Facile Synthesis of Calcium Hydroxide Nanoparticles onto TEMPO-Oxidized Cellulose Nanofibers for Heritage Conservation

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ABSTRACT: Calcium hydroxide is used in diverse applications including heritage conservation where supplying it in the form of nanoparticles allows easy carbonation with atmospheric air contacts. The effects of cellulose nanofibers on the precipitation of calcium hydroxide nanoparticles were investigated by varying the reaction time, concentration, and carboxylation content of cellulose nanofibers. Cellulose nanofibers were very effective in producing calcium hydroxide nanoparticles with less than 50 nm sizes out of calcium nitrate–sodium hydroxide precipitation reactions. The formation of smaller-size calcium hydroxide nanoparticles is believed to be the result of heterogeneous nucleation and growth of calcium hydroxide particles on cellulose nanofibers.

The liquid-phase nucleated and grown calcium hydroxide nanoparticles were also deposited onto cellulose nanofibers. The resulting calcium hydroxide nanoparticles were carbonized and generated calcite under atmospheric carbon dioxide in an efficient way.

INTRODUCTION

Calcium compounds including calcium hydroxide are used in diverse applications where supplying them in the form of nanosized particles brings unique advantages in their respective applications. Calcium hydroxide is not only an important component of Portland cement but is also used in the conservation of cultural heritage buildings, dental materials, and plasters. Their high surface area to volume ratios of penetration easily into the cracks and damaged zones of mortars and plasters. Their high surface area to volume ratios offer strong reactivity with atmospheric carbon dioxide and bring excellent binding properties.

Several methods have been used for the synthesis of metal, metal oxide, and metal hydroxide nanoparticles in liquid phases. Those can be briefly classified as co-precipitation by synthesis of metals, precipitation of metals by reduction, radiation-assisted reduction, precipitation of oxides, sol–gel processing, reactions in constrained environments (e.g., emulsion systems), templating, and stabilizing the synthesis with polymers. In the case of calcium hydroxide nanoparticles, less than 150 nm sizes are synthesized from CaCl₂ at high temperatures (150–170 °C) in glycol systems or micro-emulsion systems. Synthesis of Ca(OH)₂ in aqueous systems and in dextran solutions produced particles larger than 250 nm sizes. Other than calcium hydroxide nanoparticles, a novel nanocomposite scaffold is developed by homogeneous deposition of hydroxyapatite (HAP) on a cellulose nanocrystal (CNC) matrix suspension.

Cellulose nanocrystals and cellulose nanofibers have been investigated for the synthesis of Ag, Au, and Pd metals, mostly to produce hybrid systems for biomedical applications. In this study, carboxylated cellulose nanofibers were used for the first time to synthesize calcium hydroxide nanoparticles by co-precipitating from Ca(NO₃)₂ and NaOH in aqueous solutions at room temperature. The objective of this study was not only to synthesize nanosized calcium hydroxide particles with a facile method but also to shed some light on the co-precipitation process in the presence of cellulose nanofibers.

EXPERIMENTAL SECTION

Materials. Cellulose nanofibers (CNFs) were prepared by using hardwood pulp as a feedstock and applying 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO)-mediated oxidation along with mechanical defibrillation. Cellulose nanofibers were lignin- and hemicellulose-free according to chemical analysis. The preparation of the cellulose nanofibers with carboxylate functionalities is given with full descriptions by Saito et al. The carboxylate contents of the oxidized cellulose nanofibers were determined by using a conductivity titration technique. CNF samples were prepared at two levels of carboxylate concentrations: 0.70 and 1.27 mmol/g. They
were referred to as CNF070 and CNF127, respectively. Cellulose nanofibers have 500−2000 nm length and 4−6 nm width (Figure S1).

Anhydrous sodium hydroxide [NaOH] and calcium nitrate tetrahydrate [Ca(NO3)2·4H2O] were purchased from Fisher Scientific Canada. Solutions (0.4 M) of Ca(NO3)2 and NaOH solutions were prepared employing deionized water.

