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Preparation and properties of calcium oxide from eggshells via calcination

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Duck eggs are one of the most versatile cooking ingredients in which residue eggshells are discarded. Raw duck eggshells were calcined at temperatures between 300 to 900 °C, for 1, 3, and 5 h. Both the raw and calcined duck eggshells were characterized by FTIR, STA, XRD, XRF, TEM, BET, a particle size analyzer, and an impedance analyzer. The proper calcination conditions are: 900 °C and 1 h, yielding calcium oxide with a purity of 99.06 % w/w. The calcium carbonate of the rhombohedral form ($CaCO_3$) transforms completely into the calcium oxide or lime of the face centered cubic form (CaO) at 900 °C, as shown by XRD diffraction patterns. The transmission electron microscopy (TEM) images of the calcium oxide reveal a moderately good dispersion of nearly uniform particles. The calcium oxide has a white color, a spherical shape, high porosity, and narrow particles size distribution. The percentage of ceramic yield of the calcium oxide is 53.53, as measured by STA (TG-DTA-DTG). The calcium oxide has a N_2 adsorption–desorption isotherm indicating the meso-porosity range. The dielectric constant and the electrical conductivity of the calcined calcium oxide are 35 and $1.0 \times 10^{-6} (\Omega\cdot m)^{-1}$, respectively, at the frequency of 500 Hz.

Keywords: *calcium oxide, pyrolysis, specific surface area, phase transformation*

1. Introduction

The egg and egg derivative consumption produce a great amount of residual shells which pose an environmental pollution as a result of microbial action. An important ingredient of an eggshell is calcium carbonate which can be potentially used in various material applications such as a filler in animal feed, pet food, printing ink, paper, glaze decoration, tiles, and as the source of calcium oxide or calcite. An eggshell waste primarily contains magnesium, calcium carbonate (limestone), and protein [1–3]. The calcium/magnesium contents in the shells can be converted into the calcium/magnesium oxide and the resultant burnt lime can be used as a liming agent. The calcium oxide obtained from calcined eggshells, whether from hen, duck, bird, goose, and partridge bird, can be potentially used in various applications: as filler in feed, fertilizer, paper, printing ink, pharmaceutical and cosmetic products, starting materials of dielectrics such as $CaSiO_3$, $CaTiO_3$, $CaAl_2O_4$, gypsum ($CaSO_4$), and as bio-catalysts [4–9]. Heung Jai *et al.*, (2007) studied heavy metals removal using a calcined waste eggshell in the treatment of synthetic wastewater containing heavy metals. A complete removal of Cd and a 99 % removal of Cr were observed within a period of 10 min [10]. An eggshell membrane generally contains about 10 % collagen, including the most common Type 1 collagen and the unusual Type 10 collagen. Collagen applications include: skin grafts, dental implants, angioplasty sleeves, cornea repair, plastic surgery, treatment of osteoporosis and pharmaceuticals, food castings, and film emulsions [11]. Other possibilities for utilizing eggshells include the production of biodegradable plastics from eggshell membrane proteins, altering the heat resistance of a food-borne bacterial pathogen with a bacteriolytic enzyme contained in an eggshell membrane, as a human dietary calcium supplement especially for post menopausal women. Eggshells also contain

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certain amounts of microelements such as strontium (Sr), fluorine (F) and selenium (Se); the membrane can be used as an adsorbent for the removal of reactive dyes from colored waste effluents as well as to eliminate heavy metal ions from a dilute waste solution [11].

Eggshells are a better source of calcium for calcium oxide (CaO), calcium carbonate ($CaCO_3$), calcium hydroxide ($Ca(OH)_2$), calcium phosphate, or hydroxyl apatite, in comparison to other sources such as carbonaceous rock, precipitated soil, teeth and bone, and crab or shrimp shells. The by-product of eggshell represents approximately 11 % w/w of the total weight (≈50–60) of a hen egg and 12.6 % w/w of the total weight (≈74.9–78) of a duck egg. The Agricultural Statistics of Thailand reported the quantities of egg production of approximately 9.8×10^9 hens' eggs and 1.5×10^9 ducks' eggs each year. Therefore, both hen and duck eggshells are approximately 60×10^6 metric tons per year in Thailand. Eggs can be produced in numerous countries in the world as an important nutrient source, and the world eggshells consumption amounts to millions metric tons per year. The by-product eggshells represent a significant amount of waste for the processors because they are traditionally useless. Most of the waste is commonly disposed of in a landfill without any pretreatment, causing odors from biodegradation, destroying microbial action, and changing the quality of soil. The advantages of eggshell waste utilization are to substitute the natural sources of calcium ($CaCO_3$, CaO, $Ca(OH)_2$), to reduce the waste problem in household, to conserve natural resources from rock and soil, to reduce the global climate warming, and to develop novelty of green ceramic materials and products: dielectrics, catalysts, biomaterials, fuel cell, and fillers.

In this work, we study the phase transformation and the electrical properties of the calcium oxide obtained by the calcination of the raw duck eggshells at the temperature range from a room temperature to 900 °C for 1, 3, and 5 h. Detailed investigations of the microstructure, chemical composition and organics (C/H/N) contents, functional groups, particle size distribution, density, specific surface area, phase transformation, and electrical properties (dielectric and electrical conductivity) are reported.

2. Experimental

2.1. Materials

Raw duck eggshells were collected from a local cafeteria. The eggshells were washed with tap water until the egg white was completely removed and dried at room temperature. After that the eggshells were broken into small pieces and crushed in a porcelain mortar into a fine powder, and kept in desiccators at a room temperature.

