COPPER WHITLOCKITE SYNTHESIZED VIA HYDROTHERMAL TRANSFORMATION OF CALCIUM HYDROGEN PHOSPHATE DIHYDRATE

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Abstract: Metal ion substitution in calcium phosphate provides a vehicle for therapeutic delivery of metal ions at low cost and with a long shelf life. The whitlockite structure can incorporate metal ions, which enables the introduction of antibacterial and antiviral agents such as copper ions. The present study describes the synthesis of copper whitlockite (CuWH) via a single-step hydrothermal transformation of calcium hydrogen phosphate dihydrate in the presence of copper ions. Hexahedral morphology of single-phase CuWH was synthesized at 220 °C for 12 h at pH 2.0 in the presence of 5 to 7 mol% Cu2+ ions, suggesting that CuWH precipitation was both dose- and pH-dependent. The CuWH structure contained protonated phosphate, which also suggests that Cu2+ ions were incorporated not only into the Ca(5) site but also the Ca(4) site. The dissolution test mimicking a bioresorption environment created by osteoclasts showed similar dissolution characteristics of Ca2+ and Cu2+ ions in acetic acid–sodium acetate buffer solution containing potassium nitrate at pH 5.5.

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INTRODUCTION

A natural occurring mineral, magnesium whitlockite [MgWH; Ca12Mg2(PO4)3(OH)2] occurs in dental calculus of human tooth enamel,1-3 human articular cartilage,4 and hyper-mineralized osteocyte lacunae in human alveolar bone.5 The synthesis of MgWH involves direct precipitation in aqueous solution in the presence of Mg2+ ions. Many studies to optimize the synthetic conditions for MgWH have been reported.6-8

The Mg2+ ion in the WH structure can be replaced by various cations such as Mn2+, Fe2+, Co2+, Ni2+, Zn2+, Sr2+, and Cd2+9-14. Substitution of a metal ion into the MgWH structure could provide a vehicle for delivery of therapeutic ions, at lower cost and with a longer shelf life compared to the drug delivery of organic antibacterial or antiviral agents. Copper has antibacterial and antiviral activity,15 therefore, copper whitlockite (CuWH) will be a potential antibacterial and antiviral agent. Although Lazoryak et al.17 reported the synthesis of copper-substituted whitlockite-like products via loading of hydrogen into copper-substituted β-tricalcium phosphate [Ca9Cu5(PO4)2] at 480 and 580 °C, direct synthesis of CuWH via a liquid-phase process has not yet been reported.

The goal of the present study was a synthesis of CuWH, which was accomplished by hydrothermal transformation of calcium hydrogen phosphate dihydrate (DCPD) in the presence of copper ions.

MATERIALS AND METHODS

Synthetic methods

Calcium phosphate dihydrate (DCPD; CaHPO4·2H2O, Art. No. C7263) and copper nitrate trihydrate [Cu(NO3)2·3H2O, Art. No. 61194] were purchased from Sigma Aldrich, Japan. Copper nitrate trihydrate (0-8 mol% against calcium ion in DCPD) was dissolved in 25 mL of ultrapure water in a polytetrafluoroethylene (PTFE) vessel (50 mL) at a filling ratio of 50 vol%, followed by adjustment of the solution pH to 1.5, 2.0, 2.5, or 3.0 by addition of HNO3 or NH4OH solution. After 0.25 g of DCPD powder was added, the vessel was transferred to an autoclave (HU-50, SAN-AI Kagaku Co., Ltd., Japan). The reaction solution was treated at a pressure of 2 MPa at 220 °C for 12 h in an oven. The precipitate was separated by centrifugation, washed with ultrapure water, and then dried in an oven at 105 °C for 24 h. The experimental parameters are summarized in Table 1.

