

Solvothermal synthesis of strontium phosphate chloride nanowire

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Abstract

Strontium phosphate chloride nanowire was synthesized via a solvothermal treatment of strontium tri-polyphosphate and Collin salt in 1,4-dioxane at 150 °C. The effects of 1,4-dioxane concentration on particle morphology, crystallinity and phase purity were investigated in this study. The specimen morphology was analyzed by transmission electron microscopy (TEM) and scanning electron microscopy (SEM). When the concentration of 1,4-dioxane was below 10%, micron-sized whisker was the dominant form. At 20–25% concentration of 1,4-dioxane, strontium phosphate chloride single-crystalline nanowire was 31 ± 12 nm in diameter and 1.43 ± 0.6 μm in length with an aspect ratio of 52.28 ± 29.41 . X-ray diffraction (XRD) pattern of this nanowire matched with that of strontium phosphate chloride (JCPDS #083-0973). When 1,4-dioxane concentration exceeded 25%, nanorod aggregate was the dominant form instead of nanowire. At 20–25% 1,4-dioxane concentration suitable strontium concentration combine with high chemical potential environment favors the formation of nanowires. By adding 1,4-dioxane impure phase such as β-strontium hydrogen phosphate, nanorod formation was suppressed. This method provides an efficient way to synthesize high aspect ratio strontium phosphate chloride nanowire. It has potential bioactive nanocomposite, high mechanical performance bioactive bone cement filler and fluorescent material applications.

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1. Introduction

Control over the morphology and crystal forms of minerals is of significance in the area of crystal engineering. Strontium phosphate chloride is structurally similar to strontium phosphate and strontium hydroxyapatite. Strontium apatites are analogous to calcium apatite, a known biocompatible material [1] that attracted our group to investigate its potential applications in orthopedics for bone fracture treatment, and other clinical areas.

Apatites ($M_5(PO_4)_3X$, where M = alkaline earths (Ca, Mg, Sr, Ba), X = halogens (Cl, F, Br) or OH) have been used as a bone cement filler, industrial phosphors [2], laser materials and migration-preventing barriers for radionuclide from nuclear waste storage [3]. Strontium apatite, strontium-

substituted hydroxyapatite [4], strontium chloroapatite and strontium phosphate [5] have been reported in several literatures. Crystalline strontium-substituted hydroxyapatite synthesized by hydrothermal method was developed in 1994 by Masanori Kikuchi group [6]. Kikuchi's method is used to synthesize large-sized strontium-substituted hydroxyapatite crystals which is not suitable for orthopedic applications.

One-dimensional (1D) nanostructures, such as nanorods, nanowires and nanofibers have attracted special interests in the recent years due to their unique properties. In particular, the enhanced mechanical properties and bioactivity on the nanoscale can be well suited for clinical applications [7]. Our group has developed strontium-containing bioactive bone cement for vertebroplasty [8] which has low monomer toxicity, low setting temperature and stimulates bone growth in the bone cement–bone interface.

There is no published information available on the solvothermal synthesis of the strontium phosphate chloride

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nanowire. Its analog—calcium hydroxyapatite nanofiber and strontium hydroxyapatite nanowire have been successfully produced by three different methods: microemulsion [9], template-based method [10] and anisotropic method. Template-based and microemulsion methods suffer from aluminum and surfactant contamination, respectively, while pure anisotropic method has limited yield. Synthesis of strontium phosphate and apatite via phosphate gel hydrolysis [11] allows higher starting material concentrations that greatly improve the yield per unit volume. This method produced single-crystalline instead of multi-crystalline nanowire from template-based method.

