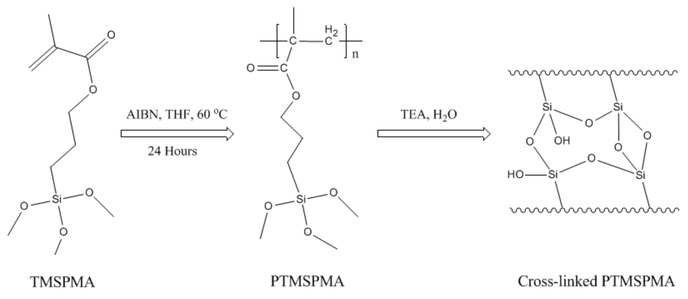
Facile Fabrication of Polymer Nano-capsules with Cross-linked Organic-Inorganic Hybrid Walls

Tianyou Chen, Binyang Du, Zhiqiang Fan

Brief Introduction

A facile method was developed for the fabrication of polymer nano-capsules with organic-inorganic hybrid walls and controllable morphologies from a cross-linkable polymer, poly[3-(trimethoxysilyl)propyl methacrylate] (PTMSPMA). With the combination of emulsion, hydrolysis and condensation reaction as well as the internal phase separation, cross-linked PTMSPMA nano-capsules with classic hollow structures, collapsed hollow structures with Kippah and muti-fold morphologies could be successfully obtained by simply mixing the toluene solution of PTMSPMA with water under vigorous stirring for 48 hrs at different temperatures. The hydrolysis and condensation of methoxysilyl groups resulted in the phase separation of PTMSPMA inside the toluene droplets and the migration of PTMSPMA to the interface of toluene and water. The cross-linking reaction of methoxysilyl groups further fixed the interfacial phase of PTMSPMA, leading the formation of PTMSPMA nano-capsules with robustly cross-linked organic-inorganic hybrid walls.

Fabrication and Characterizations



Scheme 1. Schematic of free radical polymerization of TMSPMA and the hydrolysis and condensation reactions of PTMSPMA.

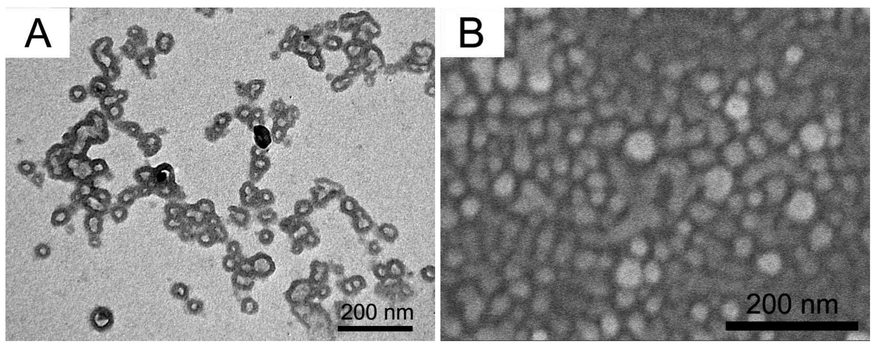


Figure 1. Morphologies of the cross-linked PTMSPMA nano-capsules obtained at 50 °C. (A) TEM image, and (B) SEM image.

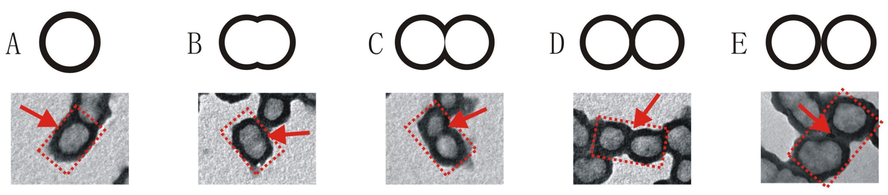


Figure 2. The fusion events of cross-linked PTMSPMA nano-capsules with classic hollow structures obtained at 50 °C.

