We report the synthesis of CaCO3@C yolk–shell particles with a microporous carbon shell through a selective etching method. The CaCO3@C exhibits an enhanced CO2 adsorption, relative to the porous CaCO3 nanoparticles or the porous carbon shell, with a capacity of 19.30 cm3 STP g−1 (0.86 mmol g−1 or 31.64 cm3 STP cm−3 sorbent) under ambient conditions (23 ± 1 °C and 1 atm CO2).

Yolk–shell nanoparticles are materials with nanoparticle cores inside hollow shells. They are promising functional nanomaterials with various functionalities both on the core and shell, which can have a wide variety of applications such as catalysis, drug/gene delivery, energy storage, biosensors, and Raman scattering (SERS) technologies.1–3 Various yolk–shell nanoparticles (YSNs) with different chemical compositions have been reported such as metal NPs@SiO2, metal oxide@SiO2, metal NPs@C, metal NPs@metal oxide, metal NPs@polymer, SiO2@metal oxide, SiO2@C and polymer@polymer4–11 by using different synthetic methods, for example, a soft templating method and selective etching methods. To date, most of the reported YSNs are limited to silica, polymer, carbon and a few metal oxides.12–14 To enrich the YSNs library and meet the requirements of practical applications, synthesis of YSNs with a new composition is desirable.

Porous carbons with various morphologies and structures have been widely investigated for CO2 adsorption and separation15 due to their large surface areas, ease of synthesis, low-cost, and high stability.16–18 The synthesis of porous carbon aerogels and xerogels via resorcinol-formaldehyde (RF) resins has been extensively reported.19,20–24 Taking the advantages of yolk–shell structures, such as large void space for accommodating of guest molecules, different functionality of both core and shell, constructing yolk–shell particle with porous carbon shell would be very promising for design of CO2 capture and conversion nanoreactors. Calcium-based materials (calcium oxide, calcium hydroxide, and calcium carbonate) have been proved as excellent sorbents for high temperature CO2 capture,26 however, their adsorption performance quickly declines with multiple reuse due to irreversible particle sintering and agglomeration at high temperatures.26,27

We herein report the first example for the synthesis of CaCO3@C yolk–shell particles. The features offered by these particles are: high surface area and pore volume, basic calcium-based core for affinity of CO2, large void space for CO2 storage, and microporous carbon shell28 for preferential passage of small molecules with respect to larger sized molecules.29 These yolk–shell particles could find application as a catalyst support (e.g., nano-metals) or in drug and gene delivery for biomedical applications,30 or high temperature CO2 capture.

As illustrated in Scheme 1, a four-step synthetic process was employed by using CaCO3 particles as core materials. First, a silica layer was coated around the CaCO3 nanospheres by a Stöber method to obtain CaCO3@SiO2 core–shell particles. Next, the CaCO3@SiO2 was coated with a RF resin via a modified Stöber method28 to produce CaCO3@SiO2@RF core–shell–shell particles. This was followed by a carbonisation process under N2 flow, which converted the RF resin into a microporous carbon shell to produce CaCO3@SiO2@C. Finally, the silica layer was removed with the treatment of hot concentrated NaOH. The detailed experimental procedures are presented in the ESI.†

CaCO3 nanospheres were prepared by the rapid mixing of solutions of CaCl2 and Na2CO3 containing surfactant poly(4-styrenesulfonic acid) sodium salt (PSS). The as-synthesised CaCO3 nanospheres have an average particle size of 450 nm as demonstrated by SEM image (Fig. 1a). The particle size distribution of the CaCO3 spheres (Fig. 1b) further confirms the uniformity of the porous CaCO3 particles. The successful preparation of CaCO3@SiO2 as well as CaCO3@SiO2@C from CaCO3 nanospheres was tracked and confirmed by TEM

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*Department of Chemical Engineering, Curtin University, Perth, WA 6845, Australia. E-mail: jian.liu@curtin.edu.au
†Electronic supplementary information (ESI) available: Materials and methods, SEM and TEM images, CO2 adsorption data. See DOI: 10.1039/c5ra02427g
characterization as shown in Fig. 2a–d. Fig. 3a and b show the SEM and TEM images of the obtained CaCO3@C yolk–shell particles. The presence of a movable core inside a thin carbon shell can be easily identified from the SEM images via the particles with broken shells, exposing the core. The TEM image shows a yolk–shell particle with a porous CaCO3 core and a golf ball like porous carbon shell. The size of the core and hollow space is ca. 240 nm and 310 nm in diameter, respectively, and the carbon shell’s thickness is around 10 nm. High angle annular dark field scanning transmission electron microscopy (HAADF-STEM) and energy dispersive X-ray spectroscopy (EDX) of the particles are shown in Fig. 3c–f, which indicates the formation of a carbon shell outside the calcium carbonate core.

