Supporting Information

Preparation of Preceramic Ferrocene-Modified Microparticles for the Development of Uniform Porous Iron Oxide Particles and Their Sustainable Recycling

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Additional experimental data:

Synthesis of ferrocenoyl chloride

5.0 g ferrocenyl carboxy acid (21.7 mmol, 1.0 eq.) was suspended in 250 mL dry DCM under an argon atmosphere and cooled at 0 °C. 6.7 mL oxalyl acid (52.8 mmol, 2.4 eq.) was slowly added and the mixture was stirred for 1 h at 0 °C and afterward 3 h at room temperature. The solvent and the excess oxalyl acid were removed under reduced pressure. The red solid was diluted in dry *n*-hexane and filtrated under a nitrogen atmosphere. The *n*-hexane was removed to obtain pure ferrocenoyl chloride (4.8 g, 19.3 mmol) with a yield of 89 %.

Surface Modification in THF

200 mg PS-oxirane particles were dispersed in tetrahydrofuran (HPLC grade) and stirred for 1 h allowing the particles to swell. The dispersion was cooled at 0 °C and 250 mg FcPA (1.53 mmol) was added. After 1 h, the mixture was stirred for 3 d at 60 °C. The brownish particles were washed five times with ethanol and THF, respectively.

Table S1. Overview of PFMMA content in different PSDVB@PFMMA precursors determined with UV-vis spectroscopy according to the literature.[1]

Particle	PFMMA content (%)
PSDVB@PFMMA-1[a]	33.62±0.11
PSDVB@PFMMA-2[a]	38.82.±0.46
PSDVB@PFMMA-3[a]	7.09±0.30
PSDVB@PFMMA-4[a]	34.65±0.14
PSDVB@PFMMA-5[a]	39.22±0.15
PSDVB@PFMMA-6[a]	50.86±0.18
PSDVB@PFMMA-7[a]	17.05±0.46

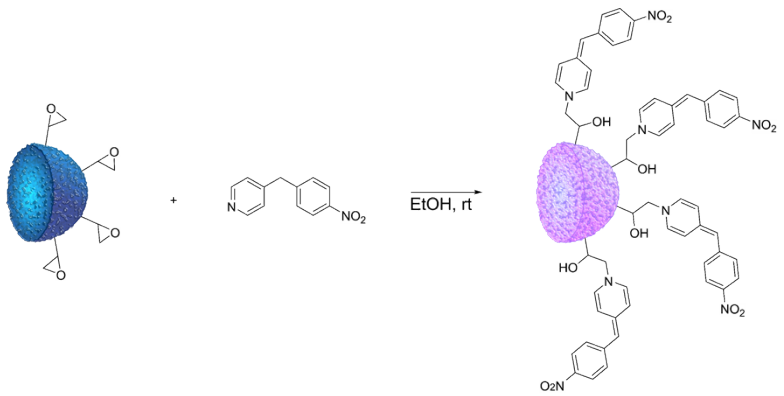

Fig. S1 *Preussmann* reaction of epoxidated PS-oxirane particles with 4-(4-nitrobenzyl) pyridine (NBP) in ethanol as proof for the presence of epoxy groups on the surfaces.

Table S2 CHNO elemental analyses of PS-oxirane particles.

	C (wt-%)	H (wt-%)	N (wt-%)	O (wt-%)
PS-oxirane01	86.72	8.11	2.49	3.55
PS-oxirane02	87.55	7.76	0.99	5.08
PS-oxirane03	88.37	7.9	1.58	4.41

