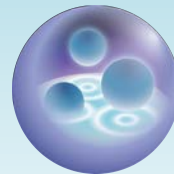




*Graduate School of Engineering,
Kobe University*



*Soft Matter Interface
Laboratory (SMIL:-)*

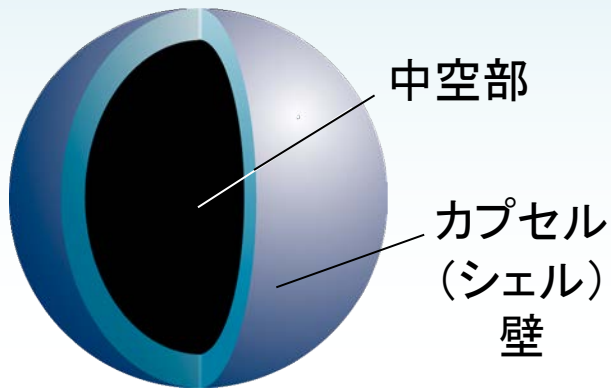
「ナノ～ミクロンサイズのシリカ粒子内包カプセル の局所場ゾルゲル反応による作製」

神戸大学大学院 工学研究科

鈴木 登代子

令和3年1月27日

中空構造を有する高分子微粒子と 有効成分内包カプセル粒子



カプセル内

ポリマー内壁近傍の影響
(バルクとは異なる環境)



内包物の物性

○ 高光散乱性

- ・ 有機白色顔料 (主に塗料分野)
- ・ 高光反射材 (主に化粧品分野)

○ 有効成分の内包化

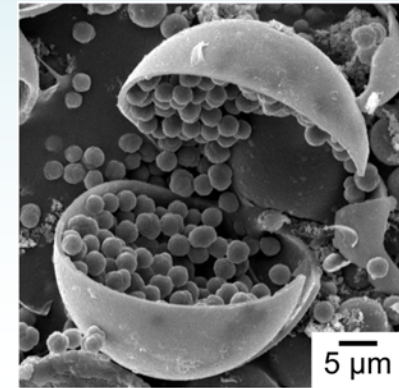
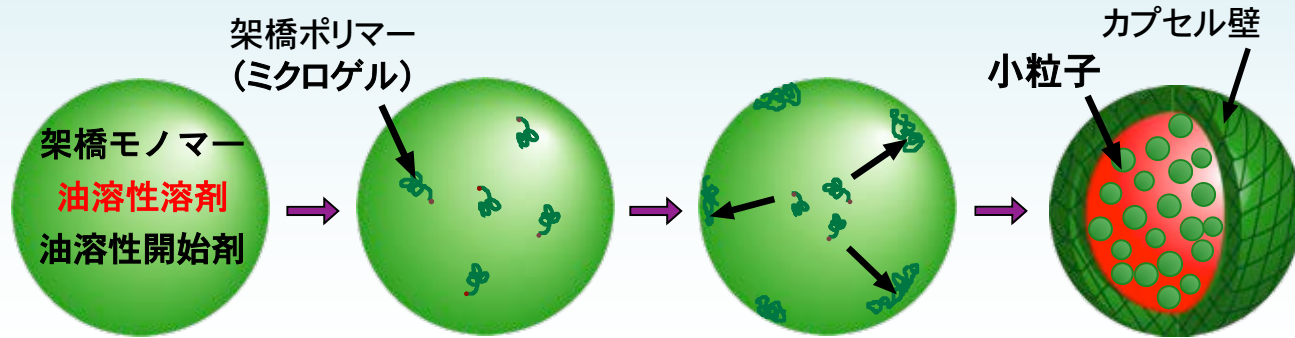
- ・ 徐放スピードの制御
(ドラッグデリバリーシステムなど)
- ・ 蓄熱材, 芳香剤
(パラフィン, 香料オイルなど)

カプセル内という特殊環境

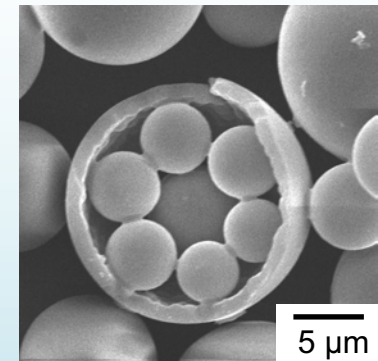
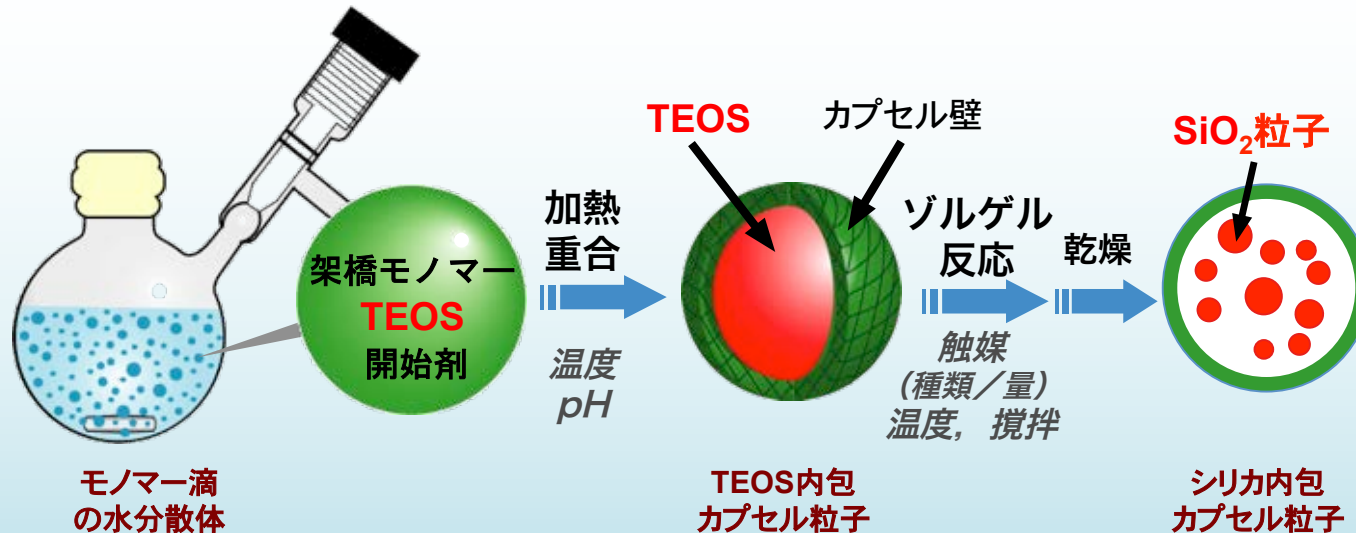
反応場

マイクロカプセルを微小反応場（リアクター）として利用

● 高分子微粒子内包カプセル粒子の一段階重合法



● カプセル内ゾルゲル反応によるシリカ粒子内包カプセルのワンポット作製





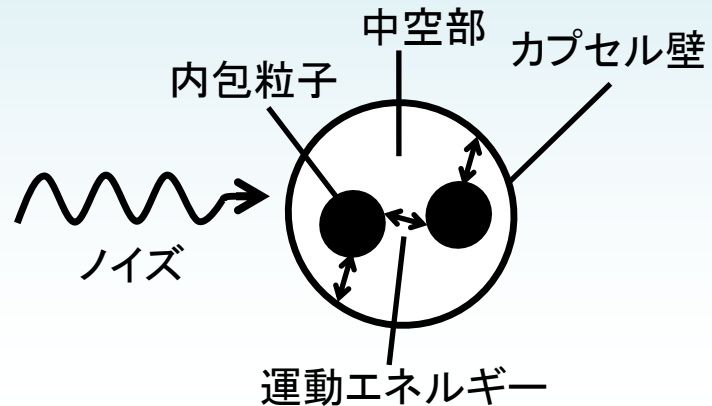
小粒子内包カプセル(ラトル状粒子)
の応用例

従来は作製に
多段階のプロセス
が必要

防音／防振材



※Authority
<http://www.ifam.fraunhofer.de/en.htm>

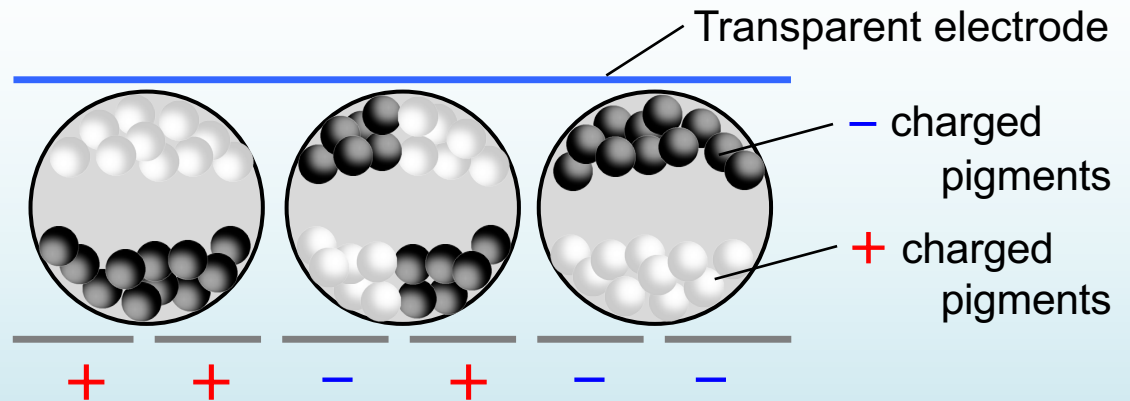


Vibration energy loss mechanism

電子ペーパー

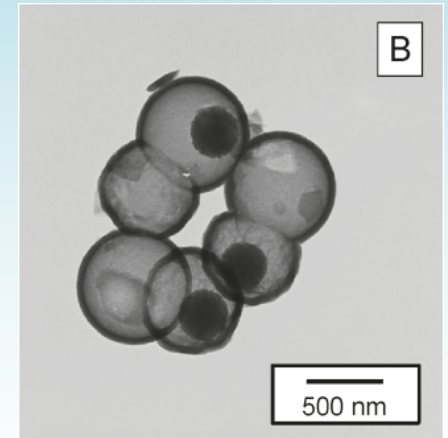
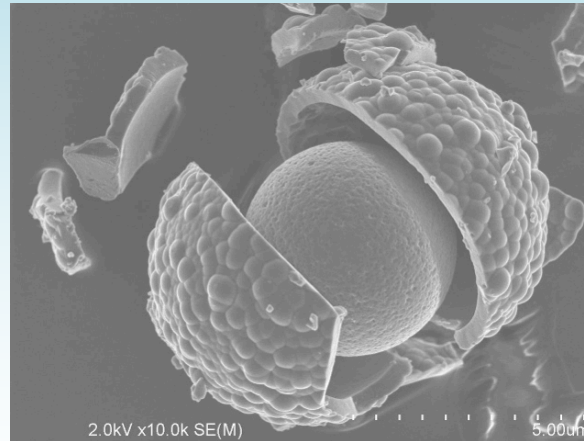
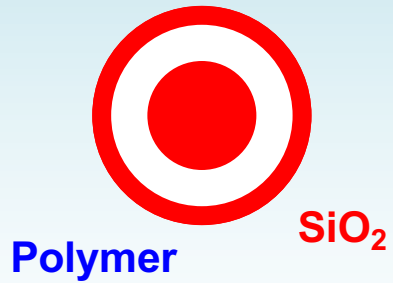


※Authority
<http://www.eink.com>



Cross-Section of Electronic-ink Microcapsules

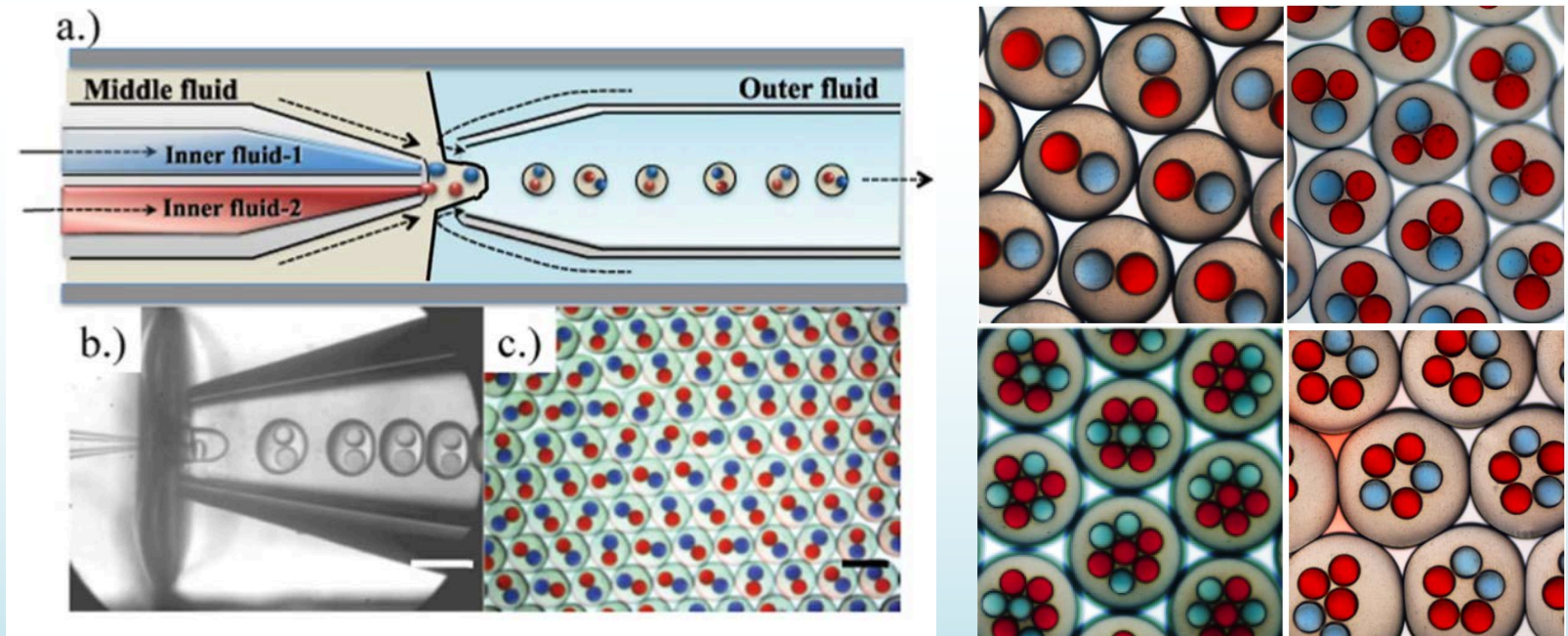
◎テンプレート法



T. Wakiya et al., *Mater. Lett.*, **65**, 1407 (2011)

Daisuke Nagao et al.,
Langmuir, **26**, 5208 (2010)

