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Preparation and characterization of carbon-coated ZnO and CaO powders by pyrolysis of PVA

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Abstract Carbon-coated ZnO and CaO powders were prepared by Poly(vinyl alcohol) (PVA) pyrolysis at 700 °C in inert atmosphere and characterized for their potential utilization in the field of antibacterial ceramics. No peaks corresponding to carbon were detected after XRD measurements of as-coated powders; that is, carbon coating is amorphous. Certain increase in specific surface area was observed after coating in all powders. Based on additional characterizations supported by SEM observations and particle size distributions, it is concluded that the formation of nanoporous structure of coated carbon layer resulted in an increase in the surface area. Some agglomeration also observed after treating powders that decreased with increasing polymerization degree of PVA used as a carbon precursor.

Introduction

There have been many research activities focused to produce coated powders for their possible utilization in unique materials development [1–6]. One of the interesting researches in this field is also a group of ceramic powders coated with carbon thin films. In almost cases, carbon films can be produced from carbon-containing gas phases by physical vapor deposition (PVD) or hydrocarbon-containing gases by chemical vapor deposition (CVD); moreover, both processes have been applied on bulk substrates easily [7–11]. Although some important efforts have been done to adapt a fluidized bed into these systems [1, 2, 4], there is still need for additional research efforts not only for more simplified methods to achieve feasible bulk quantities, but also to be able to produce compositionally more diverse coated powders. Polymer pyrolysis is a well-known method and was successfully applied to many ceramic systems to produce unique powders starting from their precursors [12–16]. Also it is reported that during the pyrolysis of polymers in an inert atmosphere, such as Poly(vinyl alcohol) (hereafter, PVA) and Poly(vinyl chloride) (PVC), some carbons remained as a residue in the system [17–19]. On PVA and PVC, it is known that a low viscosity liquid phase forms during their pyrolysis. Therefore, it is possible for powder surfaces to be wetted and coated by this liquid. By using this simple mixing method, several ceramic powders were coated with carbons so far in literature [20–25], whereas the formation and the morphologies of ceramic powders coated with carbon were not characterized in details.

In the present work, ZnO and CaO powders were selected to be coated via PVA pyrolysis. Improvement is necessary for ZnO and CaO powders, which show strong antibacterial activity [26–28] without the presence of light; therefore, carbon coating was applied against their easy dissolution and hydration reactions

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[29, 30]. The samples after coating, namely ZnO and CaO powders coated with carbon, were characterized in order to get the antibacterial ceramics with insolubility in all pH regions and hydration resistance.

Experimental

Preparation of carbon coated powders

ZnO, CaO and PVA powders with different polymerization degrees of 2000, 22,000 and 95,000 were selected as starting materials in this study. In all cases prior to coating operation, ceramic and polymer powders were mixed with a mass ratio of 1 by using an alumina mortar until the homogenous mixture obtained. The coating operation was realized by heating these homogeneous mixtures at 700 °C for 3 h with a heating rate of 5 °C min^{-1}, which always was in an argon gas under a flowing rate of 50 cm^3 min^{-1}. ZnO and CaO powders coated with carbon thin films were then obtained by the pyrolysis through the liquid phase of PVA. All powders after heating were coated with carbons, turning their color to black, and kept in separated particles. There were no powders sticking to alumina boats. The detailed preparation procedure was described in previous report [31].

Characterization of samples

The crystalline structure of as-coated powders was studied by X-ray diffraction measurement (XRD: RIGAKU, RINT 2000) and their morphology was examined under field emission-scanning electron microscope (FE-SEM: HITACHI-4500). The specific surface areas and the particle size distributions (PSD) were determined from the adsorption isotherm of nitrogen gas at 77 K (BET: SHIMAZU, SS-100) and by a laser distribution particle size analyzer (PSD: SHIMAZU, SALD 2100), respectively.

Results and discussion

Carbon-coated samples

It is known that three reactions of dehydration, dehydrogenation and decomposition of PVA molecules occur at the temperature below 450 °C [18, 19]. The surface of ceramic particles is covered by the viscous polymeric liquid of PVA, which was formed during the reactions described above, and the carbon layer with the pyrolysis of PVA liquid is coated on the surface of particles. It is reported that residual amount of carbon around 4–5 mass% may stay after the pyrolysis of PVA in an inert atmosphere [19].

