ESI – Electronical Supporting Information

Surfactant-Assisted Liquid-Phase Exfoliated Nano-Sized Bi_2S_3 for Electrocatalytic Hydrogen Evolution

Mengjiao Wang [1,*], Matteo Crisci [1], Matilde Pavan [1], Zheming Liu [2], Jaime Gallego [1] and Teresa Gatti [1,3,*]

[1] Institute of Physical Chemistry and Center for Materials Research (LaMa), Justus Liebig University, 35392 Giessen, Germany
[2] Nanochemistry Department, Istituto Italiano di Tecnologia, 16163 Genova, Italy
[3] Department of Applied Science and Technology, Politecnico di Torino, 10129 Torino, Italy

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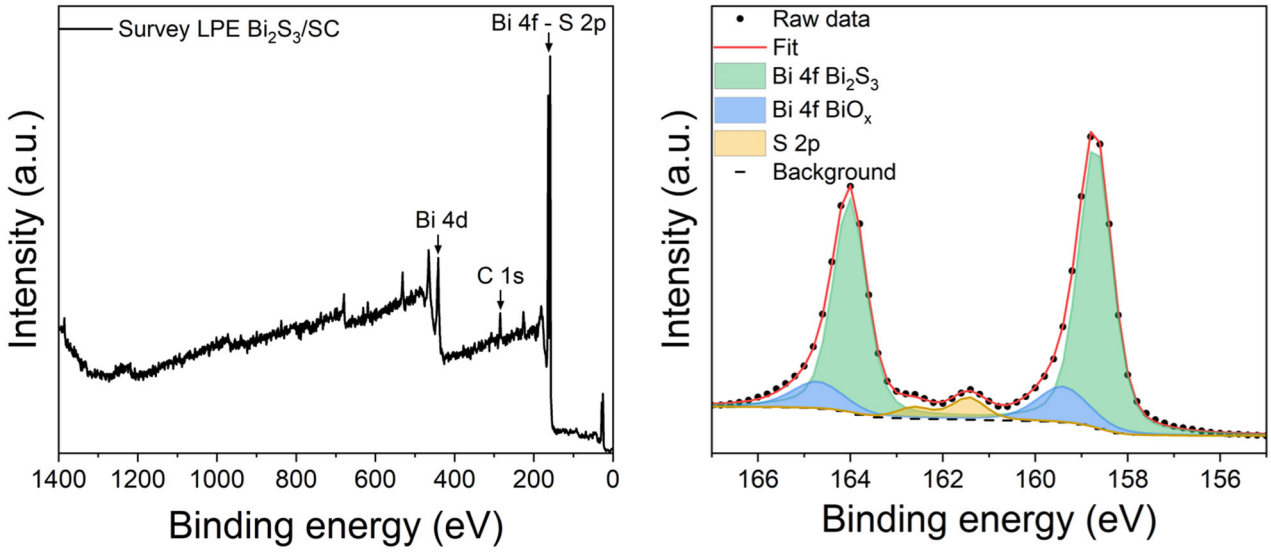

Figure S1. XPS spectrum of LPE Bi_2S_3/SC. a) XPS survey data, and b) high-resolution XPS spectra of Bi 4f and S 2p.

Table S1. Zeta potential (ζ), average size (from DLS), band gap (from UV-Vis-NIR), concentration and yield with different concentrations of surfactant of LPE Bi_2S_3/SDS. All the exfoliations were performed with a shear mixer (SM) for 3 h. The concentration of Bi_2S_3 in all the experiments is fixed to 0.33 mg/mL.

SDS (mg/mL)	ζ (eV)	Size (nm)	Eg (eV)	Exfoliated Bi_2S_3 (mg/ml)	Yield %
1.0	-46	190	1.6	0.010	3.1
2.0	-56	185	1.6	0.011	3.4
4.0	-60	220	1.5	0.014	4.5
8.0	-56	183	1.8	0.012	3.6

Figure S2. Pictures of Bi_2S_3 suspensions prepared with SDS (1.0, 2.0, 4.0 and 8.0 mg/mL from left to right) in water.

