

Article

Using Phosphogypsum as a Source of Calcium Sulfate When Synthesizing Calcium Molybdate Nanoparticles

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Abstract: Calcium molybdate (CaMoO_4) is of significant interest due to its unique properties and numerous industrial applications, such as catalysis, electrochemistry, and optoelectronics. In this study, we developed an economical and environmentally friendly method to synthesize calcium molybdate from Moroccan phosphogypsum (PG) industrial waste and sodium molybdate, all at room temperature. Comprehensive analysis through X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), Raman vibrational spectroscopy, and scanning electron microscopy (SEM) revealed the high purity of the synthesized calcium molybdate, with particle sizes of only 12 nm. Additionally, optical characteristics were studied using ultraviolet-visible spectroscopy (UV-vis), which showed an optical band gap of $E_{\text{gap}} = 3.96 \text{ eV}$ for CaMoO_4 . These results confirm the successful synthesis of calcium molybdate nanoparticles from Moroccan phosphogypsum, demonstrating an effective pathway to valorize this industrial waste into a valuable material. This approach contributes to environmental sustainability by reducing dependence on rare chemicals while offering innovative solutions for the industry's sustainable development.

Keywords: calcium molybdate; phosphogypsum; nanoparticles; optical band gap; sustainable development



Citation: Belaoufi, Y.; Bensemlali, M.; Hatimi, B.; Mortadi, H.; Labjar, N.; Nunzi, J.-M.; El Idrissi, M.; Aarfane, A.; Bakasse, M.; Nasrellah, H. Using Phosphogypsum as a Source of Calcium Sulfate When Synthesizing Calcium Molybdate Nanoparticles. *Reactions* **2024**, *5*, 462–471. <https://doi.org/10.3390/reactions5030024>

Academic Editors: Annalisa Volpe, Caterina Gaudiuso, Maria Chiara Sportelli and Diogo M.F. Santos

Received: 2 July 2024

Revised: 24 July 2024

Accepted: 6 August 2024

Published: 7 August 2024



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1. Introduction

The efficient utilization of industrial waste materials has been an important research focus in recent years due to growing concerns about environmental pollution and resource depletion. Phosphogypsum (PG), a by-product of the phosphate fertilizer industry, is a highly abundant waste product, most of which is discharged into the environment without any prior treatment, containing significant amounts of calcium sulfate and various trace elements [1,2]. The development of value-added applications for PG has received considerable attention, including the synthesis of functional materials such as nanocalcite, hydroxyapatite, fluorapatite, brushite, calcium hydroxide, and potassium sulfate [3–10].

Calcium molybdates are very interesting materials due to their attractive characteristics, such as high chemical stability [11], luminescence [12], and non-toxicity [13]. Therefore, this material was widely employed in various applications, including laser host materials [14], luminescence materials [15,16], scintillation detectors [17], energy storage [18,19],

and water treatment [20,21]. A variety of methods were used for calcium molybdate synthesis, such as hydrothermal [22,23], czochralski [24,25], microwave assisted [26,27], sonochemical [28,29], electrochemical [30,31], sol gel [32,33], and co-precipitation [34,35].

However, the conventional methods for CaMoO_4 synthesis usually require high-purity raw materials and complicated reaction conditions, which generate high costs and limit the scalability of the process. Co-precipitation is the most widely used method for calcium molybdate elaboration due to its simplicity, low energy need, scalability, and ease of use in industrial manufacturing. Accordingly, Swathi et al. have synthesized calcium molybdate starting from pure CaCl_2 and Na_2MoO_4 , in addition to expensive reagents such as polyethylene glycol [36]. Otherwise, M. Ghaed-Amini et al. have prepared calcium molybdate in two-step processing. Firstly, $\text{Ca}(\text{Sal})_2$ was synthesized from calcium nitrate and salicylaldehyde solutions. Secondly, $\text{Ca}(\text{Sal})_2$ and ammonium heptamolybdate, polyvinylpyrrolidone (PVP), sodium dodecylsulfate (SDS), and cetyltrimethylammonium bromide (CTAB) were deployed for calcium molybdate elaboration. Consequently, the use of pure raw materials and expensive reactive materials increases the elaboration cost and then limits the applicability of the method despite its numerous advantages [37]. Therefore, it is essential to develop a simple synthesis method that can address these limitations while using low-cost raw materials. Phosphogypsum can be effectively used as a source of calcium sulfate in various syntheses to replace expensive raw materials, provided the material is properly purified and the synthesis process is well optimized. This approach not only offers a cost-effective raw material but also contributes to waste reduction and sustainable industrial practices.