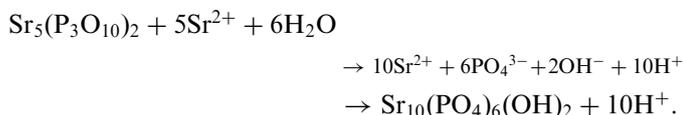
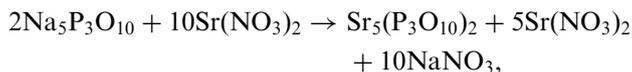
Strontium chloro(hydroxyl) apatite wet synthesis study showed that presence of OH⁻ can considerably influence the crystallinity and stabilization of a particular phase, and can act as an accelerator for converting amorphous calcium phosphate to crystalline form. In this study, we investigate the influence of 1,4-dioxane on strontium phosphate chloride crystal morphology to develop a novel method to synthesize high aspect ratio strontium phosphate chloride nanowire. In a previous strontium tri-polyphosphate hydrolysis micron whisker study, 1,4-dioxane has shown its potential of producing high aspect ratio calcium hydroxyapatite whisker at pH 4–6. By investigating the solvent effect, we were able to synthesize high aspect ratio nanowire with a high yield in the bone cement reinforcement application.

2. Experimental procedures

2.1. Preparation

Collin salt (Sr₆H₃(PO₄)₅·2H₂O) was synthesized by mixing ACS grade Sr(NO₃)₂ solution with (NH₄)₂HPO₄ solution at pH 7.5 according to a method stated in literature [12]. The precipitate was filtered out by a 1 μm filter that acts as a growth medium for nanowire [13].

Analytical grade Sr(NO₃)₂ (0.395 g) and 0.5 g NH₄Cl was dissolved into 22.5 mL distilled water and sodium tri-polyphosphate solution was prepared by dissolving 0.162 g Na₃P₃O₁₀ solution in 22 mL distilled water. Strontium tri-polyphosphate gel was prepared by mixing strontium nitrate solution and sodium tri-polyphosphate solution. One gram of Collin salt nanocrystal, 15 mL of 1,4-dioxane were added to the gel mixture. Ethylenediamine (0.5 mL) was added as a buffer system to maintain the gel pH at 9–10 during solvothermal treatment to suppress formation of micron whisker. Control specimen was prepared by replacing 15 mL 1,4-dioxane with distilled water.



The resultant mixture was transferred into a stainless Teflon-lined autoclave maintained at 150 °C for 24 h. The reaction mixture was air cooled to room temperature. The pH dropped to 8.73–9.04 from 9.41 (Table 1). The resultant product was filtered out, washed with distilled water and dried in oven at 120 °C for 24 h.

2.2. Characterization

The phases' purity and its chemical identity of the samples were characterized by Philips powder X-ray diffractometer PW1830 with Cu K_α radiation (λ = 1.54056) at a scan rate of 0.05°/s in the 2θ range of 20°–60°. The X-ray diffraction (XRD) pattern was compared with JCPDS database for chemical identification.

Transmission electron microscopy (TEM) specimen was prepared by dispersing nanowire in absolute ethanol with assistance of ultrasonics, then placing a drop of dispersion on an amorphous carbon-coated copper grid. Morphology of the sample was studied under Philips Technai 20 operating at an accelerating voltage of 200 kV. The lattice structure of the samples was determined at high resolution mode. The size distribution of nanowire was analyzed by measuring 100 nanowire particles under TEM. Leo 1530 FEG was used to analyze the specimen in a larger area to study the non-dispersed state. Specimens were stick to the carbon-coated conductive tape on the aluminum stub holder. The loosen powder was removed by blowing with compressed air. All specimens were observed at 12 kV and 20,000 × magnifications.

Strontium to chloride ratio was determined by EDS. FTIR spectrum was collected on BIO-RADFTS-7 to evaluate the functional group of the nanowire. Raman spectrum was collected on a Renishaw Raman System 1000 Spectroscopy. The wavelength of laser diode was set at 540 nm. The spectrum was processed by Biorad software for background subtraction. The Sr concentration in aqueous solution and 20% 1,4-dioxane concentration was determined by ICP-AES according to APHA method 3120.

