




Research Article

New approach to nanolime synthesis at ambient temperature

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Abstract

This study explored the viability of synthesising nanolime at ambient temperature by raising calcium solubility through the formation of complexes with dissolved sugars. Micro-Raman findings confirmed the formation of nanolime particles whilst the percentage of $\text{Ca}(\text{OH})_2$ formed, observed to vary with synthesis conditions, was calculated with thermogravimetry. Nanoparticles were synthesised most productively (77%) in a 5% sugary solution at a temperature of 25 °C and a 4 h reaction time. The hexagonal nanoparticles synthesised ranged in size from 200 to 25 nm. Portlandite formation is related to calcium complex formation with less mannitol than sucrose needed to form similar NPs of $\text{Ca}(\text{OH})_2$. The sugary media also favoured the formation of amorphous calcium carbonate.

Keywords Nanolime · Room temperature · Sugary solution · Micro-Raman · Thermogravimetry

1 Introduction

Products to protect and conserve historic-artistic heritage materials must be designed and developed with care, for inappropriate use may hasten deterioration. Whilst the earliest treatments were organic substances [1], in light of the issues that arose around substrate compatibility (mainly stones), today inorganic compounds are deemed more suitable and physically and chemically more substrate-compatible, although they have been less thoroughly researched [2].

One of the materials most commonly used in protection and conservation treatments is lime [$\text{Ca}(\text{OH})_2$, also known as portlandite], primarily as a surface coating or a limestone consolidant [3–5]. Its application poses two basic problems, however: low water solubility and slow carbonation. With a water solubility of 1.7 g/L at 20 °C, $\text{Ca}(\text{OH})_2$ requires large quantities of water to obtain an acceptable calcium concentration in the solution. Carbonate in turn is known to depend on CO_2 concentration and relative

humidity [6], both of which are difficult to control in outdoor environments. Different additives producing rapid carbonation have been studied [7, 8] following different strategies such as diethyl carbonation addition.

Nanolime synthesis is presently being explored to develop a treatment compound as the possible solution to those two problems. Nano- $\text{Ca}(\text{OH})_2$ can be synthesised homogeneously or heterogeneously. In the former, the hydroxide precipitates out of an aqueous solution containing a strong base (NaOH) and a highly soluble calcium salt (CaCl_2 or $\text{Ca}(\text{NO}_3)_2$). Heterogeneous precipitation is based on CaO hydration in excess water. Most research has been conducted using the homogeneous procedure. In Salvadori and Dei [9] pioneered nanolime synthesis in an alcoholic medium, applying the method for synthesising nano- $\text{In}(\text{OH})_3$ described by Pérez-Maqueda [10]. They successfully synthesised $\text{Ca}(\text{OH})_2$ nanoparticles from 30 to 60 nm at 150 °C. Under the experimental conditions designed for synthesis, namely supersaturation, high temperature and slow mixing time, $\text{Ca}(\text{OH})_2$ nucleation was

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favoured over particle growth, inducing the precipitation of nano-sized calcium hydroxide particles [10–15]. The aggregated nanoparticles were subsequently dispersed (peptised) in an alcoholic medium. Although nanolime was initially regarded as inert in alcohol, Rodriguez-Navarro et al. [16], studying the effect of an alcoholic medium on $\text{Ca}(\text{OH})_2$ nanoparticle formation, observed the presence of Ca alkoxides able, among others, to retard the carbonation rate.

Building on those synthesis studies, in Daniele et al. [17] found that the aforementioned nanoparticles could be efficiently carbonated. Applying the homogeneous procedure and dissolving calcium chloride in Triton X-100, Daniele and Tagliere [18] synthesised hexagonal nano- $\text{Ca}(\text{OH})_2$ at 90 °C, obtaining particle sizes of under 200 nm and reducing nanoparticle preparation time by 25%. Recently the effects of natural polysaccharide on the formation of vaterite at 95 °C has been reported [19].

To date, nanolime has been synthesised at temperatures of around 100 °C [9, 20, 21] or higher [22] to decrease calcium solubility. Ambient temperature synthesis, based on the use of exchange resins, has been proposed only recently [23].

