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Rapid, Room-Temperature Formation of Crystalline Calcium Molybdate Phosphor Microparticles via Peptide-Induced Precipitation**

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Nature provides numerous examples of organisms that synthesize intricate mineral structures (biominerals) with micro- to nanoscale features through the use of specific biomolecules.[1] While such control over mineral formation under ambient conditions exceeds current man-made assembly technologies, the known biominerals (only about 60 different minerals have been identified to date) do not possess compositions that are particularly attractive for many man-made devices.[2] Nonetheless, nature's exquisite control over biomineral formation has inspired the search for biomolecules capable of directing the assembly of non-natural inorganic materials. Peptides that exhibit specific affinities for synthetic materials (e.g., ZnO, Cr_2O_3, GeO_2, Ag, GaAs) have been identified by several authors through bacteriophage or cell surface display (biopanning) methods.[3] However, the use of such display methods to identify specific peptides that induce the formation of crystalline multicomponent metal oxide compounds (i.e., materials widely used in functional devices) at room temperature and ambient pressure has not been reported in the literature. In this work, a phage display method has been used to identify peptides that bind to, and promote the direct and rapid room-temperature formation of $CaO \cdot MoO_3$ (powellite) microparticles from aqueous precursor solutions. Microscale calcium molybdate-based powders are attractive as phosphor particles for advanced lighting and display applications (e.g., as stable and efficient red-light-emitting phosphors stimulated by light-emitting diodes for lighting applications),[4] as catalysts in petrochemical processing (e.g., as an ester-exchange copolymerization catalyst),[5] and as nontoxic corrosion-inhibiting pigments (e.g., for paints on steels used in marine applications).[6] While the syntheses of calcium molybdate-based powders has been accomplished by methods based on solid-state reaction, coprecipitation, combustion synthesis, or pyrolysis of organic precursors, such powder processing has involved high-temperature firing for extended times (e.g., 500–1000 °C for 2–8 h).[7] New chemical approaches that allow for the rapid room-temperature synthesis of calcium molybdate, as well as other functional multicomponent transition-metal oxide compounds, would enable such compounds to be directly formed on low-temperature substrates (e.g., flexible plastics and cloths) or concurrently with low-temperature materials (e.g., coprecipitation with low-melting organic or inorganic salts). Furthermore, the identification of peptides that locally induce the precipitation of such multicomponent oxide compounds could allow for organized functional structures at room temperature, that is, the patterning of such peptides onto surfaces, followed by peptide-induced mineralization, would yield functional multicomponent oxides with tailored morphologies.

The search for $CaMoO_4$-forming peptides involved the use of a commercially available phage display peptide library to identify peptides that exhibit strong binding to $CaMoO_4$ powder. After five rounds of selective panning, four unique phage clones with an affinity for calcium molybdate were isolated. The amino-acid sequences of the four displayed peptides (labeled CM1 to CM4), are listed in Table 1.

Precipitation assays were conducted to assess whether these peptides would promote the formation of $CaMoO_4$ from aqueous precursor solutions. A 25 μL quantity of a 2 mg mL^{-1} solution of a given peptide in water was introduced into an aqueous solution of 0.5 M calcium acetate and 0.2 M ammonium paramolybdate at pH 7 and room temperature. For each of the four CM peptides, precipitation occurred within 20 min of exposure to the otherwise stable calcium acetate–ammonium paramolybdate precursor solution. To confirm that such precipitation resulted specifically from the presence of the biopanned peptides, the following control experiments were conducted. Instead of the CM peptide solutions, 25 μL quantities of either: i) water, or ii) a 2 mg mL^{-1} solution of a control peptide, CON1 or CON2 (see Table 1), were added to the

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Table 1. Amino-acid sequences and isoelectric point (pI) values of calcium molybdate-binding peptides.

