Supporting Information

High surface area of carbonaceous Cr_2GaC composite microspheres synthesized by sol-gel chemistry

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Sol-Gel Synthesis of Cr_2GaC-based Microspheres

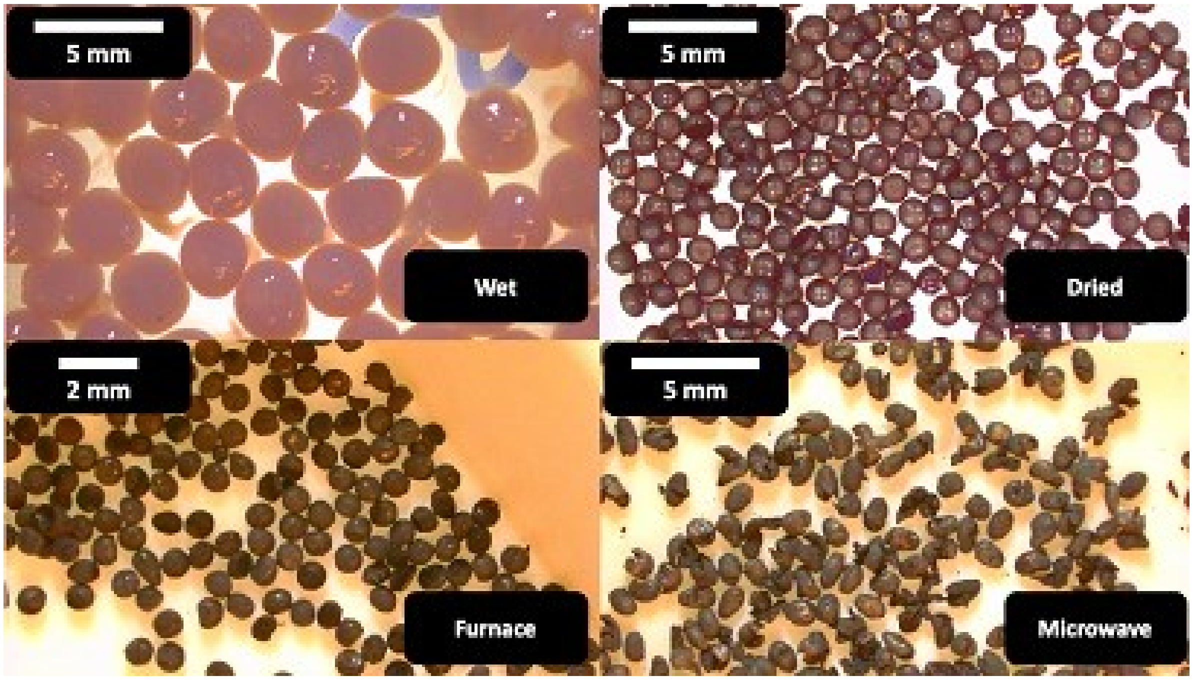

Figure S1. *Images of the 17-gauge derived Cr_2GaC Microspheres in four different states (wet, dried, furnace treated, and microwave treated)*

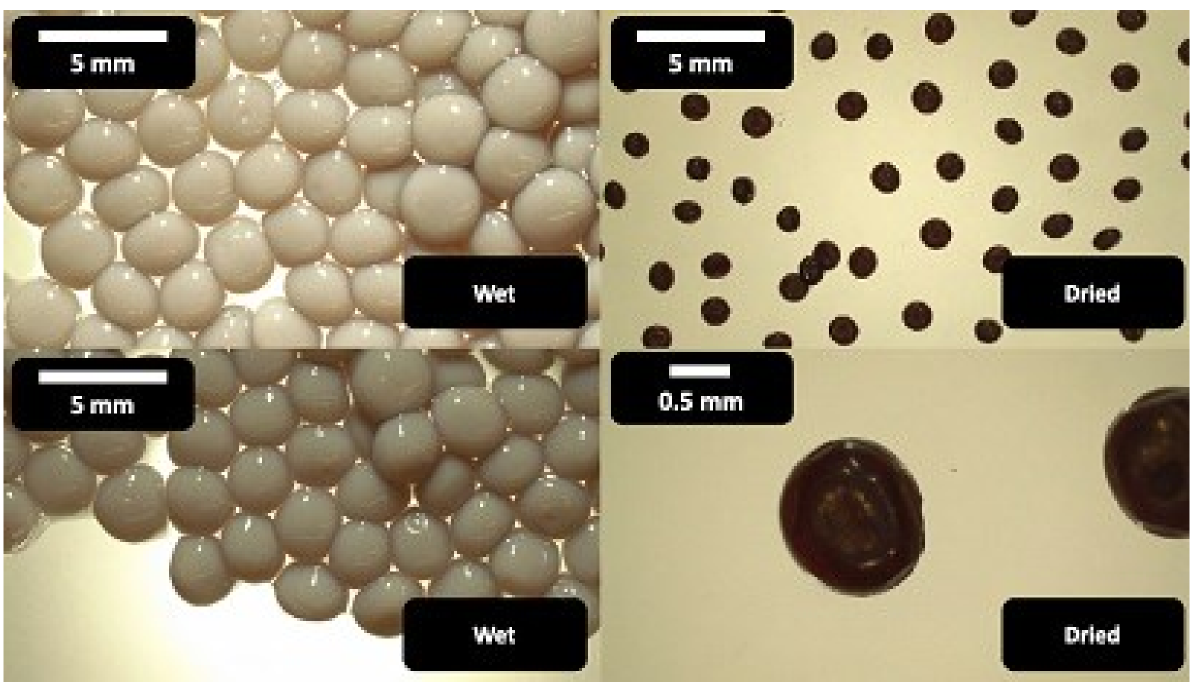

Figure S2. *Images of the 18-gauge derived Cr_2GaC Microspheres in two different states (wet, dried)*

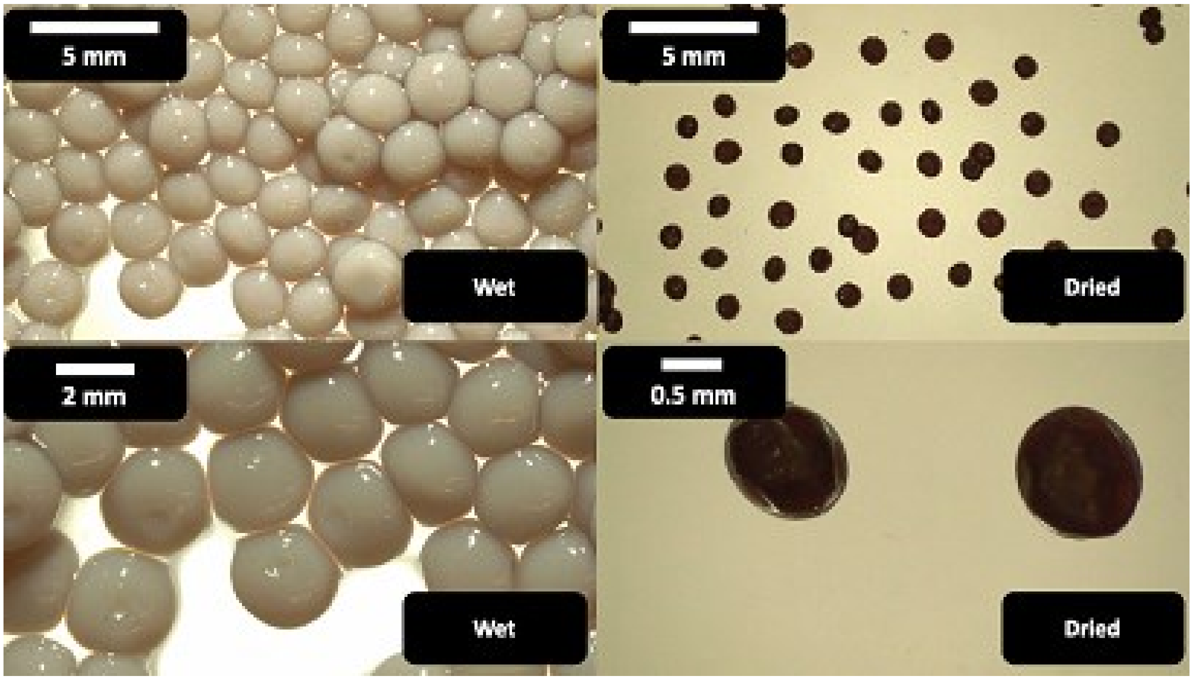

Figure S3. *Images of the 20-gauge derived Cr_2GaC Microspheres in two different states (wet, dried)*

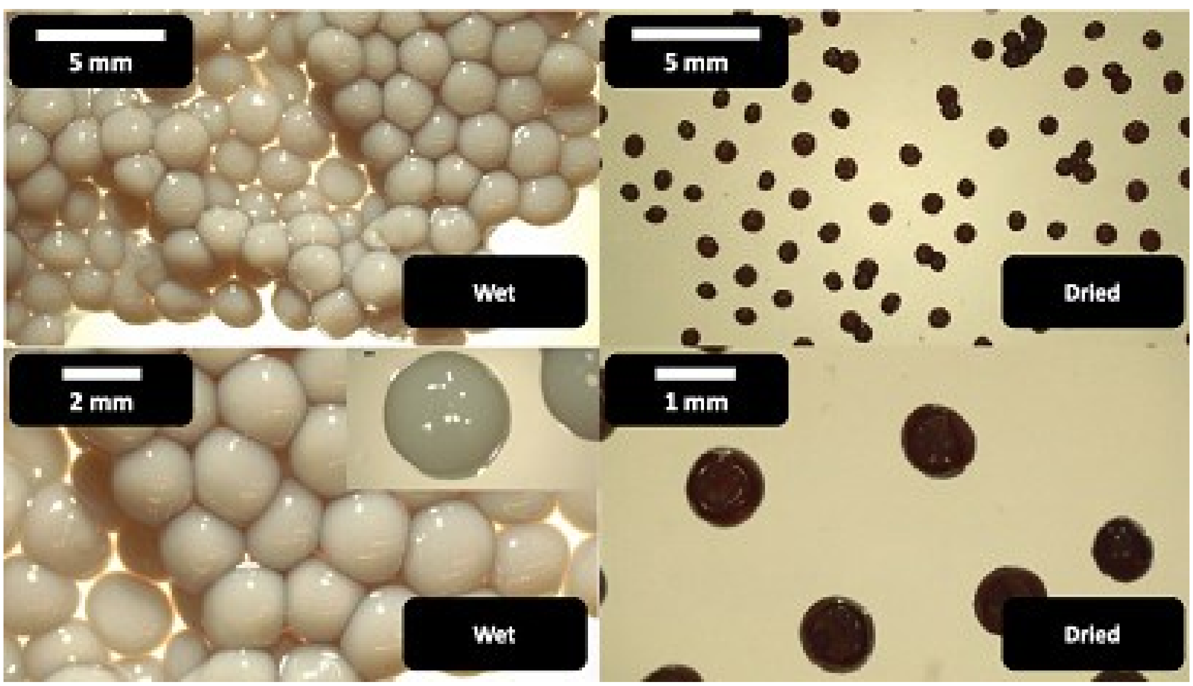

Figure S4*. Images of the 23-gauge derived Cr_2GaC Microspheres in two different states (wet, dried)*

