Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information

Synthesis of Monodisperse Mesoporous TiO_2 Spheres with Tuneable Sizes between 0.6 and 3.1 μm and Effects of Reaction Temperature, Ti Source Purity, and Type of Alkylamine on Size and Monodispersity

Myun Pyo Hong, Jang Yong Kim, Koteswararo Vemula, Hyun Sung Kim, and Kyung Byung Yoon*

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Table SI-1. Reaction conditions for the synthesis of MMTSs in the references cited in this work and the sizes and size distributions of the obtained MMTSs.

Ti source	additives	solvent	Temp (˚C)	Size (nm)	Size distribution	Ref in text
$TiCl_4$	HCl, Na_2SO_4	H_2O	98	up to 3800	σ = 15-25%	1
$TiCl_4$	-	H_2O vapor	96.5	60-600	polydisperse	2
$Ti(OEt)_4$	H_2O	ethanol	25	385-494	σ = 10%	3
$Ti(OEt)_4$	hydroxypropyl cellulose, H_2O	propanol	25	150-400	σ = 10%	4
$Ti(OEt)_4$	LiCl, H_2O	ethanol	r.t	700-2500		5
$Ti(OEt)_4$	NaCl or HCl, H_2O	ethanol	25	800-1200	σ = 15%	6
$Ti(O\textit{i}Pr)_4$	hexadecylamine, KCl, H_2O	ethanol	r.t	800		7
$Ti(O\textit{i}Pr)_4$	PS (S30RPC) beads	-	60	12000		8
$TiCl_4$	PS beads	-	60	5000		9
$Ti(O\textit{i}Pr)_4$	PS (S15RPC) beads	-	60	7100		10
$Ti(O\textit{i}Pr)_4$	mesoporous carbon	-	-	500-800		11
$TiOSO_4$	glycerol, ethyl ether	ethanol	110	2000-5200		12
$Ti(O\textit{i}Pr)_4$	dodecylamine,NH_4F	ethanol	r.t	270	± 20 nm	13
$Ti(O\textit{i}Pr)_4$	methyl amine	acetonitrile ethanol	r.t	250		14
$Ti(O\textit{i}Pr)_4$	methyl amine	acetonitrile ethanol	r.t	260-980		15
$Ti(O\textit{i}Pr)_4$	hexadecylamine, KCl, H_2O	ethanol	r.t	830	± 40 nm	16
$Ti(O\textit{i}Pr)_4$	hexadecylamine, KCl, H_2O	ethanol	r.t	320-1150	± 40 nm	17
$Ti(OBu)_4$	acetylacetone, H_2O	butanol	140	300		18
$Ti(Bu)_4$	POPOPO, H_2O	ethanol	35-40	~275		19
$Ti(OBu)_4$	ethylene glycol, H_2O	acetone	r.t	200-500		20
$Ti(OBu)_4$	citric acid, NH_4OH, H_2O	ethanol	r.t	~300	polydisperse	21
$Ti(Bu)_4$	NH_4HCO_3	ethanol	180	~100		22
$Ti(OBu)_4$	ethylene glycol, H_2O	acetone	r.t	~500		23

SI-2. Experimental Details

2.1 Materials

Titanium isopropoxide (TIP, JUNSEI) was purified according to the following procedure. First, TIP (100 g, 98.0%) was distilled at 150 °C under vacuum (1×10^{-2} Torr), and stored in a Schlenk flask (100 mL) filled with dry Ar. Ethanol was distilled on activated 4A molecular sieves under dry Ar and stored in a Schlenk flask (100 mL) under Ar. The Schlenk flasks containing purified TIP and ethanol, respectively, were kept in a glove box charged with dry Ar. A series of *n*-alkyl-amine ($C_nH_{2n+1}NH_2$, n = 8, 10, 12, 14, and 16) were purchased from Aldrich and used as received.

