

Stabilizing Cubic γ -Ga₂O₃:Cr³⁺ Spinel Nanocrystals by Size Confinement into Mesoporous Silica Nanoreactor Channels

Michele Crozzolin,¹ Camilla Belloni,¹ Jian Xu,^{2,3} Takayuki Nakanishi,⁴ Jumpei Ueda,⁵ Setsuhisa Tanabe,³ Federico Dallo,⁶ Eleonora Balliana,⁷ Asia Saorin,¹ Flavio Rizzolio,^{1,8} Davide Cristofori,¹ Pietro Riello,¹ Alvise Benedetti,¹ Michele Back,^{1,*}

¹ Department of Molecular Sciences and Nanosystems, Ca' Foscari University of Venice, Via Torino 155, 30172, Mestre – Venezia, Italy

² International Center for Young Scientists (ICYS), National Institute of Materials Science (NIMS), Tsukuba, Ibaraki 305-0044, Japan

³ Graduate School of Global Environmental Studies, Kyoto University, Yoshida nihonmatsu-cho, Sakyo-ku, Kyoto 606-8501, Japan

⁴ Advanced Phosphor Group, National Institute of Materials Science (NIMS), Tsukuba, Ibaraki 305-0044, Japan

⁵ Graduate School of Advanced Science and Technology, Japan Advanced Institute of Science and Technology (JAIST), 1-1 Asahidai, Nomi, Ishikawa, 923-1292 Japan

⁶ Institute of Polar Sciences - National Research Council (ISP-CNR), Via Torino 155, 30172, Venezia-Mestre, Venice, Italy

⁷ Department of Environmental Sciences, Informatics, Statistics, Ca' Foscari University of Venice, Scientific Campus - Via Torino 155, 30170 Venezia Mestre, Italy

⁸ Pathology Unit, Department of Molecular Biology and Translational Research, Centro di Riferimento Oncologico di Aviano (CRO) IRCCS, via Franco Gallini 2, 33081 Aviano, Italy

