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# Journal Name

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Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2012, Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

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# Preparation and characterization of novel spica-like hierarchical vaterite calcium carbonate and hydrophilic poly (vinylidene fluoride)/ calcium carbonate composite membrane

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Pure vaterite CaCO<sub>3</sub> microcrystals with unusual spica-like hierarchical morphology were synthesized via a simple precipitation method, in which NaHCO<sub>3</sub> and ethanol played a key role. Oriented attachment mechanism was responsible for the novel structure. Organic–inorganic composite membrane (PVDF/CaCO<sub>3</sub>) was prepared and its hydrophilicity was increased dramatically.

The ability to synthesize mesostructures from nanoparticles as primary building units is a key issue of both fundamental and technological interests. Among the possible mechanisms leading to self-organization, the oriented attachment is efficient.<sup>1</sup> This theory describes a nanoparticle mediated process where primary nanoparticles associate after nucleation by mesoscale assembly into an iso-oriented crystal or, if polymers or other additives are present, transforming into what is defined as a mesocrystal.<sup>2</sup> While in these systems, the adjacent nanoparticles are self-assembled by sharing a common crystallographic orientation and docking of these particles at a planar interface. The driving force for this spontaneous oriented attachment is that the elimination of the pairs of high energy surfaces will lead to a substantial reduction in the surface free energy from the thermodynamic viewpoint.<sup>3</sup> Many materials, such as TiO<sub>2</sub>,<sup>4</sup> ZnO,<sup>5, 6</sup> ZnS,<sup>7</sup> PbS,<sup>8</sup> PbSe,<sup>9</sup>  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>,<sup>10</sup> and Sb<sub>2</sub>S<sub>3</sub><sup>11</sup> have been synthesized via this mechanism.

By far the most abundant biogenic minerals are calcium carbonates, which is one of the most studied minerals because it is one of the major inorganic substances produced in biological organism<sup>12</sup> as well as it has widespread potential technical applications in fields like paints, plastics, rubbers, and papers.<sup>13</sup> CaCO<sub>3</sub> has three anhydrous crystalline polymorphs, in order of

increasing stability: vaterite, aragonite and calcite.14 The vaterite form can crystallize in either an orthorhombic or a hexagonal structure, and vaterite particles do not show well-defined morphologies, and usually aggregate into spherical particles.<sup>1</sup> Vaterite is rarely found in either biological or non-biological systems,<sup>16</sup> as it easily and irreversibly transforms into a more thermodynamically stable phase when in contact with water. However, vaterite is expected to be used for various purposes because it has features such as high specific surface area, high solubility, high dispersion, and small specific gravity compared with the other two crystal phases.<sup>17</sup> In recent years, several approaches have been taken to address polymorph stabilization and to mimic the elaborate morphologies of vaterite, for example, by using organic additives or templates. For instance, many organic additives such as surfactants,<sup>18</sup> biomolecules,<sup>19,20</sup> double hydrophilic block copolymers,<sup>21,22</sup> and homopolymers<sup>23,24</sup> have been implemented into in vitro syntheses. Furthermore, the constructed organic surfaces, such as self-assembled monolayers,<sup>25-27</sup> Langmuir monolayers,<sup>28, 29</sup> and polymers<sup>30, 31</sup> are widely used as templates for directional crystallization and assembly. However, the templates or organic additives used in experiments may lead to costly, complicated procedures, time consuming, stringent conditions and pollutants generated from the elimination of the templates. Therefore, it is highly desirable to seek a simple synthetic route for practical applications. But so far, a systematic evaluation of the best way to stabilize specific polymorphs or to design processes to produce specific morphologies without templates or organic additives is still lacking.<sup>2</sup>

Among the various polymers in use today for ultrafiltration, microfiltration and pervaporation membranes, poly (vinylidene

