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การเตรียมอนุภาคซิลิกาที่มีรูพรุนขนาดเมโซจากยางธรรมชาติอิพ็อกซิไดซ์และซิทิลไตรเมทิล แอมโมเนียม โบรไมด์

Mesoporous silica particles (MSPs) prepared by diol-functionalized natural rubber (ENR50-diol) and cationic surfactant (CTAB) dual templates

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บทคัดย่อ

ยางธรรมชาติอิพ็อกซิไดซ์และซิทิลไตรเมทิล แอมโมเนียม โบรไมด์ ถูกใช้ร่วมกันในการสังเคราะห์อนุภาคซิลิกาที่มีรูพรุนขนาดเมโซ ผ่านวิธีการสังเคราะห์แบบ StÖber method อนุภาคซิลิกาที่มีรูพรุนขนาดเมโซนี้ สังเคราะห์โดยใช้ยางธรรมชาติอิพ็อกซิไดซ์ที่มีปริมาณของหมู่ฟังก์ชันไฮดรอกซิลที่แตกต่างกัน คือ 22 และ 32 เปอร์เซ็น ซึ่งทำการสังเคราะห์เทียบกับการสังเคราะห์อนุภาคซิลิกาที่ไม่มีการเติมซิทิลไตรเมทิล แอมโมเนียม โบรไมด์ และการสังเคราะห์ที่ใช้เพียงซิทิลไตรเมทิล แอมโมเนียม โบรไมด์ จากการศึกษานี้พบว่า อนุภาคซิลิกาที่ได้จากการสังเคราะห์ร่วมกันของยางธรรมชาติอิพ็อกซิไดซ์และซิทิลไตรเมทิล แอมโมเนียม โบรไมด์ มีลักษณะของรูพรุนในอนุภาคที่แตกต่างกัน 2 ขนาด ซึ่งประกอบด้วย รูพรุนขนาดใหญ่ประมาณ 50 นาโนเมตร ที่ได้จากส่วนของยางธรรมชาติอิพ็อกซิไดซ์ และรูพรุนขนาดเล็กประมาณ 2-4 นาโนเมตร ที่เกิดจากส่วนของซิทิลไตรเมทิล แอมโมเนียม โบรไมด์ พื้นที่ผิวจำเพาะของอนุภาคซิลิกาที่สังเคราะห์ได้จากยางธรรมชาติอิพ็อกซิไดซ์และซิทิลไตรเมทิล แอมโมเนียม โบรไมด์ ร่วมกัน มีปริมาณเพิ่มมากขึ้นจากประมาณ 20 ถึง 268.50 ตารางเมตรต่อกรัม และมีปริมาตรรูพรุนเพิ่มขึ้นจาก 0.04 ถึง 0.25 ลูกบาศก์เซนติเมตรต่อกรัม

ABSTRACT

Diol-functionalized natural rubber (ENR50-diol) and Cetyltrimethyl ammonium bromide (CTAB) were used as dual templates for the synthesis of mesoporous silica particles (MSPs) through the modified StÖber method. The MSPs were synthesized using ENR50-diol/CTAB dual templates with 22% and 32% degree of diol, compared using only ENR50-diol (without CTAB) and using only CTAB. ENR50-dio/CTAB dual template provided MSPs with two different mesopore structures, i.e., large mesopores with pore size ~50 nm obtained from ENR50-diol and the small mesopores 2 - 4 nm generated from CTAB. The specific surface area of MSPs particles with using

ENR50/CTAB dual templates were obtained in order of magnitude from ~20 to 268.50 m^2/g and the pore volume from 0.04 to 0.25 cm^3/g.