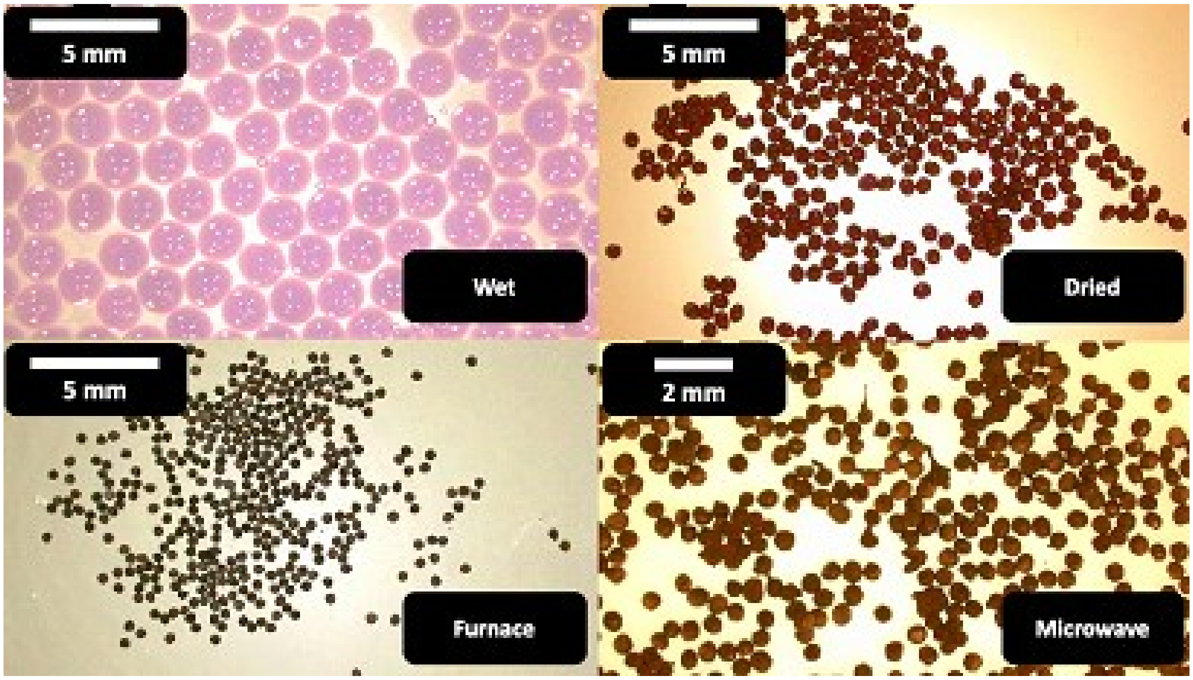

Figure S5. *Images of the 26-gauge derived Cr_2GaC Microspheres in four different states (wet, dried, furnace treated, and microwave treated)*

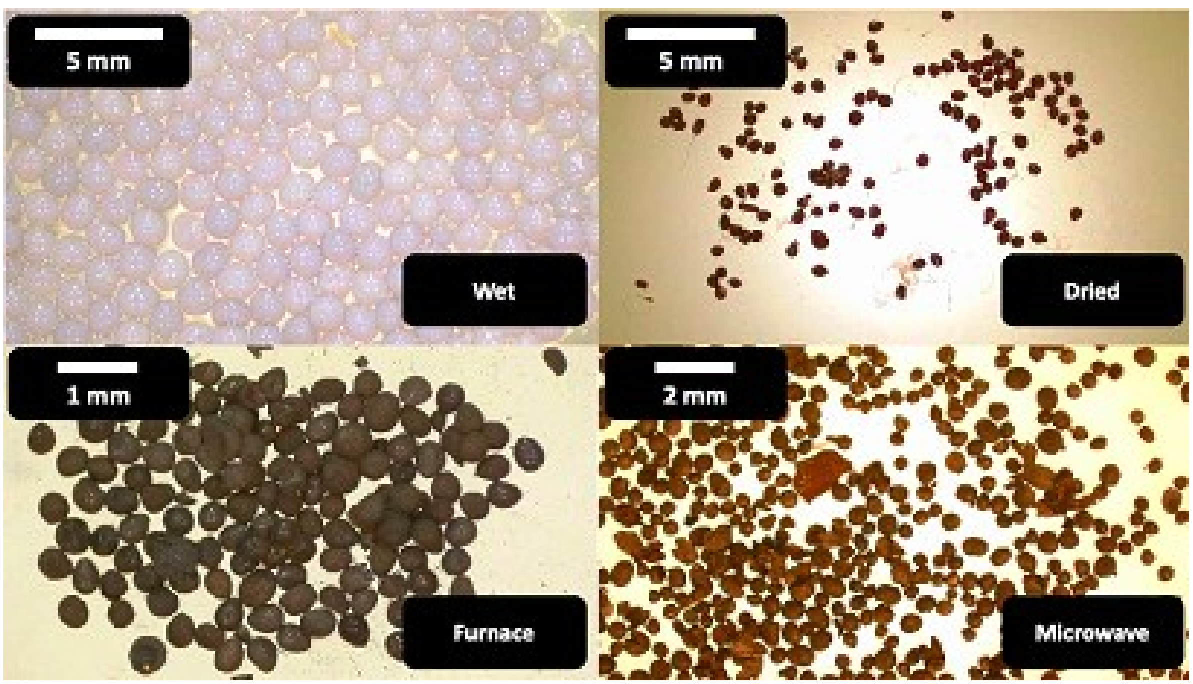

Figure S6. *Images of the 30-gauge derived Cr_2GaC Microspheres in four different states (wet, dried, furnace treated, and microwave treated)*

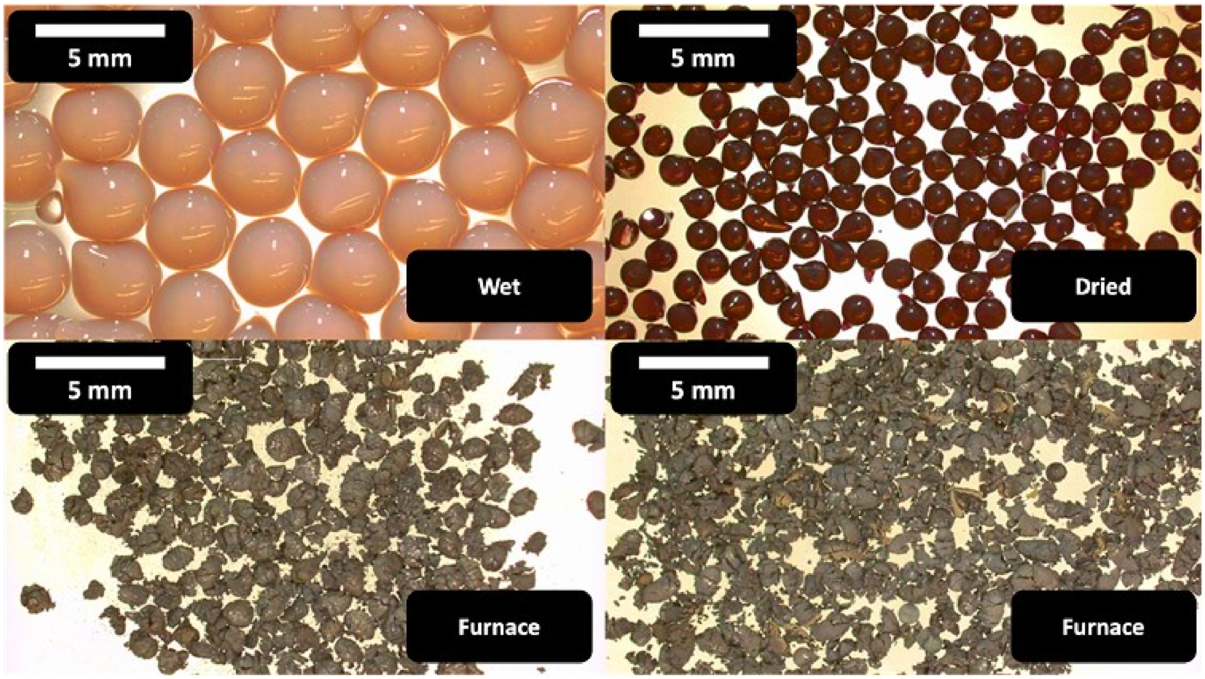

Figure S7. *Images of the 14-gauge derived Cr_2GaC Microspheres in three different states (wet, dried, and furnace treated)*

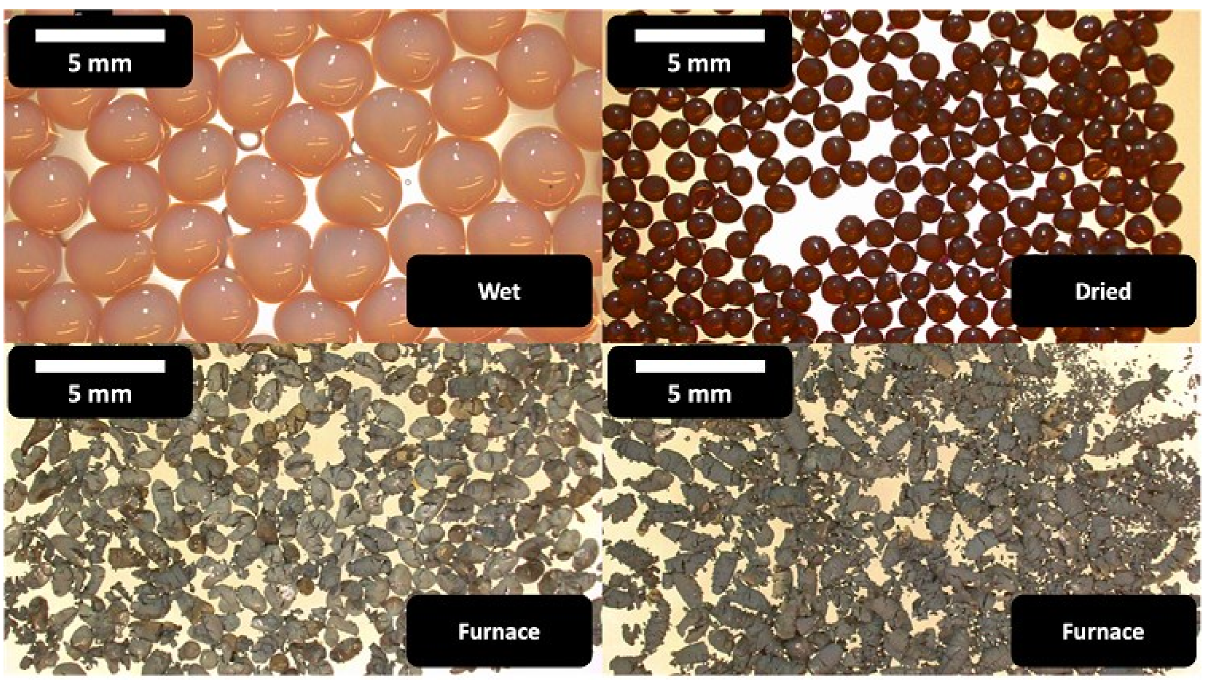

Figure S8. *Images of the 16-gauge derived Cr_2GaC Microspheres in three different states (wet, dried, and furnace treated)*

Performing the Cr_2GaC microsphere synthesis there is a clear threshold where the spheres lose the ability to retain their spherical nature. The 14- and 16-gauge sizes (1.77 mm and 1.35 mm) experience a large degree of tailing when adding spheres of this size to the dilute NH_4OH. This is shown clearly in Figure S7-S8 when observing the spheres in a dried state. Upon combustion of the 14 and 16 gauge the spheres appear completely destroyed, Figure S7-S8, observing spheres in the furnace heated treated state. 17-gauge derived spheres are the cutoff for microsphere production as the size of the sphere is sufficient to avoid spherical collapse. This however, is not a majority of the spheres as cracks prevalent upon closer inspection in the furnace and microwave synthesis routes, Figure S1. 18-gauge microspheres exhibit no spherical collapse and showcase the ability to handle the outgassing of different species that result from sol-gel synthesis.

