

# A biomimetic approach to strengthen and protect construction materials with a novel calcium-oxalate–silica nanocomposite



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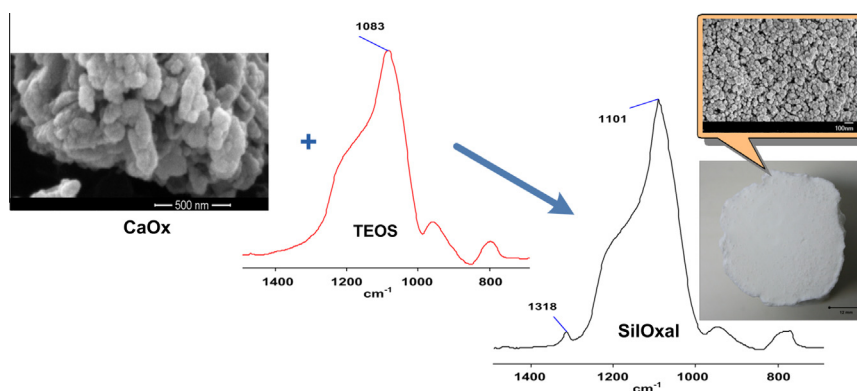
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## HIGHLIGHTS

- Nano-calcium oxalate monohydrate colloidal solution was synthesised in alcohol (CaOx).
- Incorporation of CaOx in TEOS yields a crack-free, stable nanocomposite (SilOxal).
- Mesoporous microstructure of SilOxal has physico-chemical compatibility with stone.
- SilOxal does not alter the microstructure of the treated stone.
- SilOxal improves the hygric properties and the tensile strength of stone.

## GRAPHICAL ABSTRACT



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## ABSTRACT

A novel biomimetic nanocomposite composed of amorphous silica and calcium oxalate has been efficiently synthesised by incorporating materials of low toxicity and cost, imitating a stable binary system occurring in well-preserved areas of monuments, plant biomineralisation and the industrial processing of sugar. A simple two-step and cost-effective reaction route involving calcium hydroxide and oxalic acid dihydrate in isopropanol as precursors yielded a colloidal solution of nano-calcium oxalate; this solution was mixed with tetraethoxysilane to produce a crack-free mesoporous xerogel with pore radius of approximately 15 nm. Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), differential thermal-thermogravimetric analysis (DTA-TG) and scanning electron microscopy (SEM) studies demonstrated that the nano-calcium oxalate embodiment into the silica matrix resulted in a crack-free nanocomposite. This nanocomposite penetrated deeply and was distributed homogeneously within the treated porous medium. The hygric properties and tensile strength of treated samples were improved without affecting the microstructural characteristics. The colour and water vapour permeability changes were ranged within acceptable limits. The physico-chemical stability and compatibility of the nanocomposite with stone created a potential strengthening agent with a partial protective effect for inorganic porous building materials.

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## 1. Introduction

Over the last few decades, the natural and anthropogenic induced weathering of architectural structures led to the introduction of silicon based polymeric resins to be used as consolidating and protective agents [1]. Among the most popular commercial products are tetraethoxysilane (TEOS) and the alkoxysilanes, which, upon the influence of atmospheric moisture, can be polymerised in the pores of the building materials to create a silica matrix that stabilises the structure [2,3]. The low viscosity of the initial sols allows their in-depth penetration and homogeneous distribution, followed by hardening and the formation of Si-O-Si links similar to those found in certain minerals in building materials. Despite their numerous advantages and improved properties (physical, chemical, mechanical, thermal and antibacterial), alkoxysilanes present important drawbacks, such as inefficient chemical bonding to calcite and a tendency to crack during shrinkage and drying [4,5]. Cracking is generated by the high capillary pressure generated by the gel network during drying. Several attempts to minimise this effect include the addition of different inorganic metal salts, oxides or metal organic alkoxides [6] and non-ionic surfactants, such as *n*-octylamine [7]. These additives produced a mesoporous matrix with uniform size and/or reduced the surface tension of the solvent, thus promoting a reduction in the capillary pressure and avoiding cracks during drying [7,8].

The purpose of this work is to develop and assess a new crack-free calcium oxalate–silica nanocomposite for strengthening both historic and modern building materials, imitating processes occurring both in nature and industry. This novel nanocomposite was derived from modification of TEOS with calcium oxalate nanoparticles, taking advantage of the low viscosity of ethyl silicate and the ability of the nano-materials to fill micro-cracks and gaps. The choice of calcium oxalate was based on previous studies that have shown that in well-preserved layers-patinas on monument surfaces, silicate phases associated with calcium oxalate were considered transformation products of protective treatments conducted in the past [9–11]. In plants, calcium carbonates, calcium oxalates and amorphous silica are the most common forms of biomineralisation because of metabolic activity [12,13]. In industry, an intrac-table and stable composite of calcium oxalate–amorphous silica was formed in industrial sugar mill evaporators [14,15].