2.2 Preparation of MAPSs

Preparation of solution A: In a glove box, distilled TIP (0.4 mL, 1.35 mmol) and dry EtOH (0.6 mL) were placed into a vial capped with a septum (this solution is designated as solution A).
Preparation of solution B: In a glove box, dry ethanol (EtOH, 20 mL, 342.5 mmol), dodecylamine (DDA, 0.124 g, 0.67 mmol), and a magnetic stirring bar were introduced into a three-necked round-bottomed flask and each neck was tightly capped with a septum. This three-necked flask was brought out from the glove box to bench and into which 0.16 mL (8.9 mmol) of distilled deionized water was added (this solution is designated as solution B).

Both the vial containing solution A and the three-necked flask containing solution were placed in an isopropanol bath whose temperatures were precisely controlled between 10 and -30 °C using an external chillier (See Fig. SI-2-1). To obtain -41 °C, acetonitrile and dry ice were used. When the temperatures of both solutions were equilibrated to that of the bath, solution A was quickly transferred to solution B with the help of a cannula while solution B was being vigorously stirred. The standard molar ratio of the reagents was $TIP:RNH_2:H_2O:EtOH = 1.0:0.5:6.6:253.7$.

2.3. Crystallization of MAPSs into MMTSs

Hydrothermal Reaction. MAPS powder (0.1g) was introduced into a Teflon-lined autoclave (30 mL capacity) containing a mixture of EtOH (0.625 mL) and DDW (1.25 mL). The heterogeneous solution was sealed and heated at 160 °C for 16 h. After cooling, the solid particles were collected by centrifugation and the particles were washed with EtOH and water and subsequently dried in an oven.
Calcination. The MMTS powder was calcined at 500 °C for 6 h with the heating rate of 5 °C/min in the atmosphere to remove any remaining organic template.

2.4. Instrumentation

The scanning electron microscope (SEM) images of zeolite films were obtained from a FE-SEM (Hitachi S 4300) at an acceleration voltage 20 kV. The N_2 sorption analysis for measuring surface area and pore diameter was performed at 77 K by BELSORP-max volumetric adsorption equipment. Powder X-ray diffraction (XRD) patterns were obtained from a Rigaku D/MAX-2500/pc diffractometer.

