Preparation of ZIF-8-coated Silica Hard-shell Microcapsule by Semi-batch Operation

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Electronic Supplementary Information (ESI)

1. Thermal conductivity and thermal resistance of ZIF-8-coated SiO_2 hard-shell microcapsules

The thermal conductivity of each material is shown in Table S1. Thermal conductivities (λ; W·K /m) of SiO_2 and ZIF-8 are much lower than those of Cu metal and Fe metal which are used for conventional heat exchanger. Meanwhile, thermal resistance is necessary to be considered for efficient heat transfer. Thermal resistance (R; m^2·K/W) is expressed as:

$$R = \frac{d}{\lambda} \quad (S1)$$

where d is the thickness for use as heat exchanger or shell of microcapsules. The estimated thermal resistance of each material is also summarized in Table S1. The estimated thermal resistance of SiO_2 and ZIF-8 when used as microcapsules were 0.20×10^{-5} and 0.61×10^{-5}, respectively. Their values were larger than the thermal resistance of copper, but smaller than that of iron when Cu and Fe are used as a conventional heat exchanger with 1 mm of wall thickness. Additionally, these values are similar to the

Table S1 Thermal conductivity and thermal resistance for each material

Material	Thickness for use	Thermal conductivity λ (W/m·K)	Thermal resistance R (m^2·K/W)
Conventional heat exchanger			
Cu metal [a]	1 mm	402	0.25×10^{-5}
Fe metal [a]	1 mm	79	1.27×10^{-5}
Shell of commercial microcapsule			
Polymethyl methacrylate [b]	1 μm	0.19	0.52×10^{-5}
ZIF-8/HSMC (This work)			
SiO_2 (shell of HSMC) [a]	2.8 μm	1.37	0.20×10^{-5}
ZIF-8 [c]	2 μm	0.33	0.61×10^{-5}

[a] Network Database System for Thermophysical Property Data developed by AIST: https://tpds.db.aist.go.jp/tpds-web/index.aspx

[b] B. Cui, C. O. Audu, Y. Liao, S. T. Nguyen, O. K. Farha, J. T. Hupp and M. Grayson, *ACS Appl. Mater. Interfaces*, 2017, **9**, 28139-28143.

[c] M. J. Assael, S. Botsios, K. Gialou and N. Metaxa, *Int. J. Thermophys.*, 2005, **26**, 1595-1605.

heat resistance of polymethyl methacrylate, which is already employed as the shell of a commercial heat storage microcapsule. Although SiO_2 and ZIF-8 have low thermal conductivity, thermal resistance of microcapsules consisting of SiO_2 and ZIF-8 can be reduced to the same level as that of a conventional metal heat exchanger by reducing the shell thickness of microcapsules. Therefore, effective heat transfer is expected by the reduction of thermal resistance and significant increase in surface area through microencapsulation.

2. Calculation procedure for “Modified IPTES amount” in Fig. 1.

The amount of 3-(2-imidazolin-1-yl)propyltriethoxysilane (IPTES) modified on the SiO_2 hard-shell microcapsules (HSMCs) in the IPTES-HSMC (N_{IPTES}; molecules/nm^2), which was “Modified IPTES amount” in Fig. 1, was expressed as:

$$N_{IPTES} = \frac{n_{IPTES} \times N_A}{S_{HSMC}} \quad (S2)$$

where n_{IPTES} is the amount of IPTES included in IPTES-HSMCs (mol), N_A is the Avogadro constant (6.022×10^{23} molecules/mol), and S_{HSMC} is the surface area of HSMCs (nm^2).

To obtain n_{IPTES} value, the thermogravimetric and differential thermal analysis (TG-DTA) measurement was conducted for each IPTES-HSMCs. Figure S1a shows the TG-DTA curves of IPTES-HSMCs prepared at 70 g/L of IPTES concentration. The

