

Short communication

Study on the morphology of CsH_2PO_4 using the mixture of methanol and polyols

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Abstract

A study concerned with controlling particle morphology and size of CsH_2PO_4 was conducted by modifying the precipitation method and varying the types of adding solvents to aqueous solutions of Cs_2CO_3 and H_3PO_4 . Polyols of ethylene glycol were mixed with methanol and added into the solution. The obtained samples were characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM). Conductivity of CsH_2PO_4 powders studied in this work is around $\sim 10^{-5}$ to 10^{-4} S cm^{-1} and differ with their morphologies. The participation of different types of polyols in the precipitation kinetics and the resulting morphologies of the particles obtained were investigated. The scheme considers methanol as a primary precipitation agent, while the polyols are assumed to play a role in controlling morphologies.

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1. Introduction

Clean energy technology has become an issue of great importance in recent decades which has several advantages over conventional systems as potential solutions to energy and environmental problems [1]. One of the factors crucial to electrochemical energy conversion device is the ion conductivity of the electrolytes. Therefore, the development of highly ion-conductive materials has long been of great interest in the fuel-cell research community. Recently, Haile et al. reported that solid acids have could be utilized as an electrolyte at around 150°C . Solid acids $\text{M}_n\text{H}_m\text{XO}_4$ are known to undergo phase transition upon heating, and this property induces a dramatic increase in the ion conductivity of the electrolyte [2]. Thus, attempts to develop materials with controlled morphologies and unique properties have been undertaken in recent years [3–6].

In this paper, it was considered that by modifying the shape and size of the powders, the proton conductivity of solid acids can be enhanced. To obtain powders of solid acids from aqueous solution, it is desirable to introduce solvents into the solution because the mass product can be obtained rapidly. Since the sol-

ubility of a solute in a solution varies depending on the types of solvents introduced, in precipitating CsH_2PO_4 , methanol decreases the solubility of CsH_2PO_4 in aqueous solution. Mixing other solvents with methanol is thought to help in adjusting this solubility control effect for methanol. Polyols of di-, tri-, and ethylene glycol were chosen because of their molecular polarity and viscosity. Because of their molecular polarity, these solvents can be mixed with water molecules and the methanol which is introduced to cause precipitation. The viscosity is expected to modify crystal growth by retarding diffusion of the substances and providing local methanol distribution.

2. Experimental

Distilled water (1.5 ml) was added to 1.629 g of Cs_2CO_3 ; this solution was stirred to dissolve Cs_2CO_3 , and then 0.68 ml of H_3PO_4 was added (see Fig. 1). Solutions of 10 ml of methanol, mixed solvents of 10 ml of methanol with 10 ml of ethylene glycol, 10 ml of diethylene glycol, and 10 ml of triethylene glycol were prepared, respectively, to investigate the effect of polyols in synthesis. The aqueous solution of Cs_2CO_3 and H_3PO_4 was then poured into the mixed polyol solvents. The precipitated products were formed immediately. The products were stirred for 1 h to yield homogeneously reacted products. The products

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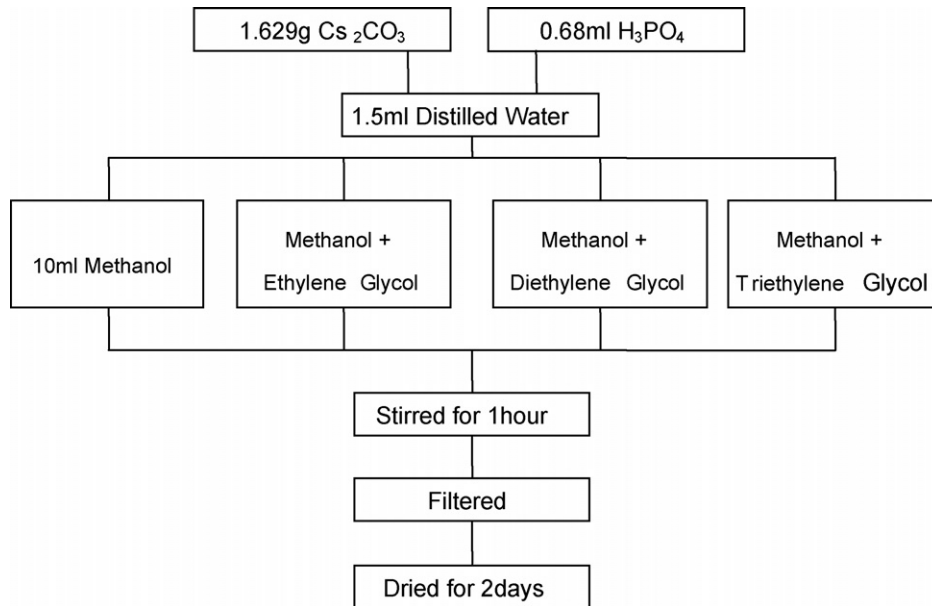


