Electronic Supplementary Information for

Optimized hot injection and HCl purification for high quality Cu_2ZnSnS_4 Nanoparticles

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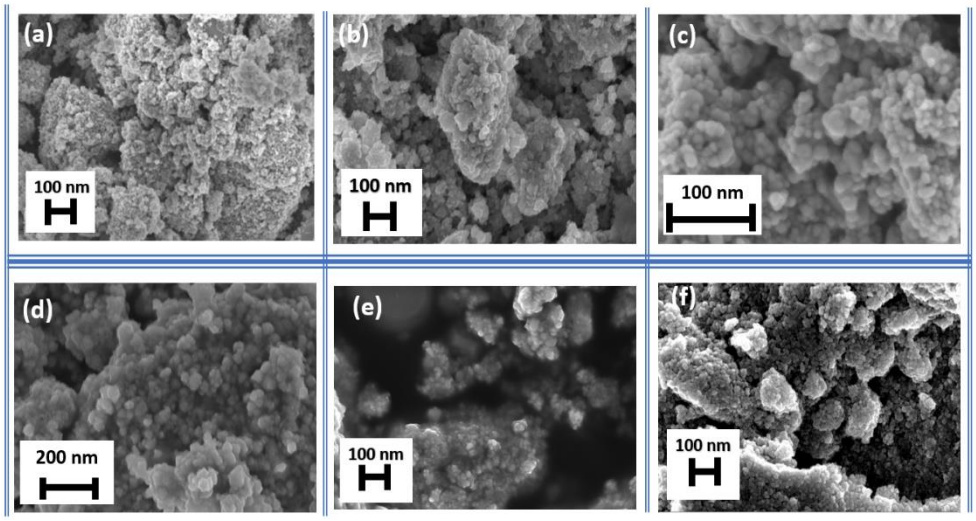
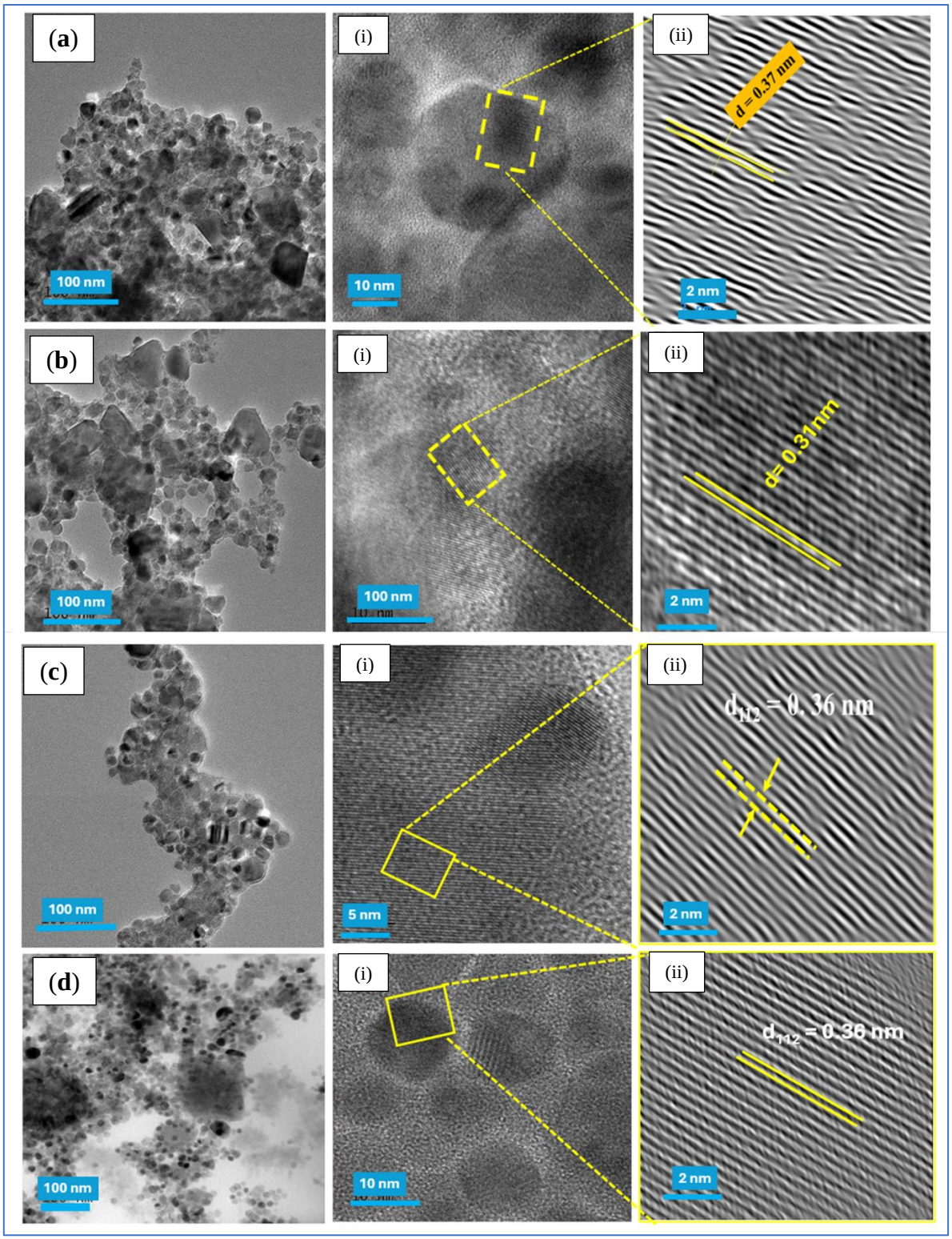