BET Report, ILP Microwave, BJH Pore Diameter Analysis, and Mass Data

Table 1. BET specific surface area and average pore size of all Cr2GaC microspheres obtained after microwave annealing with varying needle gauge sizes.

Gauge Size (mm)	Bet Surface Area (m^2/g)	T-Plot Micropore Area (m^2/g)	T-Plot External Area (m^2/g)	Micropore Volume (cm^3/g)
1.4	467	286	181	0.132
1.27	465	245	219	0.112
0.91	462	266	196	0.122
0.64	429	248	181	0.114
0.46	447	222	226	0.101
0.31	445	241	204	0.110

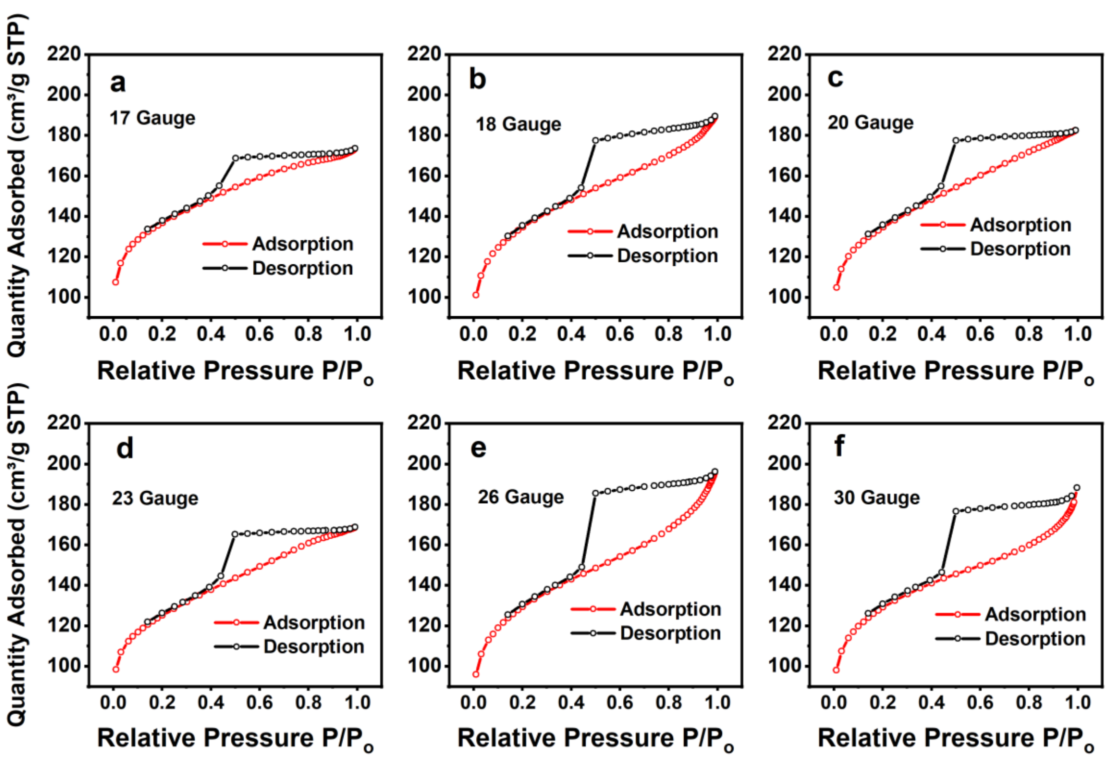

Figure S9. Isotherm Linear Plots of Cr2GaC microspheres obtained after microwave annealing using (a) 17-Gauge (b) 18-Gauge (c) 20-Gauge (d) 23-Gauge (e) 26-Gauge (f) 30-Gauge.

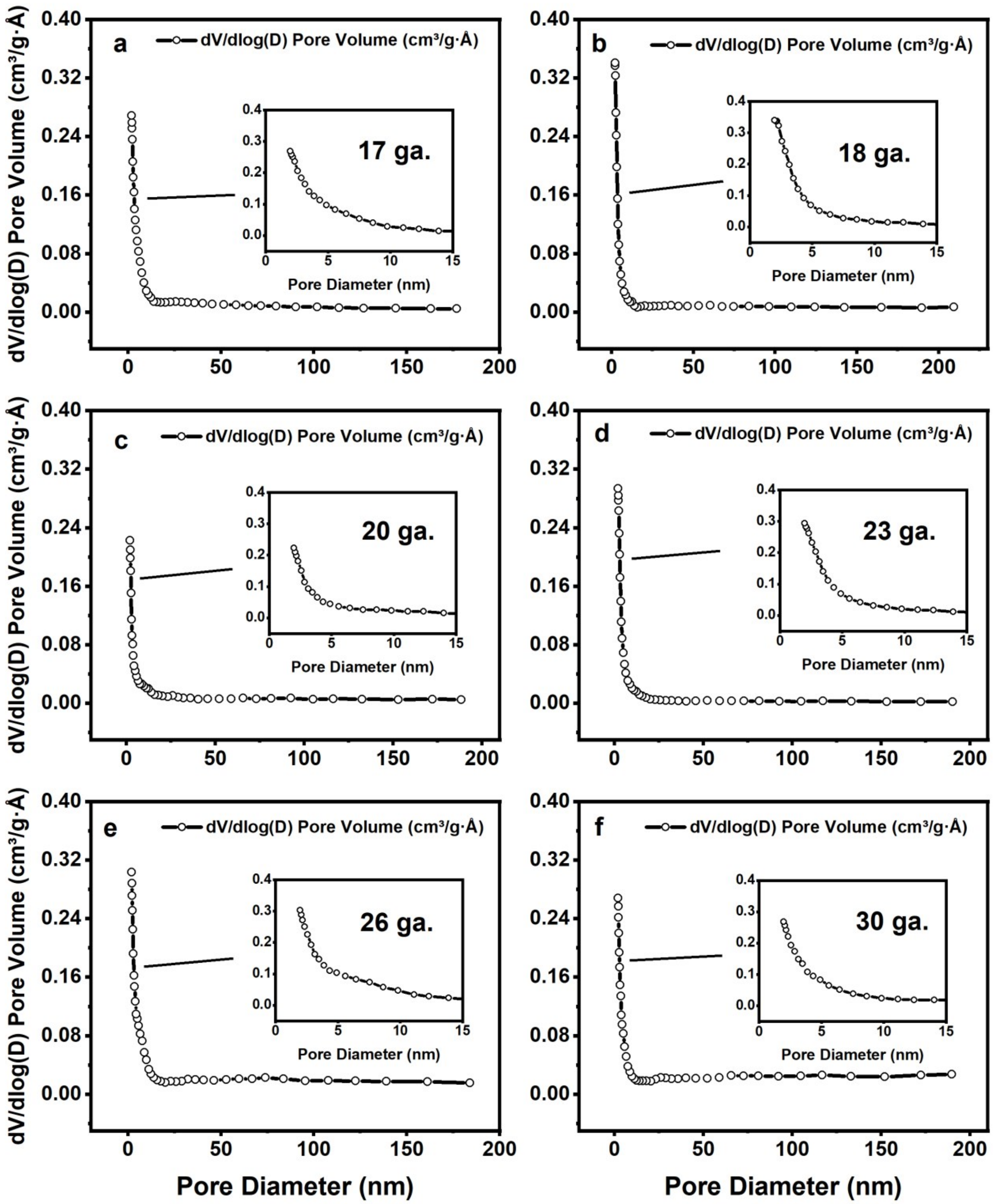

Figure S10. *Adsorption Branch BJH Pore Analysis plots of furnace synthesized Cr_2GaC microsphere. All sizes range are (a) 17-gauge (b) 18-guage (c) 20-gauge (d) 23-gauge (e) 26-gauge (f) 30-gauge (1.4-0.31 mm).*

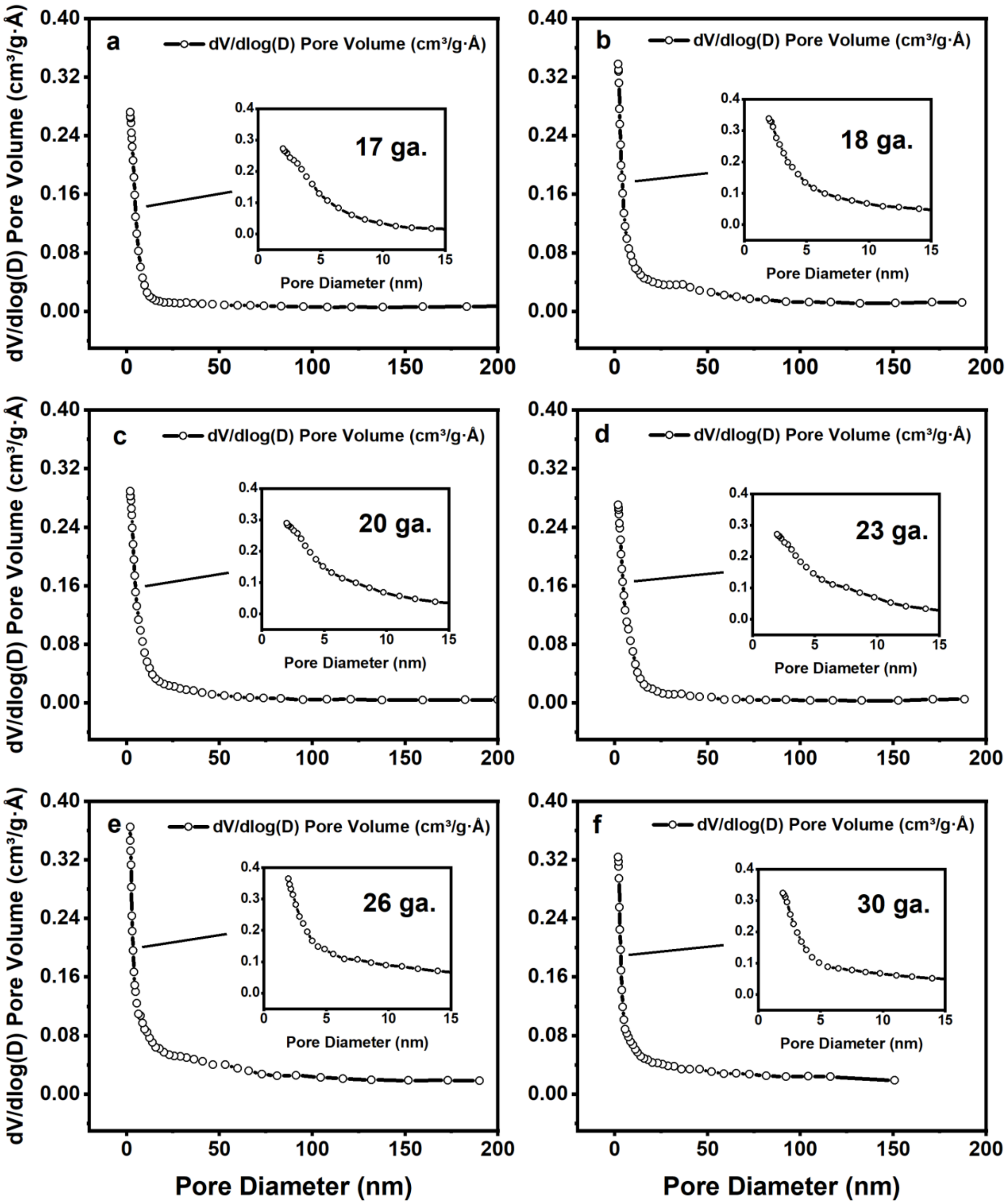

Figure S11. *Adsorption Branch BJH Pore Analysis plots of microwave synthesized Cr_2GaC microsphere. All sizes range are (a) 17-gauge (b) 18-guage (c) 20-gauge (d) 23-gauge (e) 26-gauge (f) 30-gauge (1.4-0.31 mm).)*

Furnace Synthesized Microsphere Rietveld Refinements

All Powder X-Ray Diffraction data was produced utilizing a Bruker D2 Phaser (2nd Generation), equipped with Cu $K_{\alpha 1,2}$ radiation and a 1D SDD detector. To perform the Rietveld refinements with a very high-signal-to-noise ratio, 8 data sets from each sample was experimentally measured and then computationally combined. All refinements were performed in Topas[1], all theoretical profiles and CIFs were obtained from ICSD[2] and Pearson Database[3]. Background and sample displacement factors were considered utilizing a 10th order polynomial initially and worked all the way up to a 15th order polynomial if plausible. The lattice parameters and scale were then refined taking advantage of a modified Thompson-Cox-Hastings pseudo-Voigt function (pv-TCHZ). Atom positionings, thermal displacement parameters (Beq), and occupancies were then refined. Values ≥ 0 for the Beq and ≤ 1 for the occupancies were accepted as reasonable for the Rietveld fit. Tables S2– S13 showcase the refinement parameters of the Cr_2GaC microspheres. This includes both the furnace and microwaved synthesized variations. Figures S12-S13 display the fits, percentages of phases, R_{exp}, and R_{wp}. GOF values are also displayed in Tables S2-S13.