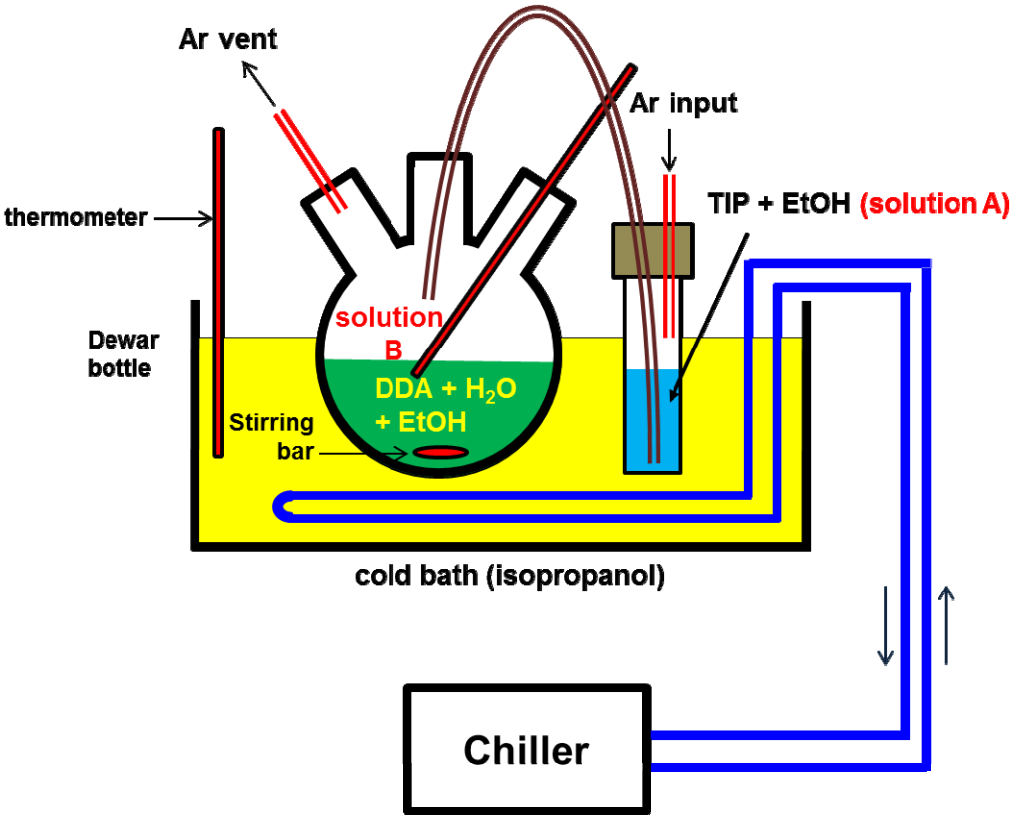

Fig. SI-2-1. Schematic illustration of the reaction setup used for the preparation of MAPSs. The temperature of the cold bath was controlled by the chiller. After both solutions A and B were equilibrated at the desired temperature, solution B was quickly transferred to the three-necked round bottomed flask containing solution B, while solution B was vigorously stirred. The temperature of solution B increased by 0.5 °C during the hydrolysis of TIP, indicating that the amount of heat generated during the hydrolysis of TIP in the three-neck flask was not significant.

SI-3. Effects of reaction conditions on the size and monodispersity of MAPSs

Table SI-3-1. Effects of mole ratio and reaction temperature on the size and monodispersity of MAPSs with dodecylamine as the additive.

Mole ratio (TIP:DDA:H_2O:EtOH)	Temperature (˚C)	Size (nm)	σ(%)	Remarks of TIP
1:0.5:6.6:253.7	23	700	28.6	Distilled
	10	720	20.1	〃
	5	780	11.5	〃
	0	900	3.6	〃
	-5	1200	2.6	〃
	-10	1600	1.9	〃
	-15	1800	1.7	〃
	-20	2040	1.5	〃
	-25	2150	7.4	〃
	-30	2580	11.6	〃
	-41	2830	28.6	〃
1:0.5:6.6:253.7	23	550	30.5	As received
	10	620	15.4	〃
	5	730	10.7	〃
	0	920	12.5	〃
	-5	1010	9.1	〃
	-10	1120	13.9	〃
	-15	1140	8.7	〃
	-20	1210	12.3	〃
	-25	1310	16.5	〃
	-30	1520	23.4	〃
	-41	1710	37.1	〃
1:0.5:4.4:253.7	23	950	20.0	Distilled
1:0.5:3.3:253.7	23	1120	8.3	〃
1:0.5:2.2:253.7	23	1450	12.3	〃
1:0.5:4.4:253.7	-20	2340	11.4	〃
1:0.5:3.3:253.7	-20	2610	25.1	〃
1:0.5:0.0:253.7	-20	no rxn	-	〃
1:0.5:6.6:507.4	23	1130	8.5	〃
1:0.5:6.6:761.1	23	1450	11.1	〃
1:0.5:6.6:507.4	-20	2690	10.3	〃
1:0.5:6.6:761.1	-20	3060	16.8	〃
0.25:0.5:6.6:253.7	23	1230	23.5	〃
0.50:0.5:6.6:253.7	23	1050	20.1	〃
0.75:0.5:6.6:253.7	23	860	17.3	〃
1.38:0.5:6.6:253.7	23	630	10.2	〃
0.25:0.5:6.6:253.7	-20	2610	20.1	〃
0.50:0.5:6.6:253.7	-20	2480	12.6	〃
0.75:0.5:6.6:253.7	-20	2120	9.5	〃
1.38:0.5:6.6:253.7	-20	1770	3.5	〃

Table SI-3-2. Effect of the type of alkylamine on the size and monodispersity of MAPSs during their synthesis at -20 °C with the mole ratio of TIP:DDA:H_2O:EtOH = 1:0.5:6.6:253.7.

