Preparation of NaF Microcapsules for High-Temperature Thermal Storage

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ABSTRACT: A novel NaF phase change microcapsule with a carbon shell (NaF@C microcapsule) was prepared by a simple approach. The carbon shell was synthesized by carbonization of a resole-type phenolic resin shell, which was encapsulated onto the surface of NaF particles by a simple phase separation process induced by tetraethoxysilane. Scanning electron microscopy, transmission electron microscopy, X-ray diffraction, Fourier transform infrared spectroscopy, X-ray photoelectron spectroscopy, differential scanning calorimetry (DSC), and thermogravimetric analysis were used to characterize the morphology, composition, crystal phase, and thermal properties of the microcapsules. The size of the NaF@C microcapsule was 3−5 μm with a core−shell structure. DSC results showed that the melting point of the prepared NaF@C microcapsule was 988 °C, and the enthalpy value was 192 J/g. The prepared NaF@C microcapsules retained the powder morphology after 30 times of heat treatment at 1100 °C, with no NaF leakage detected, and the micromorphology remained stable, presenting good thermal stability. The NaF@C microcapsules can be used in the fields of thermal protection and thermal management in extreme high-temperature environments such as aerospace and solar energy.

1. INTRODUCTION

Energy storage technology is gaining more and more importance in recent years.1,2 As the medium of energy storage technology, phase change materials (PCMs) attract much attention because of the large amount of latent heat for energy storage and temperature control during the phase change process.3 Due to the volume stability during the phase change process and the high phase change enthalpy, solid−liquid PCMs are mainly used. Solid−liquid PCMs include organic phase change materials and inorganic phase change materials. While organic materials including paraffin, fatty acids, esters, and alcohols are mainly used for low-temperature thermal energy storage applications,4,5 inorganic materials including hydrated salts, molten salts, metals, and alloys are mainly used for high-temperature thermal energy storage applications.6,7 Compared with organic phase change materials, the inorganic salts present a higher phase change enthalpy value and better thermal conductivity.8

To avoid the melt flow caused by the solid−liquid phase change process, the PCMs must be packaged in a container. Bulk packaging, porous material adsorption, and microencapsulation are developed.9,10 Microencapsulation not only resolves problems such as solid−liquid phase change material melt flow and permeation leakage but also increases PCM stability and improves compatibility with the matrix material and can be used in energy storage, environmental temperature control, and thermal protection.11,12 There were a lot of low-temperature phase change microcapsules reported.13−16 Phase change materials (PCMs) that consisted of an n-octadecane and n-hexadecane mixture as the core were encapsulated with styrene−divinyl benzene shells by an emulsion polymerization method.13 Microencapsulated phase change materials with paraffin as the core and poly(methyl methacrylate) (PMMA) and copolymers as the shell were prepared by emulsion polymerization using redox initiators at low temperatures.14 Paraffin wax microcapsules encapsulated by polymers were also prepared by the microfluidic method and in-situ polymerization.15 Capric acid was encapsulated by graphene oxide (GO)-modified urea−formaldehyde resin by in situ polymerization.16 Compared with the low-temperature phase change microcapsules, the synthesis of high-temperature phase change microcapsules is difficult, which is subjected to the stability of the shell, such as high-temperature resistance, corrosion

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resistance, and compactness. With the great efforts of scientists, some high-temperature microcapsules have been prepared. For example, sodium phosphate dodecahydrate was encapsulated by silica with interfacial polymerization and the sol–gel method. Al–Si/Al2O3 microcapsules were prepared by the sol–gel method. Al/Al2O3 microcapsules were also prepared by a self-sacrificial oxidation method. The high-temperature microcapsule with the highest phase change temperature reported was LiF@GO@SiO2 with the phase change temperature of 848 °C. The three multiwalls were encapsulated onto the LiF particle surface layer by layer.