Fig. S1: Scanning electron microscopy images of CZTS NPs obtained with different injection temperatures at scales of 100 nm and 200 nm; (a) 210 °C, (b) 225°C, (c) 235 °C, (d) 240 °C, (e) 260 ° and (f) 270 °C.


(a)
100 nm
(i)
10 nm
(ii)
d = 0.37 nm
2 nm
(b)
100 nm
(i)
100 nm
(ii)
d= 0.31nm
2 nm
(c)
100 nm
(i)
5 nm
(ii)
d312 = 0. 36 nm
2 nm
(d)
100 nm
(i)
10 nm
(ii)
d112 = 0.36 nm
2 nm

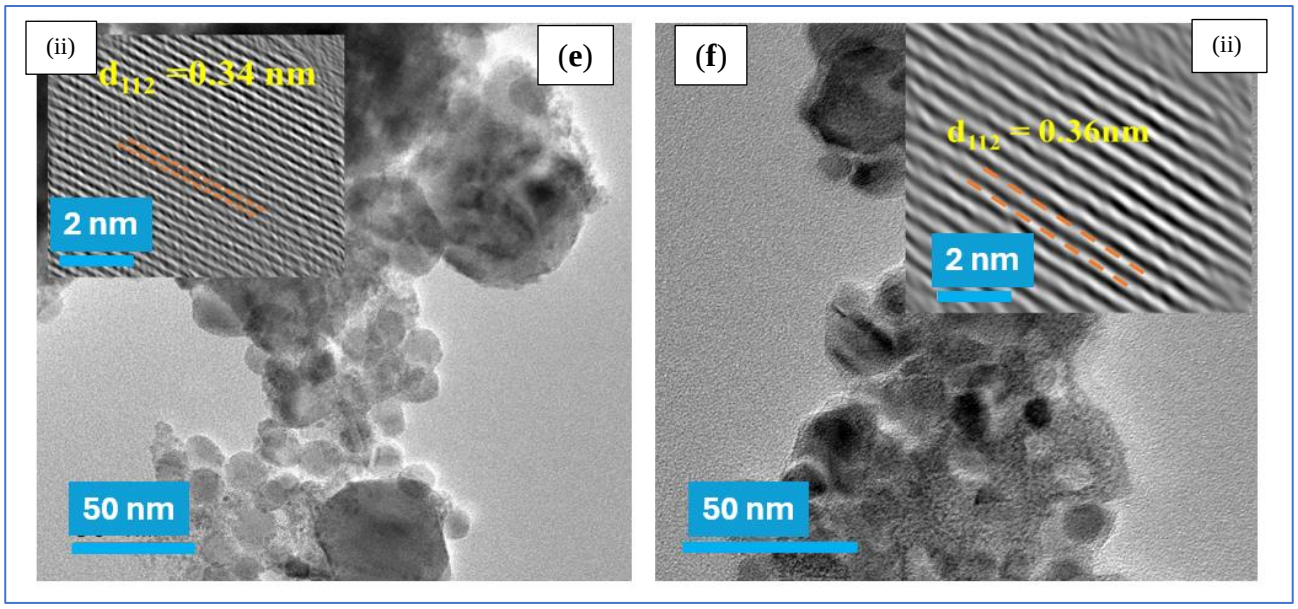


