

## Supporting Information

Mechanochemical synthesis of the NiSn, CuSn bimetallic and NiCuSn trimetallic nanocomposite using various type of additives

Katalin Musza<sup>a,b</sup>, Márton Szabados<sup>a,b</sup>, Adél Anna Ádám<sup>a,b</sup>, Péter Bélteky<sup>c</sup>,  
Zoltán Kónya<sup>c,d</sup>, Ákos Kukovecz<sup>c</sup>, Pál Sipos<sup>b,e</sup> and István Pálinkó<sup>a,b\*</sup>

<sup>a</sup>*Department of Organic Chemistry, University of Szeged, Dóm tér 8, Szeged, H-6720 Hungary*

<sup>b</sup>*Material and Solution Structure Research Group and Interdisciplinary Excellence Centre, Institute of Chemistry, University of Szeged, Aradi vértanúk tere 1, Szeged, H-6720 Hungary*

<sup>c</sup>*Department of Applied and Environmental Chemistry, University of Szeged, Rerrich B. tér 1, Szeged, H-6720 Hungary*

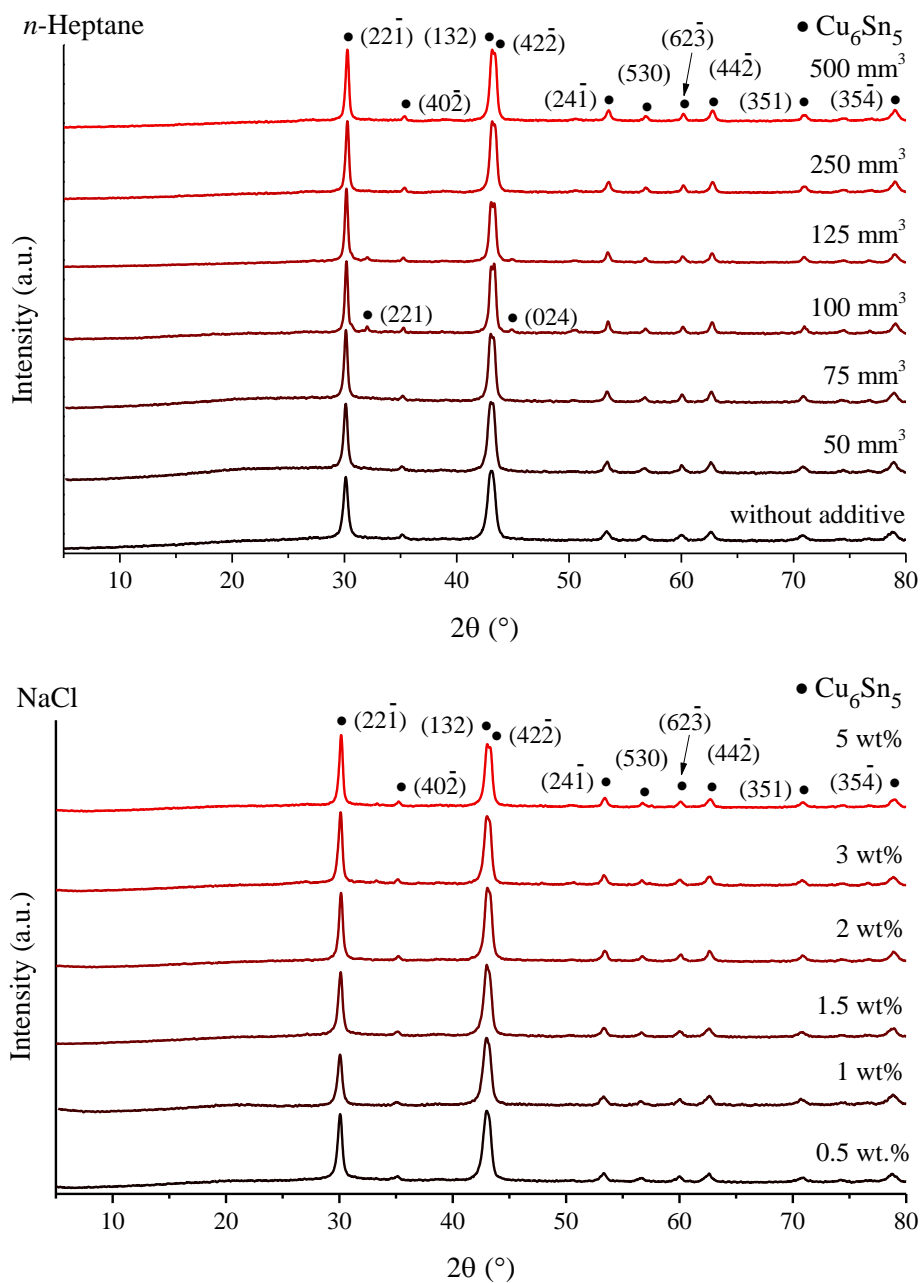
<sup>d</sup>*MTA-SZTE Reaction Kinetics and Surface Chemistry Research Group, Rerrich B. tér 1, Szeged, H-6720 Hungary*

<sup>e</sup>*Department of Inorganic and Analytical Chemistry, University of Szeged, Dóm tér 7, Szeged, H-6720 Hungary*

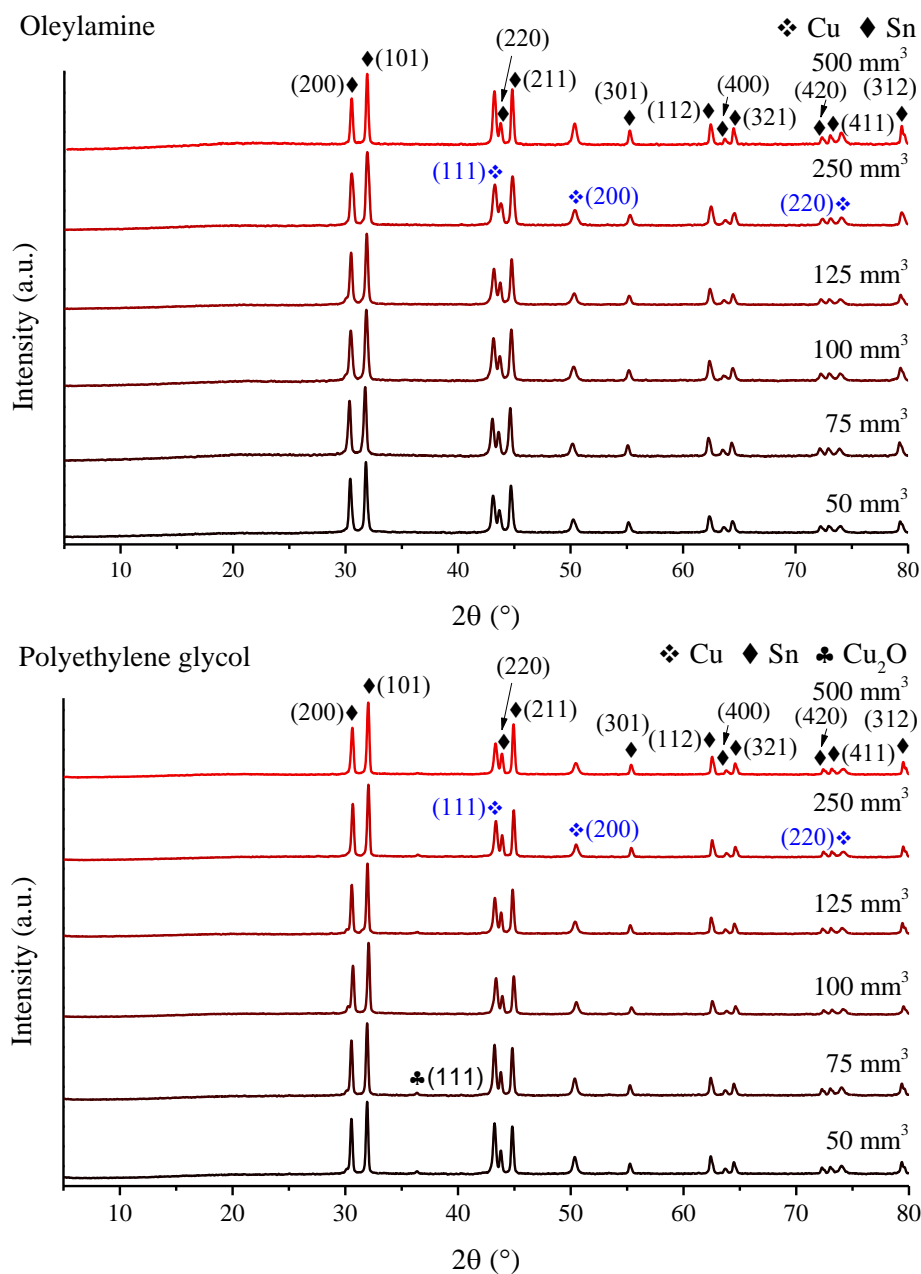
---

\*Corresponding author.

E-mail address: [palinko@chem.u-szeged.hu](mailto:palinko@chem.u-szeged.hu) (I. Pálinkó)

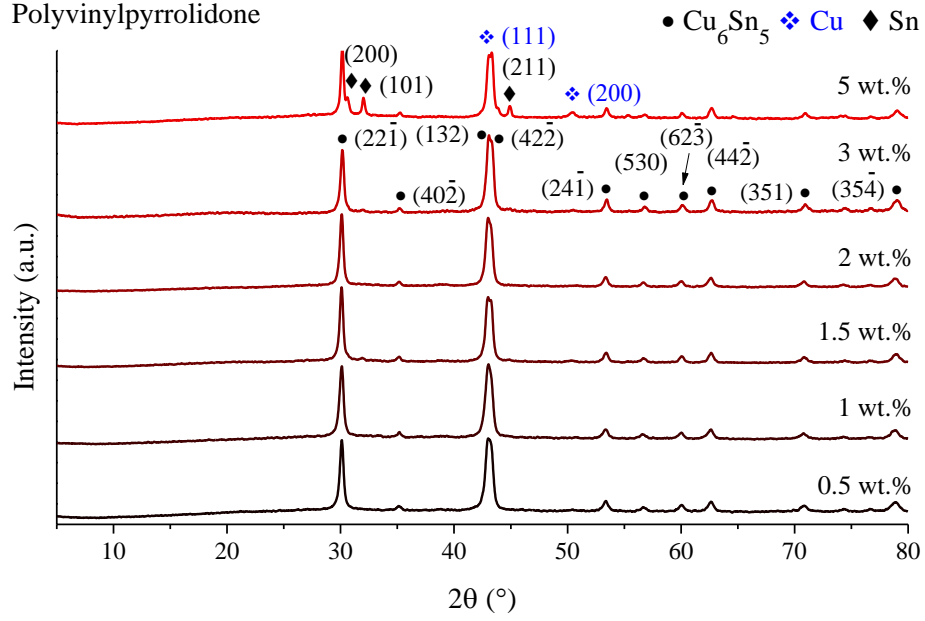


**Fig. S1** X-ray diffraction patterns of the milled Cu-Sn starting reagents without and using *n*-heptane and NaCl as milling additives.