คำสำคัญ: อนุภาคซิลิกา รูพรุนขนาดเมโซ ยางธรรมชาติอิพ็อกซิไดซ์ ซิทิลไตรเมทิล แอมโมเนียม โบรไมด์ โครงแบบร่วม เตตระเอทิล ออโทซิลิเกต

Keywords: Mesoporous silica, Epoxidize natural rubber, CTAB, Dual templates, TEOS

INTRODUCTION

Mesoporous silica particles (MSPs) have been applied for various applications, for examples, drug delivery, the catalyst supports and the separation and chromatography due to their tunable pore sizes, high surface area and pore volumes (Chen et al., 2004; Hesemann et al., 2014; Liang et al., 2008; Thomas et al., 2008; Xia et al., 2016). MSPs are typically prepared using the modified StÖber method (StÖber et al., 1968) employing various soft templates as mesopore-generating agents, such as emulsion droplets, surfactants and block copolymers (Tan and Rankin, 2005; Yoon et al., 2006; Yang et al., 2008; Ten et al., 2010; Li et al., 2015). In further development, MSPs have been synthesized using dual-template method which gains a vast variety of morphology and pore structures. Among the MSPs synthesized using the dual-template, CTAB is widely included as one of the templates owing to its specific interaction toward the silicate species, e.g., polystyrene spheres/CTAB (Zhang et al., 2009), poly (acrylic acid)/CTAB (Guo et al., 2010), polystyrene-b-poly(acrylic acid) (PS-b-PAA)/CTAB (Niu et al., 2010) and anionic sodium polyacrylate (NaPAA)/CTAB (Zhang et al., 2012). Each template in the dual system serves different role; that is, the polymer is the template for a formation of particles with the controllable morphology while CTAB provides a template for the mesopores (Li et al., 2010; Song et al., 2014; Zhang et al., 2009).

In present study, ENR50-diol/CTAB dual templates were employed for the synthesis of MSPs by the modified StÖber method using TEOS as the silica precursor. ENR50 offered a uniform particle size of MSPs through the self-assembly of ENR50 molecules induced by diethylenetriamine (DETA). CTAB could corporate with ENR50 via hydrophobic interactions and serve as the pore generating agent. Mesoporous silica particles (MSPs) with a high surface area and large pore volume were obtained in this ENR50-diol/CTAB dual templates.

EXPERIMENT

Materials

Tetraethyl orthosilicate (TEOS, 99%) and diethylenetriamine (DETA, 99%) were purchased from Sigma-Aldrich. Cetyltrimethyl ammonium bromide (CTAB, 98%) was purchased from Ajax Finochem. Epoxidized natural rubber with 50% epoxidation (ENR50) was obtained from Thai Hua Rubber, Thailand. Methanol (MeOH, 99.9%) and tetrahydrofuran (THF) were supplied by RCI Labscan, Thailand. Hydrogen peroxide (H_2O_2) was purchased from Carlo Erba Reagents.

Preparation of diol-functionalized ENR50 (ENR50-diol)

Commercial ENR50 was subjected to the molecular weight reduction by UV-induced degradation (Ravindran et al., 1988) prior to oxirane ring opening to diol groups. The degraded ENR50 in THF was mixed with 3.3% w/v acetic acid solution and the reaction was allowed to proceed at 80 °C for 24 h under nitrogen atmosphere. After the reaction, the solution was washed with DI water and dried at 60 °C for 48 h. ENR50-diol were analyzed by ^{1}H-NMR using Varian NMR-400 MHz spectrometer (Agilent) and the amount of hydroxyl group was determined by Equation (1)

$$\% \text{ diol of ENR50} = \frac{A_f}{A_e + A_f + A_g} \times 100 \quad (1)$$

where A_e is the integral peak of epoxide group at δ 2.7 ppm, A_f is the integral peak of hydroxyl group at δ 3.7 ppm and A_g is the integral peak of isoprene unit at δ 5.1 ppm (Gan et al., 1997).

Particle formation from ENR50-diol

The solvent exchange method was employed to form ENR50-diol particles. Typically 0.1 %w/v of ENR50-diol solution was prepared by dissolving dry ENR50-diol in 20 mL of THF. Next, ENR50-diol solution was poured into a dialysis tube (regenerated cellulose with MWCO = 10,000 g/mol) and dialyzed against methanol at room temperature for 2 days with a daily change of the solvent. Using the dialysis allows a formation of ENR50-diol particles while a fraction of ENR50-diol with MW < 10,000 g/mol was removed. DETA (0.02 M) was added into ENR50-diol solution during the particle formation in order to maintain the integrity of ENR50-diol particles.