3. Results and discussion

Fig. 1a shows the powder XRD pattern of a synthesized product crystallized at 150 °C under 15 h hydrothermal treatment is in good agreement with that of the bulk hexagonal Sr₅(PO₄)₃Cl (space group P63/m). The diffraction peaks can be indexed as the strontium phosphate chloride *a* = 9.8774, *c* = 7.189 (JCPDS card no 083-0973)

Table 1
Changes in the pH of the solution in different 1,4-dioxane concentration

Treatment temperature		5%	10%	15%	20%	25% ^d	30%	50%
150 °C	Initial pH	9.37	9.39	9.4	9.35	9.4	9.42	9.38
	Final pH	8.9	8.85	8.88	9.04	8.9	8.85	8.73

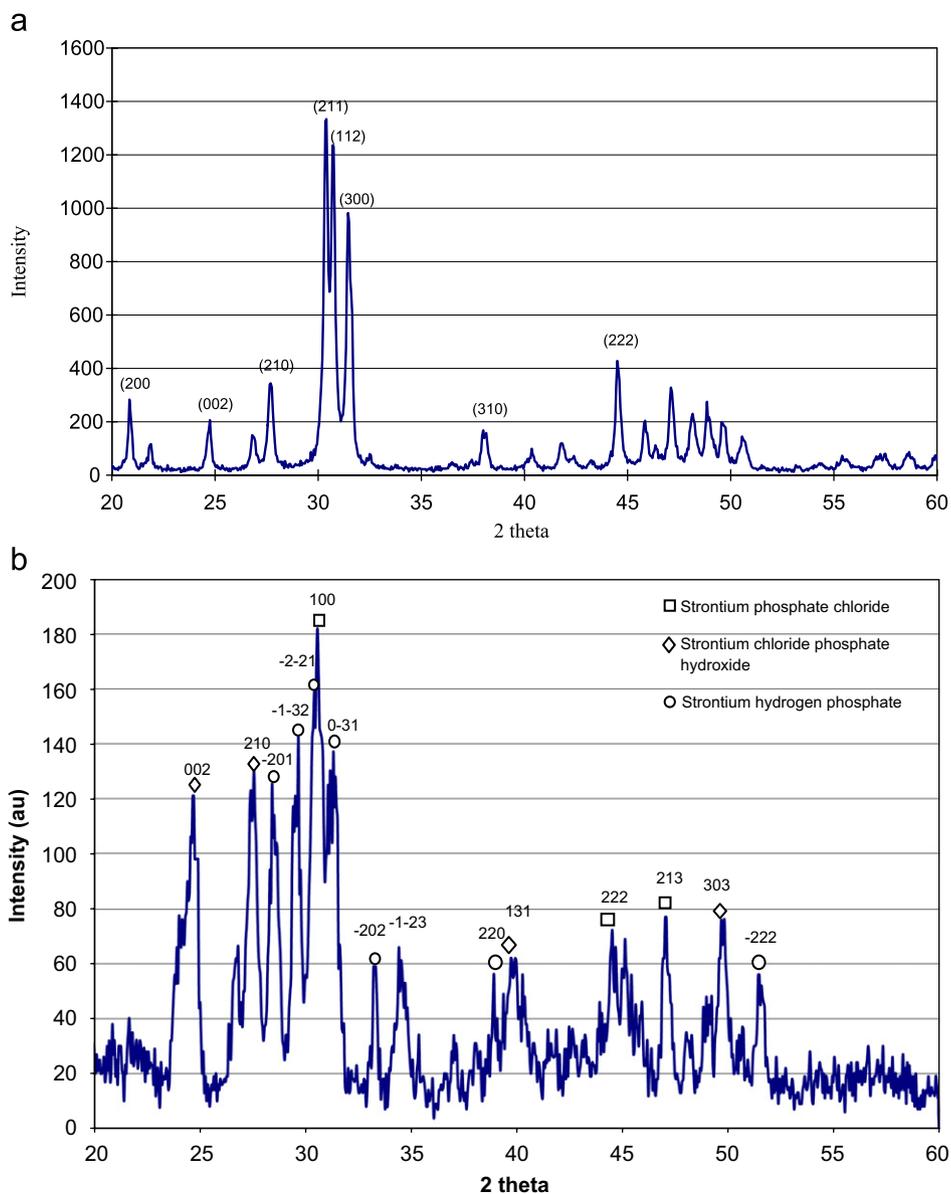


Fig. 1. (a) XRD of nanowire (20% 1,4-dioxane) and (b) XRD of nanowire without 1,4-dioxane.