In this context, the present research depicts the synthesis of calcium molybdate nanoparticles (CaMoO_4 -NPs) from Moroccan phosphogypsum as a source of calcium sulfate using a new coprecipitation method. This method allows blending all the reagents in one step and at room temperature without the need for chemical reagents such as surfactants or coating agents, pH adjustments, or thermal treatment. After coprecipitation, the resulting CaMoO_4 -NPs are easily separated by filtration, washed, dried at 105°C , and characterized to confirm their structure and purity. This novel method offers sustainable and economic efficiency; those criteria are both desirable for environmental protection and large-scale production of materials devoid of impurities.

2. Materials and Methods

2.1. Starting Materials

Sulfuric acid (H_2SO_4 98%) and sodium hydroxide (NaOH 99%) were acquired from Prolabo, while sodium molybdate (Na_2MoO_4) was supplied by Sigma Aldrich. The phosphogypsum waste was obtained from the Moroccan phosphate fertilizer industry located in El Jadida, Morocco. The PG consists of a fine-grained white or off-white powder that is relatively dense, has a low porosity, and has an acidic pH. The chemical composition of PG was analyzed using ICP, and the main components and trace elements are detailed in Table 1. Based on this data, PG is mainly composed of calcium sulfate (expressed as CaO and SO_3) and small amounts of impurities.

Table 1. Chemical composition of Moroccan phosphogypsum (%).

PG	CaO	SO ₃	P ₂ O ₅	TOC	Al ₂ O ₃	Fe ₂ O ₃	K ₂ O	F	MgO	Na ₂ O	SiO ₂
%	32.40	43.89	0.66	0.14	0.13	0.83	0.12	0.12	0.17	0.11	0.25

2.2. Preparation of Calcium Molybdate Nanoparticles

The collected PG was treated with sulfuric acid (67%), followed by washing with water and drying at 105°C for 24 h to remove any moisture. Hence, the obtained calcium sulfate was grounded and sieved to a particle size of $40\ \mu\text{m}$. Calcium molybdate was prepared using a simple co-precipitation method, as shown in Figure 1. Specifically, 0.073 moles of calcium sulfate (CaSO_4) were combined with 100 mL of deionized water and 0.073 moles

of Na_2MoO_4 . The resulting mixture underwent continuous stirring at 500 rpm for 48 h at room temperature, while the solution's pH was controlled using NaOH. The synthesis process can be represented by the following reaction (1):

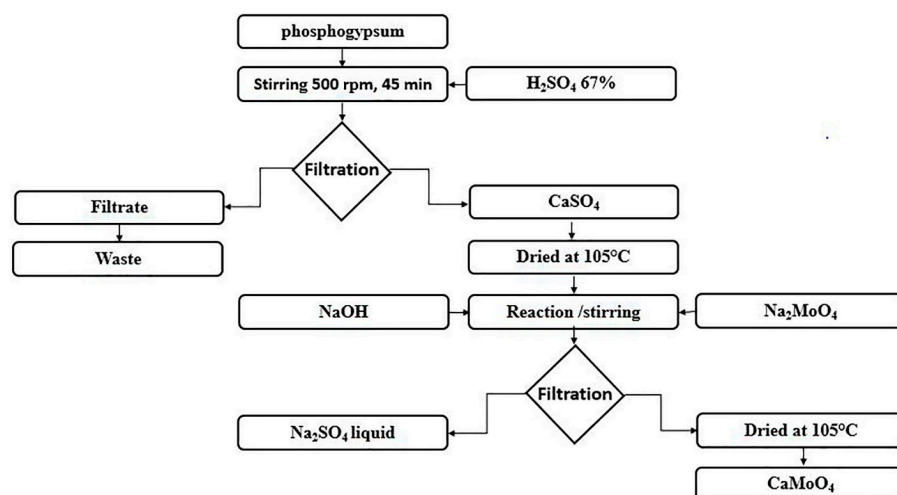
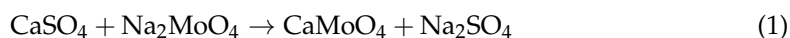


