Supplementary Information for

Efficient Thermal Energy Conversion and Storage Enabled by Hybrid Graphite

Nanoparticles/Silica -Encapsulated Phase-Change Microcapsules

Kunjie Yuan [*a], Qiuyang Chen [a], Aijia Zhang [a], Nan Xiao [a], Xuelin Zou[*c], and Zhiqun Lin[*b]

[*]Corresponding authors

[a] Department of Materials Science and Engineering, University of Science and Technology

Beijing, Beijing 100083, China

E-mail: kyuan@ustb.edu.cn

[b] Department of Chemical and Biomolecular Engineering, College of Design and Engineering,

National University of Singapore, Singapore 117585, Singapore

E-mail: z.lin@nus.edu.sg

[c] Guangdong Provincial Key Laboratory of Distributed Energy Systems, School of Chemical

Engineering and Energy Technology, Dongguan University of Technology, Dongguan 523808,

P. R. China.

E-mail: zouxl@dgut.edu.cn

Experimental Section

Materials

Paraffin was purchased from Huayong Paraffin Co, Ltd. Span80 (CP) was purchased from Tianjin Fu Chen Chemical Reagents. Tween80 (CP) was purchased from Tianjin Fuyu Fine Chemical Co, Ltd. Polyvinyl alcohol (PVA) AH-26(GR) and sodium chloride were purchased from Sinopharm Chemical Reagent Co, Ltd. Tetraethoxysilane (TEOS, CP), acetic acid glacial and sodium dodecyl sulfate, were purchased from Guangzhou Chemical Reagent Factory and Shanghai Richjoint Chemical Reagents Co, Ltd. Nano-graphite ($\leq$30 nm) was purchased from Nanjing XFNANO Materials Tech Co., Ltd, respectively.

Synthesis

SiO_2 sample was prepared by the polycondensation of TEOS. A typical procedure for preparing microencapsulated paraffin/NG@SiO_2 is as follows: 3.0 g of PVA was dissolved in 197 mL of distilled water. 9.2 g of paraffin/NG mixture (10 % of mass fraction of NG) and 6.0 g of mixed surfactants (Span 80 and Tween 80 weight ratio is 0.45: 0.55) were heated to 70 °C to form organic mixture. The aqueous PVA solution was added to the organic mixture, which was emulsified mechanically at stirring rate of 600 r/min to form an O/W emulsion. While stirring, 2.0 g of sodium chloride solution (2.5 mol/L) was added to the emulsion. After stirring for 30 min, 15 g of TEOS and 0.2 g of acetate acid solution (10.0 mass%) were added drop by drop into the emulsion system to start the hydrolysis and condensation of TEOS. After the addition, the reaction mixture was heated to 55.0 ℃ at stirring rate of 300 r/min for 5h. The resultant microcapsules were filtered, washed sequentially with distilled water and ethanol, for

three times, and dried at 50.0°C for 24 h. For comparison, the paraffin@SiO$_2$ sample was prepared by the same procedure yet without nano-graphite (NG).

Characterization and measurements

The morphology and microstructure of microencapsulated PCM composites and nano-graphite (NG) were observed using a field emission scanning electron microscopy (SEM) (LEO 1530 VP, Netherlands) and s transmission electron microscopy (TEM) (Tecnai G2 F30 S-TWIN, USA), respectively. The core-shell structure of microcapsules was characterized by FT-IR spectra, X-ray diffraction, and Raman spectra. The FT-IR spectra were recorded on a Bruker 550 from 400 to 4000 cm^{-1} using KBr pellets, the X-ray diffraction (XRD) patterns of the samples were carried out on X-ray diffractometer (D8 ADVANCE), and the Raman spectra of the products were recorded at ambient temperature on a LabRAM Aramis Raman spectrometer with an argon-ion laser whose wavelength is 514.5 nm. The phase change temperature and latent heat of the products were measured using a differential scanning calorimeter (DSC; Q20, TA). For DSC measurements, 5-8 mg for every sample was sealed in an aluminum pan for characterization at a heating rate of 10 °C·min^{-1} under a constant stream of nitrogen at a flow rate of 50 mL·min^{-1}. The UV-vis spectroscopy was performed on a UV-2450 spectrophotometer (SHIMADZU). The thermal conductivity of solid samples was characterized by a hot wire method on a thermal constant analyzer (TPS 2500, Hot Disk, Sweden). Prior to the thermal conductivity measurement, microcapsules were compressed to form a cylinder.

The photo-thermal conversion performance of samples was conducted as follows: First,

the microencapsulated composites were dispersed into the deionized water to form stable suspensions with a tiny surfactant of sodium dodecyl sulfate. The phase change microencapsulation-based suspension (i.e., in deionized H_2O) can be regarded as a novel heat transfer fluid for the direct solar thermal collectors. Second, the thermal conductivity and specific heat of the new heat transfer fluids were measured by a thermal constant analyzer and DSC. Then, a simulated solar irradiation was used to test the photo-thermal conversion performance of the suspensions. As shown in **Figure S1**, the experimental apparatus can be divided into two components: the photo-thermal conversion system and the data collection system. The photo-thermal conversion system consists of a foam insulation system, a quartz beaker, and a light source. A radiometer (ST-80C, Photoelectric Instrument Factory of Beijing Normal University) was used to measure and verify the power of the light irradiation from simulated light source (SOLAREDGE 700, Perfectlight). The power of the solar simulator was measured to be 1000 ± 20 $W\cdot m^{-2}$. The data collecting system consist of thermocouples and computer. The suspensions with the same mass were put into the quartz beaker. The heat storage process proceeded when turning the light on. The temperature changes of the samples during these periods were recorded by thermocouples. The thermophysical property (i.e. thermal conductivity, specific heat) and the photo-thermal performance of the suspensions were investigated by thermal constant analyzer, DSC and the photo-thermal device shown in **Figure S1**. When the temperature of phase change slurry is higher than room temperature, inevitably, there will be a small amount water to evaporate and evaporation increases as the temperature increases. However, the evaporation enthalpy from H_2O cannot be calculated. Moreover, partial sunlight irradiation will be reflected on the surface of the fluid,