Fig. S2: TEM images of so-obtained CZTS NPs synthesised under different injection temperatures: (a) 210 °C, (b) 225 °C, (c) 235 °C, (d) 240 °C, (e) 260 °C and (f) 270 °C, respectively; (i) high-resolution (HR)TEM image of CZTS NPs; (ii) lattice fringes in a single nanoparticle.

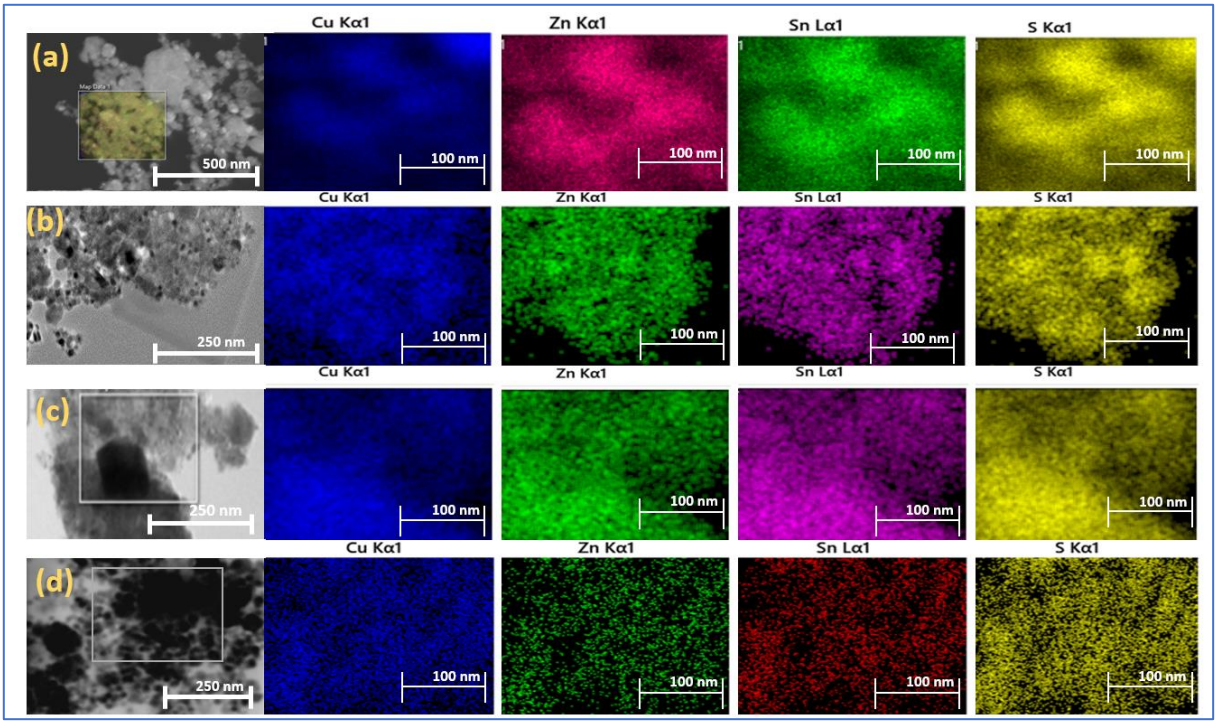


Fig. S3: STEM-EDS elemental map of CZTS NPs synthesised under different injection temperatures: (a) 210 °C, (b) 235 °C, (c) 240 °C and (d) 270 °C. The images were obtained on JEOL JEM-2100PLUS with an emission voltage of 200 kV.

