Supplementary Information (SI) for Environmental Science: Nano.

Safe-by-design assessment of SiO_2@ZnO multi-component nanomaterial used in construction

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Three-tiered approach from nanoGEM standard operating procedure framework

In order to assess the potential exposure of the different scenarios selected, a three-tiered approach was followed. As Tier 1, specific questionnaires filled in by the workers of CIAC company to identify the likely points of (MC)NMs emission are reported in Tables S1-S2.

Table S1 – Questionnaire with information on the company, the main activity and the corresponding processes involved to produce the MCNM-based mortars.

Administrative / Company Information	
Industrial Sector	*CONSTRUCTION*
Activity Information	
Type of materials your company handle or produce	*Inorganic additives for the construction sector*
List the different products or chemical elements that are handled in your process (specify with a star '*' those that are nanostructured)	Photocatalytic materials* Insulating materials. Corrosion inhibitors. additives to improve mechanical properties*
Process Information ***(Fill as many as processes/contributing scenarios for each process you may have)***	
Exposure scenario 1 (ES1): Additive preparation	
Process Description	*Covering particles of mesoporous SiO_2 NM with $ZnAc{\cdot}2H_2O$ and then, heating at 600 ºC to make SiO_2-ZnO MCNM.*
In what physical form are the products handled (powders, pellets, solution)	*Powders*
In what type of packing are the materials received or packed after production	*Bags*
How are the materials transferred to the production line (e.g. automatic feeder, manual)?	*Manual*
Total amount of materials used/produced per shift	*On demand*
What is the end-product for this process?	*Building mortar additives*
What is the amount and nature of waste materials?	*Without waste, yield 100%*
Are there subcontractors operating on the pilot line (maintenance, cleaning …)?	*No*
Please describe maintenance and cleaning operations and their frequency	*Monthly inspection of extractor hood*
Have you experienced incidental situations (spills, metal fire …) and do you have safety procedures implemented (please describe)?	*No incidental situations*
Tasks within ES1: Measuring solids and liquids	
Physical form of the material	*Dust*
Amount used	*On demand, about 200-500 grams*
Volume of the room	*About 10 m^3 (balance room)*

General air ventilation (building / room) – renewal rate	*2 open doors*
What type of air filtration is in place (efficiency)?	*No filtration in this place*
Level of automation	*0*
Level of containment	
Collective protective equipment (process related)	
Exposure duration	*1 or 2 minutes*
Types of PPE used	*mask*
Can the release of dust and/or aerosols into the workplace air be reasonably excluded?	
Other risks that might be encountered in the workplace?	*No*
Tasks within ES1: Mixing	
Physical form of the material	*Solid (dust) and liquid*
Amount used	*Amount measured on the last scenario*
Volume of the room	*120 m^3 (chemical lab)*
General air ventilation (building / room) – renewal rate	
What type of air filtration is in place (efficiency)?	*extractor hood*
Level of automation	*0*
Level of containment	
Collective protective equipment (process related)	*extractor hood*
Exposure duration	*1-2 minutes*
Types of PPE used	*extractor hood, filter mask*
Can the release of dust and/or aerosols into the workplace air be reasonably excluded?	*yes*
Other risks that might be encountered in the workplace?	*no*
Exposure scenario 2 (ES2): Calcination	
Physical form of the material	*Solid*
Amount used	*Amount obtained in the previous scenario*
Volume of the room	*130 m^3*
General air ventilation (building / room) – renewal rate	
What type of air filtration is in place (efficiency)?	*extractor hood*
Level of automation	*0*
Level of containment	
Collective protective equipment (process related)	*extractor hood*
Exposure duration	*1 minute*
Types of PPE used	*extractor hood, filter mask*
Can the release of dust and/or aerosols into the workplace air be reasonably excluded?	*yes*
Other risks that might be encountered in the workplace?	*no*
Exposure scenario 3 (ES3): Mortar formulation	
Process Description	*Inclusion of photocatalytic additive in mortar*
In what physical form are the products handled (powders, pellets, solution)	*Powders and liquids*
In what type of packing are the materials received or packed after production	*bags*
How are the materials transferred to the production line (e.g. automatic feeder, manual)?	*manual*
Total amount of materials used/produced per shift	*3 kg*
What is the end-product for this process?	*Building mortar*

What is the amount and nature of waste materials?	*big*
Are there subcontractors operating on the pilot line (maintenance, cleaning …)?	
Please describe maintenance and cleaning operations and their frequency	*Cleaning equipment, every use*
Have you experienced incidental situations (spills, metal fire …) and do you have safety procedures implemented (please describe)?	*no*
Tasks within ES3: Weighing	
Physical form of the material	*Dust and liquid*
Amount used	*3 kg*
Volume of the room	*20 m^3*
General air ventilation (building / room) – renewal rate	*Temperature and humidity-controlled room*
What type of air filtration is in place (efficiency)?	
Level of automation	*0*
Level of containment	
Collective protective equipment (process related)	
Exposure duration	*1-2 minutes*
Types of PPE used	*mask*
Can the release of dust and/or aerosols into the workplace air be reasonably excluded?	*yes*
Other risks that might be encountered in the workplace?	*no*
Tasks within ES3: Mixing with water	
Physical form of the material	*Dust and liquid*
Amount used	*Amount measured on previous step*
Volume of the room	*20 m^3*
General air ventilation (building / room) – renewal rate	*Temperature and humidity-controlled room*
What type of air filtration is in place (efficiency)?	
Level of automation	*100%*
Level of containment	
Collective protective equipment (process related)	
Exposure duration	*3 minutes*
Types of PPE used	*mask*
Can the release of dust and/or aerosols into the workplace air be reasonably excluded?	*yes*
Other risks that might be encountered in the workplace?	*no*
Tasks within ES3: Mold	
Physical form of the material	*Paste*
Amount used	*Amount mixed on the previous step*
Volume of the room	*20 m^3*
General air ventilation (building / room) – renewal rate	*Temperature and humidity-controlled room*
What type of air filtration is in place (efficiency)?	
Level of automation	*100%*
Level of containment	
Collective protective equipment (process related)	
Exposure duration	*5 minutes*
Types of PPE used	*mask*
Can the release of dust and/or aerosols into the workplace air be reasonably excluded?	*yes*
Other risks that might be encountered in the workplace?	*no*

Table S2 – Questionnaire on occupational exposure assessment information.

1. INFORMATION ON ACTIVITY WITH NANOMATERIALS

ACTIVITY RELATED TO NANOMATERIALS

☐ **Manufacturer** ☐ **Downstream user** ☒ **Research and development**

☐ **Maintenance of facilities with NMs**

QUANTITY OF NANOMATERIAL PRODUCED OR USED

Around 3 kg

MANUFACTURING PROCESSES AND OPERATIONS RELATED TO NANOMATERIALS

X MANUFACTURING

X HANDLING

☐ MANTEINANCE OF FACILITIES WITH NMs

PROCESS TYPE

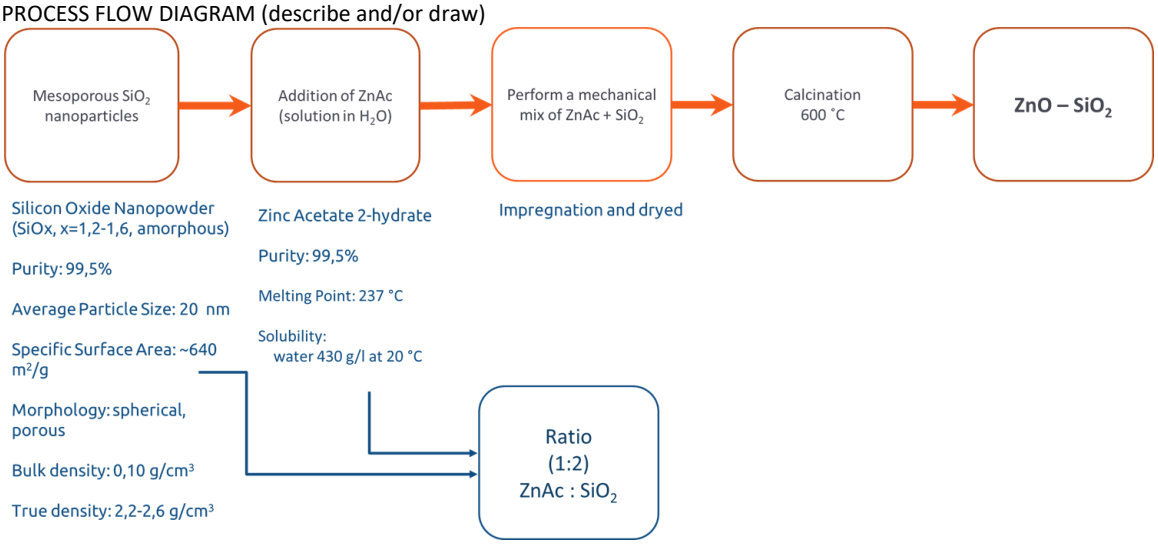
☐ **Continuos** ☐ **Discontinuos** ☑ **Discontinuos regular**

LEVEL OF PROCESS AUTOMATION

☐ **Automatic** ☑ **Semiatomatic** ☐ **Manual**

PROCESS TEMPERATURE ºC: room temperature

PROCESS FLOW DIAGRAM (describe and/or draw)



OBSERVATIONS: Closed system controlled via interface

NANOMATERIAL PROPERTIES/TOXICOLOGY/ECOTOXICOLOGY

Physical-chemical properties of the nanoparticle:

- ☐Shape: spherical
- ☐Size: below 20nm
- ☐Surface area: agglomerates, nanoporous layer
- ☐Solubility: material dependent
- ☐Is it functionalized or treated? No

Is the toxicology of nanomaterial known? No. If yes, please complete the next part of the questionnaire:

- ☐ Acute inhalation toxicity:
- ☐Acute dermal toxicity: Clic and write.
- ☐Acute toxicity by ingestion: Clic and write.
- ☐Genotoxicity: Clic and write.
- ☐Cytotoxicity: Clic and write.

Is the ecotoxicology of nanomaterial known? No. If yes, please complete the next part of the questionnaire:

☐Ecotox. acute in fresh water: Clic and write.

☐Bioaccumulation: Clic and write.

☐Ecotox. in invertebrate soil organisms: Clic and write.

LIMIT VALUE (Occupational Exposure Limits or OELs) (if you know it): Clic and write.

Source:Clic and write

Unknown:☒

OBSERVATIONS: Used materials: noble metals and metal oxide: see

2. INFORMATION ABOUT THE TASKS AND TASK LOCATION WITH NANOMATERIALS

DESCRIPTION THE TASK WITH THE NANOMATERIAL:

TASK LOCATION: Indoor

DIMENSIONS OF THE LOCATION:

length (m)5 width (m) 3 height (m) 3.

NUMBER OF WORKERS IN THE LOCATION: 2.