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fluoride) (PVDF) is a remarkable one because of its recognized good chemical stability, high hydrolytic resistance and desirable mechanical properties.<sup>33, 34</sup> However, the main shortcoming of this polymer is its hydrophobic nature which in turn makes it more susceptible to fouling.<sup>35</sup> Various methodologies have been developed to improve the surface hydrophilicity of PVDF membranes in the past, such as chemical surface treatment and the addition of hydrophilic additives.<sup>36, 37</sup> Nanoparticle incorporated membranes, i.e., organic-inorganic composite membranes, have become a new domain of interest in membrane technology. Various inorganic nanoparticles with good hydrophilicity such as Al<sub>2</sub>O<sub>3</sub><sup>38</sup>, SiO<sub>2</sub><sup>39</sup> and  $TiO_2^{40}$  were used to fabricate with PVDF. As one of the most abundant inorganic biominerals, CaCO<sub>3</sub> is almost in soluble in water due to the surface atoms of CaCO<sub>3</sub> tend to get hydroxylated to form Ca-OH groups in water. This great property can result in a considerable increase in hydrophilicity and antifouling properties.<sup>41,</sup> However, there are rare reports focusing on the intrinsic hydrophilicity of CaCO<sub>3</sub>.<sup>43</sup> Therefore, we aim to develop PVDF/CaCO<sub>3</sub> composite membranes by mixing the prepared CaCO<sub>3</sub> particles with PVDF (dissolved in DMF) via phase inversion method<sup>44</sup> for its hydrophilicity might improve the water permeation of hydrophobic membranes. To the best of our knowledge, so far there are few reports on CaCO<sub>3</sub> nano/microparticles in the

membrane technology.<sup>42</sup> In this paper, we present a simple route for fabricating spica-like hierarchical vaterite CaCO<sub>3</sub> microcrystals via the precipitation reaction of CaCl<sub>2</sub> with Na<sub>2</sub>CO<sub>3</sub> in the mixed solvent of water/ethanol and NaHCO<sub>3</sub> under 50 °C water bath in which the oriented attachments are involved. Measurements of XRD, FT-IR, SEM and TEM are performed to characterize the structure and morphology of the products. A possible growth mechanism, oriented attachment process, for the higher-order structured has been discussed. Furthermore, reasonable explanations are provided to demonstrate the formation of the stable polymorph of vaterite. In addition, the obtained products were used to prepare PVDF/CaCO<sub>3</sub> composite membrane by the phase inversion method. The hydrophilicity of the membrane was highly improved.

After the reagents were mixed in the specified order, allowing the  $CaCO_3$  crystals to grow by stirring for 0.5 h at 50 °C generated perfect spica-like hierarchical structures. The morphology of the



Fig. 1 (a) Low-, (b) Medium- (c) High-magnification SEM images and TEM image (inset in b) of the as-prepared spica-like hierarchical  $CaCO_3$  microcrystals.  $Na_2CO_3$  (2.0 mmol) and  $NaHCO_3$  (4.5 mmol, 0.2 M) were dissolved in a 50 mL conical bottle containing 15 mL of double-distilled water, and then absolute ethanol (7.5 mL) was added to the conical bottle (R= 1/2 pH = 10.65). After complete mixing, 1.1 M CaCl<sub>2</sub> aqueous solution (2 mL) was added dropwise to the above solution and stirred

product is presented in Fig. 1a, which indicated the high yield and uniformity. The magnified SEM image showed that the as-prepared products were spica-like hierarchical morphology, which length were of approximately 3-7 µm (Fig. 1b and inset TEM image). A close-up view of the products presented that the coarse surfaces were constituted of a lot agglomerated nano-aggregations (Fig. 1c). The phase of the synthesized CaCO<sub>3</sub> microcrystal was identified by XRD characterization. The Bragg reflections were marked with C, A and V, which correspond to the calcite polymorph, aragonite polymorph and vaterite polymorph, respectively. As shown in Fig. 1d, every diffraction peak was in agreement with the standard diffraction patterns of vaterite (JCPDS 25-0127),<sup>45</sup> the characteristic peaks at  $2\theta$ of 20.77, 24.70, 26.90, 32.60, 38.65, 43.65, 48.75, 49.70, 55.50° were corresponding to (004), (110), (112), (114), (211), (300), (304), (118) and (224) crystallographic nucleation planes of vaterite phase, respectively, indicating that the composition of the CaCO<sub>3</sub> microcrystals was pure phase of vaterite without impurities.