2.2. Instruments

A laboratory muffle furnace (Linn High Thermo GmbH, LM 412.27, model DC021032 with a thermocouple type K, NiCr-Ni) was used to calcine samples at temperatures from 27 °C to 1000 °C. Physical properties of the samples such as color, softness, and odor were studied. The samples were calcined in an alumina crucible for 1, 3, and 5 h at a heating rate of 10 °C/min.

Cumulative and fractional distributions were measured using a particle size analyzer (Mastersizer S long bed, model Polydisperse 2.19). The samples were dispersed in an aqueous medium and vibrated in an ultrasonic bath for 20 min.

Fourier transform infrared spectra (FTIR) were recorded on a spectrometer (Perkin Elmer, model Spectrum One) with a spectral resolution of 4 cm^{-1}, using a single-crystal potassium bromide mode.

Chemical compositions were obtained using an X-ray fluorescence (XRF) (Philips, model PW 2400) at a tube current of 1000 A with an acquisition lifetime of 30 s. The XRF diffraction pattern was used to determine the percentages of chemical compositions. The samples (raw duck eggshell and duck eggshell calcined at 900 °C for 1 h) were ground into powders and compressed into sample molds prior to testing. The elemental analysis (EA) was carried out on a C/H/N analyzer (Perkin Elmer, model PE 2400 series II). The elemental analysis was used to measure the organic C/H/N compositions.

X-ray diffraction (XRD) was taken and analyzed using a Bruker AXS analyzer (D8 Discover) with a VANTEC-1 Detector. Samples were analyzed using a double-crystal wide-angle goniometry with the 2θ scan from 10°–80° at a scan speed of 5° 2θ/min in

0.05° or 0.03° 2θ increments using CuKα radiation (λ = 0.15406 nm). The detected peak positions were compared with those of the International Center for Diffraction Data Standard (JCPDS) patterns to identify the crystalline phases.

Micrographs were obtained using a transmission electron microscope (TEM, JEM-2100) equipped with EDS for the X-ray microanalysis. The preparation of TEM samples of the raw material and the catalyst was carried out on a grid. An acceleration voltage of 80 to 200 kV with magnifications from 50 to 1.5 million times were used.

The thermal properties were measured using a differential scanning calorimeter (DSC, NETZSCH 409) and a simultaneous thermal analyzer (STA, NETZSCH 409). The samples were tested with a heating rate of 10 °C/min under air atmosphere.

True density of samples was measured with a gas pycnometer (Quantachrome, Ultra pycnometer 1000).

The specific surface area, the adsorption and/or desorption isotherms, the pore size, and the surface distributions were measured using an AUTOSORB-1 (QUANTACHROME), which measures the quantity of gas adsorbed onto or desorbed from the solid surface. The volume–pressure data were analyzed by the AUTOSORB-1 software to give the BET (Brunauer–Emmet–Teller) surface area (single and/or multipoint), the Langmuir surface area, the adsorption and/or desorption isotherms, the pore size and surface area distributions, the micropore volume, and the surface area. The determination of the surface area of solid materials involves the use of the BET equation as follows:

$$\frac{1}{W\left((P_o/P)-1\right)} = \frac{1}{W_mC} + \frac{C-1}{W_mC}\left(\frac{P}{P_o}\right) \qquad (1)$$

where W is the weight of gas adsorbed at a relative pressure, P/P_o, W_m is the weight of adsorbate constituting a monolayer of surface coverage, and C is a constant related to the energy of adsorption in the first adsorbed layer.

The specific surface area, S, of the solid was calculated from the total surface area and the sample weight, according to Eqs. (2) and (3) as follows:

$$S = S_t/W \qquad (2)$$

$$S_t = \frac{W_mNA_{cs}}{M} \qquad (3)$$

where S is the specific surface area of the solid, S_t is the total surface area, W is the sample weight, N is Avogadro's number (6.023×10^{23} molecules/mol), M is the molecular weight of the adsorbate, and A_{cs} is the area occupied by one adsorbate molecule (16.2×10^{-20} m^2 for N_2 and 19.5×10^{-20} m^2 for Kr) [13].

The electrical properties were measured using an impedance analyzer (HP, model 16451B) with an LCR meter (HP, model 4284A). The samples were prepared, according to ASTM B263-94, as thin discs with a diameter of 5.00 mm and a thickness of 0.50 mm. The electrical properties were measured at frequencies from 500 Hz to 106 Hz under an AC electrical field of 2 A.

2.3. Calcination process

Approximately 1.00 g of cleaned and crushed powder of raw duck eggshells was put into an alumina crucible and calcined in a muffle furnace under air atmosphere at various temperatures from 300 up to 900 °C, for 1, 3, and 5 h at a heating rate of 10 °C/min. After calcining, the sample crucibles were brought out from the muffle furnace and cooled down in air for a period of 10-20 min to avoid the hydrolysis, as shown in Eqs. (4) and (5). The raw duck eggshells and the calcined samples were subsequently characterized by STA, XRD, FTIR, TEM, BET, the particle size analyzer, and the impedance analyzer.

$$CaCO_3 \xrightarrow{\text{Calcination}} CaO + CO_2 \qquad (4)$$

$$CaO + H_2O \xrightarrow{\text{Hydrolysis}} Ca^{2+} + 2OH^- \qquad (5)$$

3. Results and discussion

3.1. Physical characterization of raw and calcined duck eggshells

Physical characterization data (color, odor, and softness) of raw duck eggshells and their calcined products from 300 °C to 1000 °C for 1, 3, and 5 h are tabulated in Table 1. A higher calcination temperature produces the samples which have a whiter

Table 1. Physical characterization of raw and calcined duck eggshells.