XRD pattern of the CaCO3@C yolk–shell particles (Fig. 3g) further confirms that the main composition of the core is CaCO3. A small amount of CaO and CaSiO3 (due to reaction of CaO with un-removed SiO2) is also present. Interestingly, when the CaCO3 precursor nanoparticles were subjected to the same calcination conditions as with the yolk–shell particles, a Ca(OH)2 phase was formed (according to the XRD data, Fig. S1† due to the loss of CO2 resulting from the continuous supply of fresh N2 in the furnace at 600 °C for a long period (4 hours). This suggests that the nanoporous SiO2 layer prevent the escape of the large CO2 molecules during carbonation of CaCO3@SiO2@RF core–shell–shell particles. As a result, the retainment of CO2 gas within the SiO2 layer led to an expansion of the space between the nanocrystals inside the core, increasing its porosity by creating channels and bridges, compared to the CaCO3 precursor nanoparticles (this can be seen by comparing Fig. 2a and d). Furthermore, some of CaO formed at the edge of the core reacted with SiO2 (that could not be removed by NaOH etching) to form CaSiO3. The porosity of the CaCO3@C yolk–shell particles were measured by nitrogen sorption, which revealed a type IV isotherm indicating their mesoporous structures31 (Fig. 3h). The pore size distribution curve in Fig. S2† shows that the material is highly microporous to mesoporous in nature. The high microporosity of the yolk–shell particles is due to the carbon shell.28 The BET surface area, density and total pore volume of the CaCO3@C YSNs are 381 m2 g−1, 0.12 g cm−3 and 0.61 cm3 g−1, respectively, while those of the CaCO3 precursor nanoparticles are 89 m2 g−1, 0.63 g cm−3 and 0.14 cm3 g−1, respectively (see Fig. S3† for N2 sorption isotherm and pore size distribution of the CaCO3 precursor).

In order to control: (1) the hollow space inside shell and (2) the thickness of shell, the synthesis parameters such as silica precursor concentration and RF ratio were varied, respectively (see Fig. S4–S6 in ESI†). It was found that the general size of the hollow space and shell thickness increased when increasing the silica precursor concentration and the RF ratio, respectively. In addition, by increasing the etching time, as shown in Fig. 4, the hollow space increases and the porous CaCO3 core gets more exposed due to the removal of the silica layer around the core. The ability to control these physical parameters is important in terms of improving the mechanical strength of the particles, and tuning its functionalities.
For further optimisation and confirmation of the core compositions, TGA of CaCO₃ precursor nanoparticles was performed as shown in Fig. S7† from which it can be seen that the CaCO₃ decomposes to CaO between ~600 °C and ~780 °C. As a result, the effect of high temperature recalcination on the CaCO₃@C yolk–shell particles was investigated. Fig. S8† shows the XRD patterns for CaCO₃@C samples recalcined under N₂ for 1 hour at 650 °C, 700 °C and 750 °C, respectively. At 650 °C, a CaO peak starts to appear and becomes more prominent at 700 °C. However, when the temperature is further increased to 750 °C, a CaSiO₃ phase forms due to reaction of CaO with remaining SiO₂ on the core surface. Hence it is shown that the phase and composition of the core can be changed from CaCO₃ to mixture of CaCO₃ and CaO, further to CaSiO₃ by simply tuning the recalcination temperature of the CaCO₃@C yolk–shell particles. The presence of CaO in the core increases its basicity, which can be an attractive characteristic for catalytic applications requiring basic conditions or high temperature CO₂ capture.