Since the reduction of ZnO via an interaction with coated carbon is possible at higher temperatures, 700 °C was selected as the upper limit during coating operations. The amount of carbon residue stayed after 700 °C was determined from pyrolysis of sole PVA powders and is plotted as a function of polymerization degree of PVA in Fig. 1. The detected C residue amount ranging from 4.46 to 5.42 mass%, showed a slight decrease with an increase in polymerization degree of PVA. All samples after treating at 700 °C looked black, irrespective of polymerization degree.

XRD patterns of ZnO and CaO powders coated with carbon were shown in Fig. 2a and b, respectively, together with different polymerization degrees of PVA being used as carbon sources. The samples after treating at 700 °C gave only diffraction peaks corresponding to oxides, such as hexagonal-ZnO and cubic-CaO. No diffraction peaks corresponding to carbons were observed via XRD, probably indicating that the carbon layer formed on particles is amorphous. The diffraction intensity was almost identical before and after treatment, suggesting the formation of carbon layer with the thickness of a few nano-meter order on their particles. In the CaO sample after treating at 650 °C, however, the peaks of $CaCO_3$ were detected in addition to those of CaO, as shown in Fig. 3.

In details, the pyrolysis of PVA can be summarized by chain stripping (elimination of H_2O), partial decomposition product, chain scission, diels-alder reactions, cyclization and aromatization (H_2 loss), where