This study explores the viability of synthesising nanolime at ambient temperature by raising calcium solubility through the formation of complexes. Calcium is known to form complexes with some sugars [24], which raise its ambient temperature solubility [25, 26] to yield more concentrated nanoparticle solutions. Additionally, organic compounds are capable of complexing ions, when possess, at least, one pair of oxygen atoms closed to neighbouring carbons [27]. In this work both sucrose (aromatic) and mannitol (aliphatic) have been selected.

The nanolime synthesised at ambient temperature in sugary solutions in this study was characterised for structure and composition (micro-Raman and DTA) as well as size and shape (TEM). Subsequent in-depth research will address the viability of deep penetration into damaged materials, high reactivity and speedy reactions.

2 Experimental

2.1 Materials

The reagents used were Merck 99% pure calcium chloride, Panreac 98% pure sodium hydroxide, Panreac 99% pure sucrose and Panreac 99% pure mannitol.

2.2 Nanoparticle preparation

Solutions of 5% or 10% sucrose or mannitol were prepared in Milli-Q ultrapure, decarbonated water and used, 10 mL per sample, to dissolve CaCl_2 to a molarity of 5 M or 3 M. A 3 M NaOH solution prepared in 50 mL of the aforementioned ultrapure water was then mixed with the sugary solution in a 250 mL Erlenmeyer flask and constantly stirred at ambient temperature for 4 h or 24 h. The variables used in nanolime synthesis are given in Table 1.

At the specified reaction time, the solutions were vacuum filtered and the solid rinsed several times with decarbonated water.

In order to determine the particle size and distribution, an image analyzer software, Digimater, was used and 10–30 particles were analysed for each sample.

Table 1 Initial sample composition, reaction times, reaction yield and particle shape

Sample	Reaction time (h)	Sucrose solution (%)	Mannitol solution (%)	$[\text{Ca}^{2+}]$ (mmol)	$[\text{NaOH}]$ (M)	Particle size (nm)	Particle shape	$\text{Ca}(\text{OH})_2$ formation (%)
S1	4	10		20	3	37–142 ± 33	Hexagonal	46.0
S2	24	10		20	3	12–45 ± 15	Hexagonal	69.9
S3	4	5		20	3	6–16 ± 5	Spherical	75.2
S4	24	5		20	3	9–32 ± 6	Spherical	60.8
S5	24	10		10	3	8–24 ± 5	Polygon	27.5
S6	24	5		10	3	13–36 ± 6	Spherical	68.6
M1	4		10	20	3	7–22 ± 5	Polygon	62.9
M2	24		10	20	3	20–70 ± 10	Hexagonal	65.8
M3	4		5	20	3	21–60 ± 12	Spherical	76.5
M4	24		5	20	3	95–182 ± 37	Polygon	48.9
M5	24		10	10	3	21–45 ± 5	Hexagonal	63.3
M6	24		5	10	3	55–97 ± 17	Hexagonal	60.0

Bold and italics indicates samples with lower particle size; bold indicates samples with higher reaction yield

2.3 Characterisation techniques

The crystal phases of the synthesised samples was determined by analysing the nanoparticles under a Renishaw InVia micro-Raman spectrometer fitted with a Leica microscope and laser diode (785 nm)- and Renishaw YAG:Nd (532 nm) laser-based excitation. The measuring conditions were: laser output power, 25 mW for the 785 nm laser and 5 mW for the 532 nm laser; acquisition time, 10 s; one accumulation; microscope magnification, 50 \times . Laser frequency and intensity were calibrated with a silicon standard prior to use.

One drop of each sample liquid was ultrasound-dispersed in 10% ethanol and deposited on a carbon-coated copper grid for study under a Hitachi-8000 transmission electron microscope to determine nanoparticle size and shape.

The yield for each synthesis procedure, defined as the amount of Ca(OH)₂ formed in the samples, was determined on a PerkinElmer thermogravimetric analyser (DTA), heating the samples in a nitrogen atmosphere from 25 to 950 °C at a rate of 10 °C/min.