indicating that the prepared nanowire is a polymorph of strontium chloride phosphate. Stronger peak of [2 1 1] indicates the nanowire growth along the *c*-axis direction. From Fig. 1b, the specimen synthesizes in the absence of 1,4-dioxane, β -strontium hydrogen phosphate (circle) JCPDS # 44-0798 and strontium phosphate chloride hydroxide (square) peak and strontium phosphate chloride peaks (diamond) was present in the XRD pattern.

The morphology, structure and size of strontium phosphate chloride nanowire were characterized with SEM and TEM measurements. Fig. 2 indicates that the product is strontium phosphate chloride nanowire with length of $1.43 \pm 0.6 \mu\text{m}$ and diameter of $31 \pm 12 \text{ nm}$ with an aspect ratio of 52.28 ± 29.41 . Usually, several nanowires were found to aggregate together, instead of being dispersed. From HRTEM (Fig. 3), the lattice spacing of the nanowire was found to be 7.219 \AA along the *c*-axis.

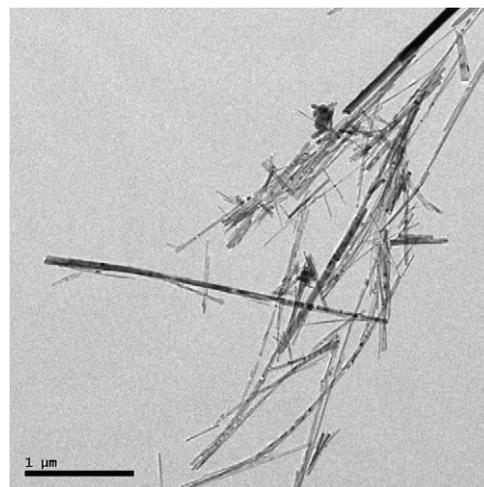


Fig. 2. TEM photo of nanowire (20% 1,4-dioxane).

Fig. 4 shows the selected area electron diffraction (SAED) pattern taken from an individual nanowire, which indicates that the strontium phosphate chloride is a single-crystal structure.

Scanning electron microscopy (SEM) photo (Fig. 5a–c) of strontium phosphate chloride showed that nanowires form aggregates that look like bundles of spaghetti. The EDS results (Fig. 5d) showed that the nanowires contained 4.17wt % chloride, and the Sr:P ratio was lowered to 1.52 due to chloride substitution [14]. PO_4^{3-} ($560, 596, 1030, 1078\text{ cm}^{-1}$) [15] and OH^- (3460 cm^{-1}) were observed in FTIR spectrum (Fig. 6) [16]. The absorption peaks were attributed to strontium phosphate chloride and minute amount of strontium phosphate chloride hydroxide impurity.

From the Raman spectrum, ν_1 phosphate mode band situated at $\sim 949\text{ cm}^{-1}$ was observed. The OH-stretch $3224, 3472\text{ cm}^{-1}$ band was observed even though we adopted 50% of 1,4-dioxane. The weakening of $-\text{OH}$ peak at 3472 cm^{-1} was shown in Fig. 7, from 0% (Blue line), 20% (Green line) and 50% (Black line). The reduction of $-\text{OH}$

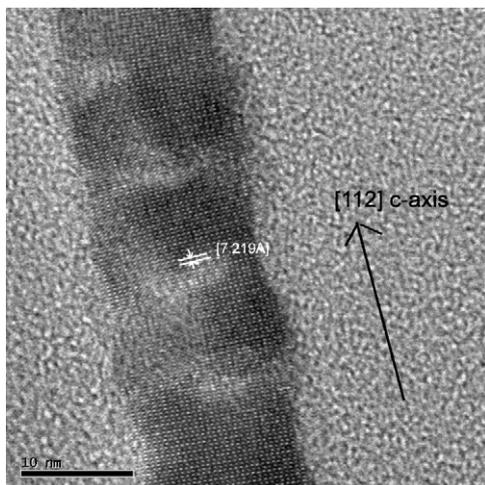


Fig. 3. HRTEM of nanowire (20% 1,4-dioxane).

