

**Highly efficient enzyme immobilization and stabilization within
meso-structured onion-like silica for biodiesel production**

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Introduction of Meso-Onion-S

By employing different concentrations and structures of meso-structure directing agents (surfactants), the surfactant packing parameters can be controlled, which enables the synthesis of mesoporous materials with various meso-structures.^{1,2} Pinnavaia group reported the synthesis of thermally stable mesoporous silica with vesicular (onion-like) structures denoted MSU-G.³ Although the silicate materials have layered structures, the porous structure was preserved after the removal of meso-structure directing agent. It was claimed that the phase of MSU-G is intermediate between lamellar phase and sponge-like three-dimensional phase. They adopted gemini amine surfactants for the synthesis of vesicular mesoporous materials. The hundred-nanometer sized vesicles are aggregated to form secondary structured particles. The reduced particle size with hierarchical structure allows facile processing and recovery without compromising rapid diffusion, which is difficult to achieve with mesoporous nanoparticles in an isolated form.³ The same group reported vesicle or onion-like mesostructured materials by using gemini surfactants as meso-structure directing agents.

However, the process is complicated because of an additional synthetic procedure for gemini surfactants.⁴ Similar onion-like vesicle-type mesostructured silica materials with large pore size (~10 nm) were synthesized via an aerosol assisted self-assembly or using a PEO-PBO-PEO surfactant.^{5,6}

Very recently, vesicle-like mesoporous silica with large pores (~10 nm) was synthesized by introducing hydrophobic additive, such as hexane and 1,3,5-triisopropylbenzene (TIPB), and used as a host for adsorption of proteins.⁷ Onion-like mesoporous silica with large pores was also synthesized from sodium silicate in the presence of α,ω -diamine surfactant.⁸

Table S1. The characterization of Meso-Onion-S, MCF and SBA-15.

	Pore volume (ml/g)	Surface area (m ² /g)	Pore size (nm)	Unit size (μm)
Meso-Onion-S	1.10	673	10	0.1-0.2
MCF	1.64	655	Window: 9.7 Mesocellular pore: 23	5.0-10.0
SBA-15	0.89	511	8.6	1.0-2.0

Table S2. The kinetic value and specific activity of immobilized lipase in Meso-Onion-S, MCF and SBA-15.

	K_m (μ M)	Specific activity (μ M/min/mg LP)
ADS-LP/Meso-Onion-S	217	38.8
ADS-LP/MCF	555	19.3
ADS-LP/SBA-15	9615	9.10
NER-LP/Meso-Onion-S	345	34.5
NER-LP/MCF	945	21.1
NER-LP/SBA-15	N. M	6.80

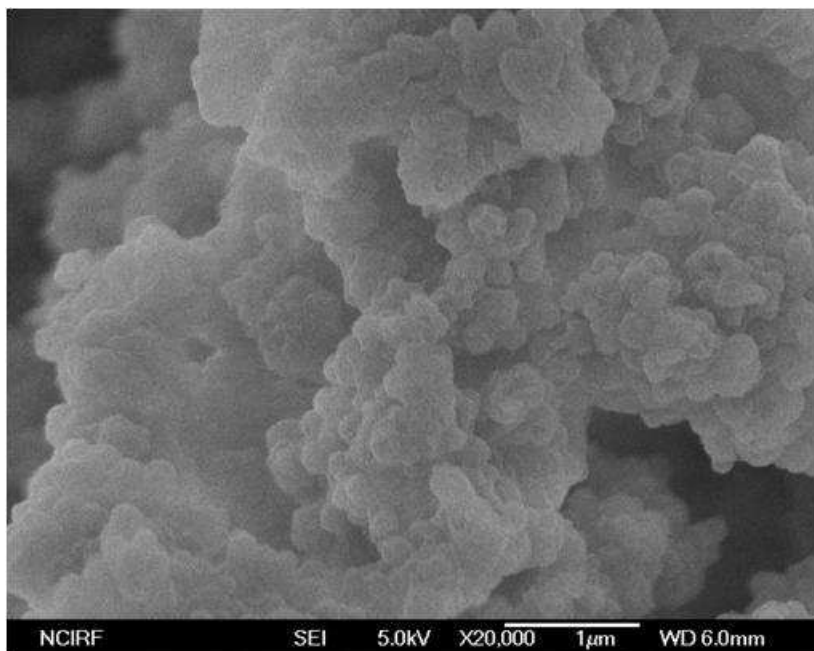


Figure S1. Scanning electron microscopic (SEM) image of Meso-Onion-S.