Synthesis of mesoporous silica particles (MSPs) from ENR50-diol/CTAB dual template

After the formation of ENR50-diol particles, 0.014 g of CTAB in 3 ml of water was added to generate mesopores inside 1 ml of ENR50-diol particles solution. Next, 40 µl of TEOS in 10 ml of methanol was then added to produce the silica via the sol-gel reaction in the presence of ENR50-diol/CTAB templates. The reaction was carried on for 24 h at room temperature. After that the resultant silica-ENR50-diol/CTAB composite particles were dried at 60 °C overnight prior to calcination at 550 °C (heating rate: 5 °C /min) for 6 h to remove the templates. To purify the synthesized silica particles, the calcined particles were dispersed in methanol and then subjected to centrifugation at 10,000 rpm to precipitate the dense silica particles and large silica aggregates. The porous silica particles were referred as MSP, MSP-22 and MSP-32 for the particles synthesized using CTAB sole template and ENR50/CTAB dual templates (The molar ratio of ENR50/CTAB is 2.0) with 22% and 32% degree of diol, respectively. The particles synthesized using only ENR50-diol were denoted as SP-22 and SP-32.

Characterization

The chemical structures and components of ENR50-diols were characterized by ^{1}H-NMR implemented on the Varian Mercury NMR-400 MHz spectrometer (Agilent Technologies) and using $CDCl_3$ as a solvent. Particle size of ENR50-diol particles were measured by dynamic light scattering (DLS) at 25 °C using Brookhaven DLS with BI-200SM goniometer and BI-9000 particle sizing software. Transmissions Electron Microscopy (TEM) images of the particles were obtained from JEOL JEM-1230. Specific surface area, total pore volume and pore size distribution were determined using N_2 adsorption-desorption method performed in TriStra II 3020 Micromeritics Instrument.

RESULTS AND DISCUSSION

The chemical structure of the samples was confirmed by ^{1}H-NMR. The NMR spectra of ENR50, ENR50-diols22 and ENR50-diols32 are presented in Fig. 1 (A), (B) and (C), respectively. The percentage of hydroxyl group in modified ENR50 was determined using Equation (1). The percentages of hydroxyl group of (B) and (C) were 22% and 32%, respectively. The diol groups content of ENR50 increases with increasing acetic acid solution. These results of the sample are summarized in Table 1.

ENR50-diol particles were investigated by TEM and DLS as shown in Fig. 2. TEM images of ENR50-diol particles without DETA (Figs. 2a and 2c) reveal a relatively large spherical particles with diameters measured by DLS (insets of Figs. 2a and 2c) being 1250 nm and 2250 nm for ENR50-diol with 22% and 32% diol, respectively. In the presence of DETA, ENR50-diol particles became smaller and more uniform as evidenced by TEM images shown in Figs. 2b and 2d. The particle diameters from DLS were 350 nm and 415 nm for ENR50-diol with 22% and 32% diol, respectively. The stability and uniformity of the ENR50-diol particles provided by DETA are due to the hydrogen bonding between amine groups of DETA and diol groups of ENR50-diol.

TEM images of MSPs synthesized using different templates are displayed in Fig. 3. TEM images of SP-22 and SP-32 in Figs. 3a and 3b reveal uniform spherical particles with diameters approximately 200 and 230 nm, respectively. It is noticed that there were some irregular pores on the particles. This suggests that ENR50-diol is capable of being the template for a formation of uniform silica particles. The diol groups in ENR50-diol particles can attract to the silicate anions, the hydrolyzed product of TEOS, and lead to a deposition of the silicate species in the particles. Consequently, the silicate species react via the condensation reaction to produce silica in the immediate presence of ENR50-diol. After a removal of ENR50-diol by the calcination, a silica particle with a spherical shape in replica to ENR50-diol particle is obtained and some large mesopores on the particle surface are produced from a burning of polyisoprene in ENR50-diol particle.