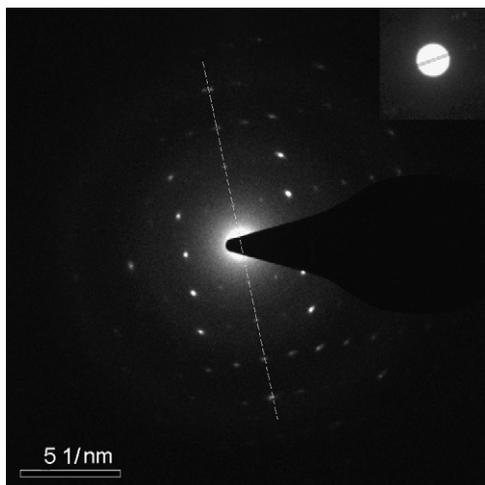


Fig. 4. SAED pattern (20% 1,4-dioxane).

band amplitude and broadening of its peak shows that the crystal became more amorphous at higher 1,4-dioxane concentrations [17].

1,4-dioxane has a lower dielectric solvent (ϵ value = 2.21) as compared with water (ϵ value = 80) [18]. The strontium ion concentration was lowered in 1,4-dioxane solution due to lower dielectric constant of the 1,4-dioxane–water mixture. The phase transformation via dissolution and reprecipitation is related to its phase stability at different pH and temperature levels. From the ICP-AES report, the strontium concentration was 0.92 mg/L for 20% 1,4-dioxane sample while the aqueous form contains 5.1 mg/L.

Collin salt, the metastable phase formed at pH 7.5, underwent a phase transformation via dissolution and reprecipitation. The difference in the thermodynamic driving force between the metastable phase and strontium phosphate chloride drive the conversion of chloride, phosphate and strontium to form strontium phosphate chloride on the surface of strontium hydroxyapatite or other nuclei. The difference in the thermodynamic force between the metastable and stable phases determines the flux of the monomer. The anisotropic reactivity of strontium hydroxyapatite or chloroapatite makes the interfacial free energy perpendicular to the c -axis higher than a -axis that favors the formation of nanowire structure.

From the Raman spectrum, the OH band broadened when the 1,4-dioxane concentration was higher than 20%. The crystal became more amorphous at 30–50% 1,4-dioxane concentrations. With the increase of 1,4-dioxane volume concentration, the crystallinity degree and crystallite size decreased, as the dissolution and precipitation process were hindered by the presence of cyclic ether. It is related to reduce solubility of strontium chloroapatite precursors in the mixture as strontium chloroapatite is a polar molecule.

4. Conclusion

The nucleation and growth condition of strontium phosphate chloride were investigated to synthesize nanowire with a high aspect ratio by controlling the 1,4-dioxane concentration. Least stable phase Collin salt dissolves and the dissolution product grows on the hydrolysis product of strontium tri-polyphosphate gel-strontium hydroxyapatite nucleus. In a suitable strontium concentration, the chemical potential favors the formation of nanowires. Due to the presence of chloride in the reaction mixture, the strontium chloride phosphate nanowire was formed instead of strontium hydroxyapatite nanowire. This method provides an efficient way to synthesize high aspect ratio strontium phosphate chloride nanowire. It has potential bioactive nanocomposite, high mechanical performance bioactive bone cement filler and fluorescent material applications.

