

Cite this: *RSC Adv.*, 2017, 7, 7857

Preparation and characterization of spherical β -cyclodextrin/urea–formaldehyde microcapsules modified by nano-titanium oxide

Xin Yu,^{ab} Houjuan Qi,^a Zhanhua Huang,^{*a} Bin Zhang^a and Shouxin Liu^a

We successfully prepared novel β -cyclodextrin/urea–formaldehyde (β -CD/UF) microcapsules modified by nano-TiO₂ using KH560 silane coupling agent by *in situ* polymerization and grafting method. The as-prepared TiO₂– β -CD/UF microcapsules displayed excellent energy storage properties with a melting enthalpy of 154.6 J g^{−1}, and the paraffin content in the TiO₂– β -CD/UF microcapsules was as high as 75.94%, indicating a high energy storage capacity. Nano-titanium oxide was successfully reacted onto the surface of the β -CD/UF microcapsules using KH560 by forming new C–O–Si and Ti–O–Si chemical bonds, which was confirmed by FT-IR and XPS technology. Besides, pH played an important role in the encapsulation of phase change paraffin by affecting the curing reaction rate of the shell materials. Also, the thermal decomposition temperature of the TiO₂– β -CD/UF microcapsules was highly improved by about 90 °C compared with that of β -CD/UF microcapsules without treatment by TiO₂ nanoparticles, mainly due to the formation of C–O–Si and Ti–O–Si chemical bonds. The as-prepared TiO₂– β -CD/UF microcapsules in this experiment might be used as an effective and potential media for energy storage.

Received 7th December 2016

Accepted 16th January 2017

DOI: 10.1039/c6ra27895g

www.rsc.org/advances

Introduction

Studies on phase change materials (PCMs) are attracting more attentions nowadays because of their potential application in buildings, textiles and thermoelectric materials.^{1–5} In general, PCMs are highly expected to release or store latent energy during the physical phase transition process yet leaving no pollution in the ambient environment.⁶ Thus, it is very intriguing to explore the stable and high enthalpy PCMs. Besides, highly desired PCMs should have some other excellent properties, such as repeated usage and being environmentally friendly.^{7–9} It would be profitable to explore suitable PCMs and effective encapsulation technology for fabricating phase change storage materials. Phase change microcapsules are an important type of PCMs, which could offer an enclosed space, much like containers, to restrict the flow ability of the encapsulated materials, such as paraffin, *n*-heptadecane and epoxy resins.^{4,10–12} Until now, there are many methods for preparing phase change microcapsules for energy storage, such as *in situ* polymerization,¹³ interfacial polymerization,¹⁴ sol–gel method,¹⁵ and *etc.* However, many PCMs always suffered from some disadvantages, such as the poor strength property, low encapsulation efficiency and low decomposition temperatures.^{5,16–18}

And some formaldehyde-contained resin-based PCMs did great harm to the ambient environment by releasing toxic gas. Generally, some organic or inorganic materials, such as cellulose, melamine, titanium oxide or silicon dioxide, could be used for decreasing the existence of free formaldehyde and enhancing the strength of the shell materials for high encapsulation efficiency.^{19–21} And thus, nano-titanium oxide and β -cyclodextrin modified urea–formaldehyde paraffin microcapsules are highly expected to have high encapsulation efficiency and little formaldehyde releasing property.

In this work, inorganic TiO₂ nanoparticles were used to modify the spherical β -CD/UF paraffin microcapsules by grafting method using KH560 silane coupling agent to enhance the strength of the TiO₂– β -CD/UF microcapsules and decrease the free formaldehyde in the shell materials. Besides, the influences of nano-TiO₂ and pH on the melting enthalpy and thermal stability of the TiO₂– β -CD/UF microcapsules were investigated by DSC and TGA instruments in detail. Besides, the possible formation procedures of the spherical TiO₂– β -CD/UF microcapsules were also proposed in the Experimental section.

Experimental

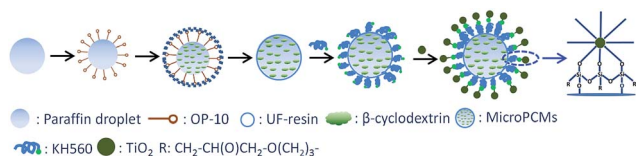
Preparation of TiO₂– β -CD/UF microcapsules

All the raw materials were commercially available and used directly without further purification in this experiment. In a typical procedure, 2.5 g urea, 6.24 mL formaldehyde (37 wt%) and deionized water were mixed with pH adjusted to ~8–9 by triethanolamine. The mixture was heated to ~70 °C for 60 min

^aKey Laboratory of Bio-based Material Science and Technology of Ministry of Education, Northeast Forestry University, Harbin 150040, China. E-mail: nefuhzh@nefu.cn

^bSchool of Chemistry and Chemical Engineering, Harbin Institute of Technology, Harbin 150001, P. R. China





Scheme 1 The schematic illustration of the formation of TiO_2 -β-CD/UF microcapsules.

with stirring, and then β-cyclodextrin was added into the mixture and stirred to form β-CD-UF solution.