NH_2-C_nH_{2n+1}	Temperature (˚C)	Size (nm)	σ(%)	Remarks of TIP
8	-20	1900	8.5	Distilled
10	″	1940	2.5	″
12	″	2040	1.5	″
14	″	1800	2.1	″
16	″	1950	7.3	″

SI-4. Lower magnification (3 K) SEM images of MAPSs

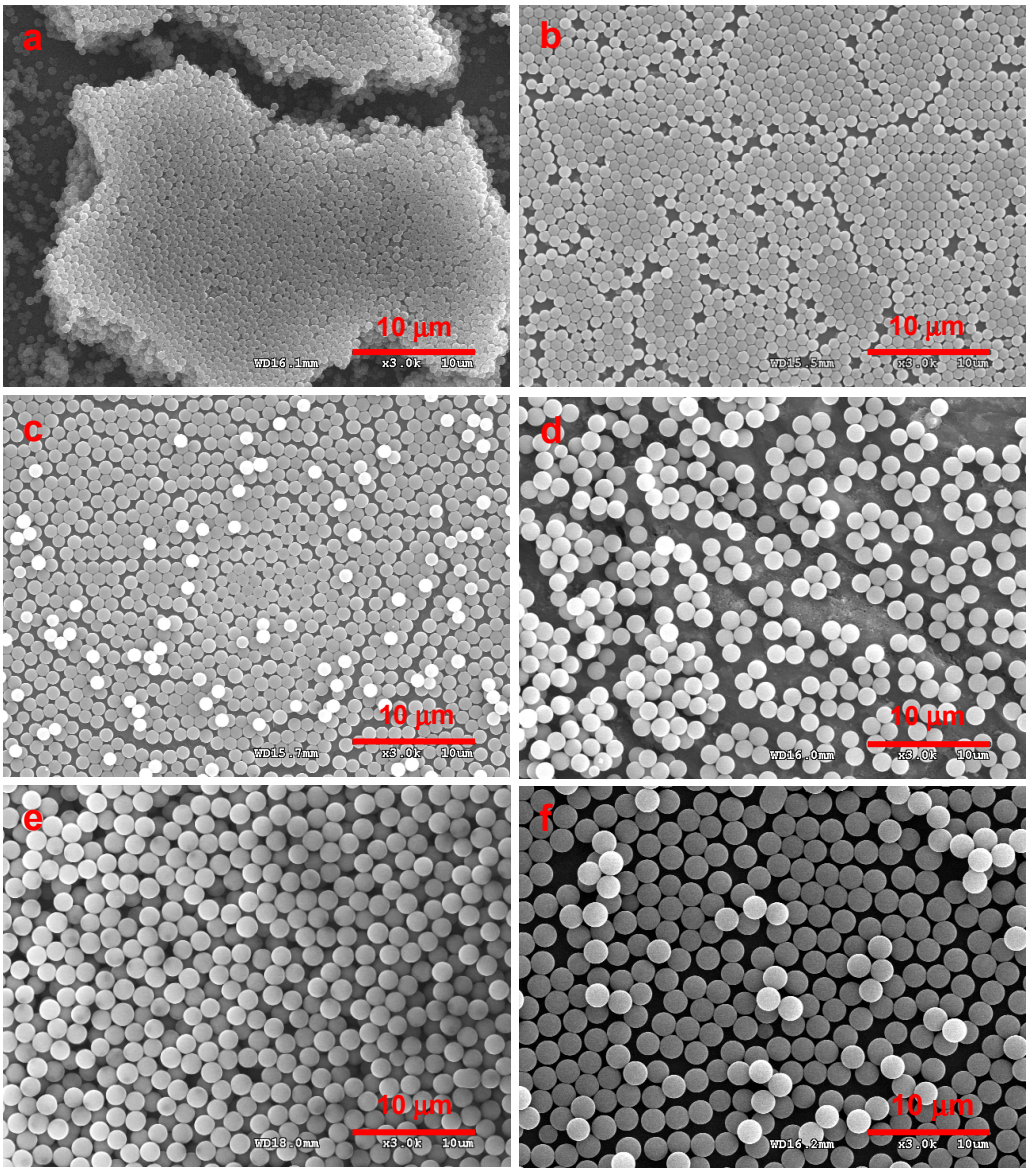

Fig. SI-4-1. Lower magnification (3 K) SEM images of MAPSs synthesized at various temperatures; 23 (a), 0 (b), -5 (c), -10 (d), -15 (e), and -20 °C (f) respectively.