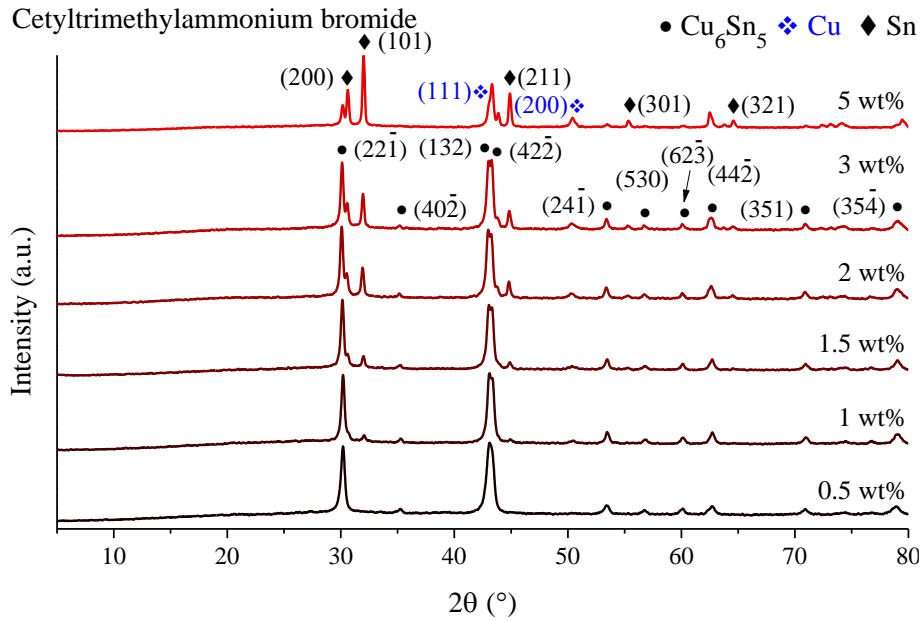


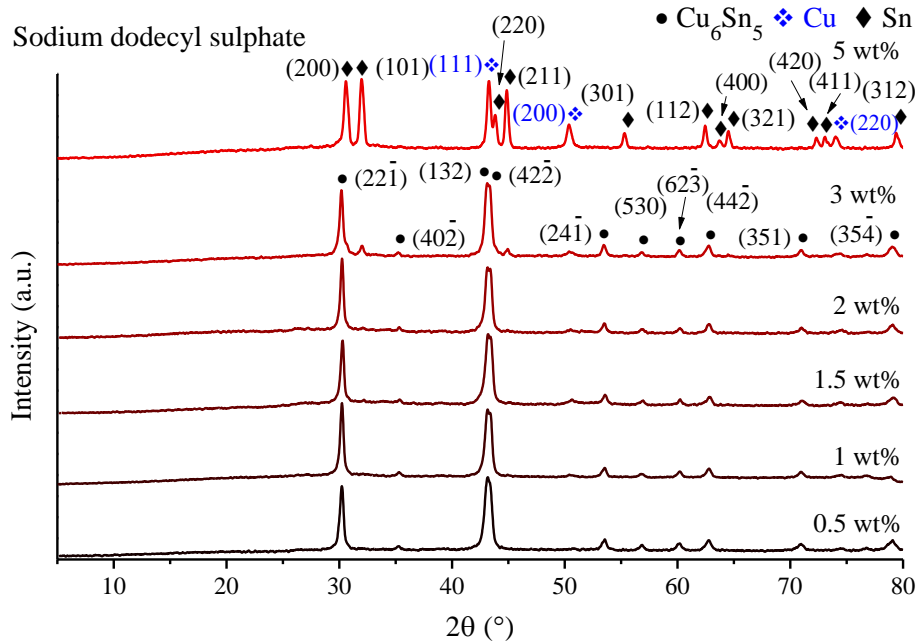
**Fig. S2** The X-ray diffractograms of the end-products of mechanochemical treatment with oleylamine or polyethylene glycol added in different amounts.

Polyvinylpyrrolidone



Cetyltrimethylammonium bromide





**Fig. S3** XRD patterns of the milling end-products in the presence of varying amounts of PVP, CTAB or SDS surfactants.

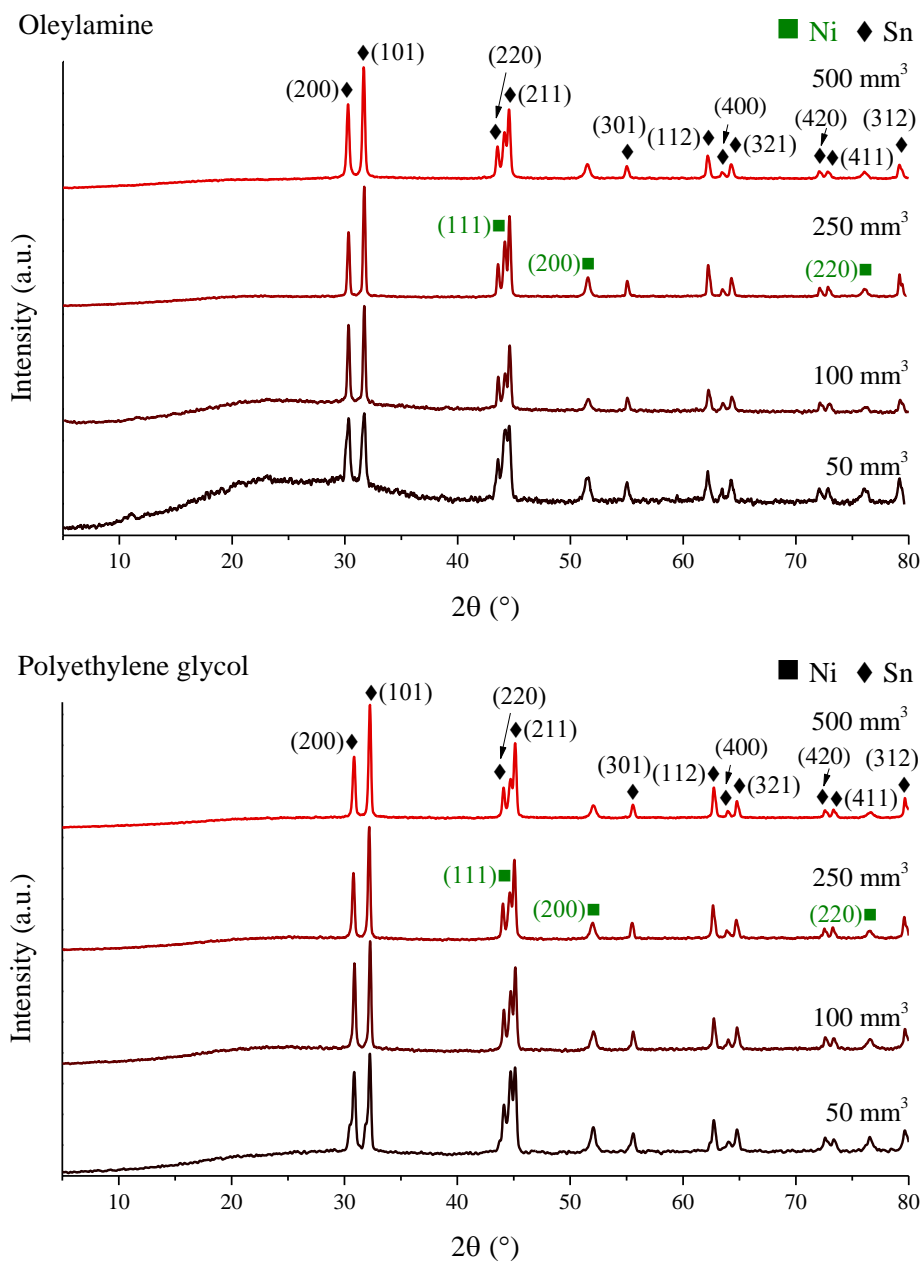
**Table S1**

Phase distribution of the samples generated and cell parameters of the  $\text{Cu}_6\text{Sn}_5$  intermetallics.

Milled systems	Crystal phase distribution (wt%)				Cell parameters			
	$\text{Cu}_6\text{Sn}_5$	Cu	Sn	Ni	a (Å)	b (Å)	c (Å)	$\beta$ (°)
Cu-Sn, <i>n</i> -Heptane (500 mm <sup>3</sup> )	92.5 ± 6.2	4 ± 0.8	3.4 ± 0.9	–	11.0445 ± 0.0189	7.2619 ± 0.0139	9.8422 ± 0.0212	98.8939 ± 0.1878
Cu-Sn, <i>n</i> -Heptane (250 mm <sup>3</sup> )	94.4 ± 4.2	3.4 ± 0.8	2.2 ± 0.9	–	11.0204 ± 0.0171	7.2756 ± 0.0155	9.8197 ± 0.019	98.9396 ± 0.161
Cu-Sn, <i>n</i> -Heptane (125 mm <sup>3</sup> )	93.4 ± 3.9	3.5 ± 0.8	3.1 ± 0.6	–	11.0168 ± 0.0175	7.2697 ± 0.0155	9.819 ± 0.0195	98.9363 ± 0.166
Cu-Sn, <i>n</i> -Heptane (100 mm <sup>3</sup> )	91.6 ± 6.0	3 ± 0.8	5.4 ± 1	–	11.0207 ± 0.0183	7.2724 ± 0.0161	9.8234 ± 0.0203	98.9217 ± 0.1731
Cu-Sn, <i>n</i> -Heptane (75 mm <sup>3</sup> )	92.4 ± 5.7	5.5 ± 0.9	2.1 ± 1.3	–	11.0268 ± 0.018	7.2759 ± 0.0159	9.8278 ± 0.02	98.9122 ± 0.1702
Cu-Sn, <i>n</i> -Heptane (50 mm <sup>3</sup> )	94.4 ± 4.2	2.9 ± 0.6	2.7 ± 0.3	–	11.0371 ± 0.0192	7.279 ± 0.0169	9.8319 ± 0.0208	98.9874 ± 0.1771
Cu-Sn, without additive	92.6 ± 5.3	5.2 ± 0.8	3.2 ± 0.9	–	11.0447 ± 0.0175	7.2735 ± 0.0156	9.8354 ± 0.0194	98.9426 ± 0.1644
Cu-Sn, NaCl (5 wt%)	93.9 ± 4.8	3.9 ± 0.3	2.2 ± 0.3	–	11.0443 ± 0.0167	7.2747 ± 0.0149	9.8339 ± 0.0185	98.9464 ± 0.1573
Cu-Sn, NaCl (3 wt%)	91.9 ± 4.9	4.3 ± 0.8	3.8 ± 0.8	–	11.0364 ± 0.0159	7.2764 ± 0.011	9.8359 ± 0.0174	98.871 ± 0.1488