OP-10, paraffin, deionized water and cyclohexane were mixed by stirring to form oil/water emulsion for ~15 min. β-CD-UF solution, ammonium chloride and resorcin were added into the paraffin dispersion by dropping and heated to ~50–60 °C with stirring for ~55 min. The nano- TiO_2 treated by KH560 was added into the reaction system and reacted for 120 min.²² The as-prepared TiO_2 -β-CD/UF microcapsules were cooled down, washed with deionized water, dried for 48 h. The samples with the dosage of 0%, 2.5%, 5%, 7.5% and 10% (TiO_2 to micro PCMs) were denoted as A0, A1, A2, A3, A4, and A5, respectively. Scheme 1 showed the schematic illustration of the formation of spherical TiO_2 -β-CD/UF microcapsules in this experiment.

Characterization

The morphology of the as-prepared TiO_2 -β-CD/UF microcapsules was investigated using FEI QUANTA 200 scanning electronic microscope (SEM) (USA) and JEM-2100 transmission electron microscope (TEM) (Japan) at 200 kV. The chemical structures and element states of the TiO_2 -β-CD/UF microcapsules were studied on a Thermo Fisher Nicolet 6700 FT-IR spectrometer (USA) and a K-Alpha X-ray photoelectron spectrometer (Thermo fisher Scientific Company, USA). The crystal structure of the TiO_2 -β-CD/UF microcapsules was studied by a Japanese Rigaku D/MAX 2200 X-ray diffractometer (XRD) (Japan). The melting enthalpy and the thermal stability were studied on a TA Q20 differential scanning calorimeter (DSC) by a heating rate of 5 °C min⁻¹ from 10 °C to 65 °C and TA Q50 thermogravimetric analyzer (TGA) (USA) in the nitrogen

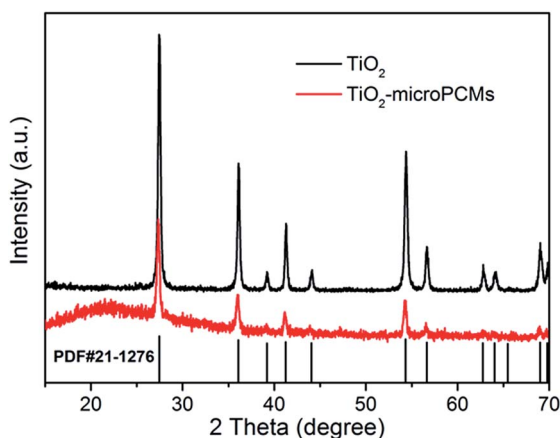


Fig. 1 XRD patterns of TiO_2 and TiO_2 -β-CD/UF microcapsules.

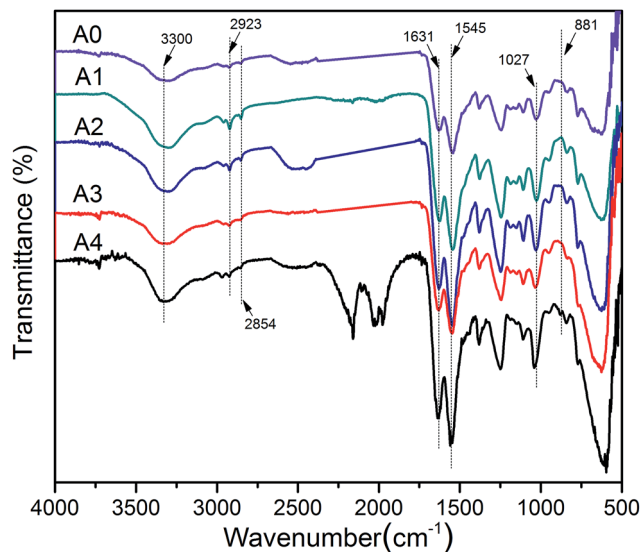


Fig. 2 FT-IR spectra of the TiO_2 -β-CD/UF microcapsules.

atmosphere. The content of the paraffin could be measured according to the following equation based on the melting enthalpy measured by DSC instrument,

$$\text{Paraffin (\%)} = \frac{\Delta H}{\Delta H_0} \times 100\% \quad (1)$$

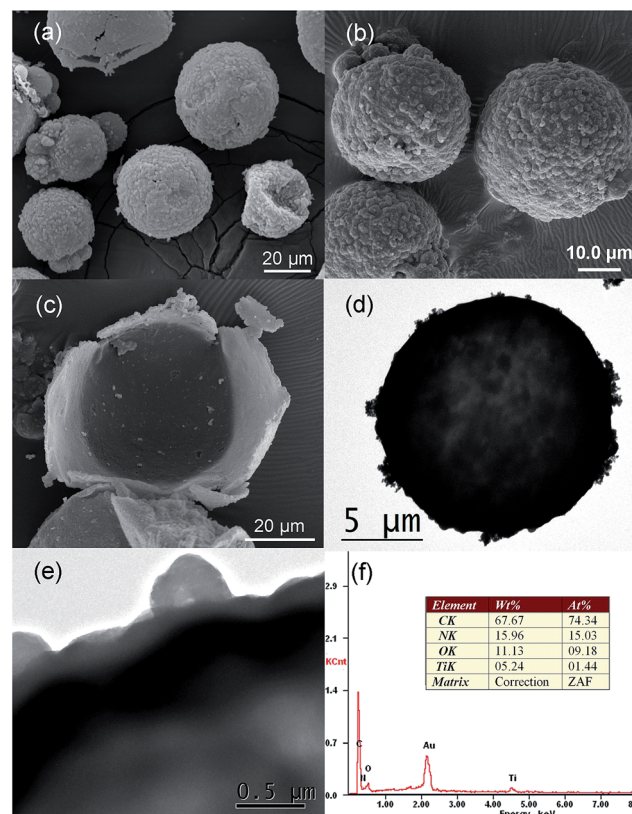


Fig. 3 Typical SEM images (a–c), TEM images (d and e) and the EDS spectrum (f) of the as-prepared TiO_2 -β-CD/UF microcapsules.