Developing a low cost and high efficient adsorbent for CO₂ capture is highly desirable in order to alleviate the crisis of climate change and greenhouse effect. Fig. 5 shows the CO₂ adsorption isotherms for the CaCO₃ precursor nanoparticles, Ca(OH)₂ (calcined CaCO₃ precursor) particles, CaCO₃@SiO₂@C and CaCO₃@C yolk–shell particles. The original CaCO₃ shows a relatively low adsorption capacity (6.30 cm³ STP g⁻¹ or 45.00 cm³ STP cm⁻³ sorbent at 23 ± 1 °C and 1 atm CO₂) even at higher CO₂ pressures due to weak physisorption of the gas on the particles. The adsorption capacity of CaCO₃@SiO₂@C is

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Fig. 2 TEM images for tracking the steps in synthesis of CaCO₃@C: (a) CaCO₃ particle, (b) CaCO₃@SiO₂ particle, (c) CaCO₃@SiO₂@RF particle and (d) CaCO₃@SiO₂@C particle. TEOS concentration = 4 mL g⁻¹ CaCO₃, RF ratio = 0.5.

Fig. 3 (a) SEM, (b) TEM, (c) HAADF-STEM images, (d–f) EDX elemental mapping of carbon, calcium and oxygen respectively, (g) XRD analysis and (h) N₂ adsorption isotherm for the CaCO₃@C yolk–shell particles. TEOS concentration = 2 mL g⁻¹ CaCO₃, RF ratio = 0.5 and etching time = 3 hours.
even lower (4.50 cm³ STP g⁻¹) sorbent at 23 ± 1 °C and 1 atm CO₂ due to the impervious layer of SiO₂ which hindered CO₂ penetration towards the CaCO₃ core; hence physisorption was mostly achieved on the surface of the carbon shell. The calcined precursor, Ca(OH)₂ particles had the lowest CO₂ adsorption capacity at 0.40 cm³ STP g⁻¹ sorbent (at 23 ± 1 °C and 1 atm CO₂), probably due to the loss in surface area resulting from particles agglomeration at high calcination temperature. However, the improvement in the CO₂ uptake is obvious with the yolk–shell particles due to removal of the SiO₂ layer for CO₂ adsorption. The CaCO₃ core of CaCO₃@C was more porous than the CaCO₃ precursor (as can be seen by comparing Fig. 2a and d). Furthermore, the core–shell architecture allowed each CaCO₃ core to be completely surrounded by a CO₂ atmosphere for enhanced adsorption. The maximum amount of CO₂ adsorbed with CaCO₃@C at ambient conditions (23 ± 1 °C and 1 atm CO₂) is 19.30 cm³ STP g⁻¹ sorbent (0.86 mmol g⁻¹ or 31.64 cm³ STP cm⁻³ sorbent). The volumetric capacity of CaCO₃ based sorbents is comparable with other sorbents such as activated carbon,⁵ much higher than high surface area zeolite 13X (with 5.00 cm³ STP cm⁻³). ²² Fig. S9† shows the determination of the optimum etching time according to CO₂ adsorption isotherms. It was found that 3 hours of NaOH etching was enough to expose the CaCO₃ core for optimum CO₂ adsorption. The CO₂ adsorption amount is due to the physisorption, which follows the sequence of CaCO₃@C > CaCO₃ precursor nanoparticles > CaCO₃@SiO₂@C > Ca(OH)₂ particles, indicating that the combination of CaCO₃ core, hollow space and carbon shells is favourable for high CO₂ adsorption at low temperature.

Conclusions

CaCO₃@C yolk–shell particles have been successfully synthesised by a selective etching method. The yolk–shell structures exhibited enhanced CO₂ uptake of 19.3 cm³ STP g⁻¹ (0.862 mmol g⁻¹ or 31.64 cm³ STP cm⁻³ sorbent) at 23 ± 1 °C under 1 atm CO₂, compared with 6.3 cm³ STP g⁻¹ for the original CaCO₃ core, or 4.5 cm³ STP g⁻¹ for the porous carbon shell. This was due to the relatively high surface area and pore volume, as well as the hollow space of the yolk–shell particle. It was shown that the core composition of the yolk–shell particles can be varied from CaCO₃, CaO, or CaSiO₃ by simply tuning the recalcination temperature. These yolk–shell particles with porous calcium-based materials core and microporous carbon shell make them potentially attractive materials for environmental remediation (SO₂, NO₂ removal), biomedical applications and nanocatalysis. Further investigation on the high temperature adsorption of CO₂, SO₂ is ongoing.

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