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Note

# Coating of ZnO Chip with Carbon and Its Effect on Longevity of a Cut Flower

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**Carbon film was coated on the surface of ZnO chip by pyrolysis of poly (vinyl alcohol) with different polymerization degrees, and then longevity of a cut flower, such as carnation, was studied by adding carbon-coated ZnO chip in the vase filled with distilled water. In the results of optimum condition for coating ZnO with carbon, it was clarified that poly (vinyl alcohol) with polymerization degree of 2000 was suitable for forming homogeneously carbon at every portion in ZnO chip. From observation of carnation, it was found that the formation of carbon on ZnO chip was effective for longevity of a cut flower.**

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## 1. Introduction

Cut flowers are necessities in much celebration, which are important for construction of friendly relations. The appreciation of given beautiful flowers wither in comparatively short time if water in a flower vase is not exchanged frequently, because cut flowers can get neither water nor nutrition due to the bacterial growth in the water. Addition of antibacterial medicine into water can consider as attractive one of the methods to make a cut flower live in a long time, without exchanging water in the vase. Antibacterial medicine, however, will cause environmental problems if the water containing the medicine flowed through river. Therefore, the development of materials that contribute to longevity of cut flowers is necessary in the situation that there is no addition of antibacterial medicine, such as quaternary ammonium salt.

We have studied antibacterial activity of ceramics so far, such as CaO, MgO, ZnO, and their solid solutions, and these ceramics showed a strong antibacterial activity without the presence of light.[1)–3)] On these ceramics, it has reported that antibacterial activity of ZnO occurred to be due to generation of hydrogen peroxide on its surface in neutrality.[4)–7)] Regarding the appreciation of flower in a long time, ZnO will be supposed to be suitable in comparison with other ceramics, because it may damage cells of flowers for an increase in pH value with hydration reaction of CaO and MgO. Since the large amount of hydrogen peroxide generated from ZnO may injure cells of the flower, it may need to control the generating amount of hydrogen peroxide. Inagaki et al.[8)] and Morishita et al.[9)] investigated pore structure of the carbons coated on ceramics through pyrolysis of poly (vinyl alcohol). They also found that the coated carbon was porous. By coating ZnO with carbon, therefore, we expected possibility to control hydrogen peroxide generated from the surface of ZnO.

In the present work, carbon thin film was coated on the surface of ZnO by pyrolysis of poly (vinyl alcohol) with different polymerization degrees, and then longevity of a cut flower, carnation, was studied by adding carbon-coated ZnO in the vase.

## 2. Experimental

Three poly (vinyl alcohol) (hereafter, PVA) with different polymerization degrees (2000, 22000 and 95000) were used as carbon sources to make carbon-coated sample. Carbon coating of ZnO was performed by covering the ZnO chip with PVA, in a mass ratio (ZnO/PVA) of 1. The ZnO chip used in present work had the size of $9\times4\times3$ mm$^3$, and the relative density was 69%. The chip covered with PVA was heated at 700°C for 3 h in a high-purity argon gas. The amount of carbon formed on ZnO chip was determined from mass loss of the carbon-coated ZnO during heating 1000°C for 1 h in air with a flow rate of 5 cm$^3$ min, i.e. burning off of carbon. BET surface area of the ZnO with and without carbon was measured based on adsorption isotherm of nitrogen at 77 K, using BEL-SORP Mini (Nihon Bel, Co.).

Carnation (Dianthus caryophyllus) was used in the longevity tests of a cut flower. After adding a carbon-coated ZnO into the vase filled with distilled water of 250 cm$^3$, carnation cut the stem in water was inserted. The longevity of carnation was examined by observing the survival situation of carnation with time. Test condition was under 70% humidity at 25°C.

## 3. Results and discussion

By X-ray diffraction measurement, diffraction peaks corresponding to ZnO with hexagonal structure were detected in the chips with and without carbon, irrespective of polymerization degree of the PVA. **Figure 1** shows photographs of the carbon-coated ZnO chips obtained by the pyrolysis of PVA. In the case of the use of PVA with the polymerization degree of 2000, ZnO chip changed from white to black in the both of the inside and the outside, indicating that the carbon formed not only the surface of ZnO chip but also the central portion uniformly. By using PVA with the polymerization degrees of 22000 and 95000, however, the surface of the chip showed gray with increasing polymerization degree of PVA. In same case, since a color at the central portion was lighter than that on the surface, the formation of carbon seems to be clearly insufficient. PVA shows fluidity at the temperature range from 200 to 250°C in inert atmosphere, and it is expected that PVA consisting of viscous fluid penetrates via pores of ZnO toward its inside. Since viscosity in polymer generally increase with increasing polymerization degree, the fluidity of PVA may decrease with increasing polymerization degree. Using PVA with low polymerization degree, the formation of carbon on ZnO chip in the inside and the outside is expected to be due to production of the low viscous fluid in PVA at 200–250°C.