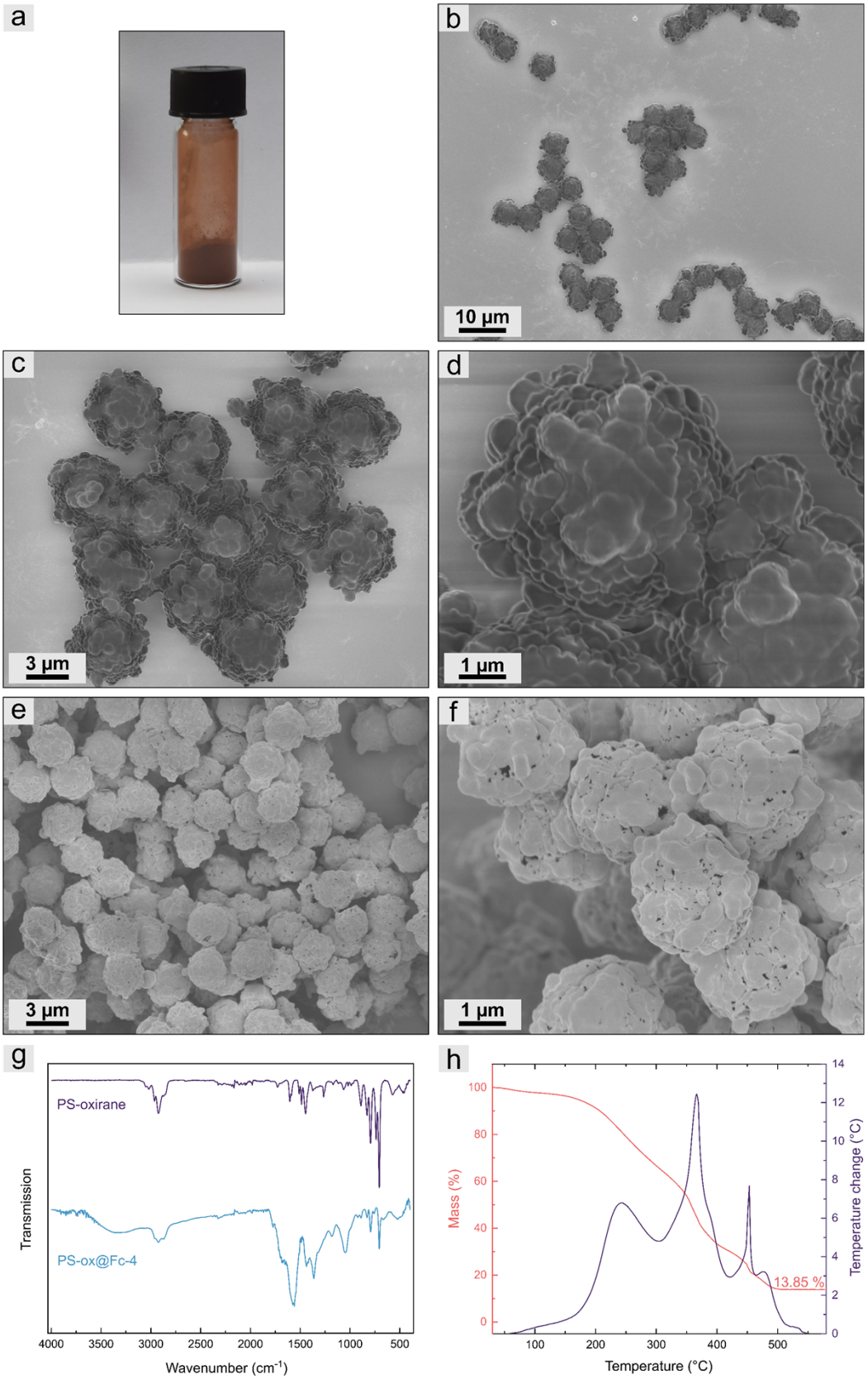

Fig. S2 a) Image of PS-ox@Fc-4 synthesized in THF, corresponding scanning electron micrographs b-d) of the precursors and e,f) the ceramics prepared in synthetic air up to 580 °C. g) Infrared spectroscopic data of PS-ox@Fc-4 and PS-oxirane and h) thermogravimetric analysis of PS-ox@Fc-4.

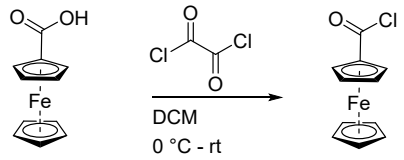

Fig. S3 Synthesis of ferrocenoyl chloride starting from ferrocenyl carboxy acid.

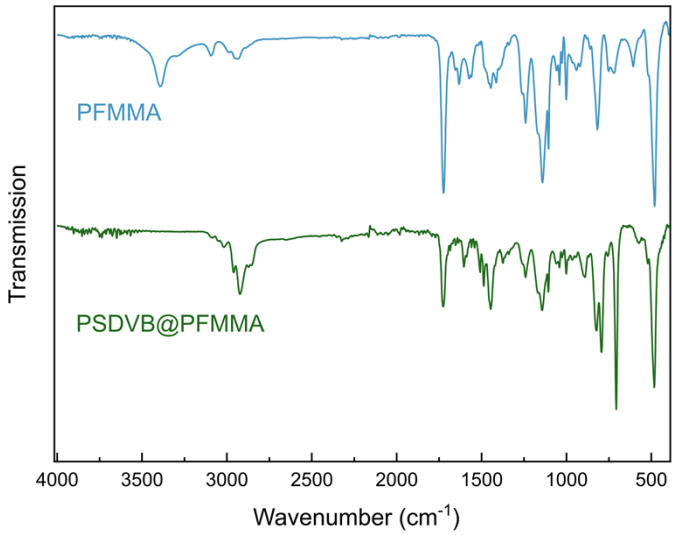

Fig. S4 Representative Infrared spectroscopic data of PFMMA and PSDVB@PFMMA particles in accordance with the literature.[1]