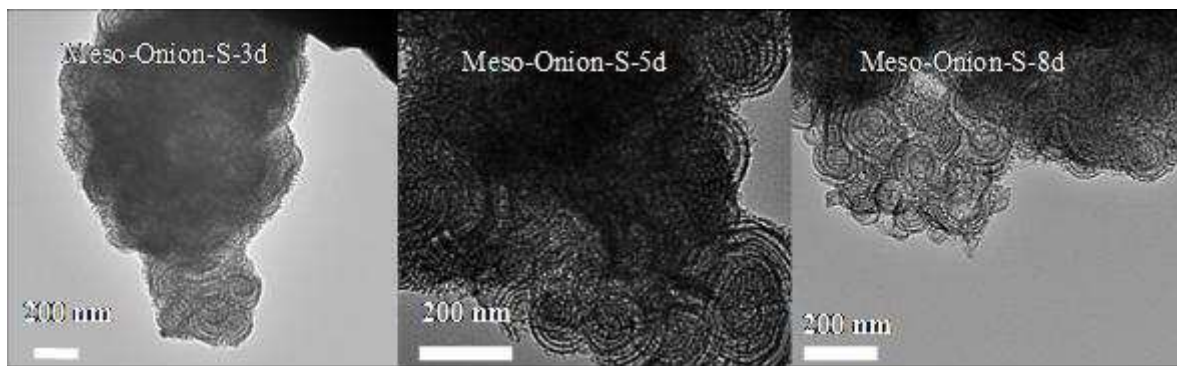


Figure S2. Transmission electron microscopic (TEM) images of Meso-Onion-S-X materials obtained at different hydrothermal reaction time (X).

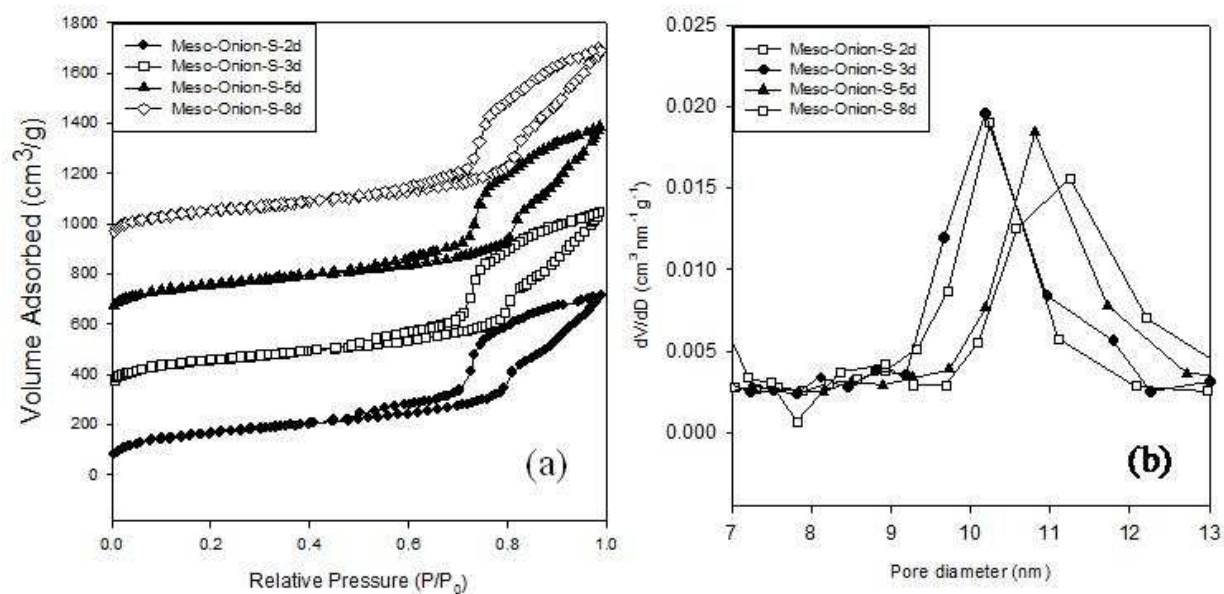


Figure S3. Nitrogen adsorption-desorption isotherms (a) and pore size distributions (b) of Meso-Onion-S-X.