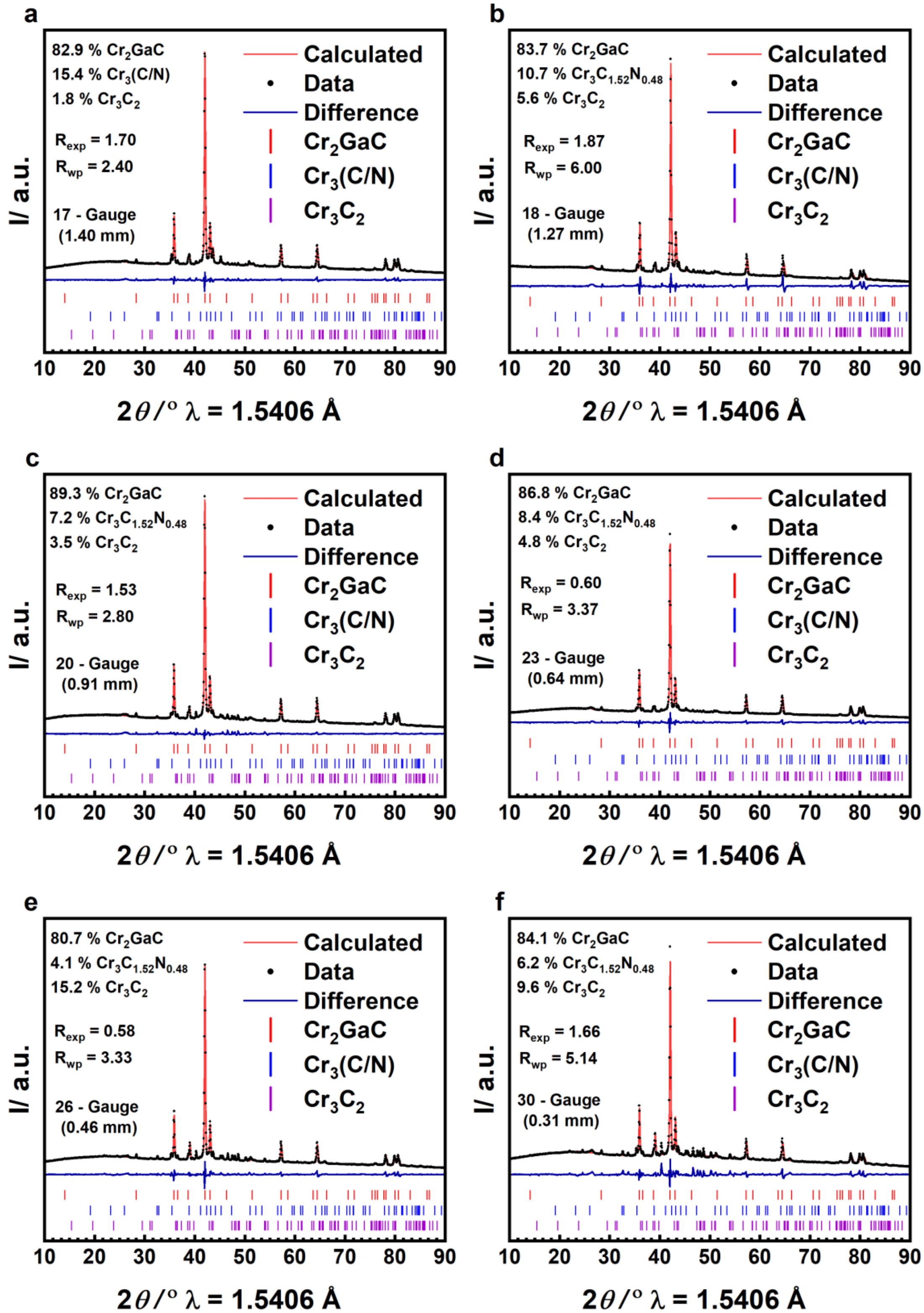

Figure S12. *Rietveld Refinement Plots and percentages of all furnace Cr_2GaC microspheres (a) 17-gauge (b) 18-guage (c) 20-gauge (d) 23-gauge (e) 26-gauge (f) 30-gauge (1.4-0.31 mm).*

Table S2: Rietveld refinement parameters of furnace-derived 17-gauge spheres

Cr_2GaC (82.9 (5) wt%)	x	y	z	Occupancy	Beq
Cr1	0.3333	0.6667	0.8690	1.00	2.115
Ga1	0.3333	0.6667	0.7500	1.00	2.997
C1	0.0000	0.0000	0.0000	1.00	1
a /Å			2.89005 (4)		
c /Å			12.6051 (3)		
a /Å			3.0770[3]		
c /Å			10.9100[3]		
R_{Bragg}			0.705		
GOF			1.42		

Table S3: Rietveld refinement parameters of furnace-derived 18-gauge spheres

Cr_2GaC (83.7 (13) wt%)	x	y	z	Occupancy	Beq
Cr1	0.3333	0.6667	0.8690	1.00	2.115
Ga1	0.3333	0.6667	0.7500	1.00	2.997
C1	0.0000	0.0000	0.0000	1.00	1
a /Å			2.88059 (11)		
c /Å			12.5694 (9)		
a /Å			3.0770[3]		
c /Å			10.9100[3]		
R_{Bragg}			2.177		
GOF			3.21		

Table S4: Rietveld refinement parameters of furnace-derived 20-gauge spheres

Cr_2GaC (89.3 (7) wt%)	x	y	z	Occupancy	Beq
Cr1	0.3333	0.6667	0.8690	1.00	2.115
Ga1	0.3333	0.6667	0.7500	1.00	2.997
C1	0.0000	0.0000	0.0000	1.00	1
a /Å			2.89128 (4)		
c /Å			12.6111 (3)		
a /Å			3.0770[3]		
c /Å			10.9100[3]		
R_{Bragg}			0.833		
GOF			1.83		

Table S5: Rietveld refinement parameters of furnace-derived 23-gauge spheres

Cr_2GaC (86.8 (9) wt%)	x	y	z	Occupancy	Beq
Cr1	0.3333	0.6667	0.8690 (3)	1.00	2.110 (13)
Ga1	0.3333	0.6667	0.7500	1.00	3.00 (17)
C1	0.0000	0.0000	0.0000	1.00	1.0 (4)
a /Å			2.88917 (6)		

c /Å	12.5988 (4)
a /Å	3.0770[3]
c /Å	10.9100[3]
R_{Bragg}	0.832
GOF	5.60

Table S6: *Rietveld refinement parameters of furnace-derived 26-gauge spheres*

Cr_2GaC (80.7 (9) wt%)	**x**	**y**	**z**	**Occupancy**	**Beq**
Cr1	0.3333	0.6667	0.8690	1.00	2.115
Ga1	0.3333	0.6667	0.7500	1.00	2.997
C1	0.0000	0.0000	0.0000	1.00	1
a /Å	2.88975 (6)				
c /Å	12.5995 (5)				
a /Å	3.0770[3]				
c /Å	10.9100[3]				
R_{Bragg}	0.764				
GOF	5.77				

Table S7: *Rietveld refinement parameters of furnace-derived 30-gauge spheres*

Cr_2GaC (84.1 (12) wt%)	**x**	**y**	**z**	**Occupancy**	**Beq**
Cr1	0.3333	0.6667	0.8690	1.00	2.115
Ga1	0.3333	0.6667	0.7500	1.00	2.997
C1	0.0000	0.0000	0.0000	1.00	1
a /Å	2.88817 (10)				
c /Å	12.5948 (8)				
a /Å	3.0770[3]				
c /Å	10.9100[3]				
R_{Bragg}	0.675				
GOF	3.10				

Microwave Synthesized Microsphere Rietveld Refinements

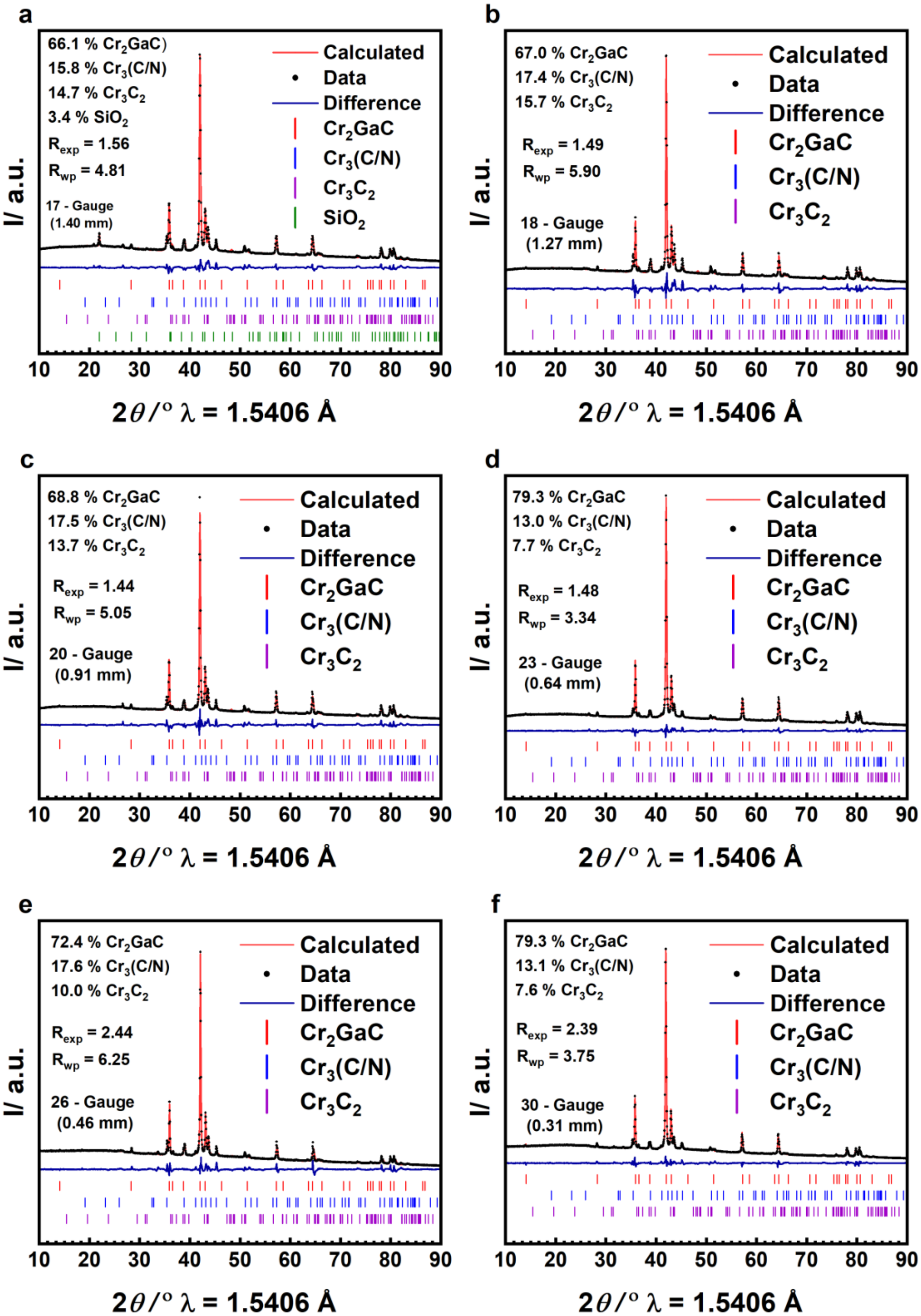

Figure S13. *Rietveld Refinement Plots and percentages of all microwave Cr_2GaC microspheres (a) 17-gauge (b) 18-guage (c) 20-gauge (d) 23-gauge (e) 26-gauge (f) 30-gauge (1.4-0.31 mm).*

