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A solvothermal method for synthesizing monolayer protected amorphous calcium carbonate clusters†

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A solvothermal method was developed for synthesizing organic monolayer protected amorphous calcium carbonate clusters using 10,12-pentacosadiynoic acid as ligand, ethanol as solvent and $NaHCO_3$ decomposition as CO_2 source, which can be extended to synthesize other monolayer protected mineral clusters.

Monolayer protected clusters (MPCs) have attracted great interest for a number of years since the pioneering work of Schiffrin and coworkers in the preparation of alkanethiolate monolayer protected gold clusters.[1] Differing from colloidal particles prepared by other routes such as microemulsion[2] or polymer stabilization,[3] alkanethiolate or alkanecarboxylate MPCs are stable in air and can be repeatedly isolated from, and redissolved in common organic solvents without irreversible aggregation or decomposition.[4] This property of MPCs opens up tremendous opportunities where they can be handled like 'molecules', and with it, MPCs have gained a variety of applications in catalysis, sensors, optical devices, electrochemistry, bioimaging, in superlattices, *etc.*[5] Nevertheless, until now, the chemical compositions of MPCs are limited to metals such as Au, Ag, Cu, Pt, Pd, *etc.*, which narrows their applicability in a vast amount of scientific and industrial fields.

Apart from the well-known metals, minerals are also an important class of nanomaterials.[6] Among them, calcium carbonate ($CaCO_3$) likely is the most important example, as it is abundant in nature as geological mineral and biomineral. For example, $CaCO_3$ is the main component of limestone, mollusc shells, water scale and also participates in the geological CO_2 cycle. In particular, $CaCO_3$ provides a model system to study nucleation and crystallization of minerals.[7] Controlling the size of $CaCO_3$ is important in biomineralization[8] and also in industry due to the high surface area and increased compatibility with matrix materials when the size is very small. Countless investigations have been undertaken to stabilize $CaCO_3$ nanoparticles at different sizes and with various morphologies.[6c] However, due to the inherent severe ionic association, precise size control of $CaCO_3$ nanoparticles at the nanoscale is quite challenging, and there are only a few reports on dispersible ultrafine $CaCO_3$ particles.[9] For instance, a complex liquid/solid/gas poly-phase reaction was used to produce overbased calcium alkylaryl sulfonate colloidal particles of 5–20 nm consisting of an organic shell and a $CaCO_3/Ca(OH)_2$ hybrid core, which have already been commercialized as detergents.[9a–c] In addition, high-gravity reactive precipitation can provide massive yields of calcite nanoparticles in a size range of 17–36 nm.[9d] Buchold *et al.* employed a microemulsion approach to synthesize monodisperse non-agglomerated $CaCO_3$ nanoparticles with a size of 25 nm.[9e] On the other hand, non-agglomerated $CaCO_3$ vaterite nanoparticles ranging from 20 to 60 nm were obtained by a wet-chemical method with heating a dispersion of calcium bicarbonate in ethylene glycol.[9f] Additive-free monodisperse amorphous calcium carbonate (ACC) nanoparticles in the range of 100–200 nm were also produced in ethanol.[9g] None of previous efforts, however, has downsized $CaCO_3$ entities to the subnanometer level or even clusters. Interestingly, the recently proposed "non-classical" nucleation pathway has already proven the existence of rather small $CaCO_3$ pre-nucleation clusters with a size of 0.6–2 nm.[7,10] This indicates that it should be possible to stabilize such small $CaCO_3$ entities by proper ligands to produce monolayer protected $CaCO_3$ clusters rather than stabilizing them *in situ* by association with inorganic silica.[11]

In this paper, we show that an easy solvothermal method can be utilized to fabricate monolayer protected ACC clusters using 10,12-pentacosadiynoic acid (PCDA) as the ligand. The chemical structure of PCDA and experimental set-up are presented in Fig. 1a and b. In brief, to a mixed ethanolic solution of 10 mM $CaCl_2$, 4 mM PCDA and 42 mM NH_4OH, 2 equimolar solid $NaHCO_3$ was added. Then, the solution was tightly sealed

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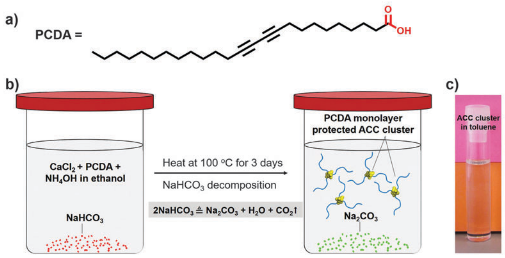

Fig. 1 (a) Chemical structure of PCDA. (b) Experimental set-up of solvothermal reaction for synthesizing PCDA monolayer protected amorphous $CaCO_3$ (ACC) clusters. (c) The photo of PCDA monolayer protected ACC clusters in toluene.