where paraffin (%) is the content of paraffin within the PCMs, ΔH is melting enthalpy of the micro PCMs, and ΔH_0 is melting enthalpy of phase change paraffin.^{23–25}

Results and discussion

Fig. 1 showed the XRD patterns of the purchased rutile TiO_2 and TiO_2 - β -CD/UF microcapsules. The as-prepared TiO_2 - β -CD/UF microcapsules displayed several distinct characteristic diffraction peaks around at 27.45° , 36.09° , 39.19° , 41.23° , 44.05° , 54.32° , 56.64° , 62.74° , 64.04° and 69.01° , which could be assigned to the (110), (101), (200), (111), (210), (211), (220), (002), (310) and (301) planes of the rutile TiO_2 (JCPDS no. 21-1276), respectively. That is, rutile nano- TiO_2 was successfully reacted onto the surface of the β -CD/UF microcapsules by forming new Ti-O-Si chemical bond using KH560 silane coupling agent, which was much like the surface modification of $\text{NdFe}_{12}\text{N}_x$ or quartz sand by KH550 silane coupling agent.^{26,27} The XRD patterns of TiO_2 - β -CD/UF microcapsules showed no other characteristic diffraction except that of nano- TiO_2 , which

confirmed the poor crystallinity of the β -CD/UF microcapsules phase change material without loading nano- TiO_2 particles.

FT-IR spectra of the β -CD/UF microcapsules and TiO_2 - β -CD/UF microcapsules phase change materials are shown in Fig. 2. The spectra of A0, A1, A2, A3 and A4 samples showed a strong, broad absorption band at $\sim 3300\text{ cm}^{-1}$, which was assigned to the -OH stretching vibrations of cyclodextrin and absorbed water molecule.^{28,29} The peaks at 2923 cm^{-1} and 2854 cm^{-1} corresponded to the asymmetric and symmetric $-\text{CH}_2$ stretching vibration,^{17,30} and the peaks of samples A1, A2, A3 and A4 were stronger than that of A0, presumably due to the formation of $-\text{CH}_2$ after cross-linking reaction between β -cyclodextrin and UF pre-polymer.³¹ The absorption peak at 1631 cm^{-1} and 1545 cm^{-1} were attributed to the C-O stretching vibration and C-N stretching vibration.²⁹ The peak at 1027 cm^{-1} corresponded to C-O-C stretching with an increase of the peak intensity accompanied by the amount increase of β -cyclodextrin.^{32,33} The peak at 881 cm^{-1} might be corresponded to Ti-O-Ti stretching vibration. Comparing with samples A0 and A1, A2, A3, A4, we could conclude that TiO_2 - β -CD/UF microcapsules were

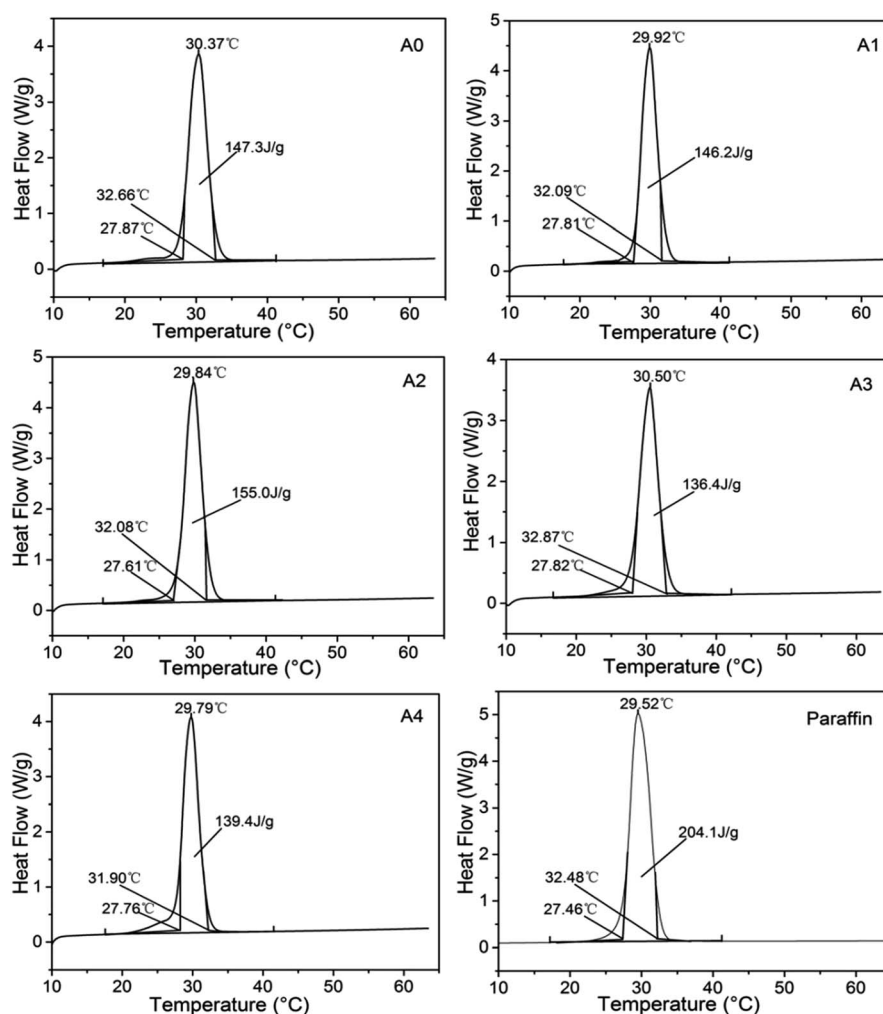


Fig. 4 The DSC curves of paraffin and TiO_2 - β -CD/UF microcapsules.