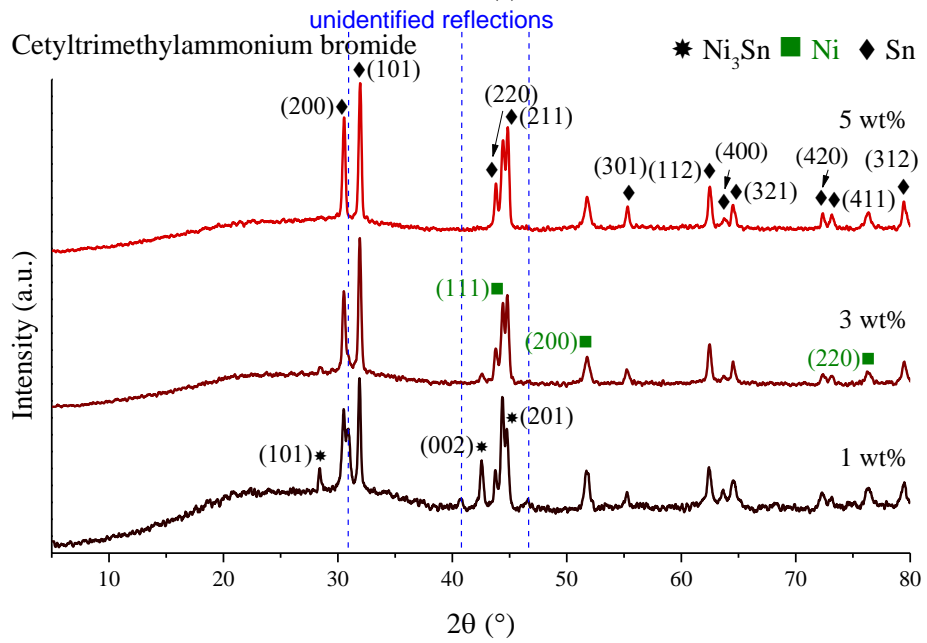
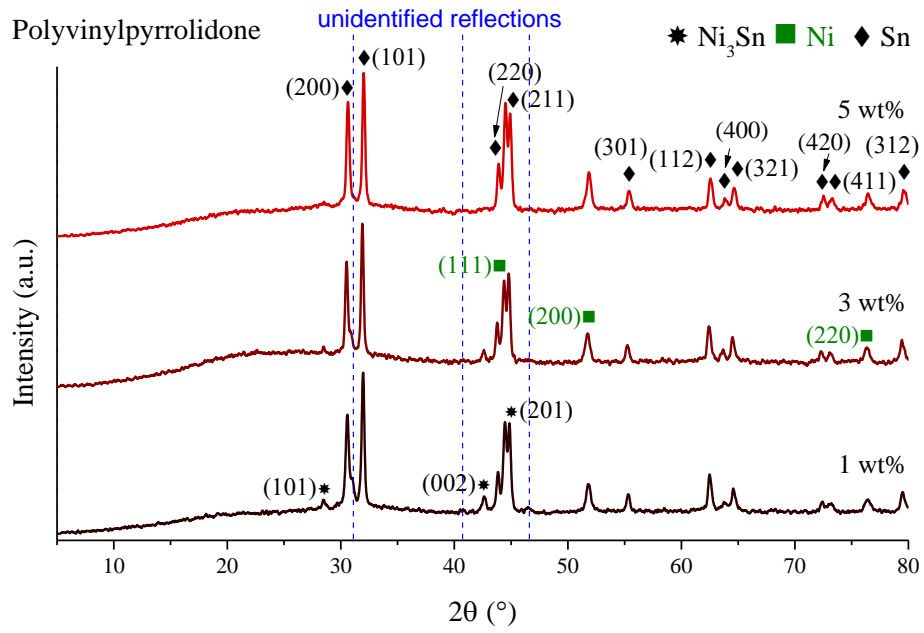
Cu-Sn, NaCl (2 wt%)	92.2 ± 5.7	3.4 ± 0.7	4.4 ± 0.9	–	11.0283 ± 0.0138	7.2852 ± 0.0112	9.8277 ± 0.0154	98.8962 ± 0.1292
Cu-Sn, NaCl (1.5 wt%)	91.1 ± 6.1	4.9 ± 0.9	4 ± 0.8	–	11.0374 ± 0.0164	7.2696 ± 0.0112	9.8349 ± 0.0178	98.9337 ± 0.1508
Cu-Sn, NaCl (1 wt%)	90.6 ± 4.8	5.5 ± 0.9	3.9 ± 1	–	11.0275 ± 0.0151	7.2841 ± 0.0102	9.8485 ± 0.0149	98.8975 ± 0.1338
Cu-Sn, NaCl (0.5 wt%)	92.5 ± 5.3	3.8 ± 0.6	3.7 ± 0.7	–	11.0562 ± 0.0184	7.2687 ± 0.0133	9.8456 ± 0.019	98.9053 ± 0.1668
Cu-Sn, CTAB (5 wt%)	22.4 ± 1.1	24.9 ± 1.0	52.7 ± 7.8	–	11.0253 ± 0.0194	7.2771 ± 0.0162	9.8283 ± 0.0208	98.9964 ± 0.1829
Cu-Sn, CTAB (3 wt%)	44.0 ± 2.4	16.7 ± 0.9	39.3 ± 6.6	–	11.0438 ± 0.0183	7.2866 ± 0.0140	9.8413 ± 0.0193	98.9956 ± 0.1666
Cu-Sn, CTAB (2 wt%)	47.7 ± 3	15.2 ± 0.9	37.1 ± 5.9	–	11.0490 ± 0.0174	7.2651 ± 0.0128	9.8428 ± 0.019	98.9174 ± 0.1688
Cu-Sn, CTAB (1.5 wt%)	61.9 ± 3.7	15.1 ± 0.7	23 ± 2.3	–	11.0351 ± 0.0176	7.2788 ± 0.0156	9.8324 ± 0.0196	98.9235 ± 0.1666
Cu-Sn, CTAB (1 wt%)	72.7 ± 4.9	14.2 ± 0.9	13.1 ± 1.1	–	11.0231 ± 0.0181	7.2756 ± 0.0159	9.8268 ± 0.0201	98.9417 ± 0.1709
Cu-Sn, CTAB (0.5 wt%)	91.6 ± 6.2	5.5 ± 0.8	2.9 ± 0.9	–	11.0479 ± 0.0182	7.2626 ± 0.0132	9.8232 ± 0.0198	98.9425 ± 0.17
Cu-Sn, PVP (5 wt%)	48.9 ± 4.3	21.9 ± 1.3	29.2 ± 4.3	–	11.0309 ± 0.0176	7.2789 ± 0.0155	9.8301 ± 0.0195	98.9284 ± 0.1664
Cu-Sn, PVP (3 wt%)	87.6 ± 4	5.5 ± 0.8	6.9 ± 1.1	–	11.0304 ± 0.0189	7.2762 ± 0.0167	9.8298 ± 0.0210	98.9288 ± 0.1784
Cu-Sn, PVP (2 wt%)	89.8 ± 5.2	4.8 ± 0.8	5.4 ± 0.9	–	11.0499 ± 0.0172	7.2677 ± 0.0126	9.8426 ± 0.0187	98.9186 ± 0.1665
Cu-Sn, PVP (1.5 wt%)	90.7 ± 4.1	4.4 ± 1.2	4.9 ± 1	–	11.0584 ± 0.0170	7.2614 ± 0.0125	9.8444 ± 0.0186	98.9740 ± 0.1584
Cu-Sn, PVP (1 wt%)	92 ± 4.1	4.1 ± 0.9	3.9 ± 0.6	–	11.0520 ± 0.0198	7.2776 ± 0.0144	9.8635 ± 0.0223	98.6979 ± 0.1909
Cu-Sn, PVP (0.5 wt%)	93.4 ± 5.2	3.9 ± 0.8	2.7 ± 0.8	–	11.0413 ± 0.0176	7.2822 ± 0.0155	9.8362 ± 0.0195	98.8818 ± 0.1661
Cu-Sn, ethylene glycol (500 mm <sup>3</sup> )	80.3 ± 5.7	6.8 ± 0.8	12.9 ± 1.2	–	11.0292 ± 0.0153	7.2701 ± 0.0115	9.8131 ± 0.0159	98.9772 ± 0.1286
Cu-Sn, ethylene glycol (250 mm <sup>3</sup> )	52.2 ± 4.3	15.6 ± 0.9	32.2 ± 4.6	–	11.0215 ± 0.0194	7.2913 ± 0.0157	9.8262 ± 0.0216	98.8528 ± 0.1831
Cu-Sn, ethylene glycol (125 mm <sup>3</sup> )	58 ± 4.6	16.9 ± 1.1	25.1 ± 3.2	–	11.0367 ± 0.0176	7.2721 ± 0.0156	9.8233 ± 0.0196	98.9154 ± 0.1668
Cu-Sn, ethylene glycol	49.3 ± 3.7	14.4 ± 0.9	36.3 ± 5.3	–	11.0287 ± 0.018	7.2726 ± 0.0158	9.8273 ± 0.0199	98.928 ± 0.1699