Table S2. Zeta potential (ζ), average size (from DLS), band gap (from UV-Vis-NIR), concentration and yield with different concentrations of surfactant of LPE Bi_2S_3/SC. All the exfoliations were performed with a shear mixer (SM) for 3 h. The concentration of Bi_2S_3 in all the experiments is fixed to 0.33 mg/mL.

SC (mg/mL)	ζ (eV)	Size (nm)	Eg (eV)	Exfoliated Bi_2S_3 (mg/ml)	Yield %
1.0	-27	140	1.7	0.021	6.3
2.0	-30	220	1.9	0.033	10.0
4.0	-48	215	1.9	0.041	12.3
8.0	-37	250	2.0	0.040	12.0

Figure S3. Pictures of Bi_2S_3 suspensions prepared with SC (1.0, 2.0, 4.0 and 8.0 mg/mL from left to right) in water. All the exfoliations were performed with a SM for 3 h and using 0.33 mg/mL of Bi_2S_3.

Table S3. Zeta potential (ζ), average size (from DLS), band gap (from UV-Vis-NIR), concentration and yield with different concentrations of bulk Bi_2S_3 of LPE Bi_2S_3/SC. All the exfoliations were performed with a shear mixer (SM) for 3 h. The concentration of SC in all the experiments is fixed to 4.0 mg/mL.

Bi_2S_3 (mg/mL)	ζ (eV)	Size (nm)	Eg (eV)	Exfoliated Bi_2S_3 (mg/mL)	Yield %
0.33	-48	215	1.9	0.04	12.3
0.67	-47	190	1.9	0.08	11.7
1.33	-40	165	1.9	0.17	12.5
2.67	-41	165	2.0	0.18	6.7

Figure S4. Pictures of Bi_2S_3 suspensions prepared with SC, 4 mg/mL, in water, using different concentrations of bulk Bi_2S_3 (0.33, 0.67, 1.33 and 2.67 mg/mL from left to right). All the exfoliations were performed with a SM for 3 h and using 0.33 mg/mL of Bi_2S_3.

Table S4. Zeta potential (ζ), average size (from DLS), band gap (from UV-Vis-NIR), concentration and yield with different exfoliation time of LPE Bi_2S_3/SC. All the exfoliations were performed with a shear mixer (SM). The concentration of SC in all the experiments is fixed to 4.0 mg/mL, while the concentration of Bi_2S_3 was fixed to 1.33 mg/mL.

Time (h)	ζ (eV)	Size (nm)	Eg (eV)	Exfoliated Bi_2S_3 (mg/mL)	Yield %
3	-40	165	1.9	0.17	12.5
6	-42	160	1.8	0.18	13.3
9	-40	175	1.9	0.19	14.0

Figure S5. Pictures of Bi_2S_3 suspensions prepared with SC, 4 mg/mL, in water, using 1.33 mg/mL of bulk Bi_2S_3. All exfoliations took place with a SM and the dispersions were centrifuged for 20 min at 500 RPM. Exfoliation times from left to right were 3, 6 and 9 hours.

Table S5. Zeta potential (ζ), average size (from DLS), band gap (from UV-Vis-NIR), concentration and yield with different aqueous solvents of LPE Bi_2S_3/SC. All the exfoliations were performed with a shear mixer (SM) for 3 h. The concentration of Bi_2S_3 in all the experiments is fixed to 0.33 mg/mL and the concentration of SC is 4.0 mg/mL.

Aqueous solvent	ζ (eV)	Size (nm)	Eg (eV)	Exfoliated Bi_2S_3 (mg/mL)	Yield %
distilled H_2O	-40	165	1.9	0.17	12.5
isopropanol 25%	-21	300	1.8	0.03	2.5
isopropanol 50%	-10	300	1.8	0.02	1.7
acetone 25 %	-35	140	1.8	0.06	4.7
acetone 50 %	-30	130	1.8	0.05	3.8
acetone 75 %	-25	143	2.1	0.01	1.1

Figure S6. Pictures of Bi_2S_3 suspensions prepared with SC, 4 mg/mL, and 1.33 mg/mL of bulk Bi_2S_3. On the top, dispersions in isopropanol aqueous mixtures, the concentration of isopropanol is 25 % and 50 % (v/v), from the left to the right. On the bottom, dispersions in acetone aqueous mixtures, the concentration of acetone is 25 %, 50 % and 75 % (v/v), from the left to the right. All exfoliations were performed with a SM for 3 h.