Clone number	Amino acid sequence	pI [a]
CM1	AAPNSPWYAYEY	4.00
CM2	SWSPAFFMQNMP	5.24
CM3	YESIRIGVAPSQ	6.00
CM4	DSYSLKSQLPRQ	8.59
CM3m1	YEAIRIGVAPSQ	6.00
CM3m2	YEAIRIGVAPAQ	6.00
CM3m3	YIVEIASGRPQS	6.00
CM3m4	YESIRISQLPRQ	8.75
CM4m	DSYSKSRLQLPQ	8.59
CON1	VLPPAIADAPLG	3.80
CON2	VVPLGMELRPRP	9.57

[a] Calculated using pI/mass program at www.expasy.ch

precursor solution. The control peptides did not exhibit specific binding to calcium molybdate and possessed isoelectric point (pI) values that spanned the range of pI values of the CM peptides. Precipitation was not observed for any of these control experiments or for the precursor solution alone, even after 6 h of incubation.

Scanning electron microscopy (SEM) revealed that the precipitates formed under the influence of the $CaMoO_4$ binding peptides were aggregates of finer particles. A secondary electron image of the aggregates formed in the presence of the CM4 peptide is shown in Figure 1a. The aggregates were comprised of fine, roughly spherical particles that were a few micrometers in diameter. Similar aggregates of spherical particles formed in the presence of the other three CM peptides. The CM3 peptide also induced the formation of aggregates comprised of larger, faceted particles (Fig. 1b). Energy-dispersive X-ray (EDX) analyses of the spherical precipitates formed in the presence of the four CM peptides, and of the faceted precipitates formed in the presence of the CM3 peptide, indicated the presence of both calcium and molybdenum, as shown in Figure 1c (note: the gold peak in the EDX pattern was due to a thin gold coating applied to the particles to avoid charging in the electron microscope). X-ray diffraction (XRD) analysis of the precipitate induced by the CM3 peptide is shown in Figure 1d. Diffraction peaks for only $CaMoO_4$ (powellite) were detected, that is, peaks for the oxides of calcium or molybdenum, or for other calcium molybdate compounds (Ca_3MoO_6, $CaMo_{3.2}O_{5.3}$, $Ca_{1.24}Mo_{1.01}O_3$[8]) were not observed. Electron diffraction analyses of particle cross sections also confirmed the presence of only $CaMoO_4$ (data not shown). Similar XRD patterns were obtained from the precipitates induced by the other CM peptides (see the Supporting Information). Hence, even though the molar ratio of Ca to Mo (1:2.8) in the starting precursor solution was molybdenum-rich relative to the stoichiometry of $CaMoO_4$, the CM peptides induced the formation of only the latter compound (i.e., the compound against which these peptides were selected by biopanning). This further indicates the specificity of these peptides for inducing powellite formation.