Besides GO mentioned in an earlier work, many carbon materials were chosen as the shell of different microcapsules due to their mechanical strength, chemical stability, and low weight. Further, compared with the traditional polymer shells, the thinner carbon shell would facilitate the energy transfer efficiency by quick thermal conductance, and the carbon shell can be used at high temperatures in the inert atmosphere. A multiform carbon nanotubes (CNTs) with GO-CNT hybrids were designed as the shell material to encapsulate long-chain alkanes. The multiform carbon nanotubes in the microspheres stabilized the capsule shell to resist volume change-induced rupture during repeated heating/cooling processes and meanwhile enhanced the thermal conductance of encapsulated alkanes which facilitated an expeditious heat exchange. CNFs were also introduced into the polyethylene ethylvinylacetate copolymer shell of microcapsules. With the addition of CNFs, both the mechanical strength and thermal conductivity of microcapsules were enhanced, and the heat storage capacity was maintained. Also, novel types of polyaniline (PANI)/carbon nanotube (CNT)-functionalized hierarchical phase change microcapsules (MEPCM-PANI/CNTs) were designed. The microcapsules showed good self-regulation capability of temperature and a high latent heat storage capacity. The addition of a carbon material to the microcapsule shell showed positive significance to the properties of the microcapsules.

In this paper, a novel NaF high-temperature phase change microcapsule with a carbon shell (NaF@C microcapsule) was prepared by a simple approach. The carbon shell was calcinated by a resole-type phenolic resin particles, which was encapsulated onto the NaF particle surface by a phase separation process, followed by an in situ curing process in the dispersion to avoid adhesion during the calcination procedure. The NaF@C microcapsule has a high phase transition temperature of 988 °C, which is much higher than that of the reported microcapsules, and good thermal stability with no leakage after 30 times of heat treatments. The successful preparation of NaF@C microcapsules improves the safety of the fluoride phase change material in use and presents a new strategy for the preparation of high-temperature phase change microcapsules.

2. MATERIALS AND METHODS

2.1. Materials. NaF, a phase change material, was provided by China Shanghai Sinopharm Chemical Reagent Co., Ltd. Phenolic resin used as a carbon source was prepared according to the literature. β-Mercaptoethylamine was provided by Shanghai Aladdin Biochemical Technology Co., Ltd., China. Anhydrous ethanol was provided by Tianjin Concord Technology Co., Ltd., Tianjin, China. Tetraethyl orthosilicate (TEOS) was provided by Shanghai Macleans Biochemical Technology Co., Ltd.

2.2. Preparation of Sodium Fluoride Microcapsules. The preparation process is shown in Figure 1. First, a resole-type phenolic resin was encapsulated onto sodium fluoride particles by solvent-induced phase separation in a beaker, followed by in situ curing of phenolic resin (NaF@PR microcapsules). Then, the above NaF@PR microcapsule powder was heated in an oven to postcure the phenolic resin shell of the microcapsule (cured NaF@PR microcapsule). Finally, carbonization was carried out in a tube furnace in argon to transfer the phenolic resin into carbon to obtain NaF@C microcapsules.

2.2.1. Preparation of NaF@PR Microcapsules. β-Mercaptoethylamine was used to chemically modify the surface of metal fluoride particles with the amino functional group, so the phenolic resin can be induced to precipitate on the surface of the particles. For non-water-soluble fluorides, such as MgF2 and LiF, water can be used as a poor solvent to induce the phase separation of phenolic resin. NaF is water-soluble, so water cannot be used. The poor solvent used to induce the phase separation of phenolic resin should be immiscible with ethanol which is the solvent of phenolic resin and does not dissolve NaF particles. TEOS was selected as the poor solvent to deposit the phenolic resin onto the NaF particles. Then, the product was heated in the mixture to in situ-cure the phenolic resin shell to avoid viscous deformation of the phenolic resin during the following heating procedure.