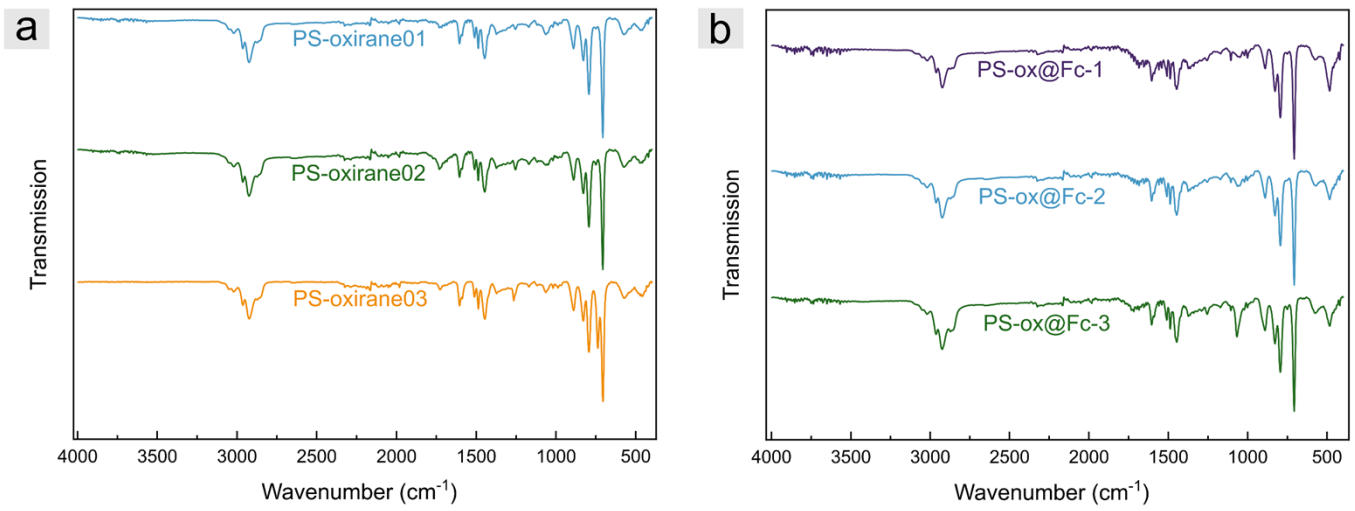

Fig. S5 Infrared spectroscopic data of PS-oxirane and PS-ox@Fc particles with different degrees of functionalizations.

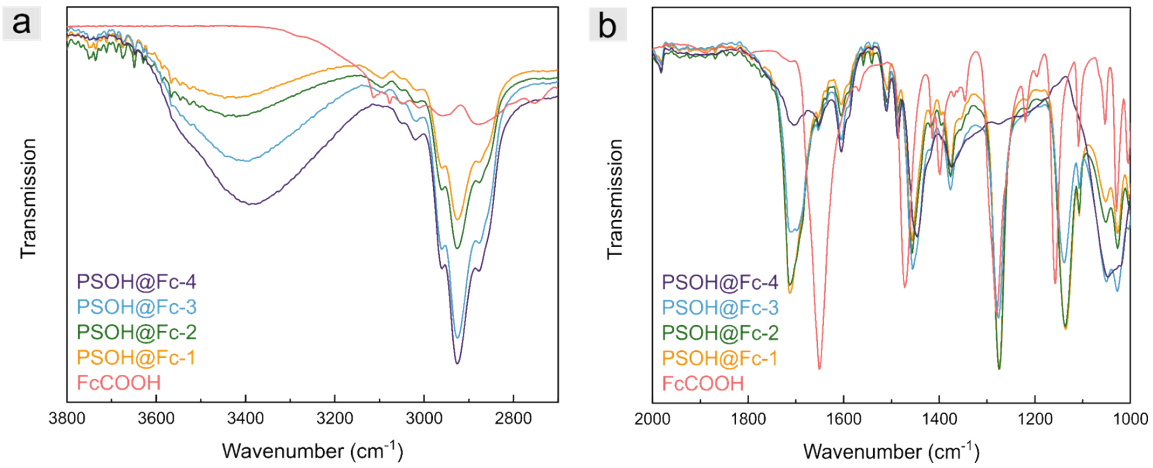

Fig. S6 Infrared spectroscopic data of PSOH@Fc particles with different degrees of functionalization and FcCOOH for comparison. a) Overview of the whole spectrum and b) partial spectrum.