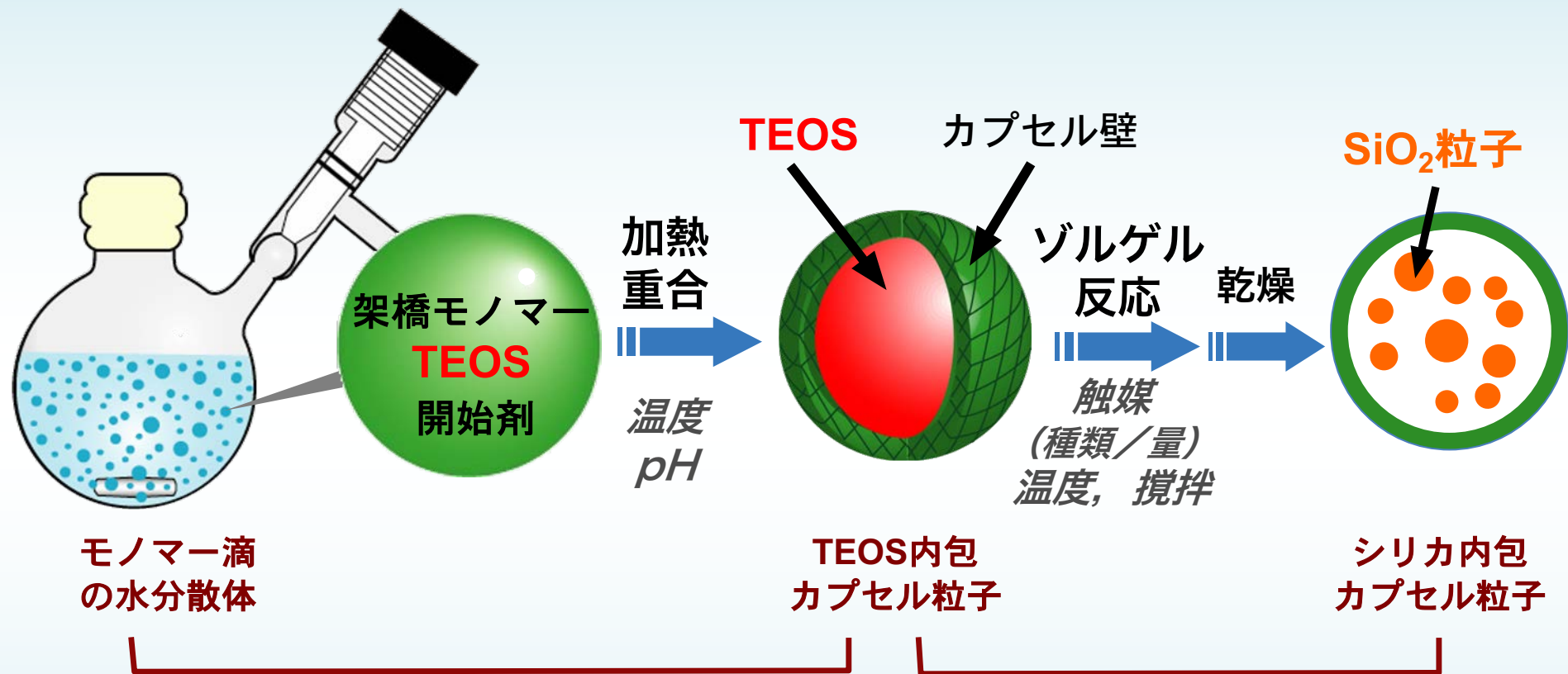
◎マイクロ流路装置の利用: ミクロな流路工学として設計法が確立



“Double Emulsions”

David A. Weitz et al, *Soft Matter*, **8**, 10719 (2012)

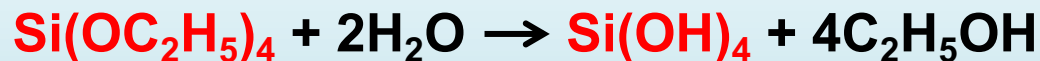
シリカ粒子内包ポリマーカプセルのワンポット作製法



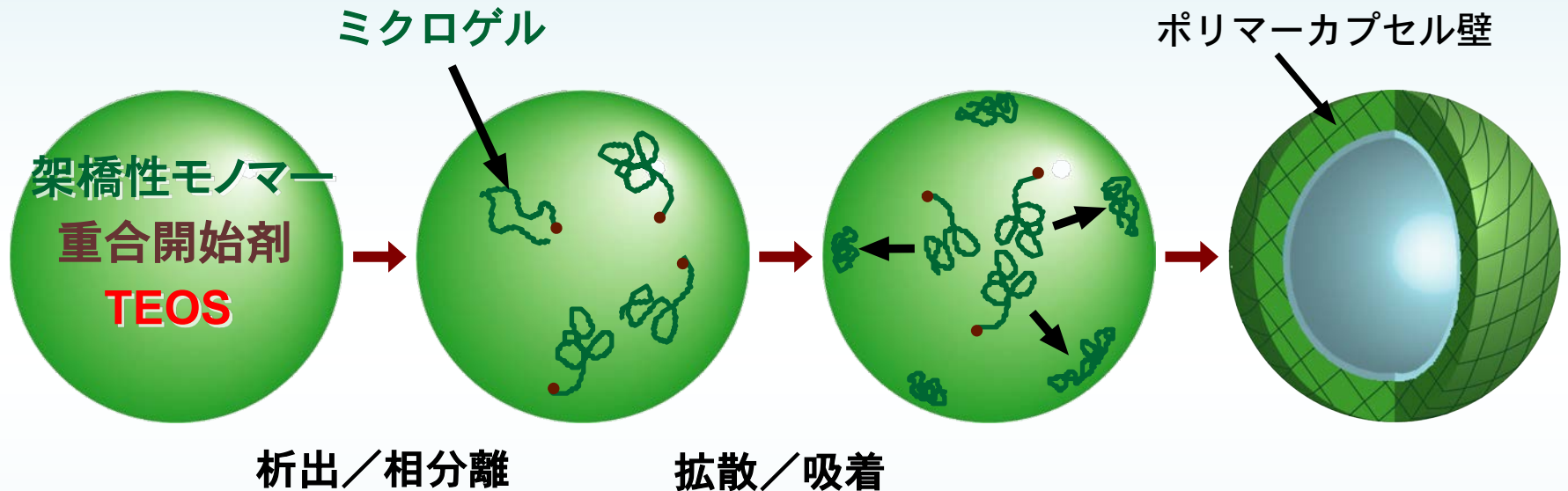
①カプセル粒子の作製

TEOS

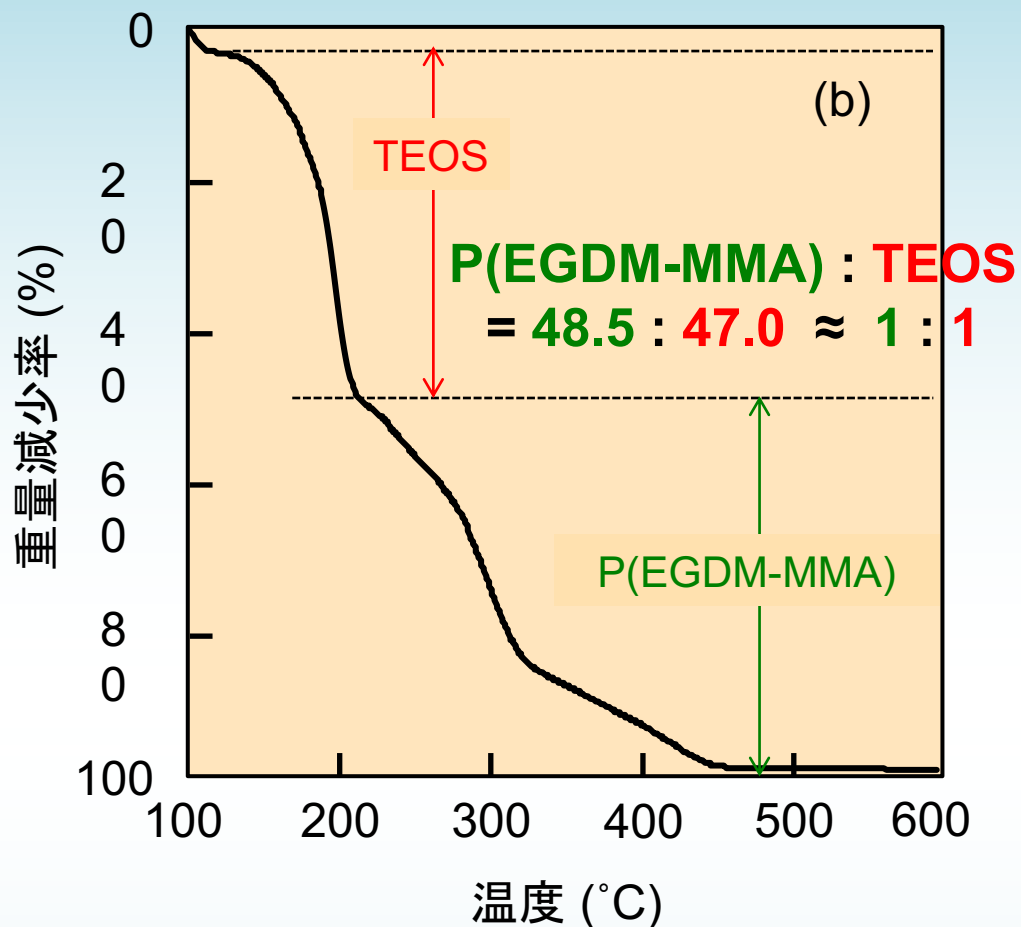
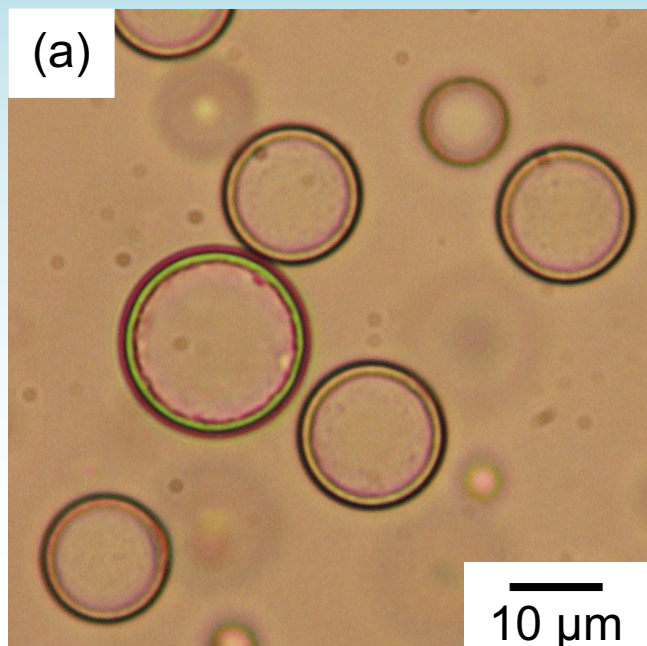
②ゾルゲル反応



相分離自己組織化法（SaPSeP法）を利用した
懸濁重合による中空構造を有する高分子微粒子の作製



Self-assembly of Phase Separated Polymer Method
(*SaPSeP Method*) 相分離自己組織化法



monomers/TEOS (w/w) 1:1

EGDM*	(g)	1
MMA	(g)	1
TEOS	(g)	2
V-70	(g)	0.08
PVA	(g)	0.06
Water	(g)	20

a) 30°C, N₂, stirring, 4 h

b) homogenizer, 4000 rpm, 5 min

Fig. **Optical micrograph** (a) of P(EGDM-MMA) particles with encapsulated TEOS and their **Thermogravimetry (TG)** curve (b)