When only CTAB was used as the template, the particles were spherical and relatively uniform as seen in Fig. 3c. MSP particles had an approximate diameter of 100 nm and contained number of small mesopores. Figs. 3d and 3e show the TEM images of MSP-22 and MSP-32 which reveal sphere-like particles with particle diameters approximately 300 and 350 nm, respectively.

The nitrogen adsorption-desorption isotherms and the pore size distributions of MSPs particles show in Fig. 4. The isotherms of SP-22 and SP-32 (Figs. 4a and 4b) exhibit type III while the isotherms of MSP, MSP-22 and MSP-32 exhibit type IV (Figs. 4c - 4e) (Zeid et al., 2012).

Accordingly, the distributions of pore sizes were calculated using BJH method from the adsorption branch of the isotherms as demonstrated on the insets of Fig. 4. It is noticed that the pore sizes of SP-22 and SP-32 were approximately 50 nm while for those of MSP-22 and MSP-32 were 2 – 4 nm. It is observed that CTAB template provided more pores than obtained from ENR50-diol. Furthermore when comparing pore abundance to MSPs particles synthesized using only CTAB, it is seen that using ENR50-diol/CTAB dual templates produced larger number of mesopores with the size of 2 – 4 nm. The physical properties of porous silica particles are shown in Table 2. Comparing with ENR50-diol template, ENR50-diol/CTAB dual templates increased the specific surface area from ~20 m^2/g to 268.50 m^2/g and increased the pore volume from 0.04 cm^3/g to 0.25 cm^3/g.

