

Electronic Supplementary Information

Carbonization of Zr-loaded thiourea-functionalized styrene-divinylbenzene copolymers: an easy way to synthesize nano-ZrO₂@C and nano-(ZrC, ZrO₂)@C composites

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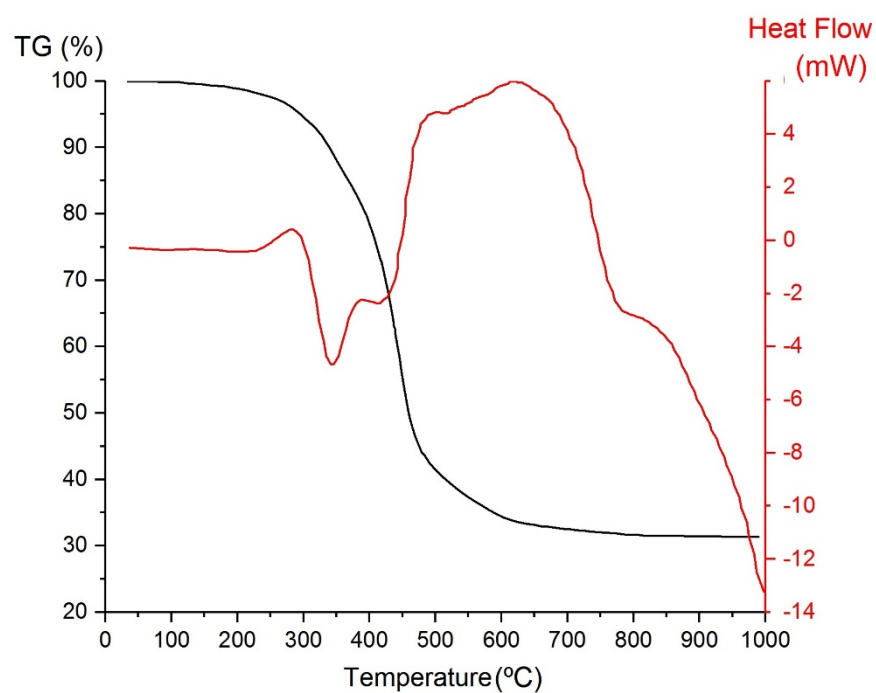
ESI Table S1 Chemical analysis of Zr-loaded thiourea functionalized styrene-divinylbenzene copolymer (average of five measurements)

Resin	C [%]	H [%]	N [%]	S [%]	Zr [%]	TU*[%]	Water [%]
Resinex-CH-80-L	60.83	6.91	5.24	6.13	2.81	14.26	20.32

