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The Stabilisation of Calcium Carbonate Vaterite Phase Via Integration of Mussel-Inspired Polydopamine

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ABSTRACT

The thermodynamically unstable vaterite calcium carbonate has vast potential for biomedical and industrial applications as it possesses high specific surface area, high dispersion, high solubility and small specific gravity. Herein, calcite and vaterite calcium carbonate polymorphs are synthesised using co-precipitation method in the presence of dopamine as a stabilising agent. The calcium carbonate was prepared by mixing Na_2CO_3 and $CaCl_2$ at room temperature of 25 °C, in the presence of dopamine as a stabiliser during (CaPA) and after (CaPB) mineralisation process. The resulted samples were characterized using Fourier transform-infrared attenuated total reflectance (FTIR-ATR), X-ray Photoelectron Spectroscopy (XPS) and Field Emission Scanning Electron Microscope (FESEM). The results revealed that dopamine was incorporated into calcium carbonate during the mineralisation process and stabilised the vaterite phase of carbonate. CaPA sample displays a massive formation of rough surface spherical vaterite phase with a diameter of 1.807 ±0.256 µm.

INTRODUCTION

Calcium carbonate can be precipitated in three anhydrous polymorphic forms which are calcite, aragonite and vaterite and the first two are more thermodynamically stable structures which commonly occur in nature (Cartwright, Checa, Gale, Gebauer, & Sainz-Díaz, 2012). Vaterite is the least thermodynamically stable polymorph and very rare in nature as it would readily transform into one of the more stable phases, commonly calcite or aragonite (Cartwright et al., 2012). However, the porous vaterite calcium carbonate particles have vast potential for biomedical and industrial applications as they possess ideal biocompatibility and biodegradability (Trushina, Bukreeva, Kovalchuk, & Antipina, 2015).

Based on this occurrence, several attempts have been made to stabilize the vaterite phase using dopamine, a mimic of 3,4-dihydroxy-L-phenylalanine (DOPA) in the adhesive protein Mefp-5 secreted from mussels (Kim & Park, 2010; Wang & Xu, 2013). During the oxidation process in an aqueous solution, dopamine spontaneously forms polydopamine that can strongly adhere to a variety of organic and inorganic materials (Lee, Dellatore, Miller, & Messersmith, 2007). The abundant functional groups especially catechol and amine groups help to stabilize the calcium carbonate phase by forming strong adhesive interaction between polydopamine and amorphous calcium carbonate during the whole biomineralisation process (Wang & Xu, 2013). Herein, we prepared calcium carbonate-polydopamine using co-precipitation method via two different routes in order to determine the effects on chemical compositions and morphological structures of the resulted compounds. The difference between the two routes is the dopamine addition order.

MATERIALS AND METHOD

Two different routes have been proposed to synthesised dopamine stabilised calcium carbonate (Figure 1).

Route A: Sodium carbonate (0.01M), calcium chloride (0.01M) and dopamine hydrochloride (2 mg/mL) were mixed in 500 mL distilled water. The solution was stirred (600 rpm) at room temperature (25 ºC) for 24 h. The precipitates were filtered and rinsed with distilled water. The obtained powders were than dried at 60 ºC for 24 h and labelled as CaPA.

Route B: Sodium carbonate (0.01M) and calcium chloride (0.01M) were stirred in 500 mL distilled water at 600 rpm at 25 ºC for 24 h. The precipitates were filtered and rinsed with distilled water. After rinsing, the precipitates were mixed with dopamine hydrochloride solution (2 mg/mL in 10 mM Tris buffer, pH 8.5) and stirred at 600 rpm for 24 h. The precipitates obtained were dried at 60 ºC for 24 h and labelled as CaPB.

The resulted samples were characterized using Fourier transform-infrared attenuated total reflectance (FTIR-ATR), X-ray photoelectron spectroscopy (XPS) and Field emission scanning electron microscope (FESEM).