Preparation of Nanolime Particles. First, 250 mL of 0.4 M Ca(NO3)2 and 100 mL of CNFs at various fiber and carboxylate concentrations were mixed and stirred for 10 min, and then 250 mL of 0.4 M NaOH was added drop by drop into the CNF suspension in Ca(NO3)2 solution. The color of the CNF suspension turned milky, and the mixture was stirred at 35 °C for a period of time. Concentrations of both Ca(NO3)2 and NaOH were 0.167 mol⋅dm−3 in the final mixture. To purify the final milky precipitate, several centrifugation and washing steps with deionized water were done to remove NaNO3 and NaOH. The summary of prepared mixtures is given in Table 1.

After the completion of reactions, samples were washed and centrifuged several times and redispersed in deionized water. Carbonation of Ca(OH)2 nanoparticles on cellulose nanofibers was evaluated by transferring samples in Petri dishes, letting them dry under natural air convection, and aging them for 90 days.

Characterization of Ca(OH)2/CNF Hybrids. The morphologies and sizes of Ca(OH)2 particles were visually inspected by SEM using a Hitachi model S-4800 instrument equipped with a field emission source operating at an accelerating voltage of 30 kV. Samples were prepared by using 10 μL of redispersed CNF/precipitation reaction mixtures after keeping in deionized water for 24 h. Samples were mounted on a glow-discharged carbon-coated Cu grid. Excess water from samples was taken out, and samples were stained by depositing a drop of uranyl acetate solution (2 wt % in water) on the grid for 5 min. The excess solution was absorbed on filter paper, and the grid was dried at room temperature for 24 h prior to obtaining the images.

FTIR spectra of CNF/precipitation reaction products before and after atmospheric air carbonation were acquired with a Varian FTIR spectrophotometer (FTS-7000) by using freeze-dried samples at room temperature under continuous nitrogen purging. Samples were scanned by using an attenuated total reflection (ATR) technique, and plots of transmission (%) versus wavenumbers were obtained in the range of 4000−400 cm−1 with a resolution of 4 cm−1 by cumulating 32 scans.

The thermal decomposition behavior of CNFs and CNF/precipitation reaction products before and after atmospheric air carbonation was determined by using a thermogravimetric analyzer (TGA 500, TA instrument). Samples (20 mg) were heated with a heating rate of 10 °C/min from 25 up to 1000 °C, while the apparatus was continually flushed with a N2 flow of 40 mL/min.

Table 1. Reaction Conditions Used for the Precipitation of Ca(OH)2 in 0.167 mol⋅dm−3 Ca(NO3)2 and 0.167 mol⋅dm−3 NaOH Mixtures

| reaction no. | reaction time (min) | CNF  | CNF addition concentration (%) | [COO−] on CNF (mmol/g) | CNF in solution (g⋅dm−3) | [COO−] in solution (mmol⋅dm−3) |
|-------------|---------------------|------|--------------------------------|------------------------|--------------------------|---------------------------------|
| 1           | 60                  |      | 0                              | 0                      | 0.167                    | 0.117                           |
| 2           | 60                  | CNF070| 0.1                           | 0.70                   | 0.333                    | 0.233                           |
| 3           | 60                  | CNF070| 0.2                           | 0.70                   | 0.333                    | 0.350                           |
| 4           | 60                  | CNF070| 0.3                           | 0.70                   | 0.333                    | 0.423                           |
| 5           | 60                  | CNF070| 1.0                           | 1.27                   | 0.333                    | 1.167                           |
| 6           | 15                  | CNF127| 0.2                           | 1.27                   | 0.333                    | 0.423                           |
| 7           | 60                  | CNF127| 0.2                           | 1.27                   | 0.333                    | 0.423                           |