Fig. 2 FT-IR spectrum of the prepared spica-like hierarchical CaCO<sub>2</sub> microcrystals.

The results were further demonstrated by FT-IR analysis as given in Fig. 2. In FT-IR spectrum, the absorption bands at 745.1, 875.3, 1086.8 and 1463.5 cm<sup>-1</sup> showed the presence of the vaterite polymorph.<sup>46</sup> No absorption bands at 854, 712, 700 cm<sup>-1</sup> and 848, 714 cm<sup>-1</sup> corresponding to aragonite and calcite, respectively, were recorded.<sup>47</sup>

To further investigate the role of bicarb and ethanol in detail, we conduct the experiment by controlling experimental parameters such as the concentration of the NaHCO<sub>3</sub> and volume ratio of ethanol/double-distilled water, various structures and morphologies of CaCO<sub>3</sub> can be obtained. The phase transition from a mixture of aragonite/calcite or aragonite/calcite/vaterite to almost pure vaterite can be nicely captured by varying the concentration of NaHCO<sub>3</sub> ([NaHCO<sub>3</sub>]) and choosing a suitable volume ratio of ethanol to distilled water (R), and the results were summarized in Scheme1 and Scheme 2.

Scheme 1. Sketch of Relationship between the Mineral Polymorph and the concentration of NaHCO<sub>3</sub>

	[NaHCO <sub>3</sub> ]=0 M	pH = 12.10	Duro arac	zoni	to		
CaCl <sub>2</sub>	[NaHCO <sub>3</sub> ]=0.1 M	pH = 10.99	Vatarita		Araganita		C-1-14-
		· · · · · ·	vaterite	+	Aragonite	+	Calcite
	[NaHCO <sub>2</sub> ]=0.2 M	pH = 10.65		••			
EG/H <sub>2</sub> O	$\rightarrow$ Pure vaterite						
	[NaHCO <sub>2</sub> ]=0.4 M pH = 10.27						
	Pure vaterite						

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 $[NaHCO_3]$  = the final mole concentration of  $NaHCO_3$  in the ethanol/water/NaHCO\_3/Na\_2CO\_3 solution. pH = the pH value of the ethanol/water/NaHCO\_3/Na\_2CO\_3 solution.

#### Scheme 2. Sketch of Relationship between the Mineral Polymorph and the Solvent Composition

	R=0	Aragonite + Calcite
CaCl <sub>2</sub> Na <sub>2</sub> CO <sub>3</sub> /NaHCO <sub>3</sub> EG/H <sub>2</sub> O		Vaterite + Aragonite + Calcite
	R=1/2 >	Pure vaterite
	R=1/1 >	Pure vaterite

R = volume ratio of ethanol to double-distilled water (v/v).

The different morphologies of the CaCO<sub>3</sub> microstructures shown in Fig. 3 were created by varying only the concentration of NaHCO<sub>3</sub>. The morphology of the products obtained without adding NaHCO<sub>3</sub>  $([NaHCO_3] = 0 M, pH = 12.10)$  was sharply changed (Fig. 3a). Unusual dendrite-shaped CaCO<sub>3</sub> aggregates composed of some bundles of CaCO<sub>3</sub> fibers were obtained. The corresponding X-ray diffraction pattern (XRD) pattern (Fig. 3b) showed only sharp aragonite reflections, indicating the phase structure was wellcrystallized aragonite (JCPDS 5-0453). When the added NaHCO3 was decreased from 0.2 M (pH = 10.65) to 0.1 M (pH = 10.99), the resulting samples were mainly composed of bowknot-like crystals and a minority of irregular crystals (marked by arrows) as shown in Fig. 3c. The corresponding XRD in Fig. 3d showed it was a mixture of aragonite, vaterite and calcite (JCPDS 83-0578). When the concentration of NaHCO<sub>3</sub> was increased to 0.4 M (pH = 10.27), defective and irregular vaterite spicules which can be confirmed by Fig. 3e and XRD measurements (Fig. 3f) were observed.