*EGDM: ethylene glycol dimethacrylate
 MMA: methyl methacrylate

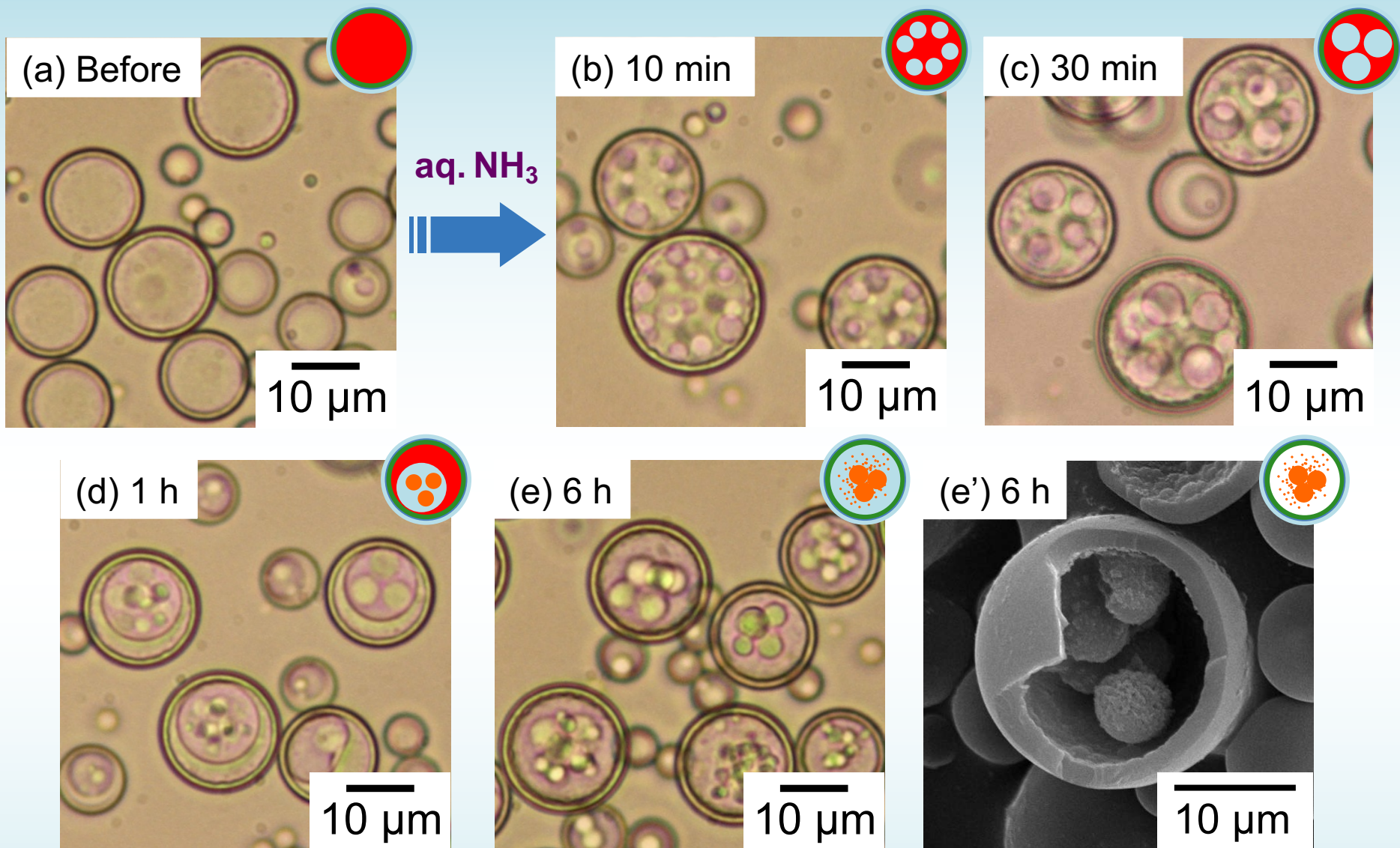
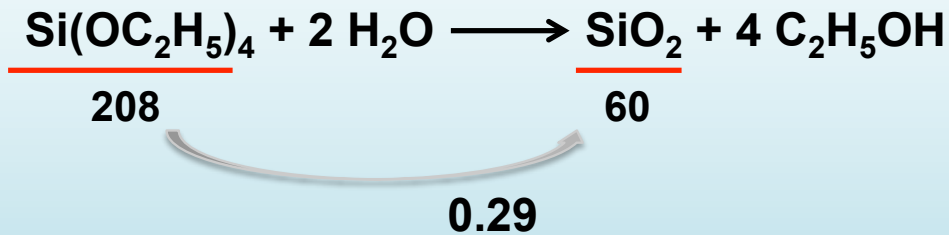
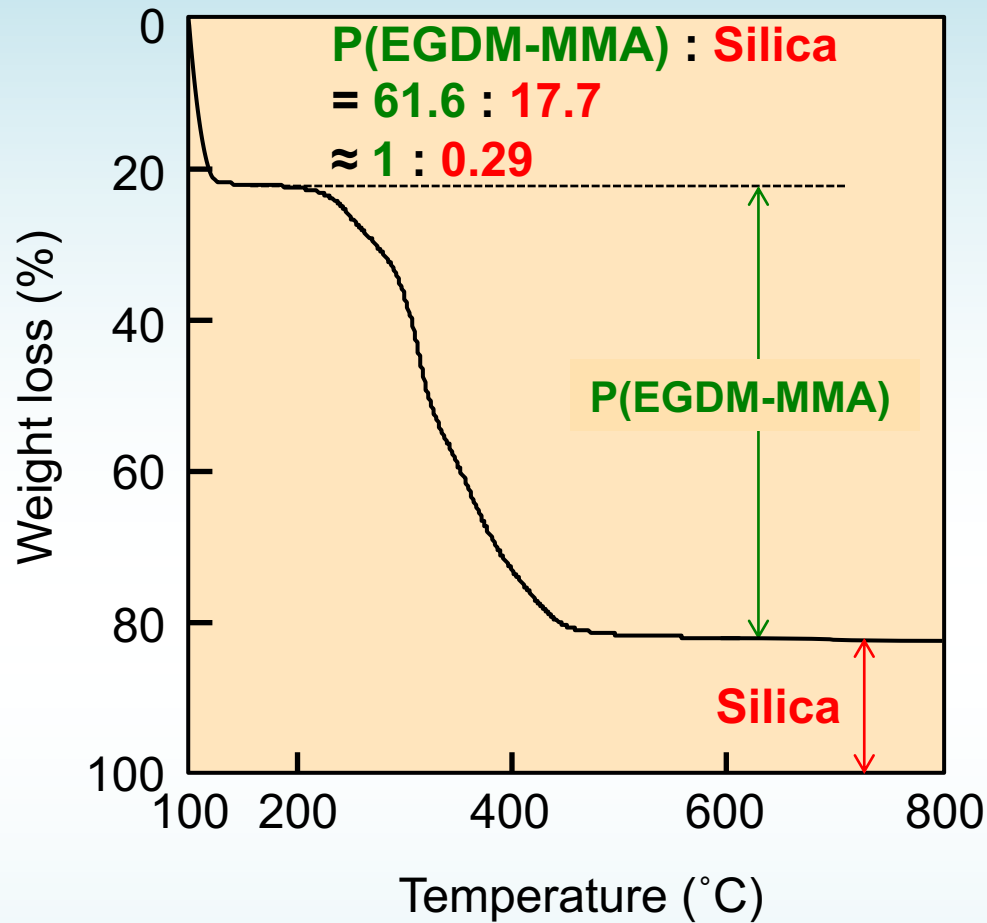


Fig. 1 Consecutive optical micrographs (a-e) of TEOS capsules before (a) and after addition of aqueous ammonia (NH_3/TEOS (molar ratio)=10) for 10 min (b), 30 min (c), 1 h (d) and 6h (e), and SEM photograph (e') of obtained particles after fracturing of polymer shell.



Weight ratio (w/w)

Before reactions:

monomers: TEOS = 1 : 1

After reactions:

polymer shell: SiO₂ = 1 : 0.29

C: 1s (285)

Si: 2s (151) Si: 2p (103)

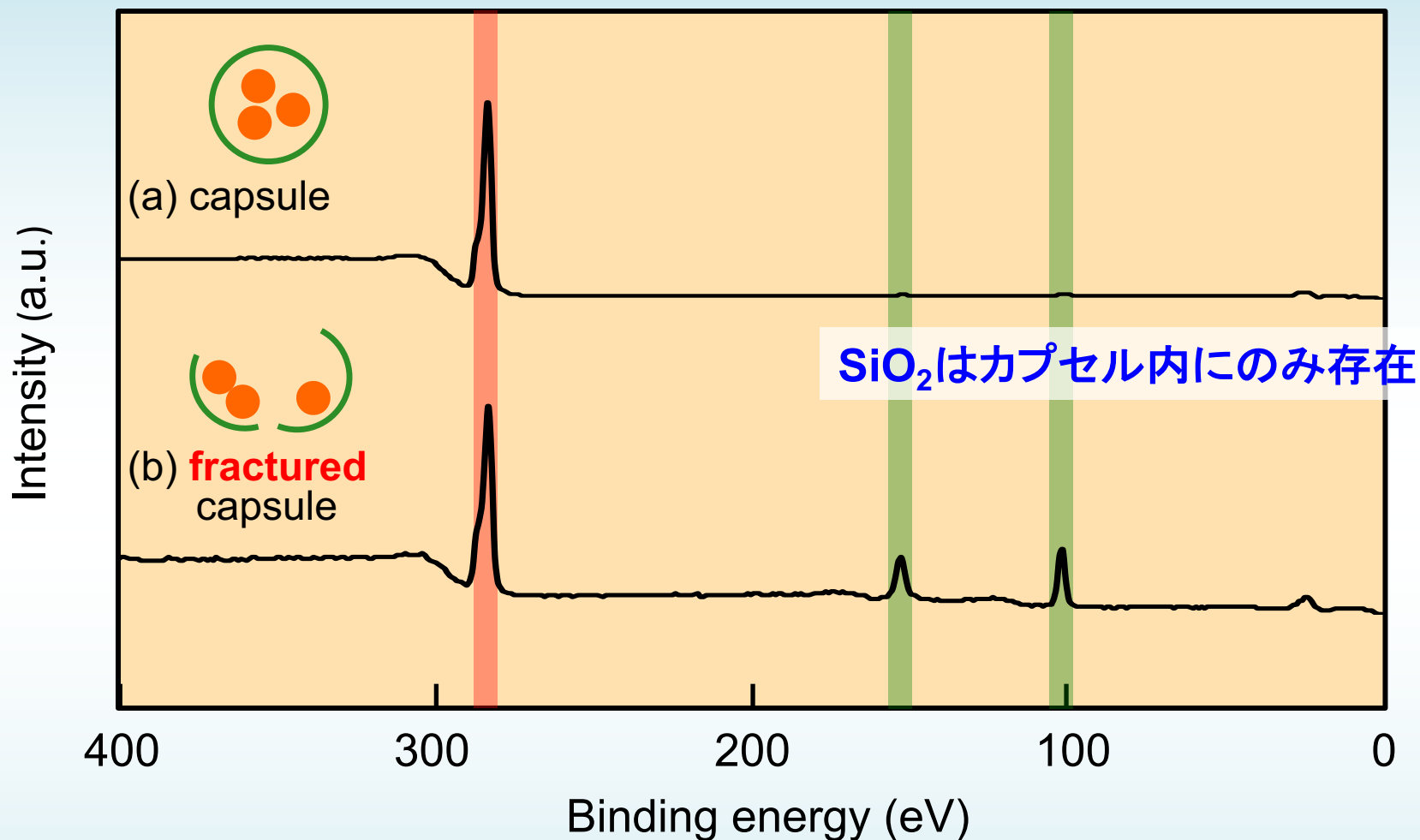


Fig. 3 XPS wide survey spectrum (MgK α) taken from P(EGDM-MMA)/SiO₂ particles, before (a) and after (b) fracture the capsule shell, prepared by sol-gel process of encapsulated TEOS with 10 molar ratio of NH₃ to TEOS