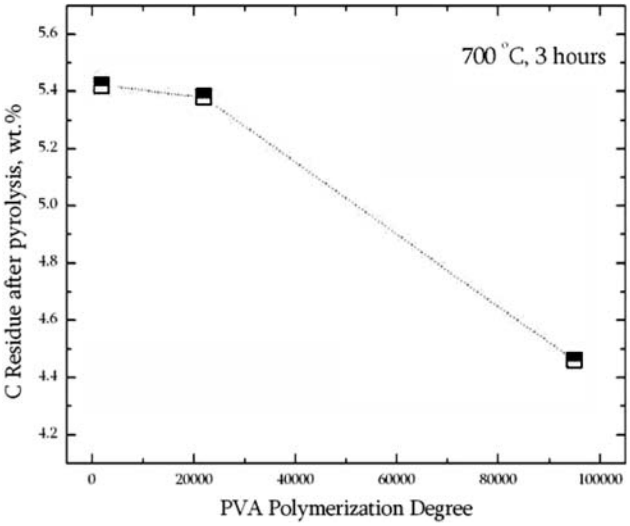

Fig. 1 Amount of carbon residue at 700 °C based on polymerization degree of PVA

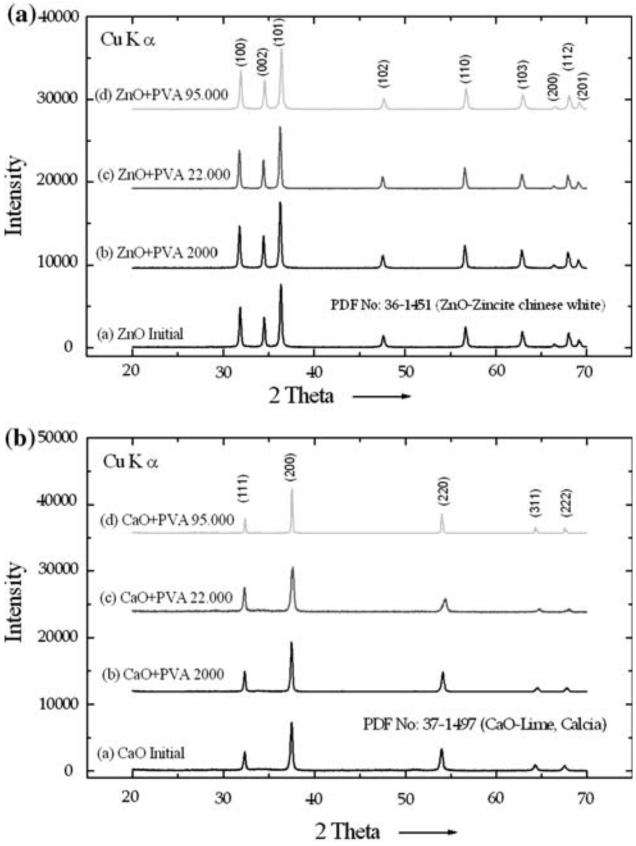

Fig. 2 (**a**) Comparative XRD results of C coated ZnO powders after 700 °C. (**b**) Comparative XRD results of C coated CaO powders systems after 700 °C

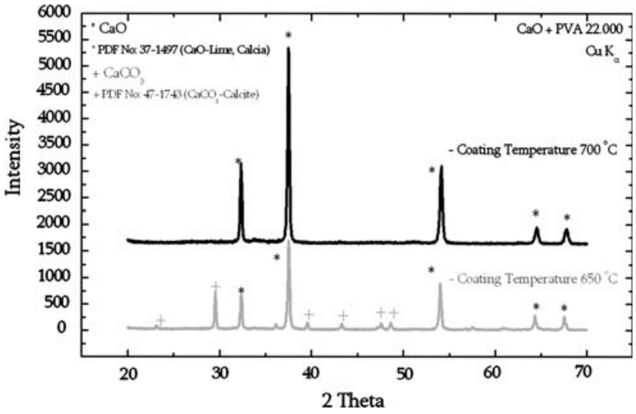

Fig. 3 XRD of C coated CaO powders after pyrolysis at 650 °C, which shows $CaCO_3$ formation

initial C/H ratio (0.5 in starting material) increases during pyrolysis temperature [18, 19]. Therefore, the reason that the diffraction peaks of $CaCO_3$ appeared at 650 °C is assumed as follows: chain stripping of PVA molecules occurs in the initial stage, and the small amount of $Ca(OH)_2$ may be formed by the reaction between CaO and H_2O which was produced due to the chain stripping, since the conversion of $Ca(OH)_2$ to the carbonate is easier than in the case of CaO. Since decomposition of $CaCO_3$ to CaO occurs above 650 °C no $CaCO_3$ peaks were observed in Fig. 2b.

SEM micrographs of ZnO and CaO powders before and after coating are shown in Figs. 4 and 5, respectively. In the case of ZnO powders (see Fig. 4), the microstructure of initial ZnO powders was different from that of the coated powders. On the other hands, particles with the size of 60–80 nm were observed in CaO powders after coating (see Fig. 5). From SEM observations, it was found that coating operation in this study affected the morphologies of ceramic powders.

Change of BET and PSD by coating of carbon

BET specific surface areas of the powders after treating at 700 °C are summarized in Table 1, together with initial powders. The specific surface area of initial CaO and ZnO powders was 1.4 and 1.2 $m^2\ g^{-1}$, respectively. By using PVA with a polymerization degree of 95,000, the surface area reached 25.5 $m^2\ g^{-1}$ in the coated CaO powder and 9.8 $m^2\ g^{-1}$ in coated ZnO powder. In the results described above, it was found that specific surface area of carbon coated sample increased with the increase in polymerization degree of PVA.

Particle size distributions of –150 μm fraction of as-coated ZnO and CaO powders comparative to their initial states are shown in Fig. 6a, b, respectively. PSD of initial ZnO powders was changed to multi modal distributions in the case of ZnO powders coated with carbon, which was prepared by the pyrolysis of PVA with polymerization degrees of 2,000 and 22,000. This change was not detected for the powders coated by using PVA with 95,000 polymerization degree. In that case, PSD of the coated ZnO prepared from PVA with 95,000 degree was observed similar to that of initial ZnO. In CaO powders, however, PSD of all as-coated samples was similar to that of initial CaO. Although a decrease in the range of small particle size was observed in as-coated CaO powders, the reason seems to be different from the formation of very fine individual carbon particles during coating operation. The change of D_{90} value in CaO powders before and after coating was less than that in ZnO powders.