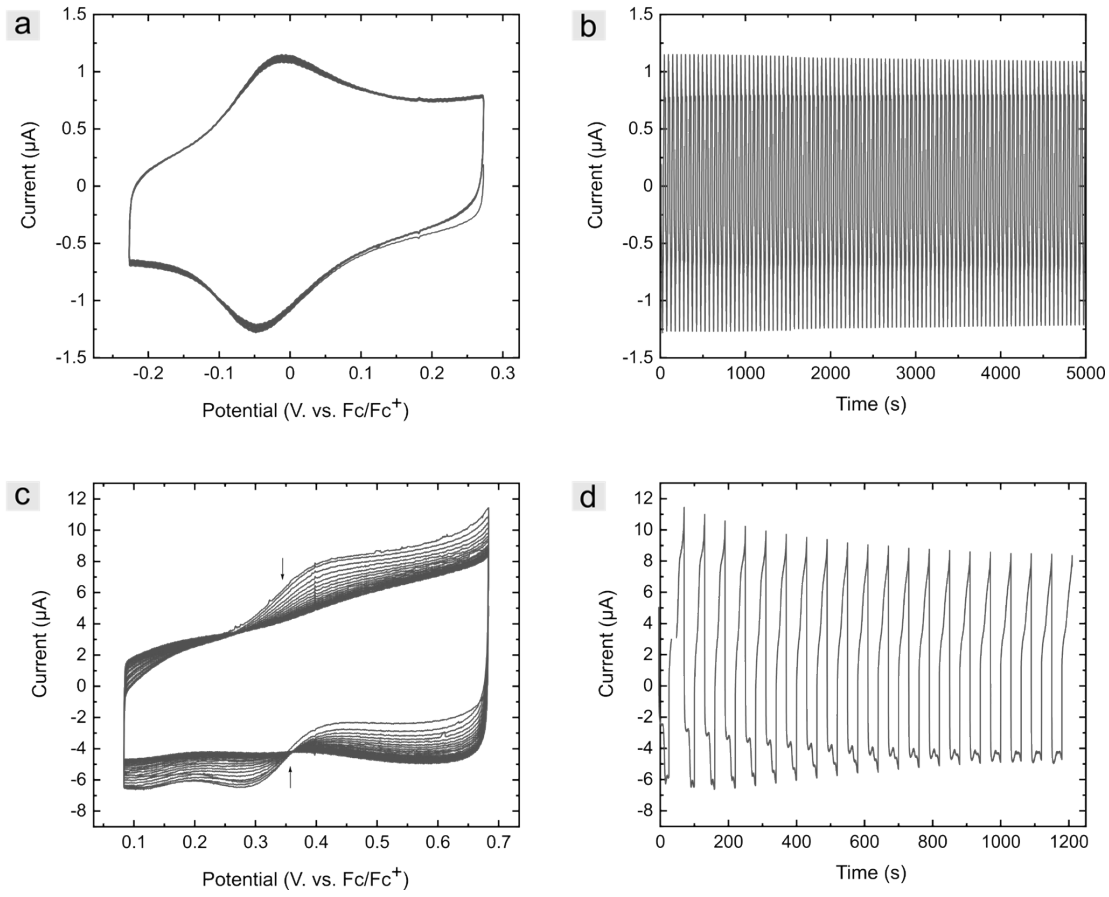

Fig. S7 Cyclic voltammetric investigations of a,b) PS-ox@Fc-2 (50 cycles) and c,d) PSOH@Fc-2 (20 cycles) in aqueous $NaClO_4$ (0.1 M) with a scan rate of 20 mV s^{-1}.

Table S3. Comparison of the residual mass of PSDVB@PFMMA-2 and the effective mass loss between 200 °C and 580 °C or 800 °C determined by thermogravimetric investigation under synthetic air with different gas flow and end temperatures.

Gas Flow (mL min^{-1})	End Temperature (°C)	Residual Mass (wt-%)	Effective Mass Loss (wt-%)
20	580	10.7	89.1
20	800	10.9	88.9
40	580	10.9	89.1
40	800	10.6	89.2

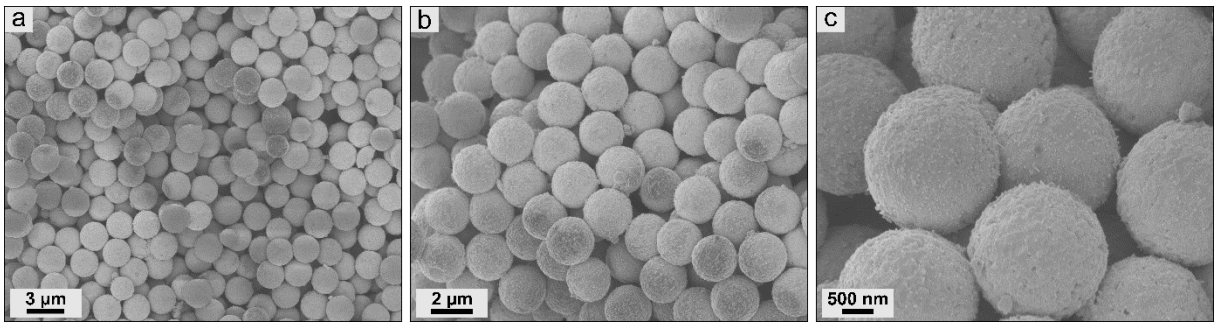

Fig. S8 Additional scanning electron micrographs of PSDVB@PFMMA-1 based ceramics synthesized under nitrogen atmosphere.