Figure 1. SEM of calcium hydroxide particles prepared with mixing 0.167 mol⋅dm−3 NaOH and 0.167 mol⋅dm−3 Ca(NO3)2 in (a) the absence of CNFs and the presence of (b) 0.167 g⋅dm−3 CNF070, (c) 0.333 g⋅dm−3 CNF070 with higher magnification, and (d) 0.333 g⋅dm−3 CNF070 with lower magnification.
were smaller than the ones (0.167 g precipitation experiment was carried out in the presence of aggregates and precipitated. In the next run, the same precipitated under these conditions. Individual calcium hydroxide particles were still in a hexagonal prismatic shape, and no generated under these conditions. Individual calcium hydroxide particles without the presence of any templates.10 with calcium nitrate dihydrate and sodium hydroxide as al., which were obtained by applying a similar chemical process with less than 10 nm size onto cellulose nano fibers. Those particles were much smaller than the nanoparticles synthesized from reaction media in glycols (~100 nm)8 and in aqueous ionic and nonionic dextran solutions (~1000 nm).9 The role of cellulose nanofibers was investigated further by increasing the CNF070 concentration in the solution from 0.333 to 1.167 g dm−3. Aggregates of much smaller particles and a network of cellulose nanofibers were seen at the CNF suspension with a concentration of 1.667 g dm−3 (Figure S2). The carboxylate functional groups on cellulose nanofibers due to TEMPO-mediated oxidation also affected both the size and morphology of Ca(OH)2 particles. Increasing the carboxylation content of CNFs from 0.70 to 1.27 mmol/g while keeping the CNF concentration in solution constant at 0.333 g dm−3 resulted again in a shape change from irregularly shaped particles to pearl-like spherical nanosized Ca(OH)2 particles. Cellulose nanofibers, CNF127, were all wrapped with calcium hydroxide nanoparticles (Figure S3).

The reaction time for the formation of Ca(OH)2 had a significant effect on the morphology of particles. Experiments were carried out by reacting 0.167 mol·dm−3 NaOH with 0.167 mol·dm−3 Ca(NO3)2 in the presence of 0.167 g·dm−3 CNF127, which has 1.27 mmol/g carboxylate groups on the cellulose nanofibers due to TEMPO-mediated oxidation also affected both the size and morphology of Ca(OH)2 particles. Increasing the carboxylation content of CNFs from 0.70 to 1.27 mmol/g while keeping the CNF concentration in solution constant at 0.333 g dm−3 resulted again in a shape change from irregularly shaped particles to pearl-like spherical nanosized Ca(OH)2 particles. Cellulose nanofibers, CNF127, were all wrapped with calcium hydroxide nanoparticles (Figure S3).

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nanometer-sized Ca(OH)$_2$ particles built on the cellulose nanofibers having approximately the same size as the nonuniform prismatic particles observed after 15 min of reaction. One of the objectives for producing calcium hydroxide nanoparticles is to utilize them as a binder for cultural heritage structures, which heals the cracks of limestones by an effective carbonation process under atmospheric conditions. Therefore, the reaction of the Ca(OH)$_2$/CNF hybrid system with atmospheric carbon dioxide is crucial. The carbonation process of Ca(OH)$_2$ nanoparticles in the CNF hybrid systems was tested by spreading them as films and aging them under atmospheric conditions for 90 days. Figure 3 shows the SEM picture of a 90 day-aged Ca(OH)$_2$ nanoparticle/CNF hybrid system, which was obtained by following experimental run 4 listed in Table 1. The carbonation process produced a stable polymorph of calcium carbonate (CaCO$_3$), calcite.

The FTIR spectra of a freshly synthesized Ca(OH)$_2$/CNF hybrid matrix (obtained by reaction 4) along with their exposure to open air for 90 days from thick and thin dried layers of films are shown in Figure 4a. The fresh sample was almost all Ca(OH)$_2$/CNF hybrid systems with the main strong adsorption peak at 3640 cm$^{-1}$, which corresponds to OH stretching of Ca(OH)$_2$ and signature bands at 1050 cm$^{-1}$ from the C−C bond and 1165 cm$^{-1}$ from the C−O−C asymmetrical stretching mode of the cellulose backbone. Exposure of dried Ca(OH)$_2$/CNF hybrid films to atmospheric air resulted in the conversion of Ca(OH)$_2$ to calcium carbonate with the main CO$_3$ peaks at 710, 870, and 1400 cm$^{-1}$. The thin layer of dried Ca(OH)$_2$/CNF hybrid film showed a total conversion of Ca(OH)$_2$ to CaCO$_3$ as opposed to a thick layer of dried film, which resulted in only a limited conversion to CaCO$_3$. The carbonation was slower in the case of a thick film than a thin film because the cellulose nanofibers delayed the diffusion of atmospheric carbon dioxide through the hybrid Ca(OH)$_2$/CNF film. Figure 4b shows the thermogravimetric analysis of a fresh Ca(OH)$_2$/CNF hybrid system, which was obtained by the reaction 4 (Table 1) procedure and its aging after 90 days under open air along with a CNF sample before the preparation of Ca(OH)$_2$/CNF hybrid materials. As can be seen, in the case of CNFs, cellulose without the presence of any Ca(OH)$_2$ decomposed over a narrow temperature range, between 280 and 360 °C. This is a very well-defined decomposition temperature range, which is due to cellulose’s very homogeneous semicrystalline structure of linked D-glucose units. The weight loss observed between 100 and 150 °C in all three samples was due to the loss of residual moisture. In the case of the Ca(OH)$_2$/CNF hybrid material, the moisture loss was ~2.1%. The fresh Ca(OH)$_2$/CNF system showed a primary weight loss around 500 °C due to the decomposition of Ca(OH)$_2$ to CaO and H$_2$O at 512 °C. In the case of the 90 day-aged sample, the magnitude of such decomposition decreased drastically at 512 °C, and another major weight loss appeared at 800 °C. It was due to the conversion of Ca(OH)$_2$ by carbonation to CaCO$_3$ after 90 days of aging under atmospheric air. Such CaCO$_3$ decomposed to CaO and CO$_2$ at 825 °C.