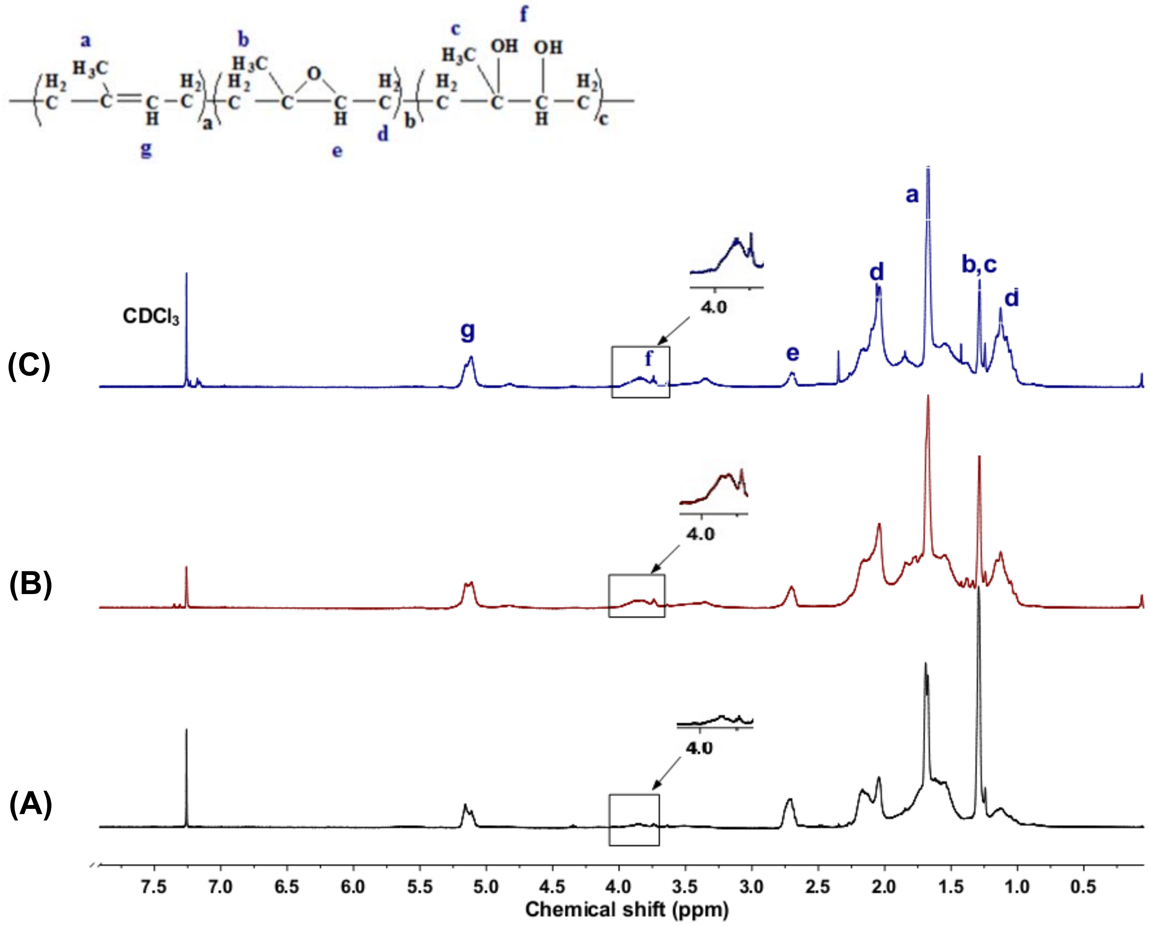


Fig. 1 ^{1}H-NMR spectra of (A) ENR50, (B) ENR50-diols22 and (C) ENR50-diols32.

Table 1 The amount of diol groups of ENR50

Sample	Isoprene unit (%)	Epoxide (%)	Diol (%)
ENR50	49.0	51.0	0.0
ENR50-diols22	48.8	29.1	22.1
ENR50-diols32	45.7	22.2	32.1