* corresponding author email: michele.back@unive.it

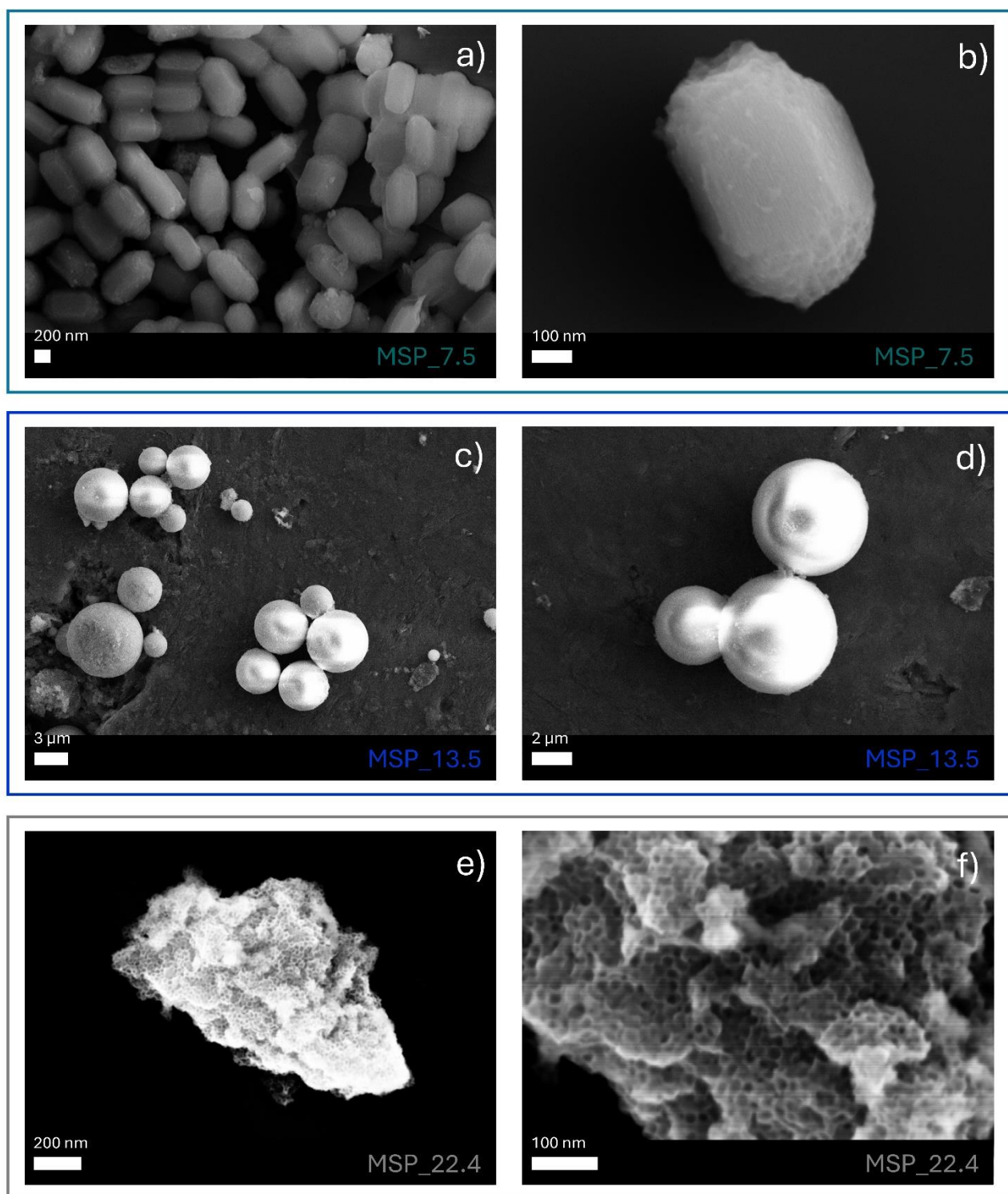


Figure S1. FE-SEM images of (a,b) SBA-15 with average pores of 7.5 nm, (c,d) MSPs obtained by using TMB/Pluronic P123 ratio of 0.3:1 and (e,f) TMB/Pluronic P123 ratio of 0.5:1.

Table S1. BET surface area, BJH pore volume and average pore diameter calculated from the N₂ physisorption measurements.

Sample name	BET surface area [m ² /g]	BJH pore volume [cm ³ /g]	Pore diameter [nm]
MSP_3.1	1236	1.035	3.1
MSP_4.2	853	0.955	4.2
MSP_7.5	873	0.976	7.5
MSP_13.5	809	0.875	13.5
MSP_22.4	932	1.653	22.4