OTHER TASKS THAT ARE PERFORMED NEAR THE TASK TO EVALUATE (WITH NMs): Clic and write.

NUMBER OF WORKERS INVOLVED IN THE TASK WITH NANOMATERIALS: 2

DURATION OF THE TASK WITHIN THE DAY: 1 to 30 minutes/day

NUMBER OF REPETITIONS OF THE TASK WITHIN THE DAY: 1.

FREQUENCY OF THE TASK: 1 day every 2 weeks

DISTANCE FROM THE WORKER TO THE SOURCE OF EMISSION (m): 1 m Choose.

QUANTITY OF PRODUCT USED IN THE TASK:

☐mg ☒g ☐kg ☐t ☐ml ☐l ☐m^3

LEVEL OF AGITATION OR ENERGY APPLIED TO THE TASK:

☐High[1] ☒Medium [2] ☐Low[3]

OBSERVATIONS: Clic and write.

DIAGRAM/GRAPH OF THE WORKING AREA[4] (describe and/or draw):

3. CONTROL MEASURES

☐ISOLATION OR CONFINEMENT: Partial

☐SEGREGATION[5]: No

☐EMISSION REDUCTION:

☐WET METHODS: Clic and write

☒ESTABLISHMENT OF PROCEDURES: A leak test is performed before printing. The pressure is checked during printing by the operator via the interface.

OBSERVATIONS:Clic and write

☐LOCALIZED EXTRACTION:

☐Integrated (on machine or tool)

☐Biological safety cabinet: Choose the type.

☐ Laminar flow cabin

☐Fume hood

☐Suspended hood

☐None

HAS A FILTER?Yes

TYPE OF FILTER: HEPA

[1] Mechanical mixing at high speed, pouring of product from big bags, spraying of products using high pressure or spray paint, boiling of liquids, mixing of products at high speed.

[2] Manual pouring of bags, mechanical mixing at low speed, fast and careless diving, aeration tanks, electroplating.

[3] Precise, slow and controlled dives; manual mixing or sieving of the product.

[4] Indicate where the emission focus of the nanomaterials, the worker, the control measures adopted, the secondary sources of nanomaterials and the measuring equipment used are located

[5] Segregation: separate the nanomaterial manipulation process from the rest of the processes

REGULAR INSPECTION AND MAINTENANCE OF EQUIPMENT No. FRECUENCY OF MAINTENANCE: Choose.. If yes, answer the following
CAPTURE SPEED (m/s): Choose.
AIR CURRENTS, VENTILATION/AIR-CONDITIONING SYSTEMS CLOSE TO THE EXTRACTION SYSTEM: Clic and write
OBSERVATIONS (deflectors, flanges, dimensions, efficiency, etc.): Clic and write

☒GENERAL VENTILATION[6]: Mechanical ventilation

HAS A FILTER?: Yes
TYPE OF FILTER: Choose.
AIR RECIRCULATION: Yes. OPERATING FLOW (renewals/hour): From 12 to 15
AIR CURRENTS, VENTILATION/AIR-CONDITIONING SYSTEMS CLOSE TO THE VENTILATION SYSTEM: Clic and write
OBSERVATIONS: Clic and write

☒TIDINESS AND CLEANLINESS[7]:

DAILY CLEANING IS PERFORMED: No
OBSERVATIONS: The lab is cleaned every 2 weeks

4. PERSONAL PROTECTIVE EQUIPMENT (PPE)

RESPIRATORY PROTECTION No

☐Self-filtering mask: Choose.
☐Mask or semi-mask with filter: Choose.
☐Assisted ventilation equipment. Mask/mask with filter: Choose.
☐Assisted ventilation equipment. Hood or helmet with filter: Choose.
☐None

EYES PROTECTION Yes

☒Universal frame glasses
☐Facial Screen
☐Full frame glasses
☐None

PROTECTIVE GLOVES Yes

Disposable Yes
Use of double glove Yes
Material: Nitrile

PROTECTIVE CLOTHING Yes

Disposable No
Type Choose.

OBSERVATIONS (Types of PPE not covered): Lab coats (VWR - general protection against dust, dirt, harmless liquid splashes, no protection against chemicals) and safety glasses are present, but rarely used.

[6] Natural and mechanical ventilation

[7] *Good*: Clean with proper procedures (HEPA filter aspirator). *Regular*: general cleaning practices. *Bad*: No specific practices

Based on the results of this survey, Tier 2 involved a monitoring campaign performed at different stages of MCNM-based mortars production and processing, as reported in Tables S3 and S4 and Figures S1-S3.
After collecting the overall data from Tier 2, the emission/exposure concentration of particles was compared to the background level, by following equation 1. This equation is included in the main text. According to the results from equation 1, if the difference between the emission/exposure concentration and the background level is bigger than three times the standard deviation of the background concentration, then the workplace or process concentration must be further assessed for the release of airborne nano-objects in Tier 3. Filter and electrostatic precipitator-based samples can be collected for chemical analysis by SEM, TEM, EDX and XRD and off-line analysis can be compared to real-time measurement results. Additional real-time instruments such as Scanning Mobility Particle Sizer, Aerodynamic Particle Size, Optical Particle Sizer or Electrical Low-Pressure Impactor (i.e., SMPS, APS, OPS or ELPI, respectively) may be used in the Tier 3 assessment. Factor three is based on the assumed level of significance of elevated exposure concentrations and is also proposed for granular biopersistent nano-objects without any specific toxicity. The factor three level was agreed upon by the nanoGEM expert team in absence of actual, robust data from comparison studies and should be revised in due time.[1] It has to be noted that the general measures and rules for workplace hygiene were applied. All laboratories have general ventilation, and they also have doors and windows to have natural ventilation. Because outdoor particles infiltrate work environments, and multiple sources of particles can be present in work areas, assessment of particle emission and exposure arising from nanotechnology processes must account for *local background particle exposure*. Particles background was measured before any activity corresponding to each room and the results are reported in Table S3 and the results of the monitoring campaign are displayed in Figures S8-S10.
Calculations of Eq. 1 for each contributing exposure scenario (CES) considered are reported in Tables S6-S8.

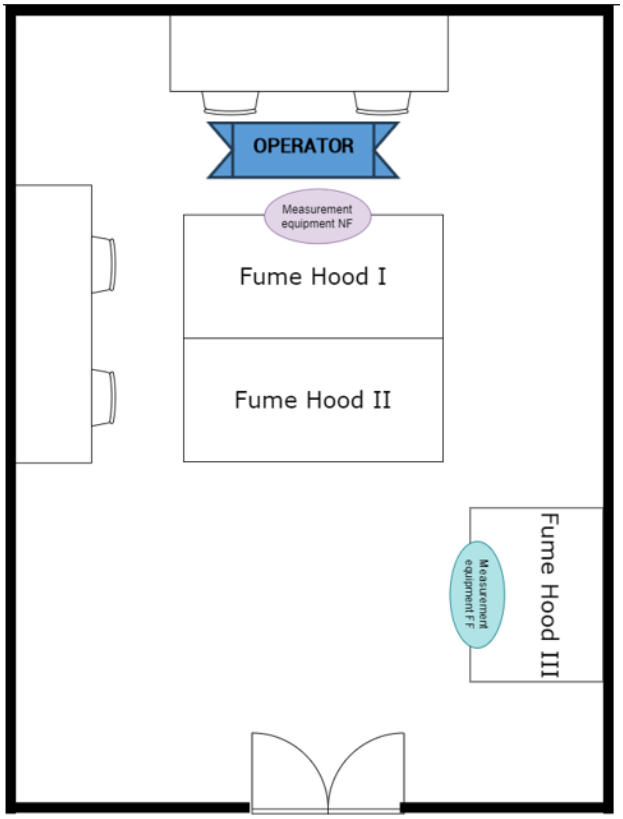


Figure S1 – Map of the laboratory for the material synthesis (exposure scenario 1). The synthesis was carried out under the fume hood #1 and the table in front of it. Monitoring equipment were placed close to fume hood #1 (near field, NF) and fume hood #3 (far field, FF).

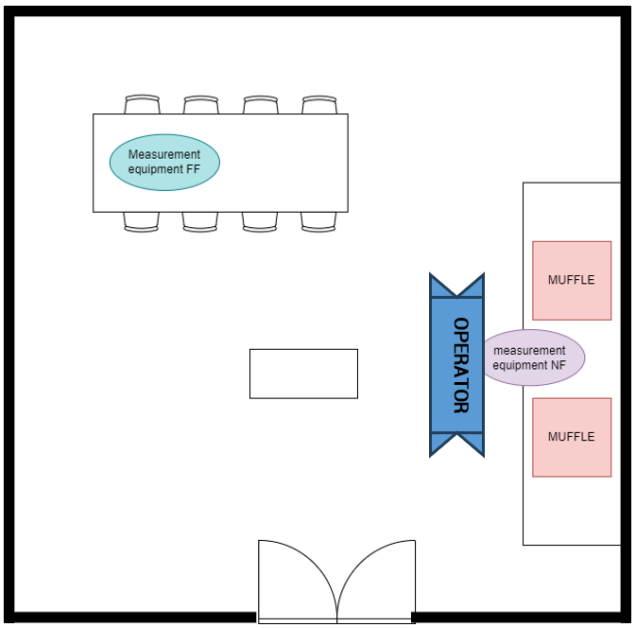


Figure S2 – Map of the laboratory for calcination (exposure scenario 2). Monitoring equipment were placed close to the muffles (near field, NF) and on a table (far field, FF).