Typically, 0.71 g of phenolic resin dissolved in 15 g of ethanol, 0.05 g of β-mercaptoprotothyamine, and 5 g of NaF were added into a 250 mL three-necked flask and stirred at a speed of 300 rpm at room temperature for 1 h. 80 g of TEOS was dropped into the solution by a peristaltic pump. Then, the temperature was elevated to 95 °C and kept for 24 h in situ-cure the phenolic resin. NaF@PR microcapsule powder with a light yellow color was gained after filtration.

2.2.2. Preparation of Cured NaF@PR Microcapsules. Curing of the microcapsule phenolic resin shell is an important process to increase the carbon residue weight of the resin and to avoid the destruction of the microcapsule structure during the carbonization process. Briefly, NaF@PR microcapsules were placed in an oven for post-curing. The specific curing procedure was carried out from room temperature to 120 °C in 30 min and kept for 2 h at 120 °C. Then, the temperature was increased from 120 to...
140 °C in 15 min and kept for 2 h at 140 °C. Then, the temperature was increased from 140 to 160 °C in 15 min and kept for 2 h at 160 °C. Finally, the temperature was increased from 160 to 180 °C in 15 min and kept for 4 h at 180 °C.

2.2.3. Preparation of NaF@C Microcapsules. The carbon shell of the microcapsule was carbonized by the resole-type phenolic resin with high carbon residue weight. Further, the carbonization of the microcapsule shell was carried out slowly to keep the carbonized microcapsule shell continuous and complete.

Typically, cured NaF@PR microcapsules were placed in a tube furnace for high-temperature carbonization in argon atmosphere. The specific carbonization procedure was heated from room temperature to 800 °C at a speed of 1 °C/min and kept at 800 °C for 1 h in argon. Finally, the black powder of NaF@C microcapsules was obtained.

2.3. Characterization. The size and shape of the microcapsules were observed by a scanning electron microscope (Hitachi, S-4800, SEM) at a working voltage of 10KV, and the surface of the microcapsule was measured by an energy-dispersive X-ray (SEM-EDS) spectrometer attached to the SEM instrument for elemental analysis. The particle size distribution of the microcapsules was measured by a laser particle size analyzer (MS3000+MV+Avios, 402019). The surface element composition of the microcapsule sample was further determined by X-ray photoelectron spectroscopy (ESCALAB250XI, VG company, XPS). The core−shell structure of the microcapsule was observed by a transmission electron microscope (Hitachi, HT7700, TEM). The chemical structure of the microcapsule sample was observed by a Fourier transform infrared spectrometer (Brook Hong Kong Co., Ltd., TENSOR27, FT-IR) in the range of 400−4000 cm⁻¹. The crystal structure of the microcapsule sample was observed by an X-ray powder diffraction instrument (Rigaku, Japan, D/max 2500, XRD). Thermogravimetric analysis (TGA) calculated the carbon shell content of the microcapsules by using a thermogravimetric analyzer (STA 409 PC, NETZSCH, TGA) in air at a heating rate of 10 °C/min from room temperature to 800 °C. Another thermogravimetric analyzer (STA449F3, NETZSCH, TGA, Germany) was used to measure the thermal stability of the microcapsule samples under a N₂ atmosphere at a heating rate of 10 °C/min. TGA−DSC combined with a simultaneous thermal analyzer (Mettler-Toledo, Switzerland, TGA-DSC3+) was used to measure the thermal stability and latent heat storage/release behavior of the microcapsule samples at a heating rate of 10 °C/min.

