

# Microwave assisted synthesis of CaO nanoparticles and use in waste water treatment

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## ABSTRACT

Clean water (i.e., water that is free of toxic chemicals and pathogens) is essential to human health. Advances in nanoscale science and engineering are providing unprecedented opportunities to develop more cost effective and environmentally acceptable water purification processes. Nanomaterials have much larger surface areas than bulk materials and exhibit novel properties due to their small size. Unique properties of nanomaterials are being exploited by the researchers for developing more effective sorbents and improving for metal ions removal. In recent years, carbon nanotubes, zeolites, and different nanoparticles have been investigated for their removal of metal ions. CaO nanoparticles were obtained by the microwave irradiation technique, using  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  and NaOH as starting materials. The formation monocrystalline CaO nanoparticles were confirmed by the XRD (X-Ray Diffraction) and HRTEM (High Resolution Transmission Electron Microscopy) as well as with SAED (Selected Area Electron Diffraction) analysis. The structure of the CaO nanocrystal was found to be cubic structure with particles size 24 nm and with surface area  $74 \text{ m}^2/\text{g}$ . A small scale study to treat synthetic acid mine water by synthesized  $\text{Ca}(\text{OH})_2$  nanoparticles shows higher efficiency to remove heavy metals than conventional use of lime. XRD results of precipitates show presence of different metal hydroxides and sulfate, precipitated as  $\text{CaSO}_4$ .

**Keywords:** Nanoparticles, CaO, XRD, HRTEM, Water treatment

## INTRODUCTION

Calcium oxide (CaO) is an exceptionally important industrial compound, is used as catalyst, toxic-waste remediation agent, an additive in refractory, in paint as well as for others fundamental applications. Ultra-fine metal oxide particles can be used as bactericide and adsorbent. Particularly CaO has also shown great promise as a destructive adsorbent for toxic chemical agent.

Few literatures are found on the preparation of nano-CaO. There are mainly two methods on the preparation of nano-CaO according to the literature. One is thermal decomposition [1,2]. The other is sol-gel. [3] CaO nanoparticles can be obtained up to about 14 nm size through sol-gel method, the cost is very high. What's more, the process is very complicated and time-consuming. So it is very difficult to apply sol-gel method in industrial

applications. Thermal decomposition method has some advantages such as simple process, low cost, and ease of obtaining high purity product, etc. So it is a promising and prospective method to be applied into industry. In thermal decomposition method, CaO is often obtained directly through calcining  $\text{CaCO}_3$ . High calcination temperature is needed. By this process, it is very difficult to get nano-scale CaO, but micrometer CaO (above 100 nm), directly through calcining  $\text{CaCO}_3$  is easily possible [4]. The microwave-assisted route is yet another method for the synthesis of metal oxides and has been gaining significance in the synthesis of oxide nanomaterials [5,6]. Microwaves have been used to accelerate organic chemical reactions for some time; because the method is generally fast, simple, energy efficient and less time consuming [7,8]. Unfortunately, the exact nature of microwave interactions with reactant during the synthesis of materials is somewhat unclear and speculative.

Mine waste water (acid mine drainage) is characterized as low pH, high acidity effluents with high sulfate content and various dissolved metals such as Fe, Al, Mn, Zn, Cu, Ni, Mg, and Cr [9,10]. Acid mine drainage, poses an environmental problem to aquatic ecosystems in coal and hard rock mining regions.

The purpose of this study is to investigate a simple and rapid synthesis method using calcium nitrate and sodium hydroxide as starting materials for the growth of the CaO nanoparticles. A small scale study to treat synthetic mine waste water by synthesized CaO nanoparticles shows higher efficiency to remove heavy metals than conventional use of lime. Result of treated water shows higher de-acidification and dischargeable concentration of heavy metals in effluent water. XRD results of precipitates show presence of different metal hydroxides and sulfate, precipitated as  $\text{CaSO}_4$ .