and put in an oil bath at 100 °C for 3 days. Two main reactions successively occurred as follows:

$$2NaHCO_3 \triangleq Na_2CO_3 + H_2O + CO_2\uparrow \quad (1)$$

$$CaCl_2 + CO_2 + NH_4OH \rightarrow CaCO_3{\cdot}xH_2O\ (ACC) + NH_4Cl \quad (2)$$

At 100 °C, $NaHCO_3$ can gradually decompose to release CO_2, which serves for the formation of $CaCO_3$. The occurrence of $NaHCO_3$ decomposition was confirmed by the powder X-ray diffraction (XRD) and thermal gravimetric analyses (TGA) of the final solid residues (Fig. S1 and S2, ESI†). We used ethanol as the solvent because it can both dissolve organic ligands and assist the formation of kinetically stable ACC.[9g,12] Once very small ACC clusters formed in the solution, PCDA could effectively protect them against agglomeration. PCDA is found to be highly specific, while other long-chain alkyl ligands like stearic acid do not show a decisive stabilizing effect. After centrifugation, the collected solid was dissolved in toluene with the assistance of sonication. Thereby, only PCDA protected ACC clusters were dissolved, while insoluble Na_2CO_3 was removed by filtration. Further purification of the product by repeated cycles of dissolution in toluene and precipitation in ethanol finally gave pure PCDA monolayer protected ACC clusters. The solution of clusters in toluene is totally transparent (Fig. 1c), indicating the very small size of $CaCO_3$. Like metal MPCs, PCDA monolayer protected ACC clusters can be repeatedly isolated from, and dissolved in organic solvents such as toluene, hexane, chloroform, dichloromethane, *etc.*

TEM (Fig. 2a and b) shows that the PCDA monolayer protected clusters are monodisperse with a mean size of 4.9 nm according to the size distribution histogram in Fig. 2d, which is also evidenced by dynamic light scattering (DLS) results (Fig. S3, ESI†). Due to the interdigitation of hydrophobic PCDA chains, the clusters tend to aggregate during drying. The selected area electron diffraction pattern (Fig. 2c) shows no crystalline features indicating the amorphous nature of the clusters. To prove the presence of Ca, we also performed energy dispersive X-ray (EDX) analysis. As shown in Fig. 2e, a signal for Ca is observable.

To obtain knowledge of the cluster structure, we compared the UV-vis and FTIR spectra of PCDA and PCDA protected ACC clusters, as presented in Fig. 3. Upon attachment to the ACC core, PCDA chains in the shell exhibit similar UV absorption peaks from diacetylene groups (Fig. 3a), revealing that they do

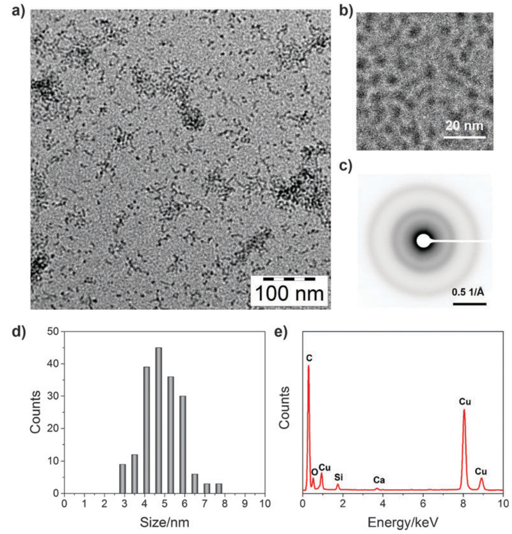

Fig. 2 (a) TEM, (b) high-resolution TEM images and corresponding (c) electron diffraction of PCDA monolayer protected ACC clusters. Electron diffraction was obtained from a round area with a diameter of 200 nm in (a). (d) Size distribution of the clusters by counting 180 particles in (a). (e) EDX profile of PCDA monolayer protected ACC clusters showing the presence of Ca. Note that the signal for Si comes from the detector, and for C and Cu, from the carbon coated copper grid.

not change significantly as a ligand of $CaCO_3$. This is important, since PCDA is a light-sensitive monomer which can easily polymerize even upon room light irradiation.[13] No obvious absorption in the visible region can be observed, which shows absence of polymerization and accords well with the good transparency of the cluster solution. The FTIR spectrum of PCDA protected ACC cluster in Fig. 3b shows features of PCDA and ACC. For instance, the C–H stretching bands arise from the PCDA shell. The stretching band of C═O shifts from 1690 cm^{-1} for COOH in PCDA to 1547 cm^{-1} for COO^- in the cluster, indicating that PCDA chains bind on the ACC core by the chelation between terminal carboxylate groups and Ca ions. The broad band between 3600 and 3000 cm^{-1} indicates the presence of structural water in the cluster, which is consistent with the amorphous nature of the $CaCO_3$ core.[12] Moreover, the ν_1–ν_4 bands of carbonate ions characteristic for ACC[14] can also be identified.