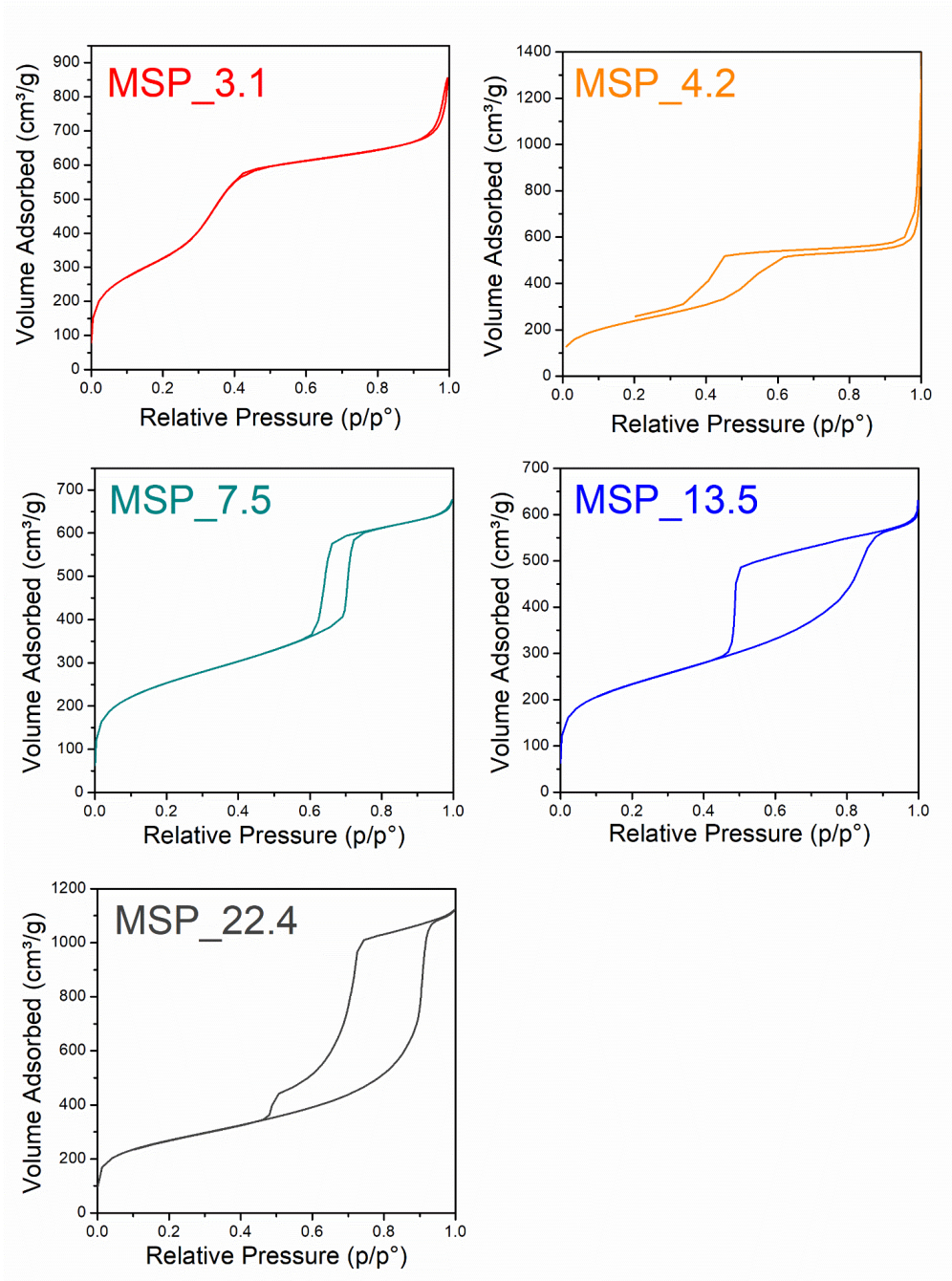


Figure S2. N₂ adsorption/desorption hysteresis of the MSPs.