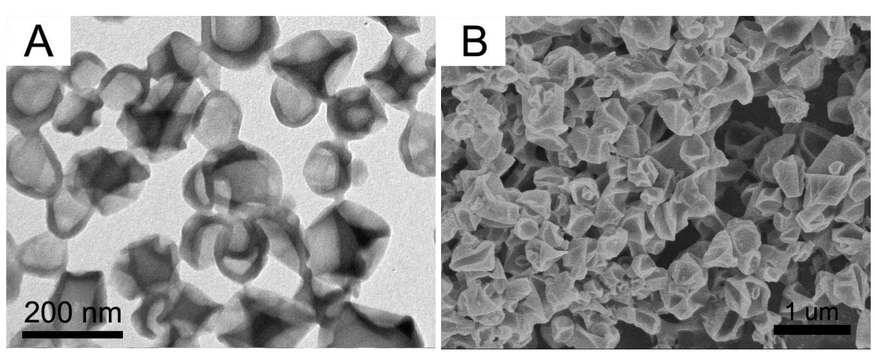


Figure 3. Morphologies of the cross-linked PTMSPMA nano-capsules obtained at 25 °C. (A) TEM image, and (B) SEM image.

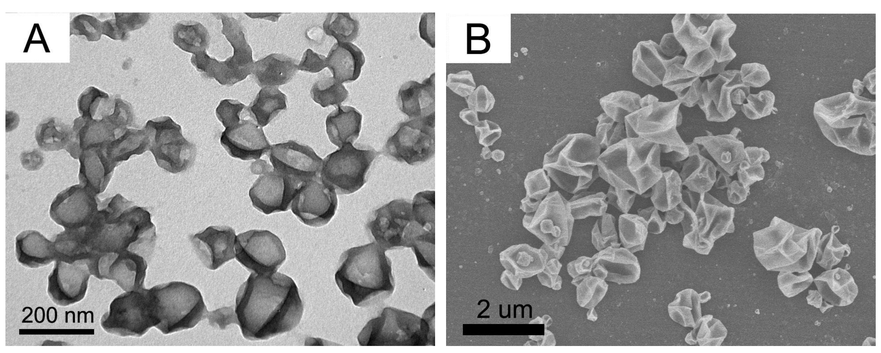
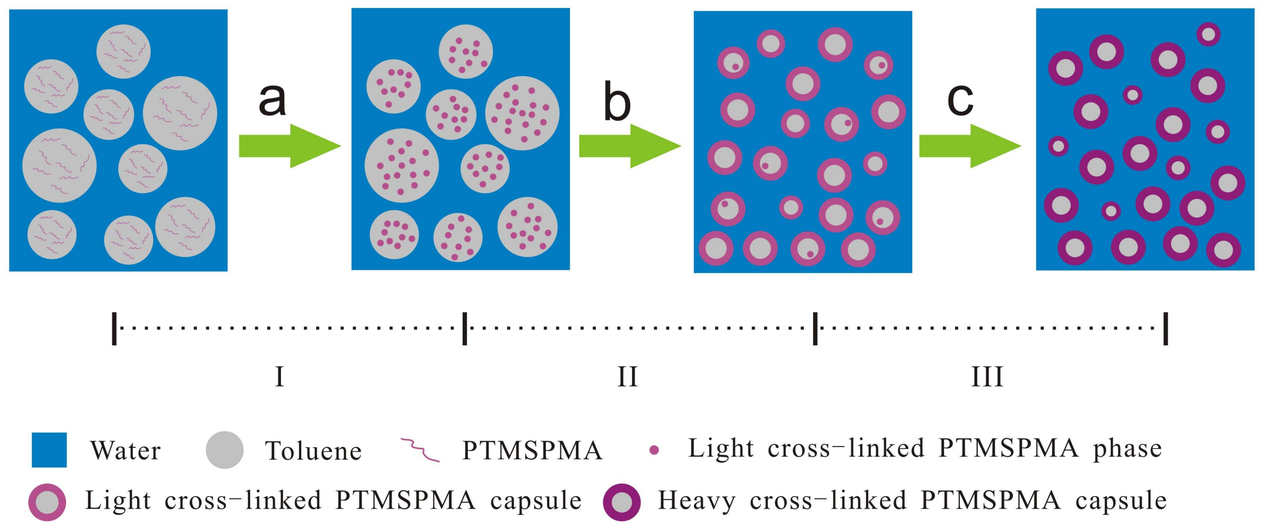
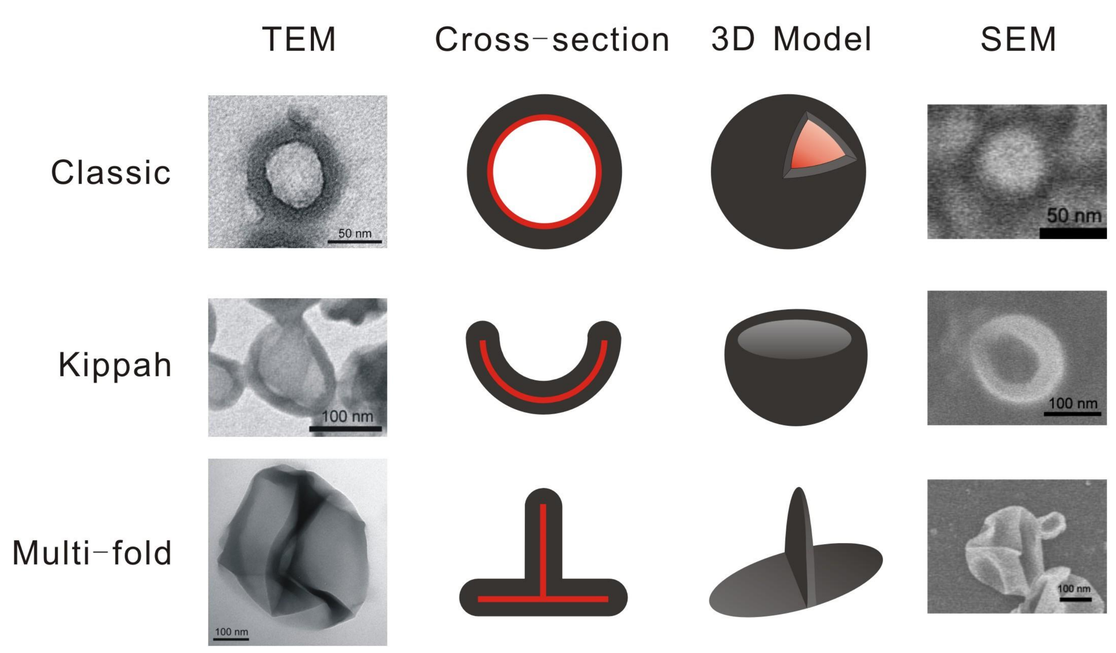