Figure 1. Schematic illustration of the main process followed for the synthesis of calcium molybdate from phosphogypsum.

The solid sample was removed from the solution by filtration and washing three times with distilled water to eliminate any remaining unreacted substances. Finally, the resulting product was dried at 105°C .

2.3. Characterization

The synthesized CaMoO_4 was analyzed using various techniques. The powder structure was characterized by X-ray diffraction using diffractometer type X-Pert Pro PAN analytical, (Bruker, Model: PANalytical X' pert PRO, PANalytical, Almelo, The Netherlands) working with $\text{CuK}\alpha$ radiation ($K\alpha = 1.54 \text{ \AA}$) at a scanning rate of $0.02^\circ/\text{s}$ and a 2θ range from 5 to 70° . The morphology was examined using scanning electron microscopy (SEM) through apparatus type VEGA3 TESCAN, (TESCAN OSRAY HOLDING, a.s., Brno, Czech Republic). In addition, the chemical function was identified by infrared spectroscopy (FTIR) via a Nicolet 380, (Nicolet 380, Versex Scientific, Los Angeles, CA, USA) Fourier spectrometer. However, Raman vibrational analysis was conducted utilizing a Bruker confocal Raman spectrometer, specifically the SENTERRA II, (Bruker, Billerica, MA, USA). The analysis covered a spectral range from 50 to 1420 cm^{-1} . A laser with resolution, wavelength, and an output power of 1.5 cm^{-1} , 532 nm , and 12.5 mW , respectively. The optical properties were investigated via the UV-vis-NIR double-beam spectrophotometer SHIMADZU 3101, (Shimadzu Europa GMBH, Duisburg, Germany). in the wavelength range of 200 – 1000 nm .

3. Results and Discussion

3.1. XRD Analysis

The prepared nanoparticles were subjected to X-ray diffraction (XRD) analysis to assess their purity and crystal size. The results are shown in Figure 2. The diffractogram reveals the presence of distinct peaks, confirming the high crystallinity of the nanoparticles produced. The observed peaks mainly correspond to calcium molybdate, according to the JCPDS 29-0351 data base, and that confirms the high purity of the elaborated NPs. The maximum reflection peaks are located at the 2θ of 18.63 , 28.72 , 31.29 , 34.31 , 39.38 , 43.14 , 45.62 , 47.08 , 49.31 , 54.20 , 56.16 , 57.96 , and 59.38° , which link to miller indices of (101), (112),

(004), (200), (211), (105), (204), (220), (116), (215), (312), and (224), respectively. Additionally, X-ray data were employed to calculate the crystallite size of the prepared NPs according to the Scherrer equation depicted in Equation (2) [38,39].

$$D = K\lambda / \beta \cos \theta \quad (2)$$

where D is the particle size ($\text{\AA}$) and K is the Scherrer constant, which is usually approximately 0.9. The wavelength of the X-ray radiation employed, represented by λ , is roughly $1.54056 \text{ \AA}$. β stands for the diffraction peak's full width at half-maximum (FWHM), and θ is the Bragg angle where the peak is noticed. The results show that the calcium molybdate nanoparticles are about 12 nm in size.