The yield of formation of Ca(OH)$_2$ nanoparticles based on the added amount of Ca(NO$_3$)$_2$ can be estimated by following the decomposition of fresh Ca(OH)$_2$ to CaO and H$_2$O from TGA. The weight loss due to H$_2$O generation around 512 °C was 22.17% from the fresh Ca(OH)$_2$/CNF hybrid system in reaction 4. Hence, the amount of Ca(OH)$_2$ in the Ca(OH)$_2$/CNF hybrid system was 91.2% according to a simple stoichiometric calculation (22.17 × MW$_{Ca(OH)_2}$/MW$_{H_2O}$). Consequently, the CNF content in the hybrid system was found to be 6.8% after accounting the moisture content of 2.1%. This gives the w/w ratio of Ca(OH)$_2$/CNF to be 13.6. The stoichiometric amount of Ca(OH)$_2$ formed was 6.72 g in the reaction pot, which also contains 0.333 g of CNF. Hence, the theoretical w/w ratio of Ca(OH)$_2$/CNF was 18.6. Therefore, one can calculate the yield of Ca(OH)$_2$ particles on CNFs to be 73% (13.6 × 100/18.6). This gave the CNF a surface coverage of 4.5 × 10$^{-14}$ g mm$^{-2}$ based on a 300 m$^2$/g specific surface area of the CNF. X-ray diffraction patterns after aging showed that the calcite (CaCO$_3$) phase was formed by carbonation of Ca(OH)$_2$ under atmospheric air and identified as rhombohedral calcite (Figure S4).

Although experiments were limited and the theory of formation of nanoparticles nevertheless was not trivial, results were still used to postulate particle formation mechanisms. The precipitation and formation of calcium hydroxide nanoparticles in the presence of carboxylated cellulose nanofiber suspensions must be discussed by considering the effects of cellulose nanofibers on the nucleation and crystal growth. Cellulose nanofibers can be considered as templates for the precipitation of calcium hydroxide, like the use of cellulose nanocrystals and cellulose nanofibers where Ag and Au metal ions were
is proportional to \(\exp(1/\ln 2)\). In another way, the precipitation reaction can be considered as co-precipitation, which involves the nucleation process. On the other side, the precipitation process is simple and solvent-free and did not employ any additional procedures.