Table S1: Angle, and FWHM of CZTS NPs synthesized at 240 °C for 30 min

Sample	Angle (2θ)	FWHM (degree)
Un treated-HCl	28.2	0.59
Treated-HCl	28.3	0.54

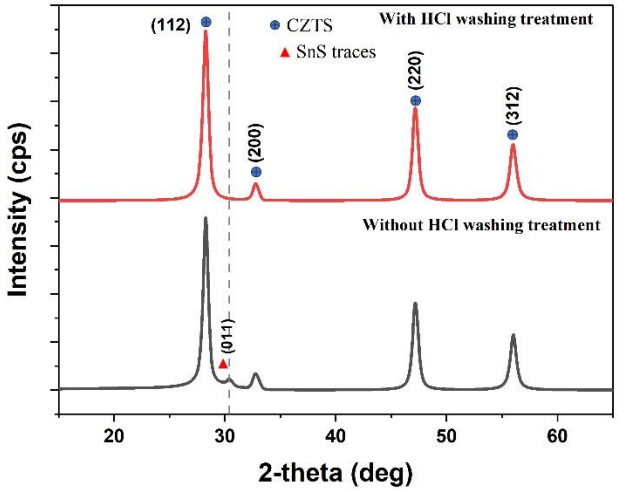


Fig. S4: XRD patterns of CZTS NPs synthesized at 240 °C; before washing with HCl solution referred as "untreated with HCl" (black line spectra) and after washing with HCl referred as "treated with HCl" (red line spectrum).

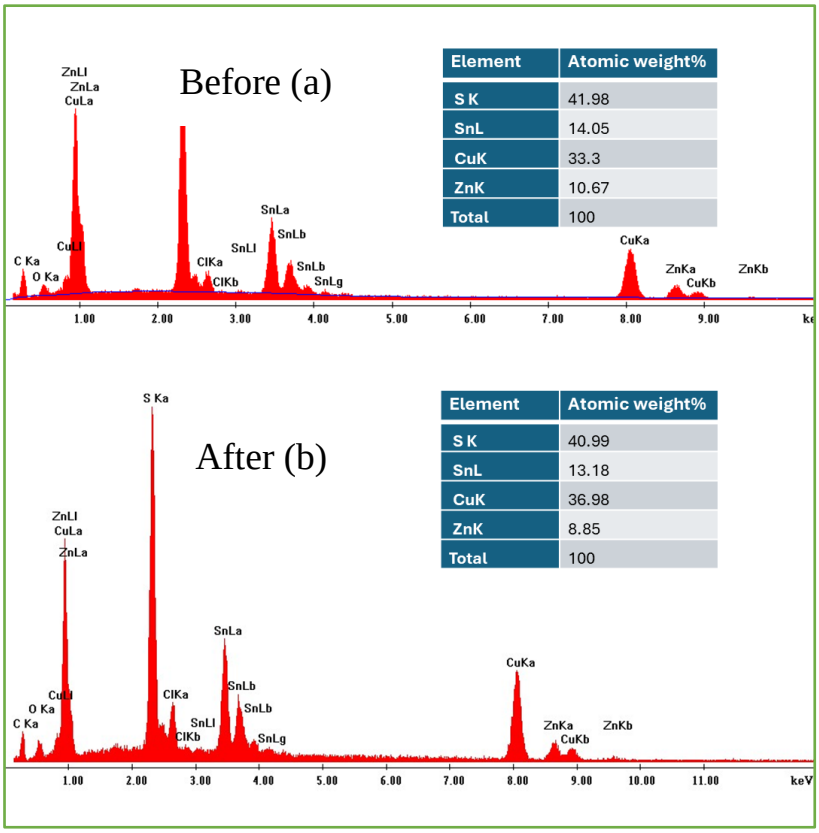


Fig. S5: EDS composition of CZTS NPs synthesized at 240 °C; (a) before and (b) after HCl treatment; the inset (tables) indicate their corresponding elemental composition before and after HCl treatment.