Table S8: Rietveld refinement parameters of microwave-derived 17-gauge spheres

Cr_2GaC (66.1 (11) wt%)	x	y	z	Occupancy	Beq
Cr1	0.3333	0.6667	0.8690	1.00	2.115
Ga1	0.3333	0.6667	0.7500	1.00	2.997
C1	0.0000	0.0000	0.0000	1.00	1
a /Å			2.88956 (13)		
c /Å			12.5973 (9)		
a /Å			3.0770[3]		
c /Å			10.9100[3]		
R_{Bragg}			1.857		
GOF			3.07		

Table S9: Rietveld refinement parameters of microwave-derived 18-gauge spheres

Cr_2GaC (67.0 (14) wt%)	x	y	z	Occupancy	Beq
Cr1	0.3333	0.6667	0.8690	1.00	2.115
Ga1	0.3333	0.6667	0.7500	1.00	2.997
C1	0.0000	0.0000	0.0000	1.00	1
a /Å			2.88924 (12)		
c /Å			12.5959 (8)		
a /Å			3.0770[3]		
c /Å			10.9100[3]		
R_{Bragg}			2.396		
GOF			3.96		

Table S10: Rietveld refinement parameters of microwave-derived 20-gauge spheres

Cr_2GaC (68.8 (12) wt%)	x	y	z	Occupancy	Beq
Cr1	0.3333	0.6667	0.8690	1.00	2.115
Ga1	0.3333	0.6667	0.7500	1.00	2.997
C1	0.0000	0.0000	0.0000	1.00	1
a /Å			2.89030 (9)		
c /Å			12.6013 (7)		
a /Å			3.0770[3]		
c /Å			10.9100[3]		
R_{Bragg}			2.088		
GOF			3.50		

Table S11: Rietveld refinement parameters of microwave-derived 23-gauge spheres

Cr_2GaC (79.3 (9) wt%)	x	y	z	Occupancy	Beq
Cr1	0.3333	0.6667	0.8690	1.00	2.115
Ga1	0.3333	0.6667	0.7500	1.00	2.997
C1	0.0000	0.0000	0.0000	1.00	1

a /Å	2.89051 (5)
c /Å	12.6053 (4)
a /Å	3.0770[3]
c /Å	10.9100[3]
R_{Bragg}	0.917
GOF	2.26

Table S12: *Rietveld refinement parameters of microwave-derived 26-gauge spheres*

Cr_2GaC (72.4 (17) wt%)	**x**	**y**	**z**	**Occupancy**	**Beq**
Cr1	0.3333	0.6667	0.8690	1.00	2.115
Ga1	0.3333	0.6667	0.7500	1.00	2.997
C1	0.0000	0.0000	0.0000	1.00	1
a /Å	2.88380 (10)				
c /Å	12.5815 (8)				
a /Å	3.0770[3]				
c /Å	10.9100[3]				
R_{Bragg}	2.619				
GOF	2.56				

Table S13: *Rietveld refinement parameters of microwave-derived 30-gauge spheres*

Cr_2GaC (79.3 (13) wt%)	**x**	**y**	**z**	**Occupancy**	**Beq**
Cr1	0.3333	0.6667	0.8690	1.00	2.115
Ga1	0.3333	0.6667	0.7500	1.00	2.997
C1	0.0000	0.0000	0.0000	1.00	1
a /Å	2.89482 (6)				
c /Å	12.6222 (4)				
a /Å	3.0770[3]				
c /Å	10.9100[3]				
R_{Bragg}	1.513				
GOF	1.56				

Microsphere SEM/EDS Imaging and Mapping

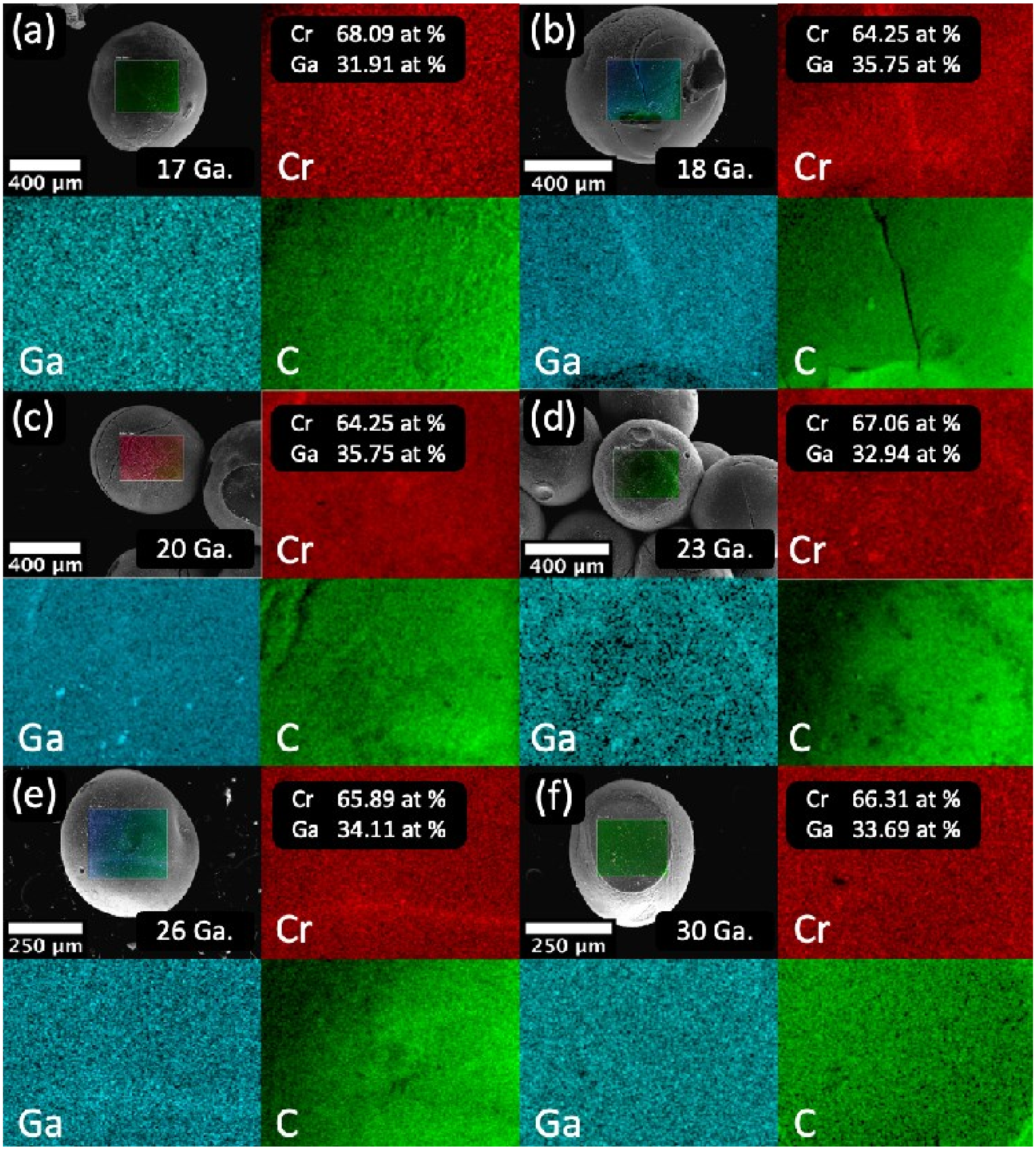

Fig S14: EDS data of Furnace spheres (a) 17-gauge (b) 18-gauge (c) 20-gauge (d) 23-gauge (e) 26-gauge (f) 30-gauge

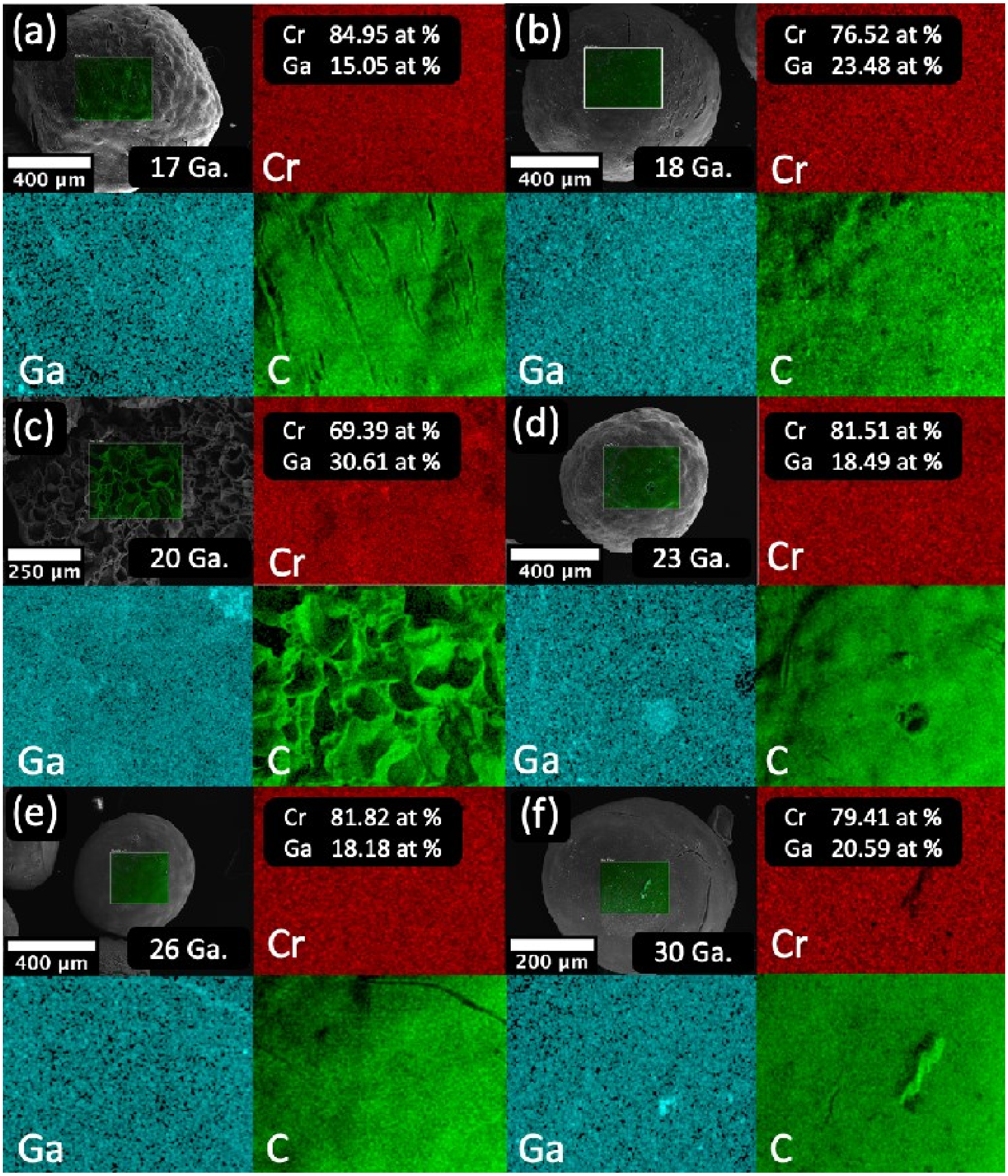

Fig S15: EDS data of Microwave spheres (a) 17-gauge (b) 18-gauge (c) 20-gauge (d) 23-gauge (e) 26-gauge (f) 30-gauge