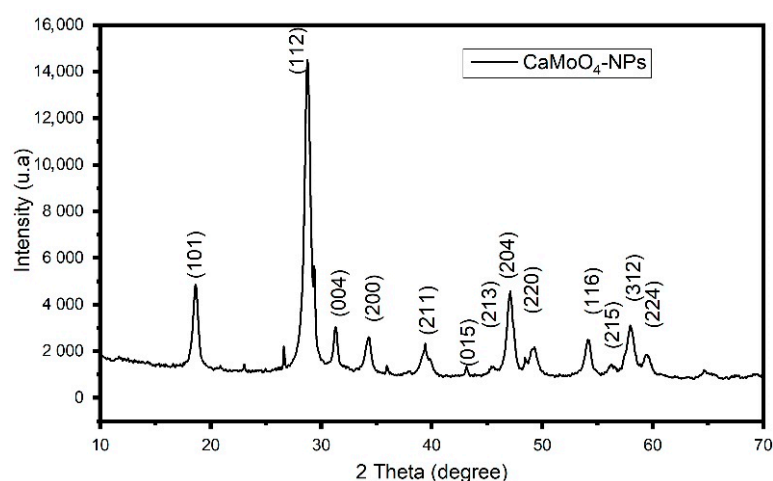


Figure 2. XRD patterns of calcium molybdate dried at 105°C .

By comparing the findings with previous research, one can conclude that the as-prepared NPs show an average size lower than prepared through the Swathi et al. method, in which polyethylene glycol (PEG) was used as a surfactant to control the homogeneity of the solution and to decrease the interaction between particles in order to control the NP size. In particular, Swathi's coprecipitation yielded a size ranging from 44 nm to 59 nm, which is four times larger than the herein elaborated calcium molybdate NPs [36]. Y. Sun et al. [40] used an electrochemical method in addition to the surfactant to control the particle size of the NPs. Adjusting the ethylene glycol content in the electrolyte solution together with the applied electric current, the optimum particle size was around 12 nm. This demonstrates the ability of our method to yield pure nano-sized calcium molybdate from inexpensive, disregarded raw materials.

3.2. UV-Vis Spectroscopy

The optical bandgap of the sample was determined based on the UV–visible absorption data using the Tauc equation: $(\alpha h\nu) = A(h\nu - E_g)^n$ [41].

Where α is the absorption coefficient, ν is the radiation frequency, n is a constant relating to the type of electronic transitions in the materials, and E_g is the band gap. Given that metal molybdate is a direct band gap material [13], $n = 0.5$. The optical bandgap energy was established as presented in Figure 3 by extrapolating the linear part of the curve $(\alpha h\nu)^2$ plotted against $(h\nu)$. Calcium molybdate nanoparticles have an energy bandgap of 3.96 eV when this linear component crosses the x-axis ($h\nu$). The calculated bandgap energy of CaMoO_4 is consistent with values reported in the literature [42–45].

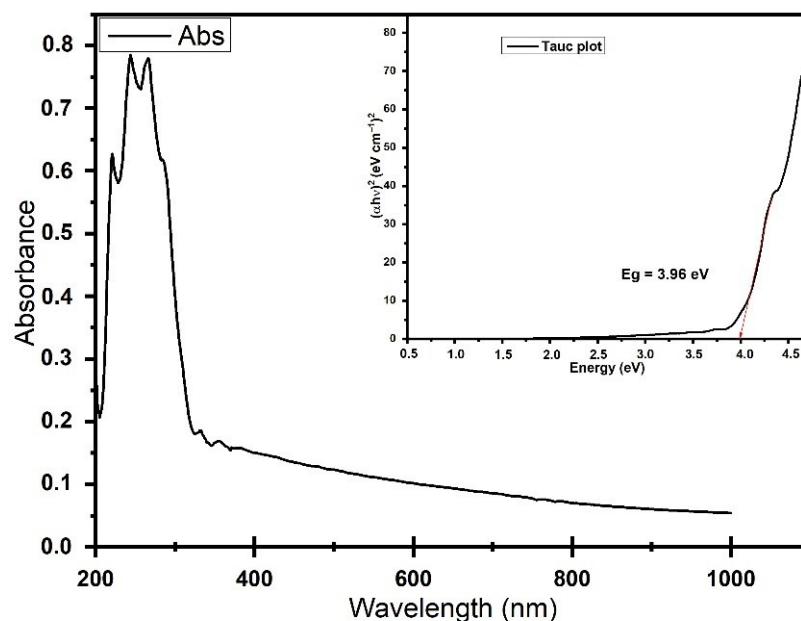


Figure 3. Absorbance spectra against wavelength and energy band gap of calcium molybdate dried at 105 °C.