RESULTS AND DISCUSSION

FTIR-ATR analysis

The $CaCO_3$, CaPA and CaPB samples were characterised using FTIR-ATR to evaluate the infrared adsorption bands corresponding to their chemical composition (Figure 1a). The hydroxyl groups (-OH) adsorption band at 3000 and 3635 cm^{-1} were observed in $CaCO_3$ sample due to the water adsorption in pure $CaCO_3$ (Barhoum et al., 2014; Li, Chengyong, Zhong-ji Qian, Chunxia Zhou, Weiming Su, Pengzhi Hong, Shucheng Liu, Lei He, Zhimeng Chen, 2014). However, these bands disappeared after the polydopamine modification processes took place in both Route A and B. The adsorption of water became difficult as the surface was covered by polydopamine layer. The adsorption bands which corresponding to the carbonate group vibrations were displayed in the region of 1430 to 711 cm^{-1}. The band which can be assigned to a doubly degenerate asymmetric stretching vibration ($v3$) in carbonate group was observed at 1393 cm^{-1} in both $CaCO_3$ and CaPB samples. However, in CaPA sample this band (asymmetric stretching, $v3$) is split into two at 1430

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and 1404 cm^{-1} which was common to vaterite polymorph. Moreover, vaterite and calcite polymorphs can be easily distinguish by observing the in-plane bending, *v*4 of carbonate group in which the adsorption band at 711 cm^{-1} and 710 cm^{-1} indicate the presence of calcite polymorph in $CaCO_3$ and CaPB respectively whereas in vaterite CaPA sample the same band is shifted to 750 cm^{-1} (Kim & Park, 2010). The adsorption band at 871 cm^{-1} is corresponding to the out of-plane bending, *v*2 of carbonate group which is common to both calcite and vaterite polymorphs and therefore can be observed in all samples (Erick S. Vasquez, Janice L. Cunningham, Justin B. McMahan & Walters, 2015; Kuriyavar et al., 2000). The emergence of C-N stretching (aliphatic amine) at 1087 cm^{-1} only in CaPA sample proved that polymerisation of dopamine took place in the early phase of $CaCO_3$ mineralisation (Kim & Park, 2010). It is different when compared to CaPB sample where there was no peak of C-N stretching can be observed. However, the presence of N1s peak can be observed in CaPB using XPS due to characterisation occurred on the surface and not within the sample. This result indicates dopamine was incorporated into calcium carbonate using Route A method and the polymerisation of dopamine happened during the mineralisation of $CaCO_3$.

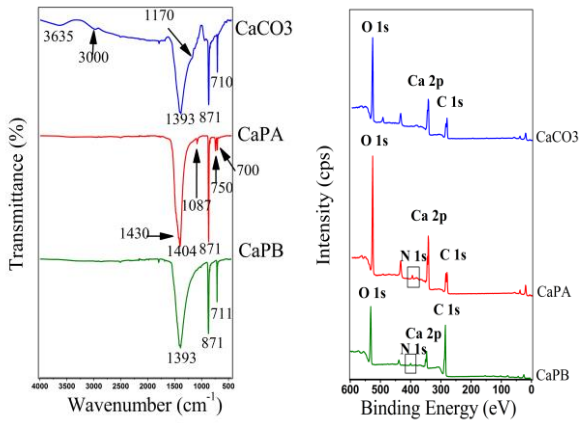

Fig. 1 (a) FTIR-ATR spectra of $CaCO_3$, CaPA and CaPB and (b) XPS survey spectra of $CaCO_3$, CaPA and CaPB