EDS Map Sum Spectrums

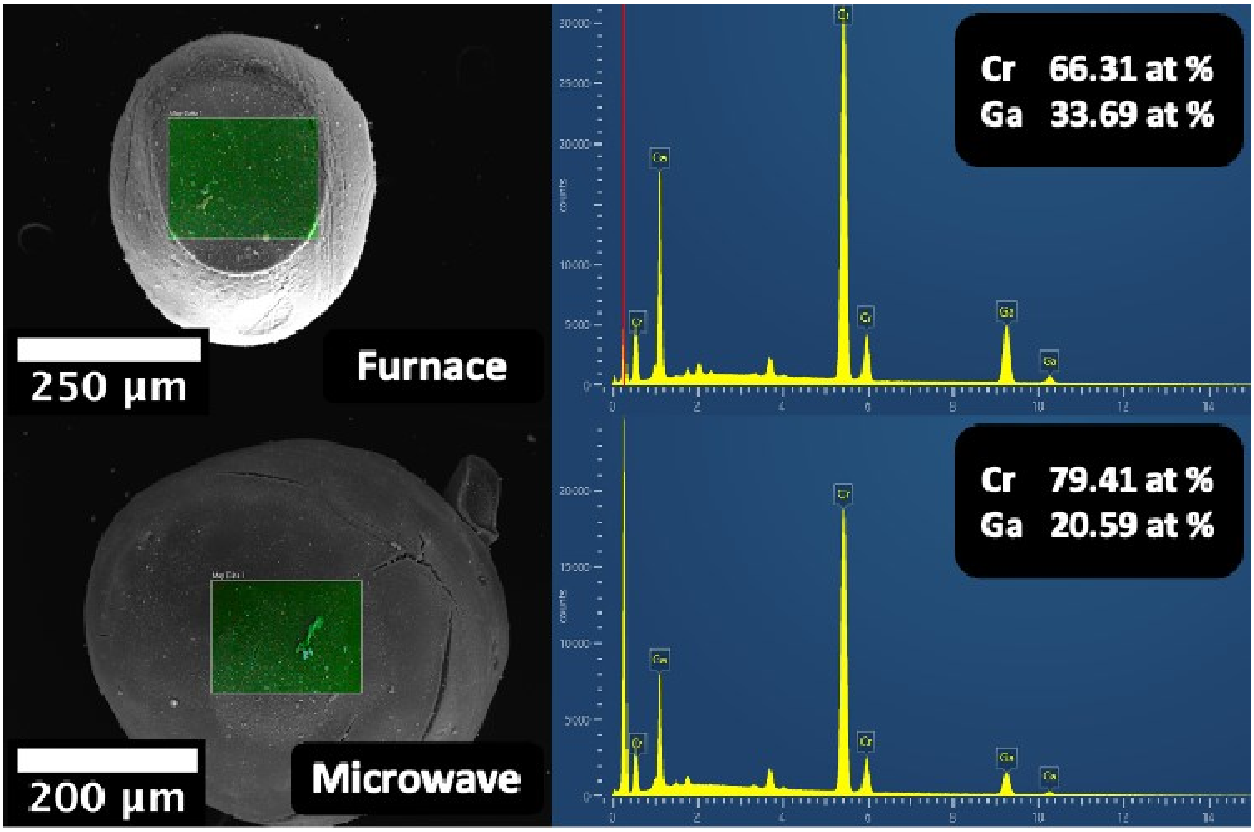

Figure S16. *EDS Imaging and Map Sum Spectrums of 17 gauge (furnace and microwave)*

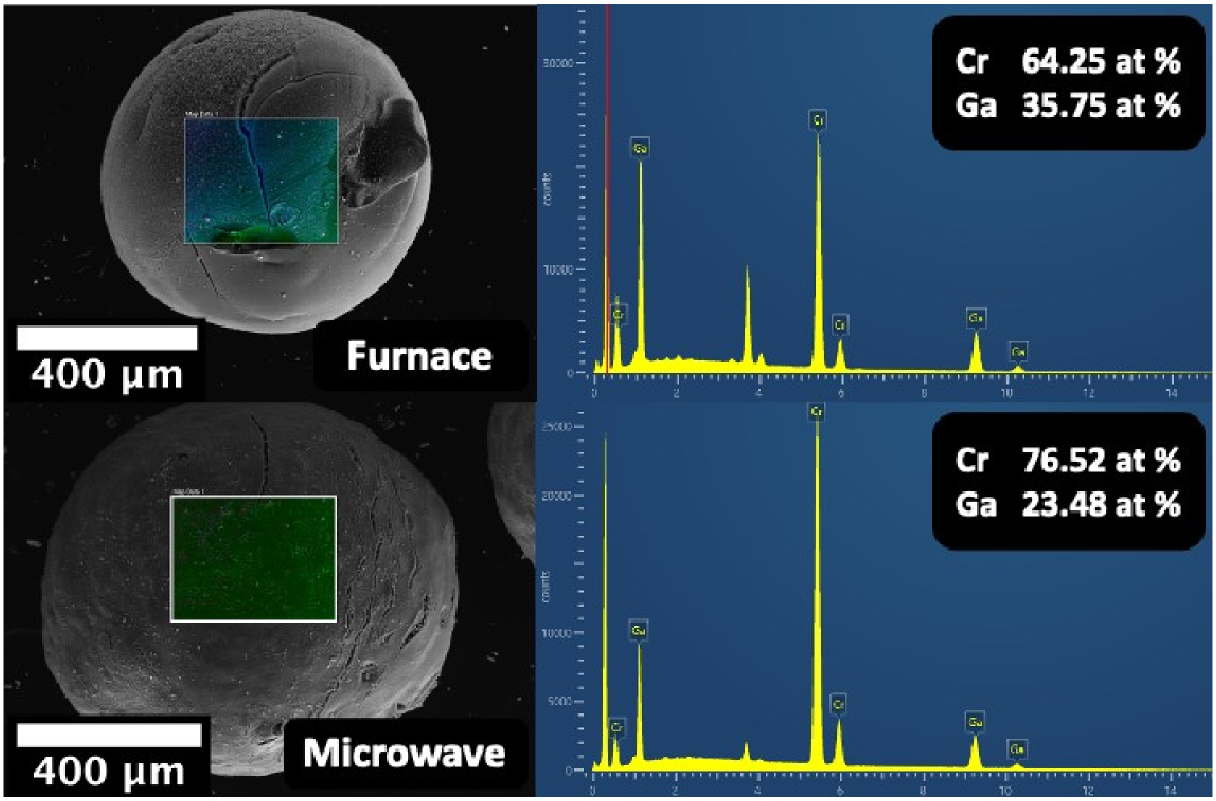

Figure S17. *EDS Imaging and Map Sum Spectrums of 18 gauge (furnace and microwave)*

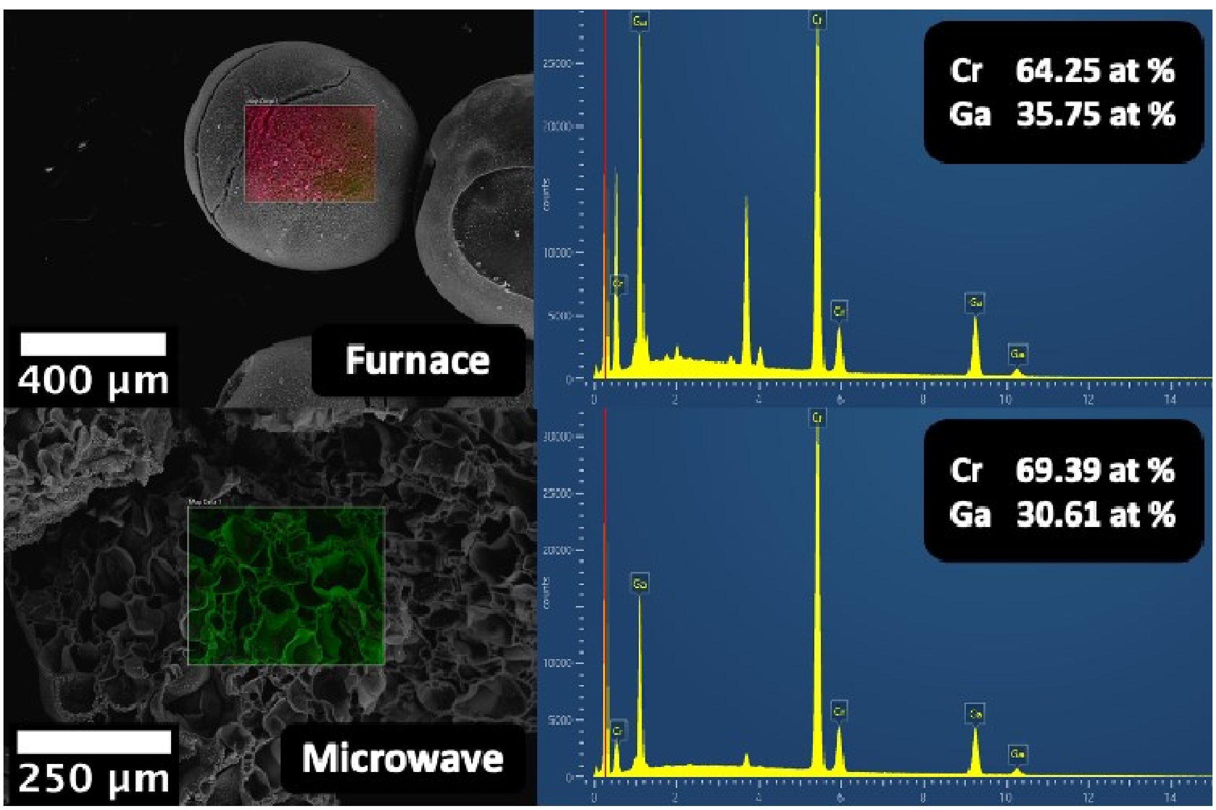

Figure S18. *EDS Imaging and Map Sum Spectrums of 20 gauge (furnace and microwave)*