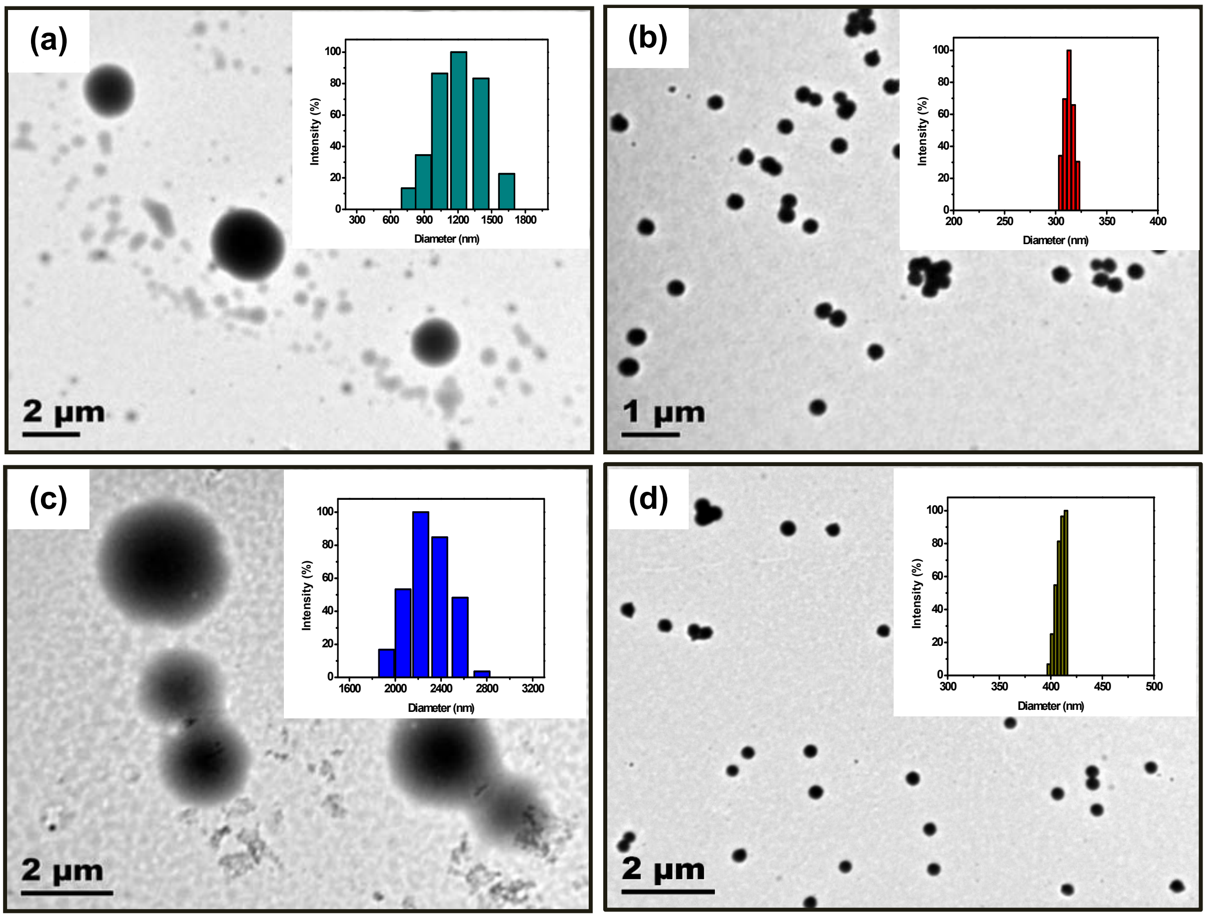


Fig. 2 TEM images and DLS histogram (insets) of (a) ENR50-diol22, (b) ENR50-diol22 with DETA, (c) ENR50-diol32, and (d) ENR50-diol32 with DETA.

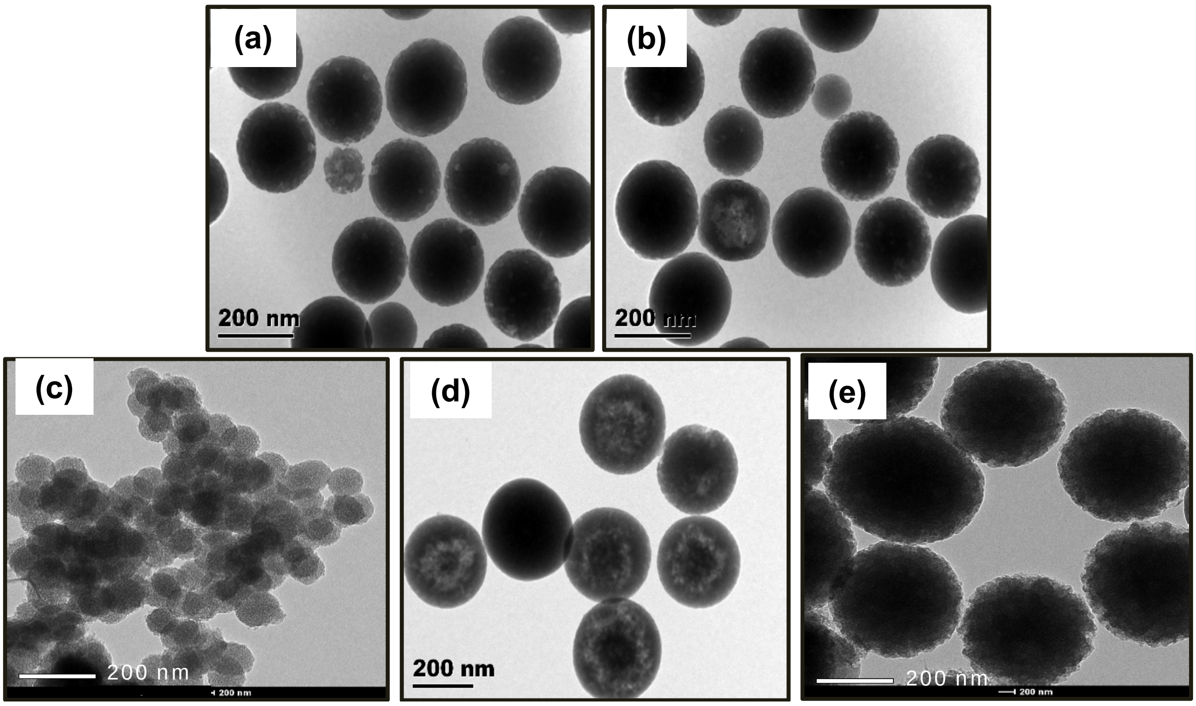


Fig. 3 TEM images of (a) SP-22, (b) SP-32, (c) MSP, (d) MSP-22, and (e) MSP-32.