XPS analysis

Survey spectra

Surface coverage and atomic percentage was studied using XPS for $CaCO_3$, CaPA and CaPB samples. Three main peaks that attributed to C 1s, O 1s and Ca 2p with different percentage were observed at 285.0 eV, 531.0 eV and 347.0 eV respectively in all samples (Figure 1b). The emergence of N 1s peak at 400.0 eV in CaPA and CaPB confirms the presence of polydopamine on the surface of particles. All samples have relatively high carbon content due to the high surface energy of the calcium carbonate surfaces which is responsible for spontaneous adsorption of hydrocarbon impurity, also known as adventitious carbon when materials are exposed to air (Ni & Ratner, 2008). However, the highest C 1s percentage (68.33 ±1.14%) observed in CaPB is not only contributed by the presence of adventitious carbon but it also correlates with the inclusion of carbon content from polydopamine molecules that covered the surface of $CaCO_3$. Moreover, after polymerisation of dopamine, the percentage of Ca 2p peak in CaPB was drastically reduced to 4.43 ±0.35% and the peak due to oxygen weakened suggesting that calcium carbonate has been mostly covered by polydopamine. In addition, the atomic percentage in CaPB is close to the theoretical value of dopamine atomic percentage (C 62.73%, H 7.24%, N 9.14% and O 20.89%). In contrast, CaPA sample showed the lowest carbon content (44.12 ±3.03%) after mixing with dopamine suggesting that polydopamine flexible chain not only concentrated on the surface of calcium carbonate but also incorporated into calcium carbonate primary particles which stabilise calcium carbonate and further possible solid-phase transformation (Erick S. Vasquez, Janice L. Cunningham, Justin B. McMahan & Walters, 2015; Wang & Xu, 2013). The content of O 1s in $CaCO_3$ and CaPA is higher compared to CaPB due to the presence of oxygen atom in carbonate ion (Baltrusaitis et al., 2007). Compared to the FTIR-ATR results, $CaCO_3$ sample showed the presence of hydroxyl (-OH) group due to the adsorption of water when the sample is exposed to moisture and this band is absence in both CaPA and CaPB samples. Therefore, the oxygen content in $CaCO_3$ not only contributed by the carbonate group but partly due to the hydroxyl group in water. However, in CaPA sample, the oxygen content could be due to the carbonate group and polydopamine chain incorporated into calcium carbonate.

High resolution spectra

In order to obtain specific chemical compositions of each samples, further investigation of C 1s, O 1s, Ca 2p and N 1s peak deconvolutions were performed. Figure 2 shows the high resolution spectra of C 1s, O1s and Ca 2p peaks in each sample. The C 1s spectra of each sample were deconvoluted to C-C, C-O, C=O and CO_3^{2-} peaks and their binding energy were listed in Table 1. As shown in Figure 4, CaPB sample displayed the highest atomic percentage of peak C-C which is 48.98% suggesting the calcite calcium carbonate particles were covered by polydopamine. Moreover, the carbonate peaks which were observed in $CaCO_3$ and CaPA samples at 289.98 eV and 289.64 eV respectively disappeared in CaPB sample. Instead, C=O peak was emerged in CaPB due to the polymerisation of dopamine under alkaline condition. During the polymerisation process, the catechol (-OH) groups are first oxidised into the quinone (C=O) groups which are further involved in intra-molecular cyclization and various cross-linking reactions (Lee, Rho, & Messersmith, 2009; Saidin, Chevallier, Abdul Kadir, Hermawan, & Mantovani, 2013; Zain, Hussain, & Abdul Kadir, 2015). The conversion of catechol into quinone group indicates the polymerisation of dopamine into polydopamine took place which subsequently serves as a platform for secondary surface-mediated reactions (Treccani, Yvonne Klein, Meder, Pardun, & Rezwan, 2013; Zain et al., 2015). Since the Ca^{2+} ions previously interacted with CO_3^{2-} ions to form calcite calcium carbonate, there is no free metal ion to bind the free quinone groups and therefore these functional groups are available for secondary surface-mediated reaction. In contrast, in the CaPA sample, the C=O peak that represents quinone cannot be observed due to the complex interaction of Ca^{2+} ions with polydopamine during the stabilisation process at the whole stage of calcium carbonate mineralisation (Wang & Xu, 2013). During this process, quinone groups together with other functional groups (carboxy, amino, imine an phenol groups) in polydopamine are responsible for Ca^{2+} ion chelation (D'Ischia, Napolitano, Pezzella, Meredith, & Sarna, 2009). The strong adhesive interaction between polydopamine and amorphous calcium carbonate takes place during the whole mineralisation process which prevents amorphous calcium carbonate dissolution and retard subsequent Ostwald ripening (Wang & Xu, 2013). According to Ostwald steps rule, from amorphous calcium carbonate, the thermodynamically unstable vaterite phase is formed first which subsequently transform into the stable calcite and aragonite phases. However, by adding dopamine, amorphous calcium carbonates does not crystallize to form the thermodynamically stable calcite, instead a less stable vaterite phase is formed. The polydopamine networks not only cover the amorphous calcium carbonate particles outside but also incorporated within the particles to stabilise the amorphous calcium carbonate phase (Wang & Xu, 2013). According to Table 1, the binding energy of C-O peak in O 1s peak is shifted to the higher binding energy (532.52 eV to 533.31 and 533.39 eV) after mixing with polydopamine in sample CaPA and CaPB due to the oxidation process during polymerisation of dopamine into polydopamine. The withdrawal of valence electron charge during the oxidation process increases the binding energy. The N 1s spectra could be resolve into two typical peaks at 399.0 eV (C-N) and 400.0