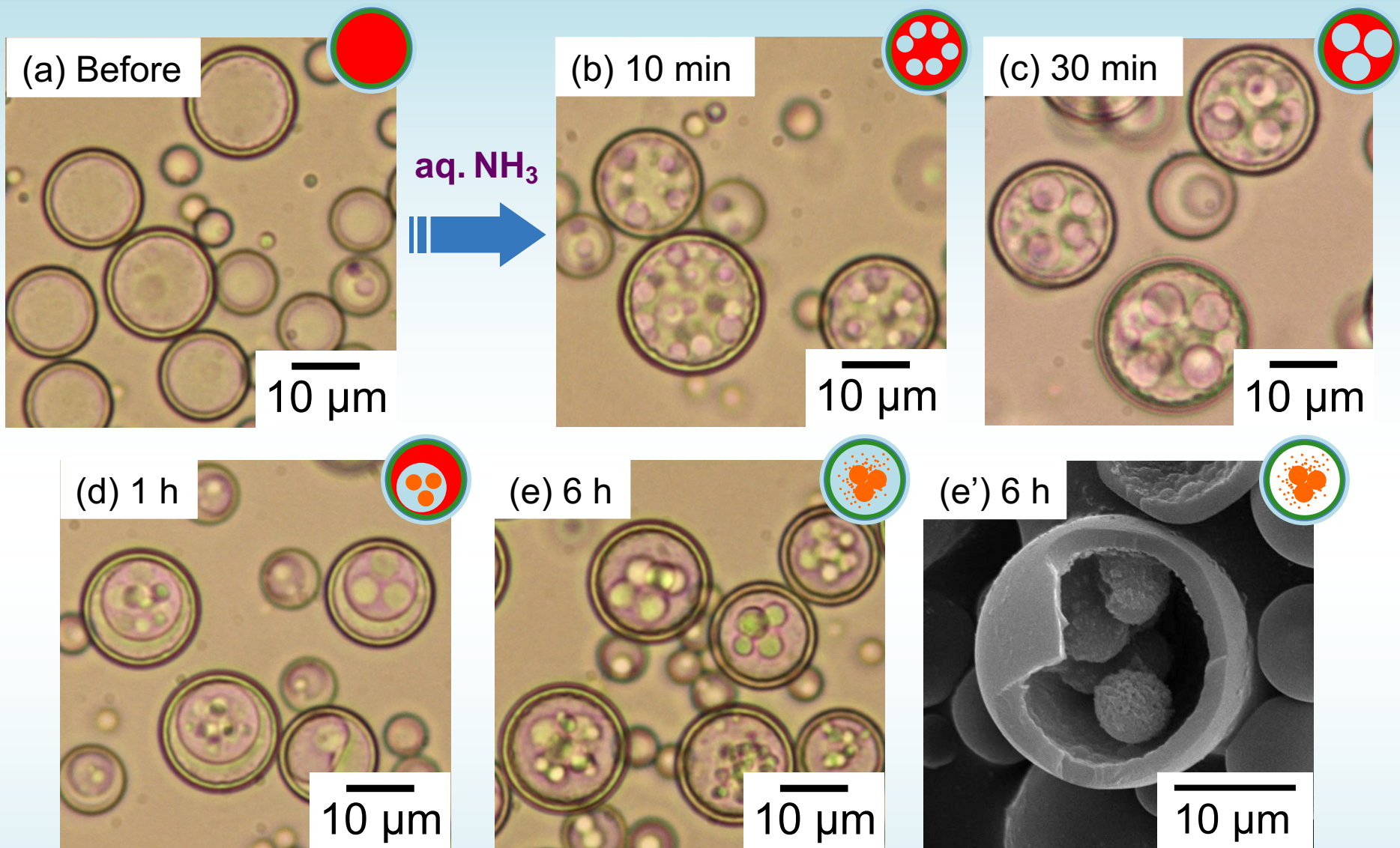
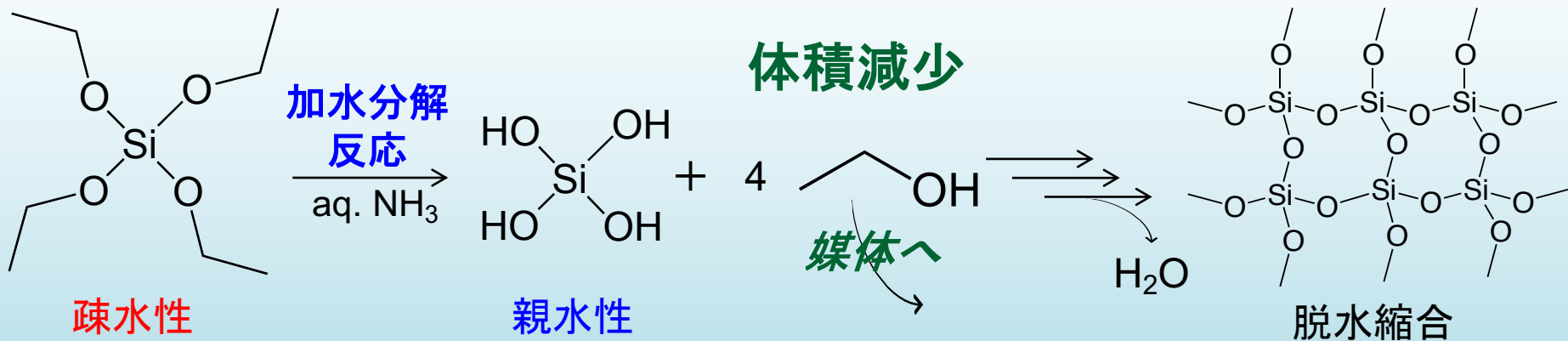
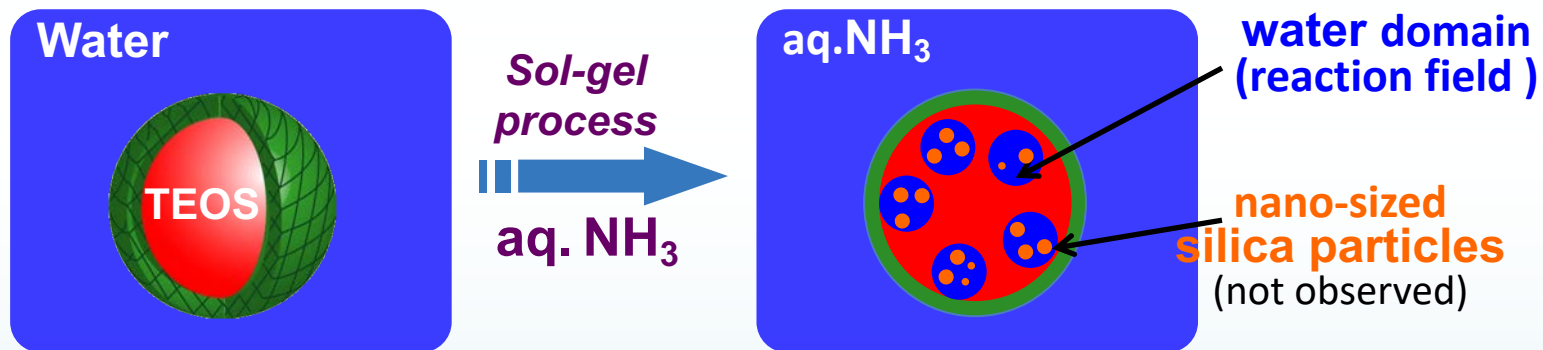
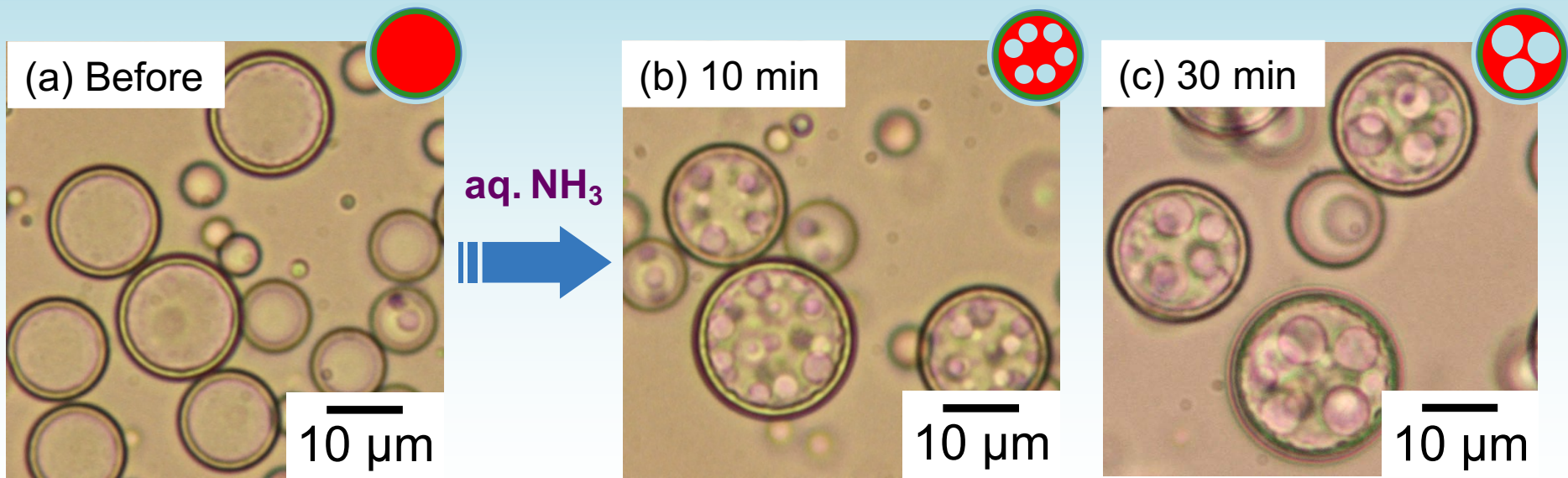


Fig. 1 Consecutive optical micrographs (a-e) of TEOS capsules before (a) and after addition of aqueous ammonia (aq. NH_3) for 10 min (b), 30 min (c), 1 h (d) and 6 h (e) and SEM photograph (e') of obtained particles after fracturing of polymer shell.

- ゾルゲル反応はカプセルの中のみ
- 全TEOSが転化



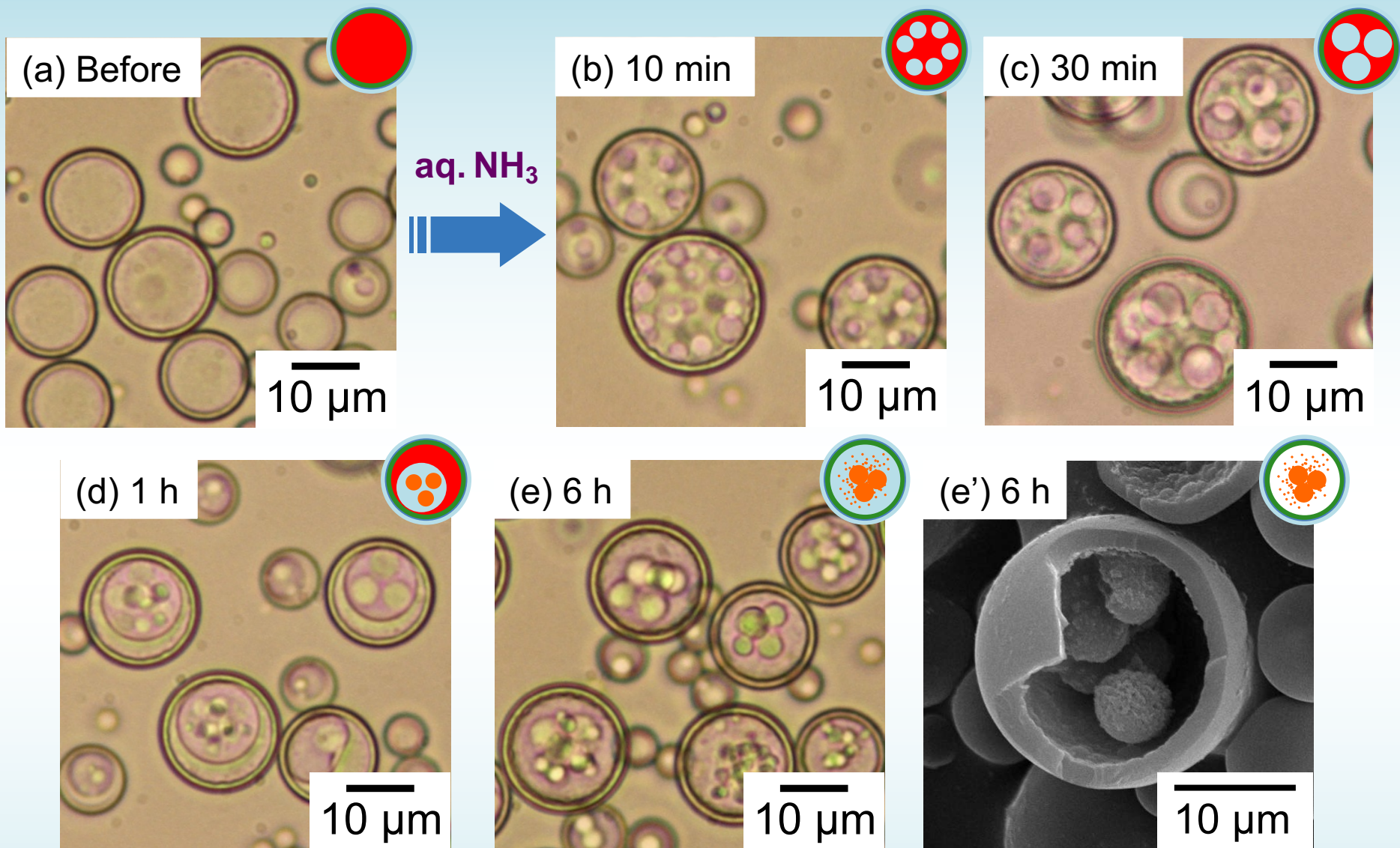
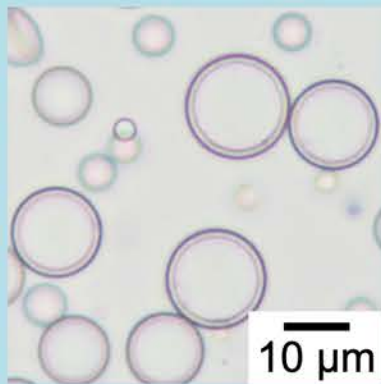
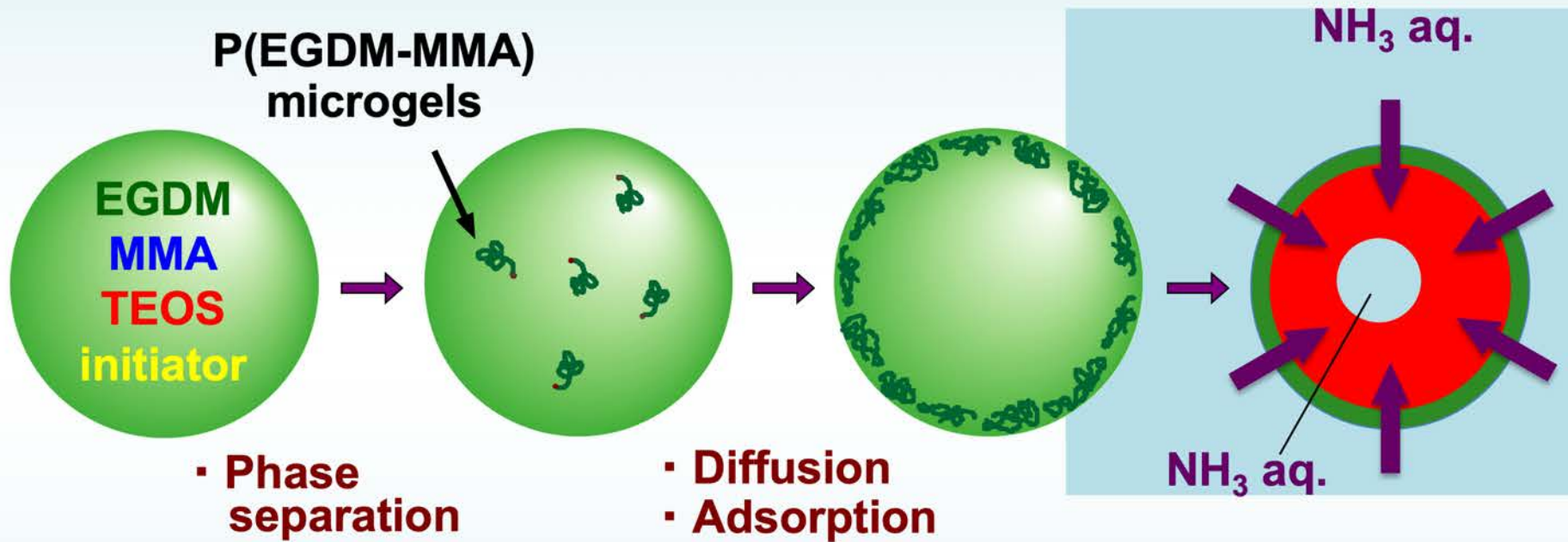