3 Results and discussion

Nano-Ca(OH)₂ was synthesised under the 12 sets of conditions described in Table 1, six in sucrose and six in mannitol.

All the micro-Raman spectra reproduced in Fig. 1 for the samples synthesised in sucrose exhibited signals characteristic of portlandite: a narrow, high intensity band at 3618 cm⁻¹ attributed to O–H bond stretching vibrations and a medium intensity, medium width band at 358 cm⁻¹,

associated with Ca–O bond lattice vibrations [28]. All the samples also contained a wide, medium intensity signal in the 1100 cm⁻¹ to 1050 cm⁻¹ range, generated by carbonate group vibrations. Enlarging the 1200 cm⁻¹ to 900 cm⁻¹ range revealed a band in some samples at 1085 cm⁻¹ or 1070 cm⁻¹. Both could be attributed to carbonate (ν_1) group symmetric stretching vibrations, the first generated by calcite [29] and the second by amorphous carbonates (ACC) [30].

The spectra for the mannitol solutions (Fig. 1) were similar under all synthesis conditions, with portlandite generating the most intense signals. As in sucrose, signals indicative of both crystalline (calcite) and amorphous calcium carbonate formation were observed, with the latter prevailing over calcite. The carbonate signals were more intense here than when the nanoparticles were synthesised in a sucrose solution. Under both sugary solutions sucrose and mannitol, portlandite is formed, as well as calcium carbonate. In order to quantify the amount of different compounds formed, thermogravimetric analysis was performed in all the samples.

The thermogravimetric curves reproduced in Fig. 2 for the nanolime-containing solutions showed similar weight loss patterns in all 12 samples. Four distinct weight loss zones could be identified on the thermograms: 25 °C to 120 °C (elimination of moisture); 120 °C to 330 °C (amorphous calcium carbonate dehydration [31]); 345 °C to 420 °C (calcium hydroxide dehydroxylation); and 430 °C to 800 °C (calcium carbonate decarbonation).

Table 2 gives the DTA-determined mass loss in the various temperature ranges, indicative of the percentage of amorphous carbonates, lime and crystalline calcium carbonate present in the sample solutions as per the equations shown below.

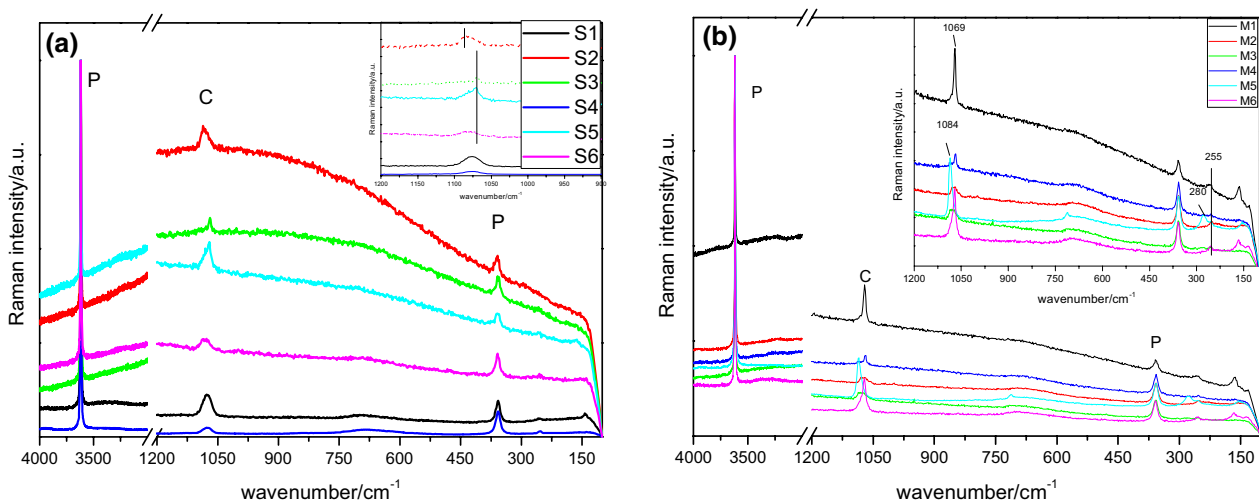


Fig. 1 Raman spectra for the nanoparticles synthesised in **a** sucrose and **b** mannitol (laser λ = 532 nm). P = Ca(OH)₂; C = CaCO₃