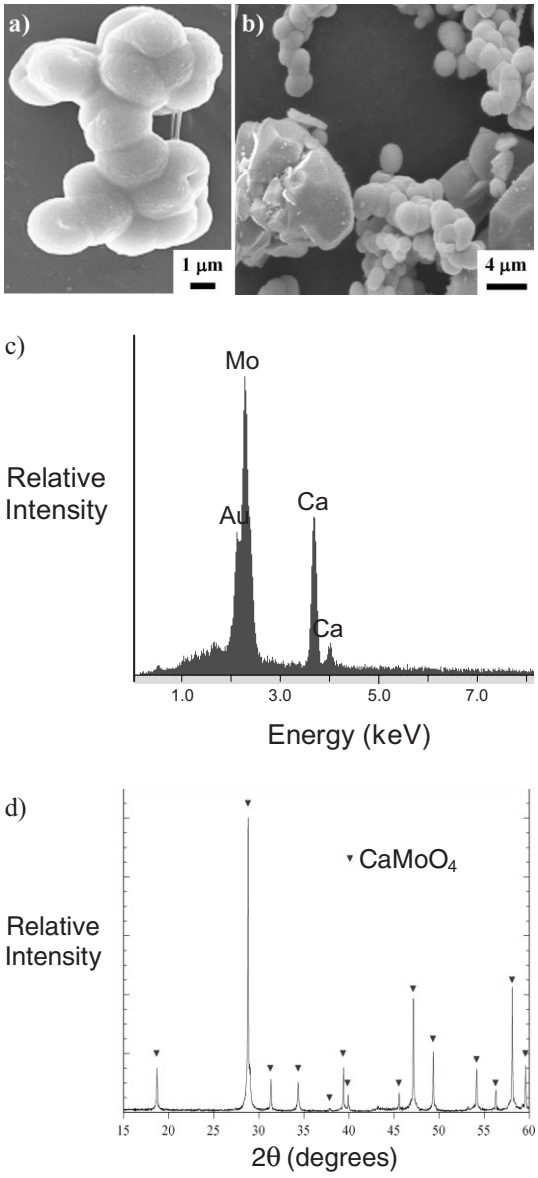

Figure 1. a,b) Secondary electron images of the precipitates generated at room temperature in the presence of the CM4 and CM3 peptides, respectively. c,d) Energy dispersive X-ray analysis and X-ray diffraction (XRD) analyses, respectively, of the precipitate generated in the presence of the CM3 peptide at room temperature.

As mentioned above, precipitation did not occur in the precursor solution (0.5 M calcium acetate, 0.2 M ammonium paramolybdate) for times as long as 6 h in the absence of the CM peptides. In order to evaluate whether pure $CaMoO_4$ would precipitate from a more concentrated precursor solution, a 2 M aqueous solution of calcium acetate was mixed with an equal amount of an aqueous 0.8 M solution of ammonium paramolybdate (i.e., the precursor concentrations were doubled, while keeping the calcium acetate to ammonium paramolybdate ratio fixed). Precipitation was observed to occur immediately upon mixing. After 2 h, the supernatant was

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removed from the precipitate, which was then dried by using vacuum centrifugation. Upon washing of the precipitate with deionized (DI) water it was observed that most of the precipitate was lost through dissolution. In a subsequent experiment under similar precipitation conditions, the precipitate was not washed after removal of the supernatant and vacuum centrifugation. XRD analysis revealed the presence of substantial amounts of ammonium molybdenum oxide hydrate ($[NH_4]_6Mo_8O_{27}\cdot 4H_2O$) and lime (CaO) along with powellite in the precipitate (shown in Fig. 2S of the Supporting Information). For comparison, the precipitate formed after only 10 min of incubation of the original precursor solution (0.5 M calcium acetate, 0.2 M ammonium paramolybdate) with the CM3 peptide was also examined by XRD analysis without washing the precipitate with DI water. The XRD pattern for this precipitate (shown in Fig. 2S of the Supporting Information) yielded diffraction peaks for only $CaMoO_4$ (i.e., the diffraction pattern was similar to that shown in Fig. 1d). Hence, while a solid mixture containing some $CaMoO_4$ could be formed from a supersaturated precursor solution, only the use of the CM-binding peptides allowed for the rapid formation of pure $CaMoO_4$ from a soluble precursor solution.

The photoluminescence emission of peptide-induced calcium molybdate particles was evaluated using 300 nm UV excitation at room temperature. A representative photoluminescence spectrum obtained from the precipitate formed in the presence of the CM3 peptide is shown in Figure 2. An emission peak centered around 530 nm (green) was observed, which is similar to that reported previously for $CaMoO_4$.[4a,7c]

To quantify the amount of $CaMoO_4$ formed in the presence of a given CM peptide, the precipitated material was dried for 16 h at 65 °C, and then subjected to thermogravimetric (TG) analyses while heating at 5 °C min^{-1} up to 600 °C in air. A representative TG analysis of the precipitate generated in the presence of the CM3 peptide is shown in Figure 3a. The weight loss due to evaporation and pyrolysis was completed upon heating to about 400 °C. The total weight loss after heating to 600 °C was only 13.5 %, which indicated that the precipitate was comprised of 86.5 wt % $CaMoO_4$. Quantitative analyses of the amount of $CaMoO_4$ formed upon exposure for 2 h to each of the CM peptides is indicated in Figure 3b. These data were obtained by measuring the weight of each precipitate after heating at 5 °C min^{-1} to 600 °C in air (i.e., after complete evaporation of the volatile constituents and pyrolysis of the organic material present with the precipitated $CaMoO_4$). While all the peptides, CM1–CM4, induced the formation of significant amounts of calcium molybdate (i.e., >6 mg $CaMoO_4$ per mg of peptide), the CM3 peptide generated the largest amount of $CaMoO_4$ (27 mg $CaMoO_4$ per mg of peptide).