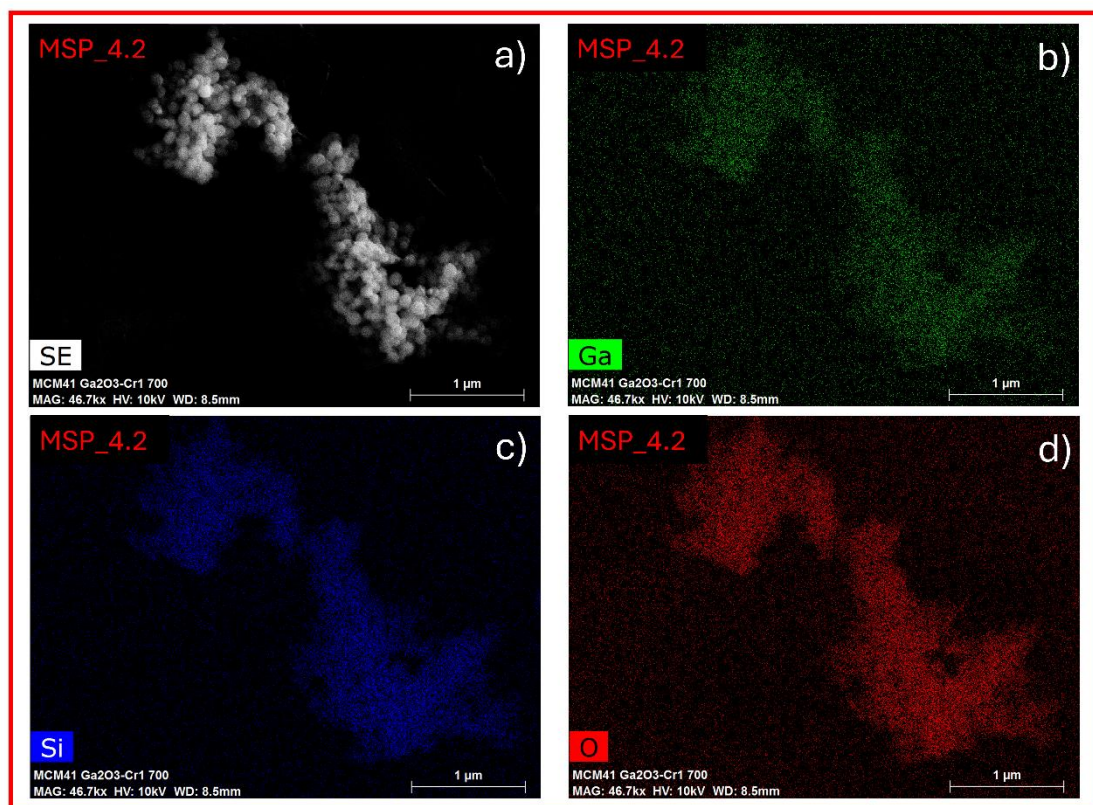


Figure S3. Representative (a) secondary electron-SEM image and corresponding EDX elemental map of (b) Ga, (c) Si and (d) O for $\text{Ga}_2\text{O}_3:\text{Cr}^{3+}$ @MSP_4.2 samples.