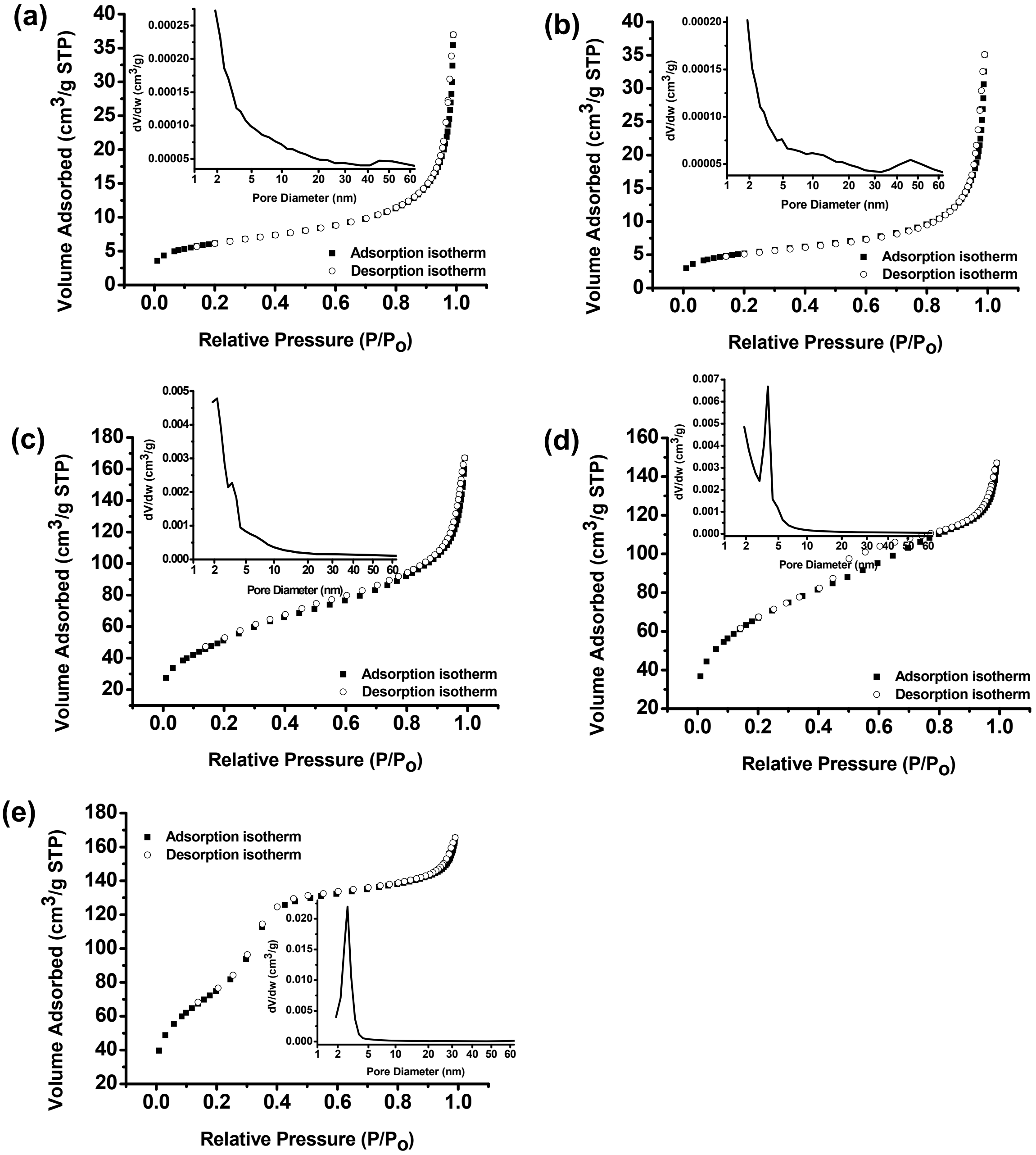
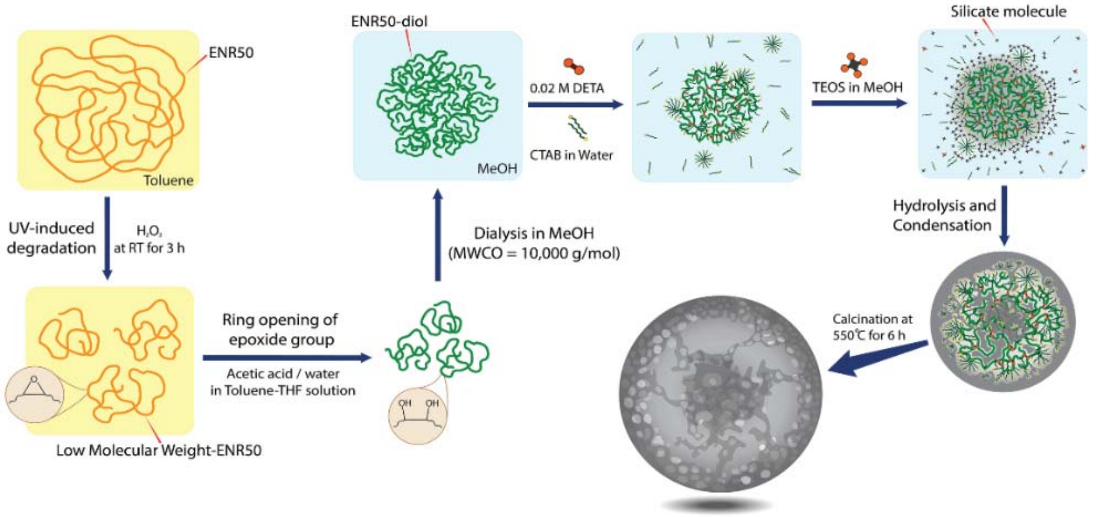