Fig. 1. Experimental procedure for polyol-mediated preparation of CsH_2PO_4 powder.

were then filtered through a ceramic membrane filter and dried for 2 days in an oven at 87°C .

The experiment to investigate the dependence of morphology on the volume change of the additive solvents of methanol and polyols was conducted by varying the volume of each solvent to 20 ml, following the same experimental procedure as Fig. 1. Additionally, while keeping the added volume of solvents of methanol, triethylene glycol and H_3PO_4 , as 20, 20, and 0.68 ml, respectively, the addition order of these solvents into the aqueous solution of Cs_2CO_3 were changed (see Fig. 2). The effect of introduction of other solvents such as acetonitrile was investigated. Directly after getting precipitates in the solution containing 25 ml of methanol and 50 ml of ethylene glycol, 25 ml of acetonitrile was put in and stirring was kept for 24 h, followed by filtering and drying.

The morphology and phase structure were examined by SEM and X-ray diffraction (XRD). XRD patterns were collected at a scanning rate of 2°min^{-1} in the 2θ range from 10° to 90° using

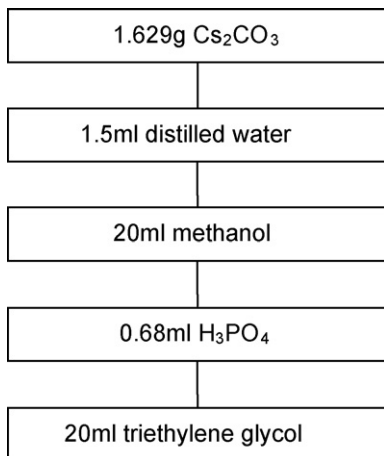


Fig. 2. Modified experimental procedure for polyol-mediated preparation of CsH_2PO_4 .

a Rigaku D/MAX Ultima β high-resolution X-ray diffractometer (Cu $\text{K}\alpha$ radiation, wavelength: 1.5406 \AA). The SEM images were obtained using a JSM-5400 scanning electron microscope.

The conductivity measurements of CsH_2PO_4 were done by AC impedance spectroscopy using a Gamry EIS300 LCR meter in the frequency range 1 Hz to 0.3 MHz and with an applied voltage of 1.0 V. Pellets were made from the powders, uniaxially pressed at 85 psi to 1 cm in diameter and 1 mm in thickness. Conductive silver paint is coated on both sides of the pellets to ensure good conductivity. Impedance spectra were analyzed using the commercially available software package, Gamry EIS300 Impedance spectroscopy software.

3. Results and discussion

The nucleation and growth mechanisms which determine the particle morphologies were strongly influenced by the reaction conditions. Methanol was chosen as the reaction medium because its polarity is thought to play a key role in removing water from solvated ions, so that ions attract each other, resulting in the nucleation and growth of particles. It is known that the presence of impurities, especially macromolecular impurities such as polymers [7], polymer capping reagent poly(vinyl pyrrolidone) [8], poly(vinyl alcohol) [9], or surfactants [10] can alter the shape of a growing crystal. In this regard, polyols such as ethylene glycol and other polyethylene glycols were employed to yield the desired particle morphology and size [8].