3. RESULTS AND DISCUSSION

3.1. Microscopic Structure of Microcapsules. The formation of the carbon shell layer of NaF@C microcapsules underwent the following procedures. First, the phenolic resin was coated on the surface of the NaF particles and in situ-solidified at a certain temperature (NaF@PR microcapsules). Then, the phenolic resin was cured (cured NaF@PR microcapsules) and carbonized into a carbon shell at a high temperature in argon (NaF@C microcapsules). Figure 2a−d presents the images of NaF, NaF@PR microcapsules, cured NaF@PR microcapsules, and NaF@C microcapsules. As shown in Figure 2a, the white NaF particles showed an irregular geometry and a smooth surface. However, the surfaces of NaF@PR microcapsules (Figure 2b) and cured NaF@PR microcapsules (Figure 2c) had some small particles on the surface, showing a rough morphology due to the inhomogeneous phase separation of phenolic resin onto the NaF particles. The NaF@PR microcapsules (Figure 2b), cured NaF@PR microcapsules (Figure 2c), and NaF@C microcapsules (Figure 2d) presented different colors but nearly the same size and morphology. Further, the NaF@C microcapsules showed a black color due to the carbon shell of the microcapsules. The Dv(50) values of the NaF and NaF@C microcapsules in anhydrous ethanol was 4.06 and 6.28 μm, respectively (Figure S1), meaning the NaF@C microcapsules were not adhered to each other apparently.

The core−shell structure of NaF@C microcapsules was confirmed by TEM, as shown in Figure 3a. The NaF@C microcapsules dispersed in hydrous ethanol were dropped onto the grid and dried for TEM observations. The TEM image of NaF@C microcapsules showed a black, opaque, irregular pattern with a particle size of around 4 μm, which was similar to the SEM image. However, the core−shell structure could not be distinguished from the TEM image of NaF@C microcapsules. Hence, the NaF@C microcapsules were dispersed in water, ultrasonicated, and washed with water many times to remove the NaF core of the microcapsule. Hollow capsules with the comparable size of the NaF@C microcapsules were left as shown in Figure 3b, and the thickness of the shell was about 30 nm. NaF is soluble in water, and carbon is not soluble in water. Therefore, the hollow capsule can be identified to be the carbon shell of the NaF@C microcapsule. Thus, the core−shell structure of the NaF@C microcapsules can be confirmed.

The NaF@C microcapsules were heated in a tube furnace in nitrogen at 1100 °C, higher than the melting point of NaF, to investigate the thermal stability of the microcapsule. The
microcapsules after 10 (Figure 4a) and 30 (Figure 4b) times of heat treatment showed the same structure as that of the original sample, presenting good thermal stability of the carbon shell. Further, the NaF@C microcapsules retained the powder morphology, with no white NaF particle leakage detected in the sample, as shown in Figure S2, while the NaF powder was melted and all agglomerated together, indicating that the prepared NaF@C microcapsules presented a compact and stable shell which can bear the melting process of NaF.

3.2. Composition of the Microcapsules. Fourier transform infrared spectroscopy was performed to investigate the composition of microcapsule samples during the preparation process. Figure 5 shows the infrared absorption peaks of NaF, phenolic resin, NaF@PR microcapsules, cured NaF@PR microcapsules, and NaF@C microcapsules.

Figure 4. SEM images of NaF@C microcapsules after many times of heat treatment: (a) 10 times; (b) 30 times.

Figure 5. FTIR absorption spectra of NaF, phenolic resin, NaF@PR microcapsules, cured NaF@PR microcapsules, and NaF@C microcapsules.

phenolic resin, NaF@PR microcapsules, cured NaF@PR microcapsules, and NaF@C microcapsules. There were no absorption peaks of organic functional groups in the NaF infrared curve. The infrared absorption peaks of NaF@PR microcapsules and cured NaF@PR microcapsules showed the composition of phenolic resin. The characteristic absorption peak at 1650 cm\(^{-1}\) indicated C=O bond stretching vibration which was produced by high-temperature oxidation of phenolic resin during curing. The characteristic absorption peak at 1004 cm\(^{-1}\) was attributed to the hydroxymethyl C–O bond stretching vibration of the cured phenolic resin, and the characteristic absorption peak at 756 cm\(^{-1}\) was the out-of-plane bending vibration of the ortho C–H bond on the phenol ring of the phenolic resin. During the curing process, the absorption peak caused by the hydroxymethyl C–O bond at 1004 cm\(^{-1}\) decreased due to the cross-linking of phenolic resin molecules. The peaks of phenolic resin disappeared in the spectra of NaF@C microcapsules.

