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Effect of carbon nanotubes on calcium carbonate/calcium silicate phase and morphology

Virginia Gomez,^a Covadonga Correas,^a and Andrew R. Barron^{a,b,c*}

^a *Energy Safety Research Institute (ESRI), College of Engineering, Swansea University, Bay Campus, Swansea, SA1 8EN, Wales, UK*

^b *Department of Chemistry, Rice University, Houston, Texas 77005, USA*

^c *Department of Materials Science and Nanoengineering, Rice University, Houston, Texas 77005, USA*

Abstract

The composition and microstructure of different CaCO₃-Ca₂SiO₄-carbon nanotube composites have been studied. Materials have been characterized by X-ray diffraction (XRD), high resolution scanning electron microscopy (SEM), thermogravimetric/differential thermal analysis (TG/DTA), and Fourier-transform infrared (FTIR) spectroscopy. The morphology and structure of the inorganic systems are affected by the presence of multiwall carbon nanotubes (MWCNT) during the hydration processes and the nature of the MWCNT/SDS interface plays a role in the curing stages of the composite enhancing the growth of calcium silicate.

Keywords: Calcium; carbonate; carbon nanotubes, silicate; microstructure, hydration.

* Corresponding author. Tel.: +44-(0)1792-606930; E-mail: a.r.barron@swansea.ac.uk, arb@rice.edu.

1. Introduction

Carbon nanotubes (CNTs) have been investigated as additives for a range of nano-composites [1-4] due to their high Young's modulus [5,6]. Several cement-based composite materials have included CNTs in their composition [7-9], since the combination of these materials offers great functional advantages over materials now employed in construction [10]. The majority of research has concentrated on the inclusion of CNTs during traditional composite processing [11,12]; however, there has been a recent interest in what the effect the presence of CNTs [13,14]. A recent work reports on the effects of carbon nanotubes (CNTs) on the microstructure and properties of carbon fiber-reinforced silicon carbide (C/SiC) composites [15]. We have reported that the synthesis of composites of CaCO₃ with fullerenes and single walled carbon nanotubes (SWCNTs) results in amorphous phases with unique and interesting morphologies [16]. These results suggested that the interface between the carbon nanomaterial and the growth medium is important, and the following work done by our group confirmed that the identity of functionalization (covalent versus non-covalent) was indeed important for CaCO₃ growth [17]. In further work we observed that with Portland cement showed that the CNTs accelerate the hydration reaction of the tricalcium silicate (3CaO.SiO₂ or C3S) and the morphology of both the tricalcium aluminate (3CaO.Al₂O₃ or C3A) and C3S hydration products were affected by the SWCNTs [18]. The effectiveness of the different dispersants on the microstructure and properties of CNTs alumina composites have been studied [19]. We have reported that surfactants typically used to solubilize CNTs also modify the morphology in the CaCO₃/SiO₂ system [20] and so it is important to differentiate between the effects of the CNTs and those of the surfactant. The hydration of the calcium silicate materials reported by Allen *et al.* determines the final morphology and particle size, which is related with various mechanical and chemical properties of cement based materials as well as other composites [21], so a study of the effect of the CNTs on the hydration processes in different CaCO₃/SiO₂ systems is of interest given the effects observed in the SiO₂ and CaCO₃ systems [16,22,23].

In the current work, we aimed to complete the reaction matrix of CaCO₃ + CNTs [13], CaCO₃ + silica source + surfactant [20], and silica + surfactant [24]. Composite materials

were synthesized using multi-walled carbon nanotubes (MWCNTs) as additives to inorganic $\text{CaCO}_3/\text{SiO}_2$ matrices, using fumed silica (FS) or silicic acid (SA) as the silica source, to determine the effects of the sodium dodecyl sulfate (SDS) surfacted MWCNT in the growth, crystallization and morphology. In addition, the effect of MWCNT/SDS on the hydration of pre-formed commercial calcium silicate (CaSiO_3) was investigated.