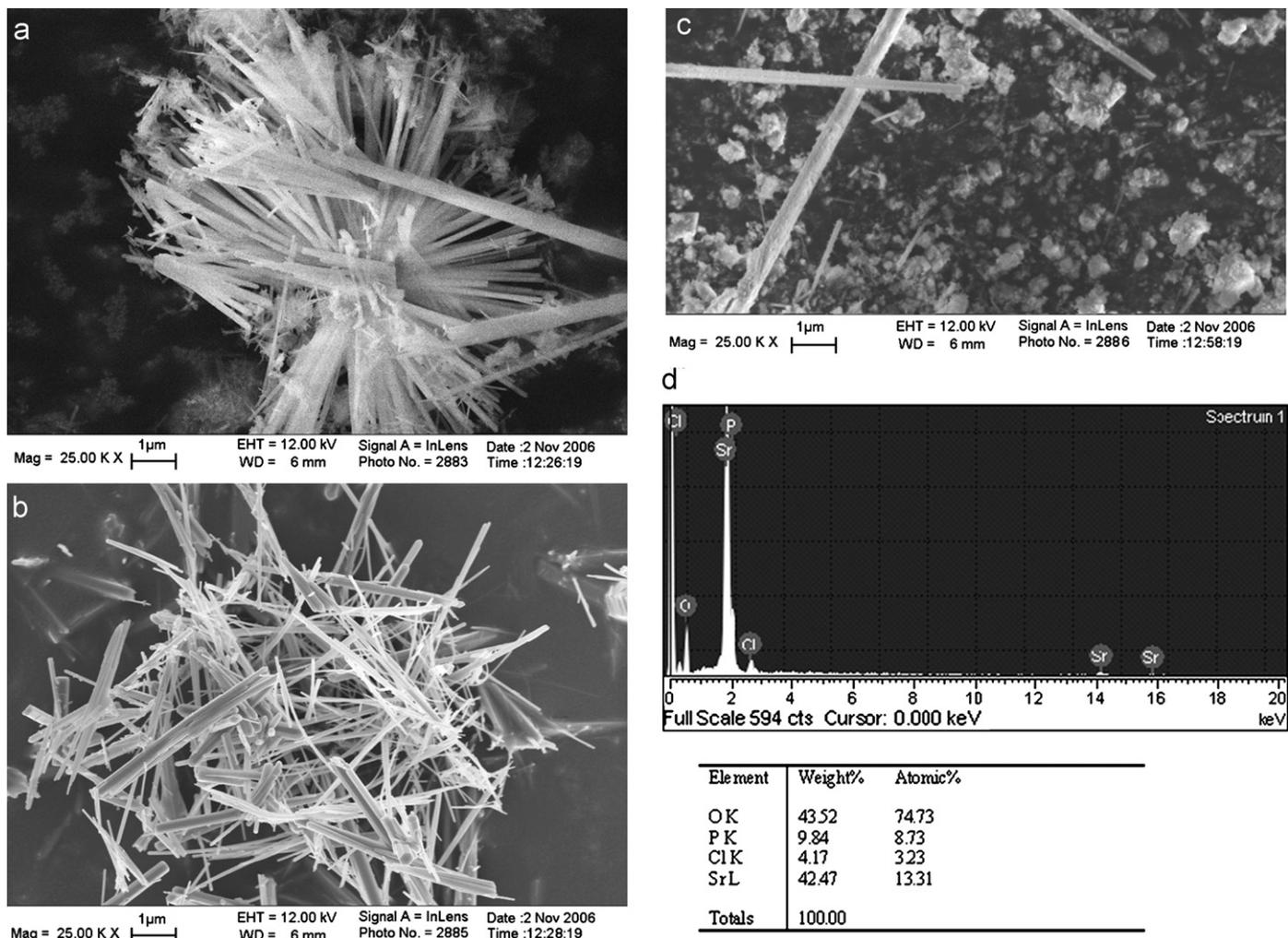


Fig. 5. SEM (a) 0, (b) 20 (c) 50% 1,4-dioxane and (d) EDX (20% 1,4-dioxane).