Number	Code	Physical characterization		
		Color	Odor	Softness
1.	000	White to light blue	Raw eggshell	Hard, Flake
2.	300_1	Gray brown	Stink	Hard, Flake
3.	300_3	Gray brown	Stink	Hard, Flake
4.	300_5	Dark gray brown	Stink	Hard, Flake
5.	500_1	Deep gray black	Stink	Hard, Flake
6.	500_3	Deep gray black	Stink	Hard, Flake
7.	500_5	Deep gray black	Stink	Hard, Flake
8.	700_1	Light gray	Slightly odor	Softer, Powder
9.	700_3	Light gray	Slightly odor	Softer, Powder
10.	700_5	Light gray	Slightly odor	Softer, Powder
11.	**900_1**	**White**	**Odorless**	**Softest, Powder**
12.	900_3	White	Odorless	Softest, Powder
13.	900_5	White	Odorless	Softest, Powder
14.	1000_1	White	Odorless	Softest, Powder
15.	1000_3	White	Odorless	Softest, Powder
16.	1000_5	White	Odorless	Softest, Powder

000 means ground raw duck eggshell at room temperature., 300_1 means calcined duck eggshell at 300 °C for 1 h., 300_3 means calcined duck eggshell at 300 °C for 3 h., 300_5 means calcined duck eggshell at 300 °C for 5 h., 500_1 means calcined duck eggshell at 500 °C for 1 h., 500_3 means calcined duck eggshell at 500 °C for 3 h., 500_5 means calcined duck eggshell at 500 °C for 5 h., 700_1 means calcined duck eggshell at 700 °C for 1 h., 700_3 means calcined duck eggshell at 700 °C for 3 h., 700_5 means calcined duck eggshell at 700 °C for 5 h., 900_1 means calcined duck eggshell at 900 °C for 1 h., 900_3 means calcined duck eggshell at 900 °C for 3 h., 900_5 means calcined duck eggshell at 900 °C for 5 h., 1000_1 means calcined duck eggshell at 1000 °C for 1 h., 1000_3 means calcined duck eggshell at 1000 °C for 3 h., 1000_5 means calcined duck eggshell at 1000 °C for 5 h.

Table 2. C/H/N contents in raw duck eggshells as measured with the elemental analyzer.

No.	% C	% H	% N
1.	13.43	0.57	0.57
2.	13.51	0.43	0.54
3.	13.99	0.47	0.78
Average	**13.64**	**0.49**	**0.63**

color, are softer, and less odorous. A higher calcination temperature and time yield a higher percentage of calcium oxide content.

The organics contents (C/H/N composition) in the raw duck eggshells were investigated with the elemental analyzer and the data are tabulated in Table 2. The average percentages of carbon, hydrogen, and nitrogen contents are 13.64 %, 0.49 %, and 0.63 %, respectively.

Table 3 shows the chemical composition of the raw duck eggshells and duck eggshells calcined at 900 °C for 1 h, revealed by the X-ray fluorescence spectroscopy (XRF). Calcium oxide content in the raw duck eggshells is very small because

Table 3. Chemical compositions of samples as measured with the wavelength dispersive X-ray fluorescence spectrometer (XRF).

Composition (% w/w)	Raw duck eggshells	Duck eggshells calcined 900_1
Na_2O	<0.01	0.04
MgO	0.10	0.20
SiO_2	0.01	<0.01
P_2O_5	0.27	0.46
SO_3	0.16	0.12
K_2O	0.02	0.04
CaO	–	99.06
$CaCO_3$	96.35	–
SrO	0.02	0.05
ZrO_2	0.02	<0.01

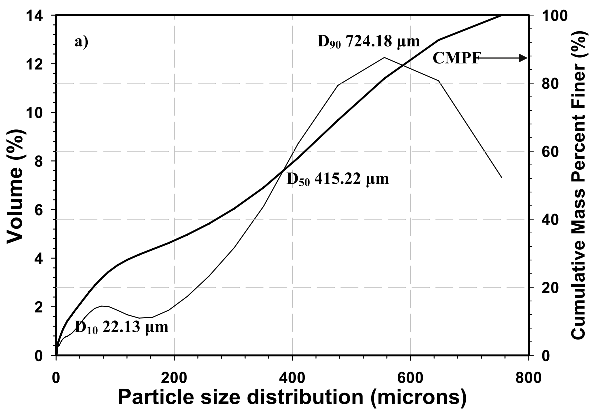
Table 4. True density of samples as measured by a gas pycnometer.

Samples	True density (g/cm^3)
Raw duck eggshells	2.25
Raw hen eggshells	2.20
Duck eggshells calcined 900_1	2.84
Hen eggshells calcined 900_1	2.16

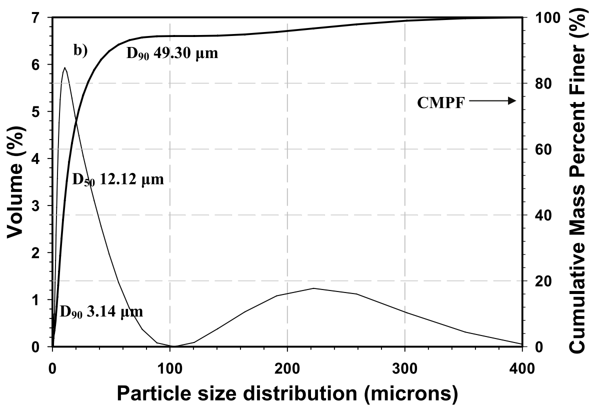
calcium mostly exists in a form of calcium carbonate at the amount of 96.35 % w/w, other oxide compounds of 0.61 % w/w, and other organic matters of 3.04 % w/w. The calcium oxide content in the duck eggshells calcined at 900 °C for 1 h is approximately 99.06 % w/w, and the other oxide compounds amounts to only 0.94 % w/w. Thus the thermal treatment of raw duck eggshells transforms the chemical composition from calcium carbonate ($CaCO_3$) to calcium oxide (CaO) almost perfectly.

