The 6th Waseda-NIMS International Symposium

'Polymeric Micelle Assembly' for Synthesis of Porous Materials with Highly Crystallized Frameworks

Yusuke Yamauchi^{1,2}*

1 National Institute for Materials Science (NIMS), 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan.

2 Department of Nanoscience and Nanoengineering, Faculty of Science and Engineering, Waseda University, 3-4-1 Okubo, Shinjuku, Tokyo 169-8555, Japan.

*E-mail address: <u>Yamauchi.Yusuke@nims.go.jp</u>

Polymeric micelles are formed in solution when the hydrophobic portions are driven to an interior structure while hydrophilic portions are turned outward facing toward the water. Recently, we have focused on the polymeric micelles as stable and rigid templates for obtaining mesoporous materials with ultra large pore sizes.[1-3] Our 'polymeric micelle assembly' approach is highly useful for preparation of novel mesoporous materials which are not easily obtained by general synthetic approaches. As one example, mesoporous gold (Au) films with tunable pores are expected to provide fascinating optical properties stimulated by the mesospaces, but they have not been realized yet because of the difficulty of controlling the Au crystal growth. Very recently, we reported a reliable synthesis of mesoporous Au films using stable micelles of polystyrene-block-poly(oxyethylene) (PS-*b*-PEO) diblock copolymers, with electrochemical deposition advantageous for precise control of Au crystal growth.[3] In the electrolyte solution, HAuCl₄ is dissolved into H_3O^+ and AuCl⁴⁻ ions and then interacts with the EO shells of the micelles through hydrogen bonding. This interaction favours H_3O^+ rather than AuCl₄, and consequently creates positively charged micelles that can be directed to the working electrode surfaces, where the AuCl₄ ions are reduced to metallic Au with the electrochemical deposition of the micelles. The resultant mesoporous Au films actually exhibit high scattering performance and thus high activity for molecular sensing. Significantly, enhanced electric field (E-field) amplitude is clearly seen inside or at the perimeter of the mesopores. In this presentation, we would like to introduce our recent progress on new mesoporous/nanoporous materials as well.[4-7]



Fig. 1 | (a) Schematic illustration for the fabrication of mesoporous Au films by using polymer micelle assemblies. (b, c) TEM images of PS-*b*-PEO micelles formed in aqueous solution (b) without and (c) with HAuCl₄ source. The Tyndall effect is also shown as an inset image.

References

- [1] J. Tang, Y. Yamauchi* et al., Angew. Chem. Int. Ed., 54, 588 (2015).
- [2] B. P. Bastakoti, Y. Yamauchi* et al., Angew. Chem. Int. Ed., 54, 4222 (2015).
- [3] C. Li, Y. Yamauchi* et al., Nat. Commun., 6, 6608 (2015).
- [4] J. Tang, Y. Yamauchi* et al., J. Am. Chem. Soc., 137, 1572 (2015).
- [5] L. K. Shrestha, Y. Yamauchi* et al., Angew. Chem. Int. Ed., 54, 951 (2015).
- [6] Y. Li, Y. Yamauchi* et al., Angew. Chem. Int. Ed., in press (2015).
- [7] C. Li, Y. Yamauchi* et al., J. Am. Chem. Soc., in press (2015).