3.3. FTIR Spectroscopy

Figure 4 shows FT-IR spectra. A prominent absorption peak in the IR spectra at 791 cm^{-1} belongs to the Mo-O antisymmetric stretching vibration of the $[\text{MoO}_4]^{2-}$ tetrahedra. A weaker peak linked to the bending vibration of Mo-O appears at 429 cm^{-1} . The stretching vibrations of absorbed water are responsible for peaks recorded near 3426 cm^{-1} , while the H-OH bending vibration is detected at 1635 cm^{-1} [41,44]. The peak at 1091 cm^{-1} can be due to the stretching and bending vibrations of Si-O-Si, while the peak region, which is typically positioned between 1000 and 1250 cm^{-1} , shows the existence of SiO_2 [46]. The absorption peak at 1446 cm^{-1} is related to vibrations of the CO_3^{2-} carbonyl group [47].

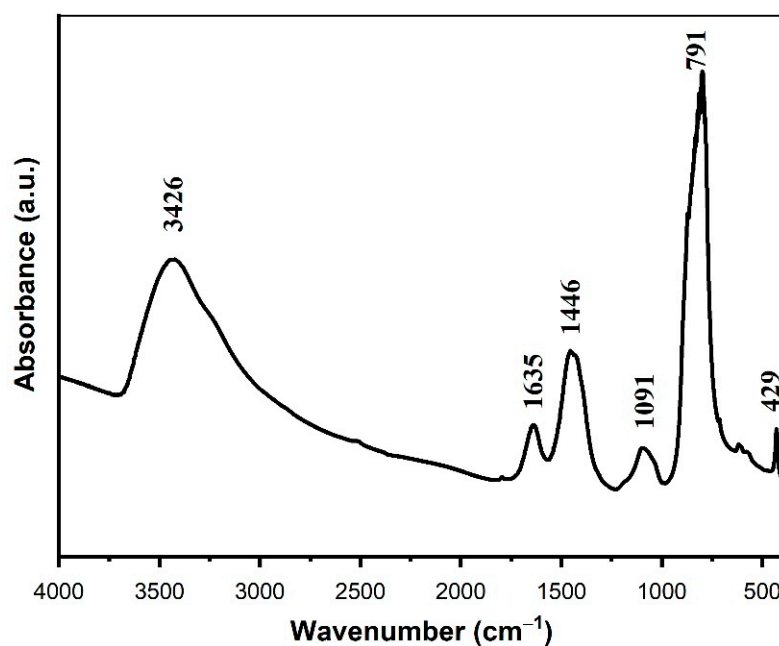


Figure 4. FTIR spectra of calcium molybdate dried at 105 °C.

3.4. FT-Raman Vibrational Spectroscopy

Raman spectra are a powerful tool for understanding the vibrational properties and structural characteristics of molecules or crystals. Anees et al. reported that the Raman spectra of calcium molybdate are classified into two main types of vibrational modes: external and internal. The first is associated with lattice phonons, involving the collective motion of $[\text{CaO}_8]$ clusters and rigid molecular cell units within the crystal structure. The second corresponds to vibrations within the units of $[\text{MoO}_4]^{2-}$ clusters, considering the center of mass in the stationary state [48]. The information provided by the FT-Raman spectrum of CaMoO_4 (Figure 5) in the range from 90 to 1100 cm^{-1} , highlighting specific vibrational modes associated with symmetric stretching of the $[\text{MoO}_4]$ tetrahedral cluster, is as follows: 141 cm^{-1} (Eg), 319 cm^{-1} (Ag), 396 cm^{-1} (Ag), and 400 cm^{-1} (Bg). The strong peaks observed at 878 , 845 , and 792 cm^{-1} are assigned to the Ag, Bg, and Eg modes, respectively. The vibrational modes 111 cm^{-1} (Eg) and 203 cm^{-1} (Bg) are characteristic of Ca-O vibrations in deltahedral $[\text{CaO}_8]$ groups. These vibrational modes and their associated symmetries provide insight into the internal vibrations of the CaMoO_4 molecule, specifically correlated with the tetrahedral $[\text{MoO}_4]$ and deltahedral $[\text{CaO}_8]$ clusters. The symmetry assignments (Ag, Bg, and Eg) indicate the symmetries of these vibrational modes based on the molecular group of CaMoO_4 . The obtained results in our current study closely correspond to previously reported ones [13,40,49,50].