The true density of the samples was measured by a gas pycnometer and the data are tabulated in Table 4. The density values of the raw duck eggshells and the raw hen eggshells are 2.25 and 2.20 g/cm^3, respectively. The density values of the duck eggshells and the chicken eggshells calcined at 900 °C for 1 h are 2.84 and 2.16 g/cm^3, respectively; the differences are caused by the anatomy, the species, the breeding, and the feeding, which influences the deposition of calcium, phosphorus, amino acid, and other nutrients during the egg formation.

The particle size distribution and the cumulative mass percentage diameters (d_{10}, d_{50}, d_{90}, and mean diameter) of the raw duck eggshells, measured with a particle size analyzer, are 22.13, 415.22, 724.18, and 383.15 μm, respectively, as shown in Fig. 1a. The particle size distribution and the cumulative mass percentage diameters (d_{10}, d_{50}, d_{90}, and mean diameter) of the particles of duck eggshell calcined at 900 °C for 1 h (900_1) are 3.14, 12.12, 49.30, and 29.16 μm, respectively, as shown in Fig. 1b. The particle size distribution and the cumulative mass percentage diameters (d_{10}, d_{50}, d_{90}, and mean diameter) of the hen eggshells calcined at 900 °C for 1 h (900_1) are 15.91, 89.03, 538.55, and 193.54 μm, respectively. The cumulative mass percentage diameters (CMPD) of calcined duck eggshells are smaller than those of calcined hen eggshells, in conformity with the true density values. The eggshells of both hen and duck are composed of three layers: a cuticle thin outer layer, a palisade thick middle layer, and an inner thin mammillary layer. However, the duck eggshells have a thicker shell layer, higher shell weight, more moisture and higher organic matter contents within the shell, more interactive bonding of the shell affecting the shell toughness, and higher true density than the hen eggshells.



(a)



(b)

Fig. 1. Particle size distribution and fractional and cumulative distributions: a) raw duck eggshells; b) raw duck eggshells calcined at 900 °C for 1 h.

The simultaneous thermal analysis (STA) plots from room temperature to 1200 °C, consisting of DTA, TG, and DTG spectra of the raw duck eggshells indicate two endothermic reactions (680 °C and 930.4 °C), as shown in Fig. 2. The DTA curve shows an onset at 861.5 °C. The first

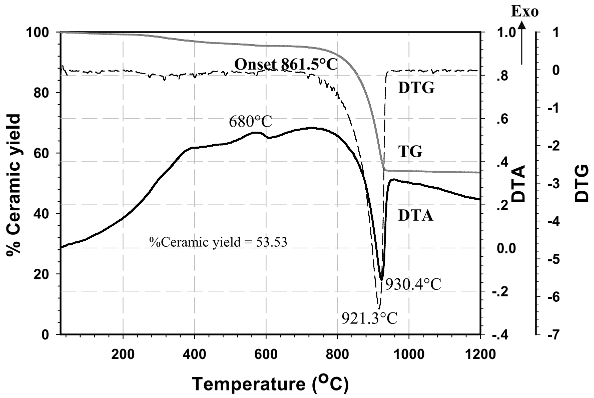


Fig. 2. Simultaneous Thermal Analysis (STA) of raw duck eggshells from 27 °C to 1200 °C at a heating rate of 10 °C/min.

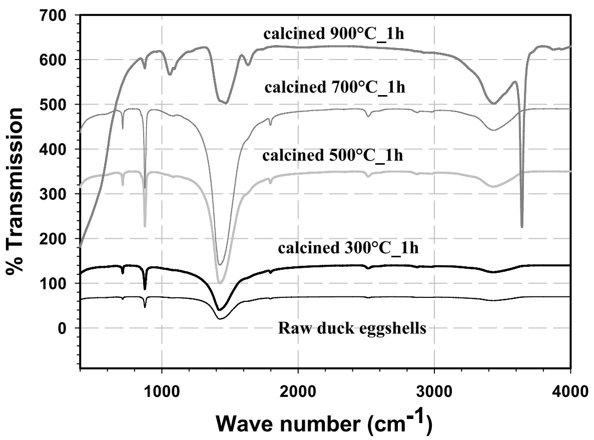


Fig. 3. FTIR spectra of raw duck eggshells and raw duck eggshells calcined at 300 °C, 500 °C, 700 °C, and 900 °C for 1 h.

stage of DTA plot expresses the moisture and the organic matter decomposition between room temperature and 680 °C, as well as the emission of CO_2 at 930.4 °C. The phase transformation from calcium carbonate ($CaCO_3$) to calcium oxide (CaO) occurs at 930.4 °C, which is consistent with the endothermic reaction. The thermogravimetric TG/DTG plot indicates the percentage of ceramic yield from room temperature to 1200 °C of the raw duck eggshells to be 53.53 % due to the single step carbon dioxide release.