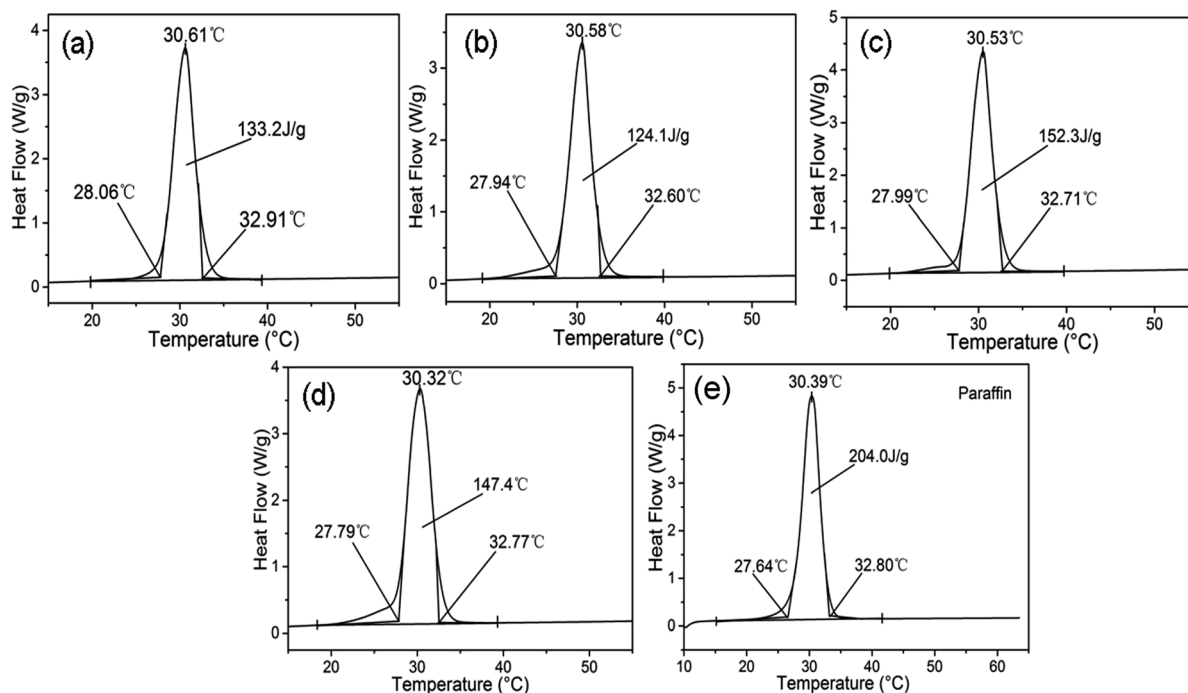


Fig. 5 Effect of pH on the melting enthalpy of the TiO_2 - β -CD/UF microcapsules: (a) 2.5, (b) 3.0, (c) 3.5, (d) 4.0.

successfully fabricated by forming new Ti-O-Si chemical bond using KH560 silane coupling agent.

Fig. 3 showed the SEM images (a-c), TEM images (d and e) and the energy spectrum (f) of TiO_2 - β -CD/UF microcapsules. As seen in Fig. 3(a) and (b), the as-prepared TiO_2 - β -CD/UF microcapsules were spherical with relatively high dispersion yet non-uniform particle size, whose morphology was much like the encapsulated phase change materials reported in the literatures.^{29,34} And the surfaces of TiO_2 - β -CD/UF microcapsules were not smooth, mainly because of the modification by nano- TiO_2 . The broken microcapsules displayed in Fig. 3(c) clearly revealed the typical core-shell structure of TiO_2 - β -CD/UF microcapsules, which offered a fixed container for the encapsulation of paraffin, and the paraffin was confined in the TiO_2 -cyclodextrin/UF microcapsules with weak flowability,³⁵ which might greatly influence the melting temperatures of the as-prepared TiO_2 - β -CD/UF microcapsules phase change material.³⁶ Fig. 3(d) and (e) showed the TEM images of TiO_2 -

cyclodextrin/UF microcapsules, which were the core-shell structure and filled with paraffin. The surface of the as-prepared sample was not smooth, which was consistent with SEM result. As shown in Fig. 3(f), the as-prepared TiO_2 - β -CD/UF microcapsules were composed of C, N, O and Ti elements, which also indicated that TiO_2 - β -CD/UF microcapsules were successfully prepared in this experiment.