As shown in Figure 6, the surface elemental composition of NaF@C microcapsules was confirmed by EDS. The NaF particles presented Na and F elements, and C, F, and Na were distributed on the surface of the NaF@C microcapsules. XPS was also performed to confirm the surface elements of the NaF@C microcapsule. As shown in Figure 7, the NaF@C microcapsules showed obvious characteristic peaks of carbon element (C 1s), oxygen element (O 1s), fluorine element (F 1s), and sodium element (Na 1s). The XPS chart showed that the characteristic peaks with binding energies 284.92, 533.05, 687.3, and 1074.45 eV corresponded to the carbon element (C 1s), fluorine element (F 1s), and sodium element (Na 1s), respectively. The characteristic peak with the binding energy 508.32 eV was the partial peak of Na. The above results showed that NaF@C microcapsules were composed by Na, F, and C. Combined with the core–shell structure of the microcapsules (Figure 3), it can be deduced that the surface of NaF was covered by a carbon shell.

XRD was performed on NaF and NaF@C microcapsule samples (Figure 8). From the XRD spectrum analysis, it is observed that the characteristic peaks of NaF 2θ = 33.4, 38.8, 56.0, 66.8, and 70.2° correspond to NaF (111), (200), (220), (311), and (222) crystal planes. All the characteristic peaks of the NaF sample and the microcapsule samples were the same and consistent with the reported characteristic peaks of NaF, meaning NaF remained stable during the preparation process.

3.3. Thermal Performance of NaF@C Microcapsules. The thermal stability of NaF@C microcapsules with different contents of carbon shell was analyzed by thermogravimetry. As shown in Figure 9a, the temperature was raised to 800 °C in air atmosphere to measure the content of carbon shell. There was almost no weight loss when NaF was heated to 800 °C. The weight loss values of NaF@C microcapsules with 10, 30, and 50% weight contents of phenolic resin against NaF were 2.1, 5.8, and 12.4%, respectively, corresponding to the percentage of the carbon shell in the microcapsules.

Then, the temperature was raised to 1150 °C in nitrogen, which was higher than the melting point of NaF, to investigate the thermal stability of the microcapsules (Figure 9b). After the heat treatment, the NaF@C microcapsules with different contents of carbon shell kept stable, with no white NaF leakage detected. 2.1% content of the carbon shell kept stable, with no white NaF leakage detected. 2.1% content of the carbon shell kept stable, with no white NaF leakage detected. 2.1% content of the carbon shell kept stable, with no white NaF leakage detected. 2.1% content of the carbon shell kept stable, with no white NaF leakage detected. 2.1% content of the carbon shell kept stable, with no white NaF leakage detected. 2.1% content of the carbon shell kept stable, with no white NaF leakage detected.
Figure 6. EDS images of microcapsules: (a) NaF and (b) NaF@C microcapsules.

Figure 7. XPS spectra of NaF@C microcapsules.

Figure 8. XRD patterns of NaF, NaF@PR, cured NaF@PR, and NaF@C microcapsules.
microcapsules was 192 J/g. Figure 10b shows the typical solidification DSC curves of NaF and NaF@C microcapsules. The solidification enthalpy value of NaF was 195 J/g, and the solidification enthalpy of NaF@C microcapsules was 183 J/g. The encapsulation rate of NaF in NaF@C microcapsule can be calculated by the following formula:

$$\text{encapsulation ratio} = \frac{\Delta H_{\text{NaF@C}}}{\Delta H_{\text{NaF}}} \times 100\%$$

The NaF@C microcapsule showed an encapsulation rate as high as 89.3%. After heat treatment for many times, no leakage of white NaF particles can be detected in the sample. These above results indicated that this NaF@C microcapsule presented a high phase transition temperature, high enthalpy value, high encapsulation rate, and high thermal stability, which made it promising in use.