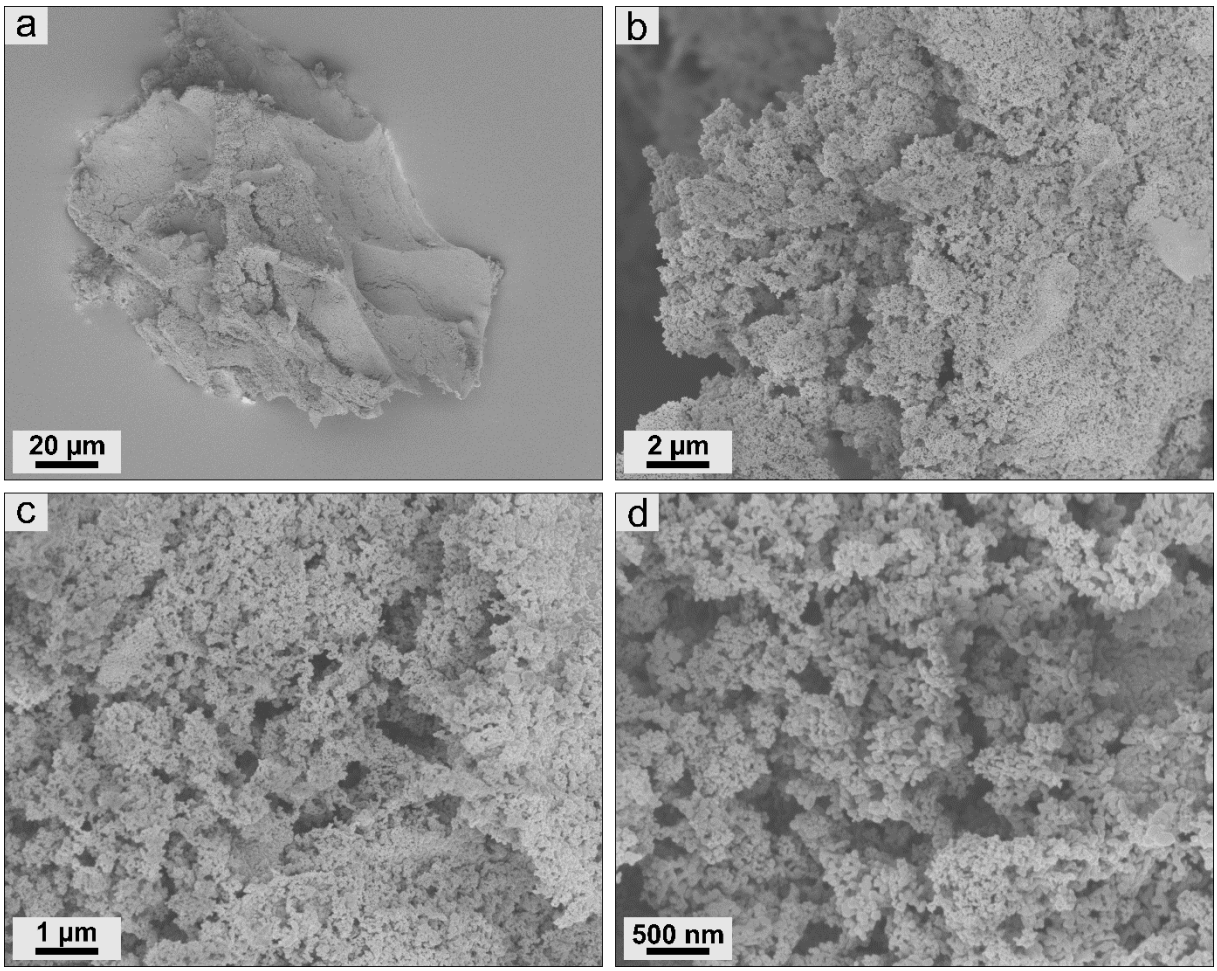

Fig. S9 Scanning electron micrographs of calcined PFMMA in synthetic air up to 580 °C.

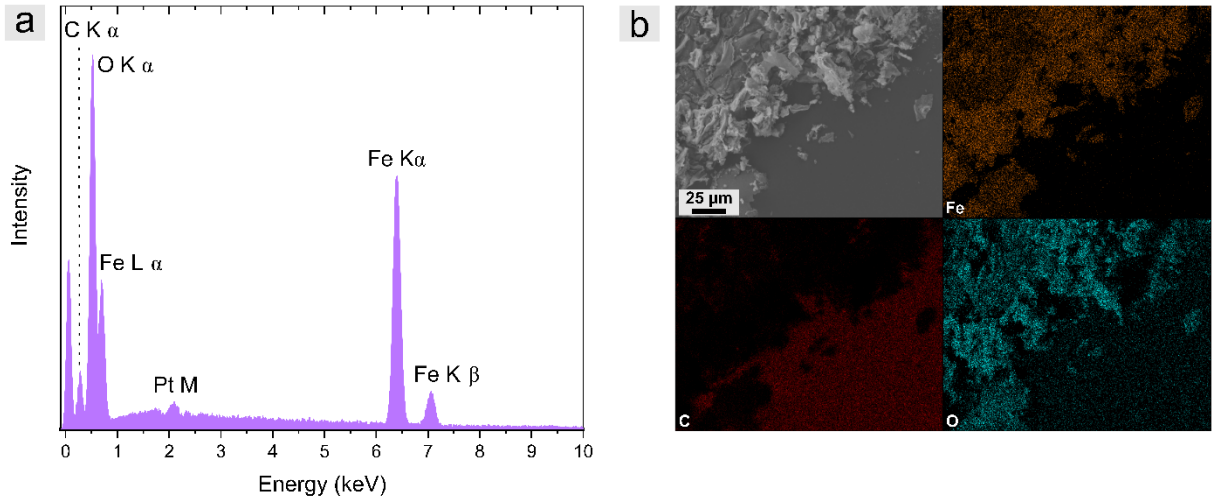

Fig. S10 Energy dispersive X-ray spectra of PFMMA-based ceramics (mean values (wt-%) of 3 measurement results: C: 12 ± 4, O: 29 ± 4, Fe: 57 ± 1, Pt:1 ± 1) and corresponding mapping images of the ceramic synthesized in synthetic air up to 580 °C.