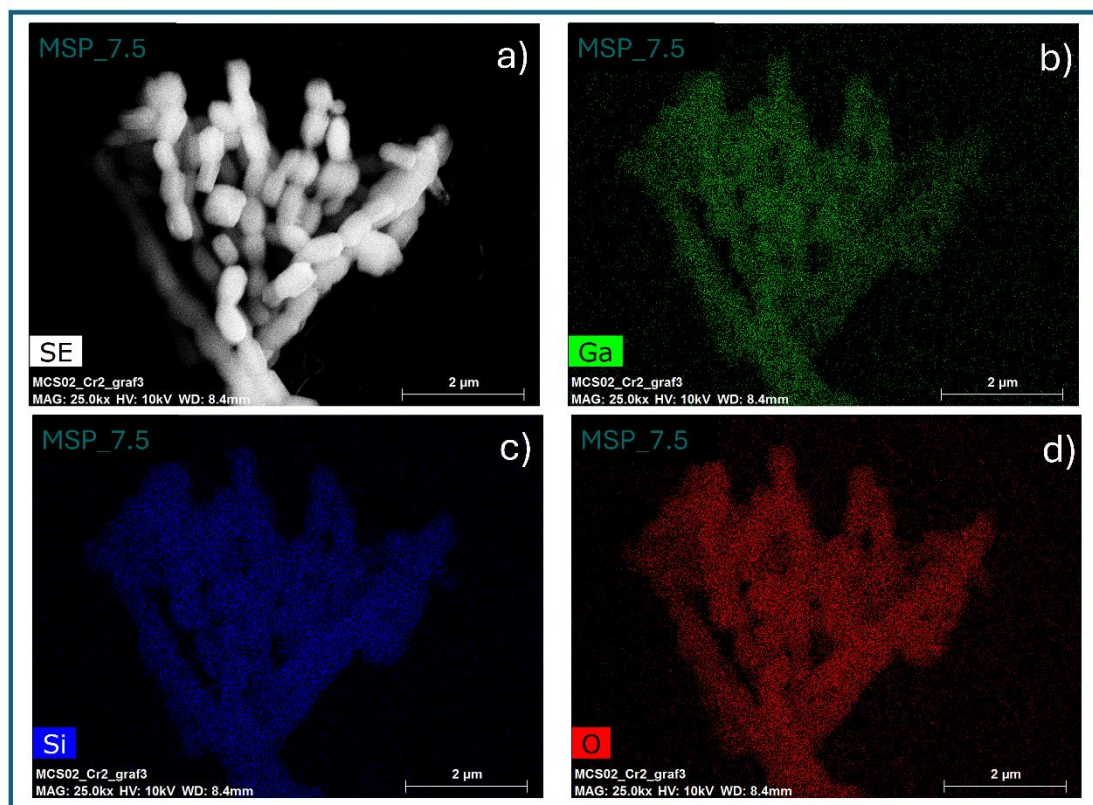


Figure S4. Representative (a) secondary electron-SEM image and corresponding EDX elemental map of (b) Ga, (c) Si and (d) O for $\text{Ga}_2\text{O}_3:\text{Cr}^{3+}$ @MSP_7.5 samples.

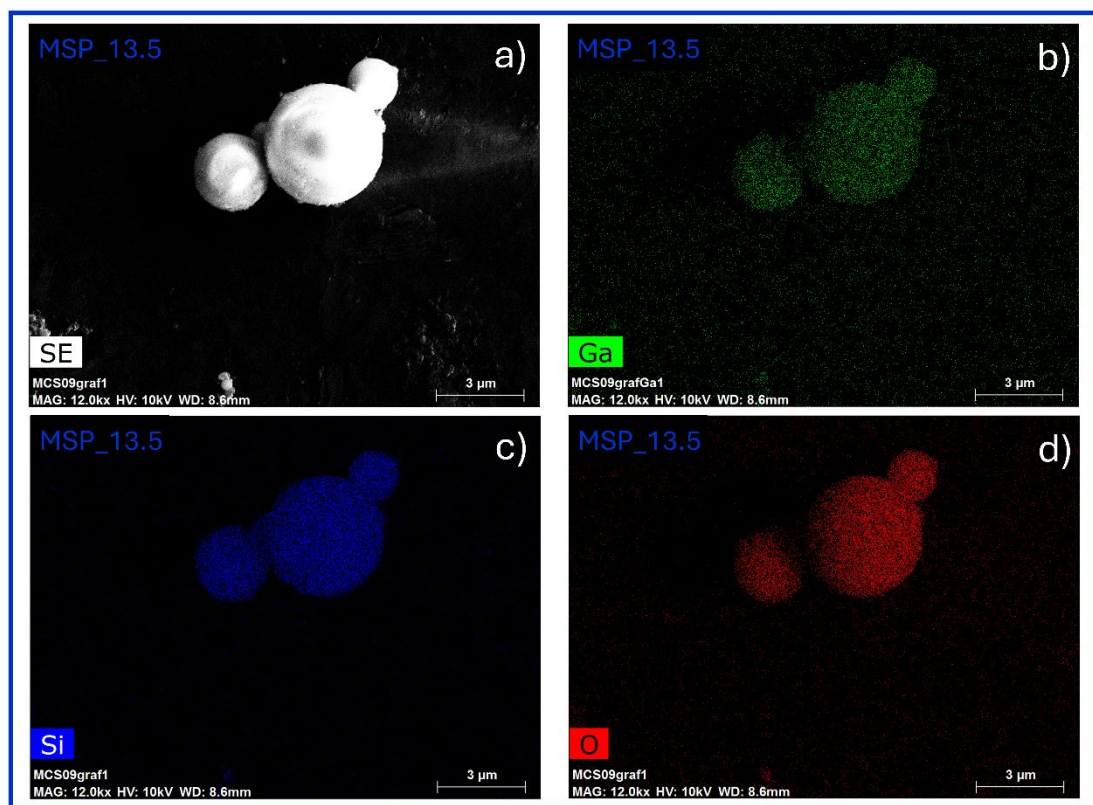


Figure S5. Representative (a) secondary electron-SEM image and corresponding EDX elemental map of (b) Ga, (c) Si and (d) O for $\text{Ga}_2\text{O}_3:\text{Cr}^{3+}@\text{MSP}_13.5$ samples.