Characterization

The crystalline phase was measured using an X-ray diffractometer (XRD; SmartLab, Rigaku Corp., Japan), equipped with a CuKα radiation source, λ = 1.5418 Å, 40 kV, and 50 mA. The crystalline phase was identified with respect to ICDD PDF reference patterns. Lattice parameters were calculated using SmartLab Studio II software (Rigaku Corp., Japan).
with an external silicon standard reference. Fourier-transform infrared (FT-IR) spectra were obtained on KBr using an FT-IR spectrometer (FT/IR-6100, Jasco Corporation, Japan) at a resolution of 4 cm\(^{-1}\). The surface morphology of the gold-sputtered CuWH particles was observed by scanning electron microscopy (SEM; JSM-6610LA, Jeol, Japan) at an acceleration voltage of 15 kV. Elemental analysis was performed by energy-dispersive X-ray spectroscopy (JED-2300, Jeol). Diffuse reflection spectra were recorded using a UV-Vis spectrometer (V-670, Jasco Corporation) equipped with an integrating sphere (ISN-723, Jasco Corporation). The MgWH synthesized by transformation of DCPD\(^6\) was used as a reference material. The reflection spectra were converted using the Kubelka-Munk function.

\(^1\)H and \(^{31}\)P magic-angle-spinning nuclear magnetic resonance (MAS NMR) spectra were collected on a 600 MHz (14.1 T) JNM-ECA600 spectrometer (Jeol) operating at 600.172 and 242.954 MHz for \(^1\)H and \(^{31}\)P, respectively. Single pulse \(^1\)H and \(^{31}\)P MAS-NMR experiments were performed at MAS frequencies of 20 kHz with a 3.2-mm-diameter zirconia tube. A 90° pulse width of 2.3 μs and a relaxation delay of 30 s were used for the \(^1\)H MAS-NMR experiment. The \(^{31}\)P MAS-NMR experiment was performed with a 90° pulse width of 3.2 μs and relaxation delay of 100 s. Adamantane [(CH)\(_2\)(CH)\(_2\)] for \(^1\)H and ammonium dihydrogen phosphate (NH\(_4\)H\(_2\)PO\(_4\)) for \(^{31}\)P were used as the secondary external references.

The dissolution of CuWH powder synthesized with 5 mol% Cu at pH 2.0 and 220 °C for 12 h was measured in a 0.08 mol L\(^{-1}\) acetic acid–sodium acetate (Ac-AcNa, pH 5.5) buffer solution containing 0.1 mol L\(^{-1}\) potassium nitrate. The Ac-AcNa buffer solution was used to mimic a bioresorption environment created by osteoclasts. Five milligrams of sample were added to 100 mL of buffer solution at 25 ± 2 °C with stirring at 430 ± 15 rpm. The amounts of calcium and copper ions released from the CuWH powders were measured using a calcium and copper ion-selective electrodes (Horiba, Ltd., Japan), in accordance with JIS T0330-3: 2012. The test was performed in three replicates.

RESULTS

The effects of copper concentration on the products were examined. Figure 1 shows XRD patterns for the powders synthesized at 220 °C for 12 h in the presence of copper between 0 and 8 mol%. Monetite (ICDD PDF 01-070-0359), WH (00-009-0169), and hydroxyapatite (HA, 00-009-0432) were formed between 0 and 1 mol%, while biphasic monetite and WH were formed in the presence of copper ions between 3 and 4.5 mol%. The amount of WH increased with increasing copper content between 0 and 4.5 mol%. At 4.5 mol%, only a trace amount of monetite was detected in the XRD pattern, together with the WH phase. Copper concentrations between 5 and 7 mol% led to the formation of single-phase WH. At 8 mol%, a mixture of monetite, WH, and an unidentified phase was formed.

| Parameter | DCPD (g) | Cu (mol%) | Initial pH |
|-----------|----------|-----------|------------|
| A change of copper concentration | 0.25 | 0, 1, 3, 4.5, 5, 7, 8 | 2.0 |
| A change of initial pH | 0.25 | 5 | 1.5, 2.0, 2.5, 3.0 |

**TABLE 1** Effects of copper concentration and initial pH on final product.

![FIGURE 1](image_url) FIGURE 1 XRD patterns for products synthesized by transformation of DCPD in the presence of 0 to 8 mol% Cu\(^{2+}\) ions. 2θ = (a) 4–60° and (b) 25–35°. ■: monetite, ▲: HA, ●: unidentified peaks.
The lattice constants of WH were plotted as a function of copper concentration together with the ICDD reference patterns of CuWH reported by Lazoryak et al. (Fig. 2). The lattice constants $a$ and $c$ tended to decrease with increasing copper concentration between 0 and 5 mol%, while they increased slightly between 5 and 8 mol%. The lattice constant $a$ was similar to that for the ICDD reference patterns, while the lattice constant $c$ was shorter than that for the ICDD reference patterns.