2. Experimental section

2.1. Materials and methods

Calcium carbonate, fumed silica (FS), silicic acid (SA) and commercial CaO-SiO_2 (c- CaO-SiO_2) were purchased from Sigma Aldrich (ACS grade) and used as supplied. Multiwall carbon nanotubes (MWCNTs) were prepared using a tabletop horizontal tube reactor (Nanotech Innovations SSP-354) as previously reported [25] and were used after acid purification [26], see Fig. 1.

[Insert Fig. 1 here]

Samples were characterized by scanning electron microscopy (SEM) using an Ultra-High Resolution FE-SEM S-4800 coupled with an energy dispersive X-ray analyzer (Inca X-ray analysis system, Oxford Instruments, Abingdon, United Kingdom) used for the EDX analysis. The crystallographic structure of the products was determined by XRD using a Bruker AXS D8 Advance diffractometer ($\text{Cu-K}\alpha$, $\lambda = 1.5418 \text{ \AA}$) with an LINXEYE detector between 10° and 70° (2θ), with 2θ increments of 0.02° and counting time of 0.5 s. Differential thermal/thermogravimetric analysis (DT/TGA) of the samples were performed on a TA Q600 instrument. The samples were heated under flowing air (100 mL/min) from room temperature to 1300°C with a heating rate of $20^\circ\text{C}/\text{min}$. The exhaust gas from the TGA was monitored using a heated sample transfer line (350°C) and a Thermoscientific i510 FTIR. Scans were taken approximately every 36 seconds for the duration of the heating cycle. This FTIR equipment was also used to carry out IR analysis of all the samples, recording spectra in the $650\text{-}4000 \text{ cm}^{-1}$ region with 16 scans.

2.2. *Sample preparation*

In a typical experiment, CaCO₃ (200 mg) was added to distilled water (250 mL) and stirred at ambient pressure under a flow of CO₂ for 1 hour. H₄SiO₄ (20 mg) were added, whilst stirring and the CO₂ bubbling for 4 hours [20]. The reaction mixture was then stirred under a CO₂ atmosphere for a further 20 hours. Finally, the sample was filtered by gravity and dried in an oven at 70 °C for 1 hour and characterized before the curing process. The reactant powders were mixed following the amounts indicated in Table 1. In order to ensure a homogeneous mixing, MWCNTs were dispersed in a 1% aqueous solution of sodium dodecyl sulfate (SDS) over 30 min in an ultrasonic bath to form 1 mg/mL dispersion. The corresponding amount of MWCNTs dispersion or SDS solution was added to the reactants mixture and placed in an ultrasonic bath for 5 min. The mixture was aged for one or two weeks under ambient indoor conditions (~20 °C, 1 atm). Finally, all samples were dried in an oven at 70 °C for 1 hour.

[Insert Table 1 here]

3. Results and discussion

Table 1 summarizes the reactions employed for the different samples for different CaCO₃/SiO₂ combinations using multiwall carbon nanotubes (MWCNTs) as an additive material.

3.1. *Effect of MWCNTs on the CaCO₃/fumed silica system*

Fig. 2 shows the SEM micrographs of sample **2** prepared from the reaction of CaCO₃ and fumed silica (FS) in the presence of SDS surfacted MWCNTs (Fig. 2a and b), in comparison with that of sample **1** prepared without the MWCNTs (Fig. 2c). As was reported previously [18], the presence of the surfactant SDS results in the formation of a textured particulate structure containing a fraction of almost spherical particles. The presence of residual SDS is confirmed from the presence of sodium and sulfur in the EDX spectrum (Fig. 2d). The sample prepared with the MWCNTs shows no spherical particles, but a sheet-like structure (Fig. 2a),

while the insertion of MWCNTs (arrows) between the hydration products can be seen in Fig. 2b. Similar results have been observed in the cement based composites literature [7].

[Insert Fig. 2 here]

The XRD for sample **2** after curing for 1 week (Fig. 3a) shows in addition to peaks associated with crystalline calcite (CaCO_3) two broad peaks. The peak at 20° is associated with silica [27], while the peak centered close to 30° is attributed to highly polycrystalline Ca_2SiO_4 [28] based upon changes that occur upon sintering (see below). The spectrum of sample **2** (in the presence of MWCNTs) is similar, although the relative intensity of this latter amorphous phase is higher, suggesting that the MWCNT favour the growth of this phase.

