SUPPLEMENTARY FILE

Role of hydrothermally prepared CeO_2 in developing chitosan-based functional coating for banana preservation

Thuong Thi Nguyen,*[ac] Bao-Tran Tran Pham,[bc] Dinh Thien Le,[de] Bang-Tam Thi Dao [de] and Chi Nhan Ha Thuc*[de]

[a] Faculty of Applied Science and Technology, Nguyen Tat Thanh University, Ho Chi Minh City, Vietnam

[b] Nguyen Tat Thanh University Center for Hi-Tech Development, Saigon Hi-Tech Park, Ho Chi Minh City, Vietnam

[c] Institute of Applied Technology and Sustainable Development, Nguyen Tat Thanh University, Ho Chi Minh City, Vietnam

[d] Faculty of Materials Science and Technology, University of Science, Ho Chi Minh City, Vietnam

[e] Vietnam National University, Ho Chi Minh City, Vietnam

*Corresponding authors: nthithuong@ntt.edu.vn (Thuong Thi Nguyen) and htcnhan@hcmus.edu.vn (Chi Nhan Ha Thuc)

SECTION A. EXPERIMENTAL SECTION

A.1. Characterization of CeO_2 Nanoparticles

The X-ray diffraction (XRD) patterns of CeO_2 nanoparticles were characterized by the D2 PHASER-XRD equipment (Bruker Co.) using Cu-Kα as a radiation source to determine their crystal structure. The zeta potential of CeO_2 nanoparticles was also measured using Zetasizer Ver. 8.02 (Malvern, Worcestershire, UK) to determine its stability in the aqueous solution. The morphology of the CeO_2 nanoparticles was observed using a scanning electron microscope (SEM, Hitachi S-4800, Japan) at 50× magnification and 3 kV voltage and transmission electron microscopy (TEM, JEOL JEM 1400) at 80 kV voltage.

A.2. Film Characterization

The morphological and structural determination of the nanocomposite films was performed using Fourier transform infrared (FT-IR) spectroscopy, XRD, and SEM. The FT-IR measurements of the nanocomposite films were executed on the FT/IR-6600 instrument (JASCO Co.) equipped with the attenuated total reflection device. The XRD and SEM characterization of the nanocomposite films was performed using the above-mentioned methods for CeO_2 nanoparticles.

The measurement of film thickness was performed by an electronic digital micrometer (Mitutoyo No. 7313A) having an accuracy of 0.015 m. The average thickness values were obtained from ten random positions.

The tensile strength (Ts) and elongation at break (Eab) of the nanocomposite films were determined according to the ASTM D882-02 standard.[1] Film specimens (12×1.5 cm) were run on a Universal testing system (Illinois Tool Works Inc.) with an initial grip distance of 5 cm and 10 mm/s crosshead speed under a 20 kN load cell.

The color indices (L, a, b) of the nanocomposite films were recorded by CR-400 colorimeter with D65 standard illumination and white standard plate ($L = 93.59$; $a = -1.46$; $b = 4.69$). The total color difference (ΔE) and whiteness index (WI) of the nanocomposite films were calculated and referred to the CS films using Eq. (A.1) and Eq. (A.2):[2]

$$\Delta E = \sqrt{\left(L_{CH-hCeO_2} - L_{CH}\right)^2 + \left(a_{CH-hCeO_2} - a_{CH}\right)^2 + \left(b_{CH-hCeO_2} - b_{CH}\right)^2} \qquad (A.1)$$

$$WI = 100 - \sqrt{\left(100 - L_{CH-hCeO_2}\right)^2 + {a_{CH-hCeO_2}}^2 + {b_{CH-hCeO_2}}^2} \qquad (A.2)$$

The light transmittance in the visible and UV regions was measured by a UV-1800 spectrophotometer in the wavelength range of 200–800 nm.

Water vapor permeability (WVP) was determined according to the method reported by Chuaynukul et al.[3], with some improvement. The film samples were sealed over the opening of a wide-mouth cup (Ø20), including 100 mL of distilled water. The as-fabricated cups were transferred to a desiccator containing 100 g of silica gel at room temperature (27 ^{o}C). The cup weight was continuously determined every 24 h for 3 d, and the average WVP values of nanocomposite films from three measurements were calculated based on Eq. (A.3):

$$WVP\ (g/s.m.Pa) = \frac{\Delta w \times x}{t \times A \times \Delta P} \times 100 \qquad (A.3)$$

where Δw (g) denotes the reduced cup weight; x (m) and t (s) are the film thickness and testing time, A (m^2) represents the contact area between the films and the cup, and ΔP is the saturated vapor pressure at room temperature (27 ^{o}C).