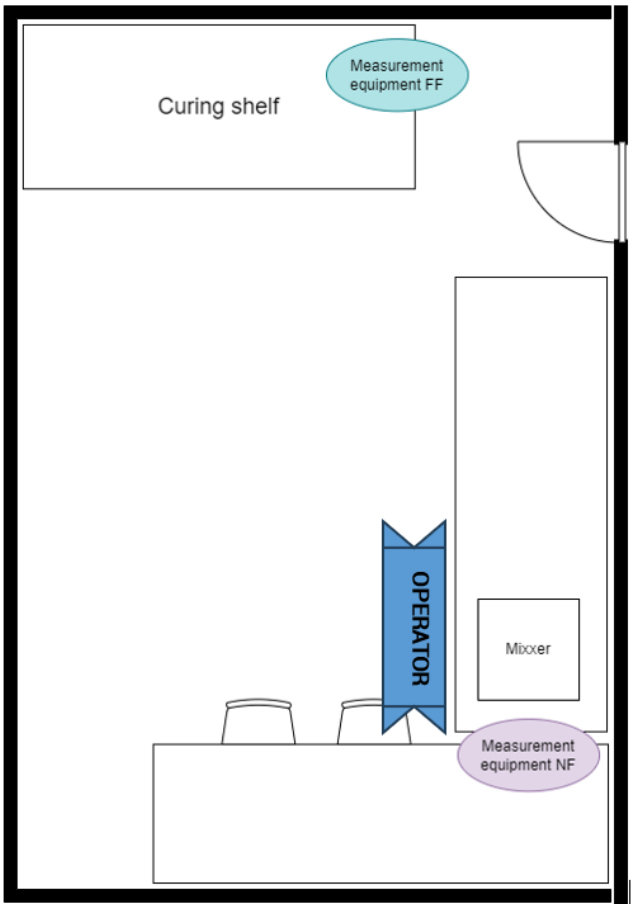
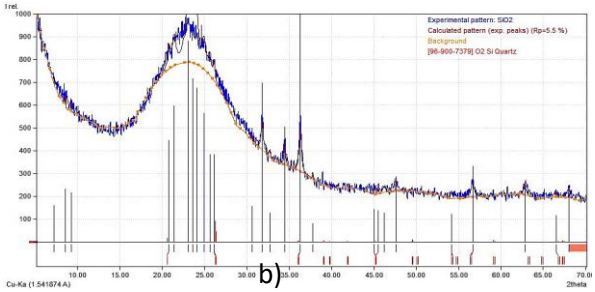
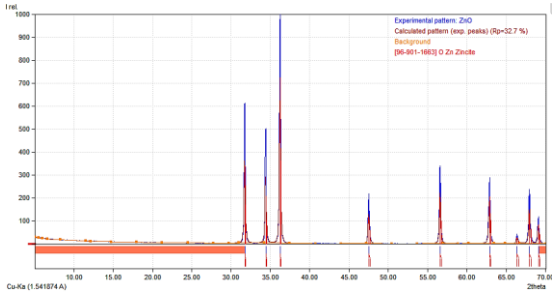


Figure S3 – Map of the laboratory for curing the test specimens (exposure scenario 3). Monitoring equipment was placed close to the muffles (near field, NF) and on a table (far field, FF).

a)



b)



c)

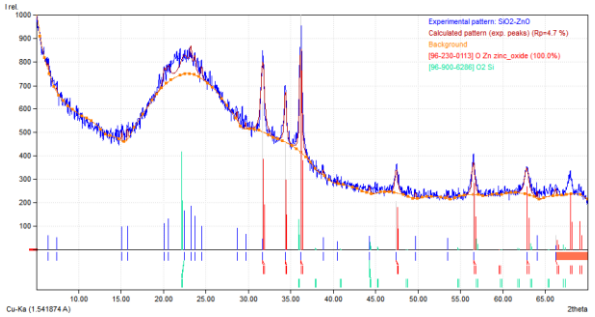


Figure S4 - XRD patterns of a) SiO_2 NM; b) ZnO NM; c) SiO_2@ZnO MCNM.

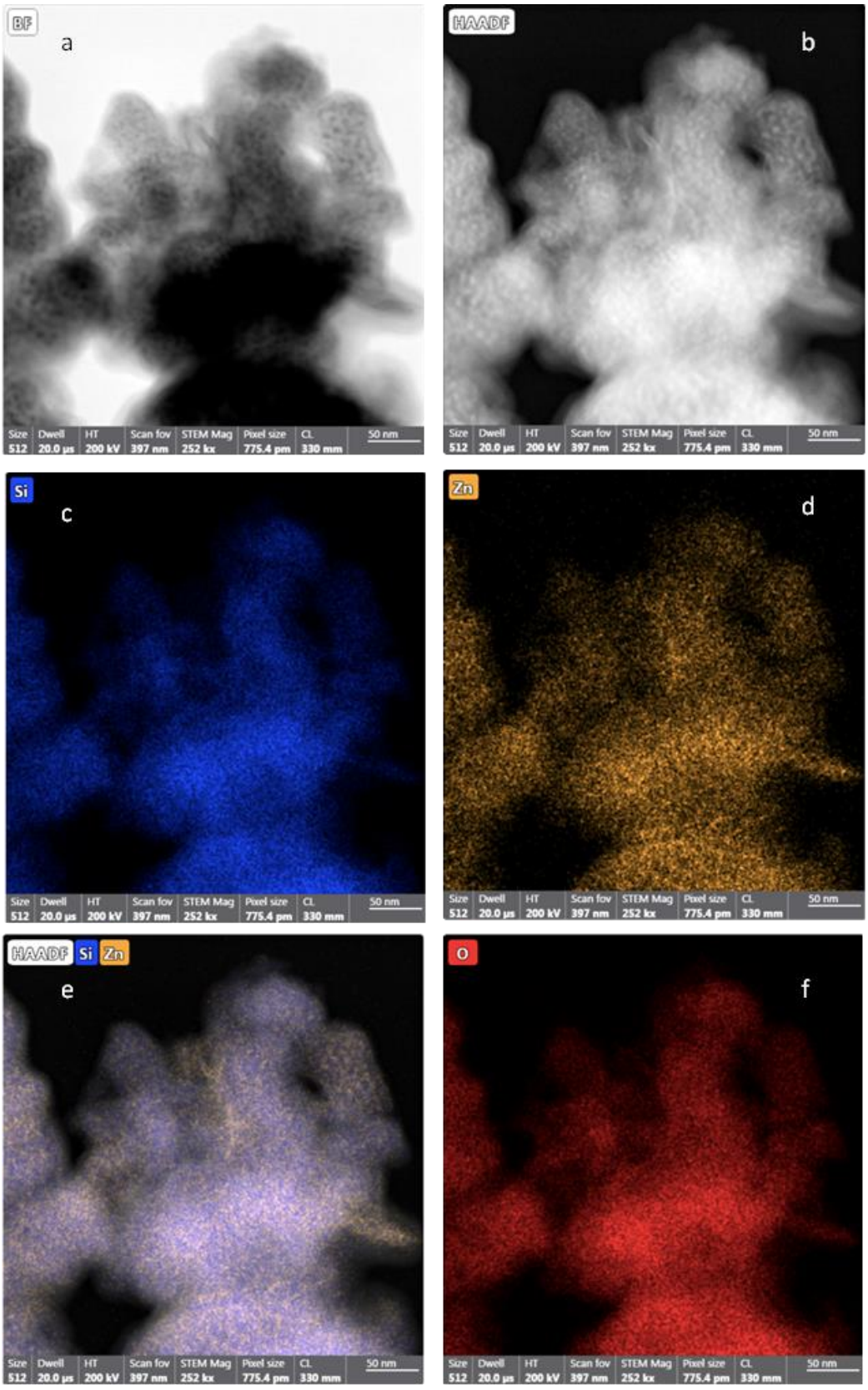


Figure S5 - EDX mapping of the MCNM. BF = bright field; HAADF = high angle annular dark field.

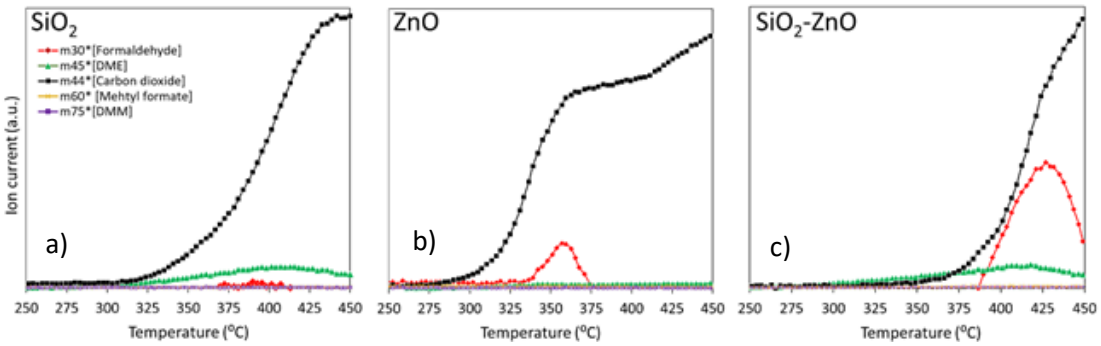


Figure S6 – Temperature-programmed reaction products of pre-adsorbed methanol analyzed by mass spectroscopy for SiO_2 (a), ZnO (b) and SiO_2@ZnO (c).

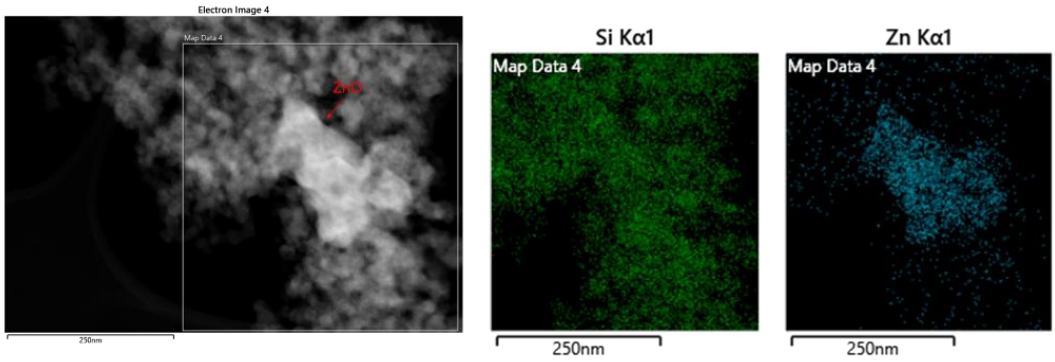


Figure S7 – STEM images of SiO_2@ZnO MCNM.

Table S3 – Particle background concentration levels for the three exposure scenarios considered. Each measurement lasted at least 15 minutes. NT: NanoTracer; CPC; Condensation Particle Counter.

Exposure scenario	Equipment	Units	Mean	Max	Min	RSD
ES1 (Material synthesis)	NT (10-300 nm)	#/cm^3	4784	6125	3507	14%
	CPC (10 nm-1 µm)	#/cm^3	3437	3626	3215	2%
ES2 (Calcination)	NT (10 to 300 nm)	#/cm^3	5718	9469	4515	23%
	CPC (10 nm to 1 µm)	#/cm^3	6106	6494	5255	2%
ES3 (Mortar formulation)	NT (10 to 300 nm)	#/cm^3	3377	4423	2450	13%
	CPC (10 nm to 1 µm)	#/cm^3	3740	4198	3095	6%

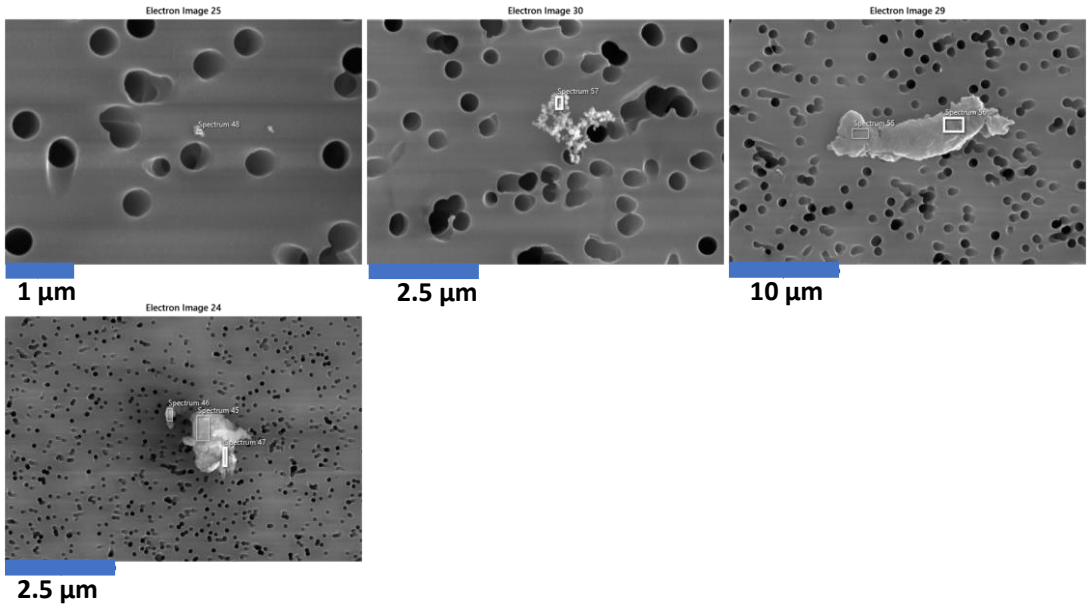


Figure S8 – Typical SEM images of background measurements in the material synthesis laboratory (ES1).