Although all four CM peptides exhibited selective binding affinities for $CaMoO_4$, and induced the rapid formation of only this compound from the precursor solution, the amino-

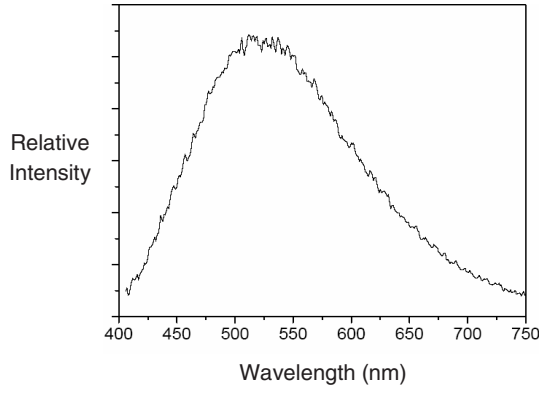

Figure 2. Photoluminescence spectrum, obtained upon stimulation with 300 nm light, of the $CaMoO_4$ precipitate generated in the presence of the CM3 peptide.

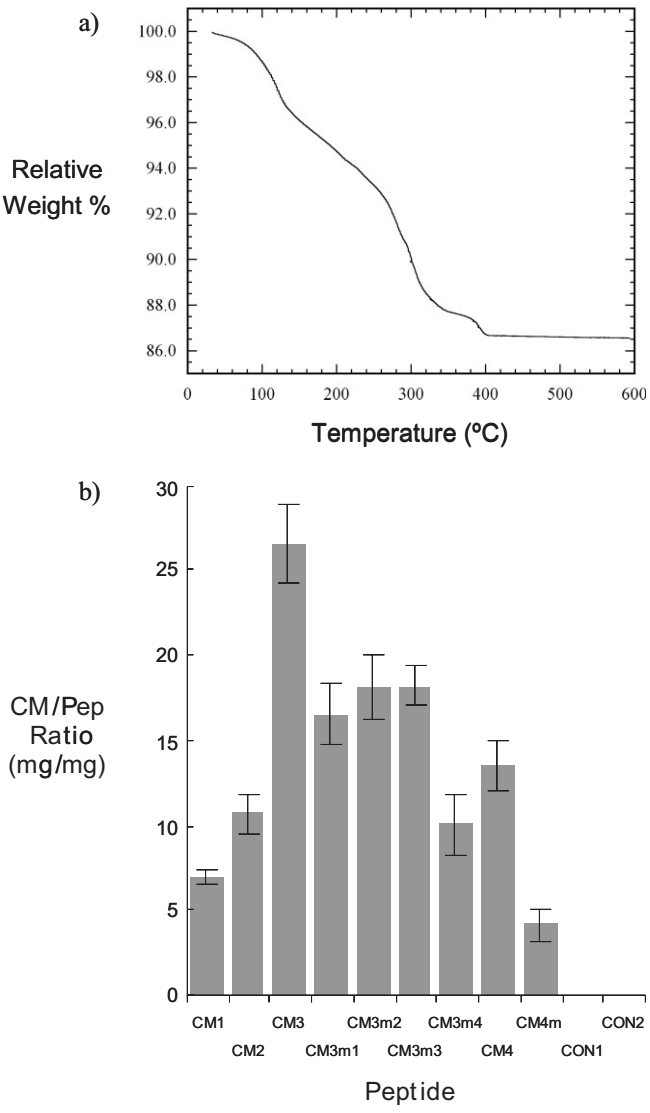

Figure 3. a) TG analysis revealing the weight loss of the dried $CaMoO_4$ precipitate generated from the CM3 peptide upon heating at 5 °C min^{-1} to 600 °C in air. b) The ratio of the weight of $CaMoO_4$ precipitate generated per weight of peptide (CM/Pep ratio) for the peptides listed in Table 1 (for similar exposure times of 2 h).