## EXPERIMENTAL SECTION

### Synthesis of CaO nanoparticles

In a typical procedure, 0.5 M  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  and 0.7 M of NaOH were separately dissolved in 50 ml de-ionized water and mixed to form 100 ml mixture (solutions). The mixture was stirred for 10 minutes at room temperature and it turned into white gels. After 10 minutes stirring at room temperature, the mixture turned into white gels. These were then irradiated by microwave energy using domestic microwave oven having frequency 2.45GHz (maximum power 800 W) in ambient atmosphere for 10 minutes. After

microwave processing, the solution was allowed to cool to reach room temperature, naturally. The resulting precipitate was collected by vacuum filtration and washed with de-ionized water and absolute ethanol, and dried in a vacuum at 80 °C for 1 h.

### Characterizations

The phase analysis and crystallinity were checked with XRD pattern using diffractometer equipped with a Co  $K\alpha$  ( $\lambda=1.789\text{\AA}$ ) source and the patterns were recorded at a scan rate  $2^\circ \text{ min}^{-1}$ . Particle size and morphology were studied with FESEM and HRTEM in the voltage range of 20-200 kV.

### Batch experiment with nano CaO

Synthetic mine waste water (Synthetic AMD) was prepared and use for the batch experiment. The aim of these neutralization batch experiments was to note pH and also changes in solution composition due to the addition of nano CaO and market available lime. At first the analyses of the above mentioned initial parameters of synthetic mine water was carried out by Orion 5 star pH meter and GBC AAS (Atomic absorption spectrophotometer). Two 1liter reagent bottles were filled with synthetic AMD and an amount of 0.1g of the nano CaO and lime were added separately and bottle cap was sealed by parafilm. The samples prepared in this manner were put on a vertically rotating shaker and were agitated (0.5 rpm) for 10 minutes. Finally, treated water was again analyzed for pH and metal contain (Tab. 2).

## RESULT AND DISCUSSION

### Characterization of CaO nanoparticles

The XRD patterns of the synthesized calcium oxide (CaO) were shown in Figure 1.

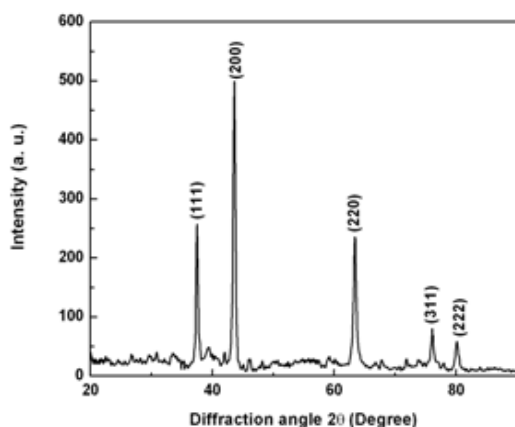


Figure1. The XRD pattern of CaO nanoparticles immediately after synthesis

The d-spacing values of the sample matched well with the standard PDF database (JCPDS file 77-2376). Unit cell parameters were obtained by least-square refinement of the

powder XRD data. XRD study revealed that the products are monophasic cubic calcium oxide (CaO) with lattice constant  $a = 4.801 \text{\AA}$  ( $Fm3m$  space group) having nanosized particles; the values in the parenthesis indicate respective Miller indices. The characteristic peaks were higher in intensity and narrower in spectral width, indicating that the products were of good crystallinity. No peaks corresponding to impurities were detected, showing that the final are high quality CaO. The average size of the particles of sample was 24 nm.

FESEM micrographs in Figure 2 have nearly cubic shapes of synthesized CaO nanoparticles with  $\sim 30 \text{ nm}$  average particle size on the cross-sections.

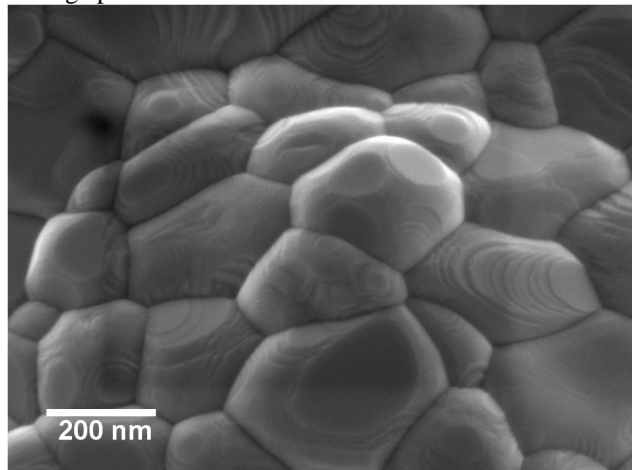


Figure 2. FESEM micrograph of synthesized CaO nanoparticles.