The co-precipitation process of calcium hydroxide involves two stages: a short burst of nucleation and growth of nuclei. The nucleation is driven by the degree of supersaturation, \(S = C/C_{eq}\) where \(C\) and \(C_{eq}\) are the \(\text{Ca(OH)}_2\) concentration at saturation and equilibrium. In our case, those were 0.333 and 0.0233 mol·dm\(^{-3}\), respectively, in the reported experiments. Thus, the driving force for the precipitation was \(\Delta C = C - C_{eq} = 0.310\) mol·dm\(^{-3}\). The rate of nucleation per unit volume, \(R_N\), is proportional to \(\exp(1/\ln 2)\) if all other reactions are kept constant. In the presence of cellulose nanofibers, the barrier to overcome for nucleation is expected to be further reduced due to nucleation on CNF surfaces. Hence, the energy needed for heterogeneous nucleation \(\Delta G_{het}\) is expressed as the product of homogeneous nucleation \(\Delta G_{homo}\) and a function of contact angle \(f(\theta)\). For a total nonwetting case \(\theta = 180^\circ\), the nucleus has no affinity for the substrate and no heterogeneous nucleation happens. On the other side, \(\Delta G_{het}\) approaches zero for a full wetting case \(\theta = 0^\circ\). Hence, the buildup of calcium hydroxide nanoparticles suggested that nuclei formation in the bulk liquid phase was drastically lowered, and CNF surfaces acted like heterogeneous nucleation sites. Calcium cations adsorbed on negatively charged carboxylated CNF surfaces are expected to be ideal sites for the nucleation (Graphical Abstract, Scheme a). As discussed by Cushing et al., there is a slow growth of the nuclei occurring either by a diffusion-controlled or surface reaction-controlled process. Experimental evidence, such as a decrease in nanoparticle size with an increase in CNF concentration, suggests that the precipitation reaction of calcium hydroxide nanoparticles in CNF suspensions was diffusion-controlled.

Another likely mechanism is the deposition of “liquid-phase nucleated” calcium hydroxide particles onto cellulose nanofibers by colloidal deposition before growing further in the liquid phase. In addition to the adsorption on CNFs, calcium ions also form bridges between the nanofibrils at high \(\text{NaNO}_3\) salt concentrations and generate three-dimensional networks. In an aqueous environment of high \(\text{pH}\), the zeta potentials of calcium hydroxide nanoparticles and carboxylated cellulose nanofibers are around +7 and −50 mV, respectively. Hence, colloidal deposition of \(\text{Ca(OH)}_2\) nanoparticles onto CNFs is favorable. These conditions most likely favor the colloidal parakinet deposition of “early-stage-grown” calcium hydroxide nanoparticles onto cellulose nanofibers inside the \(\text{Ca}^{2+}\) cross-linked networks of cellulose nanofibers (Graphical Abstract, Scheme b).

**CONCLUSIONS**

Carboxylated cellulose nanofibers in \(\text{Ca(NO}_3\text{)}_2\) solutions at room temperature were used for the first time to harvest calcium hydroxide nanoparticles with less than 50 nm particle size and in the form of deposits on the CNF surfaces. The process is simple and solvent-free and did not employ any surface active agent. If desired, \(\text{Ca(OH)}_2\) hybrid systems can also be used by drying and reintroducing them into another polar organic solvent such as ethanol or butanol instead of water. In addition, the presence of CNFs in the hybrid system can offer better rheology control if the formation of nanolime films is desired. The resulting calcium hydroxide nanoparticles were effectively carbonized and generated calcite under atmospheric conditions. The formation of smaller-size calcium hydroxide nanoparticles is believed to be the result of more than one mechanism; nevertheless, both of them depend on the adsorption of \(\text{Ca}^{2+}\) cations onto carboxylated cellulose nanofibers. First of all, adsorption of calcium cations initiates heterogeneous nucleation of CNF surfaces and growth of \(\text{Ca(OH)}_2\) particles around fiber surfaces. Second, calcium ions bridge between the nanofibers at high \(\text{NaNO}_3\) salt concentrations and generate a three-dimensional network. This condition most likely favors the colloidal deposition of liquid-phase nucleated calcium hydroxide nanoparticles onto cellulose nanofibers inside the \(\text{Ca}^{2+}\) cross-linked networks of cellulose nanofibers. Further studies are warranted to elucidate and control the formation of nanoparticles with those two mechanisms by investigating the counterions coming from calcium salts, temperature, mixing conditions, and preparation procedures.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.9b02643.

SEM of TEMPO-oxidized nanofibers and effect of CNF concentration on \(\text{Ca(OH)}_2\)/CNF hybrids (Figure S1); effect of carboxylate concentration on \(\text{Ca(OH)}_2\)/CNF hybrids shown with SEM images (Figure S2); X-ray diffraction patterns of \(\text{Ca(OH)}_2\)/CNF obtained by using reaction 4 and after aging under atmospheric air (Figure S3) (PDF)

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**Notes**

The authors declare no competing financial interest.

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