FTIR of samples **1** and **2** (Fig. 4a) confirms the presence of calcite, as the main asymmetric band (ν_3) and symmetric vibration (ν_4) of CO_3 at 1391 and 711 cm^{-1} are characteristic of crystalline calcium carbonate phases [29,30]. A broad band, centered at 1083 cm^{-1} , appears in the spectrum of the sample without MWCNT and is associated to silica in the presence of a modifier oxide, such as calcium compounds [31]. This band is significantly diminished in the spectrum of the sample with MWCNT (sample **2**) indicating that the amount of silica is lower, probably due to Ca_2SiO_4 (C2S) formation. The remaining bands (1795 , 1390 , 1085 and 870 cm^{-1}) represent the vibrations of the carbonate ions, except a 1217 cm^{-1} peak, corresponding to the skeletal vibration of the bridge S-O stretch in the SDS molecule [32].

[Insert Fig. 4 here]

3.2. Effect of MWCNTs on the CaCO_3 /silicic acid system

The SEM micrographs of samples **3** and **4** after curing for 1 week are shown in Fig. 5. As has been reported [20] the addition of SDS to a CaCO_3 /silicic acid (SA) reaction results in the formation of large ($20\text{ }\mu\text{m}$) crystallites (of calcite, see below) in a matrix of smaller particles of less well defined shapes (Fig. 5a and b). In dramatic contrast, the presence of the

MWCNTs results in a ribbon morphology, several microns in length and hundreds of nanometres wide (Fig. 5c and d). This latter observation is reminiscent of silica coated CNTs [22,23], which is expected since SA was used to grow silica coatings on SDS-solubilized SWCNTs. Thus, it would appear that the initial formation of SiO₂-coated MWCNTs is followed by silicate growth on the template, while excess CaCO₃ crystals may be seen as large crystallites (ca. 10 μm).

[Insert Fig. 5 here]

The XRD of samples **3** and **4** follow the trends observed for samples **1** and **2**, i.e., the presence of the MWCNTs appears to enhance the formation of Ca₂SiO₄ (C2S) see Fig. 3b. The FTIR spectra show the calcite bands (see above) together with the SDS bands, which are more intense in the case of the sample with MWCNT. The peaks at 2956, 2917, 2850 and 1467 cm⁻¹ corresponding to CH₂ stretching and bending modes which is characteristic of a polar environment, the 1216 cm⁻¹ peak corresponding to skeletal vibration involving the bridge S–O stretch, the 995 cm⁻¹ peak corresponding to C–C band stretching and 832 cm⁻¹ peaks corresponding to asymmetric C–H bending of the CH₂ group [32]. In this case, in sample **4** (with the MWCNTs) apart from the 1081 cm⁻¹ band, corresponding to silica in presence of Ca²⁺, it is possible to observe a group of bands around 1050 cm⁻¹, which have been associated to silicate modes in other works [31].

3.3. Effect of MWCNTs on the hydration of preformed CaCO₃-SiO₂

A commercial sample of CaO-SiO₂ was hydrated for one week in the presence of SDS (sample **5**) or SDS-MWCNT (sample **6**). In the presence of SDS the hydration of CaO-SiO₂ appears similar to prior to hydration, and consists of a particulate structure. In contrast, the presence of MWCNTs results in the formation of a small number of smooth platelet regions. The identity of these features appears to be associated with the formation of Ca₂SiO₄ (C2S), since sintering both samples to 1300 °C (Fig. 6b and d) results in an increase in these regions for both samples and coincides with C2S crystallization.

[Insert Fig. 6 here]

XRD patterns of these samples after the curing clearly showed the promoting effect of the MWCNT in the Ca_2SiO_4 growth (Fig. 3c), even if the broadness of the peaks suggest a poorly crystalline (i.e., very small crystal domains) sample. Sintering the CaO-SiO₂ sample to 1300 °C results in the formation of crystalline Ca_2SiO_4 larnite (JCPDS 33-0302) along with SiO₂ cristobalite (JCPDS 101-0938) and CaSiO_3 pseudowollastonite (JCPDS 900-2250). Interestingly, the presence of MWCNTs appear to inhibit significant crystallization of the Ca_2SiO_4 . The FTIR spectrum of samples **5** and **6** show the broad band at 1000-1300 cm^{-1} associated with the stretching vibration of Si-O-Si.