The DSC curves of the TiO_2 - β -CD/UF microcapsules with different dosage of nano- TiO_2 were shown in Fig. 4. The melting temperature and enthalpy of phase change paraffin are 29.52 °C and 204.1 J g⁻¹. The melting temperatures of the samples A0, A1, A2, A3 and A4 were 30.37 °C, 29.92 °C, 29.84 °C, 30.50 °C and 29.79 °C, and the melting enthalpy of samples A0, A1, A2, A3 and A4 were 147.3 J g⁻¹, 146.2 J g⁻¹, 155.0 J g⁻¹, 136.4 J g⁻¹ and 139.4 J g⁻¹, respectively. The melting enthalpy of the TiO_2 - β -CD/UF microcapsules in this experiment was much higher than those of phase change materials in the literatures.^{37,38} The melting enthalpy of sample A2 was higher than those of

Table 1 Recent studies on phase change materials for energy storage

Energy storage materials (ESMs)	ΔH_{ESMs} (J g ⁻¹)	ΔH_{PCMs} (J g ⁻¹)	PCMs	References (year)
CMC-MF/paraffin	83.46	135.8	Paraffin	(2013) ²⁹
PMMA/ <i>n</i> -octacosane	86.4	201.6	<i>n</i> -Octacosane	(2009) ¹¹
SiO_xR_y / <i>n</i> -octadecane	107.5	209.7	<i>n</i> -Octadecane	(2015) ¹⁷
PMMA/eicosane	84.2	242.8	Eicosane	(2011) ³⁴
PMMA- SiO_2 paraffin	71	121	Paraffin	(2015) ¹⁹
PMMA/ <i>n</i> -dodecanol	98.8	248	<i>n</i> -Dodecanol	(2012) ³⁵
PMMA/C-SEM	116.25	176.68	Capric-stearic acid	(2015) ⁴⁴
PS/fatty acid	87–98	180–192	Fatty acid	(2014) ⁴⁵
OPP/SA	111	189.36	Stearic acid	(2015) ⁴⁶
TiO_2 -micro-PCMs	155.0	204.10	Paraffin	This work



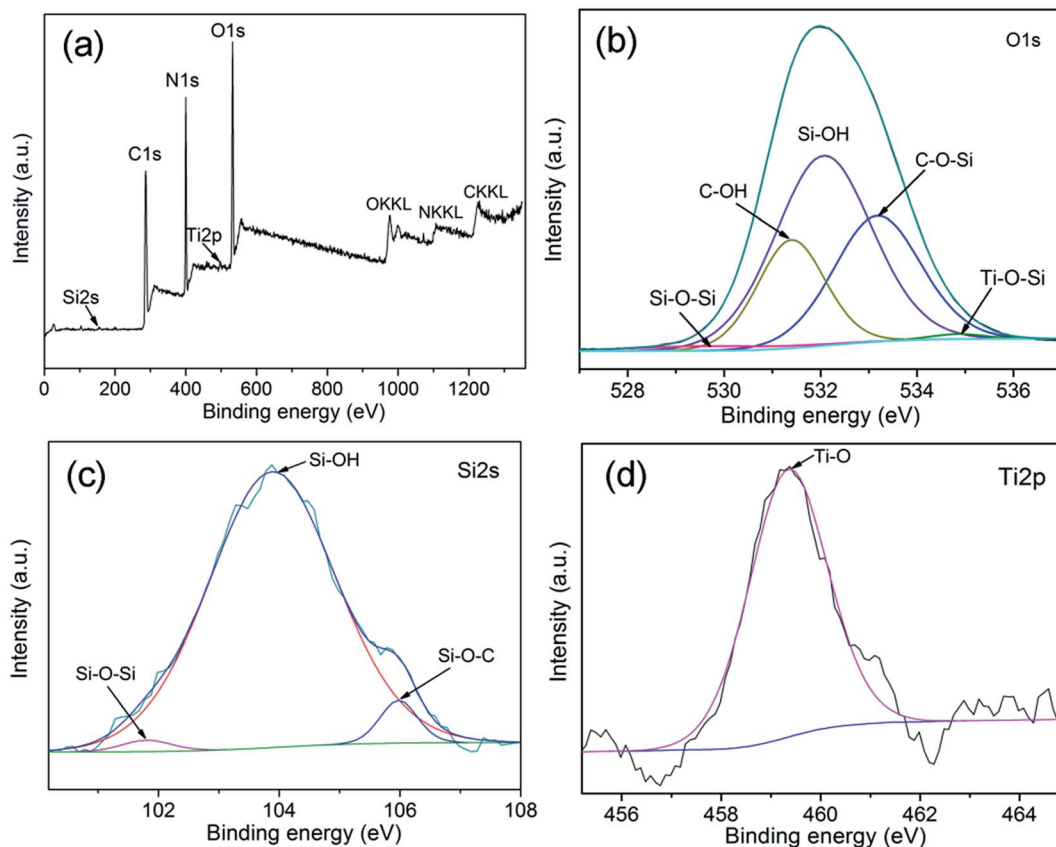


Fig. 6 XPS spectra of the TiO_2 - β -CD/UF microcapsules: (a) survey, (b) O1s, (c) Si2p and (d) Ti2p.