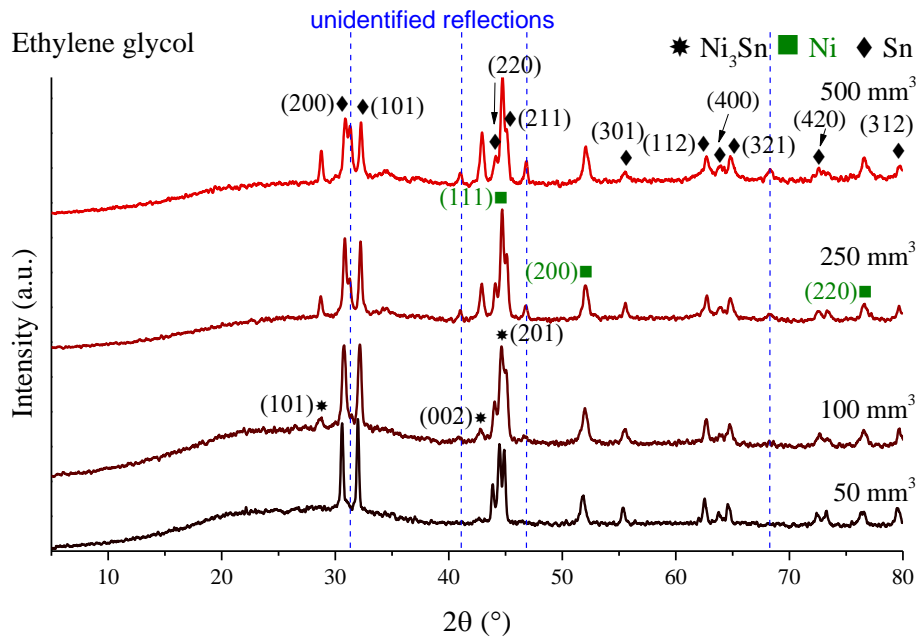
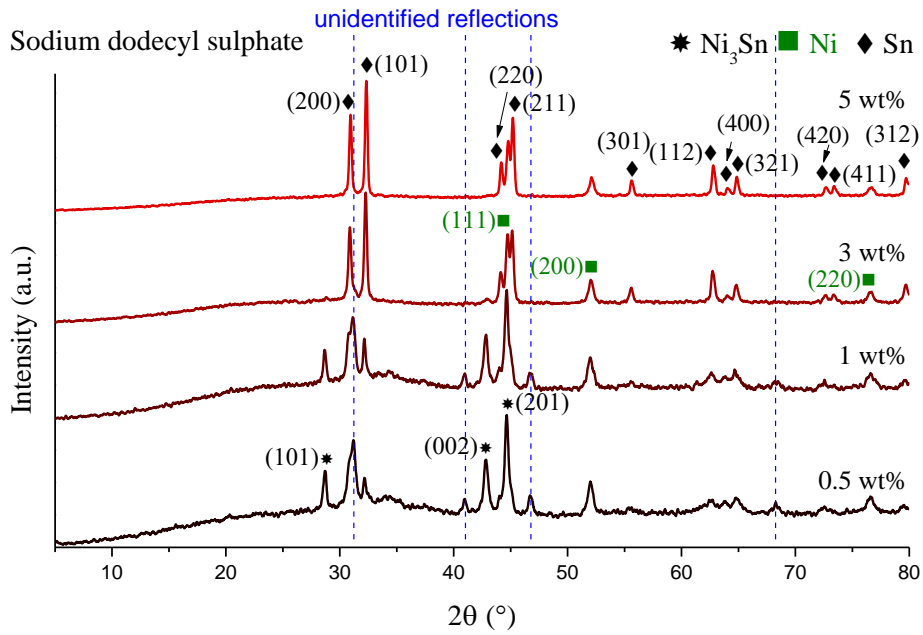
(100 mm <sup>3</sup> )									
Cu-Sn, ethylene glycol (75 mm <sup>3</sup> )	46.1 ± 4.1	19.2 ± 1.0	34.7 ± 4.8	–	11.0201 ± 0.0174	7.2764 ± 0.0152	9.8245 ± 0.0202	98.9408 ± 0.1705	
Cu-Sn, ethylene glycol (50 mm <sup>3</sup> )	28.7 ± 1.5	24.4 ± 1.1	46.9 ± 7.4	–	11.0457 ± 0.0168	7.2645 ± 0.0127	9.8444 ± 0.0188	99.014 ± 0.1479	
Cu-Sn, SDS (3 wt%)	71.5 ± 5.5	14.2 ± 1.1	14.3 ± 2.3	–	11.0521 ± 0.017	7.2777 ± 0.0124	9.8230 ± 0.0185	98.8733 ± 0.1549	
Cu-Sn, SDS (2 wt%)	82.1 ± 5.9	11.3 ± 1	6.6 ± 1.0	–	11.0476 ± 0.0164	7.2749 ± 0.012	9.8274 ± 0.0179	98.7477 ± 0.1493	
Cu-Sn, SDS (1.5 wt%)	83.2 ± 5.9	11 ± 1.1	5.8 ± 0.9	–	11.0424 ± 0.0173	7.281 ± 0.0119	9.832 ± 0.0189	98.8282 ± 0.1614	
Cu-Sn, SDS (1 wt%)	89.6 ± 6.1	4.2 ± 0.8	6.2 ± 1	–	11.0334 ± 0.0164	7.2737 ± 0.0121	9.8189 ± 0.0183	98.8928 ± 0.1535	
Cu-Sn, SDS (0.5 wt%)	92.2 ± 6.2	3.4 ± 0.8	4.4 ± 0.9	–	11.0341 ± 0.0118	7.2893 ± 0.0104	9.8173 ± 0.0127	98.8699 ± 0.0998	
Ni-Cu-Sn, CTAB (5 wt%)	17.3 ± 0.9	29.8 ± 1.9	28.7 ± 4.6	24.2 ± 1.3	11.0370 ± 0.0274	7.2847 ± 0.0138	9.8302 ± 0.0269	98.8655 ± 0.2025	
Ni-Cu-Sn, PVP (5 wt%)	25.1 ± 0.8	17.6 ± 0.8	33.4 ± 5.8	23.9 ± 0.9	11.0227 ± 0.0096	7.2950 ± 0.0087	9.8288 ± 0.0096	98.8752 ± 0.0791	
Ni-Cu-Sn, ethylene glycol (50 mm <sup>3</sup> )	32.5 ± 2.7	19.5 ± 1.9	25.8 ± 5.2	22.2 ± 1.7	11.0369 ± 0.0101	7.2964 ± 0.0088	9.8036 ± 0.0115	98.9424 ± 0.0887	
Ni-Cu-Sn, SDS (5 wt%)	59.9 ± 3.4	9.1 ± 1.4	9.9 ± 3	21.1 ± 2.7	11.0360 ± 0.0121	7.3022 ± 0.101	9.8149 ± 0.0129	99.0189 ± 0.1095	
Ni-Cu-Sn, without additive	66.4 ± 3.8	4.1 ± 0.7	4.2 ± 0.8	25.3 ± 1.9	11.0441 ± 0.0295	7.2723 ± 0.0162	9.8324 ± 0.0313	98.7267 ± 0.2361	
Ni-Cu-Sn, <i>n</i> -heptane (125 mm <sup>3</sup> )	67.6 ± 4.9	3.2 ± 0.7	4.4 ± 1.1	24.8 ± 1.1	11.0425 ± 0.0149	7.2850 ± 0.009	9.8359 ± 0.0138	98.7452 ± 0.1284	
Ni-Cu-Sn, NaCl (5 wt%)	71.8 ± 5	3.5 ± 1.2	3.4 ± 1.1	21.3 ± 1.6	11.0281 ± 0.0160	7.2739 ± 0.0134	9.8362 ± 0.0172	98.7116 ± 0.1427	

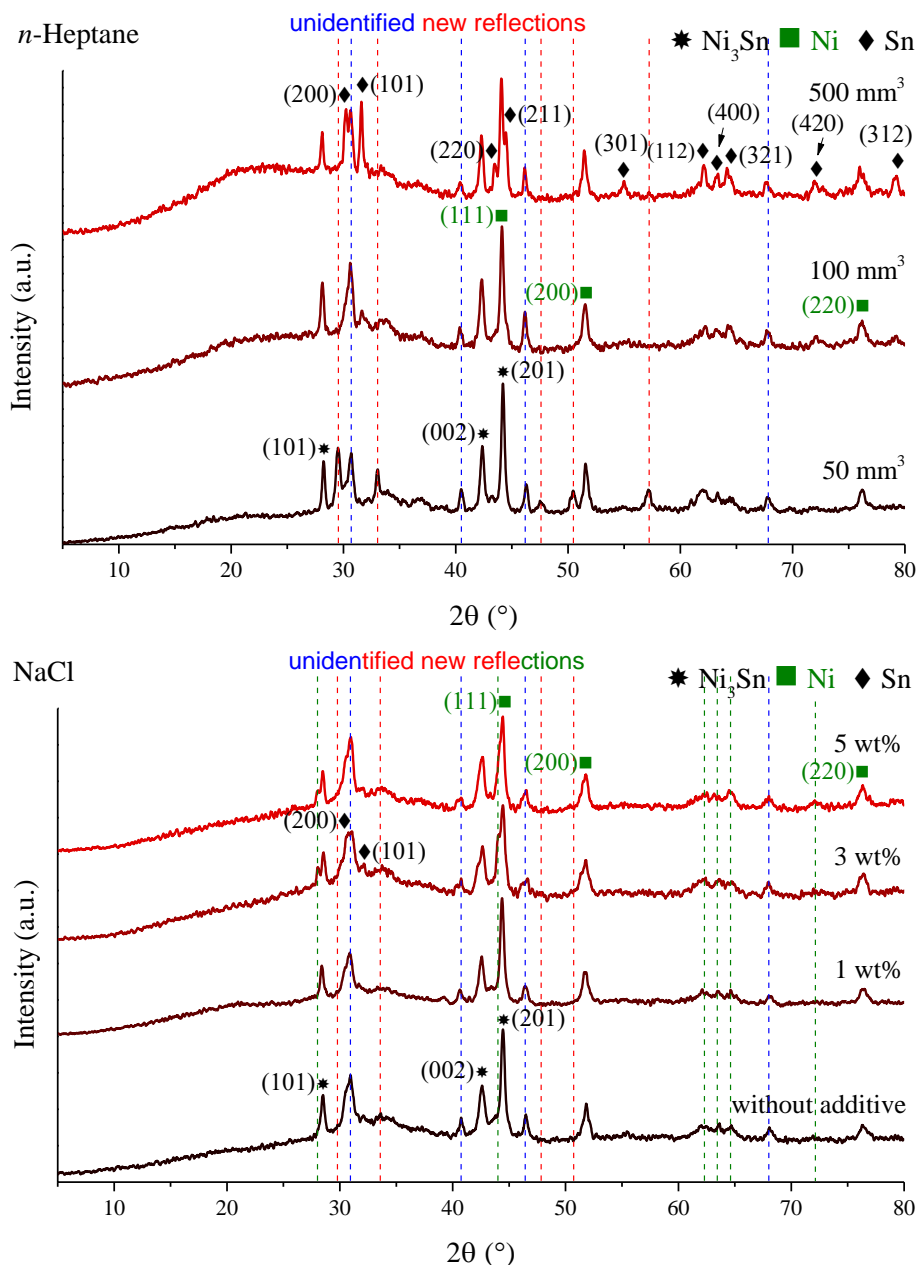


**Fig. S4** X-ray diffraction patterns of the milled Ni and Sn starting reagents using oleylamine or polyethylene glycol as milling additives.