SI-5. Transformation of MAPSs to MMTSs by a hydrothermal reaction and calcination.

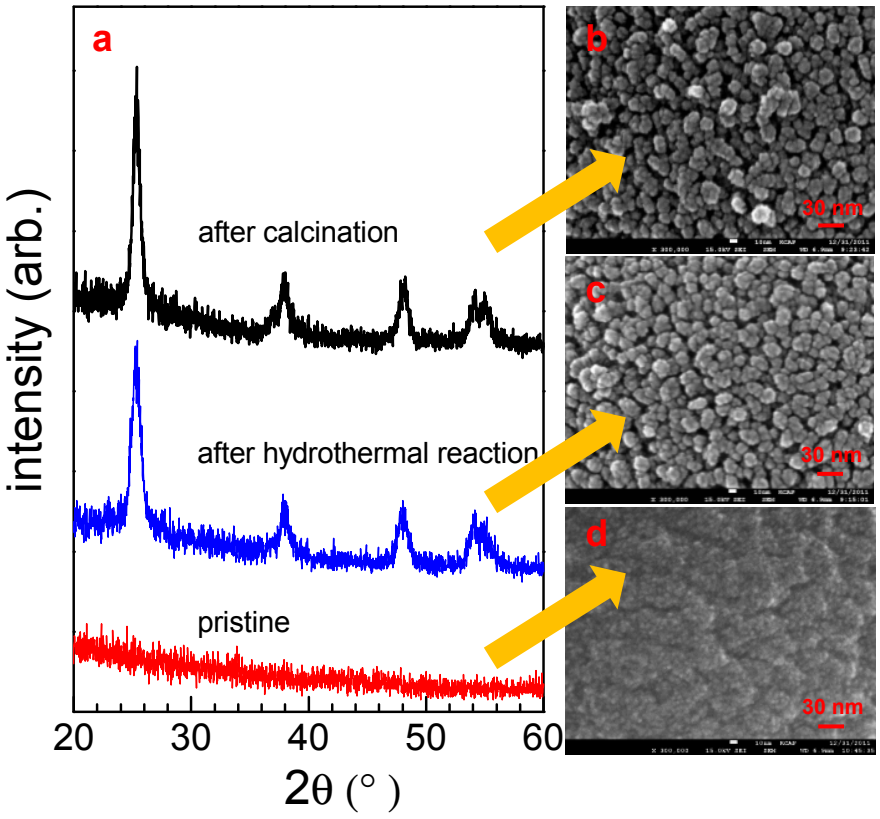

Fig. SI-5-1. XRD powder diffraction pattern (a) and the corresponding SEM image of MAPS after hydrothermal reaction and calcination (b-d, as indicated).

SI-6. SEM images of MAPSs and MMTSs.