samples A1, A3, and A4, probably because of nano- TiO_2 and β -cyclodextrin increasing the encapsulation efficiency of urea-formaldehyde resin. The sample A2 displayed only one endothermic peak, and the melting temperature was at about 29.84 °C. In general, the phase change paraffin gradually became disordered rotator phase during the heating process, yet no new chemical bonds formation between β -CD/UF resin and paraffin, much like microencapsulated paraffin@ SiO_2 phase change composite.³⁶ However, when the dosage of nano- TiO_2 exceeded 7.5%, the encapsulation of phase change paraffin was affected, resulting in the decline of the melting enthalpy for samples A3 and A4. The possible reason was that nano- TiO_2 was in favor for increasing the strength of the microcapsules and the degree of cross-linking reaction to reduce free-formaldehyde concentration yet detrimental for the curing reaction rate, as depicted in the samples A3 and A4. And the content of paraffin in the microcapsules could reach as high as ~75.94% according to melting enthalpy of TiO_2 - β -CD/UF microcapsules compared with that of paraffin (eqn (1)) by DSC measurement, indicating the as-prepared TiO_2 - β -CD/UF microcapsules was a promising and effective energy storage media.^{39,40}

We also investigated the effects of pH on the encapsulation of paraffin within the TiO_2 - β -CD/UF microcapsules by evaluating the melting enthalpy of the as-prepared TiO_2 - β -CD/UF microcapsules. As shown in Fig. 5, the TiO_2 - β -CD/UF microcapsules showed the similar endothermic peaks during the

solid-liquid melting process. The melting temperatures of samples (a), (b), (c) and (d) were 30.61 °C, 30.58 °C, 30.53, and 30.32 °C, which was very close to that of pure paraffin.^{27,41,42} The enthalpy of samples (a), (b), (c) and (d) were 133.2 J g⁻¹, 124.1 J g⁻¹, 152.3 J g⁻¹ and 147.4 J g⁻¹, which were much lower than that of pure phase change paraffin (204.0 J g⁻¹), yet higher than those of PCMs in the Table 1, showing its great advantages of the as-prepared TiO_2 - β -CD/UF microcapsules. As seen in Fig. 5,

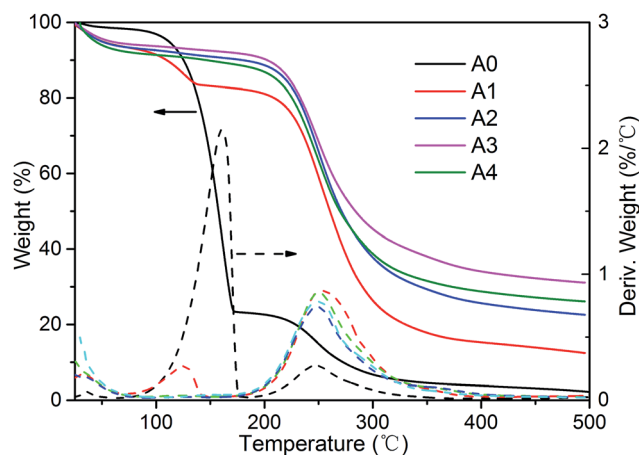


Fig. 7 TGA and TGA curves of the β -CD/UF microcapsules and TiO_2 - β -CD/UF microcapsules.



when pH exceeded 3.0, the melting enthalpy of the samples (c) and (d) were much higher than those of the samples (a) and (b), presumably mainly due to the suitable curing reaction rate of the β -CD/UF resin and high encapsulation efficiency. And thus, pH played an important role in forming the core-shell micro-encapsulation phase change materials.^{13,29,33,43} Besides, the content of paraffin in the TiO_2 - β -CD/UF microcapsules could reach up to 74.66%, which also indicated the TiO_2 - β -CD/UF microcapsules might be used in energy regulating field.

We also investigated the chemical composition and element states of the TiO_2 - β -CD/UF microcapsules by XPS technology. As shown in Fig. 6(a), the as-prepared TiO_2 - β -CD/UF microcapsules were composed of C, N, O, Si and Ti elements. Fig. 6(b) displayed the O1s XPS spectra of TiO_2 - β -CD/UF microcapsules. The fitting peaks of O1s spectra at 529.89 eV, 531.45 eV, 532.09 eV, 533.24 eV and 534.95 eV were assigned to oxygen atoms in the Si-O-Si, C-OH, Si-OH, C-O-Si and Ti-O-Si chemical bonds,³⁰ further confirming the formation of C-O-Si and Ti-O-Si chemical bonds. We might conclude that nano- TiO_2 successfully reacted onto the surface of the β -CD/UF microcapsules using KH560 by forming C-O-Si and Ti-O-Si chemical bonds.^{30,47} The peaks of Si2p spectra at 101.83 eV, 103.89 eV and 105.99 eV were assigned to silicon atoms in the Si-O-Si, Si-OH and Si-O-C chemical bonds.^{27,30,48–50} The peak of Ti2p spectra at 459.33 eV corresponded to titanium atoms in the Ti-O-Ti chemical bond,⁵¹ which was consistent with XRD and FT-IR results. It could be concluded that the TiO_2 - β -CD/UF microcapsules were successfully fabricated by forming C-Si-O and Si-O-Ti chemical bonds using KH560 silane coupling agent.