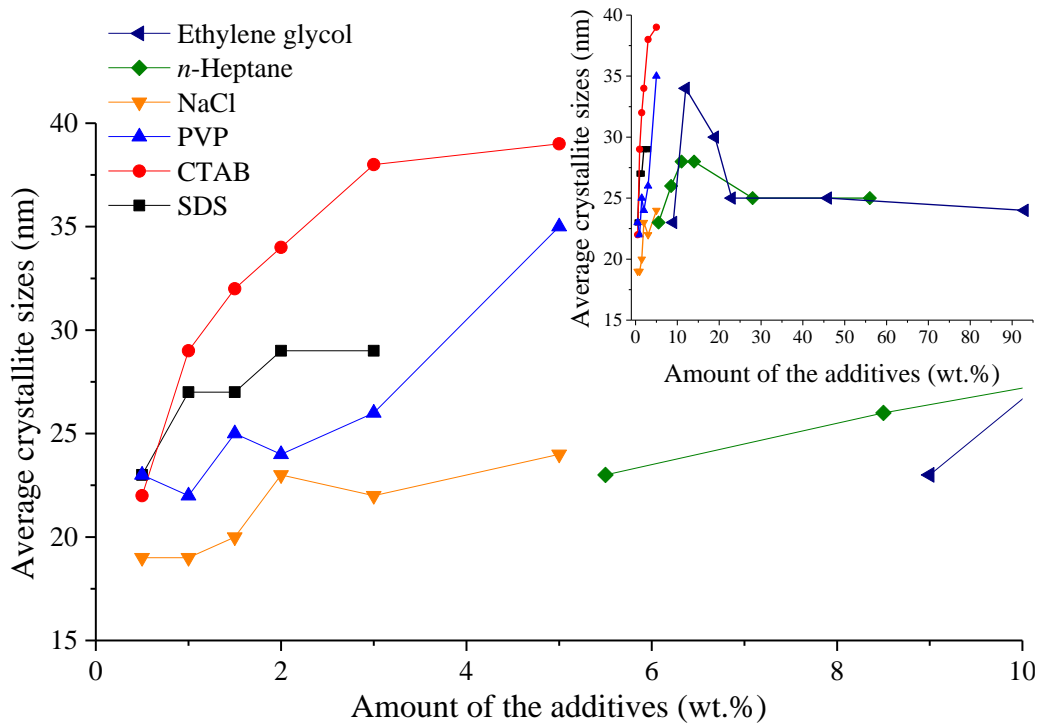
**Fig. S5** XRD patterns of the milling end-products in the presence of varying amounts of PVP, CTAB, SDS, ethylene glycol, *n*-heptane or NaCl additives and in the absence of additive.

**Table S2**

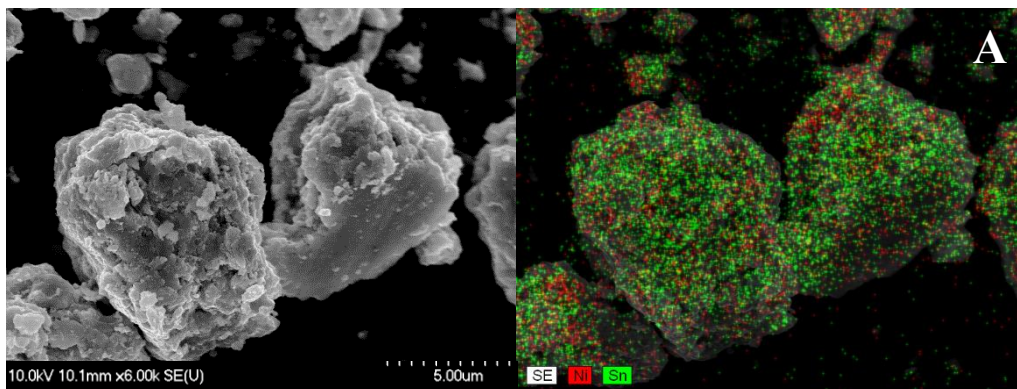
Lattice parameters of the formed hexagonal Ni<sub>3</sub>Sn intermetallics.

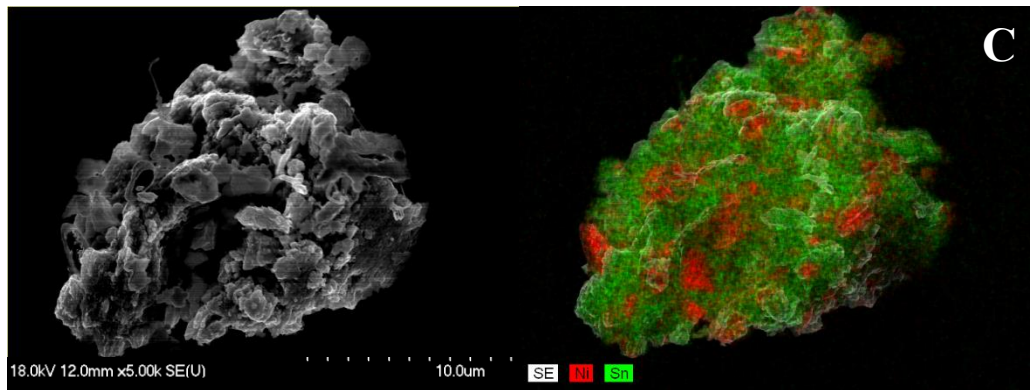
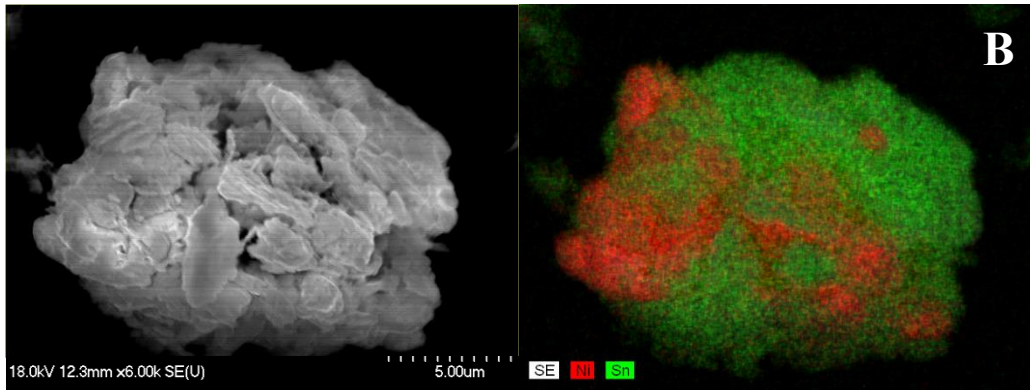
Milled systems	Lattice parameters			Lattice parameters			Lattice parameters	
	a (Å)	c (Å)		a (Å)	c (Å)		a (Å)	c (Å)
Ni-Sn, PVP (3 wt%)	5.3056 ± 0.007	4.2281 ± 0.0045	Ni-Sn, CTAB (3 wt%)	5.3087 ± 0.0196	4.2357 ± 0.0126	Ni-Sn, SDS (1 wt%)	5.3245 ± 0.0122	4.2194 ± 0.0097
Ni-Sn, PVP (1 wt%)	5.3263 ± 0.0112	4.228 ± 0.0072	Ni-Sn, CTAB (1 wt%)	5.3359 ± 0.0121	4.2369 ± 0.0129	Ni-Sn, SDS (0.5 wt%)	5.3131 ± 0.0114	4.2201 ± 0.0121

Ni-Sn, ethylene glycol (500 mm <sup>3</sup> )	5.3556 ± 0.0037	4.2376 ± 0.0023	Ni-Sn, <i>n</i> -heptane (500 mm <sup>3</sup> )	5.3634 ± 0.0015	4.2341 ± 0.001	Ni-Sn, NaCl (5 wt%)	5.3536 ± 0.0123	4.2268 ± 0.0078
Ni-Sn, ethylene glycol (250 mm <sup>3</sup> )	5.3626 ± 0.0078	4.2328 ± 0.0049	Ni-Sn, <i>n</i> -heptane (100 mm <sup>3</sup> )	5.3553 ± 0.0015	4.2348 ± 0.001	Ni-Sn, NaCl (3 wt%)	5.3435 ± 0.0172	4.226 ± 0.0109
Ni-Sn, ethylene glycol (100 mm <sup>3</sup> )	5.3614 ± 0.0145	4.2359 ± 0.0092	Ni-Sn, <i>n</i> -heptane (50 mm <sup>3</sup> )	5.3558 ± 0.0044	4.228 ± 0.0028	Ni-Sn, NaCl (1 wt%)	5.3555 ± 0.0023	4.2274 ± 0.0015
Ni-Sn, without additive	5.3594 ± 0.0042	4.2385 ± 0.0026						

