

Electronic supplementary information (ESI)

For

**Fabrication of porous thin films of block copolymer at the  
liquid/liquid interface and construction of composite films  
doped with noble metal nanoparticles**

Qian Wang,<sup>a</sup> Xingjuan Zhao,<sup>a</sup> Xiao-Kai Zhang,<sup>b</sup> Yong-Il Lee<sup>c</sup> and Hong-Guo  
Liu<sup>\*a</sup>

<sup>a</sup> Key Laboratory for Colloid and Interface Chemistry of Education Ministry, Shandong  
University, Jinan 250100, P. R. China

<sup>b</sup> College of Physics and Electronics, Shandong Normal University, Jinan 250014, P. R.  
China

<sup>c</sup> Anastro Laboratory, Department of Chemistry, Changwon National University, Changwon  
641-773, Korea.

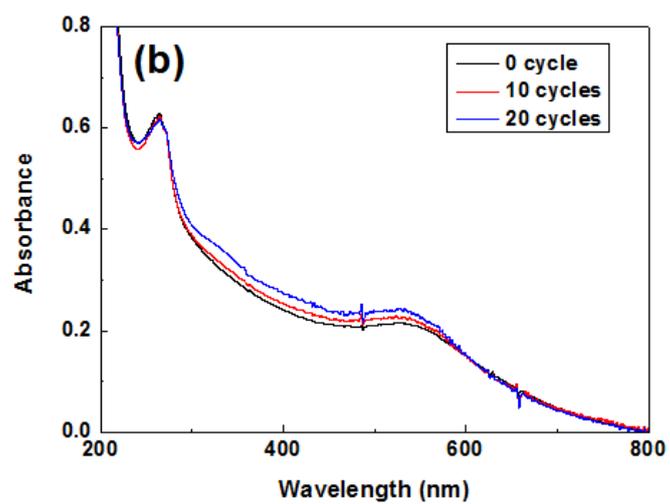
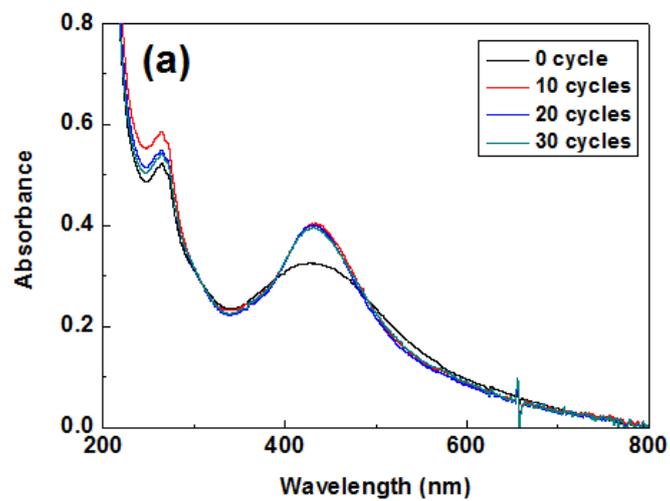


Figure S1 UV-vis spectra of the composite thin films of PI-b-P2VP/Ag (a) and PI-b-P2VP/Au (b) formed through route 1 after catalyzing the reduction of 4-NP for different cycles.