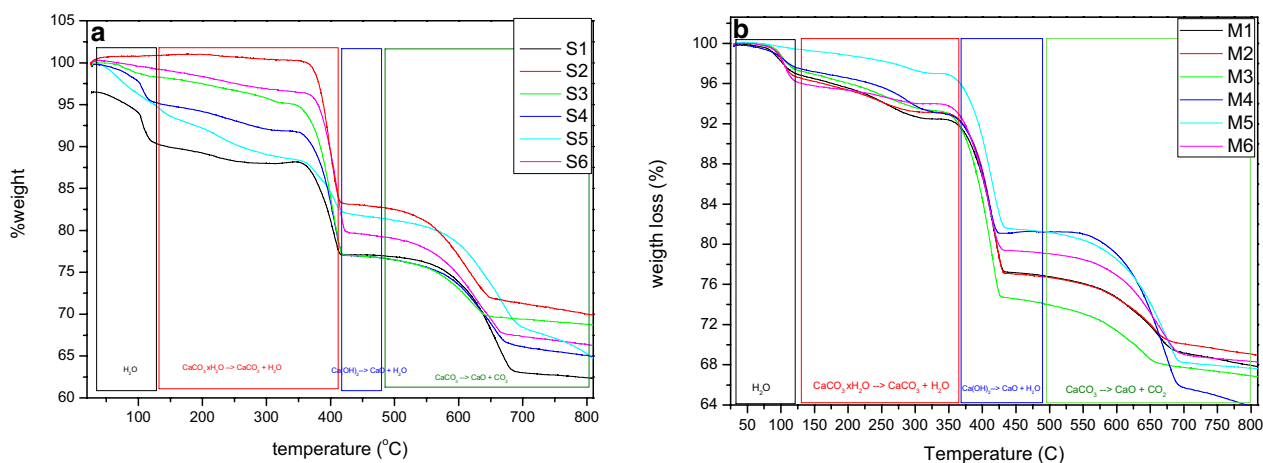
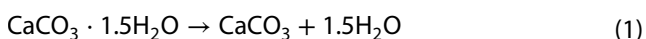


Fig. 2 Thermogravimetric curves for nanolime-containing a sucrose and b mannitol solutions

Table 2 DTA-determined percentages of ACC, Ca(OH)₂ and CaCO₃

% of mass (T in °C)	S1	S2	S3	S4	S5	S6
%H ₂ O (25–120 °C)	5.9	0	1.7	4.3	5	0.7
% ACC (120–330 °C)	11.3	0	15.1	16.9	29.6	13.2
% Ca(OH) ₂ (345–420 °C)	46.04	69.89	75.23	60.84	27.54	68.65
% CaCO ₃ ^a (430–800 °C)	22.3	30.0	3.6	10.3	21.8	16.8
	M1	M2	M3	M4	M5	M6
%H ₂ O (25–120 °C)	3.1	3.3	2.7	2.4	0.5	3.9
% ACC (120–330 °C)	20.7	17.4	19.3	21.2	11.7	9.9
% Ca(OH) ₂ (345–420 °C)	62.9	65.8	76.5	48.9	63.3	60.0
% CaCO ₃ ^a (430–800 °C)	0.44	1.0	1.4	18.4	20.1	15.3

^aCrystalline calcium carbonate



Further to the weight loss data in the 345 °C to 420 °C range (Table 2), lime formation were greater than 50% except in all synthesis solutions except S1 (t=4 h, 10% sucrose), S5 (t=24 h, 10% sucrose) and M4 (t=24 h, 5% mannitol). The data also showed that the highest amount of calcium hydroxide in both cases was obtained when synthesis was conducted for 4 h at 5% sugar with the highest calcium concentration (S3 and M3). According to those findings, a 5% concentration of sucrose dissolved sufficient calcium to synthesise nanolime. Amorphous calcium carbonate was formed in all cases as well as crystalline carbonate.