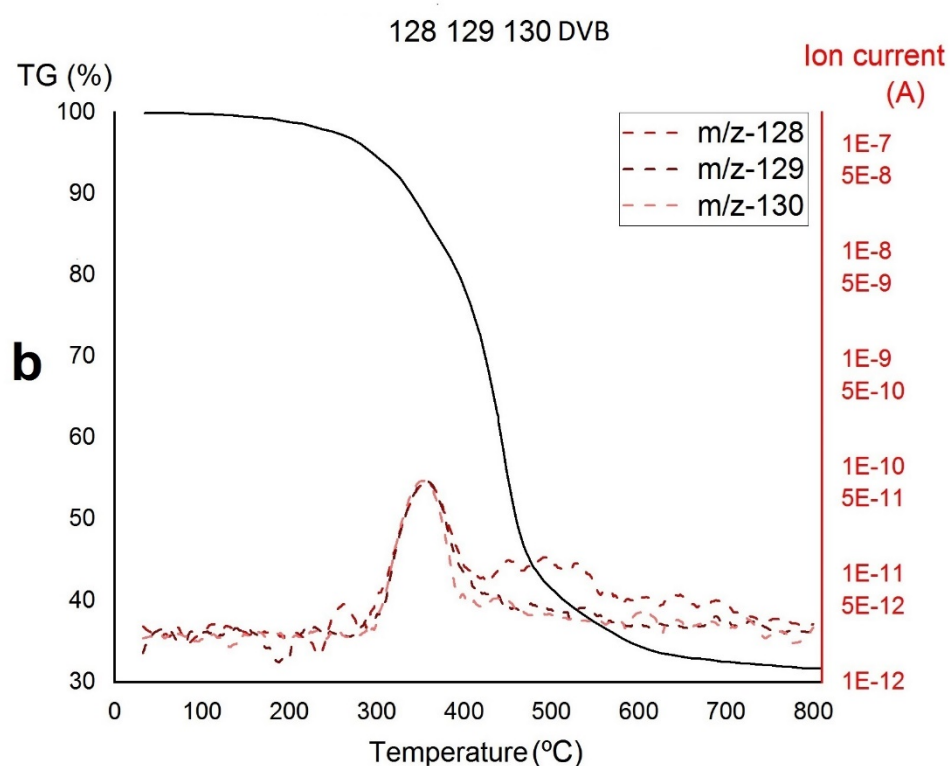
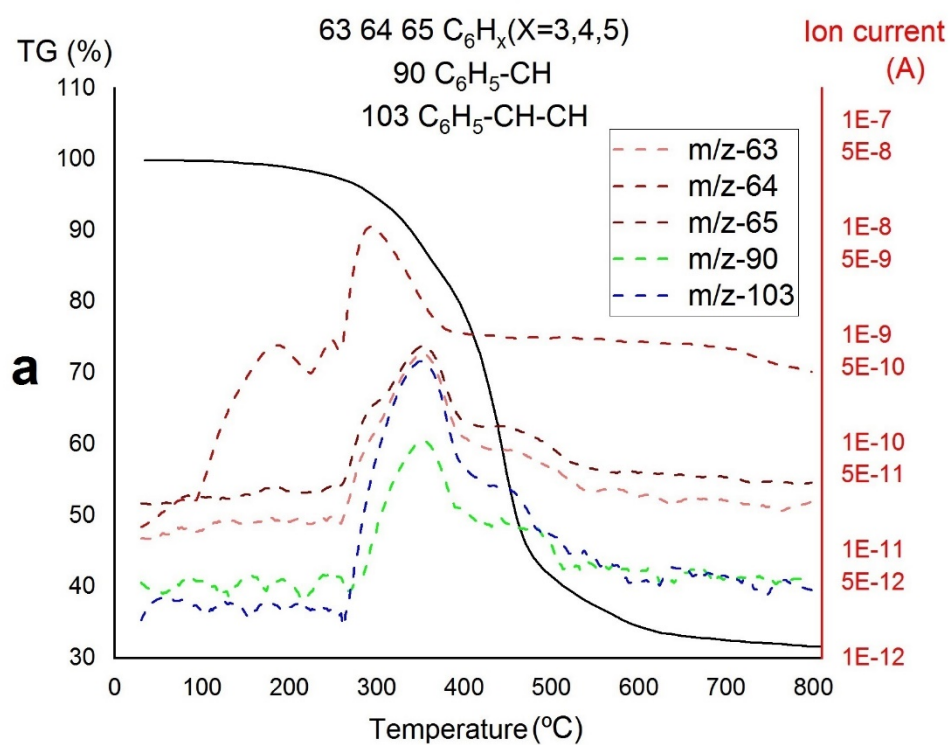
TU: percentage of thiourea active group m/m in the resin.

ESI Table S2 Raman peak positions (in cm^{-1}) and intensities for $(\text{ZrO}_2)\text{@C}$ and $(\text{ZrO}_2, \text{ZrC})\text{@C}$ composite samples