TGA and matrix-assisted laser desorption/ionization time-of-flight mass spectroscopy (MALDI-TOF MS) measurements were

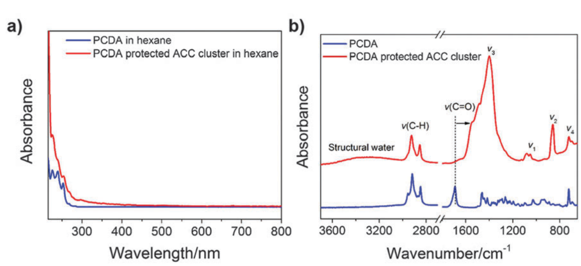

Fig. 3 (a) UV-vis spectra of PCDA and PCDA protected ACC clusters in hexane. (b) ATR-FTIR spectra of PCDA crystals and dried PCDA protected ACC cluster.

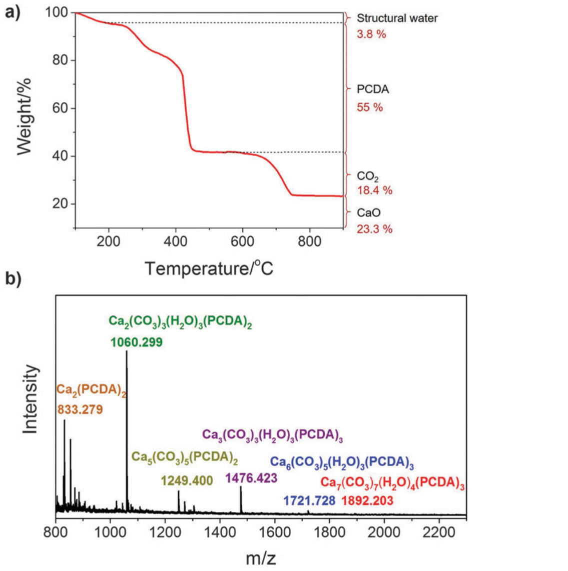

Fig. 4 (a) TGA curve (air flow) and (b) MALDI-TOF MS spectrum of PCDA monolayer protected ACC clusters. Corresponding assignments of main dissociated species are also presented. Note that the probable presence of HCO_3^- and OH^- may bring an uncertainty of 1–3 Da between calculated and experimental data.

performed to explore the chemical composition of PCDA monolayer protected ACC clusters (Fig. 4). Under air-flow, the TGA trace reveals successive mass losses due to the removal of structural water, PCDA degradation and $CaCO_3$ decomposition (Fig. 4a). The corresponding atomic ratio of $[CaCO_3]:[H_2O]:[PCDA]$ was calculated to be 2.8 : 1.4 : 1. When compared to synthetic ACC with a typical formula of $CaCO_3{\cdot}H_2O$,[14–15] in the PCDA protected ACC cluster, the number of structural H_2O is only half of that of $CaCO_3$. Indeed, according to simulation results, N_{water}/N_{Ca} decreases drastically as the size of ACC decreases in the lower nanometer level (<1.5 nm).[16] The composition is also in accord with the MALDI-TOF MS spectrum (Fig. 4b). The assignments of the main dissociated species reveal that the maximum number of $CaCO_3$ units in the clusters is 7, whereas the number of structural water molecules varies, with a maximum of 4, and the number of PCDA chains is always smaller than 3. As the ionization process leads to the dissociation of most clusters, the formula $(CaCO_3)_7(H_2O)_4(PCDA)_3$ should represent the actual composition of the PCDA monolayer protected ACC cluster, which agrees well with the atomic ratio calculated from TGA. An ACC structure with about 7 $CaCO_3$ units has a size of ~1 nm according to previous molecular simulation.[16] The fully stretched PCDA molecule with a rigid all-*trans* conformation has a size of about 3 nm—based on TEM investigations, however, the PCDA chains in the cluster are assumed to adopt a curved *gauche* conformation with an average size of 1.5–2 nm. The models for the all-*trans* and *gauche* conformations of PCDA chains are also presented (Fig. S4, ESI†).

In summary, we discovered a solvothermal method to prepare monolayer protected amorphous $CaCO_3$ clusters using PCDA as the ligand, ethanol as the solvent, and $NaHCO_3$ decomposition as CO_2 source. The resulting clusters with an average size of ~4.9 nm show very good stability and transparency in toluene and can be repeatedly precipitated from, and dissolved in common organic solvents, like typical MPCs based on metals. Structural characterizations suggest that the cluster has a hydrated ACC core and an organic PCDA shell with *gauche* conformations. The chemical formula of the cluster was estimated to be $(CaCO_3)_7(H_2O)_4(PCDA)_3$. Our method presented here extends the scope of MPCs, and its potential to be applied to the synthesis of mineral MPCs.

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