Initial particle size of ZnO was observed in the range of 1–12 μm by SEM (D_{50} = 5.85 μm in PSD measurement). In detailed observation with high magnification, these particles showed the aggregate of many small ZnO particles. During the pyrolysis of PVA, the temporary viscous polymeric liquid formed

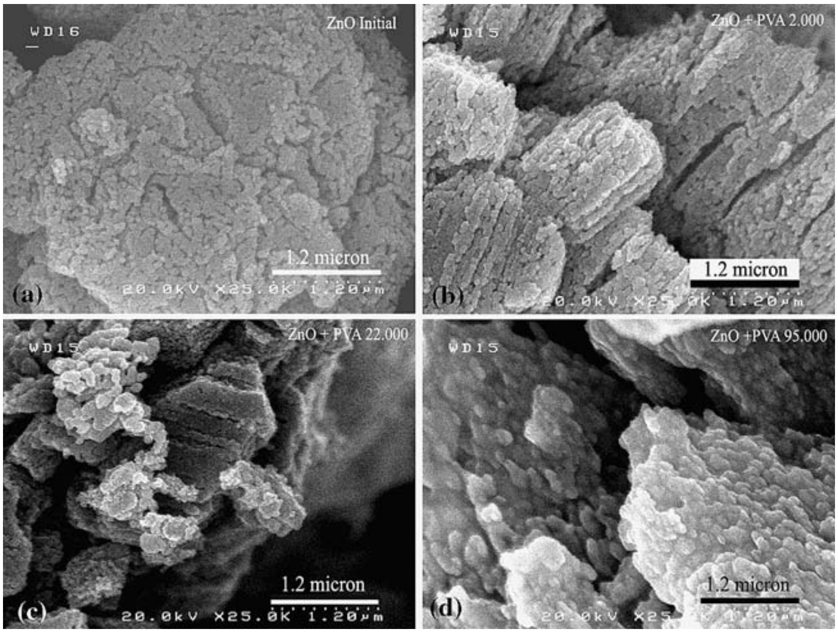

Fig. 4 Microstructure of initial and after pyrolysis ZnO powders. (**a**) Initial ZnO, (**b**) after pyrolysis with PVA 2,000, (**c**) after pyrolysis with PVA 22.000, (**d**) after pyrolysis with PVA 95,000

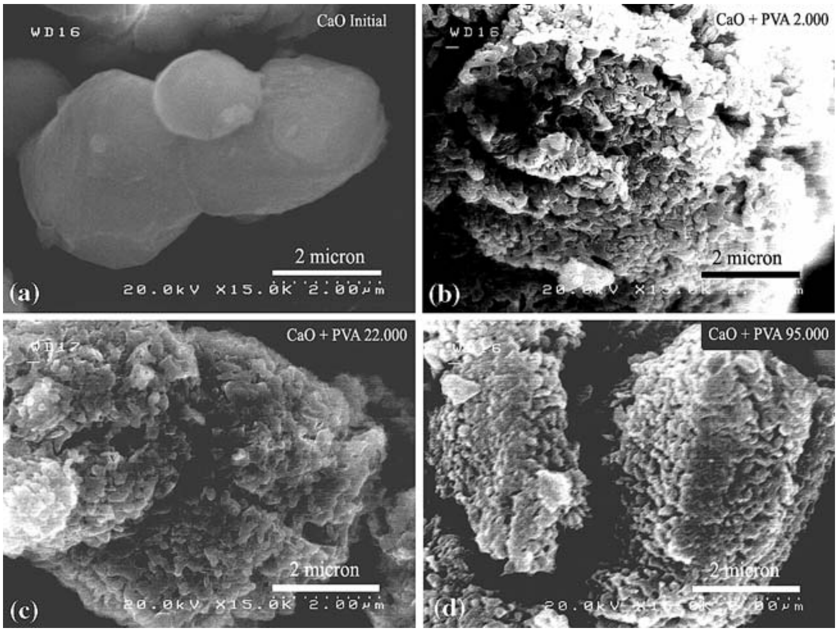

Fig. 5 Microstructure of initial and after pyrolysis CaO powders. (**a**) Initial CaO, (**b**) after pyrolysis with PVA 2,000, (**c**) after pyrolysis with PVA 22,000, (**d**) after pyrolysis with PVA 95,000