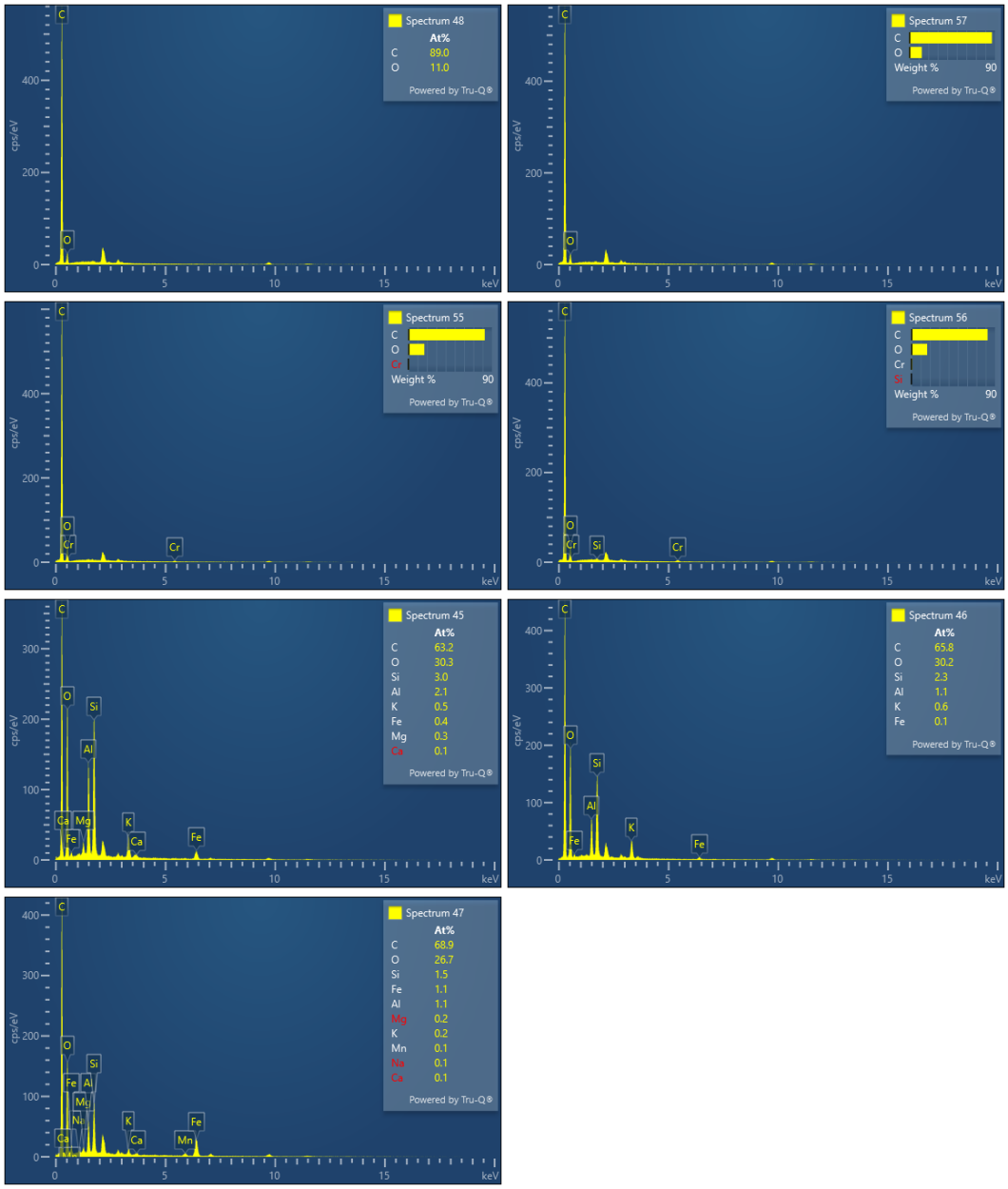


Figure S9 – EDX spectra corresponding to SEM images depicted in Figure S8 (ES1).

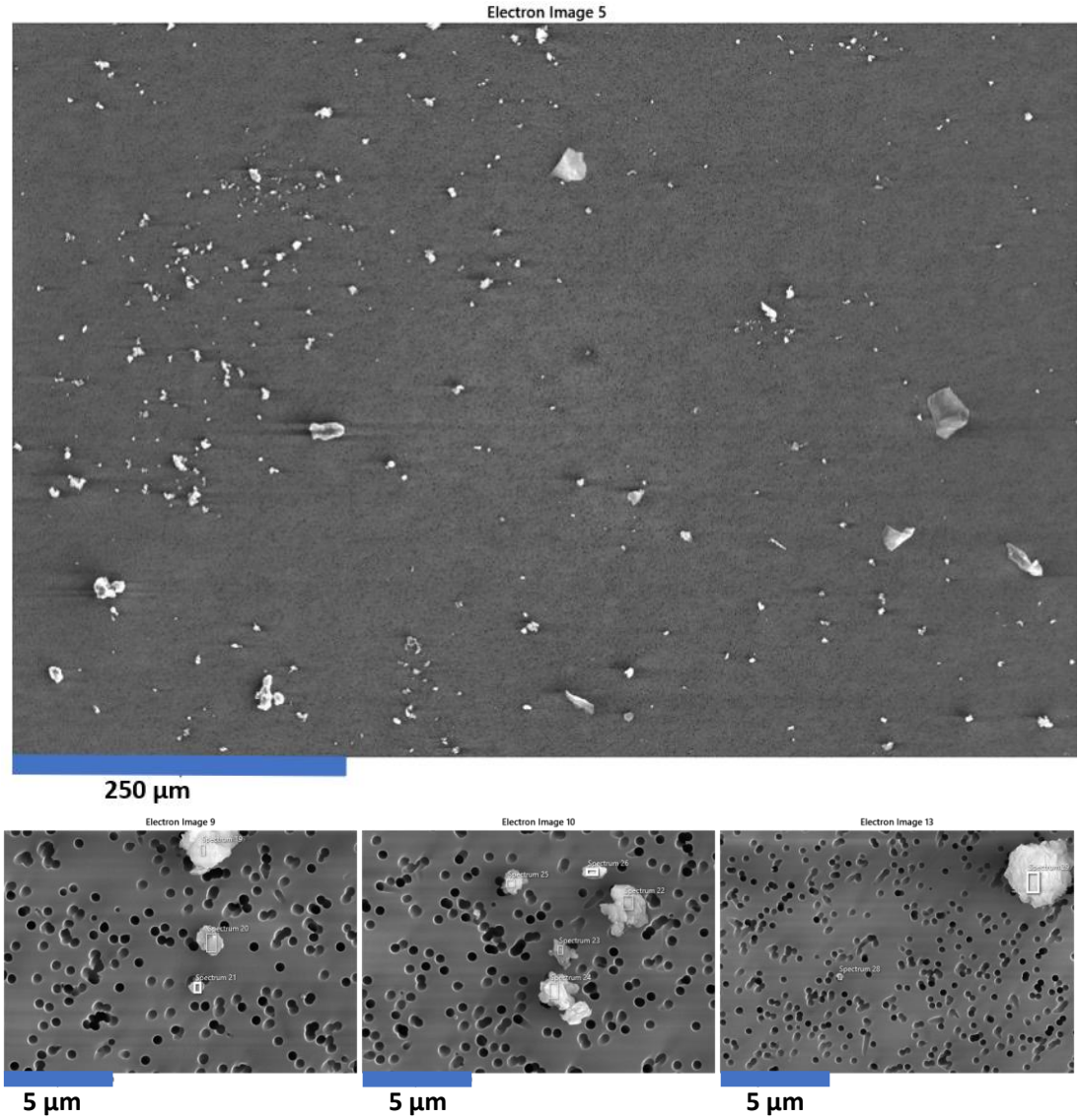


Figure S10 – Typical SEM images of background measurements in the characterization laboratory (ES2).