Representing the amount of Ca that forms portlandite versus initial amount of Ca per mol of sucrose or

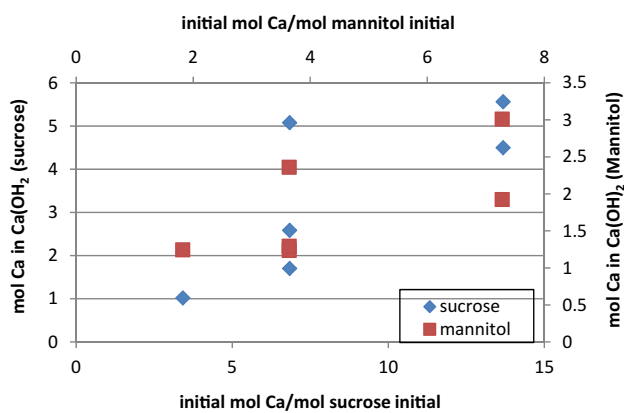


Fig. 3 Initial mol Ca/mol sugary solution versus mol Ca in portlandite

mannitol (Fig. 3) is observed that more $\text{Ca}(\text{OH})_2$ is formed as the initial mol Ca/mol sugary solution increases, then portlandite formation is related to calcium complex formation. According to Pannetier [24] a calcium-sucrose complex is formed with different calcium molecules, depending on the calcium/sucrose ratio. Assuming calcium-sugary solution complex formation from Pannetier results, and trying to understand the effect of sucrose or mannitol in calcium complexation, the ratio of the mol of calcium that forms portlandite against the mol of sugary solutions was calculated. Then Table 3 shows the amount of calcium that forms a complex with the sucrose or mannitol to form the nanoparticles of $\text{Ca}(\text{OH})_2$ showing that mannitol needs less moles of calcium to form NPs of $\text{Ca}(\text{OH})_2$. Six-calcium coordination promotes sucrose polymerization [21] and further the complexes formed involves between 1 and 5 mol of calcium per sucrose mol. For the mannitol, as a monomeric molecule, calcium complexation is lower than for sucrose with 1.2–3 mol of calcium per mannitol mol. At this point computer simulations and modelling approaches will be required to improve our understanding of the influence of sugary solutions on the nanolime formation.

According to the DTA curves reproduced in Fig. 4, sample M5 had no peak in the range (25 °C to 120 °C) associated with adsorbed water loss. The exothermal peak attributed to ACC conversion to crystalline calcium carbonate [30] was not visible on this curve either, for at around 340 °C it overlapped with the peak denoting exothermal calcium hydroxide dehydroxylation. The absence of peaks at 186 °C and 166 °C, the melting points of sucrose and mannitol, respectively, was an indication that neither sugar was present in the solid samples.

Table 3 Mol Ca that forms nanoparticles of $\text{Ca}(\text{OH})_2$ versus mol of sucrose or mannitol

Sample	Mol Ca in CH/mol sucrose
S1	1.70
S2	2.58
S3	5.56
S4	4.50
S5	1.02
S6	5.08
Sample	Mol Ca in CH/mol mannitol
M1	1.24
M2	1.29
M3	3.01
M4	1.92
M5	1.25
M6	2.36