Table 1 Surface area results of both initial and as-coated composite powders

Sample	Specific surface area (m^2/g)
CaO (Initial)	1.4
CaO + PVA 2,000	23.1
CaO + PVA 22,000	23.3
CaO + PVA 95,000	25.5
ZnO (Initial)	1.2
ZnO + PVA 2,000	8.0
ZnO + PVA 22,000	9.6
ZnO + PVA 95,000	9.8

can be easily penetrated to the potential capillaries between nano size ZnO particles. On the other hand, D_{90} value of CaO powders was too much, comparing with ZnO powders (see Fig. 6). The potential capillary effect strongly appears in the smaller particle, because the clearance between these particles is narrow. The large amount of viscous liquid formed during pyrolysis of PVA remains in the capillaries among particles, and many pores is formed by the decomposition of the liquid. Therefore, the reason that the BET value of ZnO powders coated with carbon was larger than that of as-coated CaO powders is supposed to be due to the

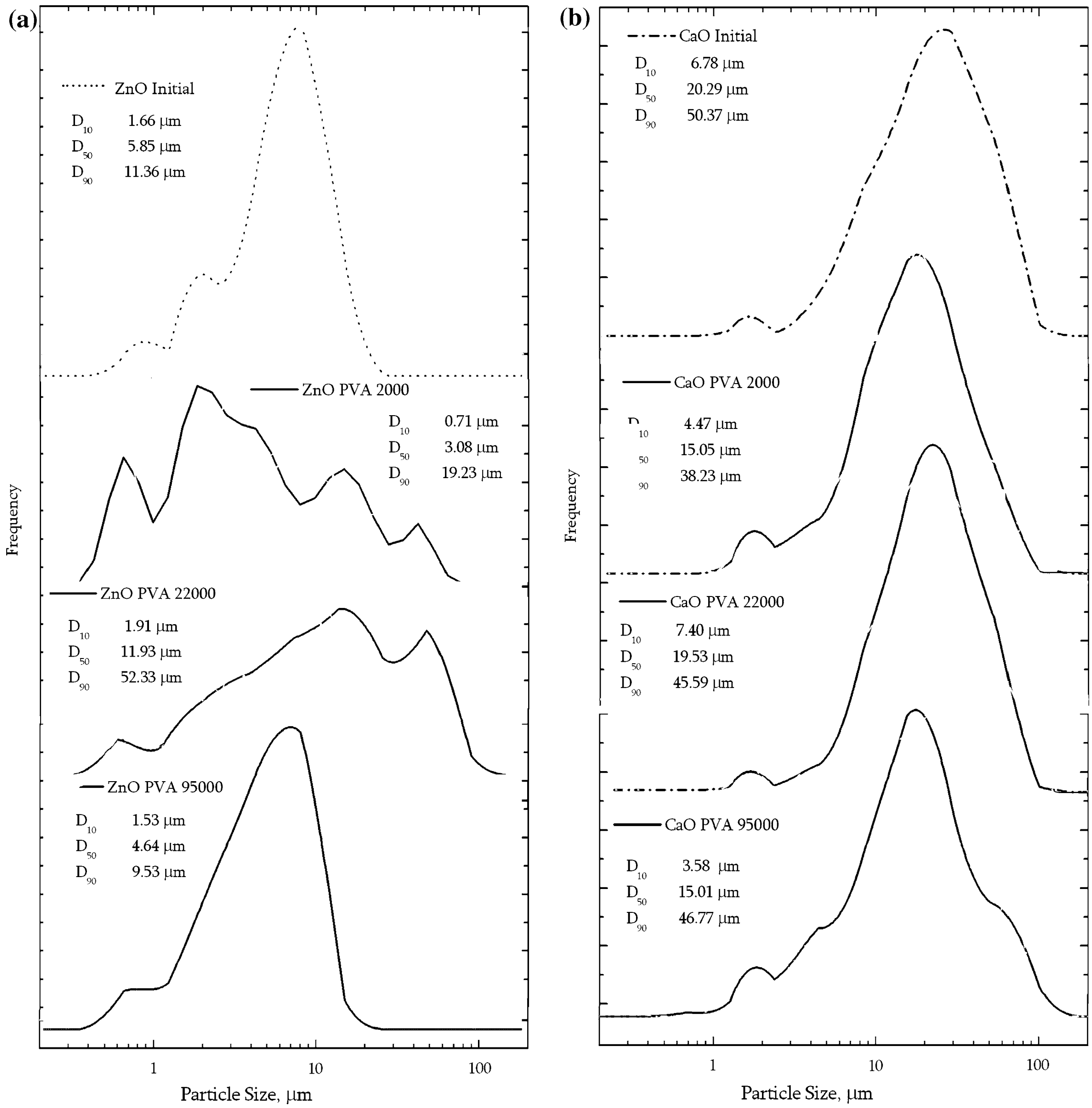

Fig. 6 Particle size distribution of initial and C coated powders. (**a**) ZnO system (**b**) CaO system

existence of the clearance filled up with viscous liquid of PVA. Some agglomeration was observed in this work. Generally, the formation of agglomeration causes the lowering of the value of BET. Although high BET values obtained in all cases after pyrolysis are contrary to this phenomena at a glance in this work, Inagaki et al. [20] reported on similar behavior that even adsorption of N_2 easily passed through carbon layer on ceramic powder. In order to investigate the agglomeration, ZnO and CaO powders after coating were separated into two fractions using 