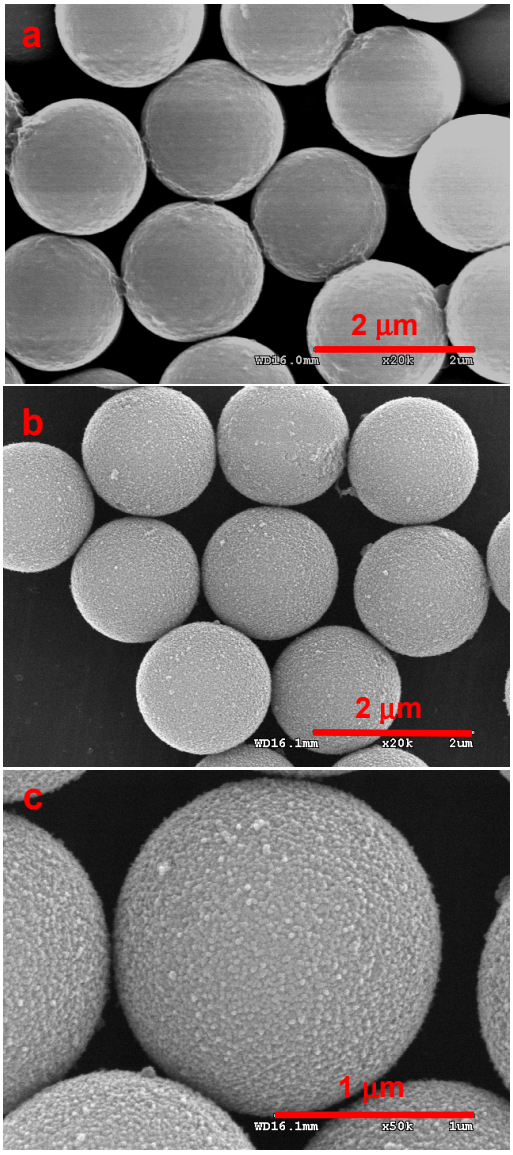

Fig. SI-6-1. SEM images of 1.8 µm MAPSs (a), 1.6 µm MMTSs obtained by hydrothermal reaction (b) and calcination (c)

SI-7. TEM images of MMTS.

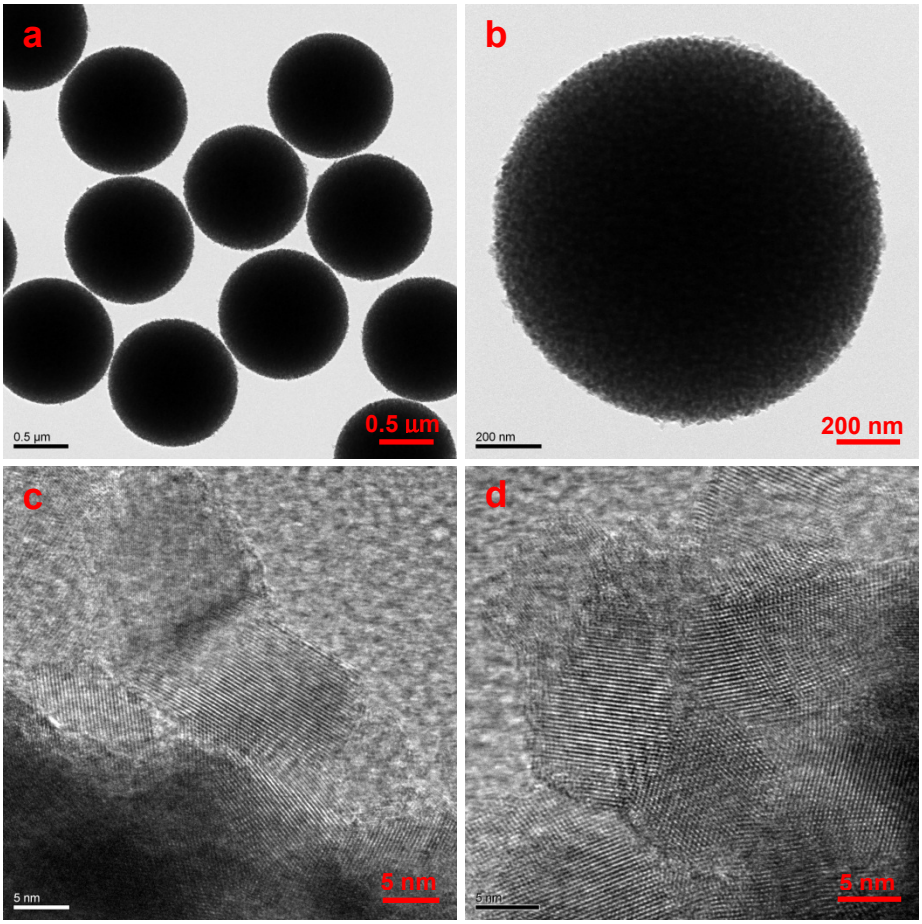

Fig. SI-7-1. TEM images of 1.1 µm MMTSs obtained by hydrothermal reaction at different magnifications (as indicated by the scale bar).

SI-8. BET pore size distribution.