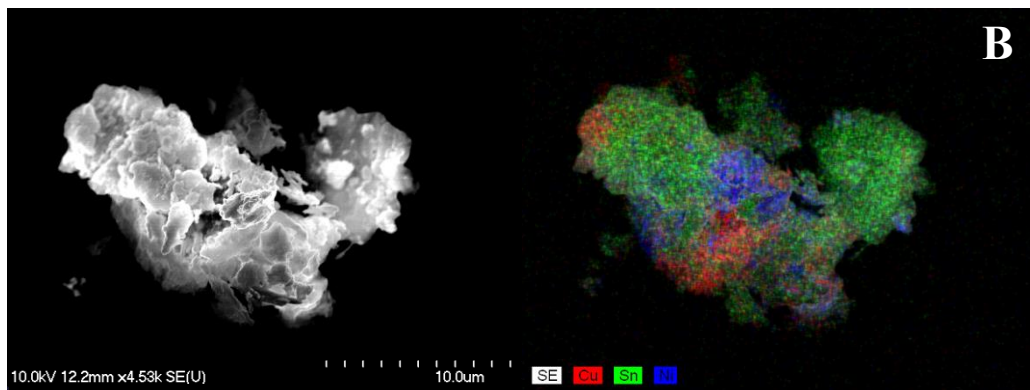
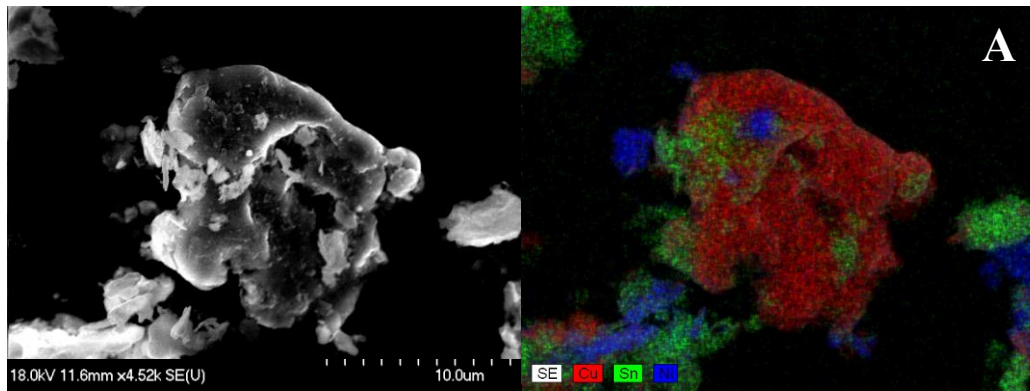


**Fig. S6** The changes of the crystallite sizes of  $\eta$ -bronze ( $\text{Cu}_6\text{Sn}_5$ ) monitored through the variation of the amount of added milling additives compared to the total mass of the starting metal reagents.

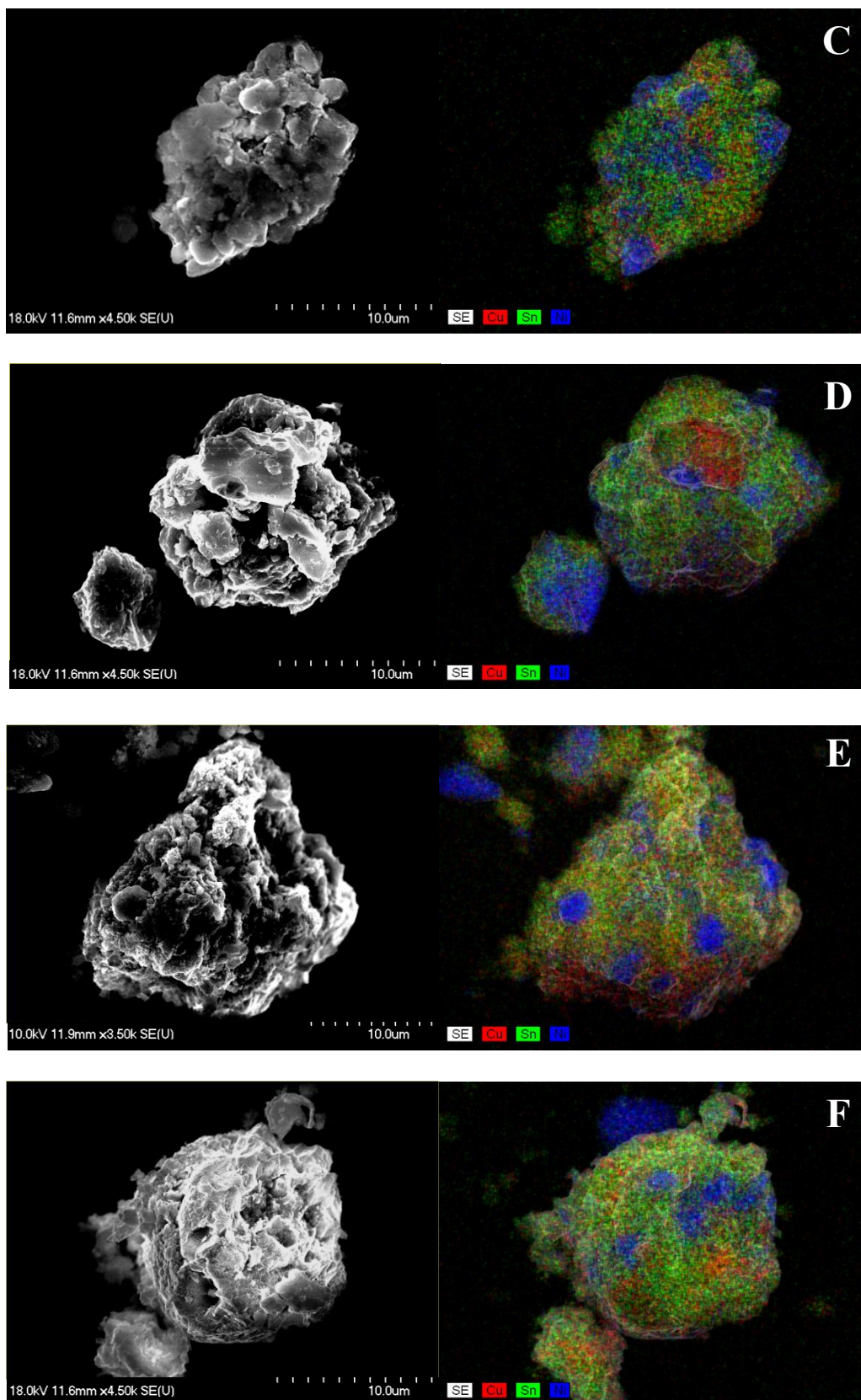




**Fig. S7** SEM images and the corresponding elemental distribution maps derived by the energy dispersive X-ray analysis of the milled Ni-Sn powders with 5 wt.% NaCl (A), 50 mm<sup>3</sup> oleylamine (B) and 5 wt.% PVP (C).

