

Electronic Supplementary Information for

**Influence of gold species (AuCl_4^- and AuCl_2^-) on self-assembly of PS-
b-P2VP in solutions and morphology of composite thin films
fabricated at the air/liquid interfaces**

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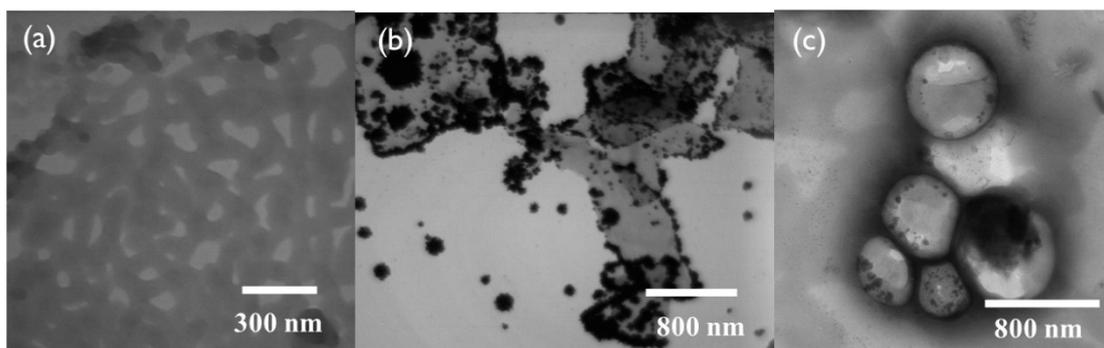


Fig. S1. TEM micrographs of the aggregates formed in the upper-phase (the aqueous solution) with HAuCl_4 (a, b) and HAuCl_2 (c), respectively.

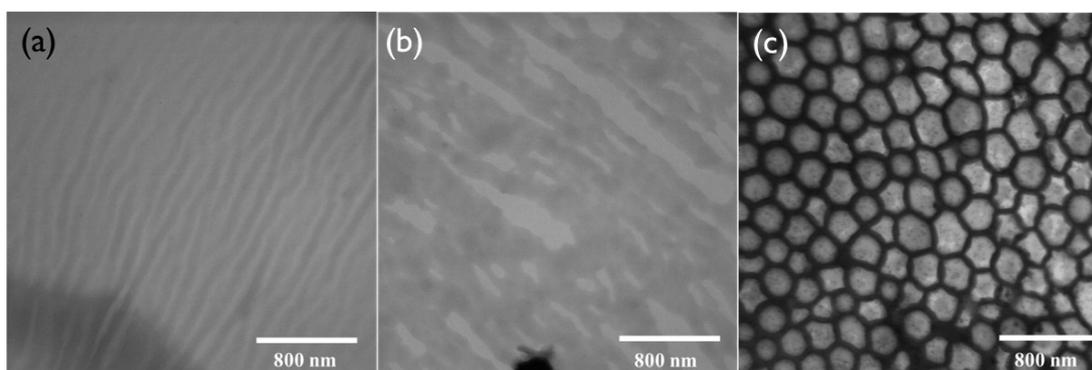


Fig. S2. TEM micrographs of thin films formed at the air/water interface with a polymer concentration of 0.4 mg mL^{-1} (a) and 0.1 mg mL^{-1} (b, c), respectively. The volumes of the aqueous solution and the organic phase are both 5 mL , $V_{\text{DMF}}/V_{\text{CHCl}_3} = 6/4$, and the AuCl_4^- concentration is 0.001 mol L^{-1} .

The concentration of PS-*b*-P2VP has an influence on the morphology of the film. As shown in Fig S2a, a nanowire array where the nanowires arranged parallelly formed at the interface when using a 0.4 mg mL^{-1} polymer solution. The formation process is the same as described in the text when using the 0.2 mg mL^{-1} polymer solution. When the polymer concentration was decreased to 0.1 mg mL^{-1} , sparse nanowires appeared (Fig S1b), because there were not efficient polymer molecules in this case. In addition to the nanowires, foam structure formed in the film (Fig S1c). This should also be attributed to the lack of the polymer molecules. Compared with the solutions with higher concentrations (0.4 and 0.2 mg mL^{-1}), less polymer molecules transferred with DMF

from the organic phase to the aqueous solution in this case. This may affect the existing state of the polymer molecules around the droplets, and affect the interaction between these molecules. The critical packing parameter p may increase, resulting in the formation of microcapsules.