TGA and DTG curves of the β -CD/UF microcapsules and TiO_2 - β -CD/UF microcapsules with different dosage of TiO_2 were displayed in Fig. 7. The β -CD/UF microcapsules without TiO_2 treatment lost its weight rapidly with two decomposition process from room temperature to 500 °C, as was shown in the DTG curves of the sample A0. When the dosage of TiO_2 was 2.5%, the DTG curve of the sample A1 had a similar DTG curve with two decomposition process, which indicated the A0 and A1 samples had similar decomposition process. However, when the dosage of TiO_2 reached 5%, the TGA curves of the A2 sample had a different decomposition process compared with the samples A0 and A1, which indicated that the content of Si-O-Ti chemical bond increased markedly with the increase of nano- TiO_2 , which greatly changed the decomposition process of the TiO_2 - β -CD/UF microcapsules phase change material.^{52,53} The thermal decomposition temperatures of the samples A0, A1, A2, A3 and A4 were ~ 131.14 °C, 224.77 °C, 220.66 °C, 223.38 °C and 219.49 °C, respectively. It could be speculated that the increase of the thermal decomposition temperatures of TiO_2 - β -CD/UF microcapsules were mainly due to the formation of the new Si-O-Ti chemical bond, which was also in good consistent of the XRD and XPS results.

Conclusions

We successfully prepared a series of novel TiO_2 - β -CD/UF microcapsules by *in situ* polymerization and grafting reaction

using KH560 silane coupling agent. The results showed that nano- TiO_2 successfully reacted on the surface of the β -CD/UF microcapsules by forming C-O-Si and Ti-O-Si chemical bonds, which highly enhanced the decomposition temperature of TiO_2 - β -CD/UF microcapsules by about 90 °C, showing great advantages compared with that of the β -CD/UF microcapsules. The melting enthalpy of the TiO_2 - β -CD/UF microcapsules could reach up to 154.6 J g^{-1} and the paraffin content in the TiO_2 - β -CD/UF microcapsules was up to 75.94% according to the melting enthalpy measured by DSC instrument. Besides, pH also had great influences on the curing reaction rate in the formation of spherical TiO_2 - β -CD/UF microcapsules, directly affecting the melting enthalpy of the TiO_2 - β -CD/UF microcapsules. The as-prepared TiO_2 - β -CD/UF microcapsules in this experiment might be used an effective energy regulating media for solar energy conversion.

Acknowledgements

The authors would like to thank the National Natural Science Foundation of China (No. 31670592); the Central University Basic Scientific Research Project of China (No. 2572017EB03); and the Research Funds for the Returned People of Heilongjiang Province (No. LC2016008).

Notes and references

- 1 D. Lencer, M. Salina, B. Grabowski, T. Hickel, J. Neugebauer and M. Wuttig, *Nat. Mater.*, 2008, **7**, 972–977.
- 2 Y. Konuklu, M. Ostry, H. O. Paksoy and P. Charvat, *Energy and Buildings*, 2015, **106**, 134–155.
- 3 A. Jamekhorshid, S. M. Sadrameli and M. Farid, *Renewable Sustainable Energy Rev.*, 2014, **31**, 531–542.
- 4 A. Sari, C. Alkan and A. Karaipekli, *Appl. Energy*, 2010, **87**, 1529–1534.
- 5 S. Mondal, *Appl. Therm. Eng.*, 2008, **28**, 1536–1550.
- 6 M. M. Farid, A. M. Khudhair, S. A. K. Razack and S. Al-Hallaj, *Energy Convers. Manage.*, 2004, **45**, 1597–1615.
- 7 D. Zhou, C. Y. Zhao and Y. Tian, *Appl. Energy*, 2012, **92**, 593–605.
- 8 T. Do, Y. G. Ko, Y. Chun and U. S. Choi, *ACS Sustainable Chem. Eng.*, 2015, **3**, 2874–2881.
- 9 S. Wi, J. Seo, S.-G. Jeong, S. J. Chang, Y. Kang and S. Kim, *Sol. Energy Mater. Sol. Cells*, 2015, **143**, 168–173.
- 10 B. Xie, G. Liu, S. Jiang, Y. Zhao and D. Wang, *J. Phys. Chem. B*, 2008, **112**, 13310–13315.
- 11 A. Sari, C. Alkan, A. Karaipekli and O. Uzun, *Sol. Energy*, 2009, **83**, 1757–1763.
- 12 L. Yuan, G.-Z. Liang, J.-Q. Xie, J. Guo and L. Li, *Polym. Degrad. Stab.*, 2006, **91**, 2300–2306.
- 13 M. Zuo, T. Liu, J. Han, Y. Tang, F. Yao, Y. Yuan and Z. Qian, *Chem. Eng. J.*, 2014, **249**, 27–33.
- 14 J. S. Cho, A. Kwon and C. G. Cho, *Colloid Polym. Sci.*, 2002, **280**, 260–266.
- 15 S. T. Latibari, M. Mehrli, M. Mehrli, A. B. M. Afifi, T. M. I. Mahlia, A. R. Akhiani and H. S. C. Metselaar, *Energy*, 2015, **85**, 635–644.