In order to probe the Ca_2SiO_4 formation, a DT/TGA has been carried out on samples **5** and **6**. From Fig. 7 it can be seen that at around 100 °C, the external water is lost in both samples occurs, with a comparable mass loss (ca. 6%). At around 250 °C, an exothermic transition with the 10-12% mass loss is due to the decomposition of the SDS and the dehydration of calcium silicate hydrates, in both samples, while the exothermic transition in sample **6** above 600 °C, corresponding to the MWCNT decomposition [34,35]. In the absence of MWCNTs (sample **5**) there is a distinct endotherm at 920 °C associated with the crystallization of Ca_2SiO_4 .

The same endotherm is only marginally above the baseline in sample **6**, consistent with the XRD results that indicate significantly lower crystalline Ca_2SiO_4 after thermolysis (Fig. 3c). In the case of CaO-SiO₂/SDS (sample **5**) there is a 2-stage exothermic decomposition (1000 and 1100 °C) in which the second step shows a significantly larger exothermic peak in the DTA. A 2-stage mass loss is also observed for sample **6**; however, the 2nd steps temperature is significantly lowered (1080 °C). This difference may be due to the Ca:Si ratio since this transition temperature increases with the increased Ca:Si ratio [37].

[Insert Fig. 7 here]

4. Conclusions

The results of the present study suggest that the presence of the anionic surfactant SDS coupled with the carbon nanotubes have a clear effect on the growth of hydrated silicates. SDS-surfacted MWCNTs acts as a template for growing silicates and alters the amount of certain phases present in the samples. For the hydration of CaSiO_3 there is an enhancement in Ca_2SiO_4 (C2S) formation, albeit poorly crystalline in nature, while the presence of MWCNTs also appears to inhibit crystallization upon thermolysis. For the reaction of CaCO_3 with fumed silica or silicic acid there is a small change in the formation of poorly crystalline (amorphous) Ca_2SiO_4 , and for fumed silica (FS) there is only a small change in morphology. However, with silicic acid (SA) the morphology is dominated by the formation of ribbon-like particles template by the MWCNTs. This process is most probably related to the known complexation of Ca^{2+} to the negatively charged SDS polar groups [38], and the importance of the surfactant modified interfacial interaction in CNT composites [39,40].

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Table 1
Samples composition.

Sample	Commercial CaSiO ₃ (mg)	CaCO ₃ (mg)	Fumed SiO ₂ (mg)	Silicic acid (mg)	1% SDS in water (mL)	MWCNT 1% SDS (mL)
1		200	20		2	
2		200	20			2
3		200		20	2	
4		200		20		2
5	200				2	
6	200					2

Legends for Figures

Fig. 1. SEM micrograph of the as purified CNTs used in the present study.

Fig. 2. SEM images of (a) sample **2** ($\text{CaCO}_3/\text{FS}/\text{SDS}\text{-MWCNT}$) after (a) one and (b) two weeks of curing and (c) sample **1** ($\text{CaCO}_3/\text{FS}/\text{SDS}$) with (d) its corresponding EDX spectrum showing the presence of residual SDS.

Fig. 3. XRD patterns for (a) samples **1** and **2**, (b) samples **3** and **4**, and (c) sample **5** and **6** as prepared and after sintering at 1300 °C.

Fig. 4. FTIR spectra for (a) samples **1** and **2**, (b) samples **3** and **4**, and (c) sample **5** and **6** as prepared and after sintering at 1300 °C.

Fig. 5. SEM micrographs of (a and b) sample **3** ($\text{CaCO}_3/\text{SA}/\text{SDS}$) and (c and d) sample **4** ($\text{CaCO}_3/\text{SA}/\text{SDS}\text{-MWCNT}$).