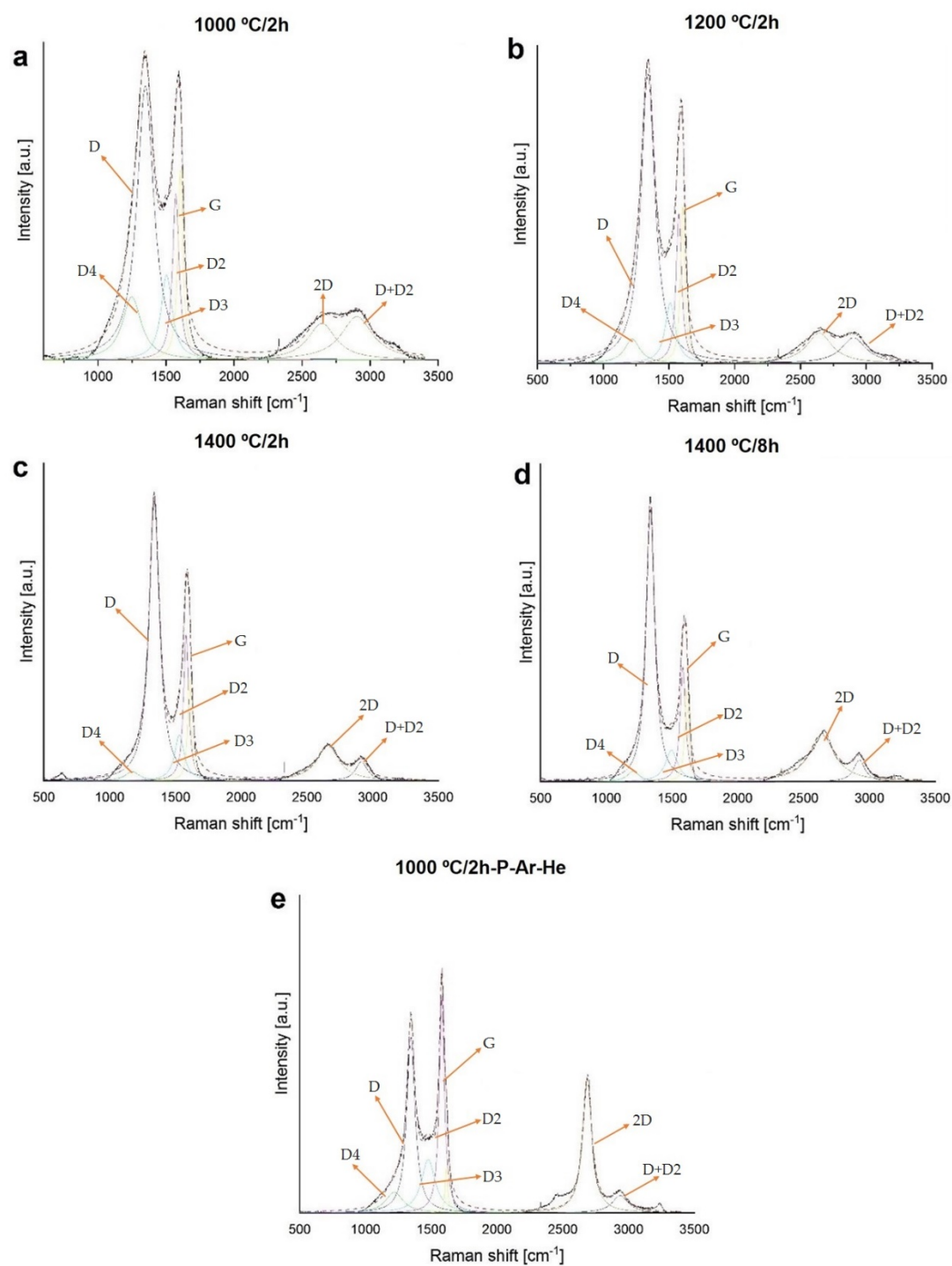
Sample	Raman shifts in cm^{-1} /intensities							Raman shift intensity ratios		
	D* (D4)	D (D1)	D'' (D3)	G	D' (D2)	2D (G1)	D+D'	$\frac{I_D}{I_G}$	$\frac{I_{2D}}{I_G}$	$\frac{I_{D''}}{I_{G+D+D'}}$
1000 °C/2h	1245 0.21	1349 0.94	1512 0.29	1576 0.54	1608 0.59	2642 0.14	2908 0.16	1.74	0.26	0.14
1200 °C/2h	1222 0.08	1336 1.09	1513 0.21	1570 0.57	1611 0.63	2640 0.11	2901 0.11	1.91	0.19	0.10
1400 °C/2h	1175 0.05	1344 1.34	1527 0.22	1576 0.69	1604 0.48	2654 0.16	2915 0.10	1.94	0.23	0.09
1400 °C/8h	1208 0.06	1336 1.62	1491 0.19	1578 0.69	1611 0.54	2632 0.28	2926 0.13	2.35	0.41	0.07
1000 °C/2h- P-Ar-He	1212 0.09	1348 0.72	1472 0.22	1583 0.87	1617 0.18	2688 0.55	2930 0.07	0.83	0.63	0.12