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acid sequences of these four peptides were surprisingly diverse (see Table 1). No apparent hydrophobic, hydrophilic, or charged sequences were conserved among all four peptides. However, all four CM peptides possessed at least two hydroxyl-bearing amino acids (serine, threonine, tyrosine). It is interesting to note that specific serine residues have been found to be critical for the complexation of molybdenum in the active sites of certain bacterial enzymes.[9a,b] Furthermore, three of the CM peptides (CM1, CM3, CM4) contained a residue with a second negatively charged carboxylate group (aspartate, glutamate) in addition to the C-terminal carboxylate group. Li et al. have previously reported that calcite-binding peptides, identified from a phage display library, exhibited an enrichment in hydroxyl-bearing, or hydroxyl- and carboxylate-bearing, amino-acid residues.[9c]

Mutations of the CM3 and CM4 peptides were used to evaluate the influence of the serine residues on $CaMoO_4$ precipitation (see Table 1). When one or both serine residues were replaced by alanine, the amount of $CaMoO_4$ formed within 2 h was reduced by 32–38 % (compare CM3m1 and CM3m2 to CM3 in Fig. 3b). When the relative positions of the amino acids were altered, without changing the amino-acid compositions, the $CaMoO_4$ yield was again significantly reduced (CM3m3 generated 32 % less $CaMoO_4$ than CM3, and CM4m generated 69 % less $CaMoO_4$ than CM4). Replacement of the last six residues at the C terminus of the CM3 peptide with the last six C-terminal residues of the CM4 peptide resulted in a 62 % reduction in the amount of calcium molybdate formed (compare CM3m4 to CM3 in Fig. 3b). However, the amount of $CaMoO_4$ formed with the CM3m4 peptide was similar to that for the CM4 peptide (note: the pI of the CM3m4 mutant was close to that of the CM4 peptide). These results indicate that the serine content, the positions of the amino-acid residues, and the acidity/basicity of the screened CM peptides influence the amount of $CaMoO_4$ formed at room temperature.

To the authors' knowledge, this work is the first report of the use of phage-display-screened peptides to induce the rapid, room-temperature formation of a specific functional crystalline multicomponent oxide compound ($CaO \cdot MoO_3$). The direct formation of such binary oxide compounds without the need for firing at elevated temperatures opens the door to the biosculpting (peptide patterning, then localized peptide-induced mineralization) of functional compounds onto or with low-temperature or chemically dissimilar materials.