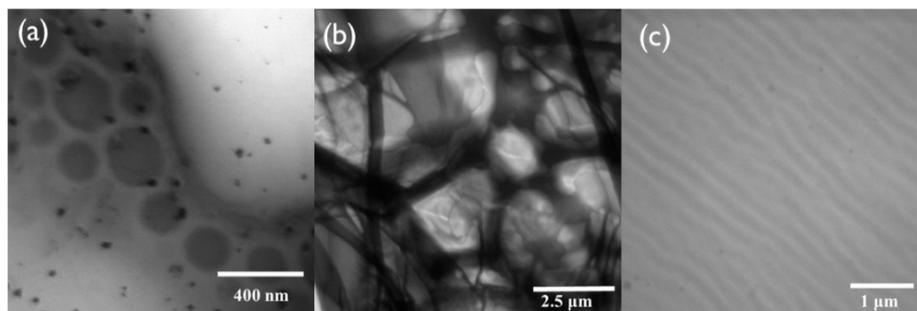


Fig. S3. TEM micrographs of thin films formed at the air/water interface: (a) $V_{\text{DMF}}/V_{\text{CHCl}_3} = 4/6$; (b, c) $V_{\text{DMF}}/V_{\text{CHCl}_3} = 8/2$. The volumes of the aqueous solution and the organic phase are both 5 mL, the concentrations of polymer and AuCl_4^- are 0.2 mg mL^{-1} and 0.001 mol L^{-1} , respectively.

The volume ratio of DMF/ CHCl_3 has a crucial influence on the formed microstructures. As shown in Fig. S3a, with a $V_{\text{DMF}}/V_{\text{CHCl}_3}$ ratio of 4/6, microcapsules were observed at the air/liquid interface. Compared with the 6/4 system, in this case, more CHCl_3 transferred into the aqueous solution with DMF and would form droplets. It is possible that DMF would not be able to diffuse into the water completely in this case because of the miscibility of DMF and CHCl_3 . The PS-*b*-P2VP molecules assembled around the remaining droplets and formed the microcapsules that adsorbed at the air/liquid interface at last. However, when the volume ratio changed to 8/2, both a foam structure and nanowires appeared in the film (Fig. S3b and c). In this case, the amount of CHCl_3 in the droplet decreased compared with that of the 6/4 system. A larger concentration of CHCl_3 caused the PS chains to freely disperse (for the 4/6 system), resulting in the formation of the microcapsules; an appropriate amount of CHCl_3 appears to behave similar to “glue” to hold the PS chains together to form micelle cores (for the 6/4 system), resulting in the formation of the cylindrical micelles. While for the 8/2 system, the interaction between the PS chains would weaken with a further reduced amount of CHCl_3 in the droplets, causing the PS chains to become freely dispersed, ultimately resulting in an increase in the value of p and the formation of microcapsules. It was concluded that the composition of the mixed solvent greatly affects the

microstructure of the films.

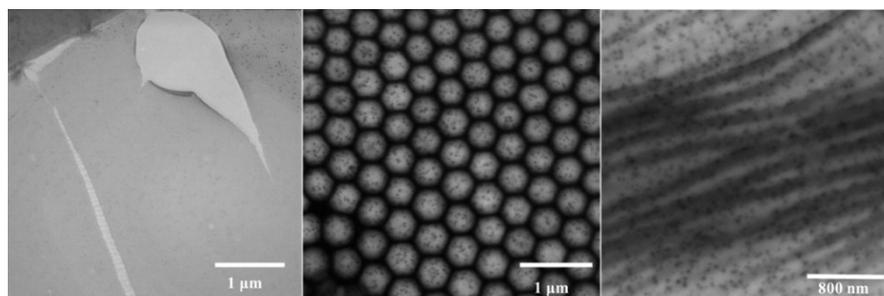


Fig. S4. TEM micrographs of thin films formed at the air/liquid interface. The volume ratios of the organic and aqueous solutions are 5/2 (a) and 5/10 (b, c), respectively. The volumes of the organic phase are both 5 mL, the concentrations of polymer and AuCl_4^- are 0.2 mg mL^{-1} and 0.001 mol L^{-1} , respectively.

The volume ratios of the organic and aqueous solutions also greatly influenced the formation of microstructures. As shown in Fig. S4a, when the volume ratio was 5/2, a laminar film formed at the interface. In this case, a smaller amount of the organic solution transferred into the aqueous solution in comparison with the typical condition, because only 2 mL aqueous solution was used as the upper phase. Thus, excepted for the background film formed through Gibbs adsorption of the block copolymer molecules, there were insufficient numbers of PS-*b*-P2VP molecules in the aqueous solution to form other aggregates. When the volume ratio increased to 5/10, a foam structure and nanowires formed in the film (Fig. S4b and c). In this case, a large amount of organic solution entered the water phase rapidly and large numbers of cylindrical micelles formed. The formation of these micelles led to the rapid consumption of a large amount of polymer molecules and AuCl_4^- ions. The depletion of the polymer molecules was possibly faster than the diffusion of DMF; and the consumption of the AuCl_4^- ions led to great decrease of the AuCl_4^- concentration around the droplets. Thus, the polymer molecules with a p value closing to 1 in this case self-assembled into microcapsules around the DMF droplets, resulting in the formation of foam structures.

It was seen that microcapsules and foam structures appeared under different conditions. However, these foam structures have different formation mechanism.