Figure 3 displays XRD patterns showing the effect of the initial reaction solution pH on the final products after reaction at 220 °C for 12 h. A mixture of monetite, WH, HA, and an unidentified phase was formed at pH 2.0, while biphasic WH and a trace amount of HA were formed at pH 2.5. At pH 3.0, monetite, WH, and an unidentified phase were formed.

The CuWH powder synthesized with 5 mol% Cu at pH 2.0 and 220 °C for 12 h was subjected to FT-IR (Fig. 4a) and UV-Vis analyses (Fig. 4b). The FT-IR spectrum showed PO$_4^{3-}$ groups ($\nu_2$: 1023, 1062, 1076, 1116, 1135 cm$^{-1}$; $\nu_1$: 921, 948, 994 cm$^{-1}$; $\nu_3$: 545, 558, 602 cm$^{-1}$) and a small shoulder peak due to protonated phosphate (HPO$_4^{2-}$) at 860 cm$^{-1}$. The UV-Vis spectrum of CuWH displayed two distinctive peaks at ~720 and ~980 nm, while no peak was observed for MgWH. According to a study by Banarafa et al., the peaks at ~720 and ~980 nm can be assigned to the Ca(4) and Ca(5) sites, respectively. Morphological observation by SEM revealed that plate-like DCPD particles with sizes of 2 to 10 µm (Fig. 5a) were transformed into characteristic hexahedral WH particles with sizes of a...
few micrometers (Fig. 5b). Similar hexahedral morphology was observed in MgWH by Hashimoto 
et al.\textsuperscript{21} and Li \textit{et al.}\textsuperscript{22} The DCPD transformation to MgWH reported by Tas\textsuperscript{7} also demonstrated the hexahedral shape of MgWH. Elemental analysis showed the incorporation of Cu\textsuperscript{2+} ions into the CuWH together with contaminating magnesium ions, which was an impurity derived from DCPD. The molar ratios Ca/P for DCPD and (Ca+Cu)/P for CuWH were 0.98 and 1.45, respectively.

The local structure of CuWH was analyzed using \textsuperscript{1}H and \textsuperscript{31}P MAS-NMR. The \textsuperscript{1}H MAS-NMR spectrum contained a broad peak at 9.9 ppm, assigned to protonated phosphate (HPO\textsubscript{4}\textsuperscript{2-}) in the CuWH structure (Fig. 6a). Figure 6b shows the broad peaks in the \textsuperscript{31}P MAS-NMR spectrum. According to the \textsuperscript{31}P MAS-NMR study of MgWH by McCubbin \textit{et al.}\textsuperscript{23} the PO\textsubscript{4} site-derived peaks were deconvoluted to three peaks centered at 2.3, 1.5, and −0.1 ppm, with an integration ratio of 22 : 40 : 38.

Similar dissolution curves of Ca\textsuperscript{2+} and Cu\textsuperscript{2+} ions were obtained in Ac-AcNa buffer solution (Fig. 7). The results support substitution of Cu\textsuperscript{2+} ions in CuWH structure and suggest that the substituted Cu\textsuperscript{2+} ions dissolved together with Ca\textsuperscript{2+} ions. The amount of Ca\textsuperscript{2+} ions released from the CuWH powders reached saturation after 16 h of dissolution test (data not shown). However, the saturation of Cu\textsuperscript{2+} ions was not observed as the copper ion-selective electrode was unstable at more than 180 min of dissolution test.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure4.png}
\caption{(a) FT-IR and (b) UV-Vis spectra of CuWH synthesized by transformation of DCPD in the presence of 5 mol\% Cu\textsuperscript{2+} ions. UV-Vis spectrum of CuWH is compared with that of MgWH.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure5.png}
\caption{Particle morphology of (a) DCPD and (b) CuWH synthesized by transformation of DCPD in the presence of 5 mol\% Cu\textsuperscript{2+} ions, and (c) EDX spectra of DCPD and CuWH.}
\end{figure}
ions. If amounts of nominal Cu$^{2+}$ ions (5 mol%) were fully substituted in the WH structure, only 47 mol% of Ca$^{2+}$ ions and 37 mol% of PO$_4^{3-}$ ions against the nominal amount of DCPD reacted to produce the CuWH $\text{Ca}_9\text{Cu}_2\text{H}_2(\text{PO}_4)_{14}$, as given in Eq. (1). The $(\text{Cu}+\text{Cu})/\text{P}$ molar ratio of 1.45, determined by EDX analysis, was similar to the value of 1.43 found for $\text{Ca}_9\text{Cu}_2\text{H}_2(\text{PO}_4)_{14}$. The DCPD as purchased unexpectedly contained a Mg impurity (Fig. 4b); therefore, Mg$^{2+}$ ions also would have been incorporated in the CuWH together with Cu$^{2+}$ ions.