Fig. 3 shows the impedance spectra of CsH_2PO_4 powders prepared from 10 ml methanol with 10 ml ethylene glycol induced precipitate. The intercept of the semicircle with the real axis (Z') is interpreted as the resistivity of the sample. In the Nyquist representation as shown in Fig. 3, the impedance data showed an arc in the high frequency region which is attributed to the bulk conductivity of the sample. The conductivities of the CsH_2PO_4 material prepared from varying the solvent ratio are given in

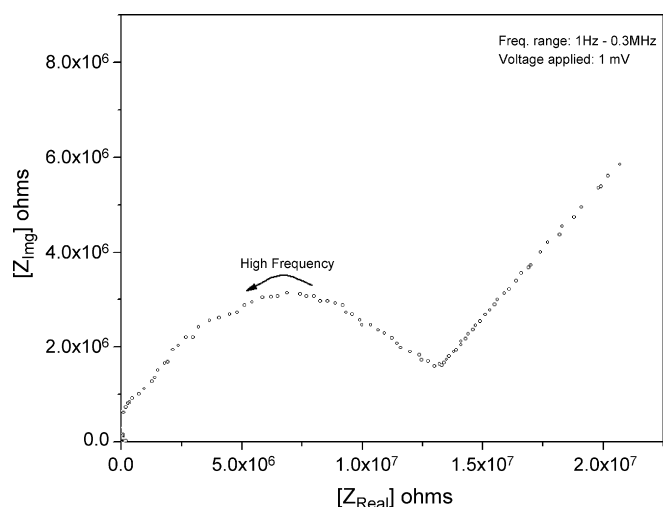


Fig. 3. Impedance spectra of CsH_2PO_4 powder prepared from 10 ml of methanol + 10 ml of ethylene glycol-induced precipitate.

Table 1
Conductivity values of CsH_2PO_4 samples prepared from various solvents

Serial number	Sample	Conductivity (S cm^{-1})
1	10 ml of methanol	1.11×10^{-4}
2	10 ml of methanol + 10 ml of ethylene glycol	0.769×10^{-5}
3	10 ml of methanol + 10 ml of diethylene glycol	0.17×10^{-4}
4	10 ml of methanol + 10 ml of triethylene glycol	0.75×10^{-4}

Table 1. There is no large difference in the conductivity values of the samples. The conductivity values differed only in magnitudes and the difference is negligible. It can be observed from Table 2 that the CsH_2PO_4 sample prepared by 10 ml methanol with 10 ml ethylene glycol showing plate-like morphology has the low conductivity compared to the other samples. Instead, the samples with small particle size of spherical morphology give relatively higher values of conductivity. Although, the conductivity values in Table 1 show clear trend of the dependence on particle size and morphologies, it needs to be investigated

Table 2
Properties of di-, tri-, and ethylene glycol [15]

	Methanol	Ethylene glycol	Diethylene glycol	Triethylene glycol
Molecular structure				
Chemical formula	CH_4O	$\text{HOCH}_2\text{CH}_2\text{OH}$	$\text{O}(\text{CH}_2\text{CH}_2\text{OH})_2$	$\text{HOCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH}$
Melting point	-98°C	-13°C	-10°C	-7°C
Boiling point	65°C	$197\text{--}198^\circ\text{C}$	$244\text{--}245^\circ\text{C}$	278°C

The melting point and boiling point indicate the increase in London force as the molecular length increases. Each polyol has two alcohol groups in the ends of the chain, which indicate that they have the same degree of partial charges per molecule. In terms of polarity per volume, ethylene glycol is the greatest, followed by diethylene glycol and triethylene glycol.

at elevated temperatures in order to understand their behaviors with contributions from the super protonic transition in operating conditions. Boysen reported that the conductivity of CsH_2PO_4 exhibited a sharp increase at the transition temperature, from 1.2×10^{-5} to $9.0 \times 10^{-3} \text{ S cm}^{-1}$ followed by a rapid decline due to dehydration [11]. Baranov et al. have reported that the CsH_2PO_4 has a conductivity of $2.3 \times 10^{-2} \text{ S cm}^{-1}$ at 230°C [12]. Our studies revealed that the conductivity of CsH_2PO_4 is approximately around 10^{-5} to $10^{-4} \text{ S cm}^{-1}$ at ambient temperature. To understand the role of hydrogen bonding in structural phase transitions, it is of important relevance to observe whether CsH_2PO_4 undergoes a super protonic transition or not.

