Mesoporous Silica Nanoparticles Synthesized By Using Templating Technique

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ABSTRACT

Mesoporous silica nanoparticles (MSNs) were synthesized in this research. TEOS was used as a precursor and two types of surfactant including CTAB and TTAB, to be used as a main structure directing agent. DMHA, PVP and S770 were employed as co-templates. To compare the effect of template type on the characteristics of synthetic nanoparticles, molar ratio of precursor to template is equally controlled. The co-condensation method combined with water-CHX biphasic condition was utilized for this synthesis. The as-synthesized particles were incinerated to remove the directing agent at about 550 °C under atmospheric pressure for 5 h. To confirm the quality of synthesized nano-silica, characteristics of nanoparticles are characterized by several analytical techniques. Morphology, particle size and composition are analyzed by SEM and TEM. Surface area, pore volume and pore size distribution are determined by BET and BJH techniques through N_2 adsorption-desorption isotherm, while phase of particles was analyzed by XRD technique. Results showed that specific surface area (SSA) of MSNs synthesized by using TTAB, TTAB+DMHA, TTAB+PVP and TTAB+S770 is about 672.30, 477.60, 431.91 and 259.71 m_2/g, respectively. Pore size distribution of the obtained MSNs are quite uniform. XRD results indicate the amorphous phase of MSNs synthesized in this work. N_2 adsorption-desorption isotherm shows microporous size on each particles. Experimental results confirm the effect of structure directing agent type on the characteristics of synthesized MSNs.

Keywords: Characteristics, Mesoporous, SiO_2, Nanoparticles, Synthesis.

MATERIALS AND EXPERIMENTS

Tetraethylorthosilicate (TEOS, $C_8H_{20}H_4Si$, M_W: 208.33 g/mol, Density of 0.932-0.934 at 20 °C) was supplied by Merck. Cetyldimethyl ammonium bromide (CTAB, $C_{19}H_{42}BrN$, M_W: 364.45 g/mol), Tetradecyltrimethyl ammonium bromide (TTAB, $C_{17}H_{38}BrN$, MW: 336.39 g/mol, 97.5% purity) and Ryoto Sugar Ester S770 manufactured by Mitsubishi-Kagaku Foods Corporation, were supported by Merck (USA), Sigma-Aldrich (Singapore) and Caltech Corp., Ltd (Thailand), respectively. Ethanol (EtOH; C_2H_5OH, M_W: 46.07 g/mol, 99.9%) and cyclohexane with purity of 99.5% (CHX, C_6H_{12}, M_W: 84.16 g/mol) were purchased from RCI Labscan. L-Arginine (LAG, $C_6H_{14}N4O_2$, M_W: 174.20 g/mol) that is used as catalyst, was supplied by Himedia (India). Dimethylhexylamine (DMHA, $CH_3(CH_2)_4CH_2N(CH_3)_2$, MW:129.24 g/mol) and polyvinyl pyrrolidone (PVP, M_W: 360,000 g/mol) were purchased from Sigma-Aldrich (Singapore). Deionized water (DI-water, 18.2 MΩ) was produced by a Sartorius H2OPRO-DI-T Arium Pro DI Ultrapure Water System.

In this study, the high surface area mesoporous silica nanoparticles (MSNs) were attempted to synthesize. Characteristics of the obtained particles were evaluated. Co-condensation method that is modified from Stöber process [1] combined with water-CHX biphasic condition [2] was utilized for the synthesis of silica nanoparticles. Main templates including CTAB and TTAB, and co-templates including DMHA, PVP and S770, and catalyst; L-Arginine (LAG), were dissolved in DI-water under stirring and then CHX was slowly poured into the solution to create a second phase on the template and DI-water mixtures. About 15-20 min after CHX was added, TEOS was added dropwise and continued stirring for 20 h. Silica nanoparticles were collected by centrifugation and washed three times with ethanol-DI-water solution. Afterwards, as-synthesized particles were washed again with RO-water and dried in electric oven at 80 °C overnight. The process of the synthesis was shown in figure 1. Synthesized particles were characterized by an analytical techniques. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were employed to study the external and internal morphology and porous structures appeared on the particles. While Brunauer-Emmett-Teller (BET) Surface Area Analysis and Barrett-Joyner-Halenda (BJH) through the resulted N_2 absorption-desorption isotherm were utilized to analyze the surface area and pore size and volume, respectively. X-ray diffraction spectroscopy was used to evaluate the phase of particles.

EXPERIMENTAL RESULTS

As shown in figure 1, three types of co-template (DMHA, PVP and S770) used in this research affect external morphological structure of synthesized MSNs particles. Smallest and biggest particle size was obtained when S770 and DMHA are used as co-template, respectively. However, external nano-structure of MSNs not well define when S770 is employed.