Solubility and swelling index were measured by the method previously reported by Mohajer et al.[4] with some improvement. The 2×2 cm film samples were dried at 45 °C and weighed on the electronic analytical balance (Ohaus No. PA214) with an accuracy of 0.0001 g to have dry mass (m_1). After that, the as-prepared film samples were soaked in the sealed holding containing 30 mL of distilled water before being stored at room temperature (27 °C) for 24h. Next, tissue was used to remove the rest water on the wet film, which was then weighed to have wet weight (m_2). Finally, these wet films were dried at 105 °C for 24 h before being weighed to have a dry weight (m_3). The solubility and swelling index of nanocomposite films were expressed by Eq. (A.4) and Eq. (A.5):

$$Solubility\ (\%) = \frac{m_1 - m_2}{m_1} \times 100 \qquad (A.4)$$

$$Swelling\ index\ (\%) = \frac{m_3 - m_1}{m_1} \times 100 \qquad (A.5)$$

A.3. Banana preservation

The coating effect on the surface morphology of bananas was observed by SEM (Hitachi S-4800 equipment). Non-, Kadozan-, CS- and CS-1.5%-hCeO_2-coated banana peels were cut into 6 mm pieces and were freeze-dried by a sublimation vacuum before being observed by SEM.

The amount of CO_2 (mgCO_2/kg.h) produced as remarked as the respiration rate of fruit was determined by a Headspace analyzer (Illinois No. GS6000). In detail, each fruit (n=5) was placed in a 2 L airtight plastic container for 120 min at 27 °C, and then the amount of produced CO_2.

The mass loss of fruit during storage was expressed by the equation (A.6):

$$Weight\ loss\ (\%) = \frac{m_0 - m_i}{m_0} \times 100 \qquad (A.6)$$

Here, m_o and mi are the weights at the initial and stored days, respectively.

The firmness of the fruit was measured by the texture analyzer (TA. XTplus) with a compression speed of 5 mm/s and a penetration distance of 10 mm.

The total soluble solids (TSS) of fruit expressed in % was determined on a hand digital refractometer (Atago No. PR-32α).

The titratable acidity (TA) of fruit was determined by the reported titration method.[5] In detail, 10 g of sliced fruit pulp was mixed with 100 mL of distilled water before being homogenized and vortexed for 1 min to obtain a homogeneous solution. Then, the titration process proceeded with 10 mL of as-prepared solution and 0.1 N NaOH using 1% phenolphthalein as an indicator. The TA (%) related to the percentage of maleic acid was calculated according to Eq. (A.7):

$$Titratable\ acidity\ (\%) = \frac{V_{NaOH\ (mL)}\ \times 0.1\ \times 0.067 \times 100}{10\ g} \qquad (A.7)$$

Here, VNaOH is the volume of NaOH solution at the equilibrium point.

The ripening level was calculated from average values of TSS and TA following to Eq. (A.8):

$$Ripening\ index = \frac{TSS}{TA} \qquad (A.8)$$

The pH of fruit pulp juices was recorded using a digital pH meter (Hanna No. HI211-02).

References

1 ASTM D882-18, in *Annual book of ASTM standards*, Philadelphia, PA: Amer. Soc. for Testing & Materials, 2018.

2 R. E. Wrolstad and D. E. Smith, 2017, pp. 545–555.

3 K. Chuaynukul, M. Nagarajan, T. Prodpran, S. Benjakul, P. Songtipya and L. Songtipya, *J. Polym. Environ.*, 2018, **26**, 1239–1252.

4 S. Mohajer, M. Rezaei and S. F. Hosseini, *Carbohydr. Polym.*, 2017, **157**, 784–793.

5 R. Thakur, P. Pristijono, M. Bowyer, S. P. Singh, C. J. Scarlett, C. E. Stathopoulos and Q. V. Vuong, *Lwt*, 2019, **100**, 341–347.