It has been observed that 10 ml of ethylene glycol mixed with 10 ml of methanol helps produce a well-developed plate-like morphology, as shown in Fig. 4(b). Fig. 4(c) shows that diethylene glycol mixed with methanol forms particles that are smaller and have a narrower size distribution with no specifically conspicuous morphologies. Particles synthesized using the mixture of methanol and triethylene glycol (Fig. 4(d)) appear to have a rod-like morphology with a considerable aspect ratio.

The XRD patterns of the products are shown in Fig. 5. All peaks are indexed to CsH_2PO_4 and are consistent with the data in the JCPDS card (no. 84-0122, $P2_1/m$ phase). However, the relative intensities of the (-201) and (111) peaks in Fig. 5(d) are shown in opposite way to the others. This indicates that the particles synthesized from the mixture of methanol with triethylene glycol have a specific preference in the growth direction. Fig. 5 shows this clearly and accords with the SEM images in Fig. 4, in which the sample synthesized from triethylene glycol shows a rod-like morphology. Therefore, di-, tri-, and ethylene glycol seem to produce different particle morphologies and sizes by providing different environments to control the crystal growth process. Di-, tri-, and ethylene glycol are known to have different viscosities, and so they have different London forces owing to their different molecular structures, as shown in Table 1 [13].

It has been reported that the London force takes about 80% of the molecule–molecule force, and the dipole–dipole interaction does 20% in aqueous solution [13]. Therefore, the London force interaction between polyols is considered to be superior to the dipole–dipole interaction between methanol and polyol, and so the miscibility of methanol with polyols (due to the molec-

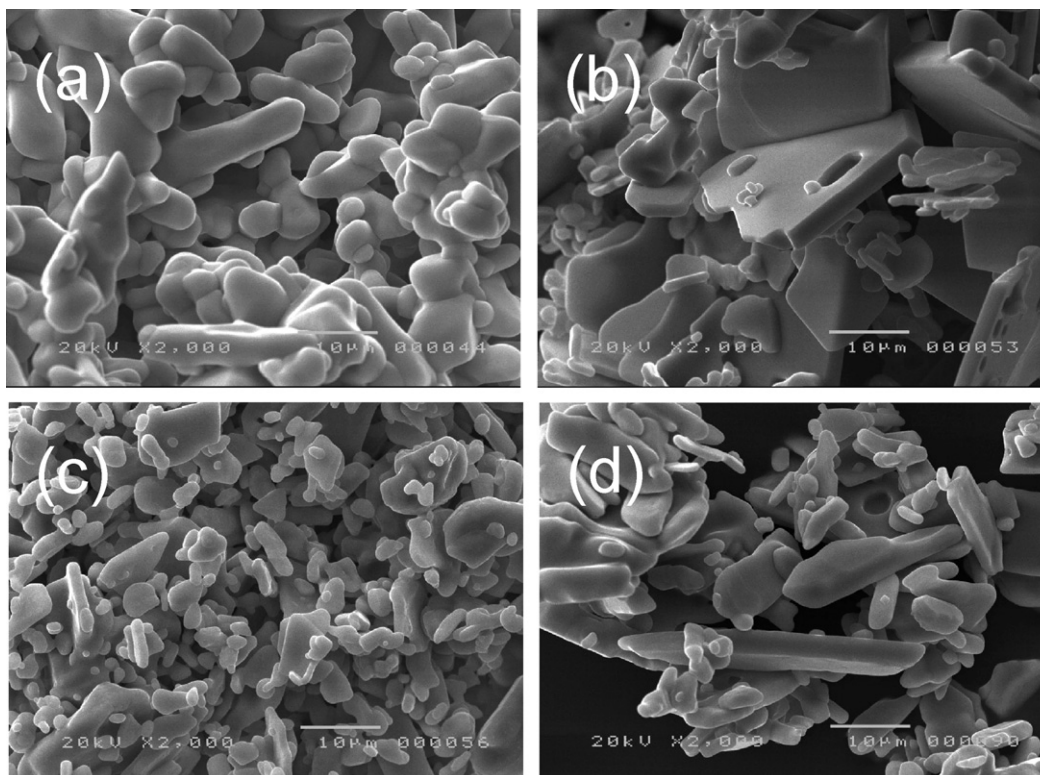


Fig. 4. SEM images of products formed by: (a) 10 ml of methanol, (b) 10 ml of methanol + 10 ml of ethylene glycol, (c) 10 ml of methanol + 10 ml of diethylene glycol, and (d) 10 ml of methanol + 10 ml of triethylene glycol. Well-crystallized plate-like morphologies (b), a smaller size and narrower size distribution (c), and rod-like morphologies (d) are observed.

ular polarity) means that they are proportionally mixed on a macro-scale, not on a micro-scale. Thus, there may be a localized disproportional distribution of methanol because of the effect of the London force interaction between polyols, although these are known to be miscible.