Structural characterization through HRTEM was rather a direct way that provides visual demonstration to estimate particle size exactly. Figure 3 shows the typical HRTEM image of the synthesized CaO nanocrystals. Bright field images of the sample indicate that the sample was dispersive single-crystal particles having cubic shapes. The selected area electron diffraction (SAED) pattern was shown in the inset a Figure 3.

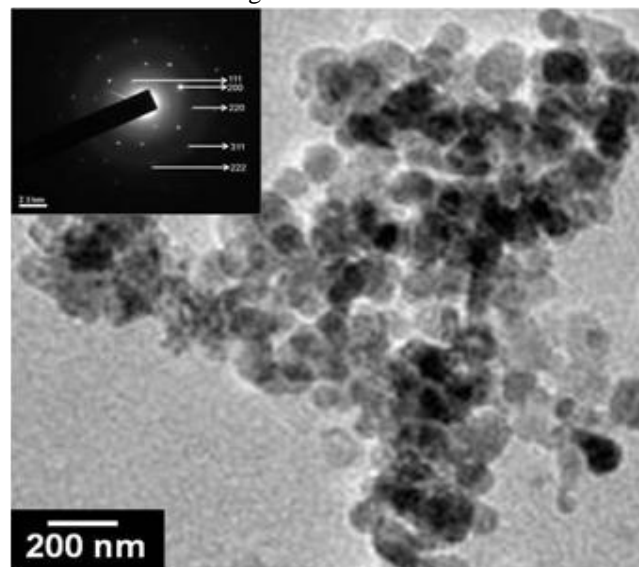


Figure 3. HRTEM micrographs of synthesized CaO nanoparticles with a selected area diffraction pattern (SAD) in inset.

To verify chemical purity, CaO powders were analyzed by FTIR. The bands due to hydroxyl and carbonate are distinctly displayed in the spectrum (Figure 4).

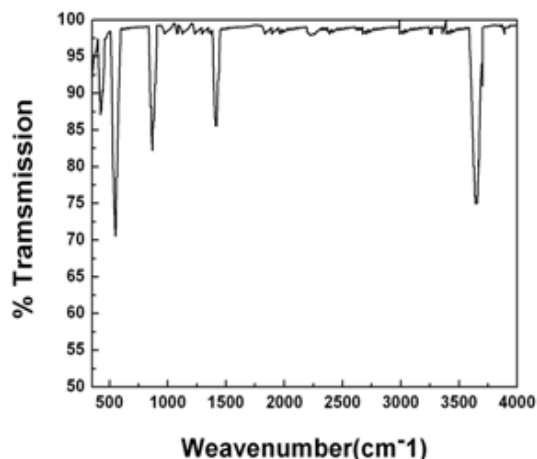


Figure 4. FTIR spectra of CaO nanoparticles.

The strong band at  $3,643\text{ cm}^{-1}$  corresponds to the O–H bonds from the remaining hydroxide. Bands at  $1,417\text{ cm}^{-1}$  and  $866\text{ cm}^{-1}$  are corresponds to C–O bond. The wide and strong band at around  $427\text{ cm}^{-1}$  and  $553\text{ cm}^{-1}$  corresponds to the Ca–O bonds (table 1).

| Peak position ( $\text{cm}^{-1}$ ) | Assignment                | Phase                            |
|------------------------------------|---------------------------|----------------------------------|
| 3643                               | OH                        | $\text{Ca}(\text{OH})_2$ [11-13] |
| 1476                               | $\nu_3(\text{CO}_3)^{-2}$ | $\text{CaCO}_3$ [12]             |
| 870                                | $\nu_2(\text{CO}_3)^{-2}$ | $\text{CaCO}_3$ [12,13]          |