Fig. 6. SEM images of (a) commercial $\text{CaO}\text{-SiO}_2$ after curing in 1% SDS solution for one week (sample **5**) and (b) after sintering at 1300 °C, and (c) commercial $\text{CaO}\text{-SiO}_2$ after being curing in 1% SDS-MWCNT solution for one week (sample **6**) and (d) after sintering at 1300 °C.

Fig. 7. Differential thermal-thermogravimetric analysis (DT/TGA) of commercial $\text{CaO}\text{-SiO}_2$ cured in the presence of SDS (a and c) and SDS-MWCNTs (b and d).

Fig. 1.

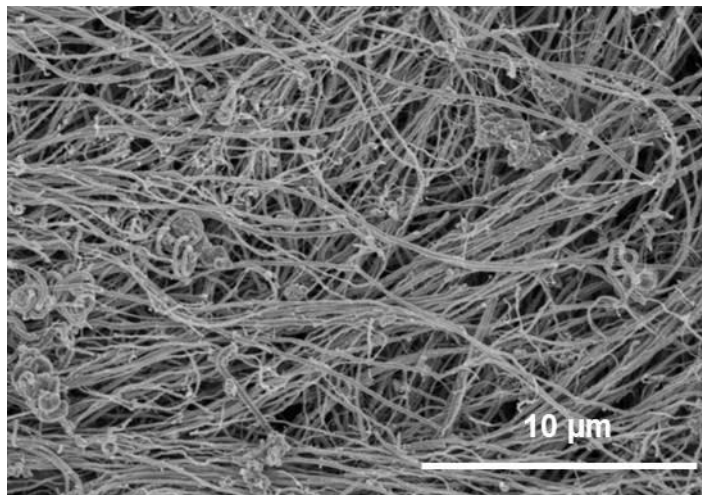


Fig. 2.