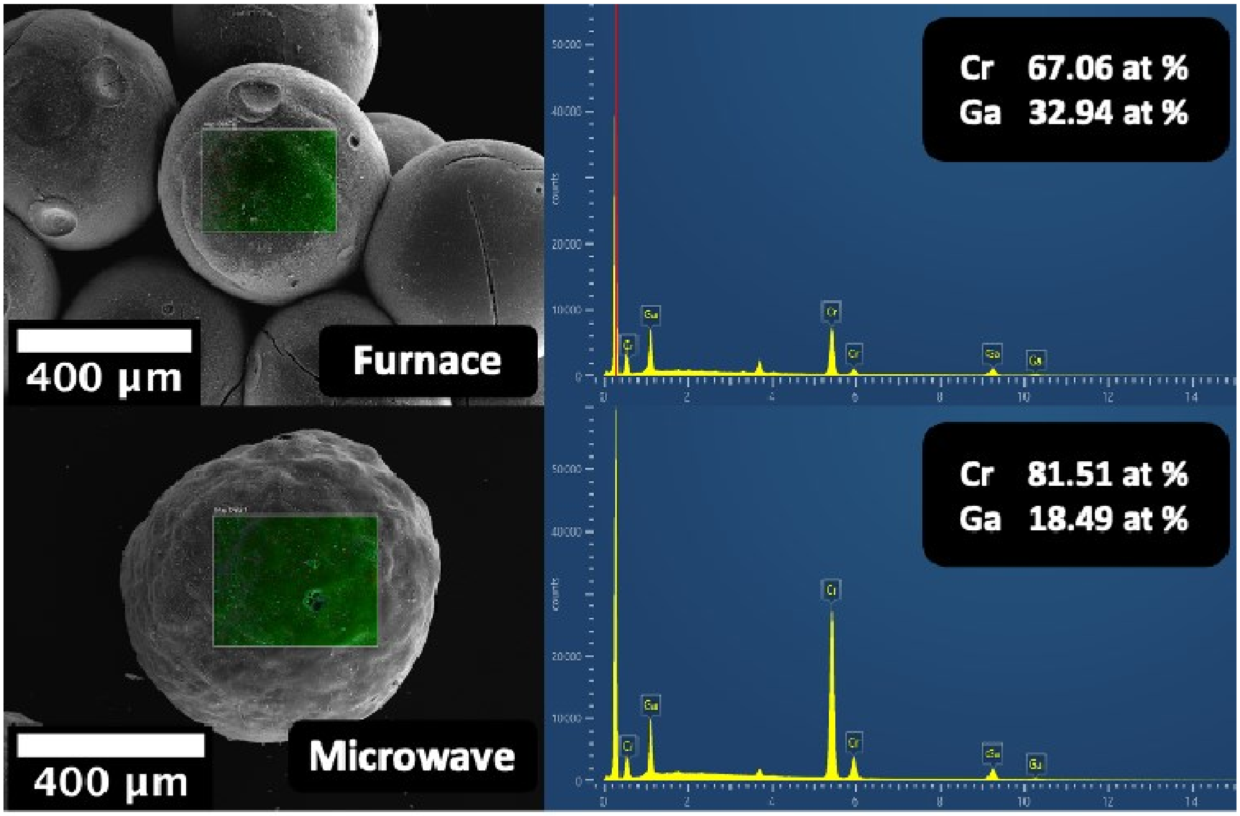

Figure S19. *EDS Imaging and Map Sum Spectrums of 23 gauge (furnace and microwave)*

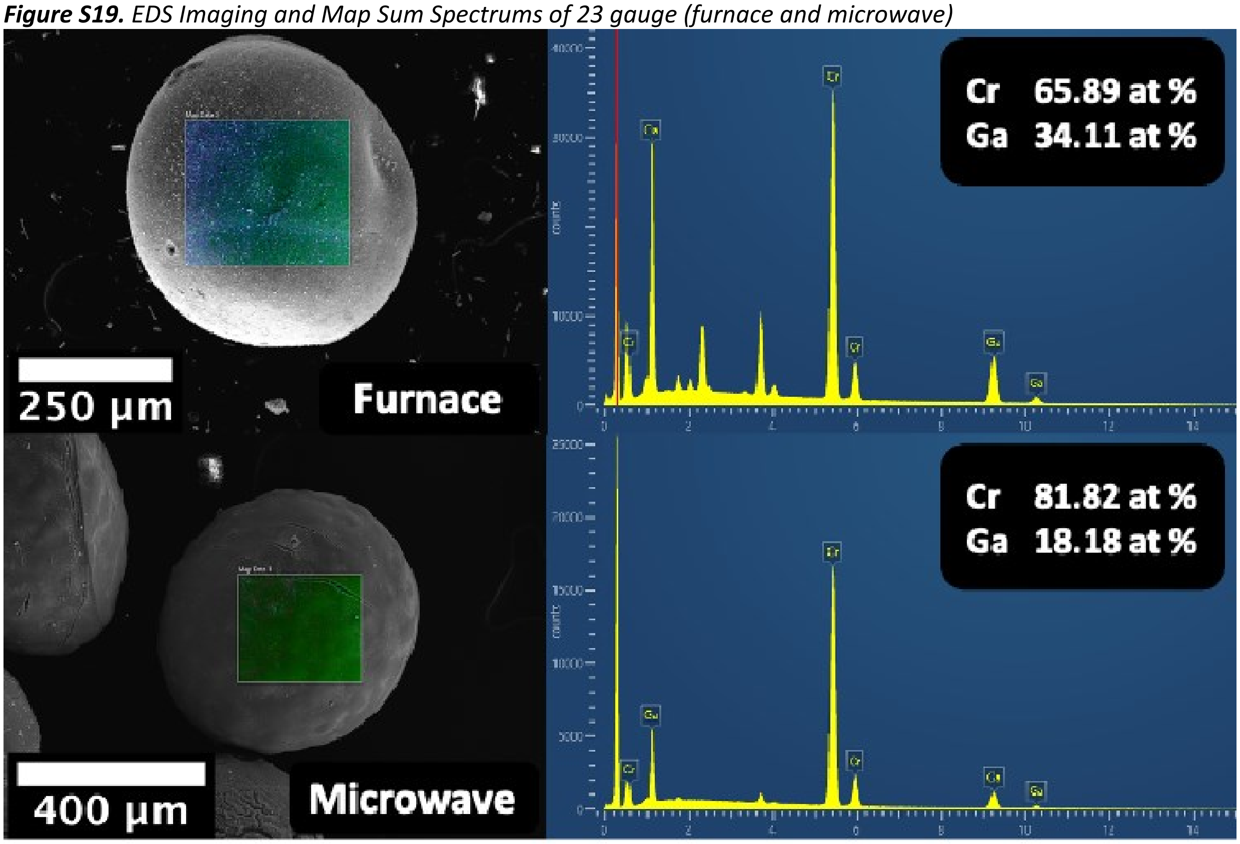

Figure S20. *EDS Imaging and Map Sum Spectrums of 26 gauge (furnace and microwave)*

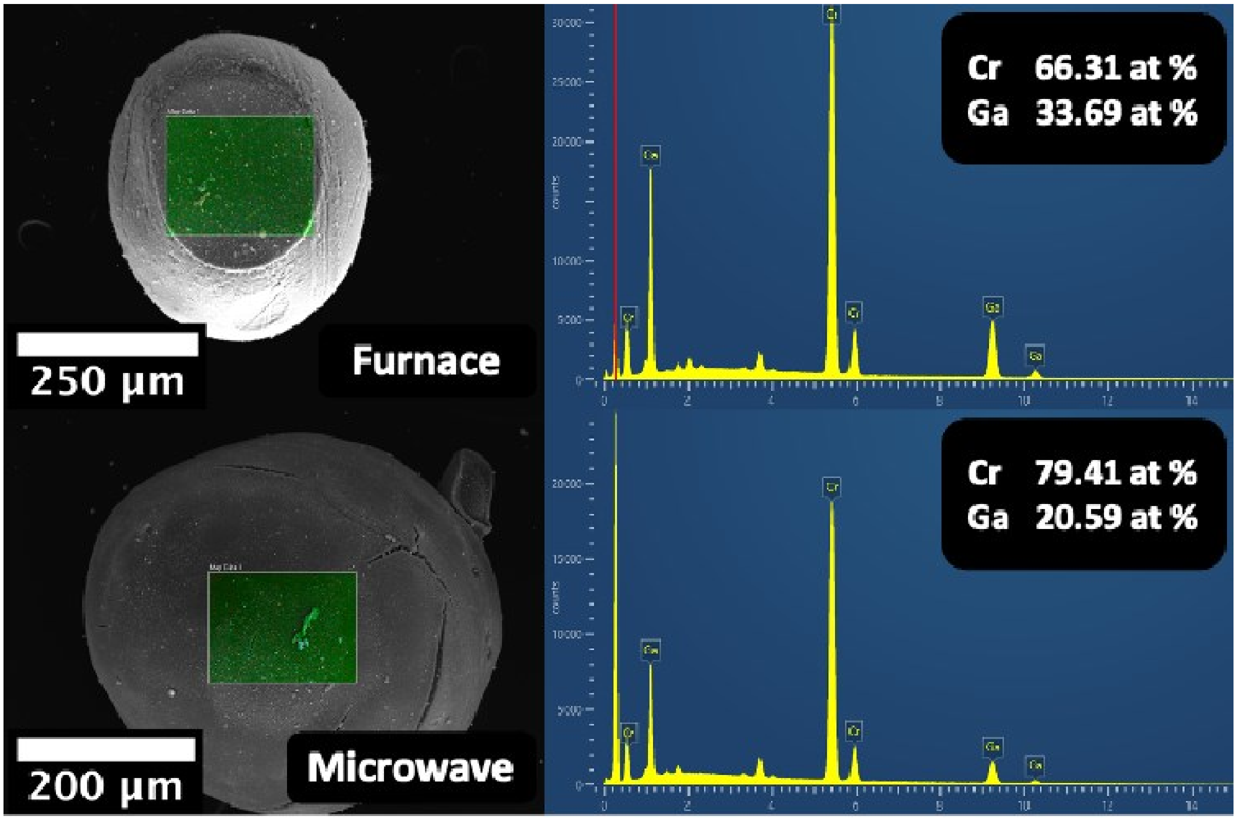

Figure S21. *EDS Imaging and Map Sum Spectrums of 30 gauge (furnace and microwave)*