Table 1 Observed infrared band positions and their assignments

### Batch experiment

Table. 2 shows chemical composition of feed and treated water when synthetic acid mine water was treated with nano CaO and lime. After 10 min shaking treated water was analyzed by AAS for heavy metal measurement and sulfate concentration was measured by spectrophotometric method. As nanoparticles have high surface by volume ratio, it is more reactive, high chemical specificity and fast sorption capacity. Heavy metal removal capacity of the synthesized nano CaO higher that lime treatment and takes very less time.

Precipitate was collected and characterized by XRD. XRD spectrum (Figure 5 and 6) of precipitates shows heavy metals were precipitated as metal hydroxide and sulfate was removed by precipitation of gypsum ( $\text{Ca}(\text{SO}_4)$ ). XRD spectrum in Fig 6 shows good amount of metal were precipitated and also sulfate ( $\text{SO}_4^{2-}$ ) were precipitated as gypsum which was not found in the Figure 5. Lime removes heavy metals but it seems to have less ability to remove sulfate from synthetic mine waste water. Nano CaO was able to remove heavy metals as well as sulfate

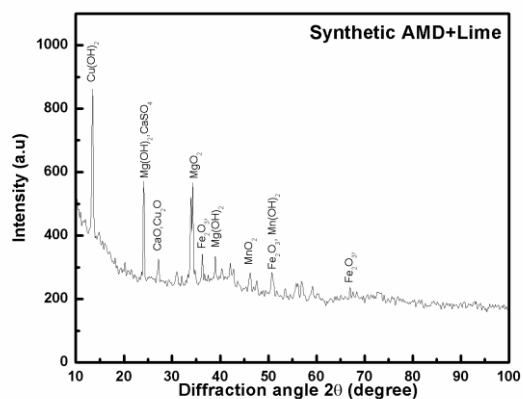


Figure 5 XRD of precipitate from lime treatment

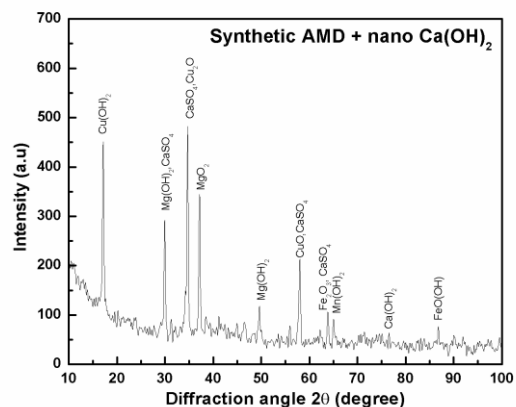


Figure 6 XRD of precipitate from nano treatment

|                          | pH   | Fe (ppm) | Cu (ppm) | Mg (ppm) | Mn (ppm) | Sulfate(mg/L) |
|--------------------------|------|----------|----------|----------|----------|---------------|
| Synthetic AMD            | 2.56 | 166.5    | 63       | 28.9     | 2910     | 1001          |
| Synthetic AMD + lime     | 8.5  | 125      | 49       | 21       | 2102     | 950           |
| Synthetic AMD + nano CaO | 10.2 | 49       | 13       | 12       | 1050     | 256           |

Table 2 Comparison of pH and selective ions with treatment of synthesized nano CaO and lime

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## CONCLUSION

Nanostructured CaO with cubic morphology was successfully produced from  $\text{Ca}(\text{NO}_3)_2$  and NaOH by using a microwave radiation in ambient atmosphere. XRD, FESEM, HRTEM, SAED and FTIR analyses revealed the presence of face centered cubic structured CaO nanoparticles with 24 nm sizes.

A novel approach toward the removal of heavy metals from mine waste water is presented. It is proved that the addition of nanoCaO into acid mine water leads to a pH increase of the solutions with the consequence of reduction of targeted anions and cations. Such processes involve mechanisms like reductive mineral precipitation and coprecipitation, insoluble hydroxide formation and adsorption.

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