FTIR spectra of the raw duck eggshells before and after the calcination are shown in Fig. 3. The characteristic peaks of the raw duck eggshells are consistent with the CAS [471-34-1] at the wavelengths from 400 to 4000 cm^{-1}. The bands at 875.08 and 1423.55 cm^{-1} are associated with the vibrations of the carbonate groups. The FTIR spectra of the duck eggshell samples calcined from 300 °C to 700 °C for 1 h reveal characteristic bands of the calcium carbonate structure at 713, 875, 1423, 1798, 2518, and 3435 cm^{-1}. The FTIR spectra of the duck eggshells calcined from 700 °C to 900 °C for 1 h show the bands at 3643 cm^{-1} strong ν(O–H), 3435 cm^{-1} ν(O–H), 1630 cm^{-1} strong ν(C=O), and 500–580 cm^{-1} ν(Ca–O).

TEM images of the raw duck eggshell samples before and after calcinations are shown in Figs. 4a and 4b at a magnification of 25000 X, and in Figs. 4a_1 and 4b_1 at a magnification of 12000 X, respectively. Before the calcination, the raw duck eggshells had a generally irregular crystal structure After the calcination at 900 °C for 1 h, as shown in Figs. 4b and 4b_1, the crystal structure changed into a porous structures; a small amount of agglomeration can be observed along with the decomposition of CO_2 as shown by STA. The formation of CO_2 can be assumed to follow an endothermic reaction as described in the reaction Eq. (4). Our TEM dispersion results resemble the SEM dispersion results reported by Heung Jai *et al.* [10].

3.2. Phase transformation of raw and claimed duck eggshells studied by XRD

X-ray diffraction patterns of the raw duck eggshell samples before and after calcinations are shown in Fig. 5. X-ray diffraction spectra of the samples were obtained with CuKα radiation (λ = 0.15406 nm) in a 2θ scan range of 5°–80°. The XRD peaks of the raw duck eggshells occur at 2θ equal to 29.399 (1 0 4), 35.981 (1 1 0), 39.417 (1 1 3), 43.171 (2 0 2), and 48.505 (1 1 6). The XRD peaks of the calcined duck eggshells can be seen at 2θ equal to 32.194 (1 1 1), 37.345 (2 0 0), and 53.843 (2 2 0). Comparing the XRD peaks in Fig. 5 with the standard peak patterns of JCPDS files, the raw duck eggshell peaks represents well the calcium carbonate or calcite ($CaCO_3$) of the rhombohedral form; R-3c; JCPDS No. 01-086-0174; the eggshell peaks calcined at 900 °C for 1, 3, and 5 h corre-