4. CONCLUSIONS

The NaF PCM with a high phase change temperature of 977 °C was encapsulated by a single layer of carbon shell that was calcinated from a resole-type phenolic resin shell which was prepared by a simple phase separation method. The core–shell structure of the microcapsule was precisely controlled by the coordination between the NaF particle and the phenolic shell, the curing process, and the calcination process. The 2.1% content of shell was compact enough to bear the phase change process of NaF in the microcapsule. The microcapsule presented high phase transition temperature, high enthalpy value, high encapsulation rate, and high thermal stability. This work presented a new preparation approach for PCM microcapsules with a high phase change temperature. The preparation procedure was simple and effective, which made it promising in practical applications.

■ ASSOCIATED CONTENT

* Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.2c02539.

Particle size data for sodium fluoride and microcapsules and macroscopic state of sodium fluoride and microcapsules after heating above the phase change temperature (PDF)

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Figure 9. TGA curves of NaF and NaF@C microcapsule samples with 10, 30, and 50 wt % phenolic resin in air (a) and in N₂ (b).

Figure 10. DSC curves of NaF and NaF@C microcapsules. (a) Melting process and (b) solidification process.
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Notes
The authors declare no competing financial interest.

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REFERENCES
(1) Gallo, A. B.; Simões-Moreira, J. B.; Costa, H. K. M.; Santos, M. M.; Moutinho dos Santos, E. Energy storage in the energy transition context: A technology review. Renew. Sust. Energy Rev. 2016, 65, 800–822.
(2) Su, J. F.; Wang, X. Y.; Han, S.; Zhang, X. L.; Guo, Y. D.; Wang, Y. Y.; Tan, Y. Q.; Han, N. X.; Li, W. Preparation and physicochemical properties of microcapsules containing phase-change material with graphene/organic hybrid structure shells. J. Mater. Chem. A 2017, 5, 23937–23951.
(3) Peng, G. J.; Dou, G. J.; Hu, Y. H.; Sun, Y. H.; Chen, Z. T. Phase change material (PCM) microcapsules for thermal energy storage. Adv. Polym. Technol. 2020, 2020, No. 9490873.
(4) Zhong, Y. J.; Zhao, B. C.; Lin, J.; Zhang, F.; Wang, H. R.; Zhu, Z. Y.; Dai, Z. M. Encapsulation of high-temperature inorganic phase change materials using graphite as heat transfer enhancer. Renew. Energy 2019, 133, 240–247.
(5) Liu, M.; Bell, S.; Segarra, M.; Steven Tay, N. H.; Will, G.; Saman, W.; Bruno, F. A eutectic salt high temperature phase change material: Thermal stability and corrosion of SS316 with respect to thermal cycling. Sol. Energy Mater. Sol. Cells 2017, 170, 1–7.
(6) Jiang, Y. F.; Sun, Y. P.; Bruno, F.; Li, S. Thermal stability of Na₂CO₃-Li₂CO₃ as a high temperature phase change material for thermal energy storage. Thermochim. Acta 2017, 650, 88–94.
(7) Chen, S. H.; Cheng, X. M.; Li, Y. Y.; Wang, X. L.; Zheng, H. H.; Zhong, H. Study on the microstructures and thermal properties of SiO₂@NaNO₃ microcapsule thermal storage materials. Int. J. Energy Res. 2020, 44, 10008–10022.
(8) Lin, Y. X.; Alva, G.; Fang, G. Y. Review on thermal performances and applications of thermal energy storage systems with inorganic phase change materials. Energy 2018, 165, 685–708.