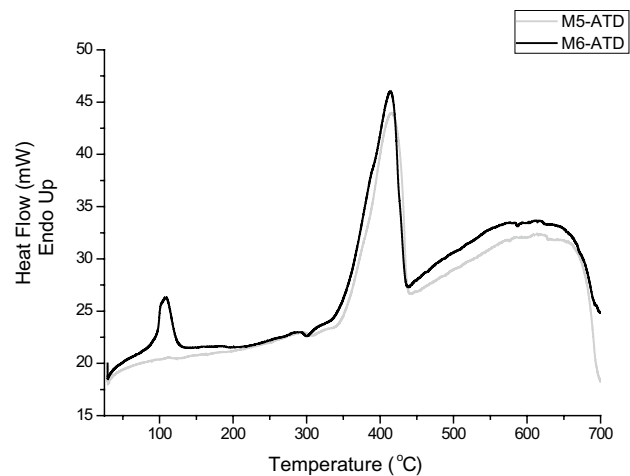


Fig. 4 DTA curves for samples M5 and M6 in the 25 °C to 700 °C range

It is also interesting to remark that ACC, which is less stable than calcite, formed during nanolime synthesis thanks to the stabilisation of this amorphous compound in the presence of organic compounds [32] (sucrose and mannitol in this study).

Nanolime particle size and shape, determined with TEM techniques, are given in Table 1 and Fig. 5. Where mannitol was the solvent, the particles were consistently hexagonal, with size varying from 10 to 50 nm, except in solution M4 (24 h, 5% mannitol) which produced very large particles, at around 200 nm. In the sucrose solutions, particle size was also generally small (approximately 5 nm to 50 nm), except where synthesis was conducted at 10% for 4 h (S1), when size ranged from 40 to 150 nm. The solutions yielding the smallest nano- $\text{Ca}(\text{OH})_2$ particles had a 5% sucrose concentration, 20 mmol of CaCl_2 and a reaction time of 4 h (S3), then it is not necessary a high sucrose solution. However, for mannitol solution, higher concentration is needed for lower particle size.

Particle morphology varied when sucrose was the solvent, whereas mannitol generated consistently hexagonal particles. Significantly, despite the differences in effectiveness of the synthetic procedures used, the nanolime obtained always exhibited more or less regular shapes.

With a 24 h reaction time and 10% sugar concentration, reducing the calcium content from 20 mmol (S2/M2) to 10 mmol (S5/M5) lowered nanoparticle formation, much more notably in sucrose (from 70 to 27%) than in mannitol (from 66 to 63%). As sucrose and calcium can combine into an adduct [24, 33] and the 10% medium (S2 and S5) contained more sugar (than the 5% medium) able to form Ca complexes, less of the element was free to generate nanolime. At a lower calcium concentration, the percentage of nanoparticles consequently declined