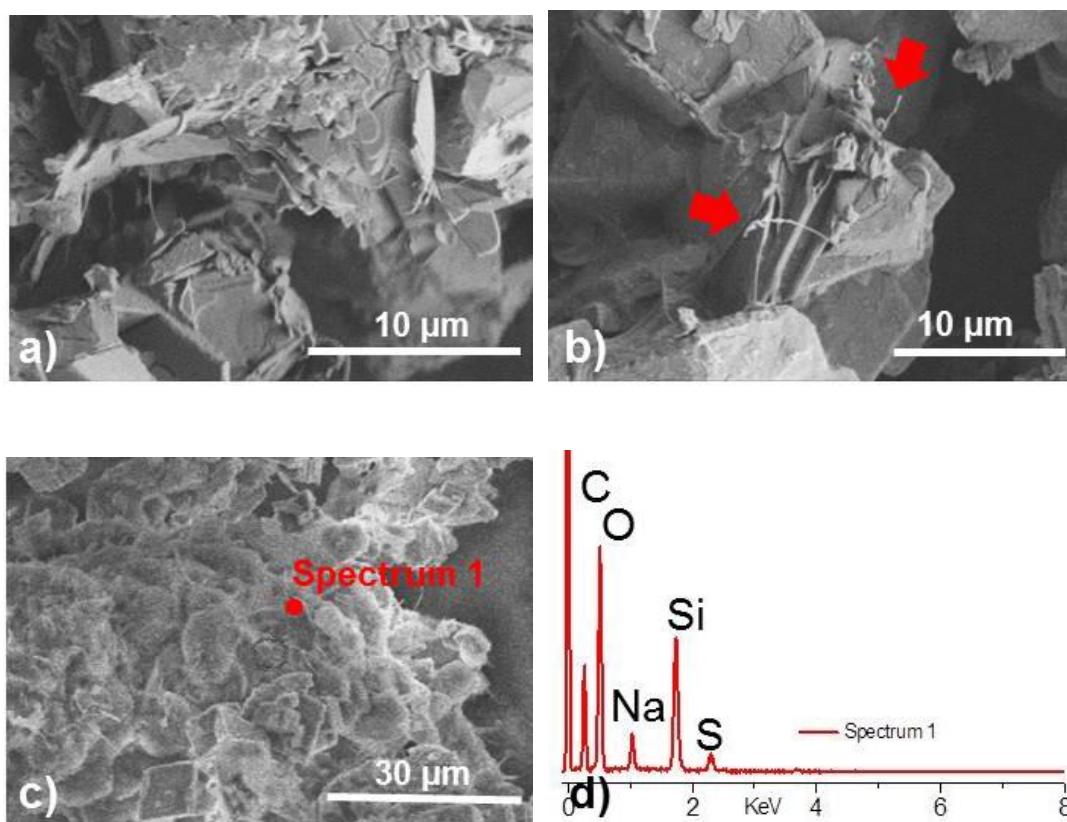


Fig. 3.

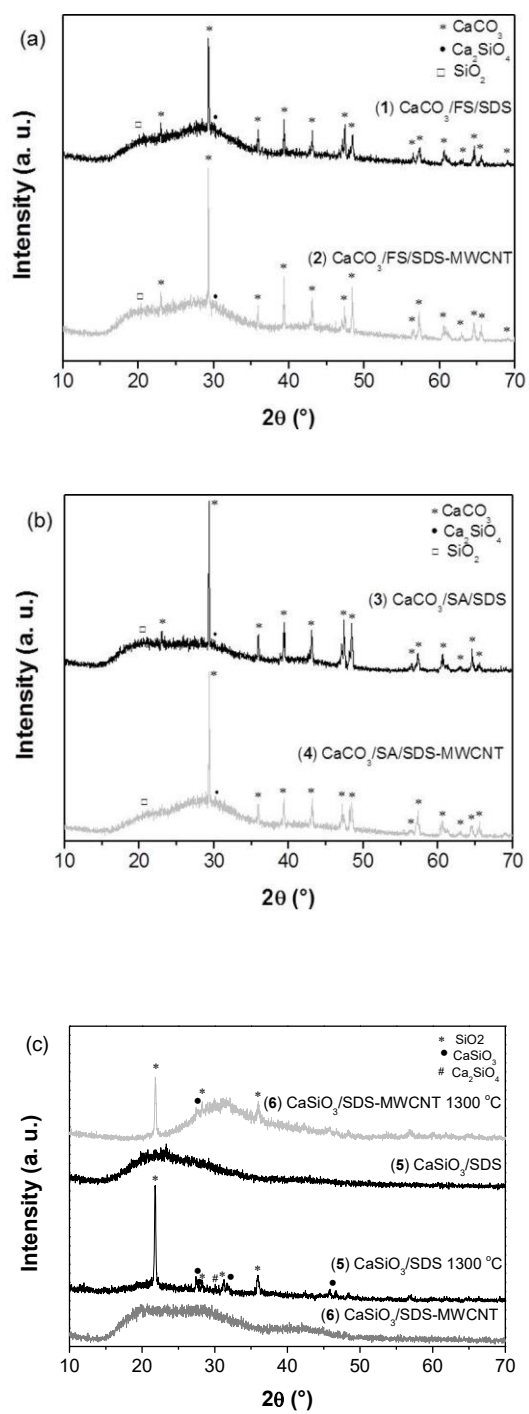


Fig. 4.