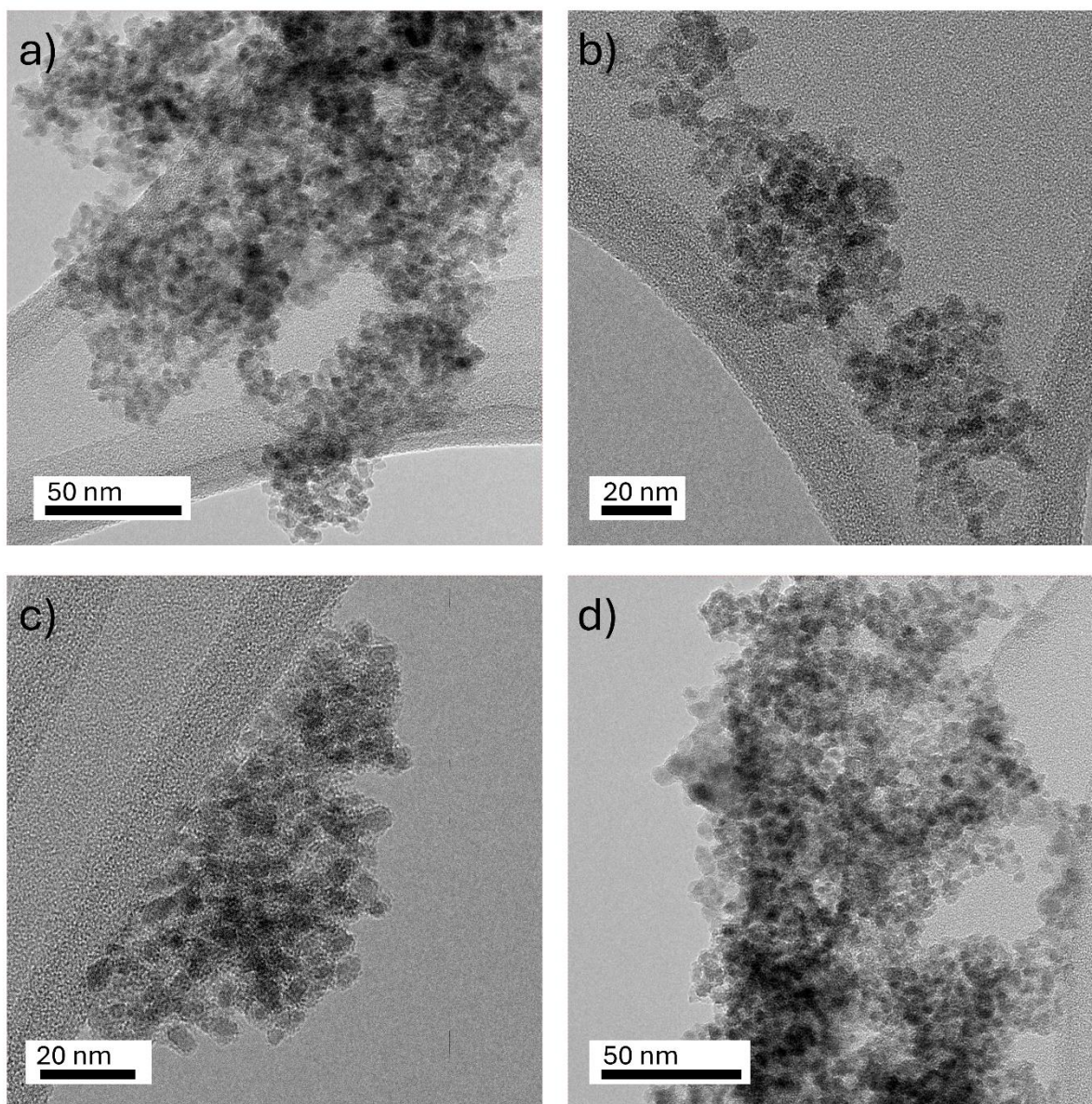


Figure S6. TEM images of the $\gamma\text{-Ga}_2\text{O}_3\text{:Cr}^{3+}$ NCs etched from the MSP_7.5.