Table S6. Zeta potential (ζ), average size (from DLS), band gap (from UV-Vis-NIR), concentration and yield with different exfoliation methods of LPE Bi_2S_3/SC. All the exfoliations were performed for 3 h. The concentration of Bi_2S_3 in all the experiments is fixed to 0.33 mg/ and the concentration of SC is 4.0 mg/mL.

Method	ζ (eV)	Size (nm)	Eg (eV)	Exfoliated Bi_2S_3 (mg/mL)	Yield %
Shear mixer	-40	165	1.9	0.17	12.5
Tip sonicator	-44	155	1.9	0.05	3.9

Figure S7. Pictures of Bi_2S_3 suspensions prepared with SC, 4 mg/mL, in water, with 1.33 mg/mL of bulk Bi_2S_3. The dispersion displayed on the left is prepared with a SM, the one on the right with a TS. Both exfoliations took place for 3 h and the dispersions were centrifuged for 20 min at 500 RPM.

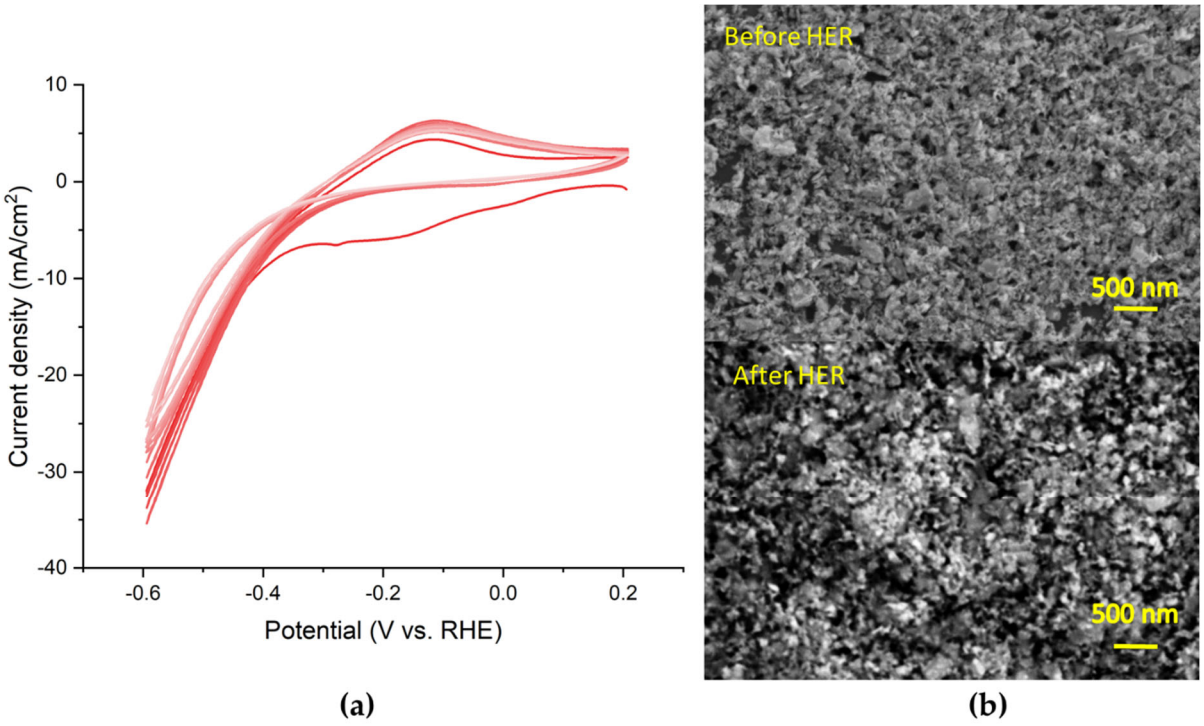

Figure S8. (a) CV curves of LPE Bi_2S_3/SC (1.61 mg/cm²) for HER electrocatalysis at a scan rate of 50 mV/s. (b) SEM image of LPE Bi_2S_3/SC before and after the CV test.