Fig. 3 SEM images of the CaCO<sub>3</sub> samples produced with different concentrations of NaHCO<sub>3</sub>: (a) 0 M; (c) 0.1 M; (e) 0.4 M. (Prepared at 50 °C, [Na<sub>2</sub>CO<sub>3</sub>] = 0.1 M, R = 1/2, t = 0.5 h). Typical XRD patterns of CaCO<sub>3</sub> products: Fig. 3b, d and f are corresponding to Fig. 3a, c, and e respectively (C: calcite, V: vaterite, A: aragonite).

It is noteworthy that the volume ratio of ethanol/double-distilled water (R = v/v) in the reaction solution is an important factor in

determining the structure and morphology of the final CaCO<sub>3</sub> products. When ethanol was replaced by the same volume of distilled water (R = 0) with other conditions remaining constant, bowknot-like and rhombohedral CaCO<sub>3</sub> crystals were formed (Fig. 4a). The XRD results (Fig. 4b) exhibited that the products were binary mixtures of calcite and aragonite. With the decrease of the volume ratio of ethanol/double-distilled water from R = 1/2 to R =1/4, defective and irregular CaCO<sub>3</sub> crystals (Fig. 4c) with a scenario of three kinds of polymorphs, i.e., aragonite, calcite and vaterite (Fig. 4d) were produced. However, if the reaction solution with R = 1 was vigorously stirred during the reaction, the hybrid of immature CaCO<sub>3</sub> spica-like hierarchical and bundle-like CaCO<sub>3</sub> crystals microcrystals was obtained as shown in Fig. 4e. The XRD pattern (Fig. 4f) indicated that pure vaterite crystals were obtained through the choice of a volume ratio of R = 1. The results showed that appropriate amount NaHCO<sub>3</sub> and ethanol were both key factors and indispensable for the formation of the spica-like hierarchical vaterite CaCO<sub>3</sub> microcrystals.



Fig. 4 SEM images of the CaCO<sub>3</sub> samples produced with different volume ratios of ethanol/double-distilled water (R = v/v): (a) R = 0; (c) R = 1/4; (e) R = 1/1. (Prepared at 50 °C, [Na<sub>2</sub>CO<sub>3</sub>] = 0.1 M, [NaHCO<sub>3</sub>] = 0.2 M, t = 0.5 h). Typical XRD patterns of CaCO<sub>3</sub> products: Fig. 4b, d and f are corresponding to Fig. 4a, c, and e, respectively (C: calcite, V: vaterite, A: aragonite).

It is well known that vaterite, a least stable polymorph, will transform into thermodynamically stable forms when in contact with water and vaterite is usually found at higher levels of supersaturation.<sup>48</sup> By adding NaHCO<sub>3</sub> in the experiment, the total carbonate content of the system essentially changed (and thus the pH value). At a given set of conditions, this will lead to higher supersaturation and thus changes in precipitation kinetics. Furthermore, in the experiment, augmenting the R value in the solvent mixture decreased the solubility of CaCO<sub>3</sub>, due to the inorganic salts have a lower solubility in ethanol than in water and hence also increased the nominal supersaturation, thus increasing the

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Fig. 5 TEM results of the CaCO<sub>3</sub> crystals (Prepared at 50 °C,  $[Na_2CO_3] = 0.1 M$ ,  $[NaHCO_3] = 0.2 M$ , R = 1/2) precipitated from the solution with different reaction times. The CaCO<sub>3</sub> particles shown in the panels of (a), (b), and (c) were obtained immediately after reaction times of 1 (a), 5 (b), and 20 (c) min, respectively. Inset in (a) indicated ED patterns of CaCO<sub>3</sub>. Panel (d) was the enlarged TEM image of the domains circled in the TEM image (Fig. 5b). The patterns 1 and 2 represented the corresponding SAED patterns for domains circled in TEM image (Fig. 5d) respectively. The blue arrows in pattern 1 indicated the diffuse rings characteristic for ACC.<sup>12</sup> Panel (e) showed the high-resolution TEM image of a part marked by circle 2 in Fig. 5d. Typical defects formed by imperfect oriented attachments, such as dislocations, were seen across some interfaces (highlighted by red arrows). The lattice spacings of 0.357 and 0.329 nm correspond to the interplane spacings of (110) and (112) faces of vaterite, respectively.