$$18\text{CaHPO}_4\cdot 2\text{H}_2\text{O} + 2\text{Cu(NO}_3)_2\cdot 3\text{H}_2\text{O} \rightarrow \text{Ca}_{18}\text{Cu}_2\text{H}_2(\text{PO}_4)_{14} + 4\text{HPO}_4^{2-} + 12\text{H}^+ + 42\text{H}_2\text{O} + 4\text{NO}_3^- \quad (1)$$

In the MgWH structure, Mg$^{2+}$ ions were incorporated into Ca(5) sites, while the Ca(4) sites were occupied by H$^+$ ions, along with inversion of the P(1)O$_4$ tetrahedra. Accordingly, protonated phosphate (HPO$_4^{2-}$) in MgWH can be detected by FT-IR spectroscopy. However, unlike the peak for HPO$_4^{2-}$ ions in the visible spectrum of MgWH, only a small shoulder peak derived from HPO$_4^{2-}$ ions was observed in CuWH (Fig. 4a). In the FT-IR spectrum of $\text{Ca}_9\text{Cu}_2\text{H}_2(\text{PO}_4)_{14}$, the HPO$_4^{2-}$ peak was not observed and the location of hydrogen was not identified by Rietveld refinement. The presence of HPO$_4^{2-}$ ions in CuWH was also confirmed by $^1$H MAS-NMR (Fig. 6a), but the peak was broader than the $^1$H MAS-NMR peak for MgWH reported by McCubbin et al. $\text{Ca}_{18}\text{Mg}_2\text{H}_2(\text{PO}_4)_{14}$ demonstrated that the Cu(5) sites were fully occupied by Cu$^{2+}$ ions in $\text{Ca}_9\text{Cu}_2\text{H}_2(\text{PO}_4)_{14}$, but $\text{Ca}_9\text{Cu}_2\text{H}_2(\text{PO}_4)_{14}$ (0.64 $\leq x \leq 0.7$) contained 68% Cu$^{2+}$ ions and 32% Ca$^{2+}$ ions. The UV-Vis spectrum suggested the incorporation of Cu$^{2+}$ ions in both the Ca(4) and Ca(5) sites in the CuWH structure (Fig. 4b), according to the report by Banarafa et al. This implies that the Ca(4) sites in CuWH were occupied.
by H' and Cu2+ ions. Furthermore, the weak HPO42− peak in the FT-IR (Fig. 4a) and 1H MAS-NMR (Fig. 6a) spectra also support partial substitution of Cu2+ ions at Ca(4) sites. In addition, the large degree of line broadening in the 31P MAS-NMR spectrum (Fig. 6b) was due to paramagnetic effects of the Cu2+ ions, which also corroborates the incorporation of Cu2+ ions into the CuWH structure. However, the line broadening prevented further analysis of the PO43− sites in CuWH.

The decreasing value of the lattice constants a and c with increasing copper concentration between 0 and 5 mol% suggests that the amount of Cu2+ ions substituted in Ca(5) sites of the WH structure increased with increasing copper concentration. Substitution of Ca2+ ions (ionic radius of 1 Å) with Cu2+ ions having a smaller ionic radius (0.72 Å) led to a decrease in lattice constants a and c. This decrease in lattice constants agreed with results from a study of copper-substituted β-TCP by Benarafa et al. In contrast, lattice constants a and c increased slightly between 5 and 7 mol%. The weak HPO42− peaks in the FT-IR (Fig. 4a) and 1H MAS-NMR (Fig. 6a) spectra indicated that Cu2+ ions were also incorporated at Ca(4) sites. The larger ionic radius of Cu2+ ions compared to H' ions caused an increase in a and c.