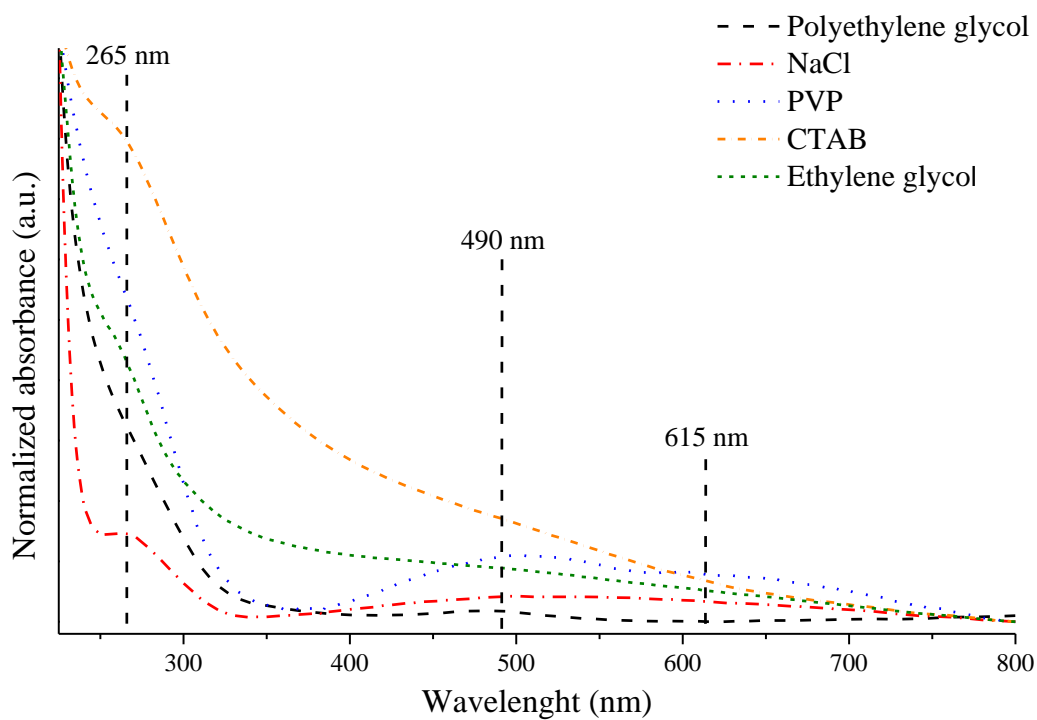




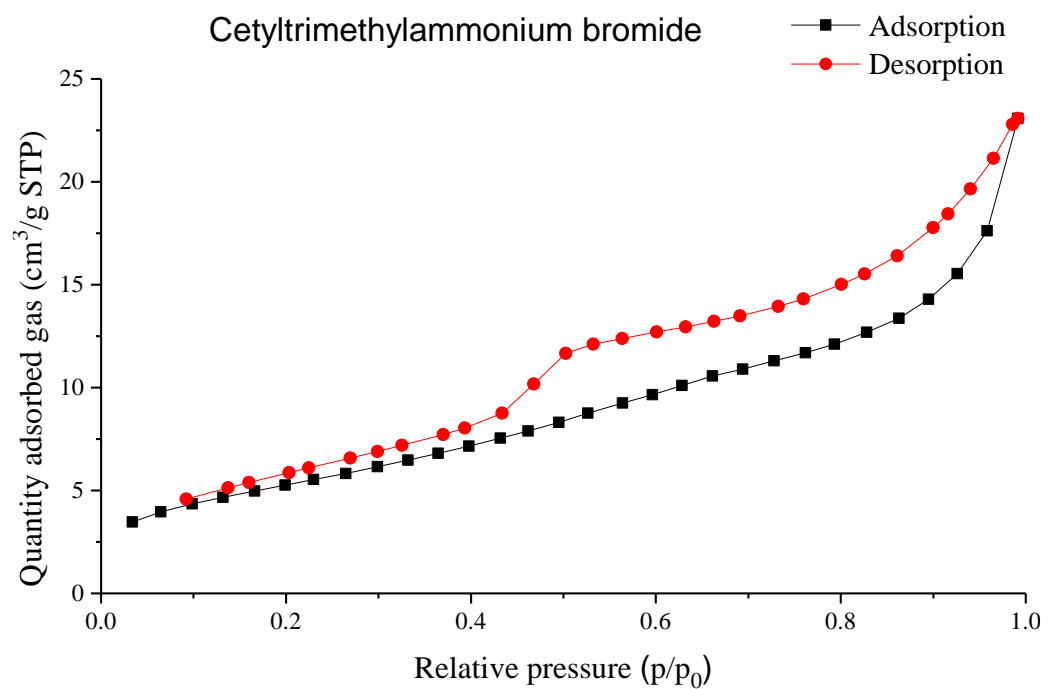
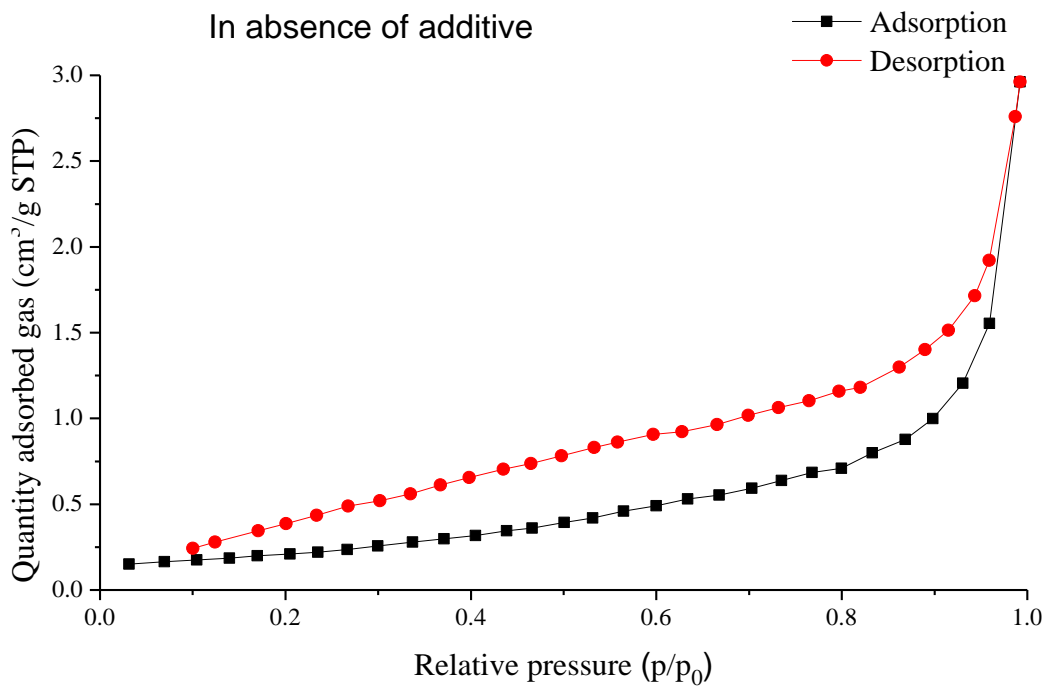


**Fig. S8** SEM images and the corresponding elemental distribution maps registered by the energy dispersive X-ray analysis of the milled Ni-Cu-Sn powders with 50 mm<sup>3</sup> polyethylene

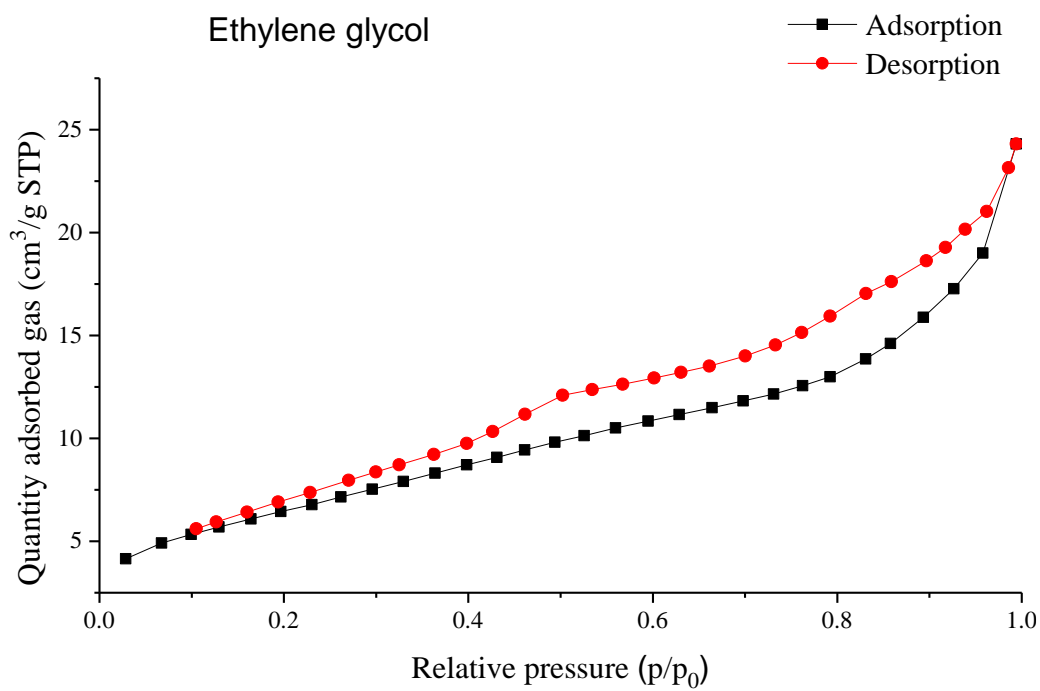
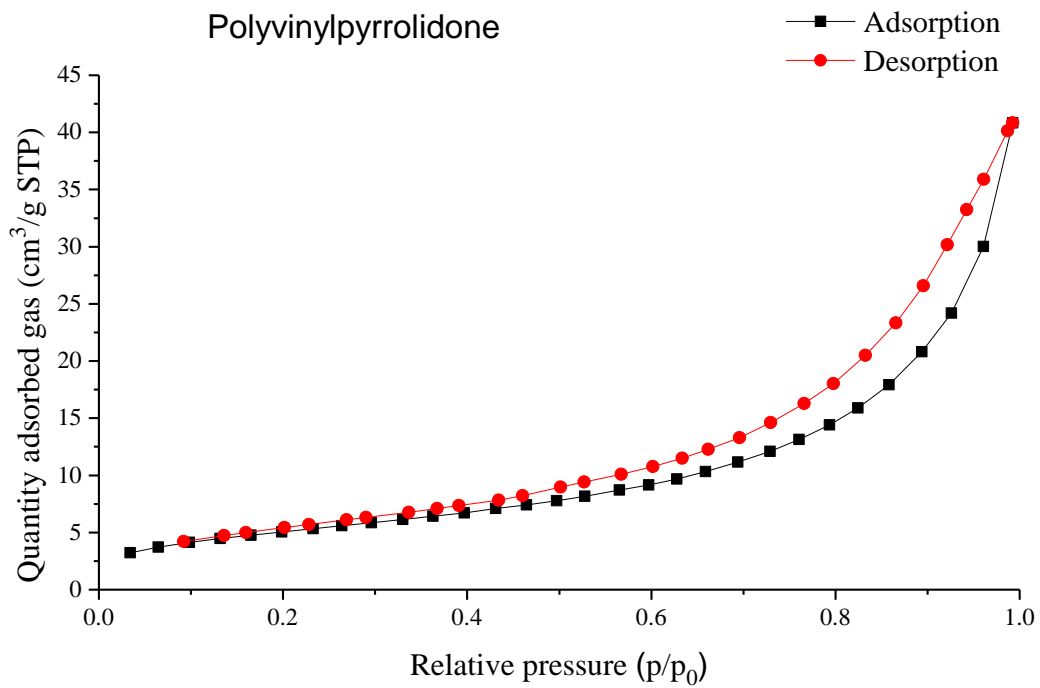
glycol (A) oleylamine (B) and ethylene glycol (C) and 2 wt.% SDS (D), PVP (E) and CTAB (F).