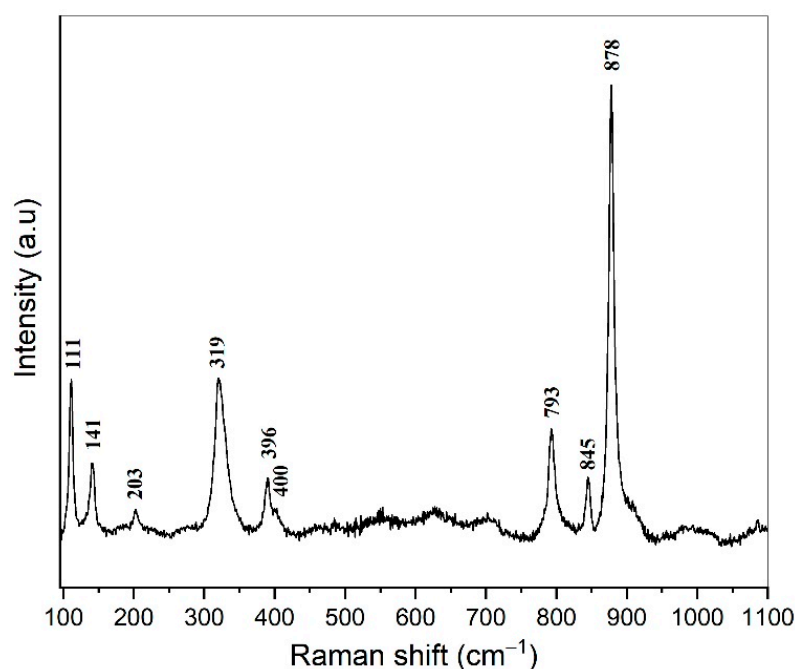


Figure 5. Raman spectrum of the tetragonal CaMoO_4 dried at $105\text{ }^{\circ}\text{C}$.

3.5. Scanning Electron Microscopy of Calcium Molybdate

The micrographs in Figure 6 depict the synthesized nanoparticles at various magnifications. The results show that the sample presented is an agglomerate characterized by its rigorous structure, homogeneity, and the presence of pores. The agglomerate's rigorous structure is reflected in the well-defined, orderly organization of its constituents. The constituent grains are tightly bonded, forming a solid network. The same color shade shows the homogeneity of the sample and means that the grains are of similar size and shape, indicating uniformity in the composition and structure of the agglomerate. In addition, the presence of pores in the sample is observed between the agglomerates, which may be the result of the presence of empty spaces between the grains. These pores can play an important role in the sample's physical and chemical properties, such as permeability and reactivity.