Table S2. Measured and tabulated crystal plane distances and corresponding (hkl) crystal planes of the $\gamma\text{-Ga}_2\text{O}_3$ phase (ICSD#152085) extrapolated from the FFT analysis of the HR-TEM images.

<i>d</i> -spacing (Å)	<i>d</i> -spacing theory (Å)	(hkl)
2.486	2.48385	(311)
1.668	1.68157	(422)
2.371	2.37811	(222)

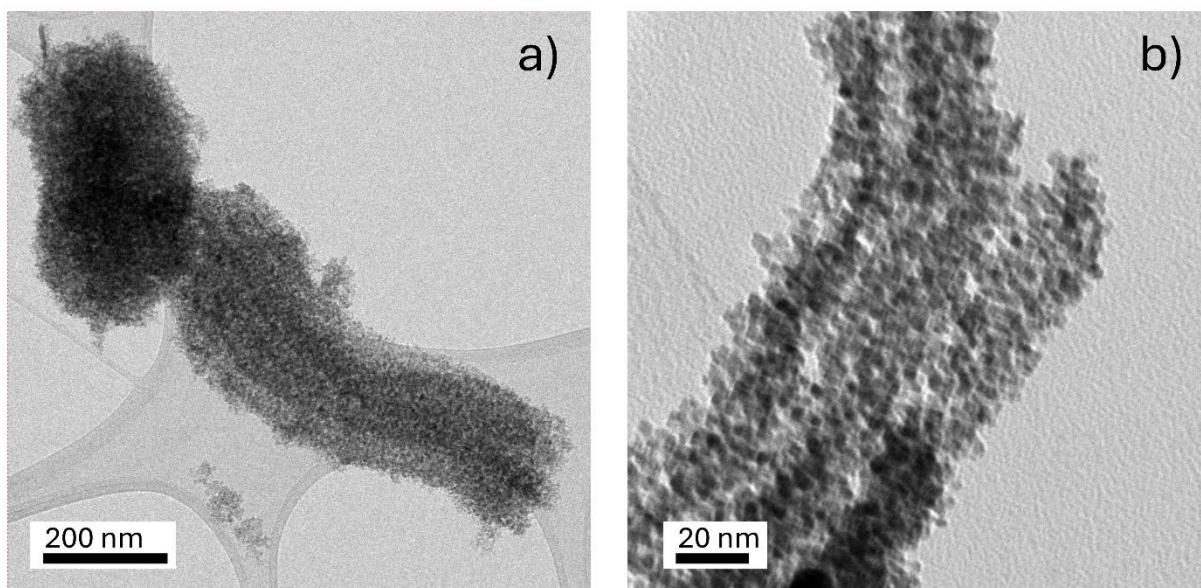


Figure S7. TEM images of the γ -Ga₂O₃:Cr³⁺ nanocasting SBA-15 replica obtained by the etching process from the MSP_7.5 without the use of ultrasonic bath.