tendency of supersaturation which favored faster precipitation of the kinetic phase, i.e., vaterite phase from the viewpoint of kinetics as reported by Xyla et al.<sup>49</sup> Thus, it made perfect sense that higher amounts of vaterite were obtained. The results demonstrate that phase switching can be achieved by changing the ratio of kinetic control. This is in accordance with a concept that the kinetic regimes, which contribute to the polymorph discrimination of calcium carbonate mineral, can be well manipulated in ethanol/water mixed solution.<sup>50</sup> Thus, the carbonate content of the system essentially changed by adding NaHCO<sub>3</sub> and solubility of calcium carbonate decreases by the addition of ethanol, thereby increasing the supersaturation, contributing to the synthesis of vaterite phase.

In this study, we proposed a possible formation mechanism of the spica-like hierarchical vaterite. Generally, there are two formation mechanisms for the crystal growth in solution system. Oriented attachment, 51, 52 the driving force for which is, from a thermodynamic viewpoint, the substantial reduction in surface free energy that the elimination of the pairs of high-energy surfaces brings about. Ostwald ripening,<sup>53</sup> which involves the growth of larger crystals at the expense of smaller crystals. The spica-like hierarchical vaterite obtained is very likely formed by oriented attachment mechanism, namely, a surface-energy-driven selfassembly. To unravel the formation mechanism of the spica-like hierarchical vaterite superstructures, the precipitates sampled at various intervals were investigated by a TEM method (as shown in Fig. 5). It was necessary to capture the initial transient before forming the spica-like hierarchical vaterite. Therefore, in situ TEM observation and selected-area electronic diffraction (SAED) detection were employed to investigate the evolution of the spicalike hierarchical structure. This was achieved initially by using a small amount of reaction solution immediately dropped onto a copper grid. Afterward, additional solvent was removed by filter

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papers and naturally dried (about 1 min). At the onset, the image of the original sample, shown in Fig. 5a, indicated that there was liquidlike substance and nearly spherical nanoparticles (around 20 nm in size) without obvious boundaries were formed. Obvious dispersion ring of ED reflected that CaCO<sub>3</sub> was in the amorphous phase (ACC, the inset of Fig. 5a). During the reacting from 1 to 5 min, association of these particles initiated the growth of vaterite spicules (Fig. 5b), using the nanoparticles in their neighborhood as feedstock. The formed ACC were deposited onto the surface of the vaterite spicules, driven by the minimizing surface energy,<sup>54</sup> then consequently, the resulting spica-like hierarchical crystals became bigger in size when the reaction time was extended to 20 min (Fig. 5c). When the TEM electron beam was focused on the top of the spica-like hierarchical crystals (circle 1 in Fig. 5d), the corresponding SAED pattern 1 indicated the amorphous nature of the vaterite particle, proving that the ACC attached to the crystals' surface.<sup>55</sup> The SAED pattern 2 recorded from those particles in the area circled in the TEM image (circle 2 in Fig. 5d) indicated that it was polycrystalline and the pattern represented d-spacings corresponding to vaterite. The marked spots (yellow arrows) can be indexed as vaterite oriented (001). The d-spacings of the other spots fit with the vaterite distances.<sup>12</sup> From HRTEM image (as shown in Fig. 5e), the lattice spacings of 0.357 and 0.329 nm correspond to the interplane spacings of (110) and (112) faces of vaterite respectively were observed. A closer look at Fig. 5e revealed an interesting feature, namely, the presence of dislocations in the domains (highlighted by red arrows). These dislocations can be easily observed from the high-magnification image as there existing clear lattice orientation in these boundary areas. The appearance of such dislocations is commonly considered to be a direct consequence of oriented attachment of particles, suggesting the occurrence of the initial particle-particle bonding.<sup>5</sup>