Figure 4. Morphologies of the cross-linked PTMSPMA nano-capsules obtained at 2 °C. (A) TEM image, and (B) SEM image.



Scheme 2. The proposed mechanism of the formation of cross-linked PTMSPMA nano-capsules via three stages, i.e. the interface energy controlled stage I, the viscosity controlled stage II, and the elasticity controlled stage III. Process **a** presents the initial hydrolysis and condensation of some methoxysilyl groups, resulting in the internal phase separation within the toluene droplets. Process **b** presents the migration of light cross-linked PTMSPMA phase to the interfacial region of toluene droplets and water, forming the interfacial PTMSPMA shells. Process **c** presents the further hydrolysis and condensation of residual methoxysilyl groups and the formation of robust cross-linked PTMSPMA shells.



Scheme 3. Summarized morphologies and structures of the cross-linked PTMSPMA nano-capsules obtained in the present work. The red portion in cross-section presents the boundary of the collapsed walls of the hollow nano-capsules.

Conclusions

The PTMSPMA nano-capsules with robustly cross-linked organic-inorganic walls were successfully obtained by simply mixing the toluene solution of PTMSPMA with water under vigorous stirring. The hydrolysis and condensation of methoxysilyl groups of PTMSPMA at the interfacial of toluene droplets and continuous water phase led to the formation of cross-linked hollow nano-capsules. The morphologies of the cross-linked PTMSPMA nano-capsules could be controlled by varying the reaction temperatures. Such nano-capsules with robustly cross-linked structures may find potential applications for the encapsulations of catalysts, dyes, and other functional species.

References

(1). Azzam, T.; Eisenberg, A., Fully Collapsed (Kippah) Vesicles: Preparation and Characterization. *Langmuir* **2010,** 26, 10513-10523.

(2). Du, J. Z.; Chen, Y. M.; Zhang, Y. H.; Han, C. C.; Fischer, K.; Schmidt, M., Organic/inorganic hybrid vesicles based on a reactive block copolymer. *J. Am. Chem. Soc.* **2003,** 125, 14710-14711.

The authors thank the National Natural Science Foundation of China for financial support.