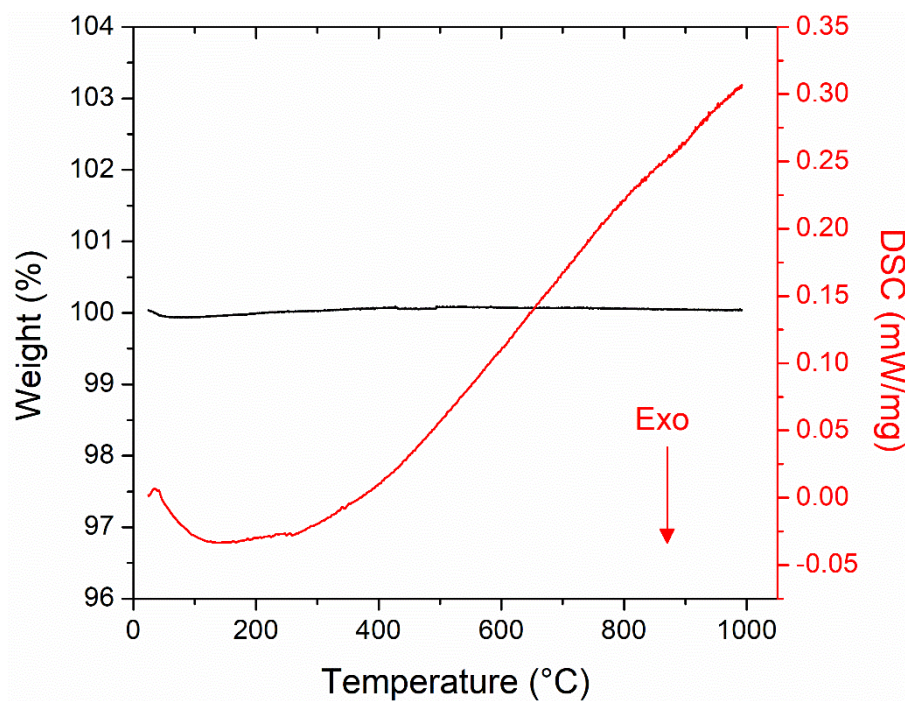


Figure S8. TG-DSC analysis of the sample.

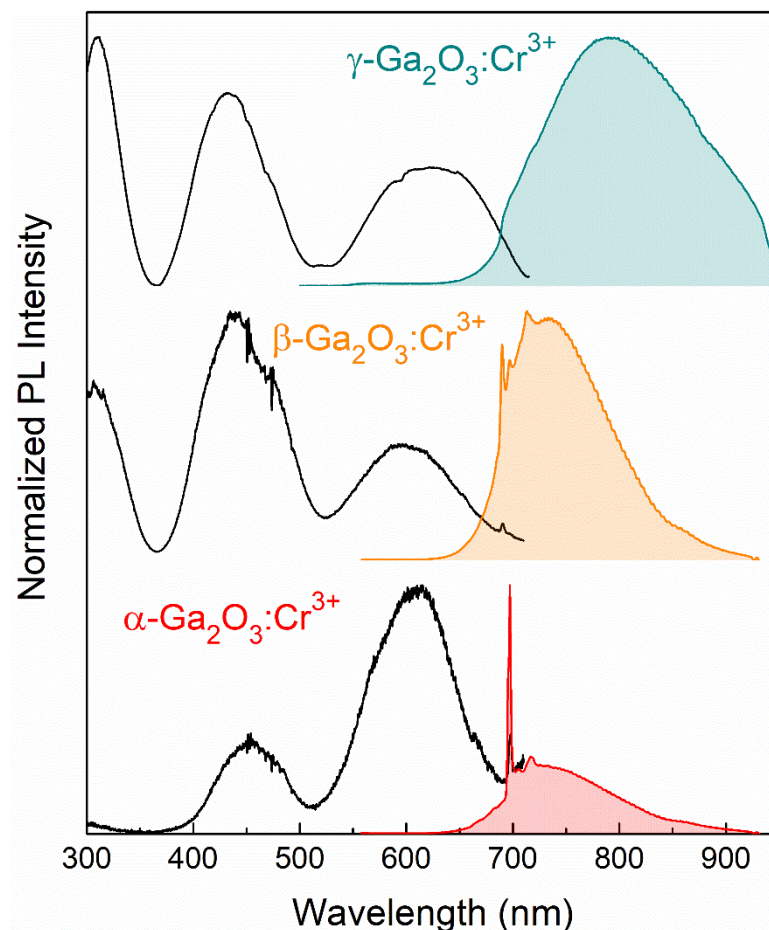


Figure S9. PL and PLE spectra of Cr³⁺ in α-Ga₂O₃ and β-Ga₂O₃ and γ-Ga₂O₃ polymorphs.