

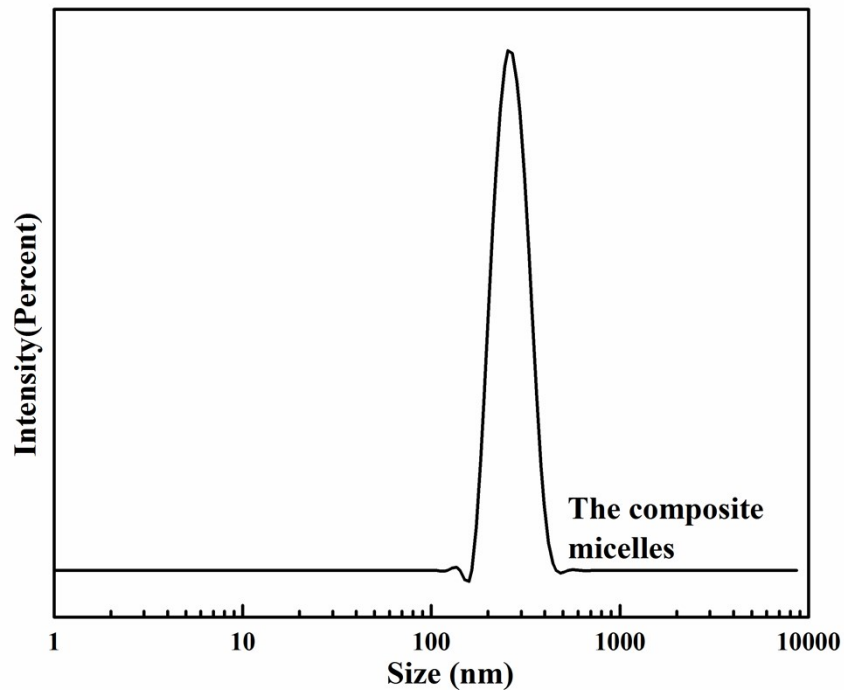
## **Supporting Information**

### **Core-template-free Synthesis of Molecularly Ethane-bridged Hollow Mesoporous Silica Spheres from Acid-hydrolyzed Precursor**

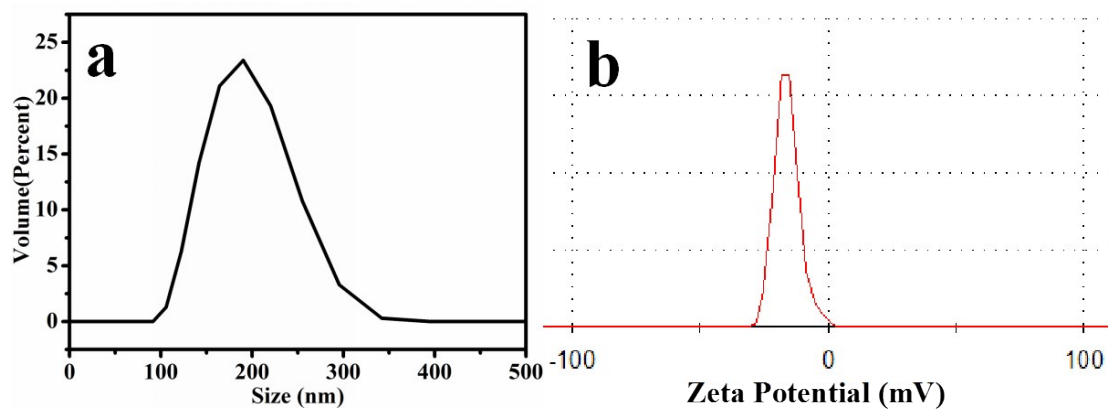
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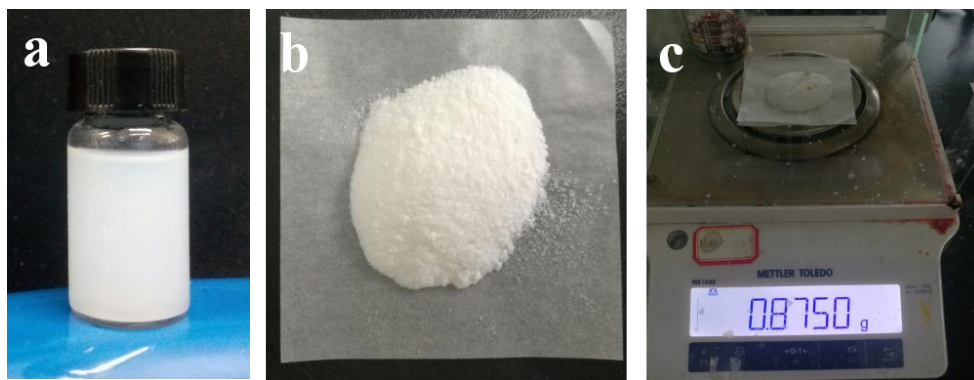
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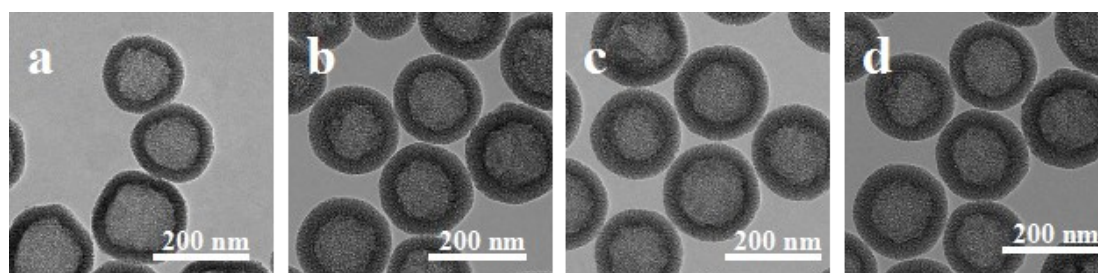
**Figure S1.** DLS size distribution of the composite micelles in TEA solution for 1h.