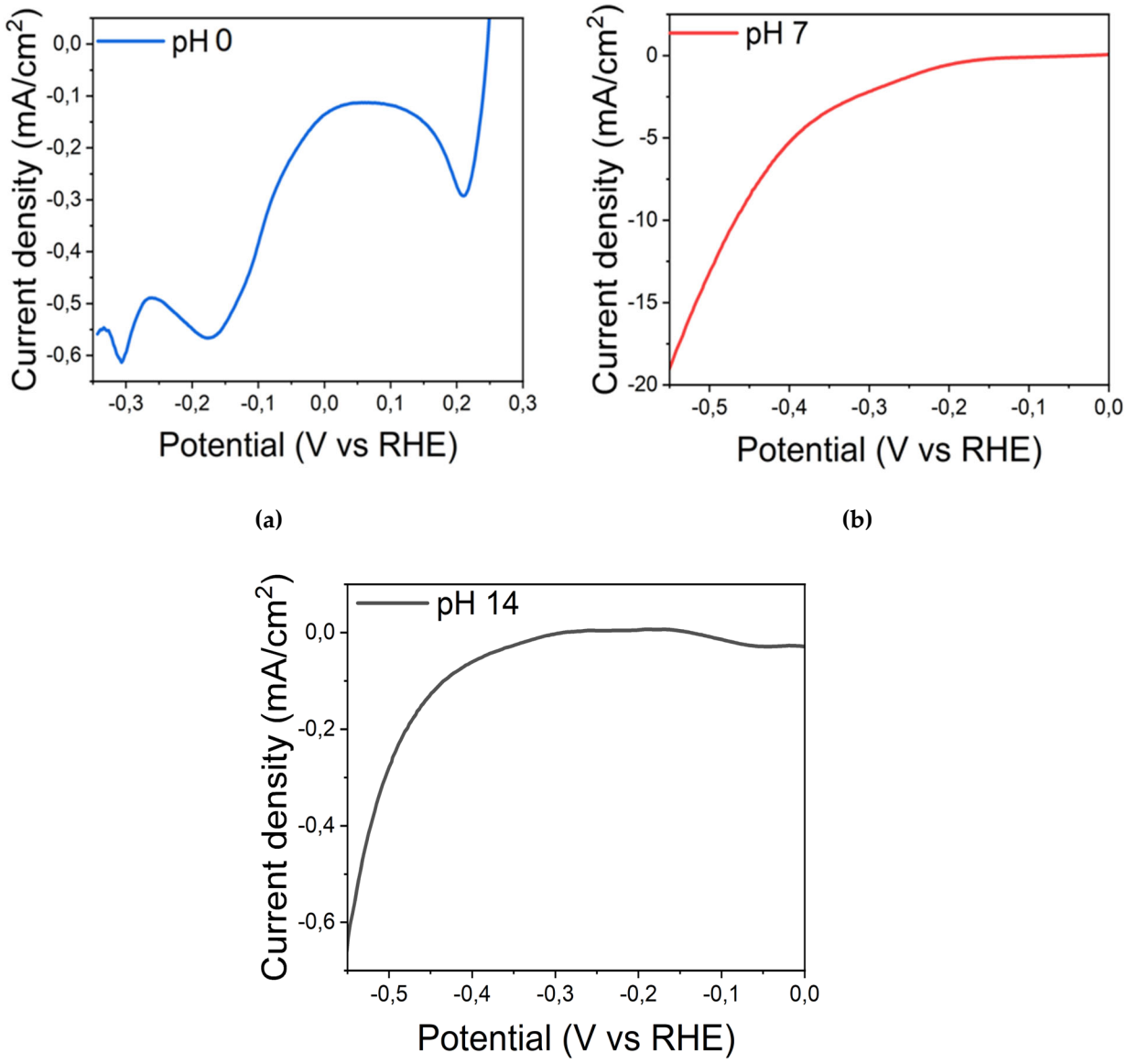

Figure S9. LSV (scan rate 10 mV/s) curves of LPE Bi_2S_3/SC (1.61 mg/cm²) for HER electrocatalysis in **(a)** pH 0 (H_2SO_4 0.5 M); **(b)** pH 7 (Na_2SO_4 0.5 M); **(c)** pH 14 (KOH 1.0 M).

Table S7. Overpotential at 1 mA/cm² and Tafel slope referred to LPE Bi_2S_3/SC HER activity in neutral conditions. The data collected refers to LPE Bi_2S_3 thin films produced using different ink loadings on a GC electrode.

Loading LPE Bi_2S_3/SC (mg/cm²)	Overpotential (mV)	Tafel slope (mV/dec)
0.72	-	-
1.43	285	220
1.61	235	125
1.79	305	275

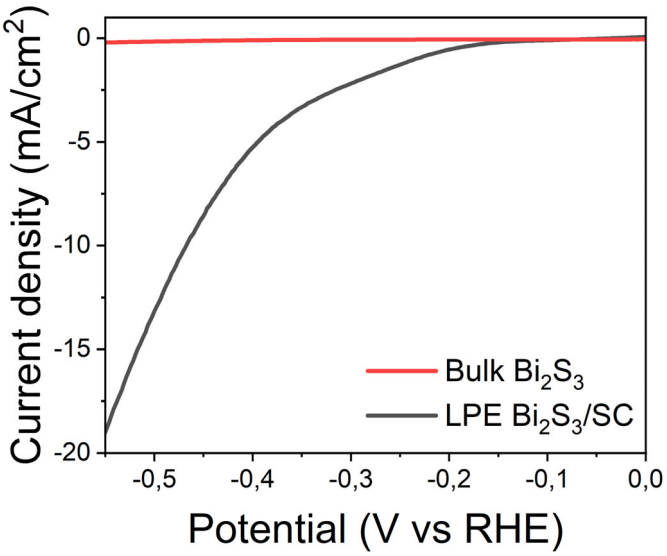

Figure S10. LSV curves (scan rate 10 mV/s) of LPE Bi_2S_3/SC and bulk Bi_2S_3 (1.61 mg/cm^2) as HER electrocatalysts in neutral condition (Na_2SO_4 0.5 M).