which is no way to record. By only considering the solar energy stored by the slurry part, the receiver (i.e. the beaker containing the phase change slurry) effective efficiency was calculated by the formula 1 below.

$$\eta = \frac{m \int C_P(T) dT}{G_s A t} \times 100\%$$ (1)

where η is the receiver effective efficiency, m represent the mass of the heat transfer fluid (i.e., the phase change slurry), $C_p(T)$ is the specific heat of the heat transfer fluid, T is the temperature of the heat transfer fluid, G_s is the irradiance of the solar simulator, A is the surface area of the receiver, and t is the time.

To test the reversible stability of samples, the microencapsulated paraffin/nano-graphite@SiO_2 was heated to 90℃ for 5 min and then cooled to 30℃ for 5 min by a temperature-controlled instrument (C50p, HAAKE). This process was repeated for 50 heating-cooling cycles and the material was then evaluated for any changes in the morphology by SEM, heat storage capacity by DSC, the encapsulation efficiency of the prepared phase change microcapsules was calculated by the formula 2 below.

$$E = \frac{\Delta H_{m,microcapsule} + \Delta H_{f,microcapsule}}{\Delta H_{m,pure} + \Delta H_{f,pure}} \times 100\%$$ (2)

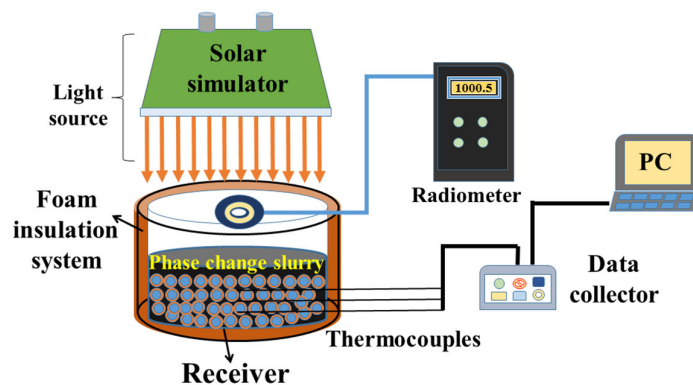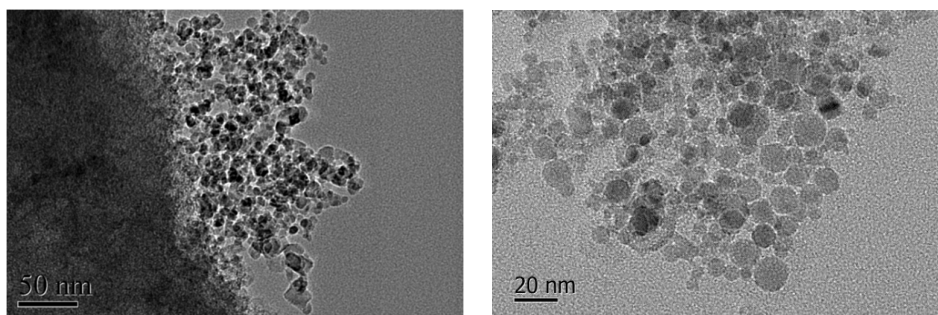**Figure S1.** Solar-driven transition diagram of the light-to-heat device.

Figure S2. TEM images of nano-graphite. Scale bars are 50 nm (left) and 20 nm (right), respectively.
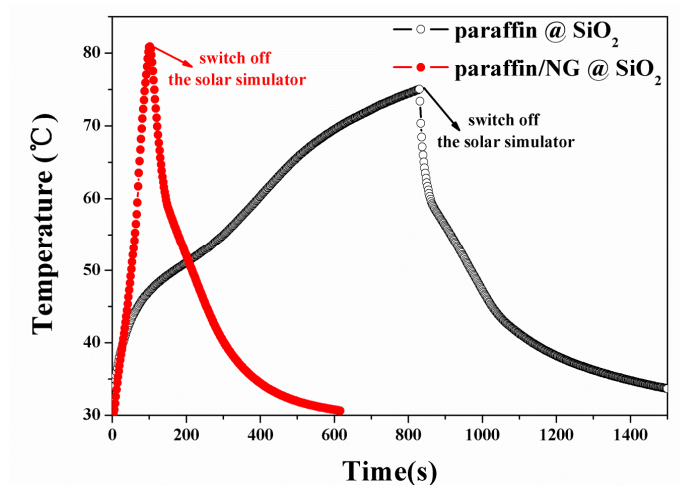

Figure S3. Photo-driven curves of paraffin@ SiO_2 and paraffin/NG@ SiO_2 composites solid powders (tested under the 1000 $W \cdot m^{-2}$ of solar intensity).