(9) Wu, M.; Xu, C.; He, Y. L. Dynamic thermal performance analysis of a molten-salt packed-bed thermal energy storage system using PCM capsules. Appl. Energy 2014, 121, 184–195.
(10) Bellan, S.; Alam, T. E.; González-Aguilar, J.; Romero, M.; Rahman, M. M.; Goswami, D. Y.; Stefanakos, E. K. Numerical and experimental studies on heat transfer characteristics of thermal energy storage system packed with molten salt PCM capsules. Appl. Therm. Eng. 2015, 90, 970–979.
(11) Farid, M. M.; Khudhair, A. M.; Razack, S. A. K.; Al-Hallaj, S. A review on phase change energy storage: materials and applications. Energy Convers. Manag. 2004, 45, 1597–1615.
(12) Pielichowska, K.; Pielichowski, K. Phase change materials for thermal energy storage. Prog. Mater. Sci. 2014, 65, 67–123.
(13) Mert, M. S.; Mert, H. H.; Yilmaz Gumus, C. Preparation and characterization of paraffin microcapsules for energy-saving applications. J. Appl. Polym. Sci. 2019, 136, 47874.
(14) Xu, D.; Yang, R. Efficient preparation and characterization of paraffin-based microcapsules by emulsion polymerization. J. Appl. Polym. Sci. 2019, 136, 47552.
(15) Shi, T. J.; Hu, P.; Wang, J. T. Preparation of Polyurea Microcapsules Containing Phase Change Materials Using Microfluidics. ChemistrySelect 2020, 5, 2342–2347.
(16) Wang, X. G.; Chen, Z. F.; Xu, W.; Wang, X. J. Capric acid phase change microcapsules modified with graphene oxide for energy storage. J. Mater. Sci. 2019, 54, 14834–14844.
(17) Liu, Z. F.; Chen, Z. H.; Yu, F. Preparation and characterization of microencapsulated phase change materials containing inorganic hydrated salt with silica shell for thermal energy storage. Sol. Energy Mater. Sol. Cells 2019, 200, No. 110004.
(18) He, F.; Chao, S.; He, X. D.; Li, M. M. Inorganic microencapsulated core/shell structure of Al–Si alloy micro-particles with silane coupling agent. Ceram. Int. 2014, 40, 6866–6874.
(19) Tian, S. S.; Jiang, Y.; Si, Y.; Guan, B.; Wang, Q.; Zhao, T. Al-microcapsules with a self-sacrificial oxidation method for high-temperature thermal energy storage. ACS Omega 2022, 7, 1908–1913.
(20) Liu, J.; Li, J. F.; Luo, Z. P.; Liu, Y. B.; Liu, Z. X.; Chen, Z. C.; Ren, Y. F.; Zhu, B. L.; Wang, R. M.; Zhang, Q. Y. A novel multiwalled LiF@GO@SiO₂ microcapsule with high phase change temperature. Sol. Energy Mater. Sol. Cells 2019, 203, No. 110188.
(21) Zheng, Z. L.; Jin, J. D.; Xu, G. K.; Zou, J. L.; Wais, U.; Beckett, A.; Hell, T.; Higgins, S.; Guan, L. H.; Wang, Y.; Shchukin, D. Highly stable and conductive microcapsules for enhancement of joule heating performance. ACS Nano 2016, 10, 4695–4703.
(22) Borreguero, A. M.; Valverde, J. L.; Rodrigues, J. F.; Barber, A. H.; Cubillo, J. J.; Carmona, M. Synthesis and characterization of microcapsules containing Rubitherm®RT27 obtained by spray drying. Chem. Eng. J. 2011, 166, 384–390.
(23) Sun, Z.; Zhao, L. J.; Wan, H. X.; Liu, H.; Wu, D. Z.; Wang, X. D. Construction of polyaniline/carbon nanotubes-functionalized phase-change microcapsules for thermal management application of supercapacitors. Chem. Eng. J. 2020, 396, No. 125317.
(24) GrenierLoustalot, M. F.; Larroque, S.; Grande, D.; Grenier, P.; Bedel, D. Phenolic resins:1. Influence of catalyst type on reaction mechanisms and kinetics. Polymer 1996, 37, 1363–1369.
(25) Tian, Y.; Huang, H. M.; Xu, X. L. Curing kinetics and curing process of phenolic impregnated carbon ablator. J. Appl. Polym. Sci. 2017, 134, 45434.