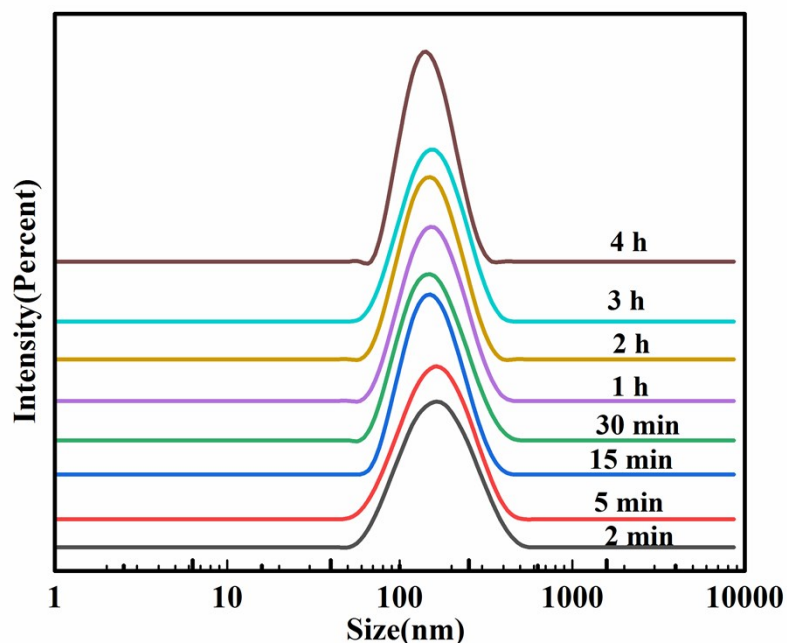
**Figure S2.** (a) DLS size distribution and (b) Zeta potential distributions of the typical MEB-HMSs. (Run 2 in Table 1)



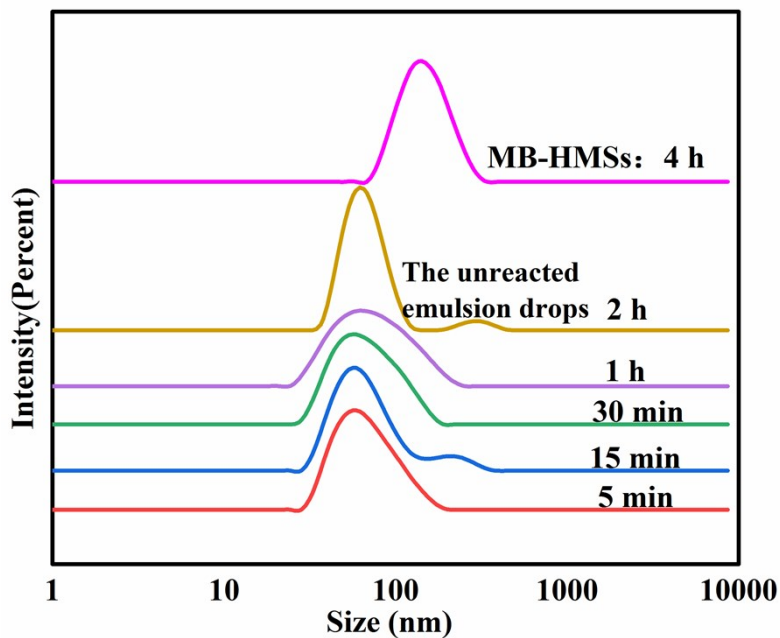
**Figure S3.** (a) The photographs of the dispersions obtained with MEB-HMSs in H<sub>2</sub>O; (b-c) The photograph of the MEB-HMSs in one-pot. Typically, the reaction solution was composed of 200mL H<sub>2</sub>O, 0.8 mL TEA, 0.24 g CTAB, and 4 mL Pluronic L-31 solution, while the acid-promoted pre-hydrolysis solution 15 mL EtOH, 5 mL HAc solution, and 0.9 mL BTEE and 0.9 mL TEOS. The content of the added pre-hydrolysis solution to reaction solution was 20 mL.