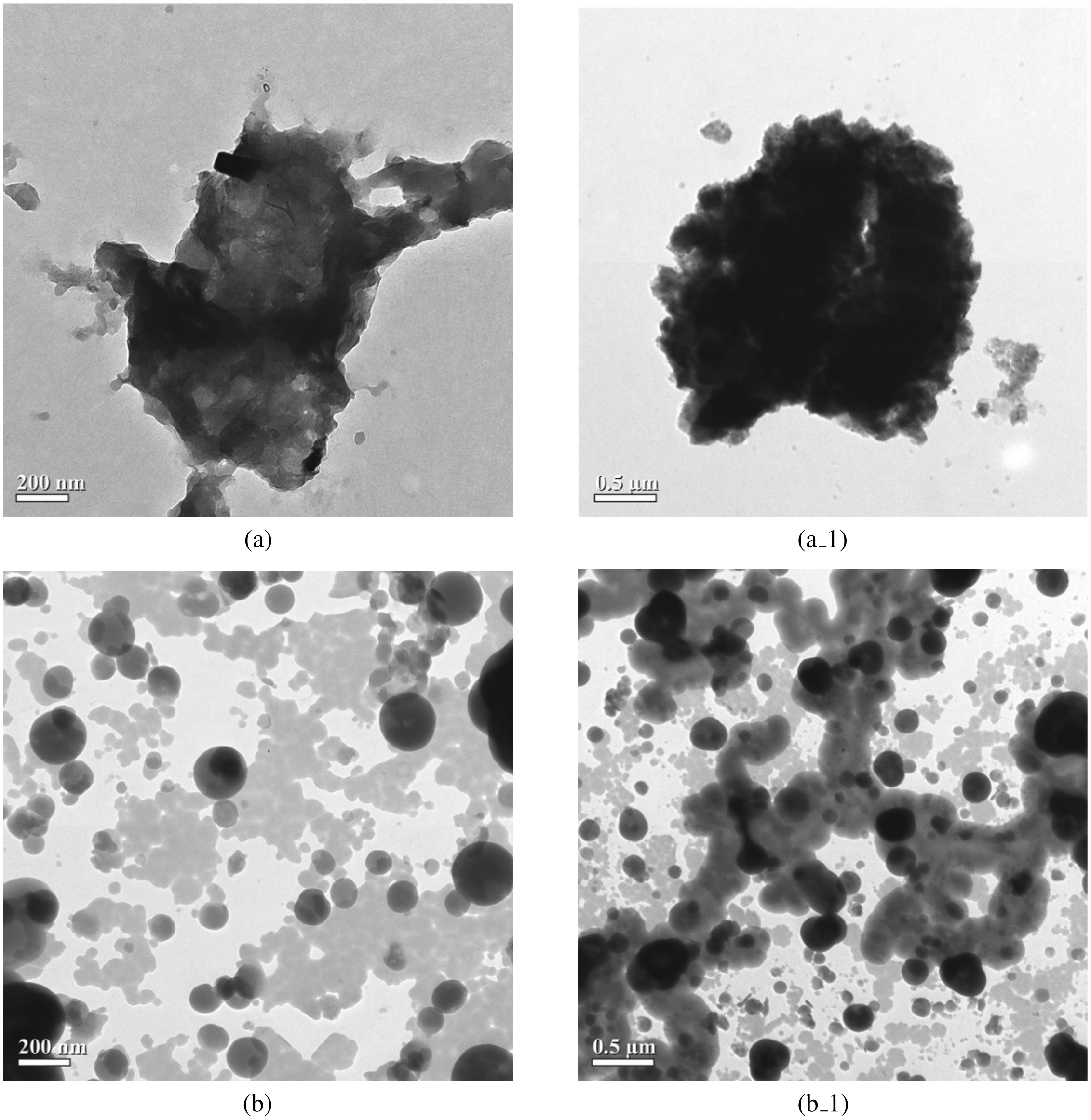


Fig. 4. TEM micrographs of raw duck eggshells and eggshells calcined at 900 °C for 1 h: a) raw duck eggshells at the magnification of 25000 X; and a_1) raw duck eggshells at the magnification of 12000 X; b) eggshells calcined at 900 °C for 1 h at the magnification of 25000 X; and b_1) eggshells calcined at 900 °C for 1 h, at the magnification of 12000 X.

spond to the calcium oxide (CaO) or the lime of the face-centered cubic form (Fm-3m; JCPDS No. 01-077-2010), with a small amount of calcium hydroxide ($Ca(OH)_2$ or portlandite) of the hexagonal form (P-3m1; JCPDS No. 01-087-0673) as a result of to the moisture absorption. The X-ray diffraction peaks of the samples calcined from 300 °C to 500 °C, for 1, 3, and 5 h, correspond to the calcium carbonate or calcite ($CaCO_3$). The XRD diffraction peaks of the raw duck eggshells calcined at 700 °C, for 1, 3, and 5 h, correspond to the lime or the calcium oxide (CaO) and the calcium carbonate or calcite ($CaCO_3$) in the meta-stable phase. A phase transformation from calcium carbonate to calcium oxide starts at 700 °C after 3 h processing. A longer calcination time at 700 °C, from 3 to 5 h, leads to a more complete phase transformation. The complete phase transformation yielding calcium oxide (CaO)

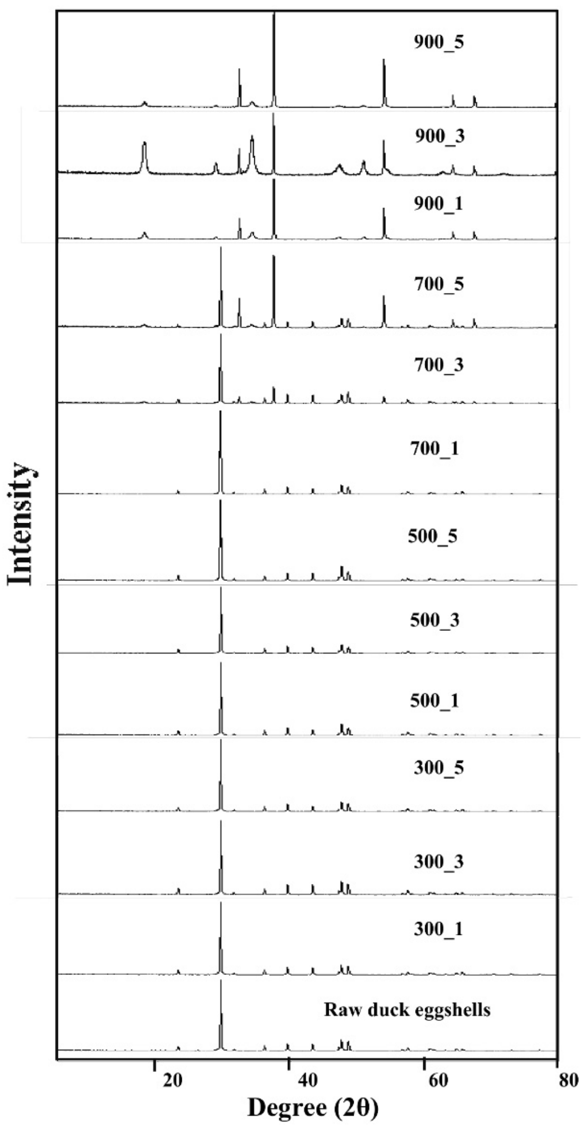


Fig. 5. XRD peak patterns and the phase transformation of raw duck eggshells and the eggshells calcined from 300 °C to 900 °C for 1, 3, and 5 h.