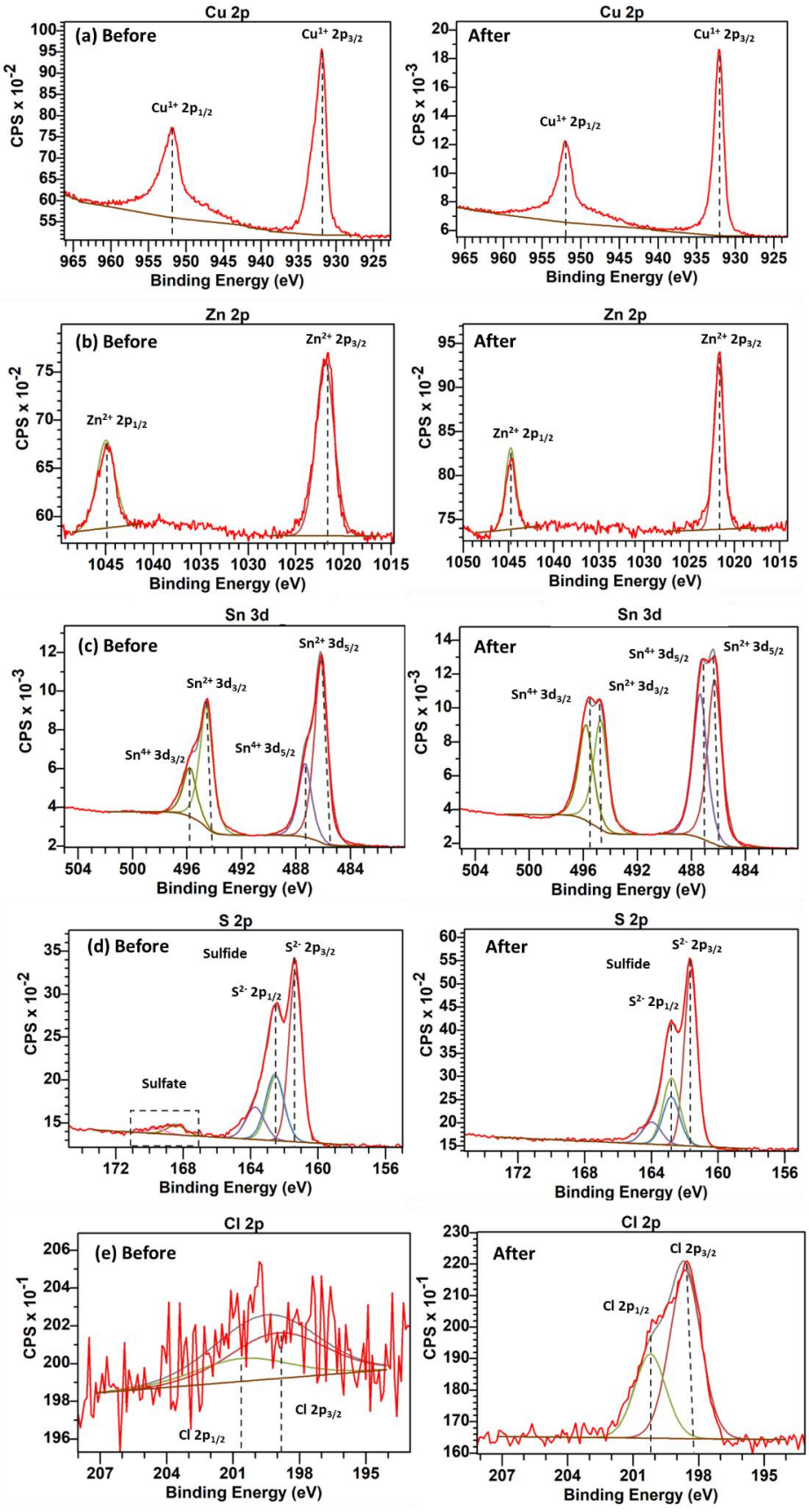


Fig. S6: High resolution XPS of (a) Cu *2p*, (b) Zn *2p*, (c) Sn *3d*, (d) S *2p* and (e) Cl *2p* core-levels in the CZTS NPs synthesized at 240 °C, before and after the HCl treatment.