Fig. 4 N_2 adsorption-desorption isotherms and average pore size distributions (inset) of (a) SP-22, (b) SP-32, (c) MSP, (d) MSP-22, and (e) MSP-32.

Table 2 Physical properties of MSPs

MSPs	Particle size from TEM (nm)	BET surface area (m^2/g)	Pore diameter (nm)	Pore volume (cm^3/g)
SP-22	200	21.95	15.31	0.04
SP-32	230	18.59	17.29	0.04
MSP	100	183.27	6.35	0.23
MSP-22	300	239.89	4.77	0.21
MSP-32	350	268.50	3.34	0.25

The formation of MSPs using ENR50-diol/CTAB dual templates can be visualized as shown in Scheme 1. Initially, ENR50-diol particles are formed via the interactions between amine groups of DETA and diol groups of ENR50 yielding a uniform spherical polymeric particles. Next, CTAB micelles was added to the dispersion of ENR50-diol particles which then incorporates into ENR50 particles via hydrophobic interactions (Li et al., 2015; Niu et al., 2010; Teng et al., 2010). After the addition of TEOS, TEOS molecules become the silicate anions via the hydrolysis reaction. The negatively charged silicate species can couple with diol groups of ENR50 particles producing large mesopores (50 nm) while interact electrostatically with positively charged CTAB molecules which lead to the formation of small mesopores with 2 – 4 nm in size.



Scheme 1 Preparation of MSPs from ENR50-diol/CTAB dual templates.

CONCLUSIONS

Mesoporous silica particles (MSPs) have been successfully synthesized using ENR50-diol and CTAB as dual templates through the modified StÖber method. The particle size of MSPs was uniform due to a formation of ENR50-diol particles while the mesopores were created by ENR50-diol and CTAB with pore sizes approximately 50 nm and 2-4 nm, respectively. The specific surface area and pore volume of MSPs synthesized using ENR50/CTAB dual templates were enhanced compared with that synthesized using CTAB sole template.

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