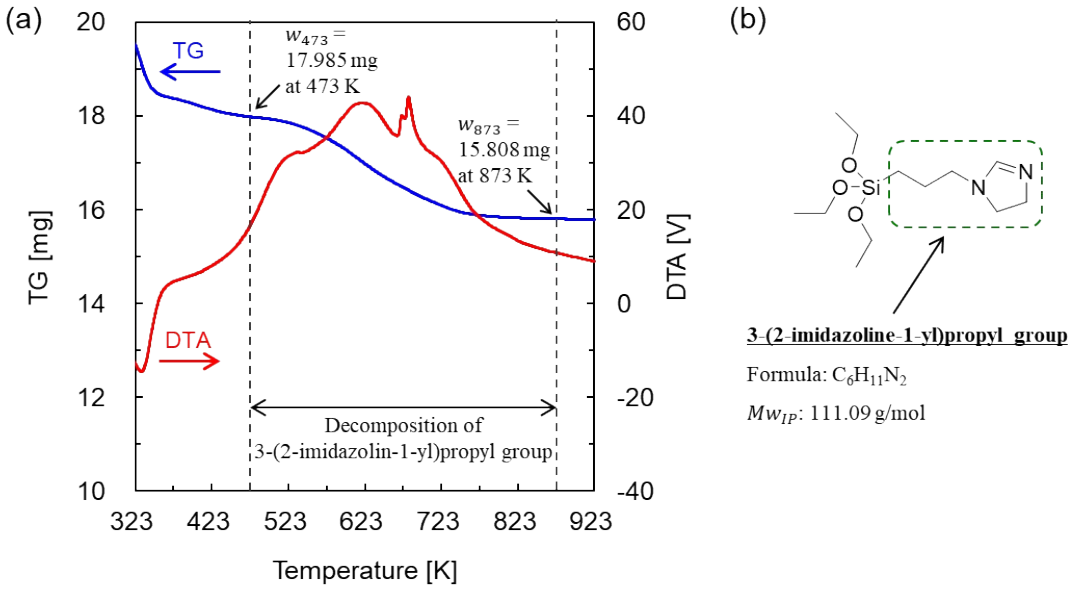

Fig. S1 TG-DTA curves of IPTES-HSMCs prepared at 70 g/L of IPTES concentration (a), and structural formula of IPTES (b). The area enclosed by the dotted line in (b) indicates the 3-(2-imidazoline-1-yl)propyl group.

weight loss observed at temperature lower than 373 K was attributed to the desorption of adsorbed water in the IPTES-HSMCs. Another weight loss was found in the temperature range 473–873 K. Tanaka et al. reported that 3-(2-imidazolin-1-yl)propyl group in IPTES (as shown in Fig. S1b) decomposed in the temperature range between 523 and 773 K in the gravimetric measurement.[38] Therefore, this weight loss was used for evaluating the amount of modified IPTES. Since no weight loss was observed at temperatures above 873 K, the TG value at 873 K was used as the weight of HSMCs. By using these results, the n_{IPTES} can be expressed as:

$$n_{IPTES} = \frac{w_{473} - w_{873}}{Mw_{IP}} \quad (S3)$$

where w_{473} is the value on TG curve at 473 K regarded as the IPTES-HSMCs weight, w_{873} is the value on TG curve at 873 K regarded as the HSMCs weight, and Mw_{IP} is the molecular-weight of 3-(2-imidazolin-1-yl)propyl group in IPTES (111.09 g/mol).

The S_{HSMC} was obtained from Eq. (S4).

$$S_{HSMC} = S_{BET} \times 10^{18} \times w_{873} \quad (S4)$$

where S_{BET} is the specific surface area of HSMCs (m^2/g) evaluated from the N_2 adsorption data using the Brunauer-Emmett-Teller (BET) method. The value of S_{BET} was 224 m^2/g.

N_{IPTES} was obtained from Eqs. (S2) – (S4).

$$N_{IPTES} = \frac{(w_{473} - w_{873})/Mw_{IP} \times N_A}{S_{BET} \times 10^{18} \times w_{873}}$$

$$= \frac{(0.017985 - 0.015808)/111.09 \times 6.022 \times 10^{23}}{224 \times 10^{18} \times 0.015808} = 3.33\ molelures/nm^2$$

3. Hmim/Zn molar ratio as a function of synthesis time during semi-batch operation.

The Hmim/Zn molar ratios in the synthesis mixture during the semi-batch operation were calculated as follows.

(a) For feeding the Hmim aqueous solution into the Zn^{2+} aqueous solution to obtain ZIF-8/HSMC-SB_{Hmim}

The Hmim aqueous solution as a supply solution was prepared by dissolving 3.62 g of Hmim in 20 mL of deionized water. The C_{Hmim} (the concentration of Hmim in this aqueous solution, mol/mL) was obtained as

$$C_{Hmim} = \frac{3.62/Mw_{Hmim}}{20} \quad (S5)$$

where Mw_{Hmim} is the molecular-weight of Hmim (82.11 g/mol).