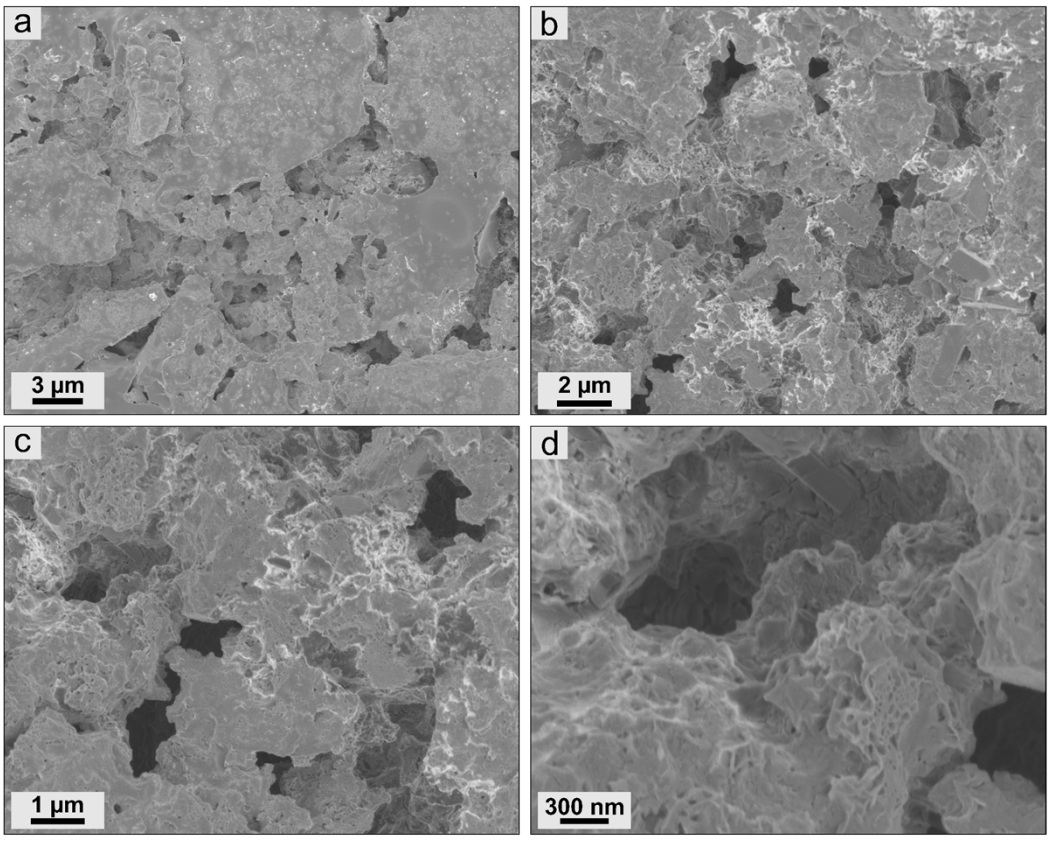

Fig. S11 Scanning electron micrographs of calcined PFMMA in nitrogen atmosphere up to 580 °C.

Table S4 Crystallographic results of X-ray diffraction measurements of the different ceramics synthesized under synthetic air[a] and nitrogen[b] atmosphere.

Particle	Phase	wt-%	Crystallite size (nm)
PSOH@Fc-2[a]	α-Fe_2O_3	100	23±1
PSOH@Fc-2[b]	Fe_3O_4	93±1	3±1
	Fe	7±1	9±1
PS-ox@Fc-2[a]	α-Fe_2O_3	100	27±1
PS-ox@Fc-2[b]	Fe	-	7±1
PSDVB@PFMMA-1[a]	Fe_3O_4	87±1	18±1
	α-Fe_2O_3	13±1	10±4
PSDVB@PFMMA-1[b]	Fe	48±2	12±1
	FeO	52±2	6±1
PFMMA[a]	α-Fe_2O_3	100	25±1
PFMMA[b]	Fe_3O_4	87±1	3±1
	Fe	13±1	11±2

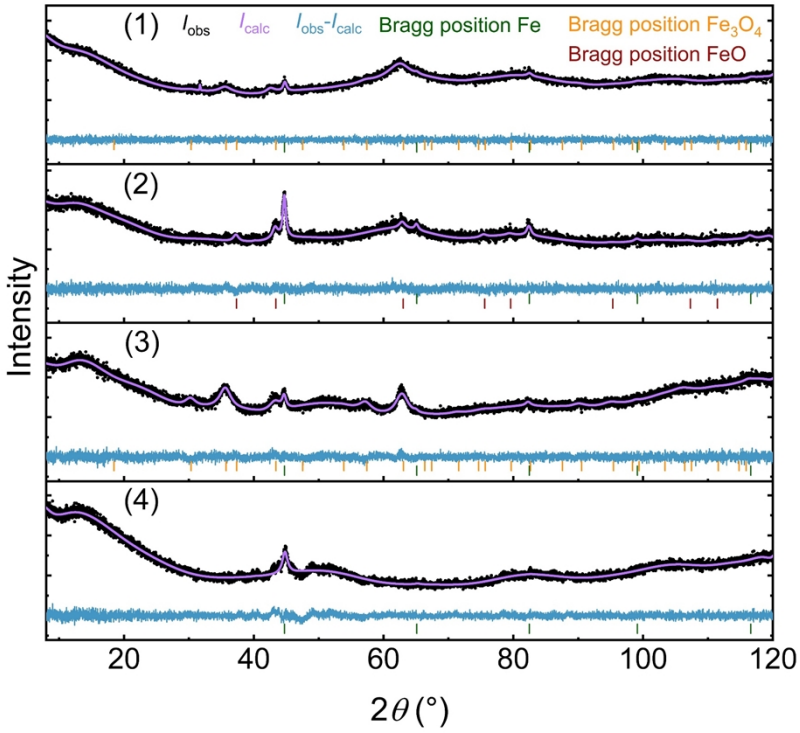

Fig. S12 X-ray diffractogram of calcined (1) PFMMA, (2) PSDVB@PFMMA-1, (3) PSOH@Fc-2, and (4) PS-ox@Fc-2 particles synthesized under nitrogen atmosphere.