TEM Imaging

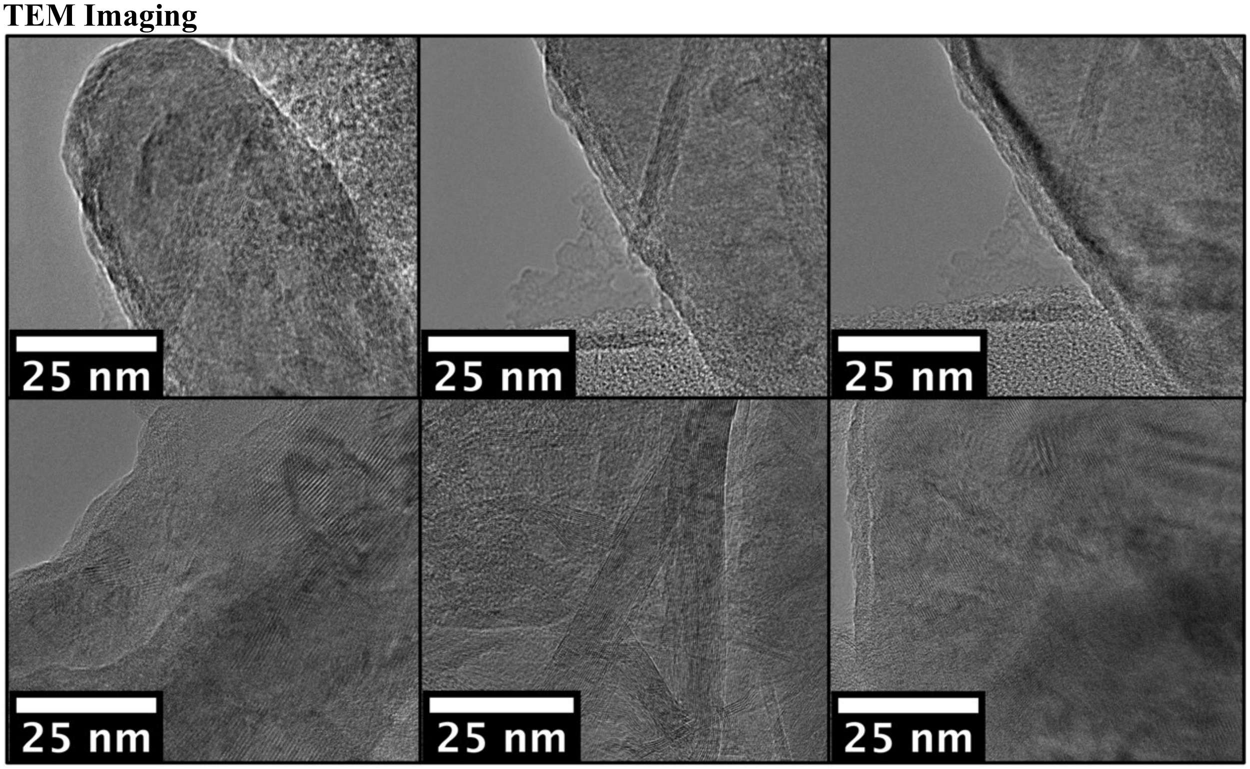

Figure S22. *TEM imaging of microwave microspheres*

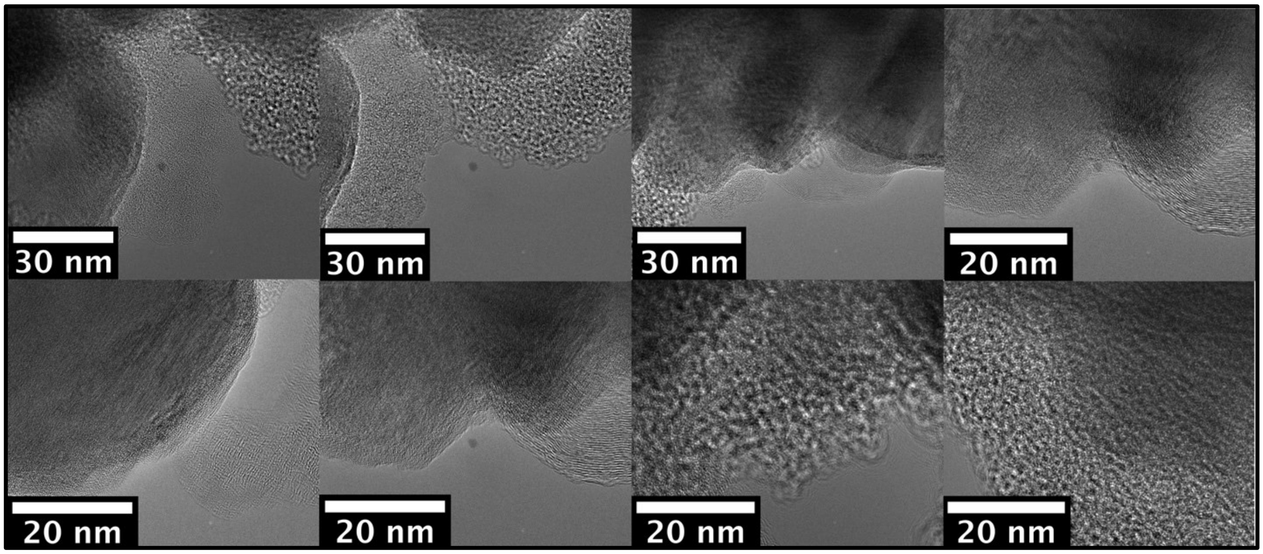

Figure S23. *TEM imaging of chitosan microspheres*

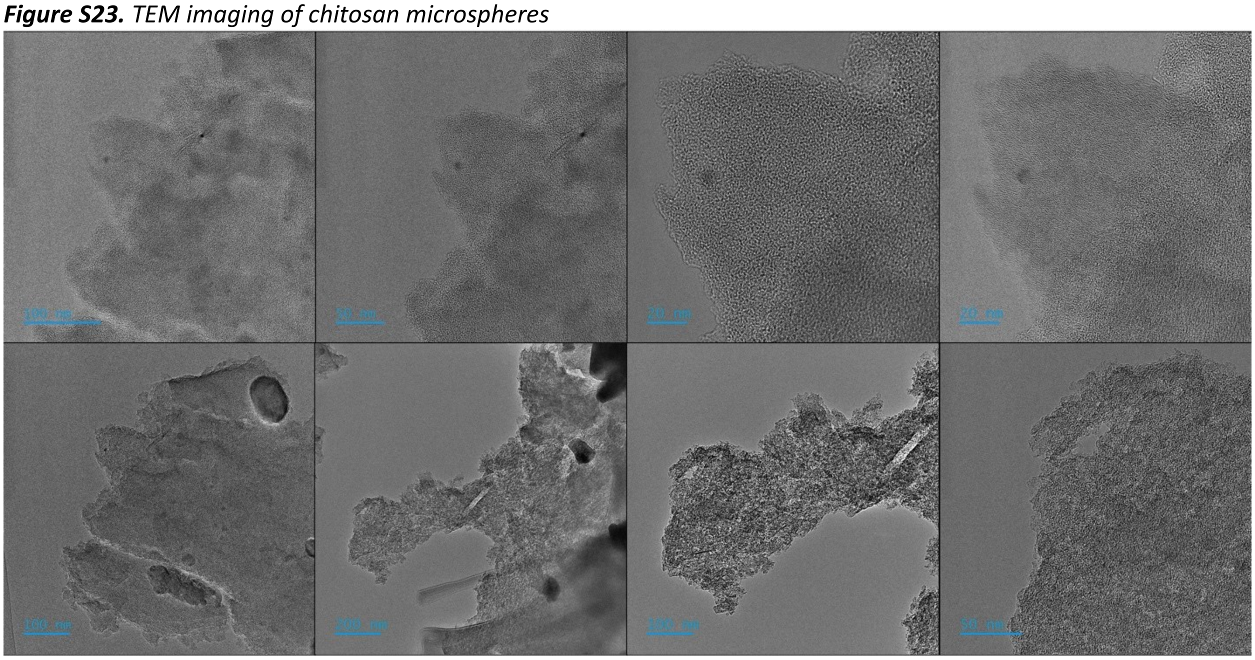

Figure S24. *HR-TEM imaging of furnace microspheres*

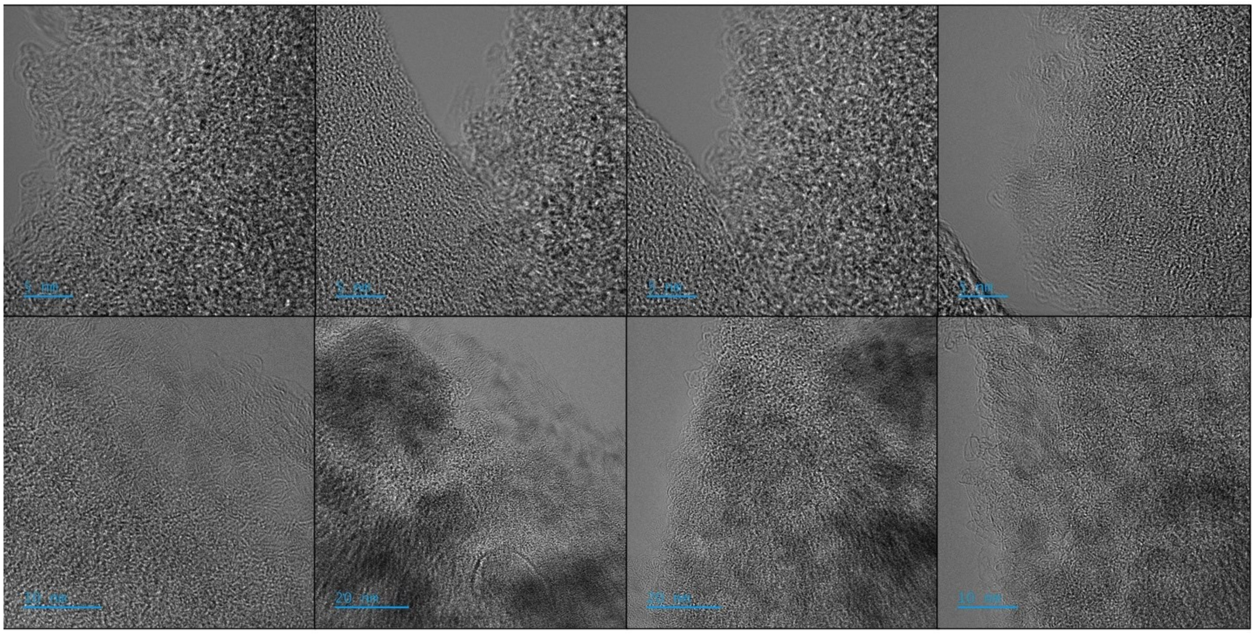

Figure S25. *HR-TEM imaging of furnace microspheres*

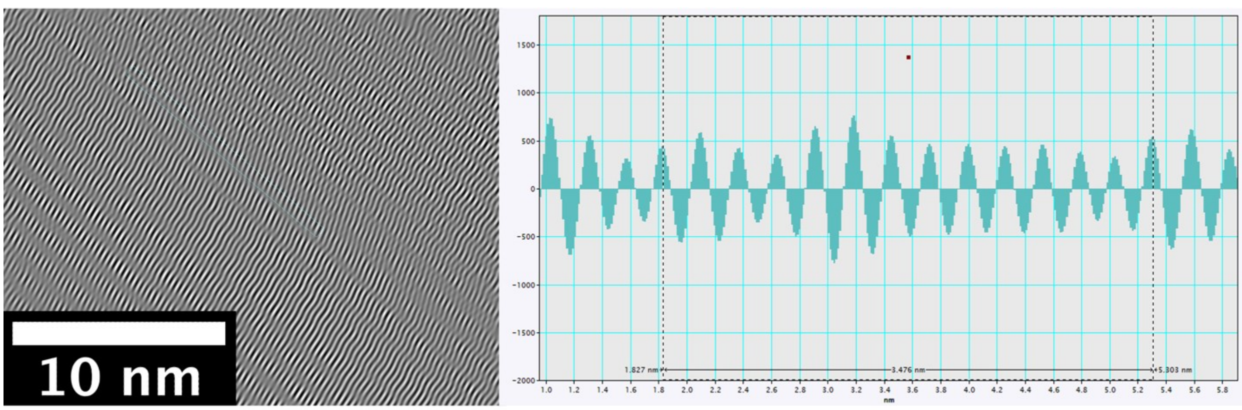

Figure S26. *Inverse Fourier Transform of HR-TEM imaging of furnace microspheres. Lattice spacing was estimated across 12 different points to get a good average.*

Figure S27. *A depiction of most of the needle gauge sizes used in synthesis.*

References

1. Coelho, A. A. TOPAS and TOPAS-Academic: An optimization program integrating computer algebra and crystallographic objects written in C++: An. *J. Appl. Crystallogr.* **51**, 210–218 (2018).

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