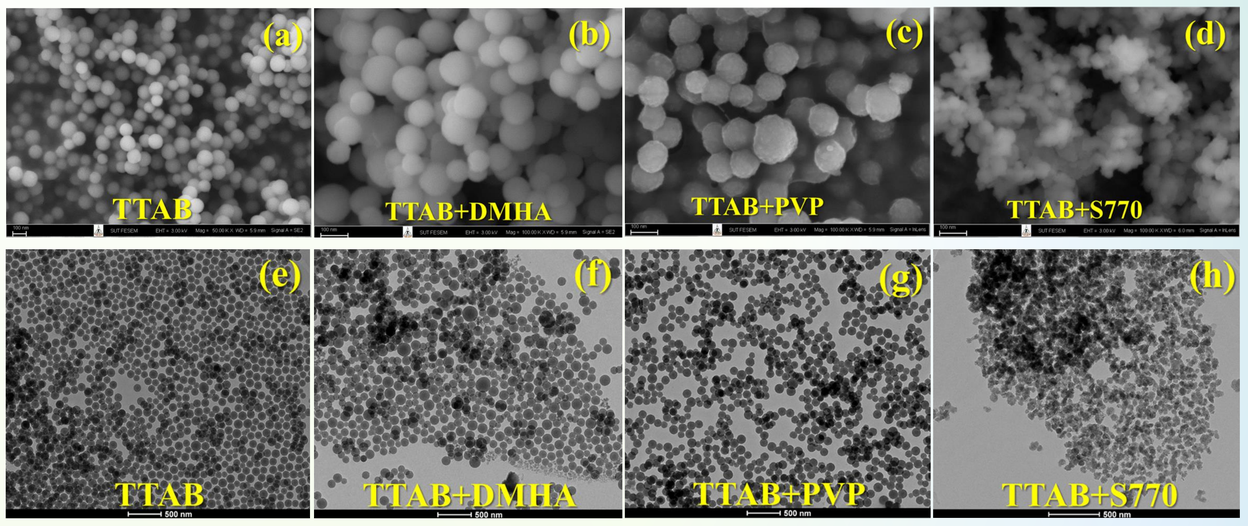

Figure 1. (SEM) External morphology of synthesized MSNs using, (a) TTAB, (b) TTAB+DMHA, (c) TTAB+PVP, TTAP + S770 and (d) CTAB, as templates and (TEM) porous structure of synthesized MSNs using, (e) TTAB, (f) TTAB +DMHA, (g) TTAB+PVP and (h) TTAB+S770.

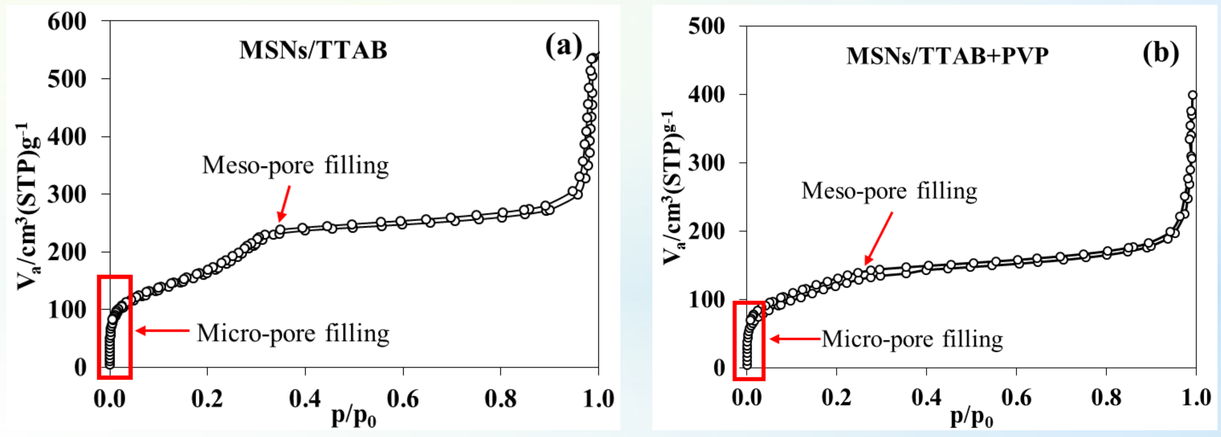

Figure 2. Nitrogen adsorption-desorption isotherm of synthesized MSNs using TTAB and TTAB+PVP as template and LAG as catalyst.

Micro/Meso-porous silica nanoparticles were completely synthesized. Profile of N_2 adsorption-desorption isotherm as illustrated in figure 2 shows clearly pore characteristics on the particles and corresponds to the type IV adsorption-desorption isotherm published by IUPAC [3]. Type IV adsorption-desorption isotherm clearly shows micro/meso-porous on the particles.

CONCLUSIONS

Micro/meso-porous silica nanoparticles (MMSNs) were completely synthesized. Catalyst and co-template affect the morphological structure, surface area, pore volume and particle size of synthesized porous silica nanospheres.

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