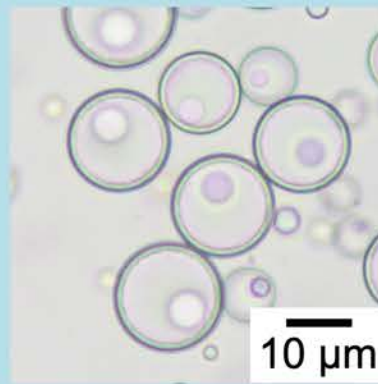
Fig. 1 Consecutive optical micrographs (a-e) of TEOS capsules before (a) and after addition of aqueous ammonia (NH_3/TEOS (molar ratio)=10) for 10 min (b), 30 min (c), 1 h (d) and 6 h (e), and SEM photograph (e') of obtained particles after fracturing of polymer shell.

**水ドメインの合一に伴って
シリカも凝集し成長**

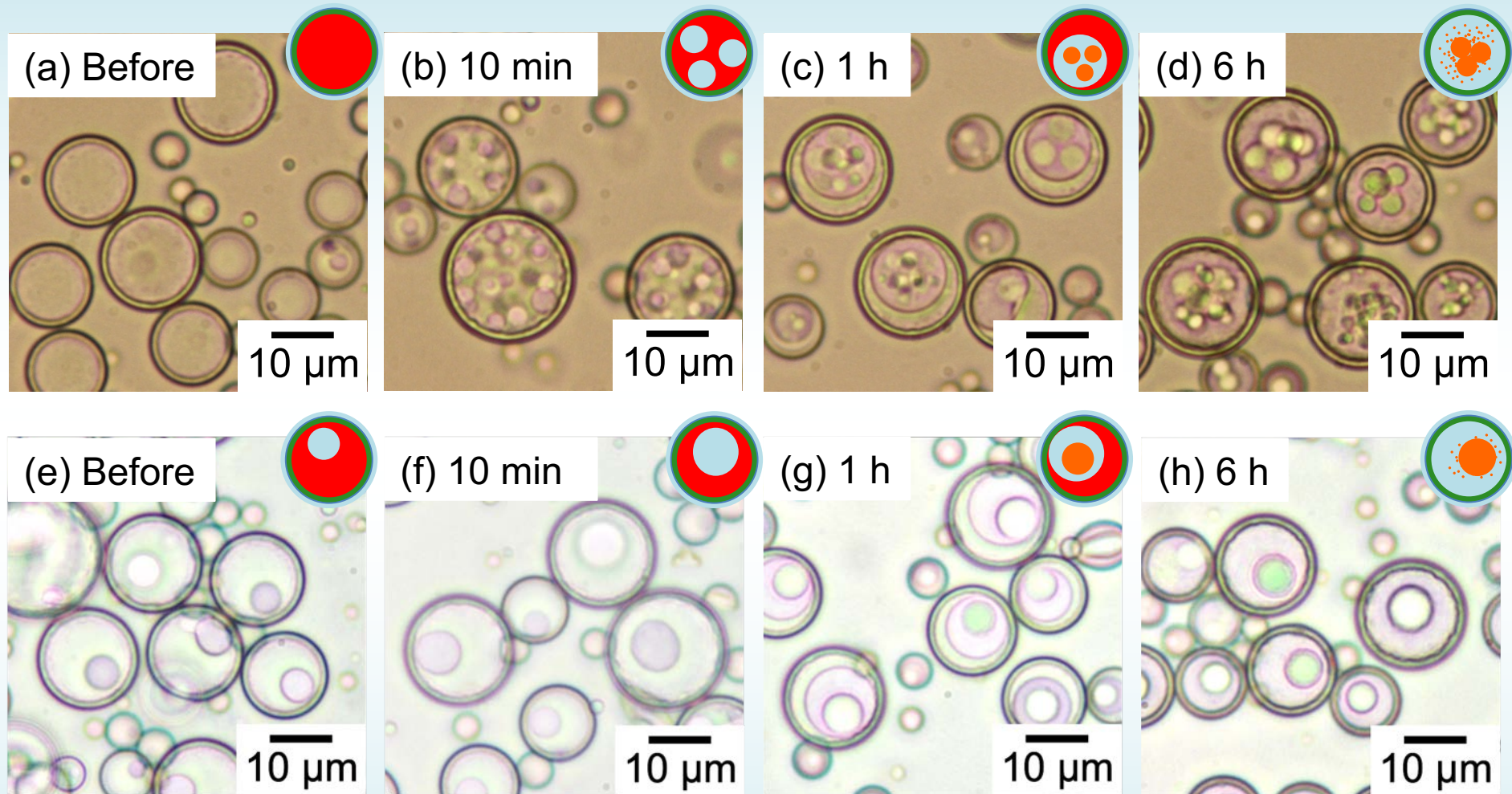
Self-assembling of Phase Separated Polymer Method (SaPSeP Method)



Cooling



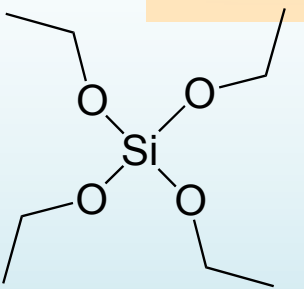
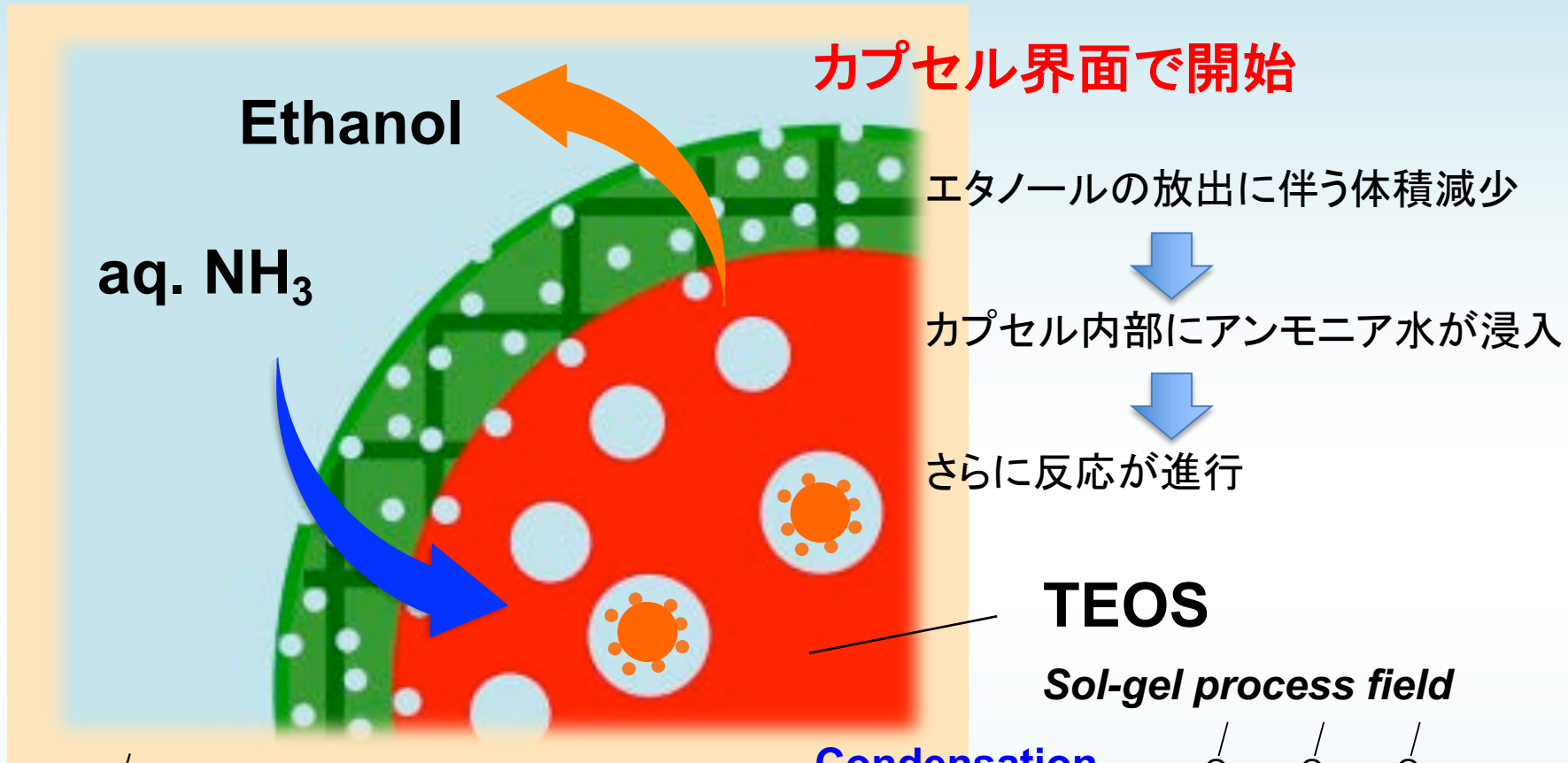
カプセルに水ドメインを存在させたらゾルゲル反応は進行するか？



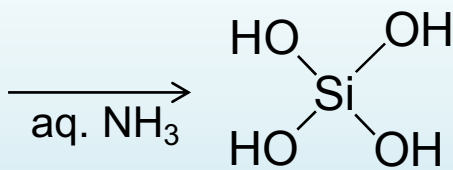
ゾルゲル反応はほぼ同じ速度で進行

$\text{NH}_3/\text{TEOS}(\text{molar ratio})=10$

カプセル内ゾルゲル反応の開始



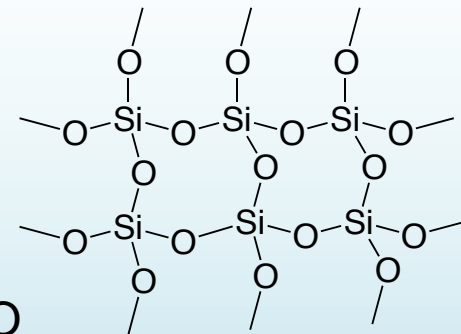
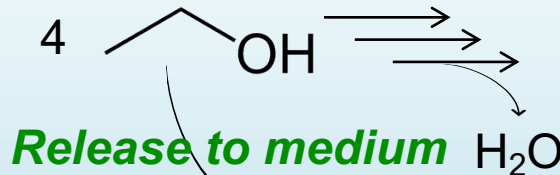
Hydrolysis



Hydrophobic

Hydrophilic

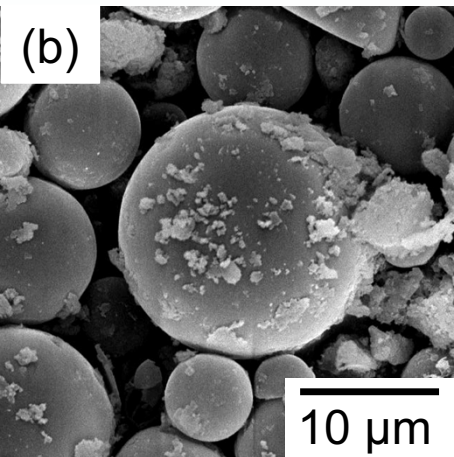
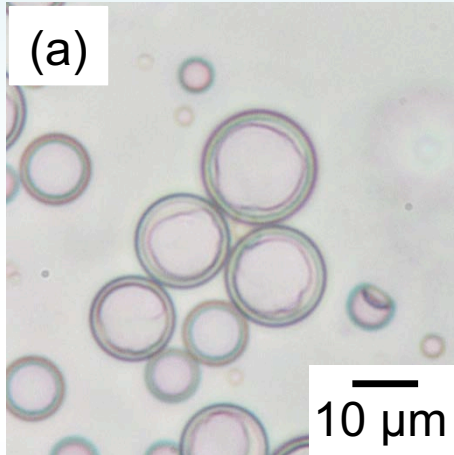
Condensation reaction