Table S8. Summary of the conditions used for all the exfoliations discussed in this work. Concentrations of starting bulk material, concentrations and types of surfactant (SDS, SC), LPE methods (SM, TS), exfoliation times and aqueous mixtures used as solvents are here listed.

Bulk Bi_2S_3 (mg/mL)	Surfactant type/concentration (mg/mL)	Exfoliation method	Exfoliation time (h)	Solvent
0.33	SDS/1	SM	3	distilled H_2O
0.33	SDS/2	SM	3	distilled H_2O
0.33	SDS/4	SM	3	distilled H_2O
0.33	SDS/8	SM	3	distilled H_2O
0.33	SC/1	SM	3	distilled H_2O
0.33	SC/2	SM	3	distilled H_2O
0.33	SC/4	SM	3	distilled H_2O
0.33	SC/8	SM	3	distilled H_2O
0.67	SC/4	SM	3	distilled H_2O
1.33	SC/4	SM	3	distilled H_2O
2.67	SC/4	SM	3	distilled H_2O
1.33	SC/4	SM	3	isopropanol 25% (v/v)
1.33	SC/4	SM	3	isopropanol 50% (v/v)
1.33	SC/4	SM	3	acetone 25% (v/v)
1.33	SC/4	SM	3	acetone 50% (v/v)
1.33	SC/4	SM	3	acetone 75% (v/v)
1.33	SC/4	TS	3	distilled H_2O
1.33	SC/4	SM	6	distilled H_2O
1.33	SC/4	SM	9	distilled H_2O