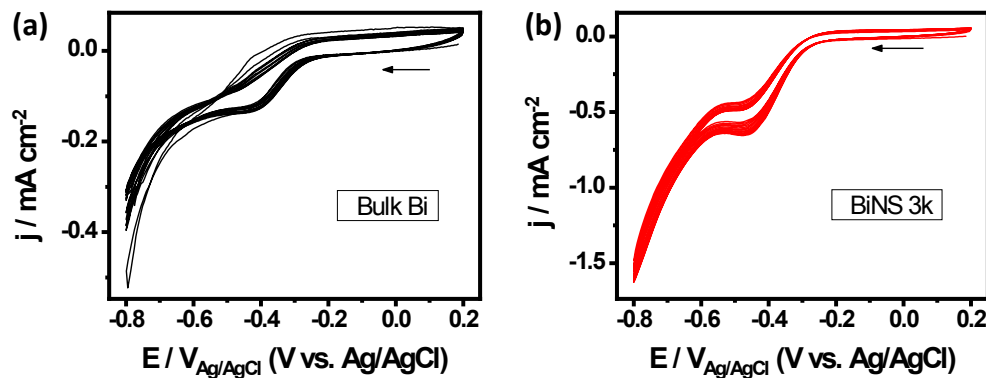


Fig. S6 Cyclic voltammetry (CV) spectra representing the pre-conditioning of (a) bulk Bi and (b) BiNS 3k catalysts, prior to the ORR activity measurements (0.1 M KOH).

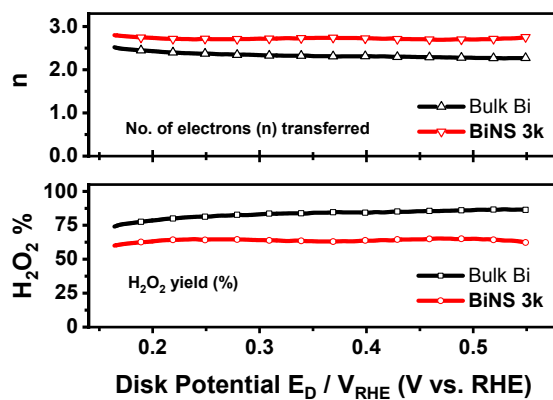


Fig. S7 The number of electrons (n) transferred (top figure) and the H_2O_2 yield (bottom figure) estimated at various applied potential.