On the other hand, the preferred orientation of the crystal can also be observed, due to the different growth rate in the preferred directions [9,14]. The anisotropy generates the difference in surface energy and/or attachment free energy of crystalline planes, leading to a directional dependence on growth rate. The area of principal crystal growth faces depends on their relative surface energies [15,16]. This report helps us to consider the occurrence of the preferred orientation of growth after introducing polyols such as triethylene glycol as shown in Fig. 4(d) and provides clues for the possibility of polyols interacting with certain faces, while there is no preferred orientation of growth after introducing methanol alone. The attachment of polyols to the more unstable faces can be expected to prevent diffusion of the substances to those faces, and the crystal growth is hindered. In contrast, the attachment-free faces continue growing. There is no perfectly stable crystallographic plane during growth, but the relatively more or less energetically stable states can be compared.

One more thing to be considered is the fact that the polarity per volume strength increases as the organic molecules become shorter. The polarity per volume of organic chemicals can influence the amount of ionically bonded particles to be dissolved [17], which means that the polarity per volume influences the particle-formation phenomena by interfering with the methanol effect of reducing the solubility. Table 1 lists the properties and molecular structures of di-, tri-, and ethylene glycol. It can be seen that the London force increases in the order of ethy-

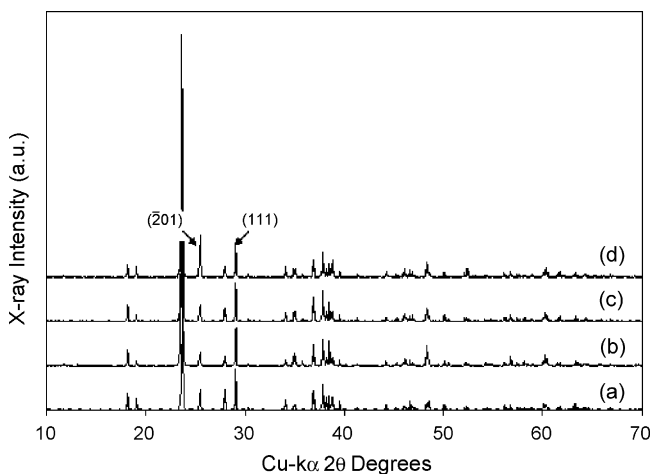


Fig. 5. XRD data of products formed by: (a) 10 ml of methanol, (b) 10 ml of methanol + 10 ml of ethylene glycol, (c) 10 ml of methanol + 10 ml of diethylene glycol, and (d) 10 ml of methanol + 10 ml of triethylene glycol. All peaks are indexed to CsH_2PO_4 and are consistent with the data in the JCPDS card (no. 84-0122, $P2_1/m$ phase). However, the relative intensities of the (201) and (111) peaks in (d) are shown in the reverse direction to the others.

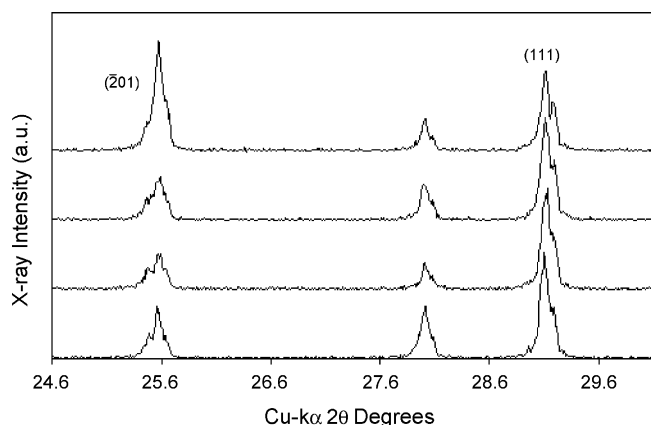


Fig. 6. XRD patterns in the 2θ range from 24.5° to 30° of: (a) 10 ml of methanol, (b) 10 ml of methanol + 10 ml of ethylene glycol, (c) 10 ml of methanol + 10 ml of diethylene glycol, and (d) 10 ml of methanol + 10 ml of triethylene glycol. The relatively increased (201) intensity of (d) indicates the influence of 10 ml of triethylene glycol in producing the directional growth of the particles.