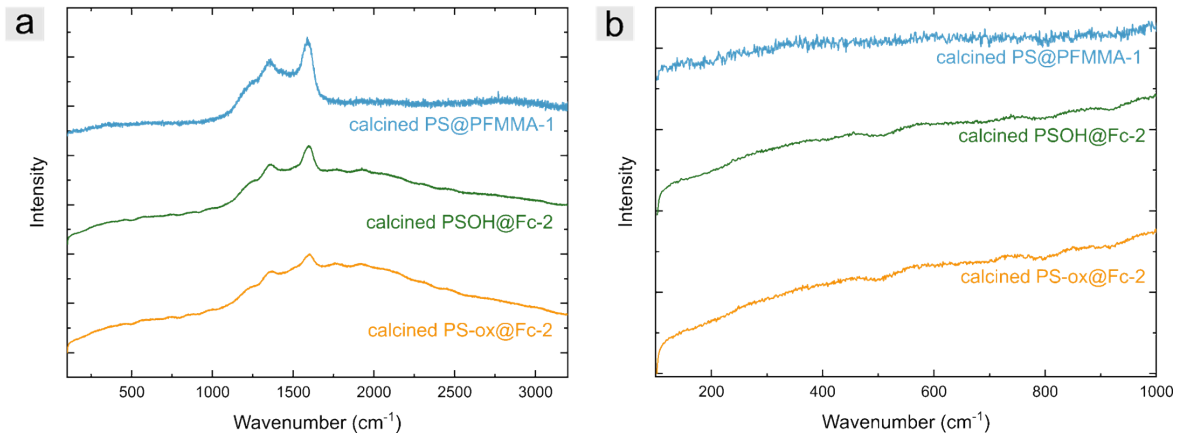

Fig. S13 Raman spectroscopy data of calcined particles in nitrogen atmosphere until 580 °C. a) Overview between 100 and 3200 cm^{-1}, b) partial spectrum between 100 and 1000 cm^{-1}, where the iron oxide signals could be expected.

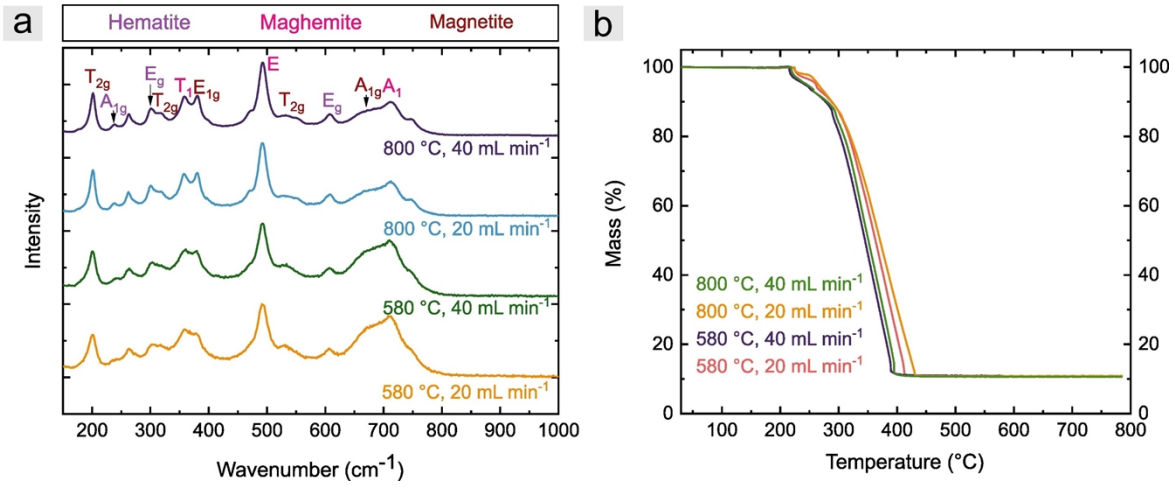

Fig. S14 a) Raman and b) thermogravimetric analyses of PSDVB@PFMMA-2 based ceramics synthesized under synthetic air in different gas flows and until different maxima temperatures.

Table S5. Overview of ceramic particle sizes (synthesized under synthetic air[a] and nitrogen[b] atmosphere).

Particle	Size (µm)	Particle	Size (µm)
PSOH@Fc-1[a]	1.53 ± 0.03	PSDVB@PFMMA-2[a]	1.65 ± 0.05
PSOH@Fc-2[a]	1.40 ± 0.02	PSDVB@PFMMA-3[a]	0.76 ± 0.03
PSOH@Fc-3[a]	1.03 ± 0.04	PSDVB@PFMMA-4[a]	1.49 ± 0.05
PSOH@Fc-4[a]	0.57 ± 0.01	PSDVB@PFMMA-5[a]	1.64 ± 0.05
PS-ox@Fc-1[a]	1.42 ± 0.09	PSDVB@PFMMA-6[a]	1.09 ± 0.05
PS-ox@Fc-2[a]	1.02 ± 0.03	PS-ox@Fc-2[b]	2.16 ± 0.05
PS-ox@Fc-3[a]	0.93 ± 0.02	PSDVB@ PFMMA-1[b]	2.31 ± 0.06
PSDVB@PFMMA-1[a]	1.63 ±0.05		