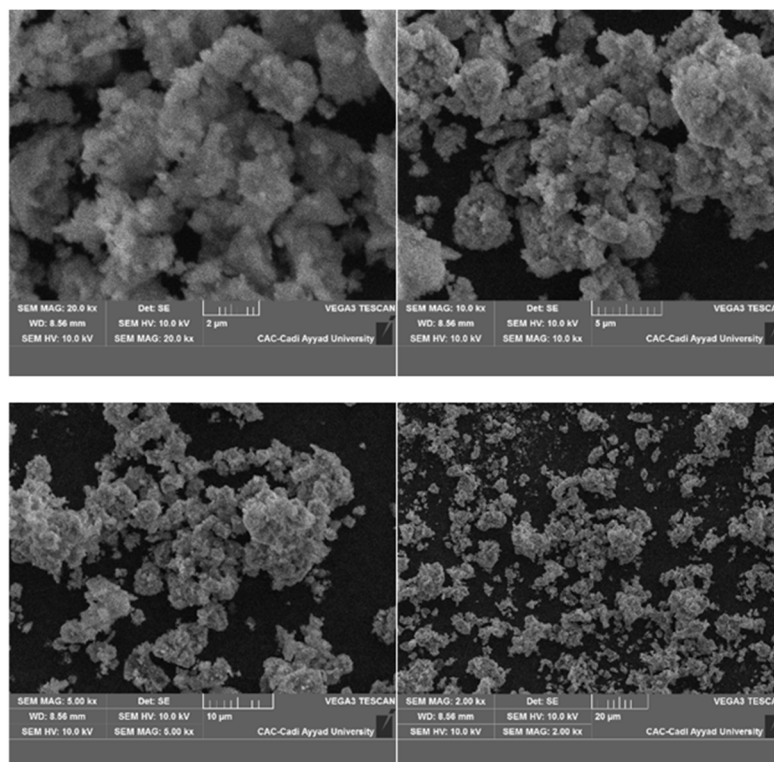


Figure 6. SEM images of calcium molybdate dried at 105 °C.

4. Conclusions

Calcium molybdate was successfully prepared by mixing PG with sodium molybdate at room temperature using a simple, low-cost, one-step co-precipitation method without any subsequent pH adjustments or aqueous additions. XRD, FTIR, and Raman spectra revealed the high purity of the compound. The size of the crystallites was estimated using the Scherer formula at 12 nm. The optical band gap was found to be 3.96 eV.

The nanoparticle size, high crystallinity, and large band gap show that the nanoparticles prepared in this work have great potential for applications in catalysis, energy storage, and electronic devices. Consequently, the synthesis of calcium molybdate from phosphogypsum using the new co-precipitation method has great potential for the production of this valuable material. The method offers several advantages, such as operational simplicity, high purity of the final product, and improved energy efficiency as compared with conventional methods. In addition, the use of phosphogypsum, a by-product of the phosphate fertilizer industry, as a raw material for the synthesis of calcium molybdate also offers significant environmental benefits by converting an industrial waste into a useful material.

Author Contributions: Conceptualization, Y.B., M.B. (Mina Bakasse) and H.N.; Methodology, M.B. (Meryem Bensemlali), B.H., N.L., A.A., M.B. (Mina Bakasse) and H.N.; Software, Y.B., M.B. (Meryem Bensemlali), H.M. and H.N.; Validation, M.B. (Mina Bakasse), A.A. and H.N.; Formal analysis, Y.B., B.H., M.E.I., A.A., M.B. (Mina Bakasse) and H.N.; Investigation, Y.B., M.B. (Meryem Bensemlali), H.M., A.A., M.B. (Mina Bakasse) and H.N.; Resources, Y.B., M.B. (Mina Bakasse) and H.N.; Data curation, M.B. (Meryem Bensemlali), N.L., A.A., M.B. (Mina Bakasse) and H.N.; Writing—original draft, Y.B., M.B. (Meryem Bensemlali), H.M., N.L., J.-M.N., M.E.I., A.A., M.B. (Mina Bakasse) and H.N.; Writing—review & editing, Y.B., J.-M.N., N.L. and H.N.; Visualization, H.N., M.B. (Mina Bakasse). All authors have read and agreed to the published version of the manuscript.

Funding: The authors have no affiliation with any organization with a direct or indirect financial interest in the subject matter discussed in the manuscript.

Data Availability Statement: All the data in this manuscript are available upon request.

Acknowledgments: The authors gratefully acknowledge the Faculty of Science Semlalia, University of Cadi Ayyad, Morocco, for SEM analysis.

Conflicts of Interest: The authors declare that there is no conflict of interest.

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