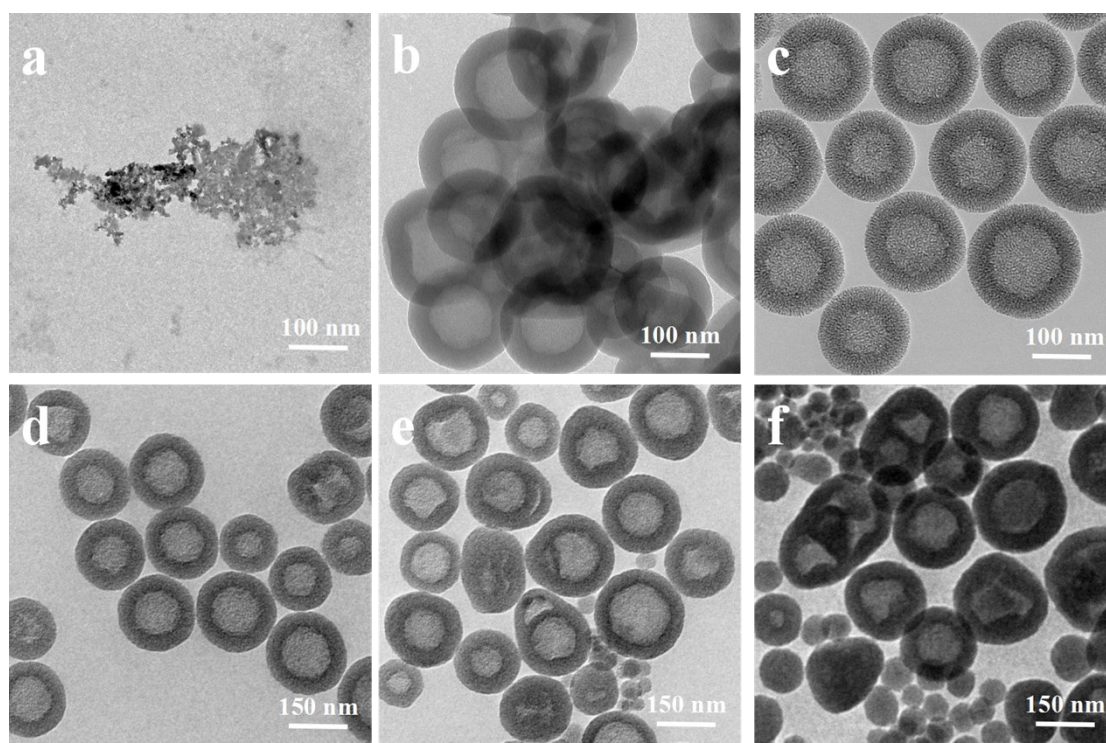
**Figure S4.** The evolutionary morphologies of the prepared MEB-HMSs as a function of reaction time: (a) 5, (b) 15, (c) 30, (d) 60 min.