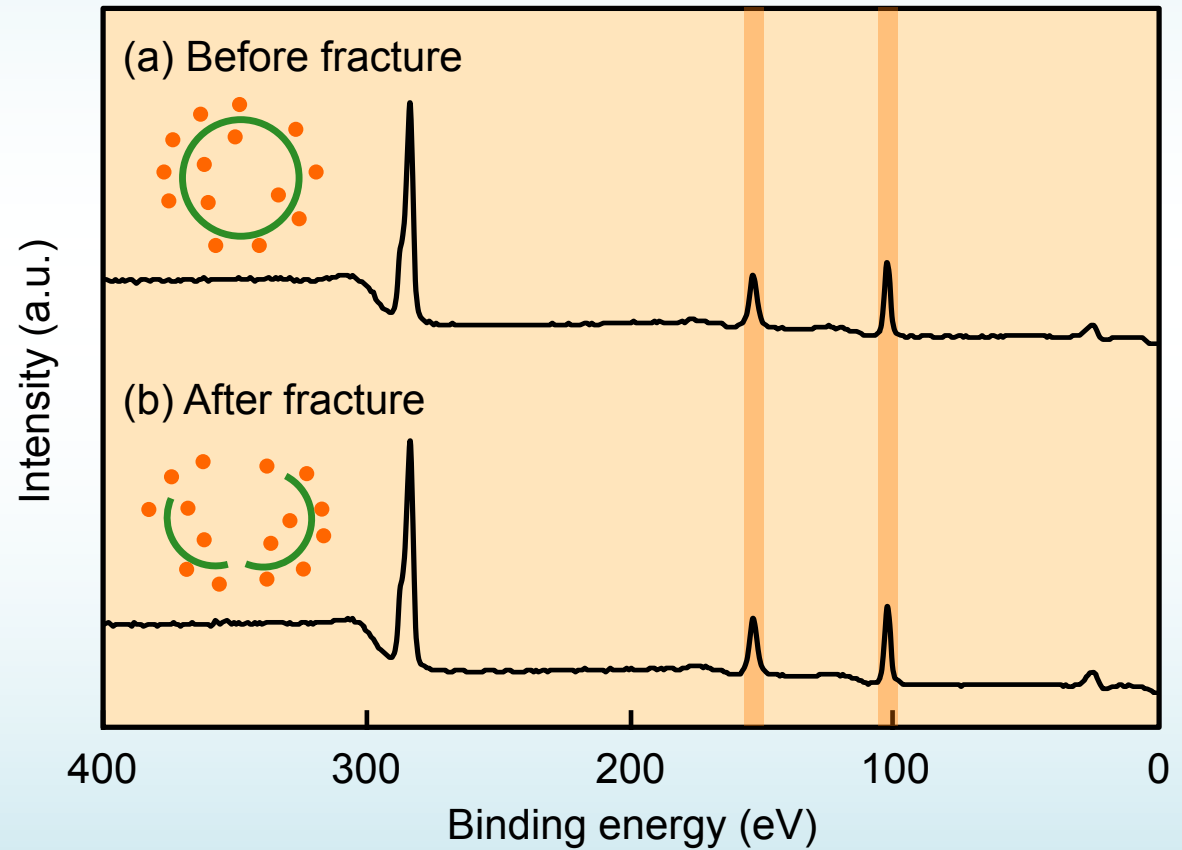
Three-dimensionally formed silica

ゾルゲル触媒量を1/200

速度低下→カプセル外部でシリカが生成
カプセル内ゾルゲル反応には適切量(速度)

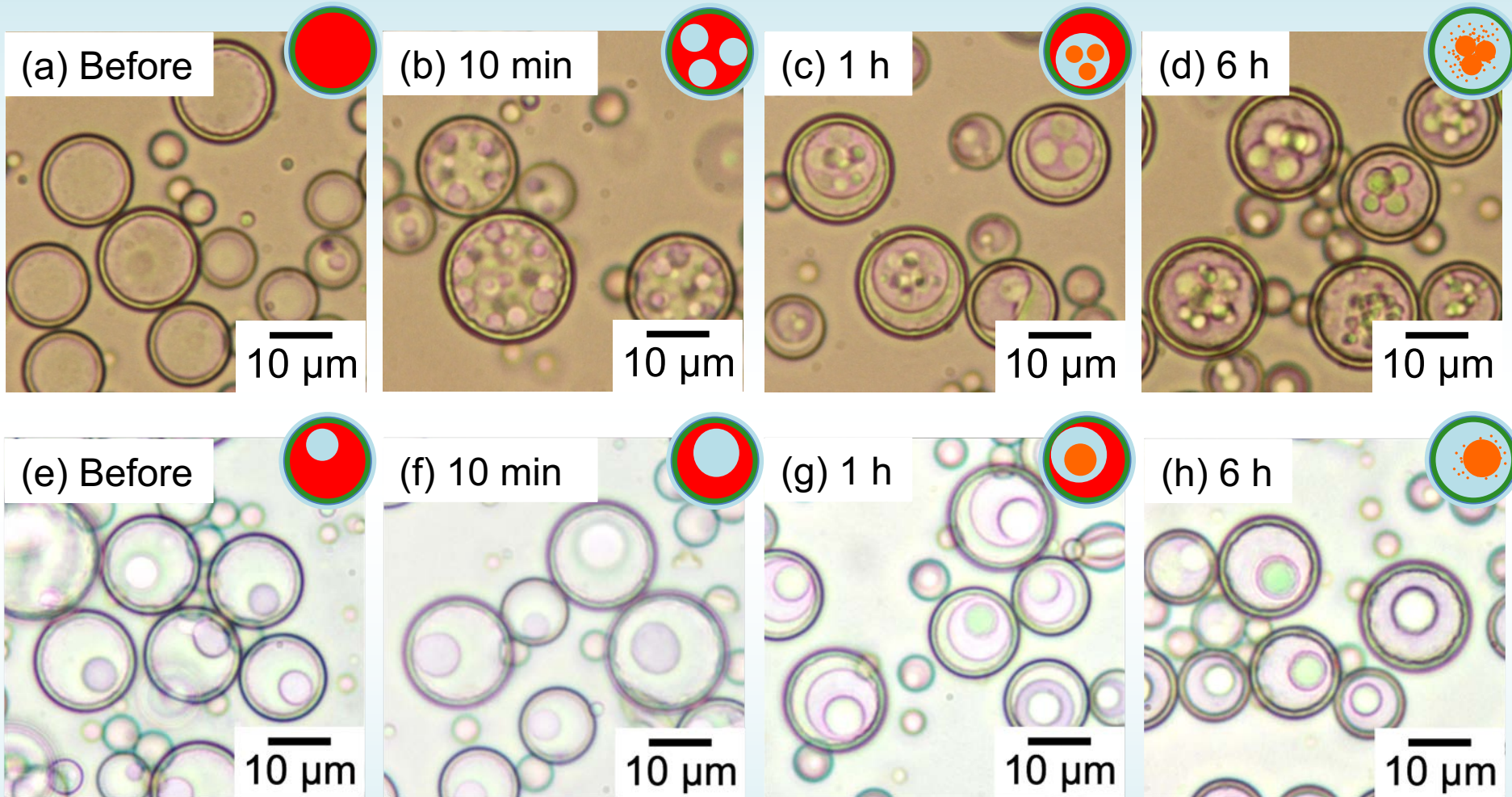


Si: 2s (151) Si: 2p (103)



96時間かけて反応

カプセルに水ドメインを存在させたらゾルゲル反応は進行するか？

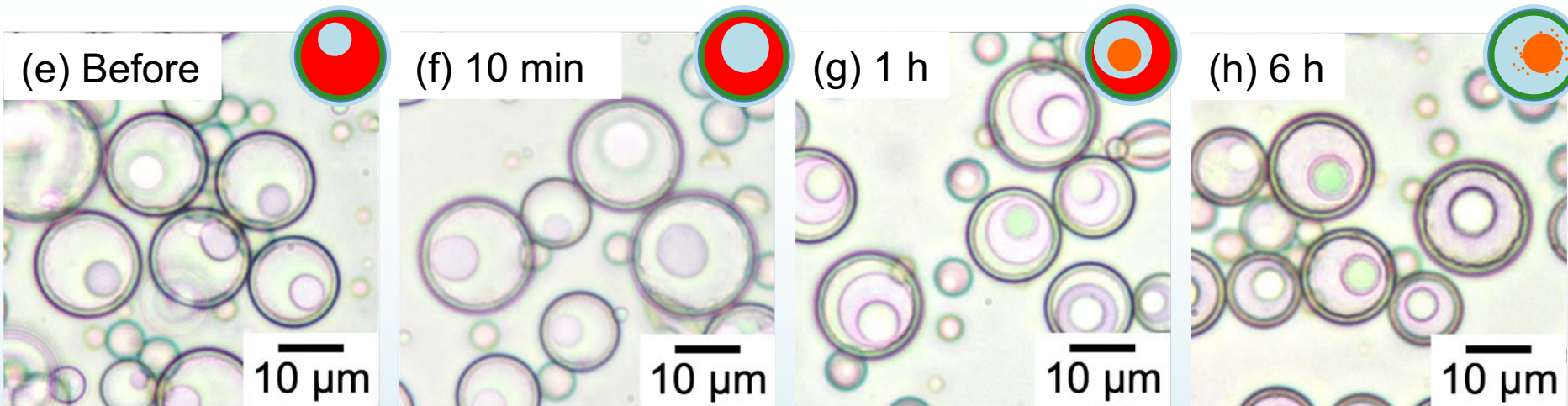
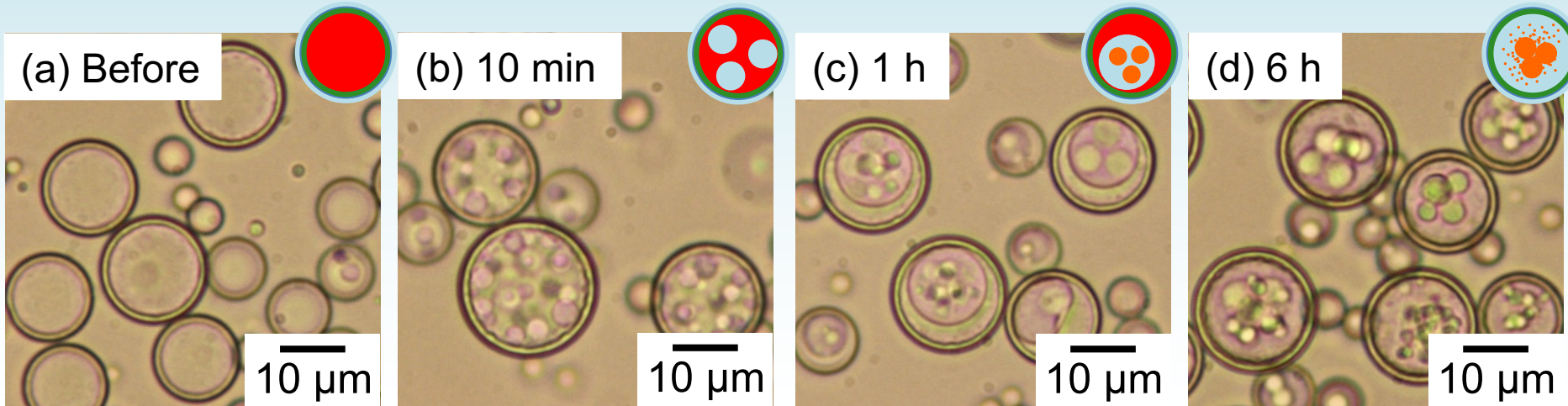


ゾルゲル反応はほぼ同じ速度で進行

ドメインがひとつのまま→1つの大きなシリカ粒子

NH_3/TEOS (molar ratio)=10

カプセルに水ドメインを存在させたらゾルゲル反応は進行するか？



water domains

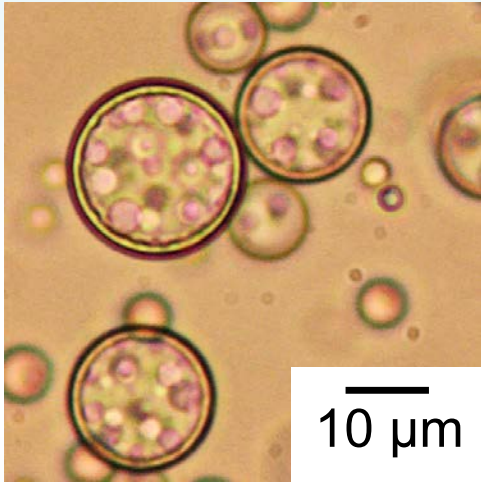
- number
- size



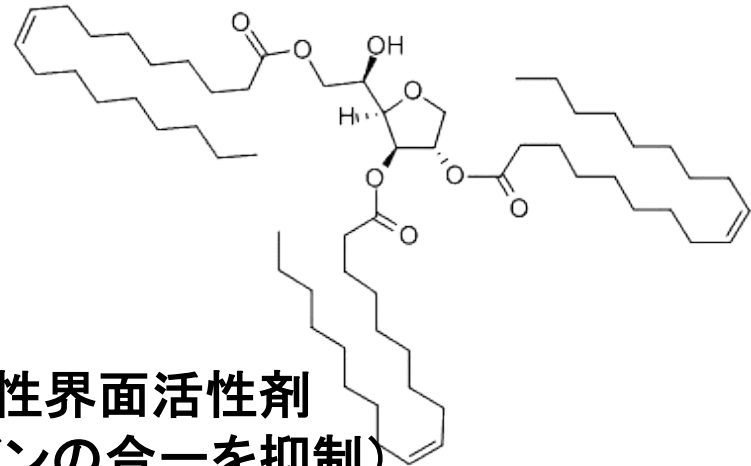
silica particles

- number
- size

Effect of oil soluble emulsifier on coagulation of water domains in capsule

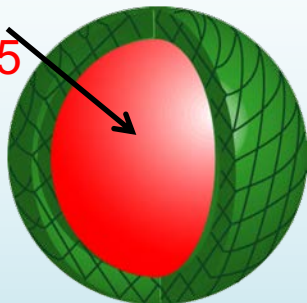


Sorbitan trioleate (**Span 85**)

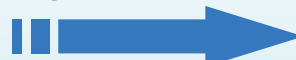


油溶性界面活性剤
(水ドメインの合一を抑制)

TEOS
Span 85



Sol-gel process



NH₃ aq.