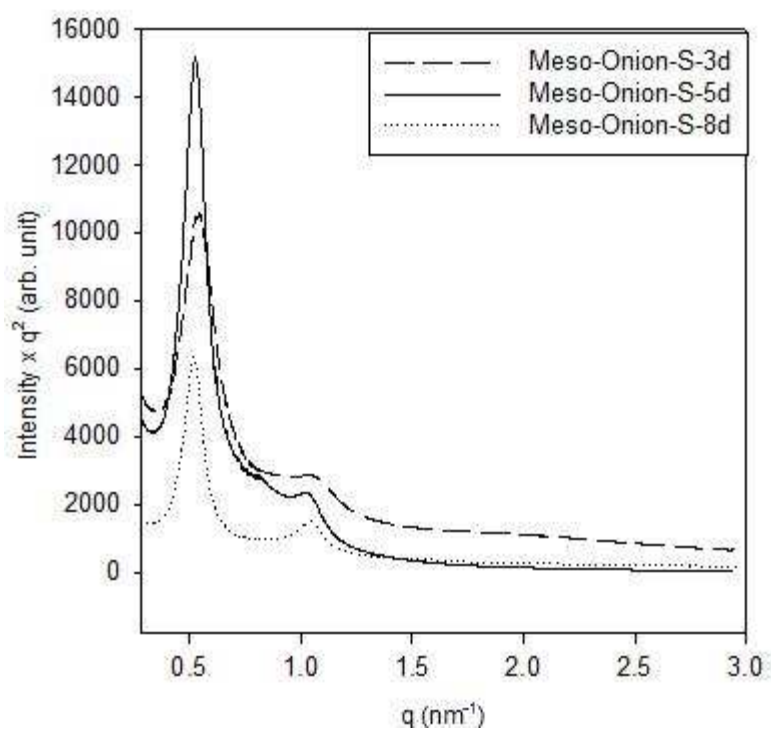


Figure S4. Small angle X-ray scattering pattern of Meso-Onion-S-X.

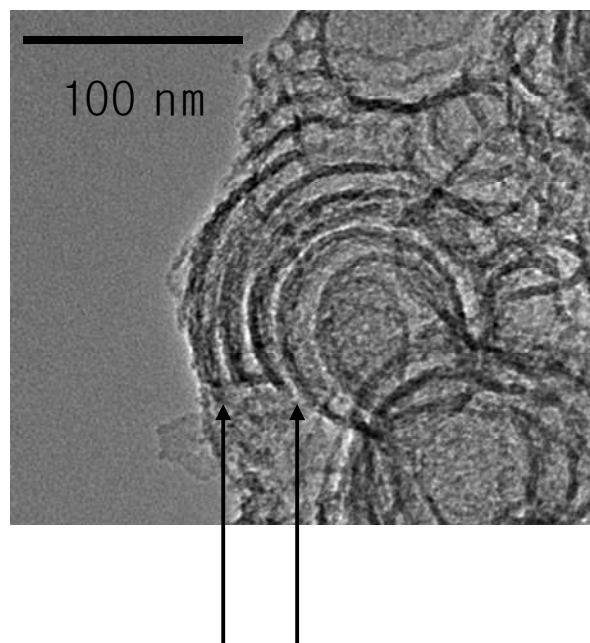


Figure S5. TEM image of Meso-Onion-S, showing the exposed mesochannels in Meso-Onion-S. The arrows indicate the exposed part of mesochannels.

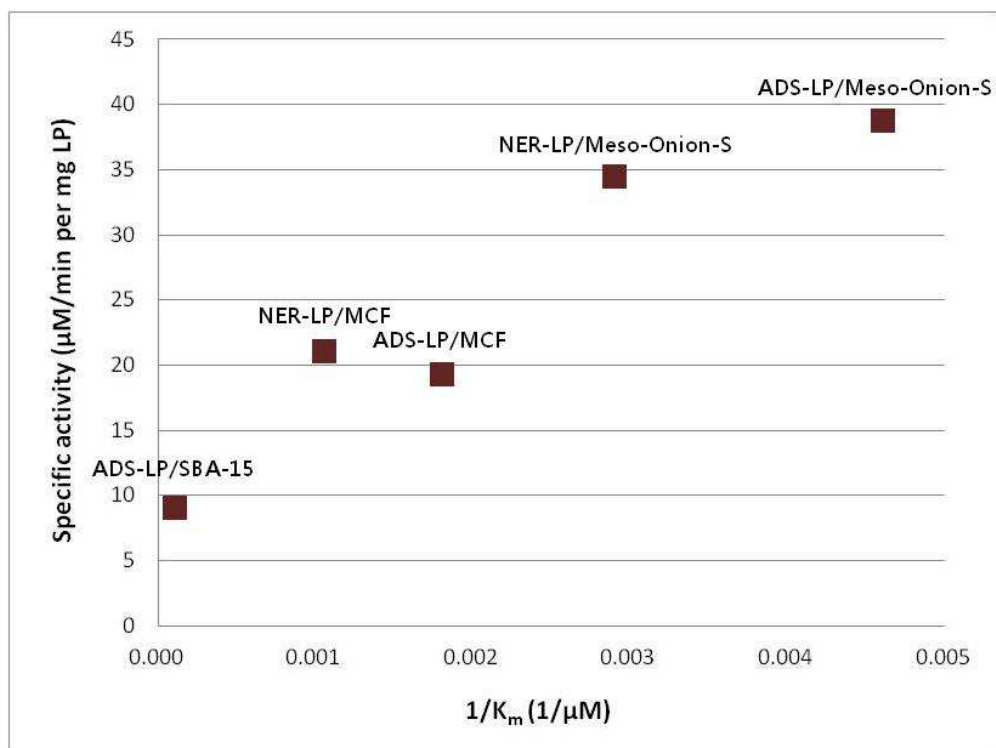


Figure S6. The correlation between the specific activity and inverse values of K_m of immobilized lipase in Meso-Onion-S, MCF, SBA-15.

References

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