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Fortunately, the unusual CaCO<sub>3</sub> crystals produced from the above reactive systems were directly captured under SEM observation (see support information Fig. S1). As the reaction time went by, the produced spica-like crystals grow bigger in size, acquired rough surfaces and the morphology became more united and regularly due to the amorphous CaCO<sub>3</sub> deposited onto the surface of the crystals during the oriented attachment process. We proposed that the crystallization of CaCO<sub>3</sub> proceeded through several steps. At the beginning of the reaction, the nanoparticles were generated via precipitation by nucleation and growth. As the nanoparticles crystallized and the number of them increased, the total surface energy of the growing nanoparticles (amorphous or crystallographic) in solution increased accordingly. To reduce the surface energy, the nanoparticles aggregated and were used to build the spica-like hierarchical structures to further reduce the total surface energy. Finally, the spica-like hierarchical vaterite were formed (Schematic illustration, see support information Fig. S2). From the above discussion, it was concluded that the oriented attachment mechanism accounted for the formation of the spica-like hierarchical superstructures.



Fig. 6 The surface SEM images of the PVDF membranes before (a) and after (b) phase inversion process by mixing with the as-prepared spica-like  $CaCO_3$  crystals. (c) and (d) are high-magnification view of the black box in (b) and (c).

In addition, the PVDF/CaCO<sub>3</sub> composite membrane was prepared via the phase inversion method by using the obtained spica-like hierarchical vaterite CaCO<sub>3</sub> microcrystals. As shown in Fig. 6a, the neat PVDF membrane had a smooth surface without any circular pores. Through phase inversion method, the CaCO<sub>3</sub> microcrystals (Fig. 6b marked by arrows) have been successfully mixed with PVDF. From Fig. 6c, we can see that the obtained CaCO<sub>3</sub> microcrystals dispersed on/in the membranes and many irregular pores randomly distributed on the surface of the PVDF/CaCO<sub>3</sub> composite membrane. The diameter of the pores on the surface of the surface of the membranes were scattered in the range of several hundred nanometers and there were still some nano-aggregations on the surface of the membrane, which may be used as building blocks for the final microcrystals (Fig. 6d).



Fig. 7 XRD patterns for the neat PVDF (a) and PVDF/CaCO $_3$  composites (b).

To further examine the crystal structure of PVDF/CaCO<sub>3</sub> composite membranes, X-ray diffraction was performed. Two major peaks around 18.6°, 20.1° and one minor peaks around 26.7° corresponding to (020), (110) and (002) planes of PVDF, were observed from the PVDF raw material membrane (Fig. 7a), in accordance with the previous research.<sup>59</sup> In the XRD pattern of PVDF/CaCO<sub>3</sub> composite (Fig. 7b), the peaks around 18.6° as well as 20.1° belonging to PVDF can still be detected and the peaks which can be assigned to the (110), (112), (114), (211), (300), (304), (118) and (224) reflections of the planes of vaterite phase<sup>45</sup> were observed simultaneously, indicating that the composites formation occurred.



Fig. 8 FT-IR spectra (a, b) and EDX spectra (c, d) of PVDF film and PVDF/CaCO<sub>3</sub> composites: (b) is high-magnification view of the black box in (a), (c) is for neat PVDF and (d) is for the PVDF/CaCO<sub>3</sub> composites.