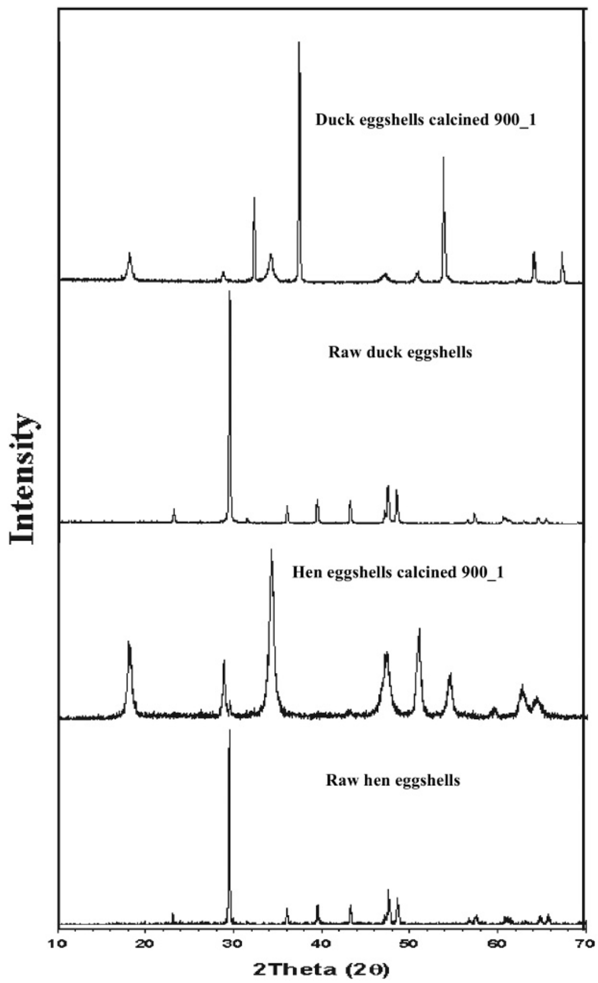
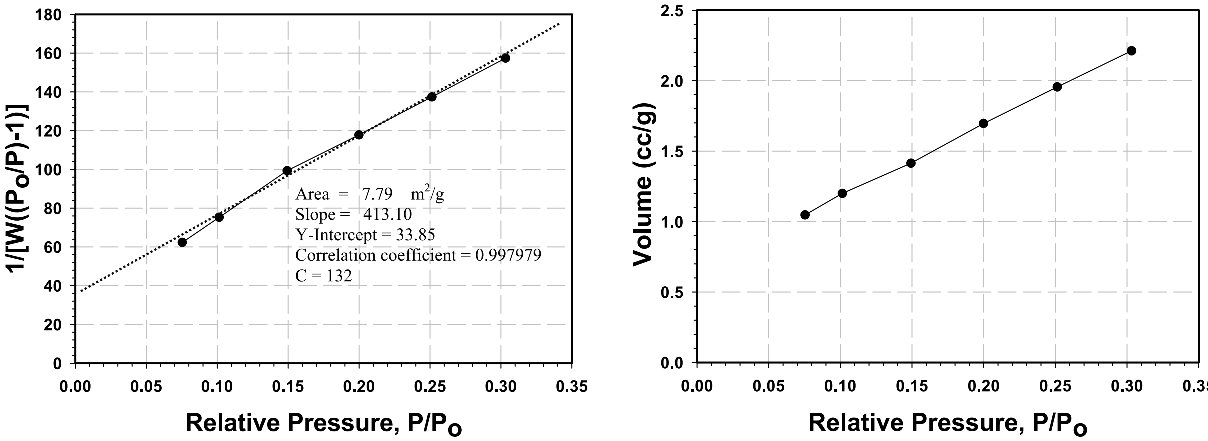


Fig. 6. Comparison XRD peak patterns between hen and duck eggshells before and after the calcination at 900 °C for 1 h.

occurs at 900 °C after 1 h calcination. Furthermore, the longer calcination time at 900 °C for 3 or 5 h yields a more calcium hydroxide ($Ca(OH)_2$) due to a reactive moisture adsorption. The phase transformation thus depends on a calcination temperature and time, which is consistent with the result obtained by the simultaneous thermal analysis (STA), as expressed by the endothermic peaks at 680 °C and 930.4 °C.

Fig. 6 shows the comparison of XRD spectra patterns between the hen and duck eggshells before and after calcinations at the same temperature of 900 °C for 1 h. The XRD results of the duck eggshells before and after calcinations are similar to the XRD results of the hen eggshells. The main peak of both raw eggshells (duck and hen) before calcination appears at $2\theta = 29.399$ indicating calcium carbonate ($CaCO_3$), calcite or a rhombohedral phase formation. Other peaks appear at 2θ = 35.981, 39.417, 43.171, 47.492, 48.505, 57.417, and 60.683.

The main XRD spectra patterns of the duck and hen eggshells, calcined at 900 °C for 1 h, are nearly the same. The main peak appears at $2\theta = 37.345$, d-value = 2.40600, and $(h\,k\,l) = (2\,0\,0)$. Other peaks appear at 2θ = 32.194, 53.843, 64.136, 67.357, 79.631, and 88.496. The peaks indicate calcium oxide or



(a) (b)

Fig. 7. a) Specific surface area of raw duck eggshells calcined at 900 °C for 1 h versus the relative pressure obtained by the BET method. b) Volume of nitrogen gas adsorption and desorption on raw duck eggshells calcined at 900 °C for 1 h at STP vs. the relative pressure obtained by the BET method.

lime (CaO), which is consistent with JCPDS No. 01-077-2010, with a small amount of calcium hydroxide ($Ca(OH)_2$ or portlandite) of the hexagonal form (P-3m1; JCPDS No. 01-087-0673), as a result of the moisture absorption. The XRD patterns of calcined hen eggshells 900_1 show only the calcium oxide phase formation, whereas the XRD peak patterns of calcined duck eggshells 900_1 show more small peaks belonging to calcium hydroxide ($Ca(OH_2)$) which are different from the XRD peak positions of the hen eggshells at $2\theta = 28.698$ (1 0 0) and 34.111 (1 0 1). However, both the eggshells undergo the identical phase transformation at the same calcination temperature and time which are 900 °C and 1 h, respectively. The duck eggshells are more prone to moisture adsorption than the hen eggshells because of different micro-organisms, weight and thickness of the eggshell, bridge bonding within the shell and particle size distribution effect on the duck shell toughness, amount of circular openings or pore effect on the reactive moisture adsorption within the shell microstructure, and true density.

3.3. Specific surface area of raw and calcined duck eggshells

The N_2 adsorption-desorption isotherms of CaO from the eggshells at room temperature (25 °C) are shown in Figs. 7a and 7b. The calcium oxide has the specific surface area, the total pore volume, and the average pore diameter of 7.79 m^2/g, 0.05, and 17.69 nm, respectively. The pore diameter of the calcium oxide is in the range of mesopore or in the range of 20 Å-500 Å (2–50 nm).