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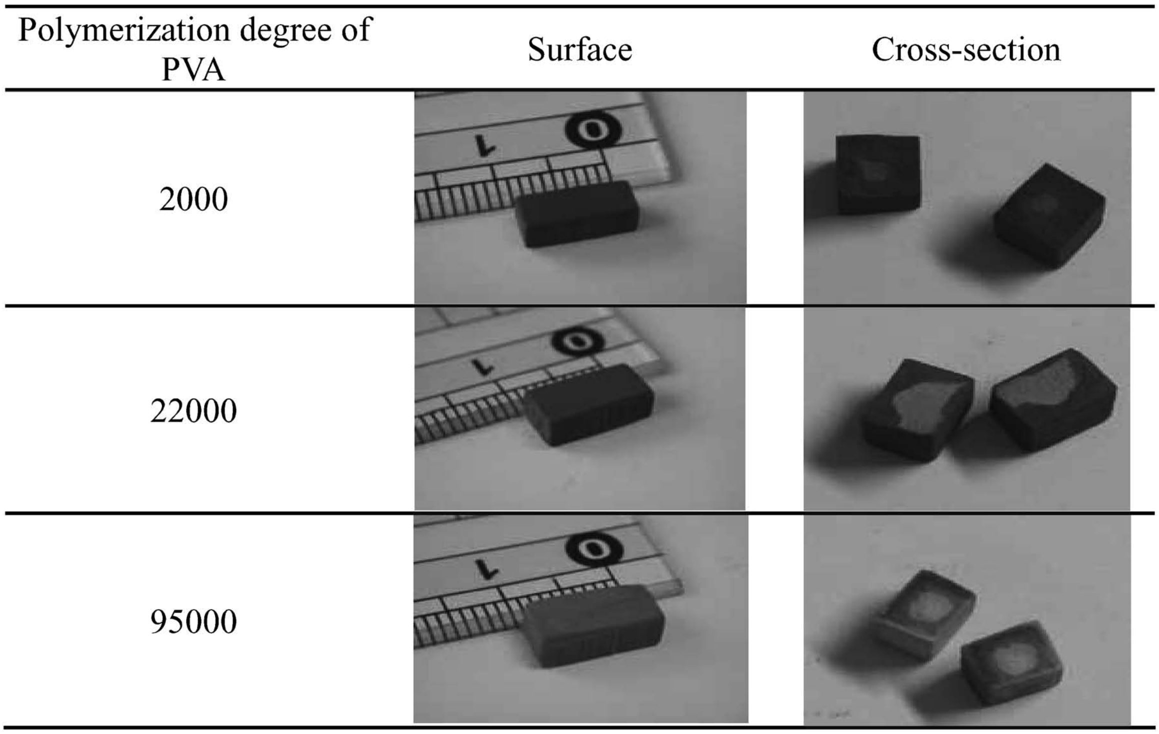


Fig. 1. Photographs at the inside and the outside of carbon-coated ZnO chips.

Table 1. Mass Gain and Specific Surface Area of Carbon-Coated ZnO

| Sample | Mass gain (%) | Specific surface area ($m^2\ g^{-1}$) |
|---|---|---|
| ZnO | 0 | 0.10 |
| ZnO-PVA(2000) | 5.0 | 13.6 |
| ZnO-PVA(22000) | 3.0 | 12.6 |
| ZnO-PVA(95000) | 2.0 | 6.30 |

**Table 1** summarized the mass gain and the specific surface area of the carbon-coated ZnO chips prepared by using PVA with different polymerization degrees, together with ZnO chip without carbon. Mass gain of the carbon-coated ZnO prepared by using PVA with polymerization degree of 2000 was a value of 5.0%. With increasing polymerization degree, the mass gain was found to decrease due to the small amount of carbon, according with the formation situation of carbon shown in Fig. 1. Specific surface area of the carbon-coated ZnO increased with decreasing polymerization degree, which reached the value of 13.6 $m^2\ g^{-1}$ in the degree of 2000, though the surface area was 0.1 $m^2\ g^{-1}$ in ZnO without carbon. There are many pores in carbon formed on the surface of ceramic powder.[10] The specific surface area is anticipated to be dependent on the amount of carbon formed on ZnO chip, i.e., increasing surface area with increasing amount of carbon.