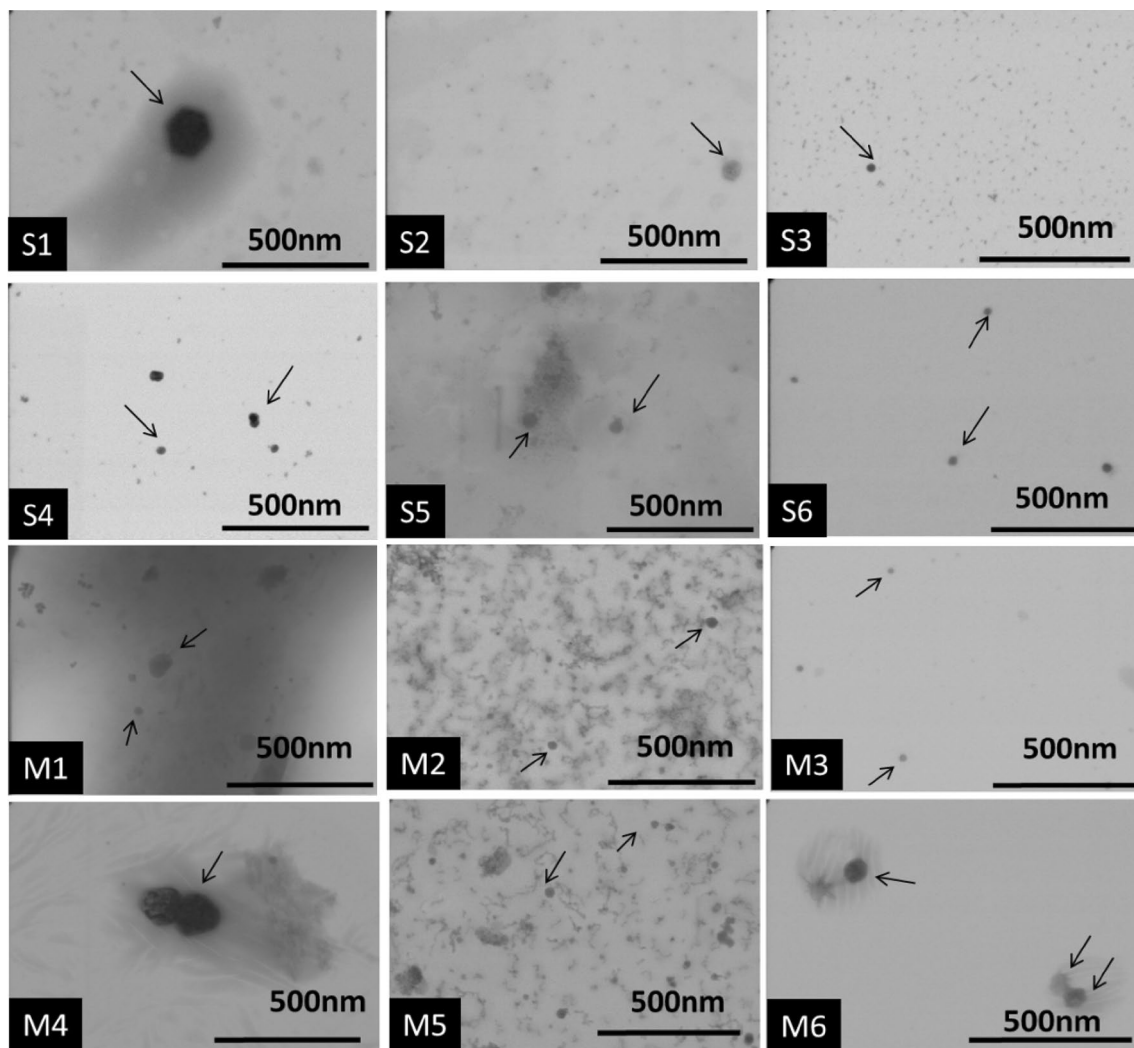


Fig. 5 TEM micrographs of the 12 samples synthesised

(from 70% in S2 to 27% in S5). In 5% solutions, in contrast, lowering the calcium concentration had the opposite effect, slightly raising the nanolime yield (from 24% in S3 to 28% in S6). Calcium adduct formation at different concentrations of the two solutions would be a line of research worth pursuing.

Whilst the type of sugar appeared to have no obvious impact on particle size, it did impact calcium hydroxide formation, for mannitol generated a higher percentage of nanolime (49% to 76%) than sucrose (27% to 75%).

4 Conclusions

Calcium hydroxide nanoparticles were obtained at ambient temperature using sucrose and mannitol in 10% and 5% solution.

Both micro-Raman and DTA studies confirmed nanolime formation at portlandite formation ranging from 27 to 77%, depending on the experimental conditions. Yield was highest at: $T = 25\text{ }^{\circ}\text{C}$; reaction time = 4 h; solvent (sucrose or mannitol) concentration = 5%; calcium content = 20 mmol; and NaOH molarity = 3 M.

The smallest nanoparticles were obtained under the following conditions: $T = 25\text{ }^{\circ}\text{C}$; reaction time = 4 h; solvent (sucrose or mannitol) concentration = 5 or 10% respectively; calcium content = 10 mmol; and NaOH molarity = 3 M. The findings confirmed the viability of synthesising nano- $\text{Ca}(\text{OH})_2$ at ambient temperature.

In mannitol the nanoparticles were consistently hexagonal, whereas in sucrose shape varied (hexagonal, spherical, polygon) depending on experimental conditions. Synthesis conducted in a 5% mannitol solution containing 20 mmol of calcium for 24 h yielded very large (200 nm) particles.

Portlandite formation is related to calcium complex formation with less mannitol that sucrose needed to form similar NPs of $\text{Ca}(\text{OH})_2$. Furthermore modelling studies will be required.

The sugar content favoured amorphous calcium carbonate formation.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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