150 µm sieve, and the result is shown in Fig. 7. The amount of powders that passed under 150 µm sieve increased with increasing polymerization degree of PVA used during pyrolysis. That is, it was found that less agglomeration is formed with increasing polymerization degree of PVA.

Conclusion

In order to improve the dissolution and hydration reaction of ZnO and CaO that was made to lower antibacterial activity, carbon thin films were successfully formed on the surface of ZnO and CaO powders by the pyrolysis of PVA in inert atmosphere at 700 °C. Carbon deposition on the powder surfaces was in amorphous.

Certain increase in specific surface area was detected after coating of both ZnO and CaO powders,

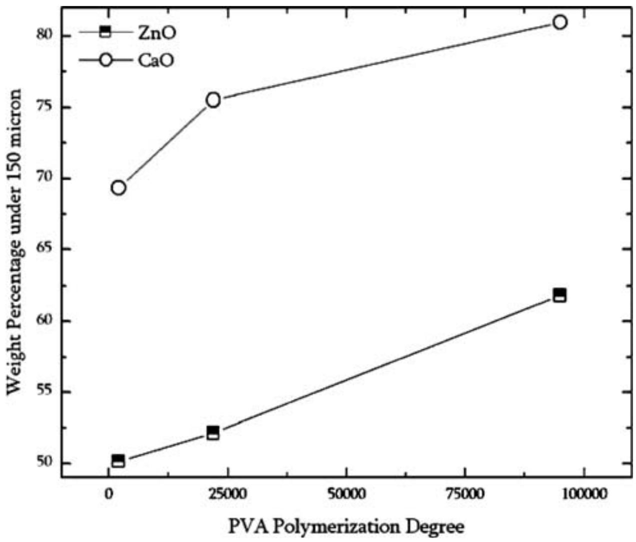

Fig. 7 Agglomeration tendency of as-coated composite powders as a function of polymerization degree of PVA used during pyrolysis

due to the formation of nanoporous structure in carbon layer that is quite motivating for improving time dependent antibacterial activity of these powders.

Based on $CaCO_3$ phase detection at 650 °C, it was found that the increase of extra surface area in CaO system in compare with ZnO system was related to this carbonate formation and its thermal decomposition. The formation of $CaCO_3$ was supposed to be dominant factor for formation of nanoscale particles leading higher surface area.

Some amount of agglomeration was observed after carbon coating of powders. A decrease was observed in agglomeration tendency with increasing polymerization degree of PVA used as carbon source.

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