lene glycol, diethylene glycol, and triethylene glycol, while the polarity per volume strength increases in the reverse order (Fig. 6).

Morphologies drawn by the variation of experimental procedures and conditions are seen in Fig. 7. The comparison between Figs. 7(a) and (b) and 4(b) and (d) verifies that the change in the amount of methanol and polyols, while keeping the volume ratio as 1:1, results in the change in morphologies. Contrast to

the plate like well crystallized morphology (Fig. 4(b)), morphology of smaller and more narrowly distributed size was obtained (Fig. 7(a)). Rod shape morphology (Fig. 4(d)) has changed to that of three dimensionally well crystallized (Fig. 7(b)).

Adoption of different procedures (Fig. 7(c)), especially in the introducing order of solvents, methanol, triethylene glycol, and H_3PO_4 , acceptably well generated deviation of the morphology-modification from the sample shown in Fig. 7(b). It is obvious that each solvent participates in modifying the morphology not only in the manner of a mixture but also in the manner of itself. In addition, post-treatment with acetonitrile generated well-modified morphology of a rod shape with a good aspect ratio (Fig. 7(d)). Organic nitriles are reported to act as solvents and are reacted further for various application including; extraction solvent for fatty acids, oils and unsaturated hydrocarbons, recrystallization of steroids, parent compound for organic synthesis, and stabilizer for chlorinated solvents. A nitrile group is strongly polarized and has an electrophilic carbon atom, hence nitriles are susceptible to the attack by nucleophiles, which is considered to recrystallize the already prepared powders.

All peaks are indexed to CsH_2PO_4 and are consistent with the data in the JCPDS card (no. 84-0122, $P2_1/m$ phase). The deviation of peaks of (-201) and (111) in Fig. 8(d), of samples having rod shape morphology (see Fig. 7(d)) is well consistent with Fig. 5(d) sample with a rod shape, which also confirms the directional preference of the crystal growth of CsH_2PO_4 particles.