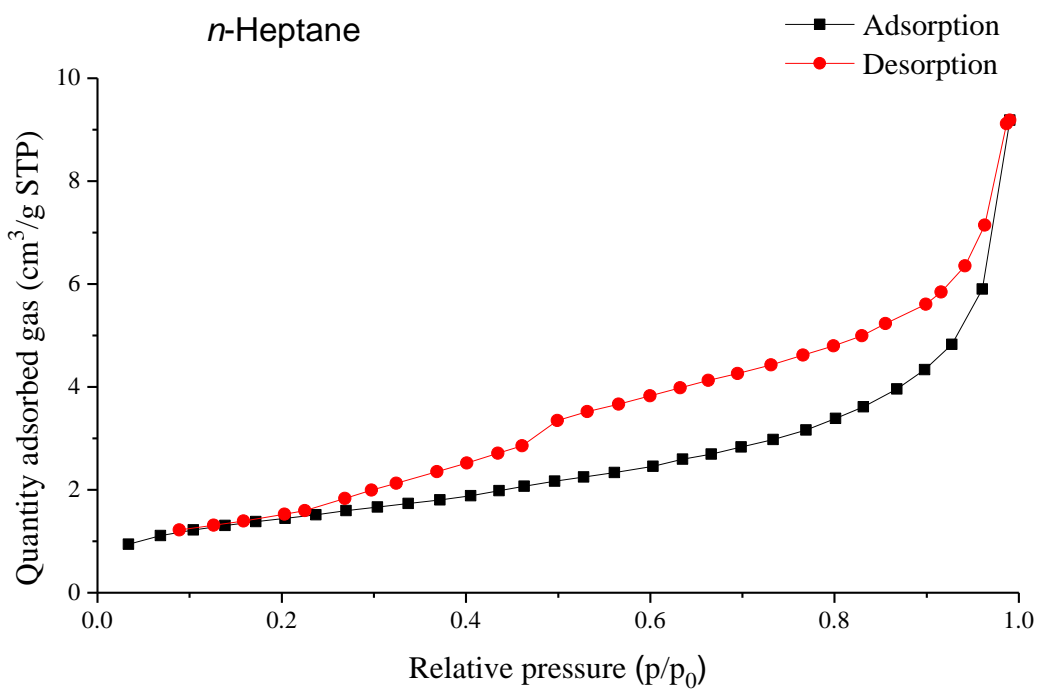
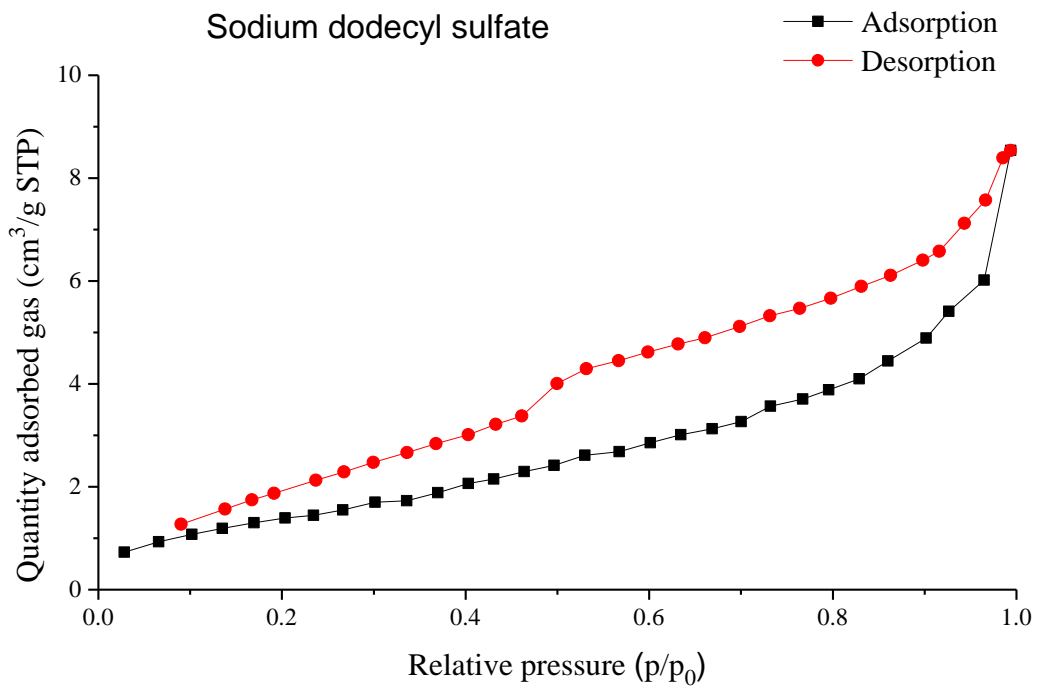


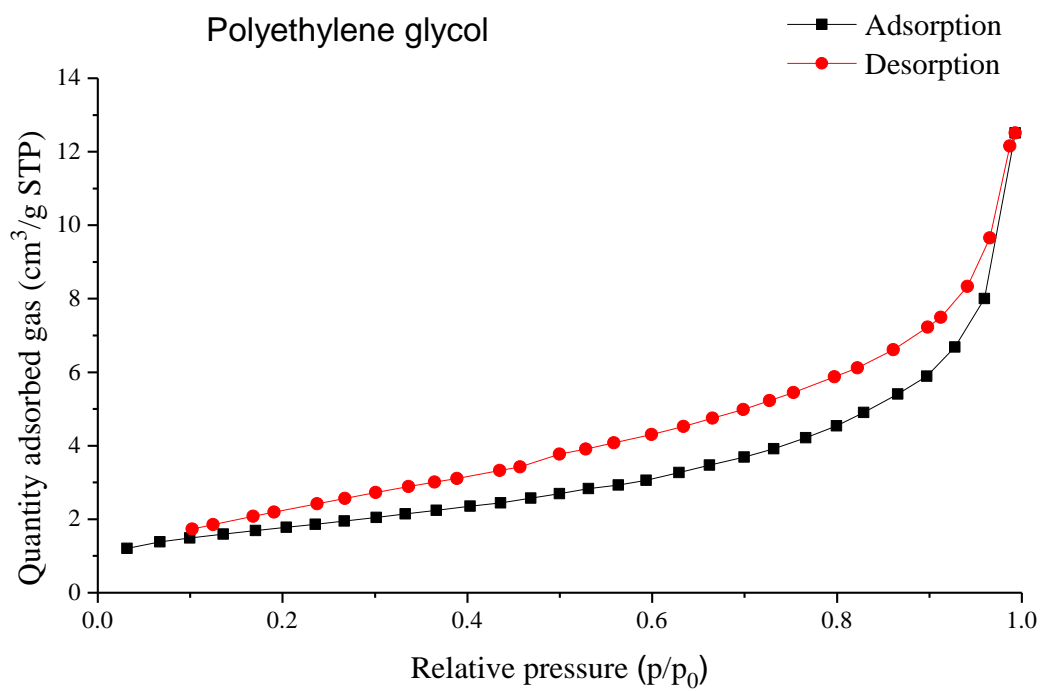
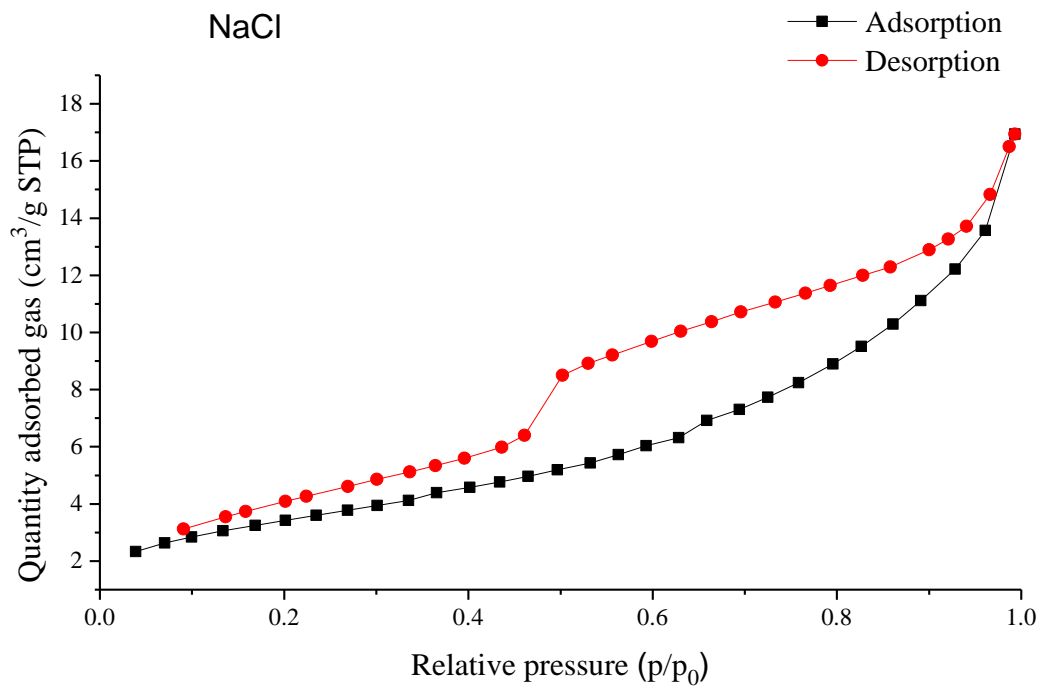
**Fig. S9** UV-visible absorption spectra of the Ni-Cu-Sn nanocomposite using polyethylene glycol (50 mm<sup>3</sup>), NaCl (5 wt%), PVP (5 wt%), CTAB (5 wt%) and ethylene glycol (50 mm<sup>3</sup>) milling additives.

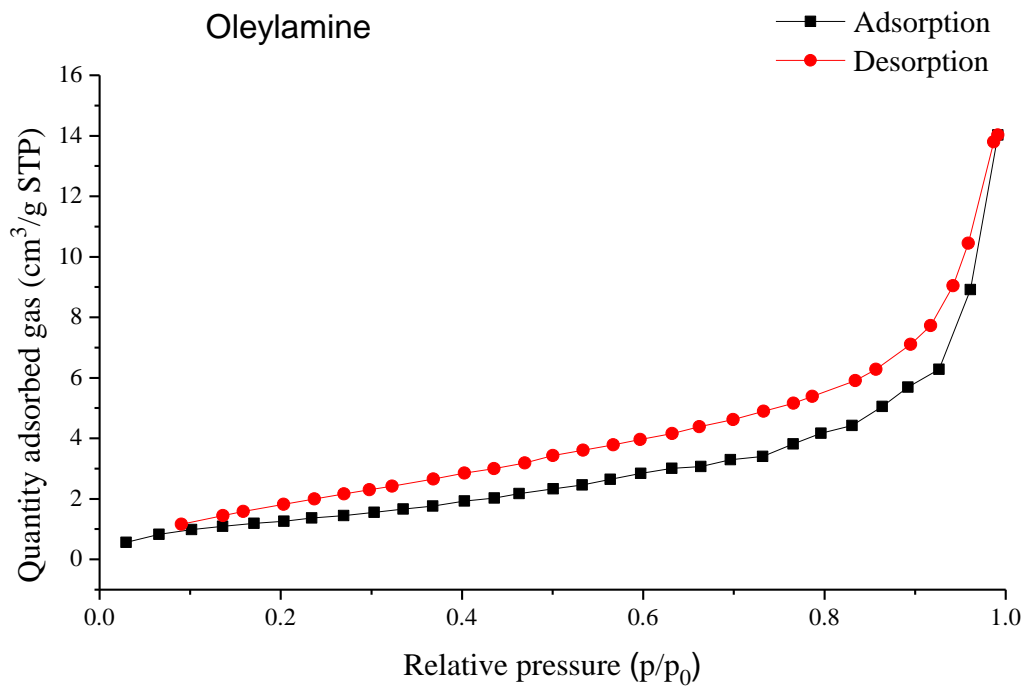












**Fig. S10** N<sub>2</sub> adsorption-desorption isotherms of the milled Ni-Cu-Sn system in the presence of CTAB (5 wt%), PVP (5 wt%), ethylene glycol (50 mm<sup>3</sup>), SDS (2 wt%), *n*-heptane (125 mm<sup>3</sup>), NaCl (5 wt%), polyethylene glycol (50 mm<sup>3</sup>) and oleylamine (50 mm<sup>3</sup>) and in the absence of additive.