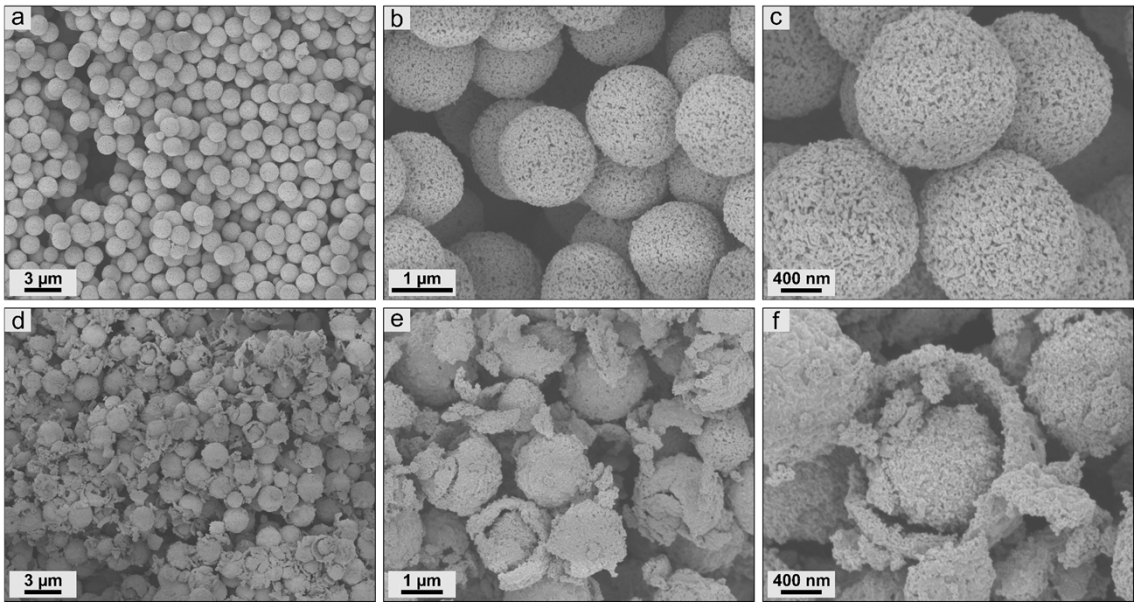

Fig. S15 Scanning electron micrographs of calcined a-c) PSDVB@PFMMA-5 and d-f) PSDVB@PFMMA-6 prepared in synthetic air up to 580 °C.

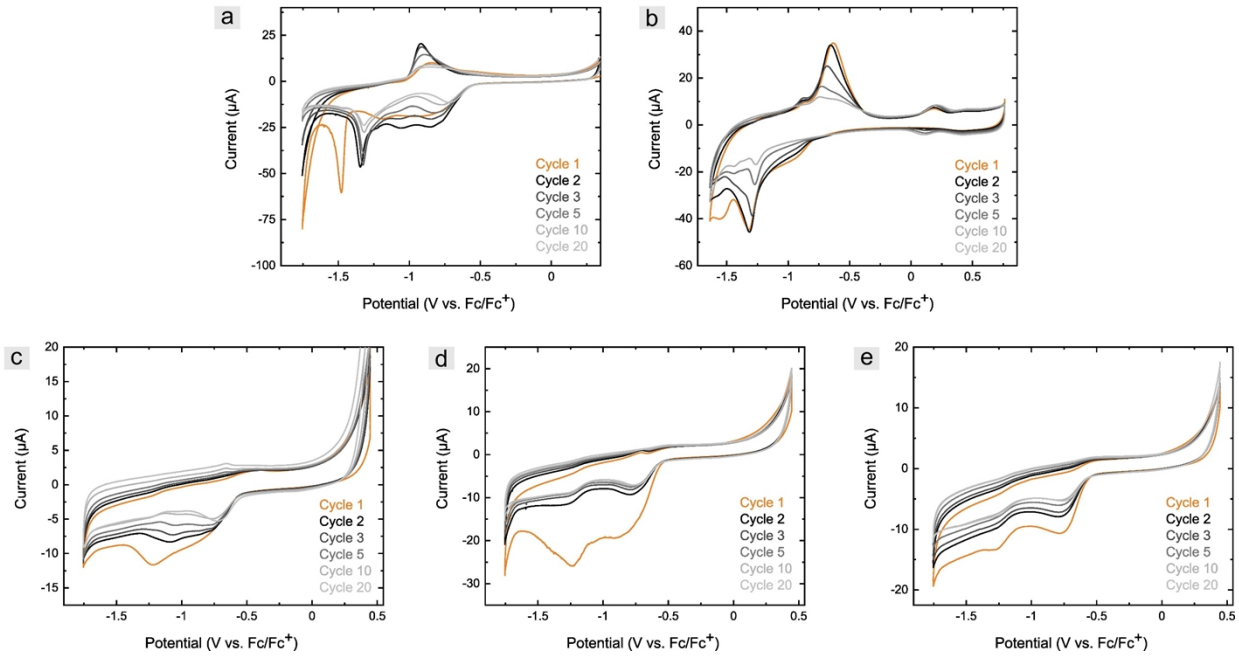

Fig. S16 Cyclic voltammetric investigation of a,b,c) PS-ox@Fc-2 and d) PSOH@Fc-2 and e) PSDVB@PFMMA-1 based ceramics synthesized in a,b) synthetic air or c-e) nitrogen atmosphere. The measurements in c-e) were carried out in alkaline solution (1 M NaOH) and a,b) were measured in 0.1 M $NaClO_4$ with a scan rate of 20 mV s^{-1}. The 1, 2, 3, 5, 10, and 20 cycles were shown, respectively.

References

1. D. Schmitt, S. M. Abdel-Hafez, M. Tummeley, V. Schünemann, M. Schneider, V. Presser and M. Gallei, *Macromol.*, 2023, **56**, 7086-7101.