From the results described above, it was clarified that PVA with polymerization degree of 2000 was suitable for forming homogeneously carbon at every portion in ZnO chip.

In order to know the formation state of the carbon at the central portion of carbon-coated ZnO chip, ZnO in carbon-coated chip was dissolved with $NH_4OH$ aqueous solution in the concentration of 0.5 mol $dm^{-3}$. SEM-micrograph of the carbon formed in ZnO chip is shown in **Fig. 2**. Pores with the diameter of about 6 $\mu$m and 1 $\mu$m were observed. The pores of 6 $\mu$m size were comparable with the grain size in ZnO chip. On the other hand, the pores of 1 $\mu$m size may correspond to portion of the neck among ZnO grain. It was found that all pores which existed in ZnO chip with low density were filled up with carbon.

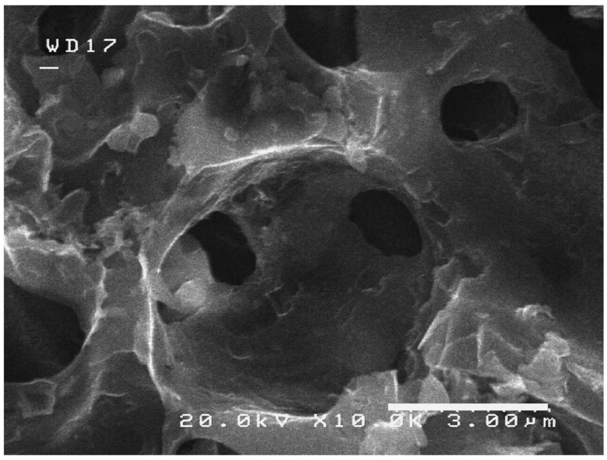


Fig. 2. SEM-micrograph of carbon portion after removing ZnO from carbon-coated ZnO chip.

Addition effect of the carbon-coated ZnO on longevity of carnation was examined using the chip prepared by pyrolysis of PVA with polymerization degree of 2000. **Figure 3** shows the situation of carnation with time in the case of addition of ZnO, carbon-coated, and no ZnO. In ZnO, the stem of carnation bent for 15 days, which corroded 30 days later, as well as