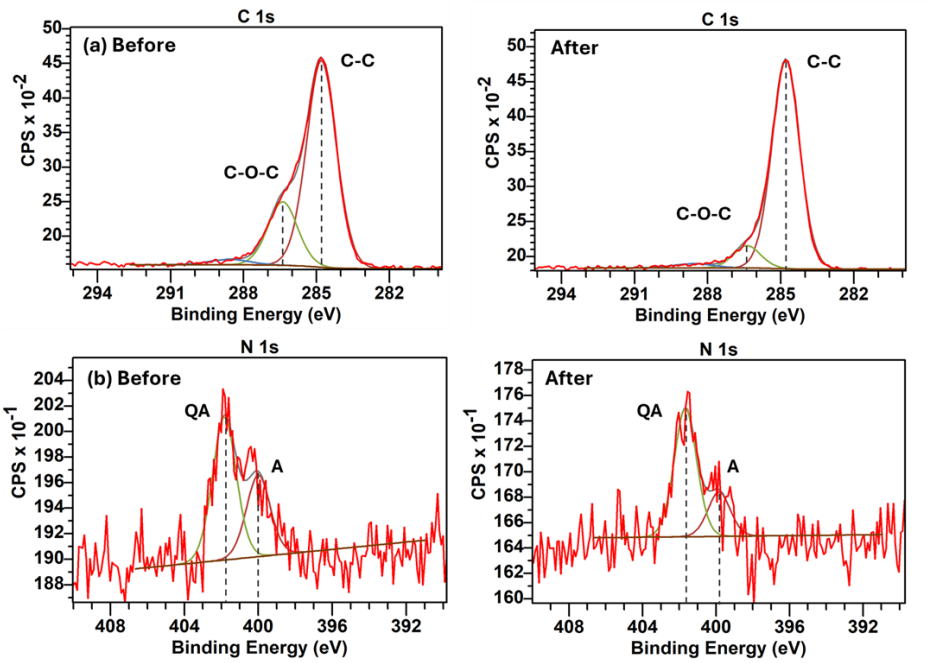


Fig S7: High-resolution XPS of (a) C *1s* (C-C and C-O-C chemical states), and (b) N *1s* (amine A and quaternary amine QA) contaminations related to residual oleylamine in the dried CZTS NPs. The spectra are compared before and after the HCl treatment.

Table S2: Peaks positions for the XPS spectra of Cu 2p, Zn 2p, Sn 3d, S 2p and the corresponding peak separation binding energies, before and after the HCl treatment.

Element	Before	Peak Separation before	After	Peak Separation after
Cu^{1+}	$2p_{3/2}$ 932.0 eV $2p_{1/2}$ 951.8 eV	19.8 eV	$2p_{3/2}$ 932.1 eV $2p_{1/2}$ 952.0 eV	19.9 eV
Zn^{2+}	$2p_{3/2}$ 1021.8 eV $2p_{1/2}$ 1045.0 eV	23.2 eV	$2p_{3/2}$ 1021.6 eV $2p_{1/2}$ 1044.8 eV	23.2 eV
Sn^{2+}	$3d_{5/2}$ 486.2 eV $3d_{3/2}$ 494.5 eV	8.3 eV	$3d_{5/2}$ 486.3 eV $3d_{3/2}$ 494.7 eV	8.4 eV
Sn^{4+}	$3d_{5/2}$ 487.4 eV $3d_{3/2}$ 495.8 eV	8.4 eV	$3d_{5/2}$ 487.3 eV $3d_{3/2}$ 495.7 eV	8.4 eV
S^{2-}	$2p_{3/2}$ 161.3 eV $2p_{1/2}$ 162.4 eV	1.1 eV	$2p_{3/2}$ 161.7 eV $2p_{1/2}$ 162.8 eV	1.1 eV

Table S3: Atomic percentage S in sulphate and in sulphide phases over the total sulphur amount, and C and N total composition, before and after the HCl treatment.