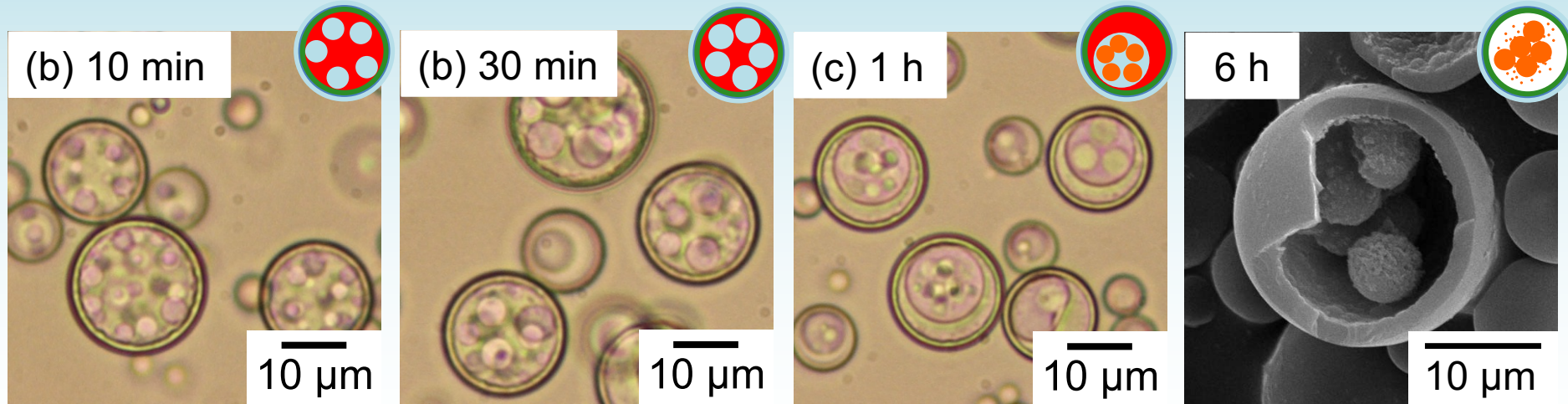
NH₃/TEOS(molar ratio)

= **10**



Span 85 添加無し

※反応速度に変化無し



Span 85 添加あり

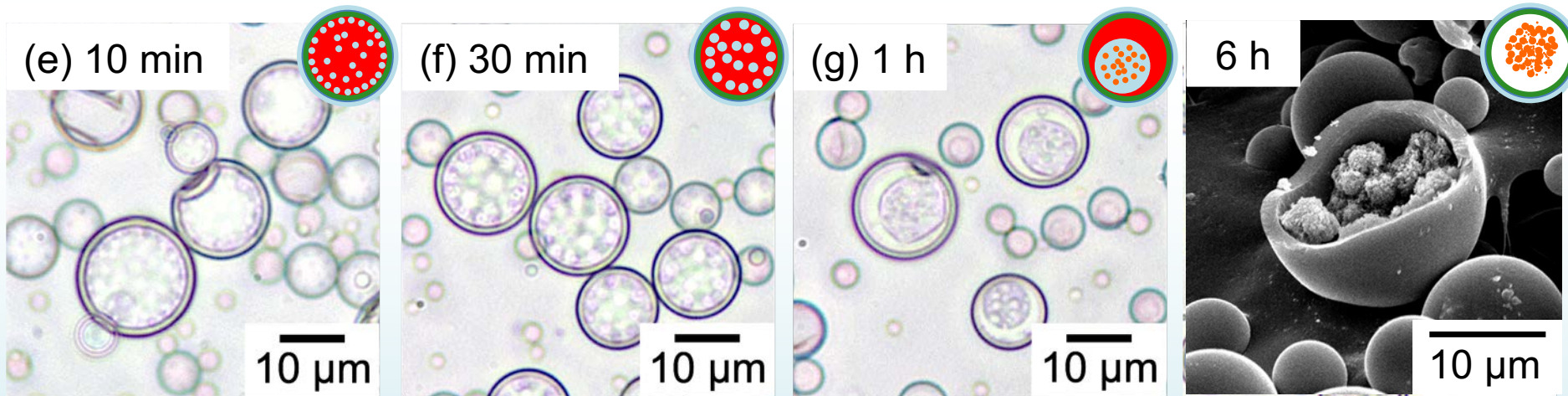
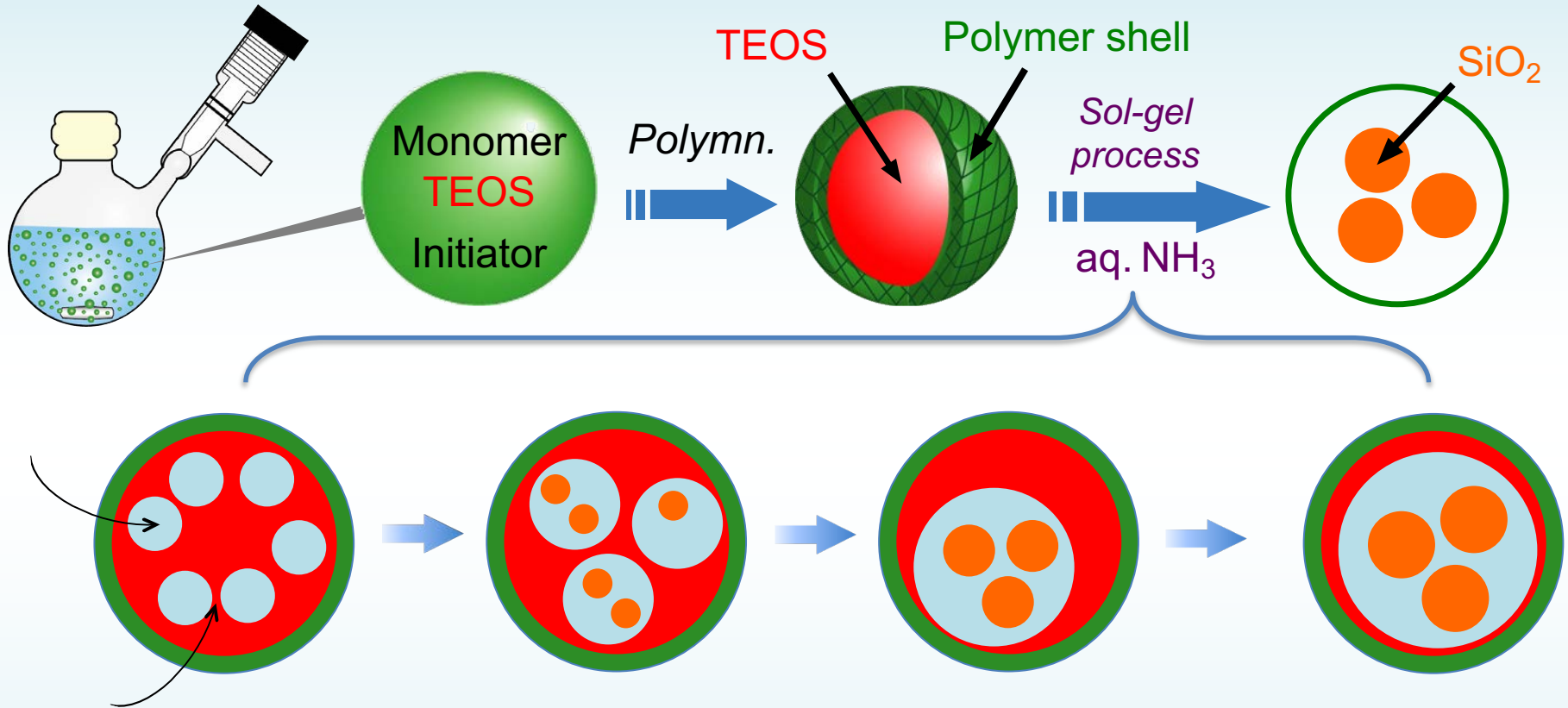


Fig. 4 Consecutive optical micrographs (a-h) of TEOS capsules after addition of NH_3 aqueous solution (NH_3/TEOS (molar ratio)=10) for 10 min (a, e), 30 min (b, f), 1 h (c, g) and 6 h (d, h), in the absence (a-d) and presence (e-h) of Span 85 in original TEOS capsules

Influence of penetration rate of water into the capsule on the morphology of silica particles



媒体の浸入速度 \propto ゾルゲル反応速度

\Rightarrow NH₃/TEOS (molar ratio) = 1, 10, 50

シリカ転化率-時間曲線

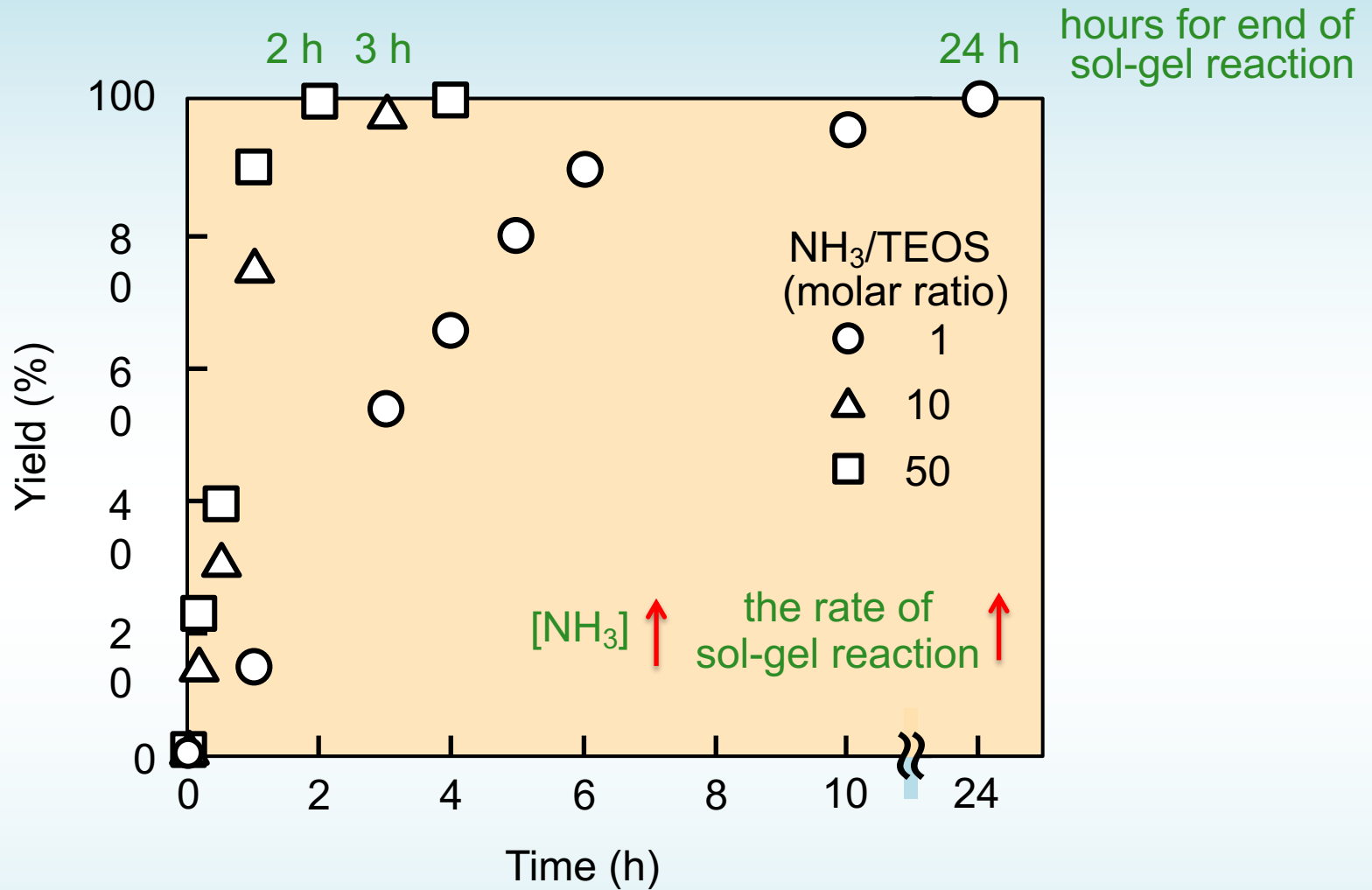


Fig. 5 **Yield versus time plots** for sol-gel processes of encapsulated TEOS in P(EGDM-MMA) capsule at 30°C with various molar ratios of NH_3 to TEOS; ○ : 1, △ : 10, □ : 50