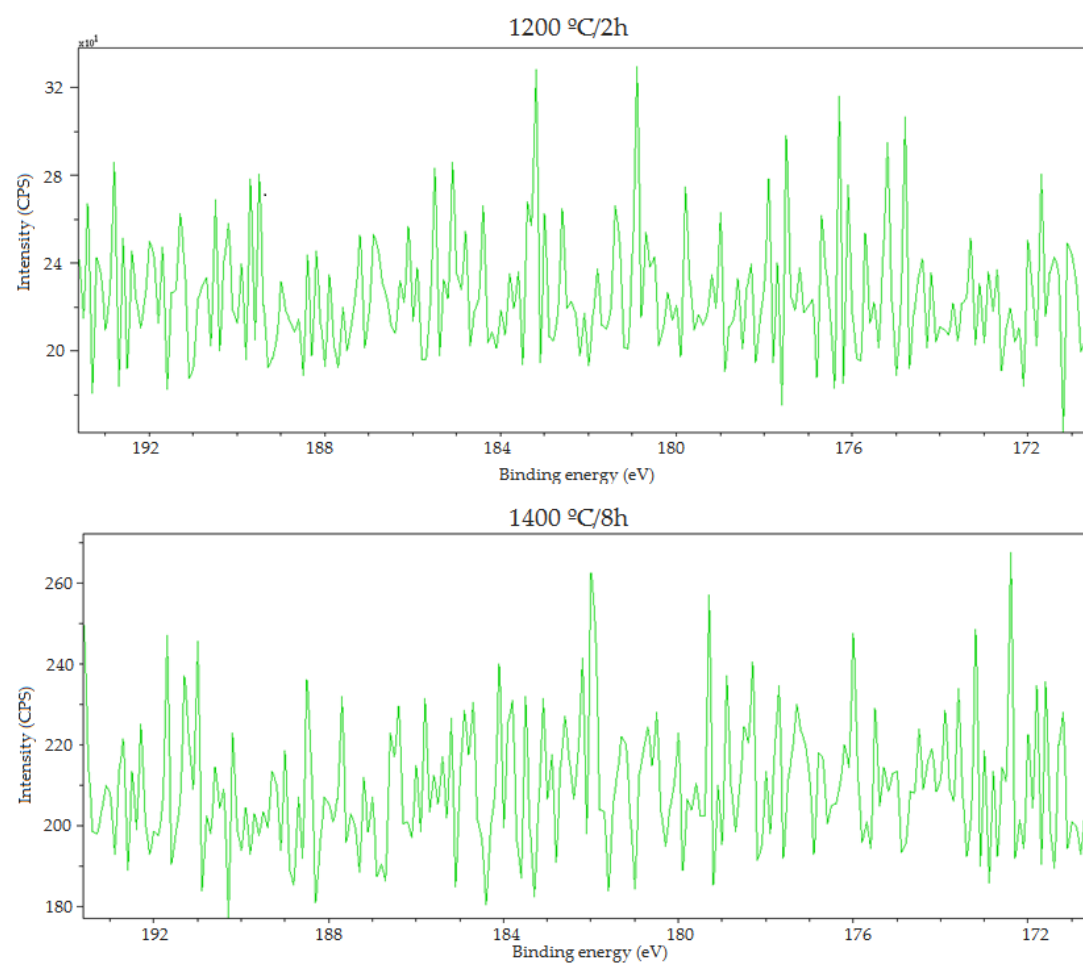
ESI Figure S1 TG-DSC of the of the Zr-loaded thiourea-functionalized styrene-divinylbenzene copolymer under N₂ atmosphere.