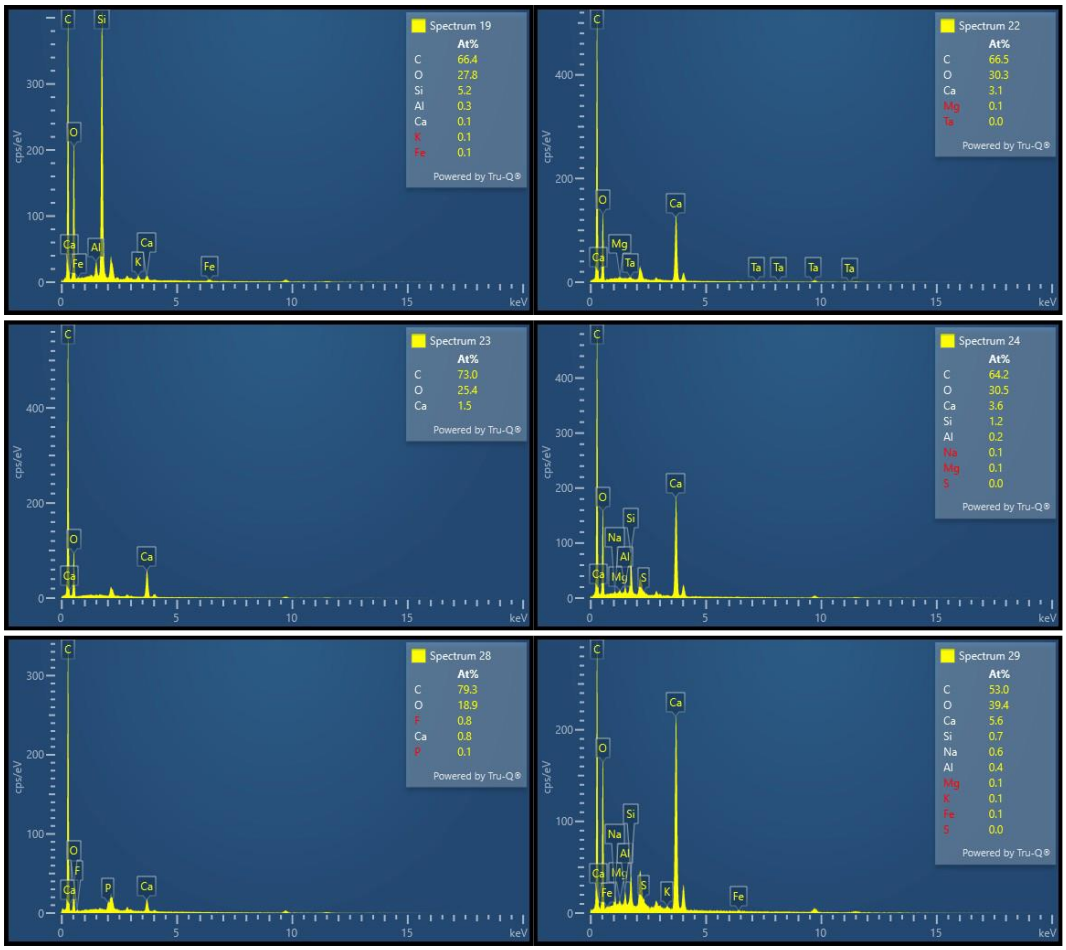


Figure S11 – EDX spectra corresponding to SEM images depicted in Figure S10 (ES2).

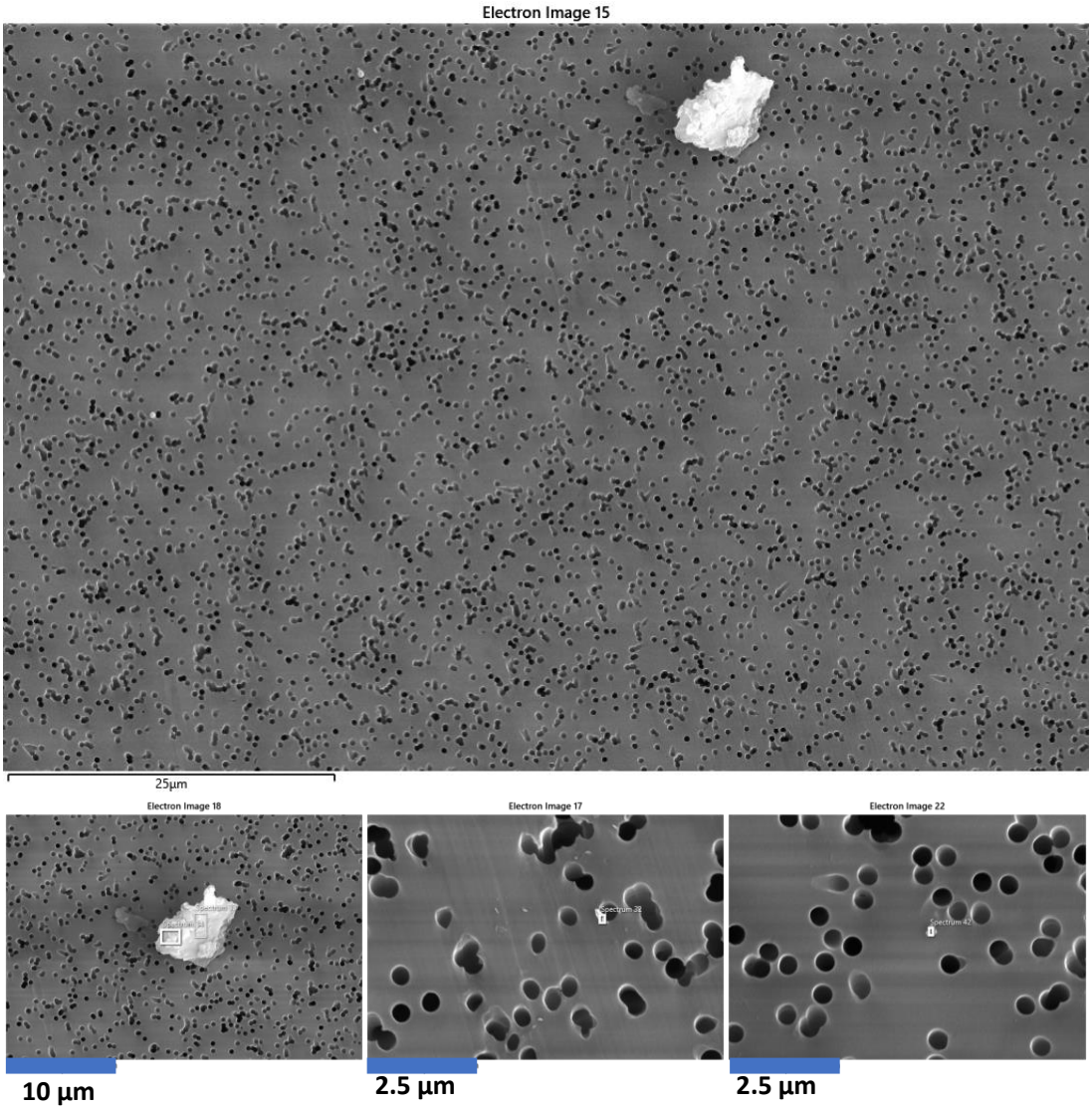


Figure S12 – Typical SEM images of background measurements in the mortar formulation laboratory (ES3).

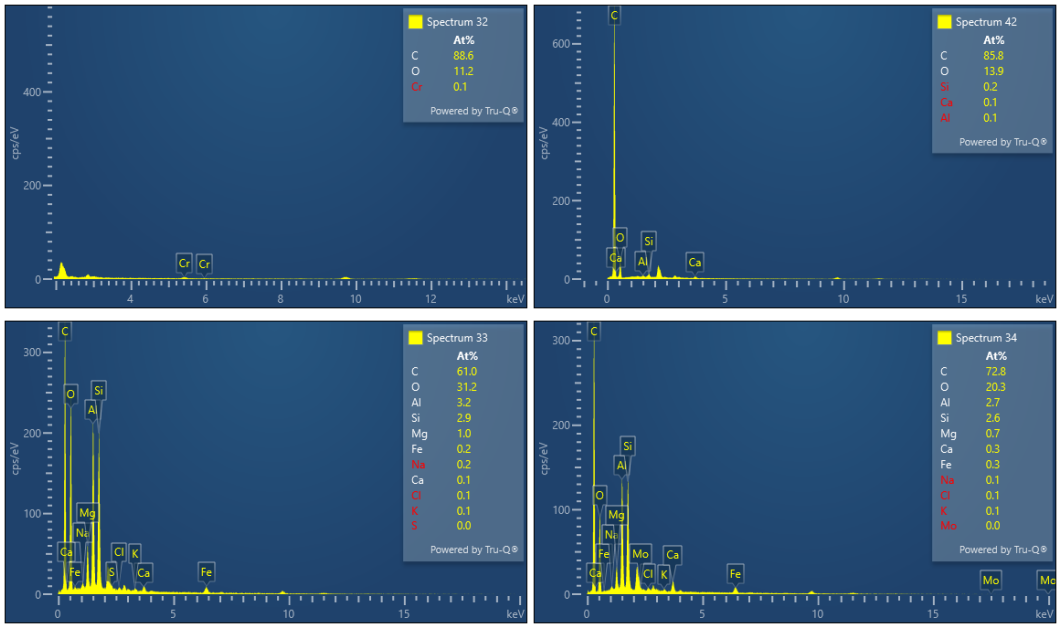


Figure S13 – EDX spectra corresponding to SEM images depicted in Figure S12 (ES3).

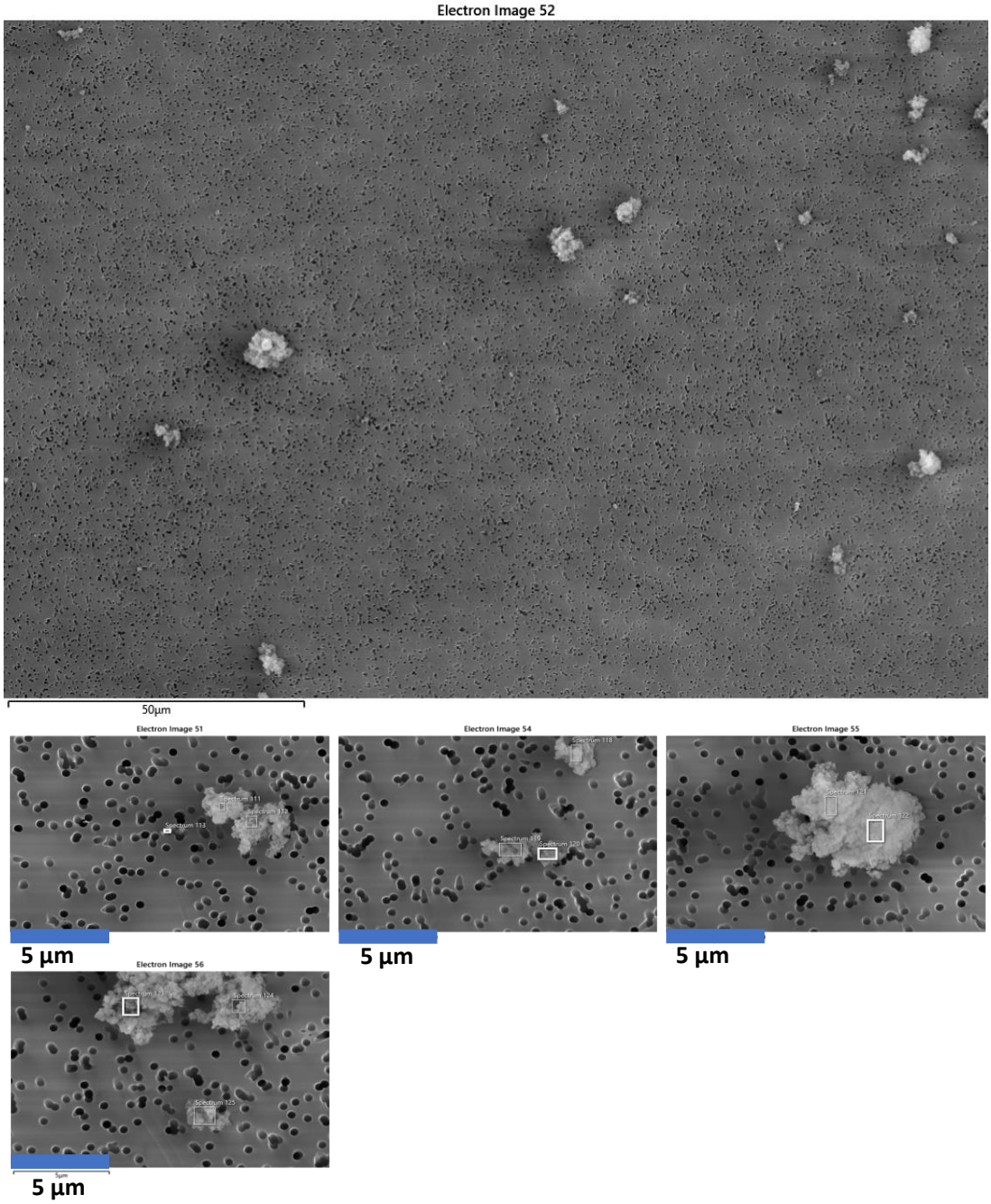
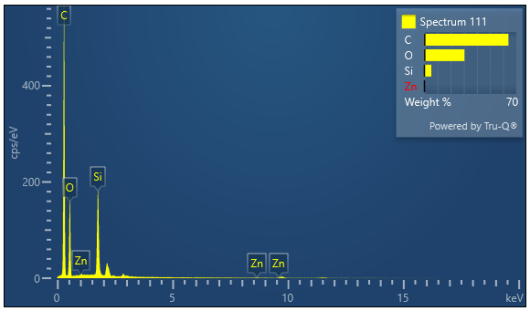
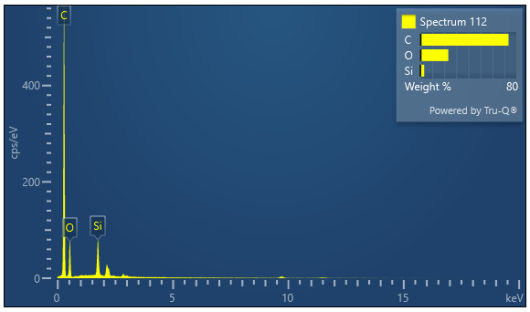
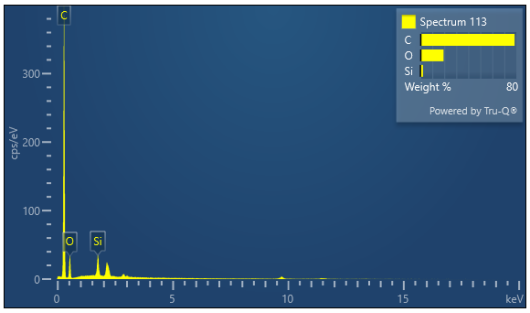
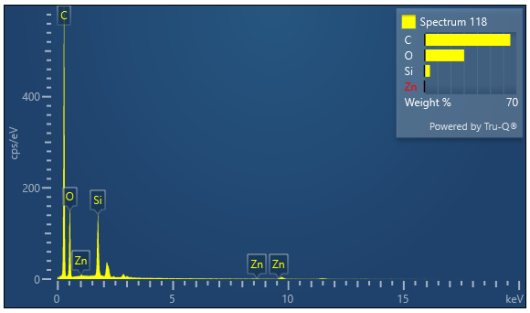