SECTION B. RESULTS

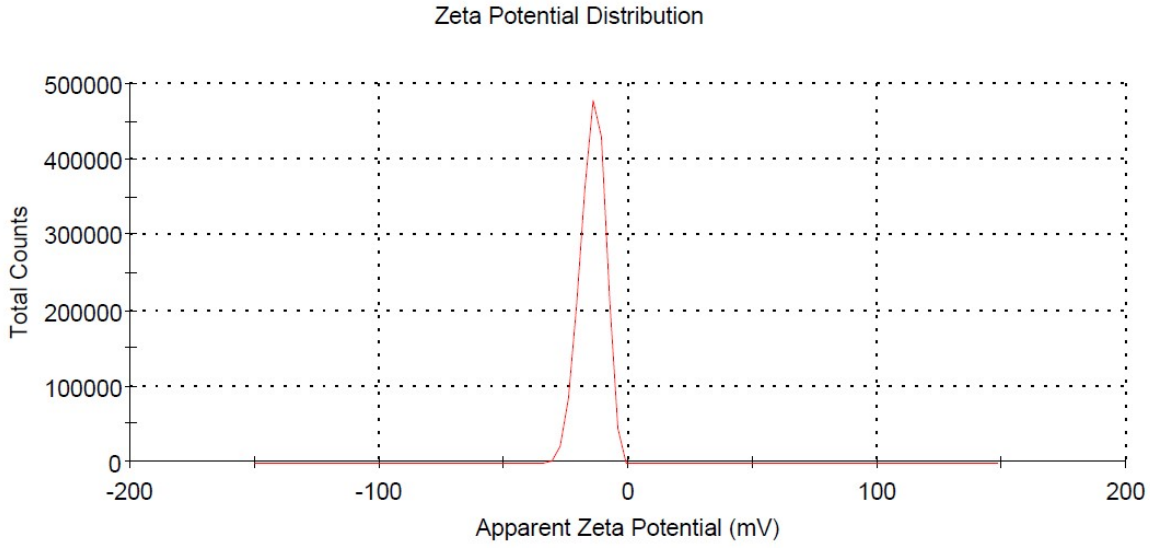

Figure B1. The zeta potential of CeO_2 prepared by the hydrothermal method

Table B1. Viscosity and pH of CS and CS-1.5%-hCeO_2 solution

Sample code	Viscosity (mPa/s) at 26°C, 100 rpm	pH
CS	257.50 ± 0.75	3.90 ± 0.01
CS-1.5%-hCeO_2	266.70 ± 1.14	3.90 ± 0.01

Table B2. The respiration rate, weight loss, firmness, total soluble solids, titratable acidity, and pH data of mango fruit during storage.

Coating × day	Respiration rate (mgCO$_2$/kg.h)	Weight loss (%)	Firmness (kg/m^2)	Total soluble solids (%)	Titratable acidity (x10^{-2} %)	pH
Control × day 0	180.90^{a} ± 0.00	0.00^{a} ± 0.00	3544.88^{a} ± 35.92	10.47^{a} ± 0.06	4.13^{a} ± 0.19	4.55^{a} ± 0.00
Kadozan × day 0	180.90^{a} ± 0.00	0.00^{a} ± 0.00	3544.88^{a} ± 35.92	10.47^{a} ± 0.06	4.13^{a} ± 0.19	4.55^{a} ± 0.00
CS × day 0	180.90^{a} ± 0.00	0.00^{a} ± 0.00	3544.88^{a} ± 35.92	10.47^{a} ± 0.06	4.13^{a} ± 0.19	4.55^{a} ± 0.00
CS-1.5%-hCeO$_2$ × day 0	180.90^{a} ± 0.00	0.00^{a} ± 0.00	3544.88^{a} ± 35.92	10.47^{a} ± 0.06	4.13^{a} ± 0.19	4.55^{a} ± 0.00
Control × day 2	299.13^{g} ± 14.21	4.44^{c} ± 0.50	304.23^{fgh} ± 27.40	15.27^{d} ± 0.59	3.75^{bcd} ± 0.07	4.90^{de} ± 0.02
Kadozan × day 2	256.74^{cd} ± 9.85	4.16^{c} ± 0.84	680.87^{d} ± 42.35	13.83^{c} ± 0.59	3.80^{bc} ± 0.04	4.89^{de} ± 0.02
CS × day 2	255.06^{cd} ± 5.78	4.13^{c} ± 0.59	906.76^{c} ± 6.78	13.93^{c} ± 0.49	3.84^{bc} ± 0.04	4.81^{bc} ± 0.03
CS-1.5%-hCeO$_2$ × day 2	238.40^{bc} ± 20.33	2.43^{b} ± 0.42	1444.16^{b} ± 155.90	11.37^{b} ± 0.40	4.09^{a} ± 0.07	4.60^{a} ± 0.10
Control × day 4	338.74^{h} ± 7.30	8.83^{e} ± 1.15	274.86^{ghi} ± 18.87	18.70^{f} ± 0.87	3.66^{cd} ± 0.04	5.18^{hi} ± 0.02
Kadozan × day 4	266.51^{def} ± 26.00	7.90^{de} ± 0.58	293.53^{gh} ± 10.06	17.37^{e} ± 0.06	3.75^{bc} ± 0.00	5.01^{f} ± 0.01
CS × day 4	270.20^{def} ± 10.65	7.87^{de} ± 0.53	323.61^{fg} ± 4.61	17.33^{e} ± 0.06	3.80^{bc} ± 0.04	4.92^{de} ± 0.11
CS-1.5%-hCeO$_2$ × day 4	247.14^{bcd} ± 13.89	5.29^{c} ± 0.35	474.31^{e} ± 30.67	13.77^{c} ± 0.47	3.91^{ab} ± 0.04	4.78^{b} ± 0.07