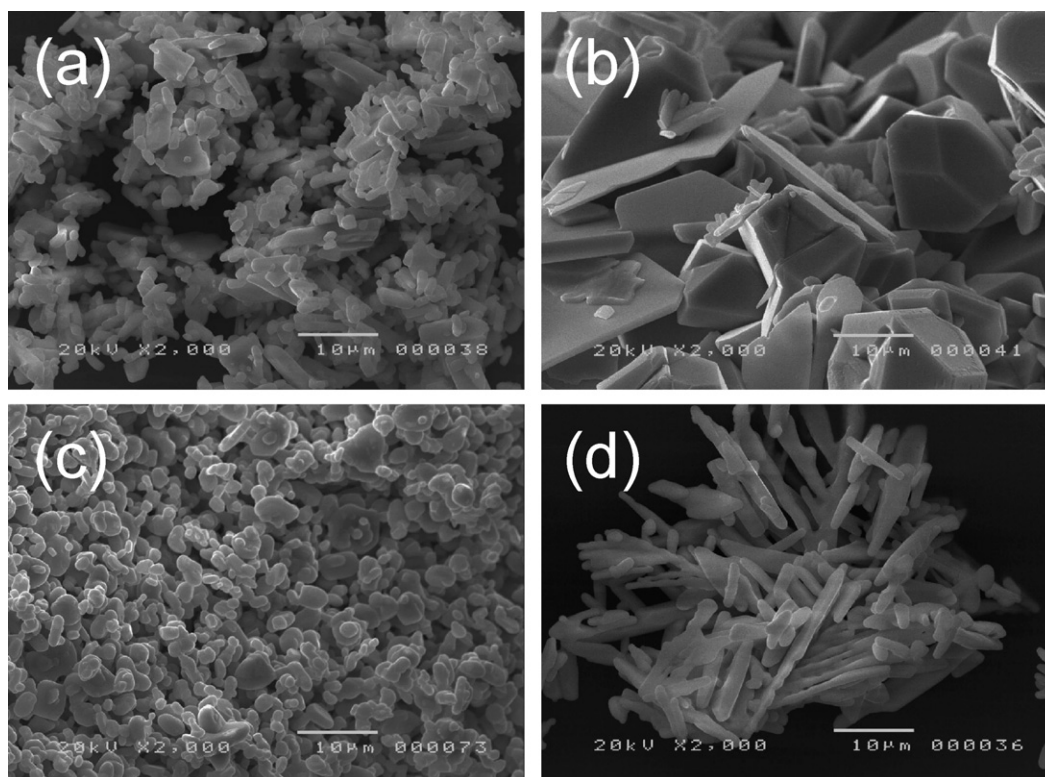


Fig. 7. SEM images of products formed by: (a) methanol/ethylene glycol: 20/20, (b) methanol/triethylene glycol: 20/20, (c) methanol/triethylene glycol: 20/20 different process from (b), and (d) methanol/ethylene glycol: 25/50, post-treatment with acetonitrile.

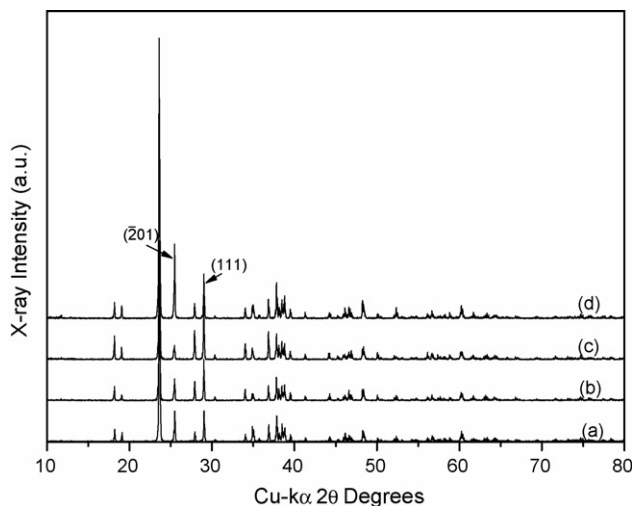


Fig. 8. XRD data of products formed by: (a) methanol/ethylene glycol: 20/20, (b) methanol/triethylene glycol: 20/20, (c) methanol/triethylene glycol: 20/20 different process from (b), and (d) methanol/ethylene glycol: 25/50, post-treatment with acetonitrile.

4. Conclusion

By controlling the nucleation and growth steps, particles with different morphologies and sizes can be prepared from a mixture of methanol and polyols. Different growth mechanisms for particles synthesized by adding methanol and the mixture of methanol and polyols have been observed. The mixture of 10 ml of ethylene glycol and 10 ml of methanol created a well-developed plate-like morphology. Diethylene glycol with methanol (10 ml of each) exhibited no conspicuous morphology but influenced particle size. Triethylene glycol with methanol (again, 10 ml of each) formed a rod-like morphology, and this directional growth was confirmed via XRD. The Impedance measurements revealed that the samples have conductivity around $\sim 10^{-5}$ to 10^{-4} S cm^{-1} depends on their morphologies and particle sizes.

The concepts of polarity per volume and the London force were adopted to explain the variations of morphologies generated by different mixtures of polyols and methanol. The London force between polyol molecules is believed to generate specific environments for the crystal nucleation and growth, and the polarity per volume strength has the effects of dissolving

ionically bonded particles. In addition, directional growth can be explained as a result of the interaction between polyols and the surface of the particles as the growth proceeds.

It was confirmed that each solvent participates in morphology modification in its own manner, which was revealed by varying the addition order of solvents into $10\text{C}_2\text{S}_2\text{CO}_3$ aqueous solution. The recrystallization effect of the acetonitrile was shown to generate rod-shape morphology due to the strong polarization of acetonitrile which remains carbon atom bonded to nitrogen atom strongly electrophilic, hence susceptible to be attacked by nucleophiles.

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