HCl treatment	Sulphate / % of total sulphur	Sulphide /% of total sulphur	Carbon / % of total composition	Nitrogen / % of total composition
Before washing	8.7	91.3	48.72	1.66
After washing	1.7	98.3	37.80	0.33

Table S4: Work Function, Valence band and Ionizing Potential by UPS for CZTS NPs powder before and after HCL washing.

HCl treatment	WF UPS	VB UPS	IP (eV)
Before	4.4 ± 0.1	0.22 ± 0.04	4.7 ± 0.1
After	4.2 ± 0.2	0.39 ± 0.13	4.5 ± 0.1

Table S5: equations for the reactions involved in the CZTS nanoparticles formation

Reactions	Temperature range
$2Cu(II) + Sn(II) \rightarrow 2Cu(I) + Sn(IV)$	From 100 to 180 °C
$2Cu(I) + Zn(II) + Sn(IV) + 4S \rightarrow Cu_2S + ZnS + SnS_2$	Above 230 °C (after S injection)
$Cu_2S + ZnS + SnS_2 \rightarrow Cu_2ZnSnS_4$	Between 230 and 280 °C

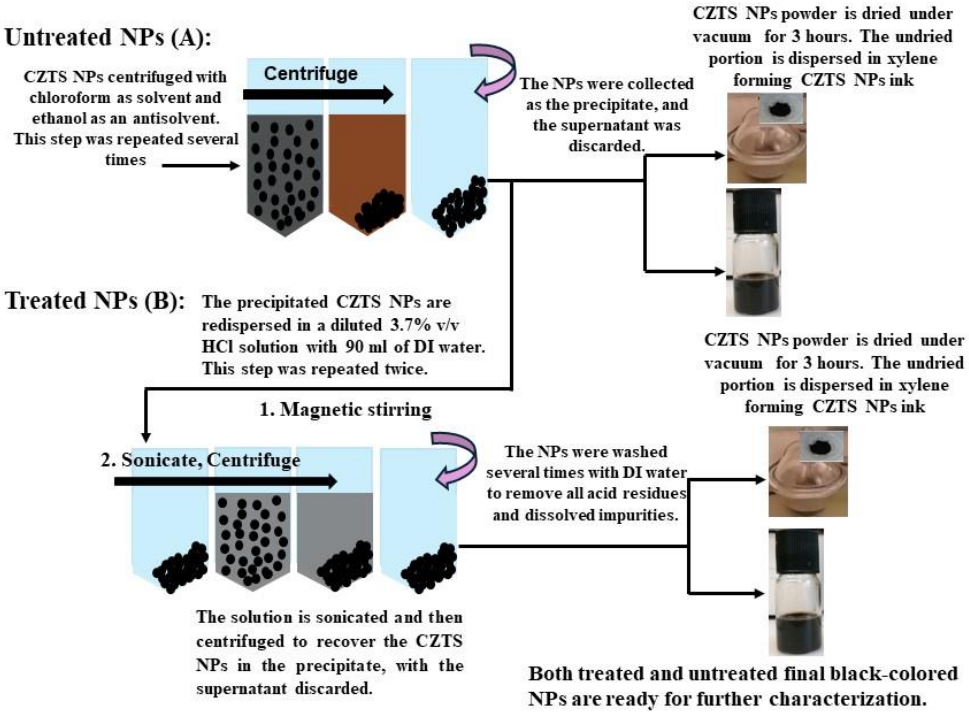


Fig. S8: The schematic of purification steps and CZTS NPs ink