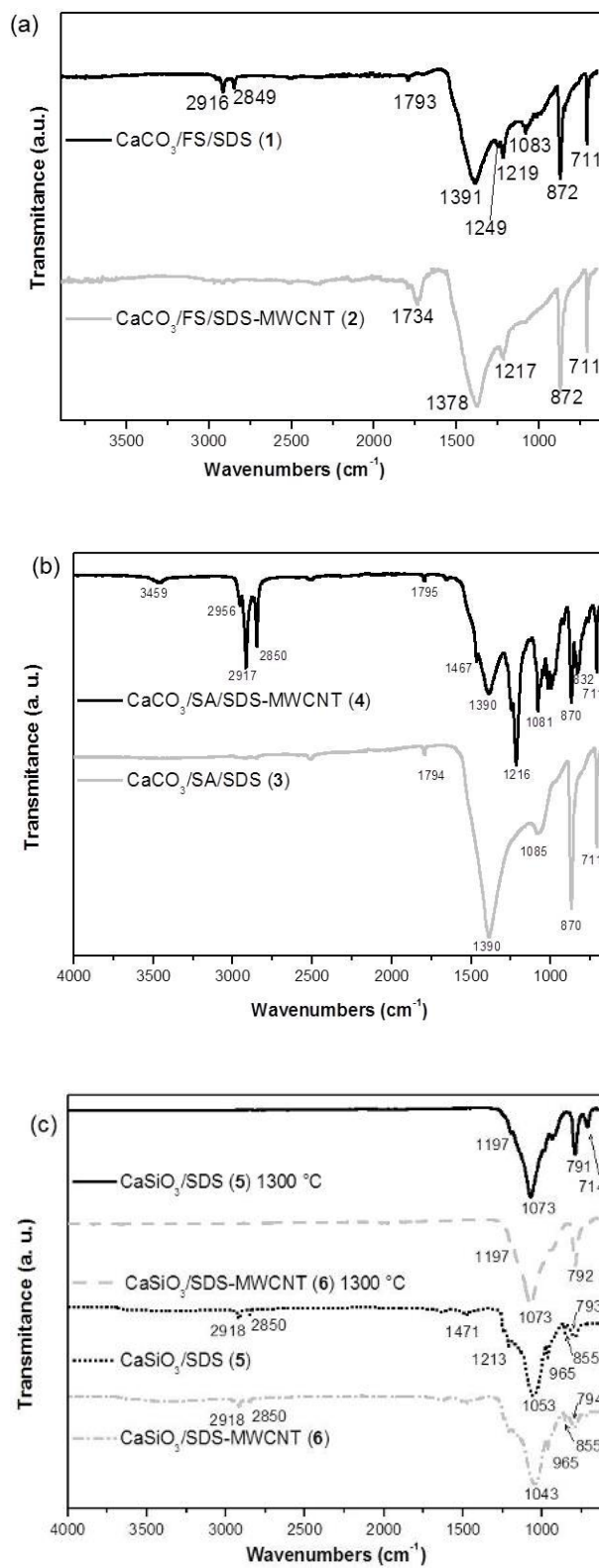


Fig. 5.