Fig. 8a and b present the FT-IR results for the pure PVDF and the composite samples (PVDF/CaCO<sub>3</sub>). The broad peak around 3400.2 cm<sup>-1</sup> (marked by arrow) seen in the hybrid membranes corresponded to both CaCO<sub>3</sub> and the -OH groups (Fig. 8a).<sup>42</sup> As shown in Fig. 8b, the presented absorption peaks in 1395.8 and 1178.6 cm<sup>-1</sup> wavenumber were belonging to PVDF polymer according to literature data.<sup>60</sup> The absorption at 1073.2 and 878.4 cm<sup>-1</sup> was sensitive to the crystallinity of PVDF and the band at 837.2 cm<sup>-1</sup> was associated with the  $\beta$ -crystal of PVDF, while the bands centered at 763.5 and 613.6 cm<sup>-1</sup> belonged to the absorption of  $\alpha$ -crystal of PVDF.<sup>61</sup> The lines in 1465.5 and 745.1 cm<sup>-1</sup> (symmetric stretching vibration of carbonate ion of vaterite) appeared in the spectrum, which revealed the presence of vaterite.<sup>46, 62, 63</sup> These results are in agreement with those obtained by XRD analysis.

In order to determine the existence of CaCO<sub>3</sub> on the PVDF membrane surface, energy dispersive X-ray spectroscopy (EDX) was used as a qualitative spatially resolved detection technique (Fig. 8c

and d). We checked the elemental composition of the raw PVDF and the hybrid membrane, and found that the peaks ascribed to calcium and oxygen atoms newly appeared in the composite membrane (Fig. 8d) compared with the neat PVDF (Fig. 8c). The appearance of Au and Na elements were caused by coating material that was made of Aurums and the reactant of sodium carbonate and/or sodium hydrogen carbonate. Thus, the EDX spectra exhibited the presence of CaCO<sub>3</sub> on the external surface of the composite membrane, which can affect the surface hydrophilia of the PVDF membrane.

Surface hydrophilicity is an important parameter for determining the flux and antifouling property of a membrane. Hydrophilicity of the membranes was evaluated in terms of water contact angle (WCA) measurements. A motor-driven syringe was used to pump liquid steadily into the sessile drop, and a sequence of images of the growing drop was then captured, as shown in Fig. 9. The observed



Fig. 9 Water contact angles of PVDF membrane and  $\mathsf{PVDF}/\mathsf{CaCO}_3$  composite membrane.

value of the pure PVDF membrane is about 92.8 °. When the composite membrane was tested, this value continuously decreased to 28.9 °.

A control experiment was performed to investigate the effect of surface morphology on the contact angle, in which virgin PVDF membrane having pore morphology (see support information Fig. S3) was prepared by the classical method-immersion precipitation inversion process.<sup>64</sup> The WCA measured by dynamic contact angle measurements showed that the WCA value of the porous virgin PVDF membrane increased from 92.8° to approximately 94.1°, when compared with the neat PVDF membrane having a smooth surface without any circular pores (Fig. 6a). This result is in good agreement with the previous report<sup>65</sup> that the contact angles on rough solids are greater than on relatively smooth surfaces. However, the spica-like hierarchical vaterite microcrystals on the hybrid membrane would make the membrane roughness, but why the final WCA value of the blend membrane was much less than the PVDF membrane with smooth surface morphology? We consider this phenonmen should be attribute to the the natural hydrophilicity of the CaCO<sub>3</sub> and also to the surface -OH groups being formed due to hydroxylation (shown as Fig. 8a).<sup>41</sup> Furthermore, both the high specific surface area and a greater hydrophilicity compared with other more stable polymorphic phases<sup>66</sup> that vaterite has and the pores on the membrane surface (Fig. 6d) which may also increase the opportunity for the contact between the internal CaCO3 and water may enhance the hydrophilicity of the blend membrane.

## Conclusions

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In this work, we described a simple method for the synthesis of spica-like hierarchical vaterite CaCO<sub>3</sub> microcrystals with lengths of approximately 3-7 µm using the precipitation reaction of CaCl<sub>2</sub> with Na<sub>2</sub>CO<sub>3</sub> in water/ethanol media. The growth mechanism for the formation of the spica-like hierarchical microstructure, oriented attachment process, has been presented. This work sheds light on the possibility of adding ethanol and sodium bicarbonate to control the kinetic balance for CaCO<sub>3</sub> polymorphs, thus to possibly control the polymorph of the final products. Therefore, the mild processing conditions used to form superstructure suggest that this strategy may be used as a green chemistry simple method to provide a convenient route for synthesizing novel materials. Highly improved membrane hydrophilicity was observed by adding the prepared spica-like hierarchical vaterite CaCO<sub>3</sub> particles into the PVDF membrane via phase inversion method as seen from WCA results. This result indicates that this method is a promising approach for fabricating hydrophilic organicinorganic composite membranes.