For all of the above reasons, nano-calcium oxalate was introduced in a synthesised nanocomposite based on TEOS, aiming to configure the pore structure of the final xerogel and provide a matrix compatible with calcareous building materials. The synthesis of nano-calcium oxalate was carried out from the reaction of calcium hydroxide with oxalic acid, followed by its incorporation into TEOS. The above reagents play a crucial role in the successive admixture with TEOS, as an excess of acid or base in the nano-calcium oxalate synthesis can promote both the catalysis of the sol-gel process of TEOS and the carbonate formation in the stone matrix. Furthermore, the nano-scale dimensions of calcium oxalate lead to better integration into the silicate matrix to achieve stability of the final product. The production of a crack-free product was augmented by the addition of the surfactant *n*-octylamine [7,8]. The innovation in this work is twofold. Firstly, the main component found on the patinas was introduced as part of an efficient consolidant, and secondly, nontoxic raw compounds were used as catalysts for the sol-gel process during the nano-calcium oxalate synthesis.

The synthesised product has been characterised and evaluated for its effectiveness as a combined consolidant and potential protective (hydrophobic) agent on a bioclastic limestone that is frequently found in the historic and modern architectural structures in the Mediterranean basin.

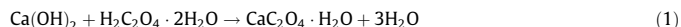
## 2. Experimental section

### 2.1. Synthesis of (a) nano-calcium oxalate and (b) hybrid silica–calcium oxalate

TEOS, *n*-octylamine (Oct) and isopropanol (ISP) (puriss. p.a.) were supplied by Sigma-Aldrich (Taufkirchen, Germany), calcium hydroxide (CH) was supplied by Fluka (St. Gallen, Switzerland), and oxalic acid dihydrate (Oxac) was supplied by Panreac (Barcelona, Spain).

The experimental part of this research included two stages: (a) Firstly, a colloidal solution defined as CaOx-s that contained as a major part calcium oxalate monohydrate (COM) nanoparticles was synthesised by the reaction of CH and Oxac in stoichiometric proportions in the presence of ISP (see Eq. (1)); (b) Secondly, TEOS and Oct were added into the CaOx-s. This synthesis, which is outlined in Fig. 1 of the supporting material, led to the formation of the final colloidal solution defined as SiOxal-s.

In the first stage, two separate alcoholic solutions were prepared by dissolving CH 1.01% w/v and Oxac 1.72% w/v in ISP. The solutions of CH and Oxac were separately stirred for 10 min under ultrasonic agitation, and then they were mixed to give the CaOx-s, which was kept under the same agitation for 12 h. Afterwards, the CaOx-s was vigorously stirred with a magnetic agitator for another 24 h; this reaction time was computed according to analyses of powders of dried CaOx-s, which indicated that in 24 h, the maximum amount of COM nanocrystals were achieved (Eq. (1)) [16]. The term CaOx-p refers to the dried powder obtained from the CaOx-s, in which the major part is COM with an amount of remaining CH.



In the second stage, TEOS was added into the entire CaOx-s solution at a molar ratio of TEOS/CaOx-p (0.5/0.03), under ultrasonic agitation for 2 h. The water produced in the reaction in Eq. (1), along with the remaining CH, can facilitate the hydrolysis of TEOS. Afterwards, Oct, acting as a surfactant [8,17], was added under vigorous stirring to obtain SiOxal-s. The mole ratio of SiOxal-s was TEOS/CaOx-p/H<sub>2</sub>O/ISP/Oct (0.5/0.03/0.09/7.15/0.05). The SiOxal-s was placed in a round-bottom flask containing a magnetic stirrer and was stirred for approximately 3 h at room temperature.

After completion of the synthesis, the SiOxal-s was cast into transparent cylindrical moulds that were 5.5 cm in diameter and 2 cm in height. The moulds were covered with perforated Parafilm to allow gentle evaporation of the solvent. Gelation and drying occurred by simple exposure of the cast sols to laboratory conditions (RH = 60 ± 5%, T = 20 ± 2 °C) until a constant weight was achieved. Gel times were determined by a visual inspection of the gel transition inside the transparent mould. After the polymerisation and drying processes, a crack-free xerogel (SiOxal-x) was produced in a period of 35–40 days.

For comparison purposes, another xerogel (TEOS-x) derived from a sol containing TEOS, ethanol (EtOH) and water in a molar ratio TEOS/EtOH/H<sub>2</sub>O (1/4/16) was also synthesised and analysed.

### 2.2. Characterisation of powders and xerogels

Initially, the viscosity of the SiOxal-s was measured with a Brookfield DV-II + Pro spindle: S18 viscometer.

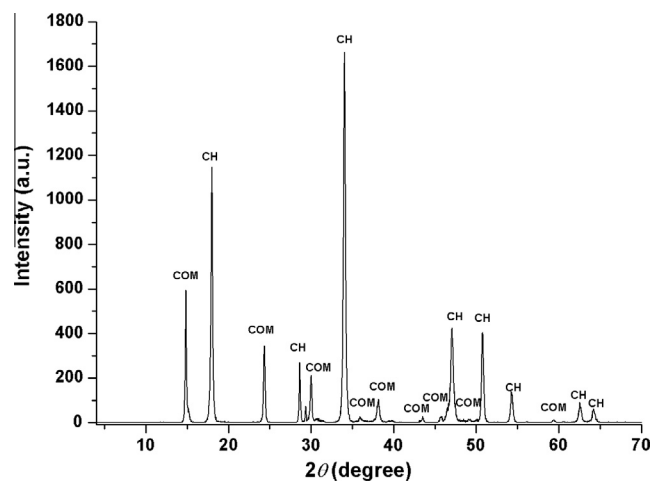


Fig. 1. XRD pattern of the synthesised CaOx-p nanoparticles containing whewellite (COM) and portlandite (CH).

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