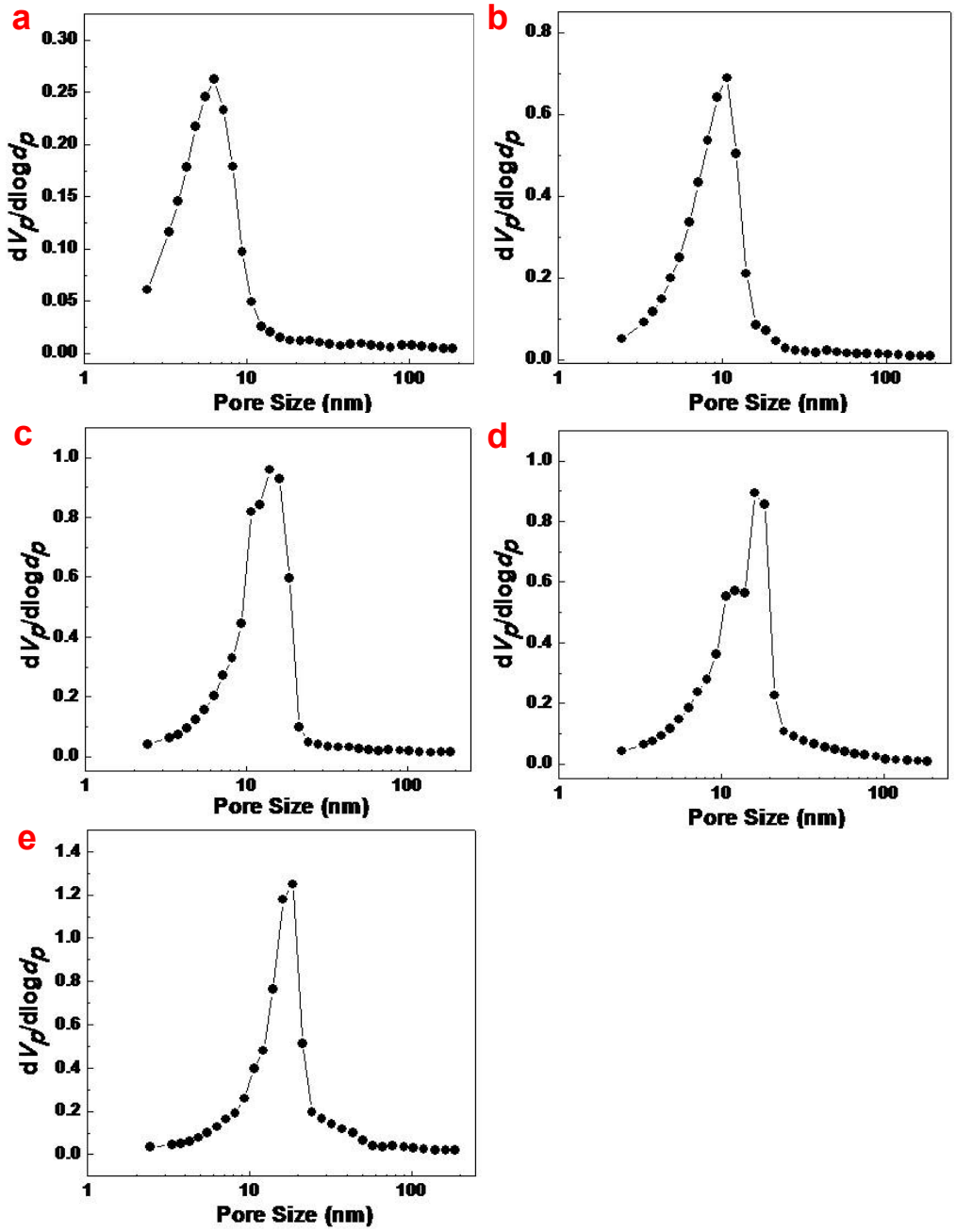

Fig. SI-8-1. BET Pores size distributions of MMTSs obtained from the reaction mixtures having different alkylamines; octylamine (a), decylamine (b), dodecylamine (c), tetradecylamine (d), and hexadecylamine (e).