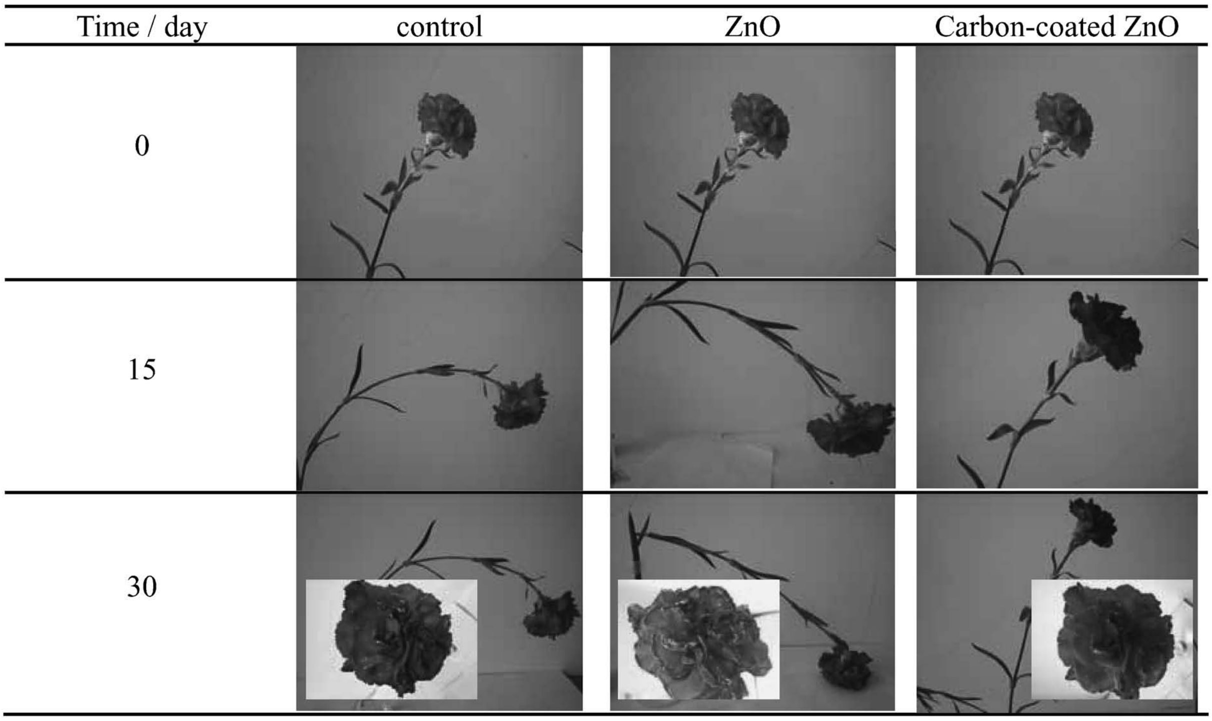


Fig. 3. Photographs of carnation in addition of ZnO, carbon-coated ZnO and no ZnO.

without addition (control). In the case of carbon-coated ZnO, however, no bend and corrosion in stem of carnation was observed for 30 days, being slight change in color of the petal portion. From this observation, it is found that the formation of carbon on ZnO chip is effective for longevity of carnation. Bacterial growth in the vase water results in the death of flowers, because of obstruction in supply from stem of water and nutrition.[11),12)] Even if large amount of hydrogen peroxide generated from ZnO strongly acts on cell of flowers, it probably lead to death of the flowers. Hydrogen peroxide generated from carbon-coated ZnO may be less than that from ZnO, because of the decrease in surface of ZnO generating hydrogen peroxide by the porous carbon coated on ZnO. Yamamoto et al.[13)] reported that carbon spheres obtained from ion-exchanged resin adsorbed the large amount of bacteria in bacterial suspension, and did not exhibit bacterial extinction on the surface of carbon spheres. This indicates that carbon can remove bacteria dispersing into water and has little adsorption effect for local bacterial growth. Bacterial growth should occur at stem soaked into water. Therefore, the reason that carbon-coated ZnO chip gave a superior effect for longevity of carnation is expected to be due to the appropriate amount of hydrogen peroxide affecting inhibition of bacterial growth without damage with cell of carnation.

## 4. Conclusion

Carbon-coated ZnO chip was prepared by pyrolysis of PVA with polymerization degree of 2000, and carbon was formed homogeneously at every portion in ZnO chip. Pores which existed in ZnO chip with low density were filled up with carbon. From observation of carnation, the longevity of a cut flower for ZnO chip with carbon was more improvement than that without carbon. The formation of carbon on ZnO chip was effective for longevity of a cut flower.

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## References


1) O. Yamamoto, J. Sawai, H. Kojima and T. Sasamoto, *J. Mater. Sci. Mater. Med.*, 13, 789–792 (2002).
2) J. Sawai, *J. Microbiol. Methods*, 54, 177–182 (2003).
3) J. Sawai, K. Himizu and O. Yamamoto, *Soil Biol. Biochem.*, 37, 1484–1489 (2005).
4) O. Yamamoto, Y. Iida and T. Sasamoto, *J. Ceram. Soc. Japan*, 112, S839–S841 (2004).
5) O. Yamamoto, A. Yamamura, H. Suzuki, K. Matsumoto and T. Sasamoto, *Electrochemistry*, 71, 2–4 (2003).
6) O. Yamamoto, M. Komatsu, J. Sawai and Z. Nakagawa, *J. Mater. Sci. Mater. Med.*, 15, 847–851 (2004).
7) J. Sawai, O. Yamamoto, B. Özkal and Z. Nakagawa, *Biocontrol Sci.*, 12, 15–20 (2007).
8) M. Inagaki, Y. Hirose, T. Matsunaga, T. Tsumura and M. Toyoda, *Carbon*, 41, 2619–2624 (2003).
9) T. Morishita, K. Ishihara, M. Kato and M. Inagaki, *Carbon*, 45, 209–211 (2007).
10) M. Inagaki, S. Kobayashi, F. Kojin, N. Tanaka, T. Morishita and B. Tryba, *Carbon*, 42, 3153–3158 (2004).
11) Y. de Witte and W. G. van Doorn, *Acta Hortic.*, 298, 155–170 (1992).
12) W. G. Van Doorn, Y. de Witte and H. Harkema, *Postharvest Biol. Technol.*, 6, 111–119 (1995).
13) O. Yamamoto, K. Nakakoshi, T. Sasamoto, H. Nakagawa and K. Miura, *Carbon*, 39, 1643–1651 (2001).