- 16 Q.-x. Zhang, J.-h. Chen, H.-b. Lu, W. Tang, Y. Lu and Y.-z. Gao, *Acta Polym. Sin.*, 2015, 692–698.
- 17 Y. Zhu, S. Liang, K. Chen, X. Gao, P. Chang, C. Tian, J. Wang and Y. Huang, *Energy Convers. Manage.*, 2015, **105**, 908–917.
- 18 S.-s. Chen, J. Hu, L. Gao, Y. Zhou, S.-m. Peng, J.-l. He and Z.-m. Dang, *RSC Adv.*, 2016, **6**, 33599–33605.
- 19 J. Shi, X. Wu, X. Fu and R. Sun, *Thermochim. Acta*, 2015, **617**, 90–94.
- 20 Y. Konuklu, H. O. Paksoy and M. Unal, *Appl. Energy*, 2015, **150**, 335–340.
- 21 F. He, X. Wang and D. Wu, *Energy*, 2014, **67**, 223–233.
- 22 M. Xu, S. Lin, S. Gong and Z. Yang, *Adv. Mater. Res.*, 2012, **399–401**, 688–692.
- 23 K. Tumirah, M. Z. Hussein, Z. Zulkarnain and R. Rafeadah, *Energy*, 2014, **66**, 881–890.
- 24 Y. Konuklu, H. O. Paksoy, M. Unal and S. Konuklu, *Energy Convers. Manage.*, 2014, **80**, 382–390.
- 25 A. Sari, C. Alkan and C. Bilgin, *Appl. Energy*, 2014, **136**, 217–227.
- 26 H. Chen, J. Zheng, L. Qiao, Y. Ying, L. Jiang and S. Che, *Adv. Powder Technol.*, 2015, **26**, 618–621.
- 27 B. Wei, Q. Chang, C. Bao, L. Dai, G. Zhang and F. Wu, *Colloids Surf., A*, 2013, **434**, 276–280.
- 28 B. Tang, L. Wang, Y. Xu, J. Xiu and S. Zhang, *Sol. Energy Mater. Sol. Cells*, 2016, **144**, 1–6.
- 29 X. Hu, Z. Huang, X. Yu and B. Li, *BioEnergy Res.*, 2013, **6**, 1135–1141.
- 30 H. Li, R. Wang, H. Hu and W. Liu, *Appl. Surf. Sci.*, 2008, **255**, 1894–1900.
- 31 R. Qin, G. Xu, L. Guo, Y. Jiang and R. Ding, *Mater. Chem. Phys.*, 2012, **136**, 737–743.
- 32 G. Fang, Z. Chen and H. Li, *Chem. Eng. J.*, 2010, **163**, 154–159.
- 33 L. Yuan, G. Liang, J. Xie, L. Li and J. Guo, *Polymer*, 2006, **47**, 5338–5349.
- 34 C. Alkan, A. Sari and A. Karaipikli, *Energy Convers. Manage.*, 2011, **52**, 687–692.
- 35 Z.-H. Chen, F. Yu, X.-R. Zeng and Z.-G. Zhang, *Appl. Energy*, 2012, **91**, 7–12.
- 36 B. Li, T. Liu, L. Hu, Y. Wang and L. Gao, *ACS Sustainable Chem. Eng.*, 2013, **1**, 374–380.
- 37 S. Karaman, A. Karaipikli, A. Sari and A. Bicer, *Sol. Energy Mater. Sol. Cells*, 2011, **95**, 1647–1653.
- 38 D. Yang, S. Shi, L. Xiong, H. Guo, H. Zhang, X. Chen, C. Wang and X. Chen, *Sol. Energy Mater. Sol. Cells*, 2016, **144**, 228–234.
- 39 C. Liu, Z. Rao, J. Zhao, Y. Huo and Y. Li, *Nano Energy*, 2015, **13**, 814–826.
- 40 Y. Konuklu and H. O. Paksoy, *Energy Technol.*, 2015, **3**, 503–508.
- 41 R. Luo, S. Wang, T. Wang, C. Zhu, T. Nomura and T. Akiyama, *Energy and Buildings*, 2015, **108**, 373–380.
- 42 B. Zalba, J. M. Marin, L. F. Cabeza and H. Mehling, *Appl. Therm. Eng.*, 2003, **23**, 251–283.
- 43 X. Hu, Z. Huang and Y. Zhang, *Carbohydr. Polym.*, 2014, **101**, 83–88.
- 44 A. Sari, C. Alkan and A. N. Ozcan, *Energy and Buildings*, 2015, **90**, 106–113.
- 45 A. Sari, C. Alkan and A. Altintas, *Appl. Therm. Eng.*, 2014, **73**, 1160–1168.
- 46 D. Djefel, S. Makhlof, S. Khedache, G. Lefebvre and L. Royon, *Int. J. Hydrogen Energy*, 2015, **40**, 13764–13770.
- 47 Y. Min, Y. Fang, X. Huang, Y. Zhu, W. Li, J. Yuan, L. Tan, S. Wang and Z. Wu, *Appl. Surf. Sci.*, 2015, **346**, 497–502.
- 48 X. Li, Z. Cao, Z. Zhang and H. Dang, *Appl. Surf. Sci.*, 2006, **252**, 7856–7861.
- 49 R. Wang, H. Li, W. Liu and X. He, *Journal of Macromolecular Science, Part A*, 2010, **47**, 991–995.
- 50 Y. Xie, C. A. S. Hill, Z. Xiao, H. Militz and C. Mai, *Composites, Part A*, 2010, **41**, 806–819.
- 51 M. Wang, Y. Hu, J. Han, R. Guo, H. Xiong and Y. Yin, *J. Mater. Chem. A*, 2015, **3**, 20727–20735.
- 52 X. Cai, D. Fu and A. Qu, *J. Wuhan Univ. Technol., Mater. Sci. Ed.*, 2015, **30**, 1234–1239.
- 53 X.-M. Tong, T. Zhang, M.-Z. Yang and Q. Zhang, *Colloids Surf., A*, 2010, **371**, 91–97.