The lattice constants for Ca9Cu2H1.42(P04)14 and Ca9Cu25H2.32(HPO4)14 reported by Lazoryak et al. were a = 10.3197(1) Å and c = 37.300(2) Å, and a = 10.3975(1) Å and c = 37.274(2) Å, respectively. The lattice constants a and c in the present study were smaller than those reported Lazoryak et al. These results may be caused by differences in the substitution sites of the Cu2+ ions or in the synthetic method.

The solubility of DCPD and β-TCP decreased with increasing temperature, i.e., the solubility constants [log K(T)] for DCPD (0.61) and β-TCP (10.61) at 25 °C decreased to 0.28 and 0.26, respectively, at 90 °C. Thus, β-TCP could precipitate together with DCPD at temperatures of 90 °C or higher. Indeed, some fractions of copper-free WH formed in the absence of Cu2+ ions (0 mol%), as shown in Fig. 1. In fact, the solubility of MgWH was less than that of β-TCP, as demonstrated by an in vivo study of MgWH. Therefore, CuWH was assumed to be thermodynamically more stable than DCPD at 220 °C in the presence of Cu2+ ions. However, the copper concentrations between 0 and 5 mol% were too low to form single-phase CuWH. Thus, DCPD, HA, and an unidentified phase precipitated together with CuWH. A concentration of Cu2+ ions between 5 and 7 mol% resulted in the precipitation of single-phase CuWH.

The initial pH of the reaction solution was also a crucial factor in the synthesis of single-phase CuWH. Jang et al. reported that MgWH was the most stable calcium phosphate phase at pH values below 4.2 and a temperature of 70 °C. Although the final pH after synthesis of CuWH was below 4.2, only the initial pH of 2.0 resulted in the precipitation of single-phase CuWH. When the synthesis was conducted at an initial pH of 1.5, 2.5, or 3.0, subphases of monetite, HA, and an unidentified phase were formed. Therefore, CuWH was considered the only stable phase at an initial pH of 2.0. Overall, the results demonstrated that CuWH precipitation was dose- and pH-dependent.

The Cu2+ ions substituted in CuWH structure dissolved together with Ca2+ ions (Fig. 7). The substitution amount of Cu2+ ions in CuWH was 9.4 mol%, calculated from the amount of released Ca2+ and Cu2+ ions, which was close to 10 mol% of CuWH Ca9Cu2H2(PO4)14. However, assuming chemical composition of CuWH Ca9Cu2H2(PO4)14, only 38.9 wt.% of Ca2+ ions and 36.3 wt.% of Cu2+ ions against total Ca2+ and Cu2+ ions in CuWH were released after 180 min. It was also reported by Lazoryak et al. that solubility of zinc-substituted β-TCP decreased with increasing zinc concentration between 0 and 10 mol%, which was due to decreased stability of the TCP structure. It is considered that Cu2+ ion substitution stabilized whitlockite structure and subsequently led to solubility decrease of CuWH. Therefore, the amounts of dissolved Ca2+ and Cu2+ ions were lower than total Ca2+ and Cu2+ ions in CuWH. In contrast, decrease in dissolution rate of CuWH was observed after 15 min of dissolution test. Bohner et al. proposed formation of an HA interfacial layer on β-TCP particles during the dissolution test, which resulted in decrease in dissolution rate. The formation of interfacial layer on CuWH particles may be among the factors that decrease in dissolution rate of CuWH. However, further analysis is needed to clarify the dissolution mechanism of CuWH.

CONCLUSIONS

Synthesis of CuWH was accomplished through a single-step hydrothermal transformation of DCPD in the presence of Cu2+ ions. The CuWH synthesized at 220 °C for 12 h in the presence of 5 to 7 mol% Cu2+ ions and a pH of 2.0 had single phase and a hexahedral morphology. The results suggest that CuWH precipitation was both dose- and pH-dependent. The CuWH contained HPO42− ions in its structure and copper ions incorporated not only at Ca(5) sites but also partially at Ca(4) sites. The dissolution of Ca2+ and Cu2+ ions had similar trend in Ac-AcNa buffer solution.

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