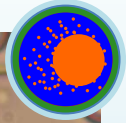
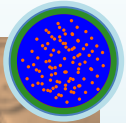
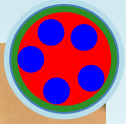
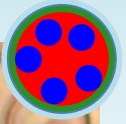
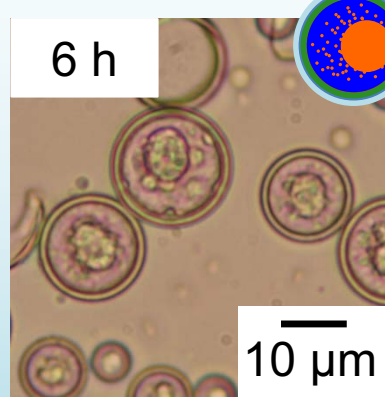
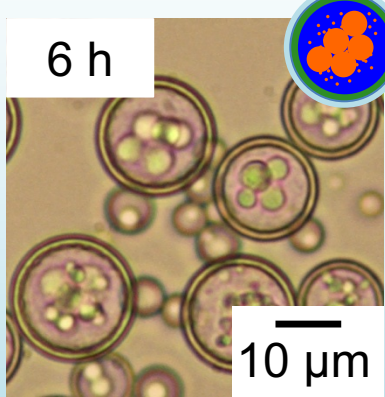
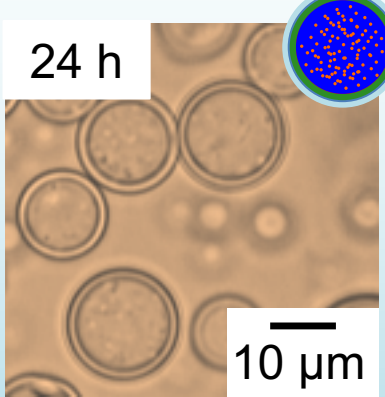
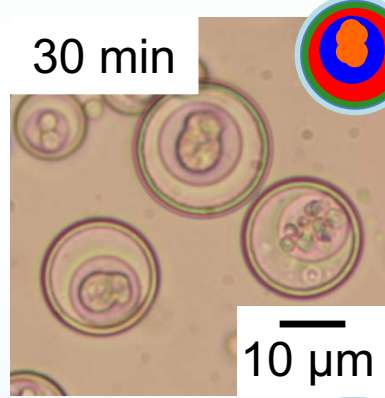
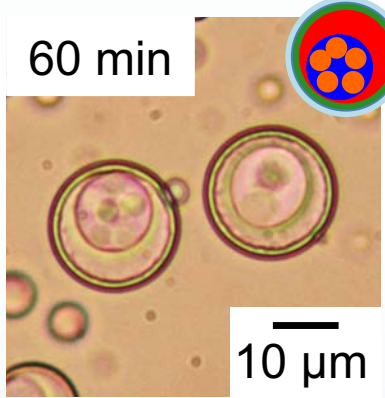
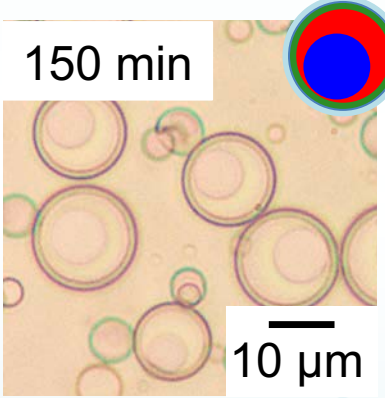
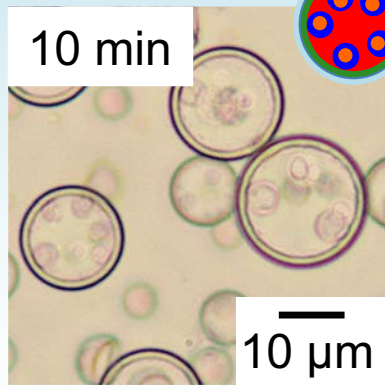
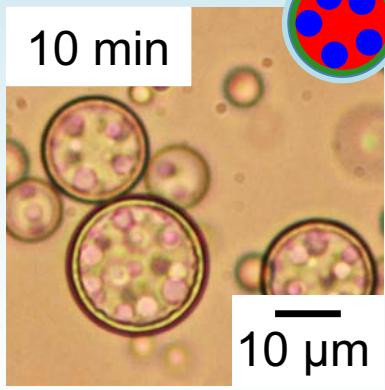
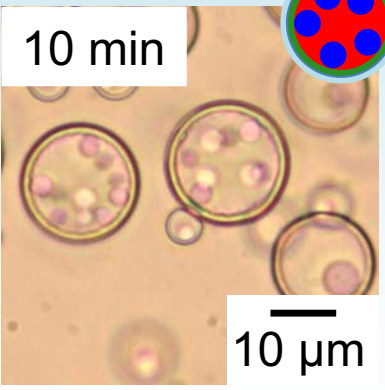
各アンモニア濃度におけるカプセル内ゾルゲル反応

NH₃/TEOS
(molar ratio)

1

10

50



NH_3/TEOS
(molar ratio)

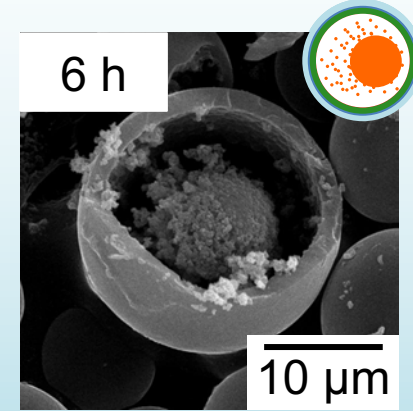
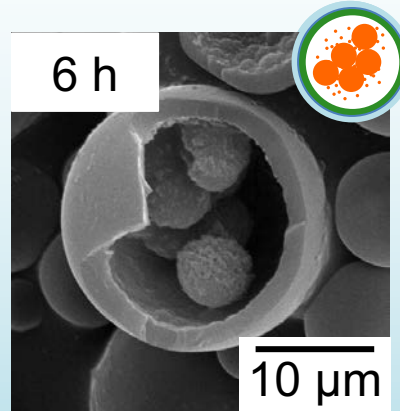
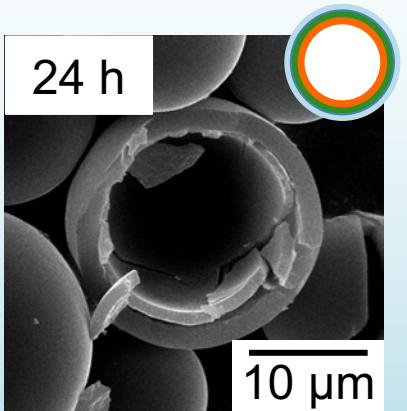
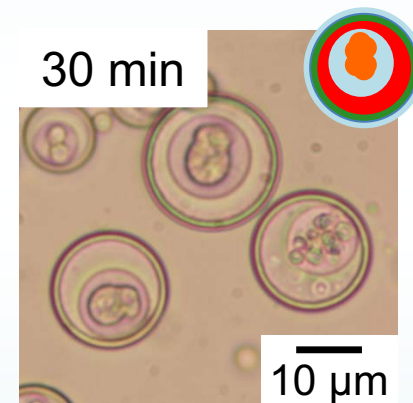
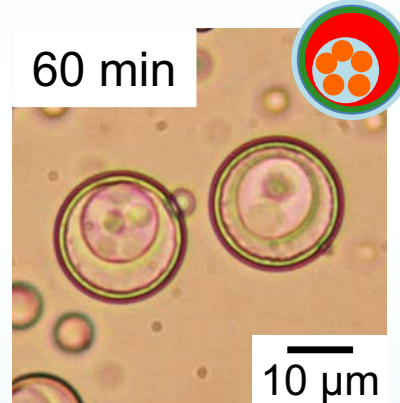
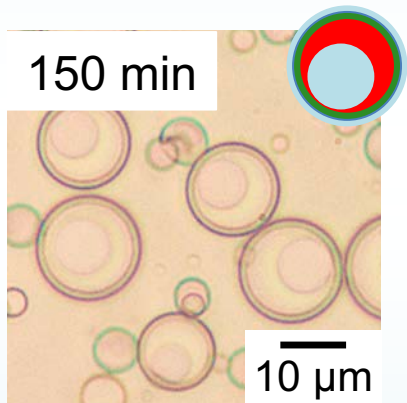
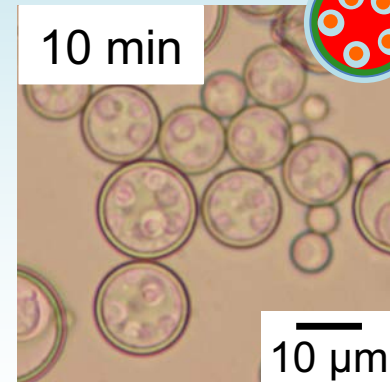
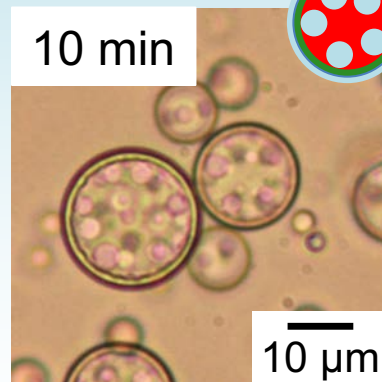
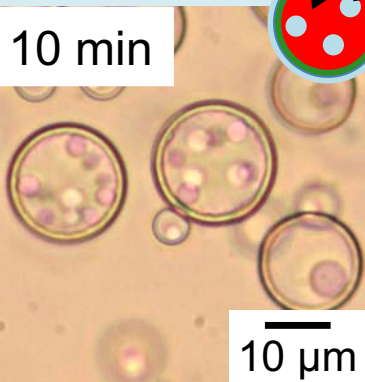
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TEOS

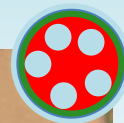
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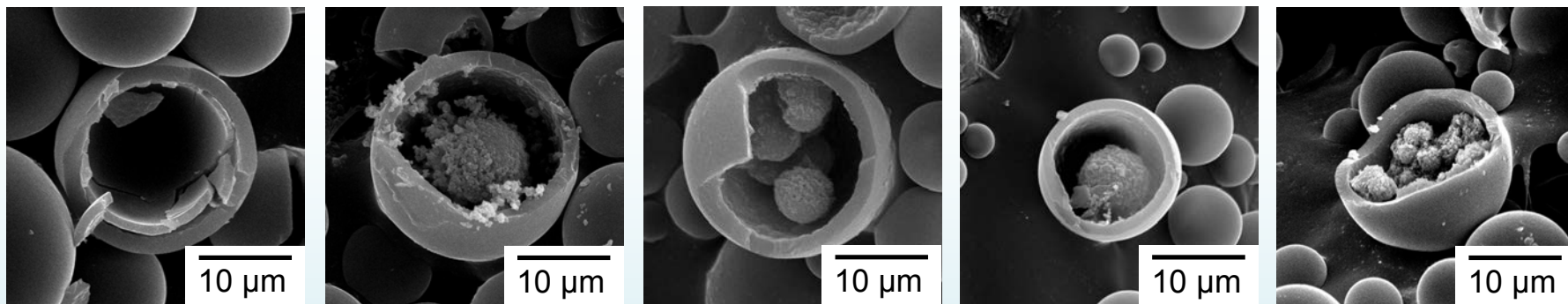
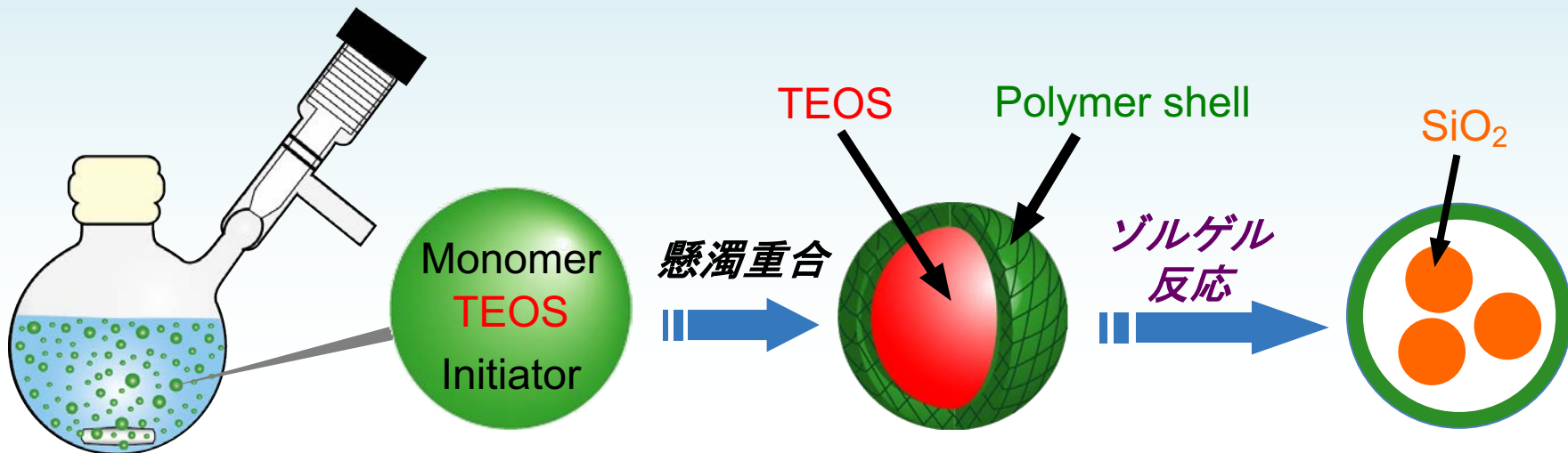
50



Reaction time



シリカ粒子内包カプセルのワンポット作製法の確立



水ドメインの合一挙動



シリカ粒子のモルフォロジー