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Short communication

Environmental benign synthesis, characterization and mechanism studies of green calcium hydroxide nano-plates derived from waste oyster shells

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ABSTRACT

Continuous dumping of oyster shells in open fields has been a global issue, causing serious problems in the water and human health. The conversion of those wastes into value-added products is highly desirable. Here, Green Calcium Hydroxide Nano-plates (GCHNPs) were first synthesized from waste oyster shells by a chemical precipitation method in an aqueous medium at 90 °C without using any additives. The crystal structure with a hexagonal portlandite ($Ca(OH)_2$) was observed by both X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FT-IR). The crystal size of around 350–450 nm and specific surface area with 4.96 m^2g^{-1} were confirmed by field emission scanning electron microscopy (FE-SEM) and Brunauer-Emmett-Teller (BET), respectively. In addition, a schematically organized new qualitative model for a mechanism was proposed to explain the genesis and evolution of GCHNPs from raw oyster shells.

1. Introduction

Solid waste management is one of the major barriers for a sustainable world. Varieties of solid waste recycling using the plastic, glass, waste tires, e-waste, paper waste etc. are in limelight nowadays (Godlewska, 2017; Kumar et al., 2017; Mohajerani et al., 2017; Pivnenko et al., 2015; Ragaert et al., 2017). Due to ever increasing human population some food wastes are becoming threats to our environment. An oyster shell, one such waste available in abundance, accounting for almost 1/3 of total bivalve's production, has been a global issue (Lu et al., 2018). According to FAO (2016), Europe produced 632,000 tonnes of bivalves in 2014. In South East Asia on an annual average basis, Japan, South Korea and Thailand produced 377,000, 347,000, and 210,000 tonnes of bivalves respectively. China being the leading producer of bivalves disposed annually about 10 million tonnes of waste sea shells in landfills (Yao et al., 2014). According to Li et al. (2015), problems arise when the shells are considered as wastes which account for about 60–70% of their original weight after utilization of these food. Severe environmental issues arise when those wastes are dumped in open dumps and public waters. As an example, the microbial decomposition of flesh remnants causes health issues such as diarrhea, malaria and dengue. In addition, hazardous gases including hydrogen sulphide, ammonia and amines are generated (Felipe-Sese et al., 2011; Varhen et al., 2017; Yoon et al., 2003). Aforementioned wastes are responsible for huge deposits of which only minor portion is being utilized with purposes such as calcium supplements, fertilizers and handicrafts (Lu et al., 2018; Yang et al., 2005). Even though those wastes can be used as fertilizers and handicrafts, recycling or reuse for waste oyster shells has a few drawbacks. Pretreatment processes should be required to remove the organic impurities. In addition, a calcination process is mandatory to use the raw oyster shells where the process requires high energy consumption. Therefore, a conversion of those wastes into a product with high economic value is highly desirable.

Nowadays nanotechnology dominates in the field of science and technology. Numerous consequences have been reported by Pandey and Prajapati (2018) with conventional nanoparticles like Fe, Cu, Zn, Pt etc. Since those nanoparticles are not eco-friendly, the dose above the threshold limit can damage the cellular physiology by the generation of reactive nitrogen and oxygen species. In addition, it has been extensively reported that the deposition of nanoparticles in organs like brain and heart causes cytotoxic effects on macrophages, which ultimately affect the human immune system (Sahu et al., 2014; Wang et al., 2010). Recently, the trend in nanotechnology is shifting towards eco-friendly nano-materials (Hajipour et al., 2012; Mane et al., 2017; Roy et al., 2017). Among a variety of eco-friendly nano-materials, calcium hydroxide ($Ca(OH)_2$) being an eco-friendly compound, has been utilized in a variety of environmental, chemical and industrial applications

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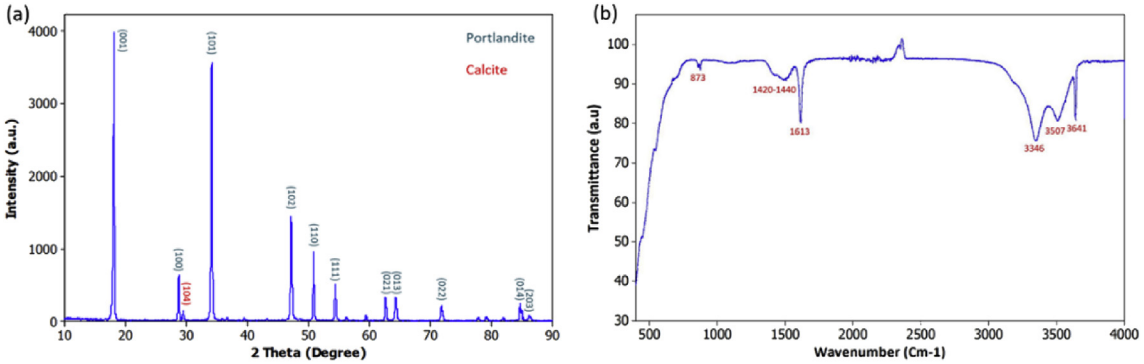

Fig. 1. (a) Powder X-ray diffraction patterns of synthesized GCHNPs and (b) FT-IR spectrum of synthesized GCHNPs.

such as treatment of sculptures, catalyst and adsorbents (Poggi et al., 2016; Samanta et al., 2017; Boynton, 1980; Ashurst and Dimes, 1990). Moreover, those Nano calcium hydroxide can also be used for heritage conservation, dentistry and water treatment (Carretti et al., 2013; Hajipour et al., 2012; Louwakul et al., 2017; Samanta et al., 2017).