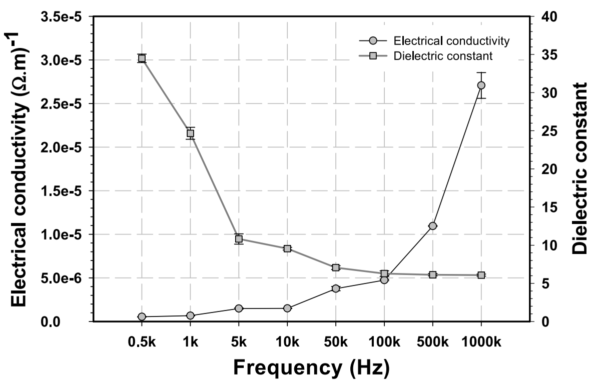


Fig. 8. Plots of the electrical conductivity and the dielectric constant versus frequencies from 500 Hz to 1 MHz, measured at room temperature.

3.4. Electrical properties of raw and calcined duck eggshells

The electrical properties (the dielectric constant and the electrical conductivity) of the duck eggshells calcined at 900 °C for 1 h measured at a room temperature and at frequencies from 500 Hz to 1 MHz, are shown in Fig. 8. The electrical conductivity and the dielectric constant, measured at the frequency of 500 Hz, are 1.0×10^{-6} $(\Omega{\cdot}m)^{-1}$ and 35, respectively. Thus, the prepared calcium oxide is a potential material to be used as a dielectric material.

4. Conclusions

Raw duck eggshells or calcite ($CaCO_3$) of the rhombohedral form, transform completely into a face-centered cubic lime (CaO) after calcination at 900 °C for 1 h. The phase transformation from calcium carbonate ($CaCO_3$) to calcium oxide (CaO) depends on the calcination temperature and time. The higher calcination temperature and longer calcination time, the more complete phase transformation is obtained. The calcium oxide made from duck eggshells has a good dispersion, good electrical properties and high porosity, as evidenced by TEM, the impedance analyzer, and BET, respectively. The particle size distribution and the cumulative mass percentage diameters (d_{10}, d_{50}, d_{90}, and mean diameter) of calcium oxide particles, obtained from the egg shells calcined at 900 °C for 1 h, are 3.14, 12.12, 49.30, and 29.16 µm, respectively. The percentage of ceramic yield is 53.53 % with the purification of 99.06 % w/w. The calcium oxide has the specific surface area, the pore volume, and the average pore diameter of 7.79 m^2/g, 0.05, and 17.69 nm, respectively. The electrical conductivity and the dielectric constant, measured at the frequency of 500 Hz, are 1.0×10^{-6} $(\Omega{\cdot}m)^{-1}$ and 35, respectively. Furthermore, the eggshells of both hen and duck are composed of three layers: a cuticle thin outer layer, a palisade thick middle layer, and an inner thin mammillary layer. The suitable calcination temperature and the time of the phase transformation from $CaCO_3$ into CaO are the same for both the eggshells, namely – 900 °C and 1 h. However, the duck eggshells have a thicker shell layer, higher shell weight, more interactive bonding within the shells, and are of higher true density than the hen eggshells. Therefore, the physical and chemical properties of the calcium oxide derived from raw duck eggshells differ slightly from the properties derived from the raw hen eggshells. The calcium oxide derived from the raw duck eggshells is supposed to be a potential material used as a dielectric material, an absorbent, a filler in a variety of industries such as paper, printing ink, rubber, pharmaceutical and cosmetic, and as a starting material for sensors, insulators, and catalysts [14, 15].

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References

[1] THAPON J.L., BOURGEOIS C.M., *Lavousier Technique at Documentation*, L'Oeuf et les ovoproducts, 1994.
[2] RIVERA E.M. *et al.*, *Mater. Lett.*, 41 (1991), 128.
[3] ADEYEYE E.I., *Bull. Chem. Soc. Ethiop.*, 23 (2009), 159.
[4] FREIRE M.N., HOLAND J.N.F., *Cerâmica*, 52 (2006), 240.4.
[5] WAN X. *et al.*, *Mater. Sci. Eng.*, 25 (2005), 455.
[6] MEISZTERICS A., SINKO K., *Colloids Surf. A: Physicochem. Eng.*, 319 (2008), 143.
[7] CHRYSAFI R. *et al.*, *J. Eur. Ceram. Soc.*, 27 (2007), 1707.
[8] SOUTHAM D.C. *et al.*, *Curr. Appl Phys.*, 4 (2004), 355.
[9] RICHARDSON I.G., *Cem. Concr. Res.*, 38 (2008), 137.
[10] PARK H.J. *et al.*, *J. Environ. Sci.*, 19 (2007), 1436.
[11] JONES D., ADAS Consulting Ltd. UK Utilization of egg shell waste from UK egg processing and hatchery establishments, Pigs, Eggs and Poultry Division, DEFRA, Whitehall Place East, London, 2002 (`www.defra.gov.uk`).
[12] MURAKAMI F.S., RODRIGUES P.O., *Cienc. Technol. Aliment.*, 27 (2007), 658.
[13] LU G.Q., ZHAO X.S., *Nanoporous Materials Science and Engineering*, Imperial College Press, 4th editions, 2006.
[14] CHEN X.D. *et al.*, *Trans. I. ChemeE. part C*, 77 (1999), 40.
[15] SU B.L. *et al.*, Microporous Mesoporous Mater., 105 (2007), 49.

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