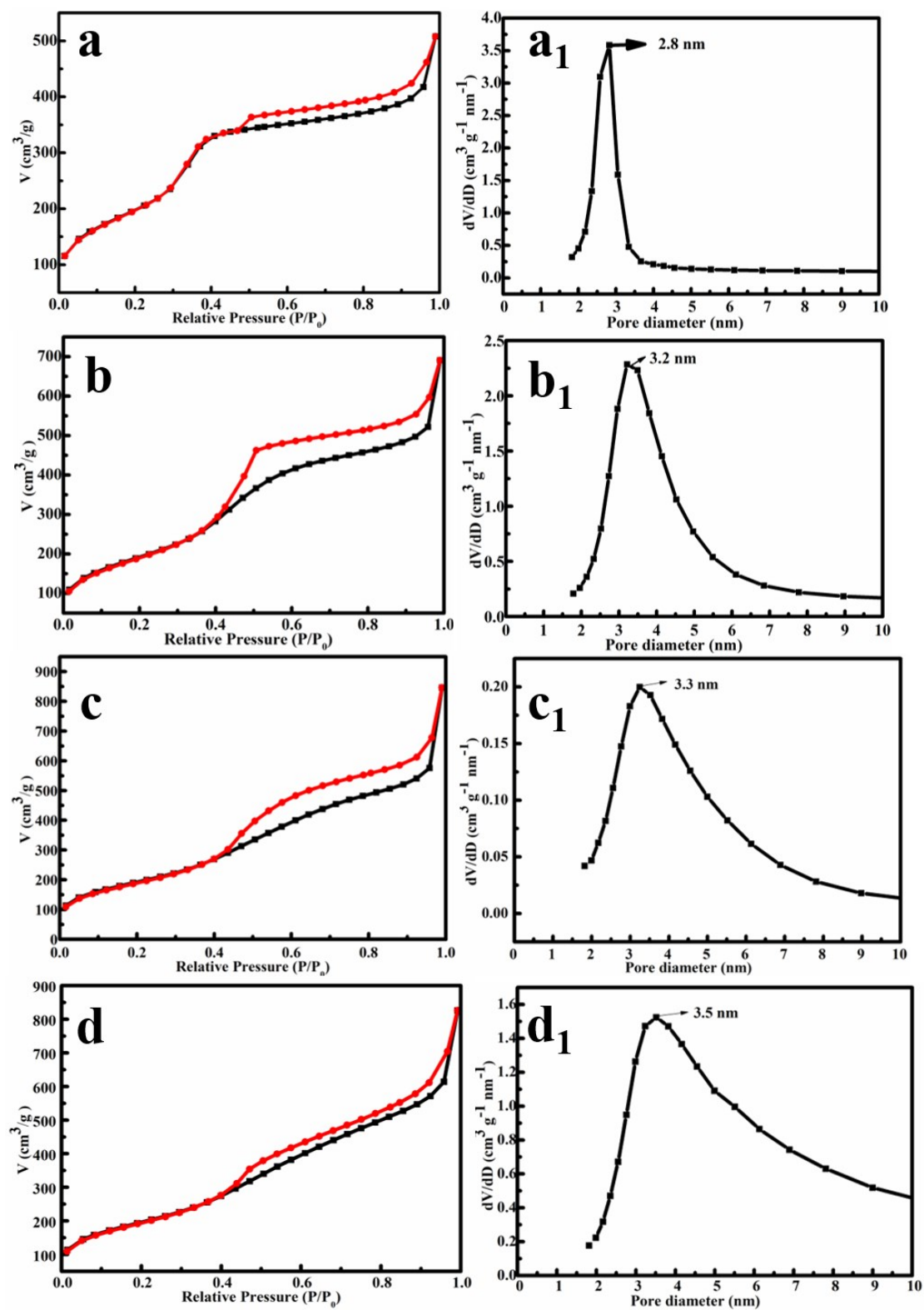
**Figure S5.** DLS size distribution of the MEB-HMSs as a functional of reaction time with addition of TEA. The result show that the size of MEB-HMSs does not show significant change with different reaction time.



**Figure S6.** DLS size distribution of the unreacted emulsion drops as a functional of reaction time without addition of TEA. The results show that the average size of the unreacted emulsion drops is smaller than that of MEB-HMSs.



**Figure S7.** TEM images of the MEB-HMSs prepared with different CTAB amount: (a) 0, (b) 0.01, (c) 0.06, (d) 0.12, (e) 0.18, (f) 0.24 g.



**Figure S8.**  $N_2$  sorption-desorption isotherm and the corresponding pore size distribution of the MEB-HMSs prepared of 0.06 g CTAB with different amount of Pluronic L-31: (a, a<sub>1</sub>) 0, (b, b<sub>1</sub>) 1.0, (c, c<sub>1</sub>) 2.0, (d, d<sub>1</sub>) 3.0 mL.

**Table S1.** Atomic compositions of the MEB-HMSs. (Run 2 in Table 1)

Analysis	Atomic percent (molar ratio %)		
	C	Si	O
XPS	42.89	19.2	37.91
EDX	28.65	18.55	52.79

**Table S2.** Structure properties of MEB-HMSs and their drug-loading capacity

Samples	BTEE /mL	TEOS /mL	Pluronic L-31 /mL	Particle size/ nm (TEM)	Shell Thickness / nm (TEM)	Particle size/ nm (DLS)	$S_{\text{BET}}$ ( $\text{m}^2/\text{g}$ )	Pore volume ( $\text{cm}^3/\text{g}$ )	Pore size (nm)	Drug-loading Capacity (%)
HMSSs-1	0.90	0	1.0	202	24	207.6	817	1.21	2.8	15.4
HMSSs-2	0.60	0.3	1.0	183	26	262.7	790	1.18	3.1	29.6
HMSSs-3	0.45	0.45	1.0	178	36	200.1	687	1.07	3.2	34.5
HMSSs-4	0.45	0.45	2.0	193	40	210.2	694	1.31	3.3	35.9
HMSSs-5	0.45	0.45	3.0	192	44	207.0	708	1.28	3.5	33.0