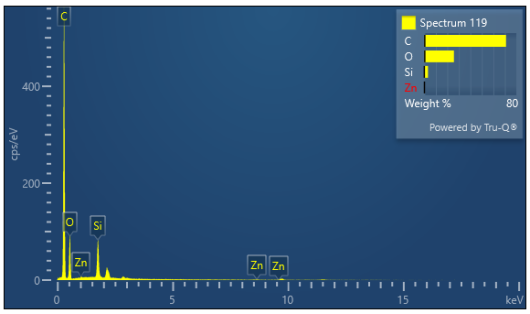
Figure S14 - Typical SEM images of measurements performed during the material synthesis (ES1).


Spectrum 111
C
O
Si
Zn
Weight % 70
Powered by Tru-Q®
cps/eV
keV


Spectrum 112
C
O
Si
Weight % 80
Powered by Tru-Q®
cps/eV
keV


Spectrum 113
C
O
Si
Weight % 80
Powered by Tru-Q®
cps/eV
keV


Spectrum 118
C
O
Si
Zn
Weight % 70
Powered by Tru-Q®
cps/eV
keV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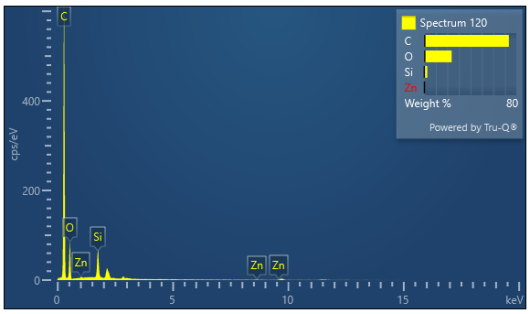
O
Si
Zn
Weight % 80
Powered by Tru-Q®
cps/eV
keV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Si
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Weight % 80
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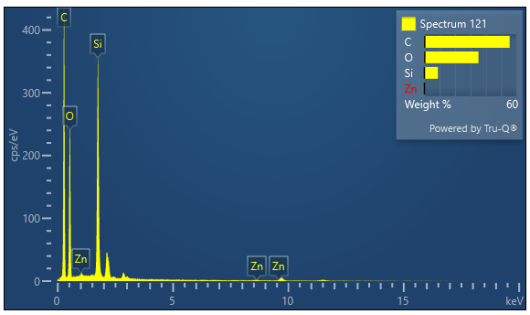
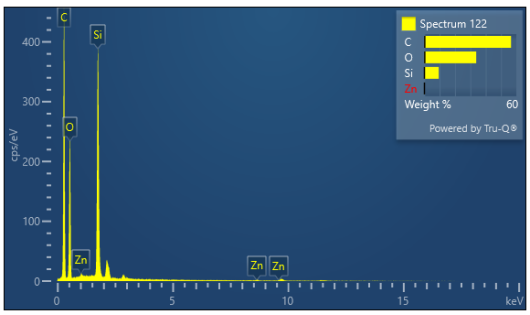
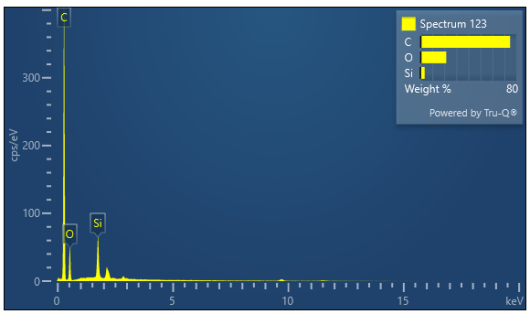
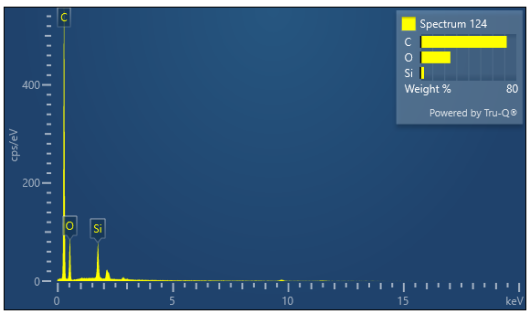
cps/eV
keV


Spectrum 121
C
O
Si
Zn
Weight % 60
Powered by Tru-Q®
cps/eV
keV


Spectrum 122
C
O
Si
Zn
Weight % 60
Powered by Tru-Q®
cps/eV
keV


Spectrum 123
C
O
Si
Weight % 80
Powered by Tru-Q®
cps/eV
keV


Spectrum 124
C
O
Si
Weight % 80
Powered by Tru-Q®
cps/eV
keV

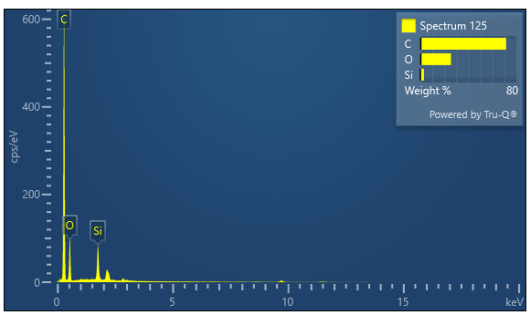

Spectrum 125
C
O
Si
Weight % 80
Powered by Tru-Q®
cps/eV
keV

Figure S15 – EDX spectra corresponding to SEM images in Figure S14 (ES1).