The Zn^{2+} aqueous solution was prepared by dissolving 0.40 g of $Zn(NO_3)_2{\cdot}6H_2O$ in 40 mL of deionized water. The $n_{Zn^{2+}}$ (the mole number of Zn^{2+} in this aqueous solution, mol) was obtained as

$$n_{Zn^{2+}} = \frac{0.40}{Mw_{Zn(NO_3)_2 \cdot 6H_2O}} \quad (S6)$$

where $Mw_{Zn(NO_3)_2 \cdot 6H_2O}$ is the molecular-weight of $Zn(NO_3)_2{\cdot}6H_2O$ (297.48 g/mol).

The obtained Hmim aqueous solution was fed into Zn^{2+} aqueous solution at a feed rate of 0.20 mL/min. Therefore, the Hmim/Zn molar ratio as a function of the synthesis time, (plotted in Fig. S2a) can be expressed using Eqs. (S5) and (S6) as

$$Hmim/Zn\ molar\ ratio\ in\ Fig.\ S2a = \frac{C_{Hmim} \times 0.20 \times t}{n_{Zn^{2+}}} \quad (S7)$$

where t is synthesis time (min).

(b) For supplying the Zn^{2+} aqueous solution into the Hmim aqueous solution to obtain ZIF-8/HSMC-SB_{Zn}

Zinc nitrate hexahydrate (0.40 g) and Hmim (3.62 g) were dissolved in 20 and 40 mL of deionized water, respectively. The $C_{Zn^{2+}}$ (the concentration of Zn^{2+} in the obtained aqueous solution, mol/mL) and the n_{Hmim} (the mole number of Hmim in this aqueous solution, mol) can be expressed using Eqs. (S8) and (S9), respectively, as

$$C_{Zn^{2+}} = \frac{0.40 \Big/ Mw_{Zn(NO_3)_2 \cdot 6H_2O}}{20} \quad (S8)$$

$$n_{Hmim} = \frac{3.62}{Mw_{Hmim}} \quad (S9)$$

The obtained Zn^{2+} aqueous solution was supplied into the Hmim aqueous solution at a feed rate of 0.20 mL/min. Therefore, the Hmim/Zn molar ratio as a function of the synthesis time (plotted in Fig. S2b) can be expressed using Eqs. (S8) and (S9) as

$$Hmim/Zn\ molar\ ratio\ in\ Fig.\ S2b = \frac{n_{Hmim}}{C_{Zn^{2+}} \times 0.20 \times t} \quad (S10)$$

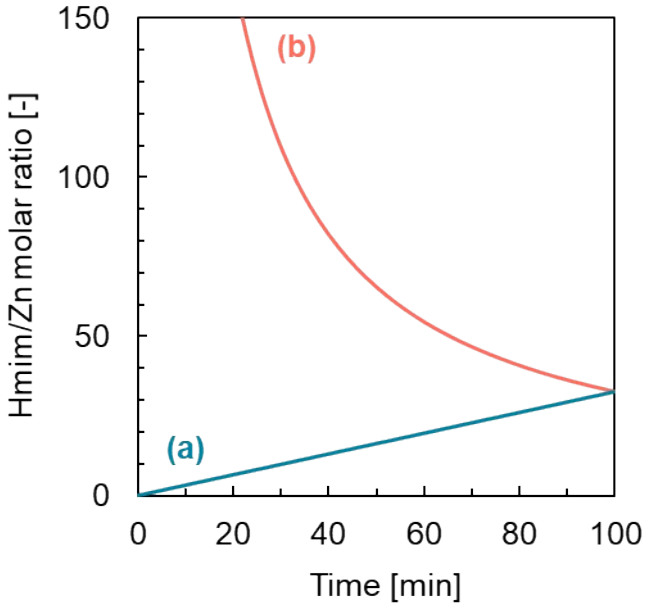

Fig. S2 Calculated Hmim/Zn molar ratio in the synthesis mixture of ZIF-8 cover layer using the semi-batch operation for feeding the Hmim aqueous solution into the Zn^{2+} aqueous solution (a) and supplying Zn^{2+} aqueous solution into Hmim aqueous solution (b) as a function of synthesis time.