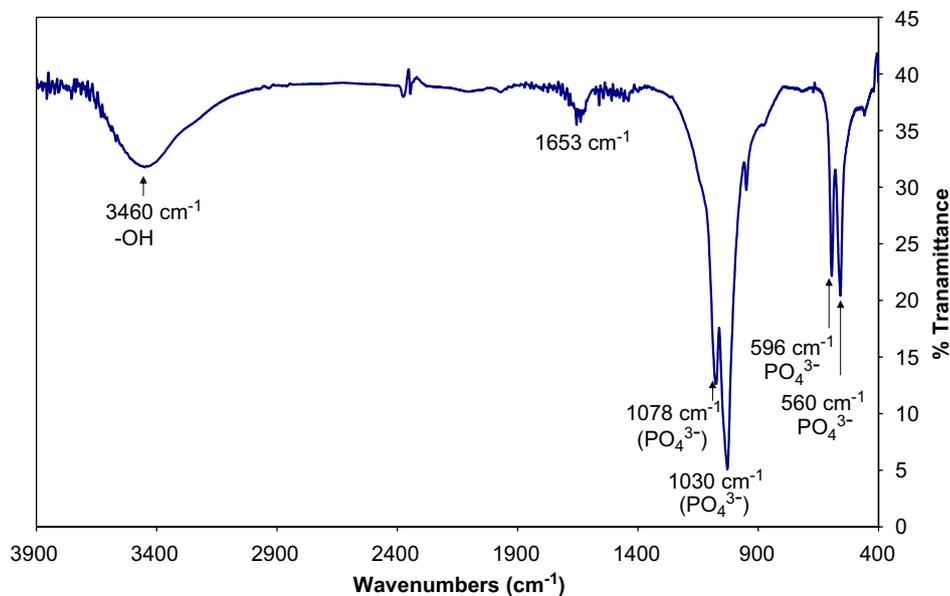


Fig. 6. FTIR spectrum of nanowire (20% 1,4-dioxane).

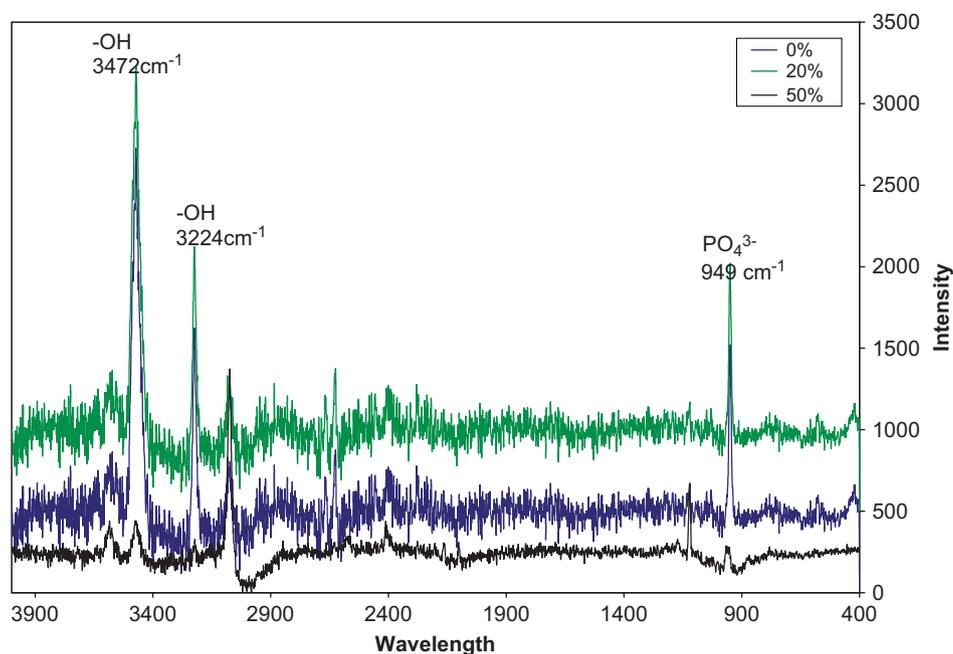


Fig. 7. Raman spectrum of different 1,4-dioxane concentration.

Acknowledgments

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