### Experimental

Synthesis Procedure: We chose a simple precipitation method, in which we fixed the temperature at 50 °C and the final concentration of Na<sub>2</sub>CO<sub>3</sub> (0.1 M, 2.0 mmol, 0.212 g) and varied the final concentration of NaHCO<sub>3</sub> (0 M,0 mmol, 0 g; 0.1 M, 2.25 mmol, 0.189 g; 0.2 M, 4.5 mmol, 0.378 g and 0.4 M, 9.0 mmol, 0.756 g) and the volume ratio of ethanol/double-distilled water (R = 0, 1/4, 1/2 and 1/1). The total volume of ethanol and double-distilled water was constant in all experiments (22.5 mL), and the alcohol was considered as part of the liquid in calculating the final concentration of the reaction mixture. This approach allowed us to address which parameter or which combination of parameters were the most effective for polymorph discrimination and the cause of morphology change. All of the chemicals were analytical grade and used without further purification. In a typical experimental procedure, Na<sub>2</sub>CO<sub>3</sub> and NaHCO<sub>3</sub> were dissolved in a 50 mL conical bottle containing double-distilled water under magnetic stirring, and then an appropriate amount of absolute ethanol was added (R= 0, 1/4, 1/2 and 1/1) to form a transparent solution A, which was then put into a 50 °C water bath with electromagnetic stirring for 10 min. Solution B was a mixture of CaCl<sub>2</sub> (11 mmol) and H<sub>2</sub>O (10 mL). The freshly prepared aqueous solution B was carried out dropwise to the solution A under strong stirring. The mixture was stirred and allowed to stand at a certain aging temperature (50 °C) in a thermostatic water bath for 0.5 h. The freshly precipitated CaCO<sub>3</sub> crystals were then centrifuged, washed several times with deionized water and ethanol alternately, and dried in the oven at 60 °C for 12 h.

Procedure for preparation of  $PVDF/CaCO_3$  composite membrane: PVDF (25 wt%) was dissolved in DMF (70 wt%) at 60 °C over a period of 45 min to obtain a homogeneous solution. 5.0 wt% of the prepared spica-like hierarchical vaterite CaCO<sub>3</sub> was added at the same temperature, sonication for 30 min, and followed by stirring for 30 min at the same temperature. After stirring, the viscous solution was cast over a glass plate using a finely polished metal rod. The glass plate was then immersed in distilled water (~25 °C) for phase inversion. Finally, the membranes were dried in vacuum oven at 30 °C for 12 h.

The morphology and microstructures of the obtained spicalike hierarchical crystals were examined using SEM (Hitachi S-4800) with an accelerating voltage of 10 kV and energy-

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dispersive X-ray (EDX) spectroscopy was utilized to analyze our products. TEM observation and SAED experiments were carried out with a JEM-2100F. The crystallographic information of the as-prepared samples was established by using powder X-ray diffraction (XRD, D8 DISCOVER with GADDS version of BRUKER Company of Germany) with graphite monochromatized high-intensity Cu K $\alpha$ . FT-IR spectrometry was performed with a Bruker TENSOR 37 FT-IR analyzer. WCA was measured by dynamic contact angle measurements using the drop shape analysis system (Kruss DSA 100, Germany) at room temperature. The WCAs were calculated using the software supplied in the instrument.

## Acknowledgements

Authors thank the testing centre of Tianjin Polytechnic University for assistance with XRD, FT-IR, FE-SEM, EDX, TEM, SAED analysis as well as WCA test.

## Notes and references

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Spica-like hierarchical vaterite CaCO3 was fabricated through oriented attachment process and a hydrophilic PVDF/CaCO3 composite membrane was prepared 39x21mm (300 x 300 DPI)