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eV (aromatic N). The C-N peak presence in CaPA sample could be attributed to the primary amine (R-NH_2) in dopamine and secondary amine (R-NH-R) connected with polydopamine and intermediate species (Kaminska et al., 2012). The aromatic N component was developed after the conversion of dopamine into tautomeric species of the intermediate species 5, 6-dihydroxyindole and 5, 6-indolquinone. This species dominated the N 1s region in both CaPA and CaPB samples suggesting the complete polymerisation process of dopamine.

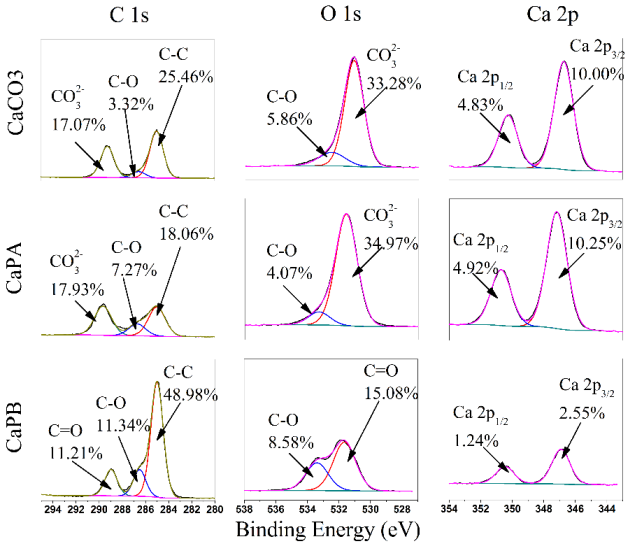

Fig. 2 High Resolution XPS spectra of $CaCO_3$, CaPA and CaPB samples

Morphological analysis

The morphological structure of $CaCO_3$, CaPA and CaPB were observed using FESEM. Figure 2a shows the mineralisation of calcium carbonate without adding dopamine in the process resulted in the development of large rhombohedral calcite crystals with size ranged of 1.0 -3.0 µm. The formation thermodynamically stable calcite polymorph occurs spontaneously according to Ostwald step rules. Compared to the rhombohedral calcite crystals with a smooth surface grown in the absence of dopamine, a massive formation of rough surface spherical vaterite phase with a diameter of 1.807 ±0.256 µm was observed in the presence of dopamine at the early stage of mineralisation in Route A (Figure 2b and 2c).

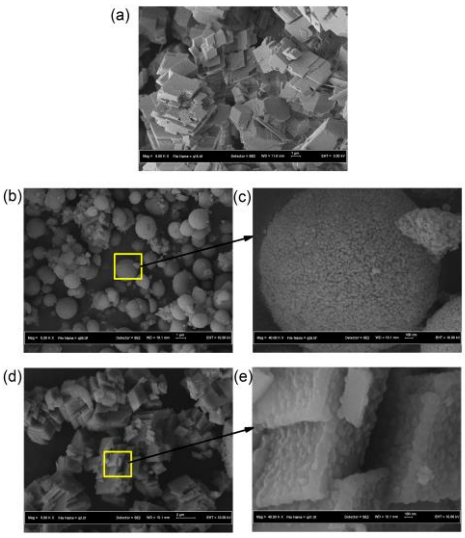

Fig. 2 FESEM images of (a) $CaCO_3$, (b-c) CaPA and (d-e) CaPB

CONCLUSION

Dopamine has been used for the synthesis of vaterite calcium carbonate. During the mineralisation process, the incorporation of dopamine plays an important role in stabilising the varterite phase by introducing the functional groups that can interact with the calcium ions. The presence of dopamine was confirmed by chemical analysis of FTIR-ATR and XPS. Based on the results, Route A produced calcium carbonate in vaterite form with average diameter of 1.807 ±0.256 µm due to the introduction of polydopamine during the mineralisation process and Route B produced large rhombohedral calcite crystals.

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