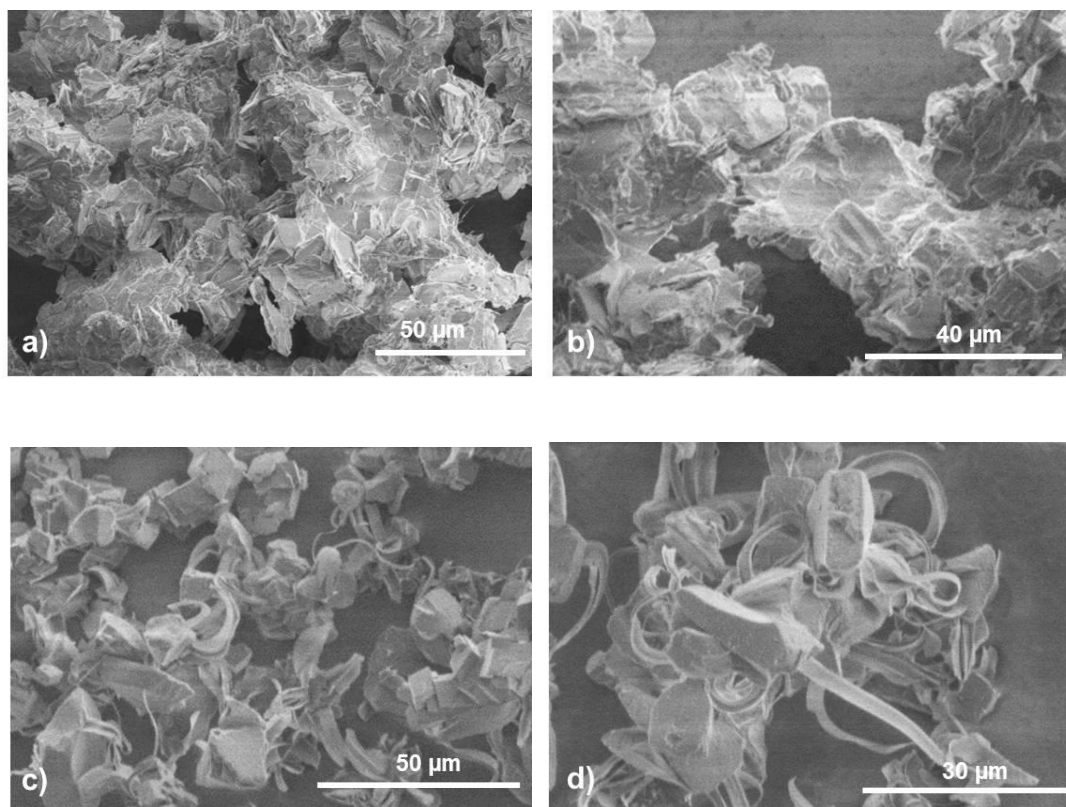


Fig. 6.

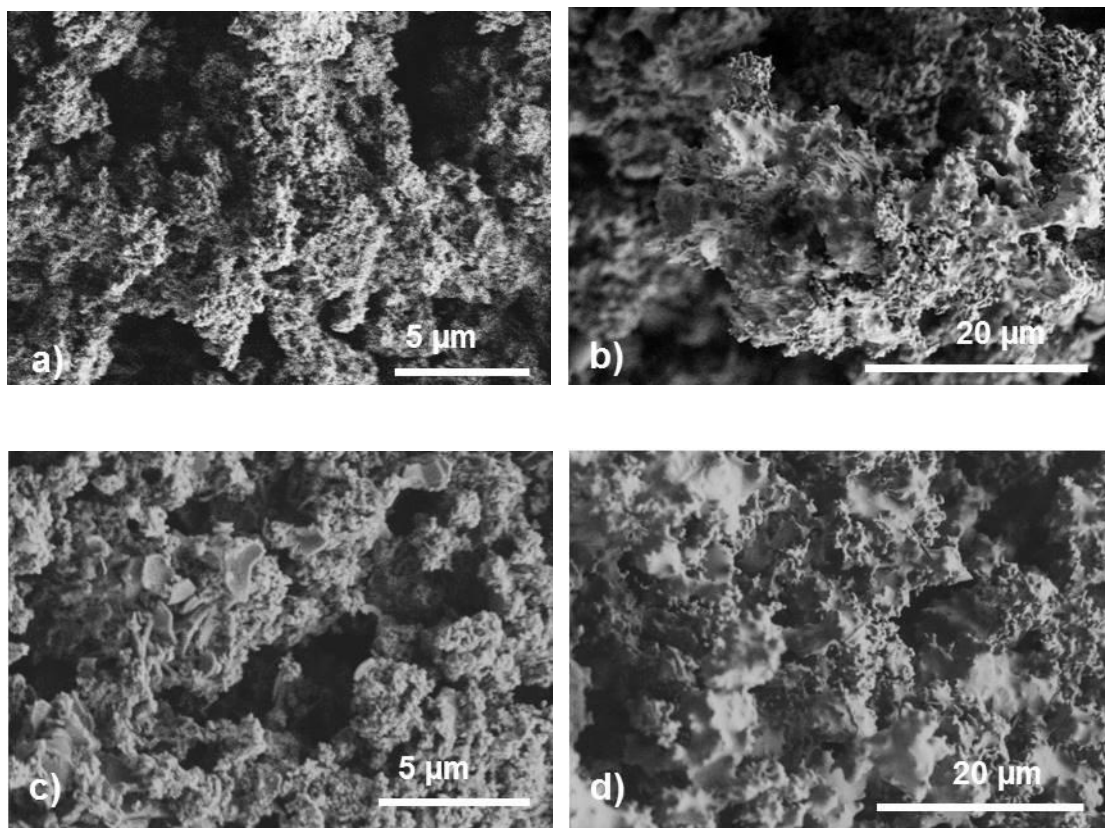


Fig. 7.