Until now, methods used for synthesizing the nano-sized calcium hydroxide have been carried out either at high temperature and high pressure or in the presence of an alcoholic and an organic solvent (Daniele and Taglieri, 2012; Poggi et al., 2016; Salvadori and Dei, 2001). Rodriguez-Navarro et al. (2013) mentioned that it is very rare to find calcium hydroxide nanoparticles as the only final product. Apart from those challenges, the time-consuming purification usually leads to high cost. The utilization of wastes along with the development of economically feasible and scalable methods is the ultimate objective.

Waste oyster shells can be a potential candidate for the synthesis of green calcium hydroxide nanoparticles (GCHNPs) due to their high concentration of calcium elements. To the best of our knowledge, no past investigation on the preparation of GCHNPs from oyster shell has been discussed. It would be highly desirable to converge the existing gap regarding an understanding of a mechanism for the formation of GCHNPs from oyster shells. In this work, our group first synthesized GCHNPs by using the waste oyster shells without using any toxic chemical elements in an aqueous medium. Characteristics of GCHNPs were investigated using X-ray diffraction (XRD), fourier transform infrared spectroscopy (FT-IR), field emission scanning electron microscope (FE-SEM) and Brunauer-Emmett-Teller (BET). In addition, for the first time, the mechanism for a formation of nanoparticles from oyster shells was discussed thoroughly.

2. Experimental

2.1. Materials

Waste oyster shell was collected directly from a local supplier in South Korea. The chemical composition of oyster shells are primarily composed of calcium carbonate with the calcite phase and tiny fractions of other oxides including K_2O, SiO_2, MgO and AlO_3. Hydrochloric acid and sodium hydroxide with 35%–37% concentration and 97% purity were provided by Junsei Chemicals Ltd, South Korea.

2.2. Synthesis

Oyster shells were carefully washed and dried at 105 °C for 5 h in an oven. In order to eliminate carbon dioxide and other volatile impurities, calcination process with 100 g of crushed shells was performed at 900 °C for 2 h 23 g of resulting powders were allowed to react with 250 ml of 1 M hydrochloric acid (HCl) with rapid mixing. It was followed by a filtration where the filtrate was heated at 90 °C as at this temperature so that the solubility of carbon dioxide (CO_2) in water from the atmosphere is minimum. The temperature around 90 °C greatly favors the synthesis of a perfect shape of nano-calcium hydroxide (Madrid and Lanzon, 2017). Finally, 250 ml of 1 M sodium hydroxide (NaOH) solution was added to the filtrate with rapid mixing. In 2–3 min mixtures became milky in color, confirming the synthesis of green calcium hydroxide nano-plates (GCHNPs). Those were then filtered off, followed by washing with deionized water until all impurities and residues were washed out. The final product was then dried in an oven at 105 °C for 5 h. The percent yield of the final product was found to be 66.67%.

2.3. Characterization

The structural analysis and identification for phases of synthesized green calcium hydroxide nano-plates (GCHNPs) were investigated by powder X-ray diffraction (XRD) utilizing Cu Kα radiation (λ = 1.5406 Å) in a range of 2θ from 10° to 90° (BD2745N, Rigaku, Tokyo, Japan). For microscopic images, samples are first spread on Aluminium stubs and coated by Platinum in a sputter coater. Micro images were then recorded through field emission scanning electron microscope (FE-SEM), (D1627, Sirion, Eindhoven, Netherlands) for analyzing the crystal structures and size at an accelerating voltage of 10 kV. Characteristic functional groups were investigated in the range of 400–4000 cm^{-1} by fourier transform infrared spectroscopy (FT-IR) (6700 FTIR, Thermo Scientific Nicolet, Massachusetts, United States). The specific surface area was evaluated through Brunauer-Emmett-Teller (BET) (Quadrasorb SI, Quantachrome Instruments, Florida, United States).

3. Results and discussion

In order to identify the crystal structure of both oyster shell and green calcium hydroxide nano-plates (GCHNP), powder X-ray diffractions (XRD) were collected. For oyster shells, as shown in Fig. S1, XRD patterns matched with those of rhombohedral calcite phase ($CaCO_3$) with space group *R*-3*c* (Space Group No. 167, PDF Card No. 00-081-2027) as a major phase with minor impurities. In the case of synthesized GCHNPs shown in Fig. 1(a), the XRD patterns resembled with hexagonal portlandite ($Ca(OH)_2$) phase with space group *P*-3*m*1 (Space Group No. 164, PDF Card No. 00-087-0673) as a major phase. The minor phase consisted mostly of rhombohedral calcite phase with space group *R*-3*c* (Space Group No. 167, PDF Card No. 00-081-2027). Moreover, for a better understanding of properties regarding nanoscale material and microstructure parameters, crystal size and lattice strain were calculated using Scherrer's Equation: $d = k\lambda/\beta\cos\theta$, where k is Scherrer's constant, λ is the wavelength of X-Ray used, β is structural broadening and θ is Bragg's angle. The crystallite size for the plane (101) of GCHNPs was determined as 43.66 nm. In addition, the lattice strain of crystal at this plane can be determined by $\varepsilon = \beta/4\tan\theta$, where, ε is lattice strain. The lattice strain for the plane (101) was found to be 2.7×10^{-3} (Bindu and Thomas, 2014; Venkateswarlu et al., 2014).