Experimental

A commercial combinatorial phage display peptide library (PhD12 kit, New England Biolabs, Beverly, MA, USA) was used to isolate peptides that bind to calcium molybdate ($CaMoO_4$) powder (99.9 % purity, Alfa Aesar, Ward Hill, MA USA). Prior to the biopanning experiments, the powder was vigorously washed (by vortexing and centrifugation) ten times with 1 mL of a tris-buffered saline Tween (TBST) solution comprising 0.2 % Tween-20 buffered at pH 7.5 with tris-hydroximethyaminoethylene (AMRESCO, Solon, OH, USA). The powder was placed in the TBST solution (5 mg $CaMoO_4$ to 1 mL TBST) and then exposed to the phage solution (10 μL of phage solution per 5 mg of $CaMoO_4$) for a total time of 1 h at room temperature on a rotator operating at 25 rpm. After such exposure, the powder was vigorously washed ten times with 1 mL of a TBST solution, containing 0.5 % Tween-20 at pH 7.5 with tris-hydroximethyaminoethylene, to remove any unbound or loosely bound phage particles. The powder was then exposed to a solution of 0.2 M glycine with HCl (pH 2.20) for 7 min to elute the phage particles adhering to the $CaMoO_4$. The eluted phage particles were transferred to a new Eppendorf tube and neutralized (to pH 7.0) with the addition of 150 μL of the TBST solution. The eluted phage particles were amplified by incubation for 4.5 h with *Escherichia coli* K12 host cells that had been grown overnight on Luria Broth (LB) medium. The biopanning process (exposure to $CaMoO_4$ powder, washing, acid elution, amplification) was repeated four times to further isolate and enrich the calcium molybdate-binding phage. After the final round of panning, *Escherichia coli* host cells were infected with the eluted phage and spread on LB (Fisher Scientific, USA) plates containing 5-Bromo-4-Chloro-3-indolyl-β-D-galactopyranoside (X-gal, Invitrogen, Carlsbad, CA, USA) and isopropyl-β-D-thiogalactopyranoside (IPTG, Invitrogen). DNA obtained from the phage clones was sequenced using an automated sequencer (ABI310, PE Applied Biosystems, Foster City, CA). Peptides were synthesized by a commercial vendor (New England Peptides, Gardner, MA, USA).

For precipitation assays, precursor solutions of calcium acetate ($Ca(C_2H_5O_2)_2 \cdot H_2O$, 99 % purity, Alfa Aesar) and ammonium paramolybdate ($(NH_4)_6Mo_7O_{24} \cdot 4H_2O$, 99 % purity, Alfa Aesar) were prepared in DI water (Nano-Pure Diamond Ultrapure Water System, Barnstead International, Dubuque, IA USA). A 100 μL quantity of a 1 M calcium acetate aqueous solution was mixed with 100 μL of a 0.4 M solution of ammonium paramolybdate at pH 7. A given precipitation assay was initiated by introducing 25 μL of a particular peptide solution (2 mg mL^{-1}) to this precursor solution at room temperature. The concentrations of individual peptides in solution were evaluated by spectrophotometric analysis at 280 nm, using the known molar extinction coefficients of tryptophan and tyrosine. The precipitates formed after 2 h in the presence of the peptides were washed three times with DI water and then with methanol. The precipitates were then dried for 16 h at 65 °C.

SEM was conducted using a field emission gun microscope (Leo 1530 FEG SEM, Carl Zeiss SMT Ltd., Cambridge, UK) equipped with an EDX spectrometer (INCA EDS, Oxford Instruments, Bucks, UK). Transmission electron microscopy was conducted with a JEOL 4000 EX instrument. XRD analyses (Philips PW 1800, PANalytical Almelo, The Netherlands) were conducted with Cu Kα radiation at a scan rate of 0.6° min^{-1}. TG analyses were conducted with a Netzsch 449C Simultaneous Thermal Analyzer (Selb, Germany). Quantitative analyses of the amount of $CaMoO_4$ formed upon exposure to each of the CM peptides were obtained by measuring the weight of each precipitate after heating at 5 °C min^{-1} to 600 °C in air. The photoluminescence emission spectrum of peptide-induced calcium molybdate particles was evaluated at room temperature, using chopped (100 Hz, Chopper Sync II, Spiricon, Logan, UT) 300 nm UV excitation from a 300 watt Xenon arc lamp (Oriel Instruments, Stratford, CT) coupled to a 1/4 meter monochromater (Cornerstone 260, Oriel Instruments). The powder specimens were excited at 45° incidence, and the resulting emission was collected at normal incidence using a collimating lens (74-UV, Ocean Optics, Dunedin, FL) and a fiber probe (LG-455-020-3, Acton Research Corp., Acton, MA). The fiber probe was coupled to an emission monochromator (Spectra Pro 500i, Acton Research Corp.), affixed with a thermoelectrically cooled photosensor module (H7422-50, Hamamatsu Corp., Bridgewater, NJ). The detected signal was acquired using a lock-in amplifier (Signal Recovery 5210, Oak Ridge, TN).

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