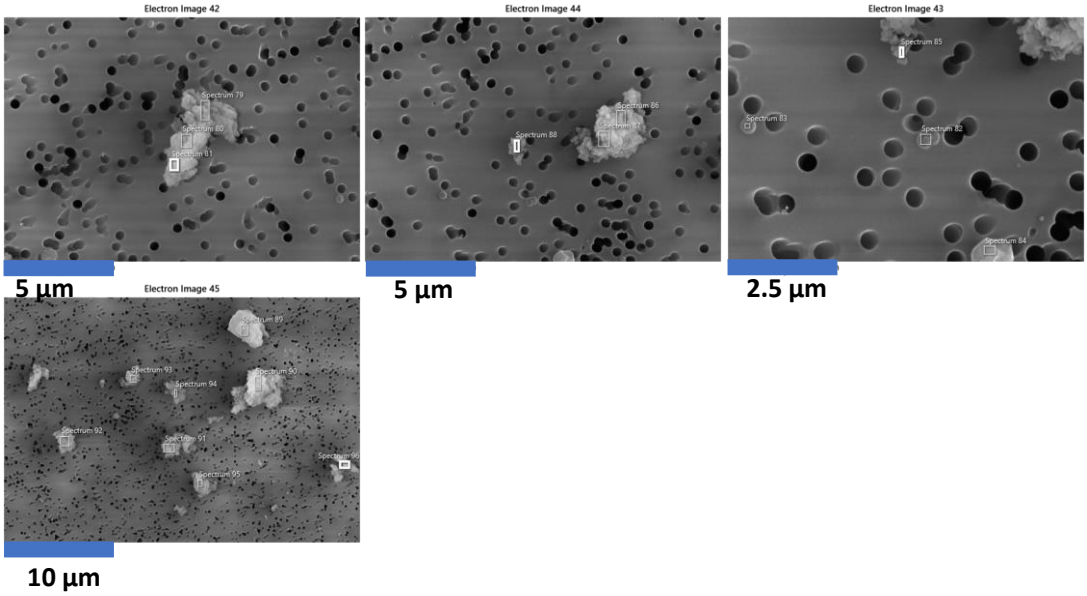
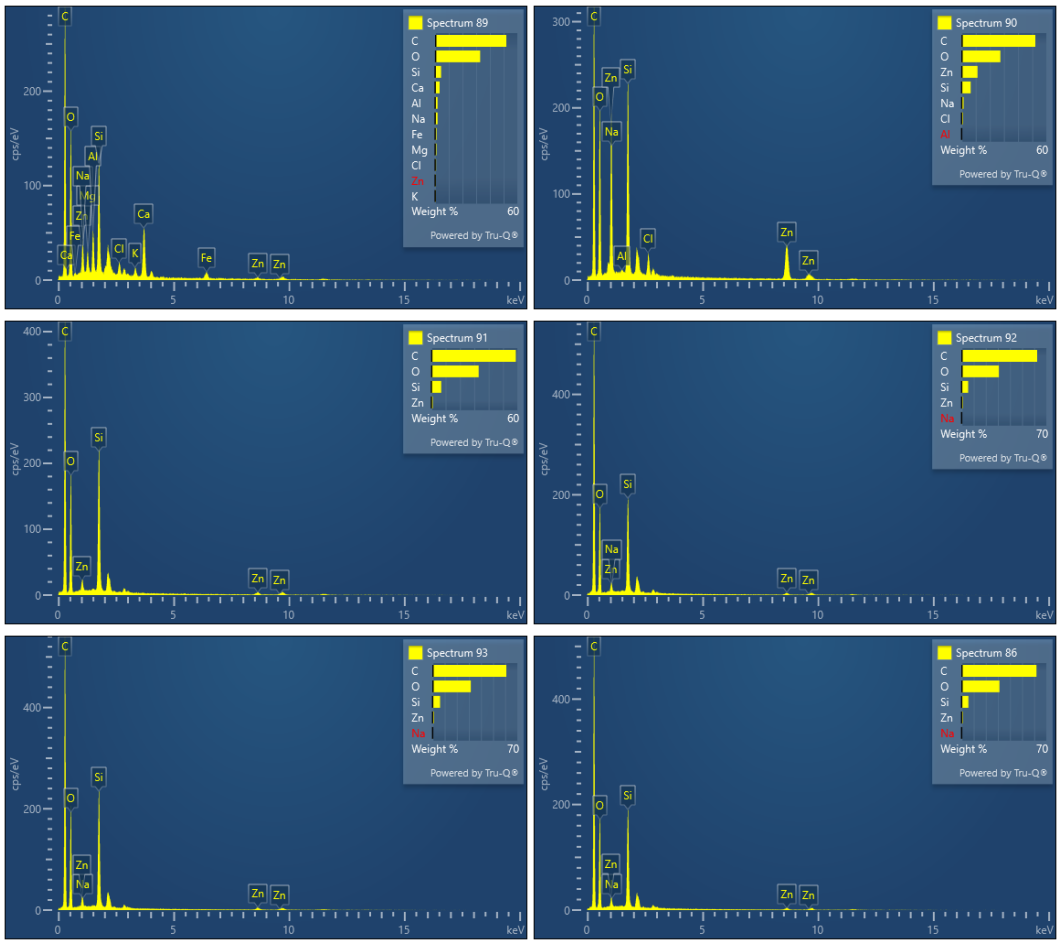


Figure S16 - Typical SEM images of measurements performed during the calcination process (ES2).



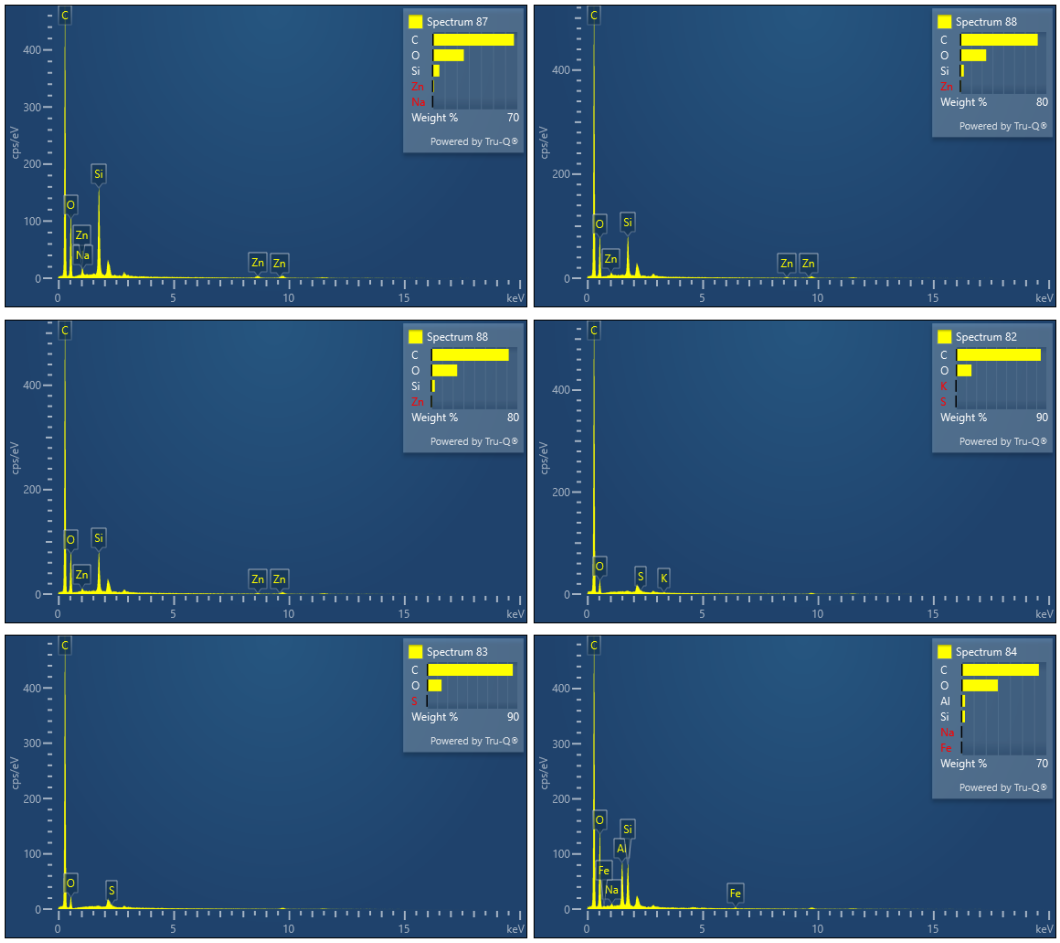


Figure S17 – EDX spectra corresponding to SEM images in Figure S16 (ES2).

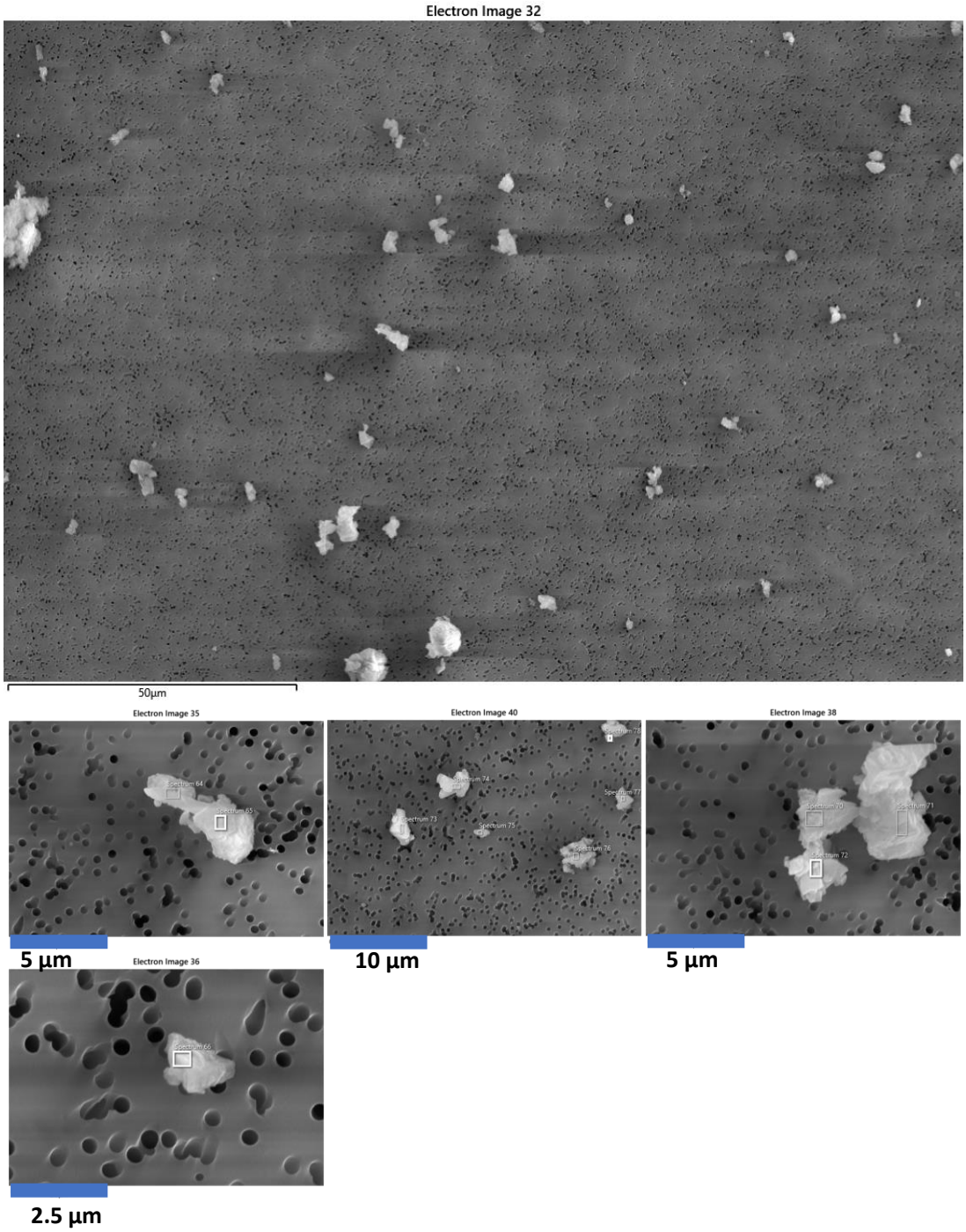


Figure S18 - Typical SEM images of measurements performed during the mortar formulation step (ES3).