Control × day 6	293.66^{g} ± 12.67	13.50^{h} ± 0.49	166.52^{k} ± 8.99	23.63^{j} ± 0.38	3.17^{ef} ± 0.17	5.46^{f} ± 0.01
Kadozan × day 6	285.62^{fg} ± 8.96	12.83^{gh} ± 1.01	185.51^{jk} ± 8.69	21.57^{g} ± 0.21	3.30^{e} ± 0.14	5.17^{ghi} ± 0.04
CS × day 6	284.66^{efg} ± 25.48	12.11^{g} ± 2.05	245.18^{hij} ± 8.12	21.60^{g} ± 0.20	3.30^{e} ± 0.04	5.10^{g} ± 0.10
CS-1.5%-hCeO$_2$ × day 6	260.32^{cd} ± 12.90	7.29^{d} ± 0.39	365.91^{f} ± 54.77	18.73^{f} ± 0.85	3.80^{bc} ± 0.14	4.87^{cd} ± 0.07
Control × day 8	-	-	-	-		-
Kadozan × day 8	228.13^{b} ± 11.05	16.35^{i} ± 1.32	144.06^{k} ± 11.02	23.50^{ij} ± 0.10	2.84^{h} ± 0.14	5.22^{hi} ± 0.02
CS × day 8	262.38^{de} ± 8.47	16.10^{i} ± 1.09	201.74^{jk} ± 7.32	23.33^{ij} ± 0.25	2.86^{gh} ± 0.17	5.19^{hi} ± 0.02
CS-1.5%-hCeO$_2$ × day 8	267.51^{def} ± 9.15	10.68^{f} ± 0.91	275.60^{ghi} ± 18.85	21.63^{g} ± 0.15	3.53^{d} ± 0.17	4.95^{ef} ± 0.02
Control × day 10	-	-	-	-		
Kadozan × day 10	-	-	-	-		
CS × day 10	-	--	-	-		
CS-1.5%-hCeO$_2$ × day 10	260.71^{cd} ± 16.14	13.51^{h} ± 0.44	241.84^{hij} ± 10.67	22.20^{gh} ± 0.62	3.30^{e} ± 0.04	5.13^{gh} ± 0.01
Control × day 12	-	-	-	-		
Kadozan × day 12	-	-	-	-		
CS × day 12	-	-	-	-		

CS-1.5%-hCeO$_2$ × day 12	251.79^{cd} ± 13.62	16.32^{i} ± 0.34	205.93^{ijk} ± 17.02	22.83^{hi} ± 0.59	3.10^{fg} ± 0.08	5.22^{i} ± 0.02

(-): spoiled fruit.

*** Different letters within each column indicate significant differences among coating formulations at different storage periods using the Tukey HSD test ($p < 0.05$).