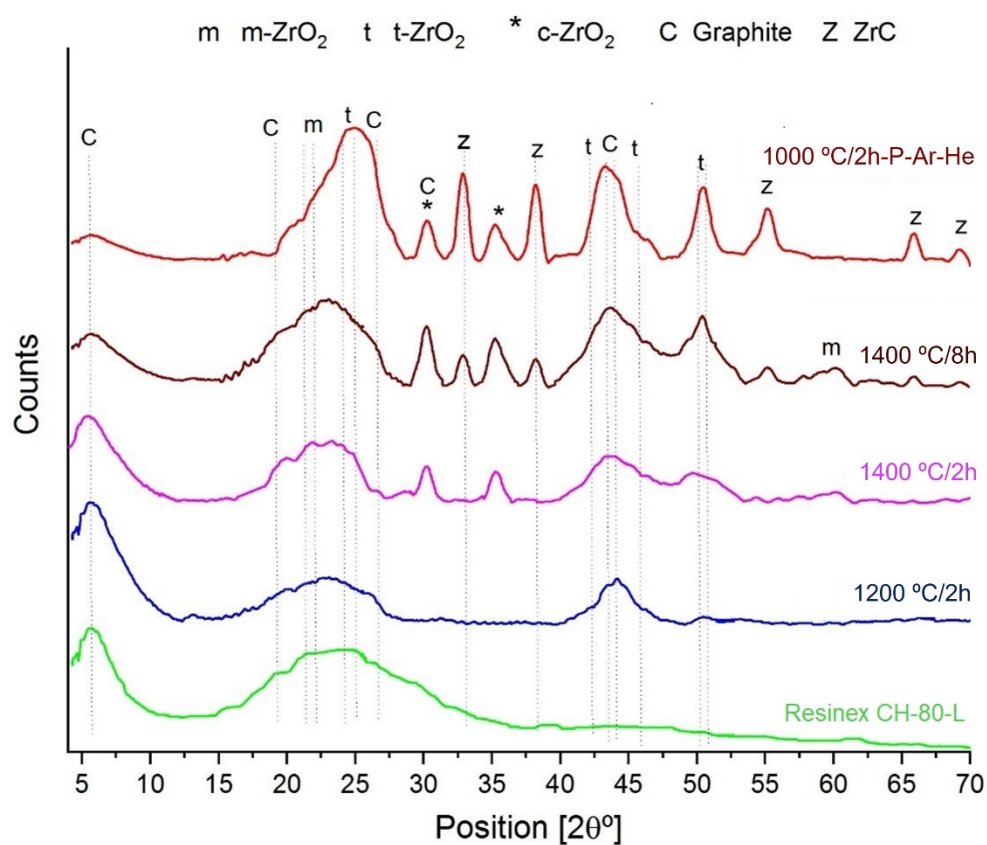
ESI Figure S2. TG-MS of the Zr-loaded thiourea-functionalized styrene-divinylbenzene copolymer: $Ph-CHCH^+$ ($m/z=103$), $PhCH^+$ ($m/z=91$), $C_6H_x^+$ ($x=3,4,5$, $m/z=63,64,65$) (**a**), and DVB fragments ($m/z=130,129,128$) (**b**)



ESI Figure S3. Raman spectra of the carbonized Zr-loaded thiourea-functionalized styrene-divinylbenzene copolymer at different temperatures and processes. 1000 °C for 2 hours (a), 1200 °C for 2 hours (b), 1400 °C for 2 hours (c), 1400 °C for 8 hours (d), plasma treated in He atmosphere (e).



ESI Figure S4. Zr 3d XPS spectra of the samples prepared at 1400 °C for 2 and 8 h heat treatment.



ESI Figure S5. XRD pattern of the samples produced by calcination of the Zr-loaded thiourea-functionalized styrene-divinylbenzene copolymer