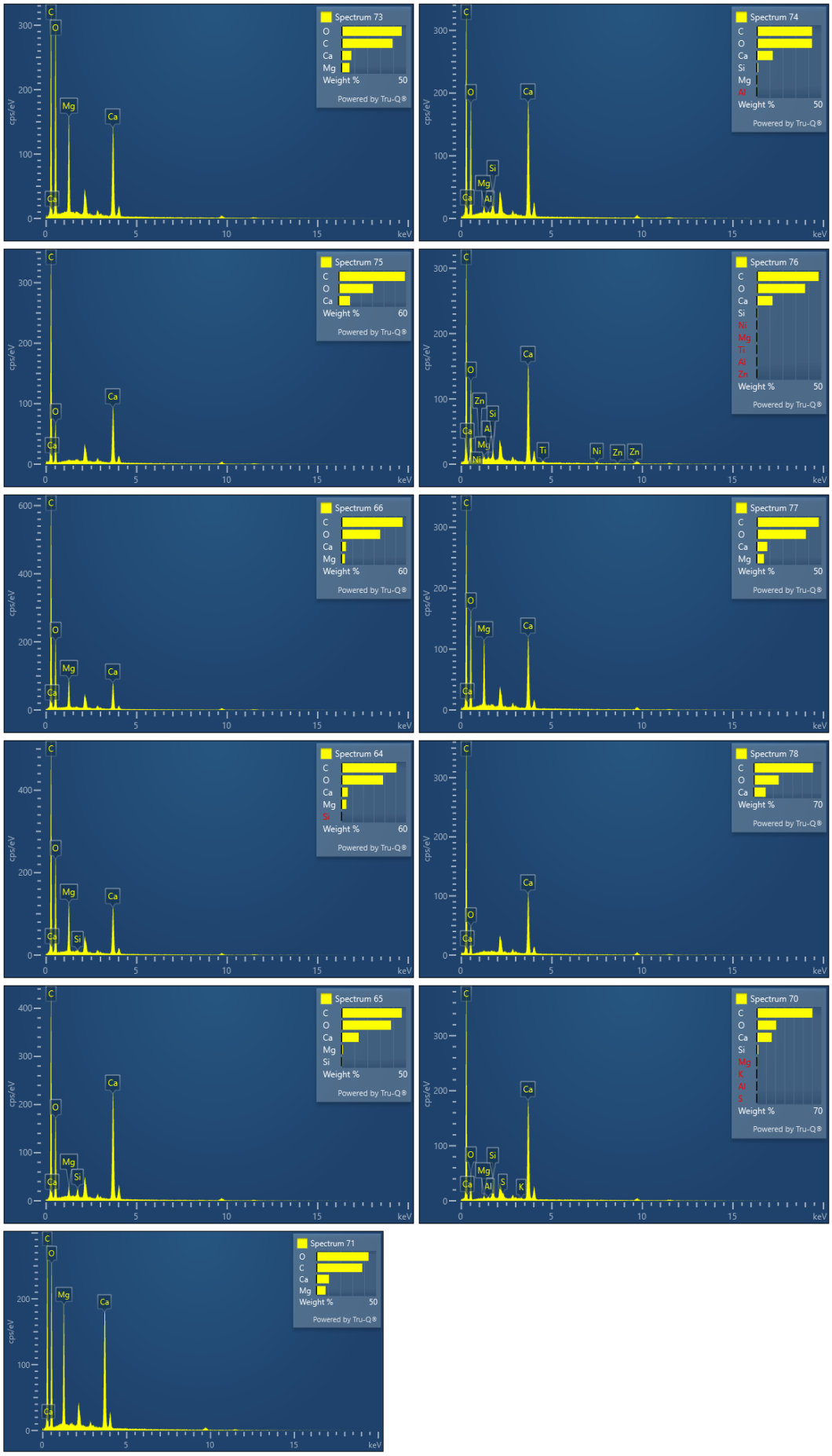


Figure S19 - EDX spectra corresponding to SEM images in Figure S18 (ES3).

Table S4 – Data collected by portable condensation particle counter (CPC) for ES1 and calculation of equation 1 for each activity performed with the relative significance (significant = the particle concentration is significantly above the particle background; not significant = the particle concentration is not significantly above the particle background).

Exposure Scenario	Contributive Exposure Scenario	Material	Results			
			BG	**Mean (#/cm³)**	**3.44E+03**	**Significance**
				Max (#/cm³)	**3.63E+03**	
				Std Dev	**7.45E+01**	
ES1	CES 1.1	SiO_2 & $ZnAc_2{\cdot}2H_2O$	NF	Mean (#/cm³)	3.34E+03	Not significant
				Max (#/cm³)	9.44E+01	
				C_{net}/C_{bg}	0.97	
				C_{netmax}/C_{bg}	0.03	
	CES 1.2	SiO_2 & $ZnAc_2{\cdot}2H_2O$	NF	Mean (#/cm³)	3.46E+03	Not significant
				Max (#/cm³)	5.24E+01	
				C_{net}/C_{bg}	1.01	
				C_{netmax}/C_{bg}	0.02	
	CES 1.3	SiO_2 & $ZnAc_2{\cdot}2H_2O$	NF	Mean (#/cm³)	3.46E+03	Not significant
				Max (#/cm³)	6.22E+01	
				C_{net}/C_{bg}	1.01	
				C_{netmax}/C_{bg}	0.02	
	CES 1.4	SiO_2 & $ZnAc_2{\cdot}2H_2O$	NF	Mean (#/cm³)	3.96E+03	Not significant
				Max (#/cm³)	1.32E+02	
				C_{net}/C_{bg}	1.15	
				C_{netmax}/C_{bg}	0.04	
	CES 1.5	SiO_2 & $ZnAc_2{\cdot}2H_2O$	NF	Mean (#/cm³)	4.34E+03	Not significant
				Max (#/cm³)	1.55E+02	
				C_{net}/C_{bg}	1.26	
				C_{netmax}/C_{bg}	0.05	

Table S5 – Data collected by portable condensation particle counter (CPC) for ES2 and calculation of equation 1 for each activity performed with the relative significance (significant = the particle concentration is significantly above the particle background; not significant = the particle concentration is not significantly above the particle background).

Exposure Scenario	Contributive Exposure Scenario	Material	Results			
			BG	**Mean (#/cm³)**	**6.11E+03**	**Exposure estimation significance**
				Std Dev	**1.49E+02**	
ES2	CES 2.1	SiO_2 & $ZnAc_2{\cdot}2H_2O$ / ZnO_2	NF	Mean (#/cm³)	6.16E+03	Not significant
				Max (#/cm³)	6.53E+03	
				C_{net}/C_{bg}	1.01	
				C_{netmax}/C_{bg}	1.07	
	CES 2.2	SiO_2 & $ZnAc_2{\cdot}2H_2O$ / ZnO_2	NF	Mean (#/cm³)	5.95E+03	Not significant
				Max (#/cm³)	6.31E+03	
				C_{net}/C_{bg}	0.97	
				C_{netmax}/C_{bg}	1.03	
	CES 2.3	SiO_2 & $ZnAc_2{\cdot}2H_2O$ / ZnO_2	NF	Mean (#/cm³)	3.30E+03	Not significant
				Max (#/cm³)	3.44E+03	
				C_{net}/C_{bg}	0.54	
				C_{netmax}/C_{bg}	0.56	
	CES 2.4	SiO_2 & $ZnAc_2{\cdot}2H_2O$ / ZnO_2	NF	Mean (#/cm³)	5.06E+03	Not significant
				Max (#/cm³)	5.35E+03	
				C_{net}/C_{bg}	0.83	
				C_{netmax}/C_{bg}	0.88	

Table S6 – Data collected by portable condensation particle counter (CPC) for ES3 and calculation of equation 1 for each activity performed with the relative significance (significant = the particle concentration is significantly above the particle background; not significant = the particle concentration is not significantly above the particle background).

Scenario	Contributive Scenario	Material	Results			
ES3			**BG**	**Mean (#/cm³)**	**3.38E+03**	**Significance**
				Std Dev	**4.52E+02**	
	CES 3.1	SiO_2 & ZnO_2 + mortar	NF	Mean (#/cm³)	3.21E+03	Not significant
				Max (#/cm³)	3.40E+03	
				C_{net}/C_{bg}	0.95	
				C_{netmax}/C_{bg}	1.01	
	CES 3.2	SiO_2 & ZnO_2 + mortar	NF	Mean (#/cm³)	3.14E+03	Not significant
				Max (#/cm³)	3.27E+03	
				C_{net}/C_{bg}	0.93	
				C_{netmax}/C_{bg}	0.97	
	CES 3.3	SiO_2 & ZnO_2 + mortar	NF	Mean (#/cm³)	3.02E+03	Not significant
				Max (#/cm³)	3.21E+03	
				C_{net}/C_{bg}	0.90	
				C_{netmax}/C_{bg}	0.95	
	CES 3.4	SiO_2 & ZnO_2 + mortar	NF	Mean (#/cm³)	3.00E+03	Not significant
				Max (#/cm³)	3.19E+03	
				C_{net}/C_{bg}	0.89	
				C_{netmax}/C_{bg}	0.95	

Hazard assessment of the MCNM precursors – *In vitro* toxicity testing (step 1)

Cytotoxicity was assessed by measuring the metabolic activity of the cells (assessed by the Alamar Blue assay). The cells were maintained in RPMI media (Sigma, RNBB2729) supplemented with 10% v/v fetal bovine serum (FBS; Gibco 413105K; heat inactivated), 1% Penicillin and Streptomycin (Gibco I think, check HW stock consumables) and 1% L-glutamine (corresponds to 2 mM L-Glutamine). The stock cultures of THP-1 cells were maintained in T75 Flasks at 37°C in the presence of 5% CO_2.

On reaching approximately 80% confluence, the non-adherent cells were tipped from the flask into a 15 ml Falcon tube and centrifuged at 900 g for 5 minutes. The supernatant was removed, and the cells were resuspended in 5 ml of RPMI medium containing 10% fetal calf serum (FCS), 1% Penicillin and Streptomycin and 1% L-glutamine (corresponds to 2 mM L-Glutamine), before counting in the presence of Erythrosine B 0.9% (cell suspension: Erythrosine B 0.9% 9:1 dilution). Cells with a viability of greater than 90% were accepted for further use before dilution to $5x10^5$ cells/mL. To differentiate the THP-1 cells to macrophage phenotype, an appropriate volume of a 100 µg/mL stock (phorbol 12-myristate 13-acetate; CAS Number 16561-29-8, Sigma P8139-1MG, (PMA)) was added to obtain the working concentration of 100 ng/ml. The resultant cell suspension was placed into a 96 well plate, 100 µL/well. The cells were placed in an incubator (37°C in the presence of 5% CO_2) for 24 hours to allow differentiation and adherence of macrophages. After 24 hours PMA-containing media was removed and replaced with 200 µL/well of fresh 10% FCS, 1% P/S, 1% L-Glut RPMI 24 hours prior to addition of treatments.

Human health and environmental aspects in the final application phase (step 3)
Dissolution investigation

Calibration curves with Zn and Si standard solutions were built by selecting 10 concentrations ranging from 0 to 25 mg/L. The wavelength selected with the best signal-to-noise ratio were 213.857 nm and 212.412 nm for Zn and Si, respectively. The limit of detection (LOD), calculated as 3 times the standard deviation of the blanks, was 0.08 $mg \cdot L^{-1}$ for Si and 0.0007 $mg \cdot L^{-1}$ for Zn.

References

1 C. Asbach, T. A. J. Kuhlbusch, B. Stahlmecke, H. Kaminski, H. J. Kiesling, M. Voetz, D. Dahmann, U. Götz, N. Dziurowitz and S. Plitzko, in *Safety of Nanomaterials along Their Lifecycle: Release, Exposure, and Human Hazards*, 2014, pp. 233–246.