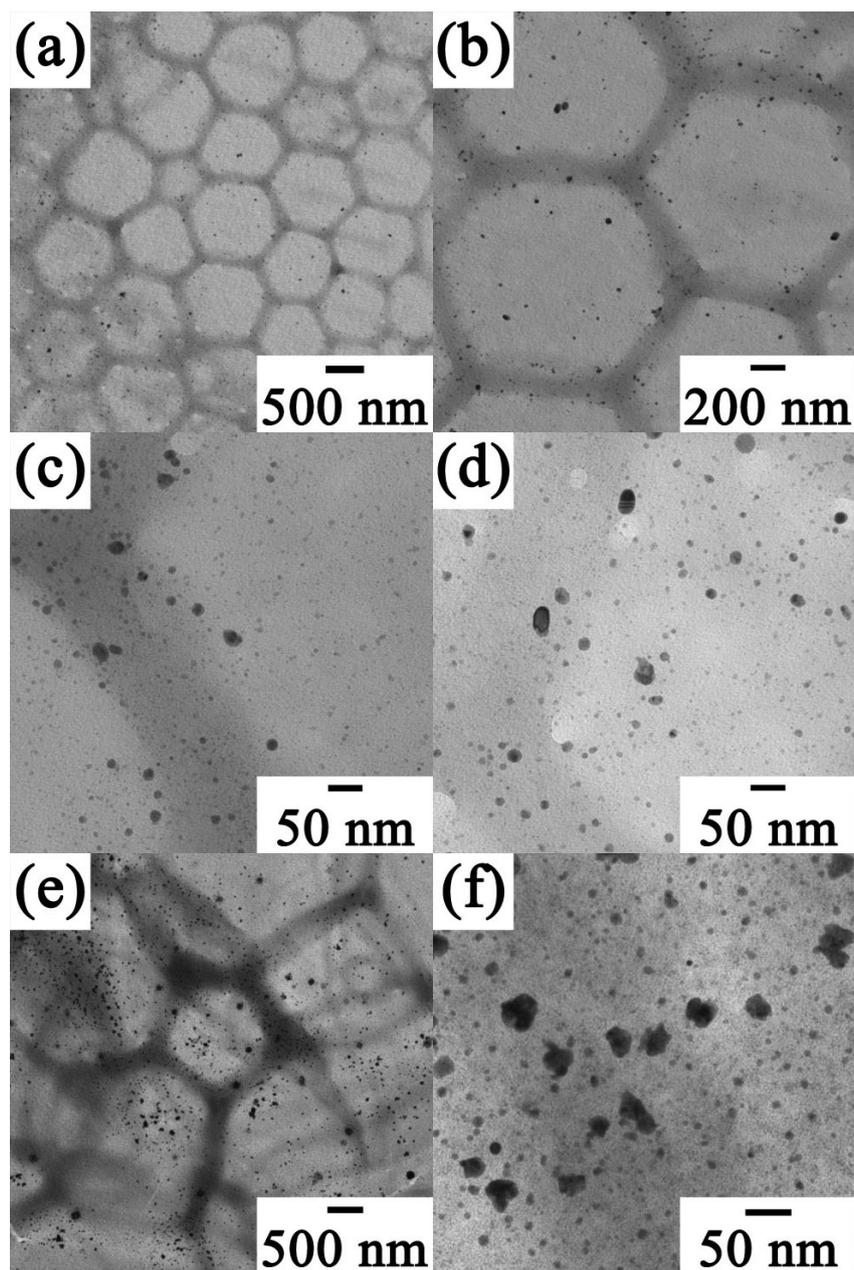


Figure S2. TEM micrographs of the composite PI-b-P2VP/Ag (a-d) and PI-b-P2VP/Au (e, f) films formed through route 1 after 30 catalytic cycles.

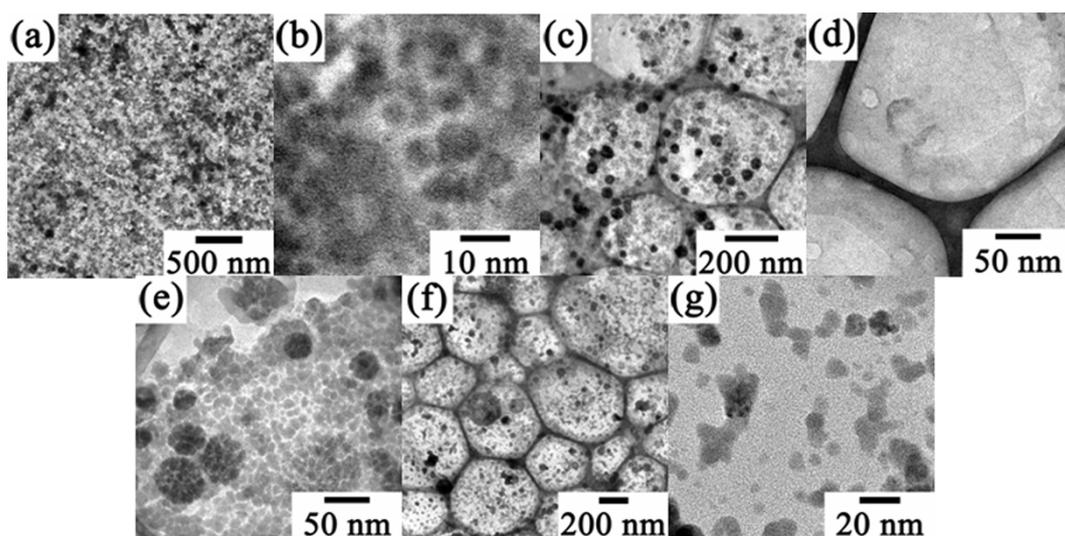


Fig. 3 TEM micrographs of as-prepared composite thin films of PI-b-P2VP/Ag (a-e) formed at the crosslinked polymer chloroform solution/ $\text{AgNO}_3$  aqueous solution interface and after treatment with  $\text{KBH}_4$  aqueous solution (f, g). The concentration of PI-b-P2VP was  $0.2 \text{ mg mL}^{-1}$ , and the  $\text{AgNO}_3$  concentrations were  $1 \times 10^{-2}$  (a, b), and  $1 \times 10^{-3} \text{ mol L}^{-1}$  (c-g).

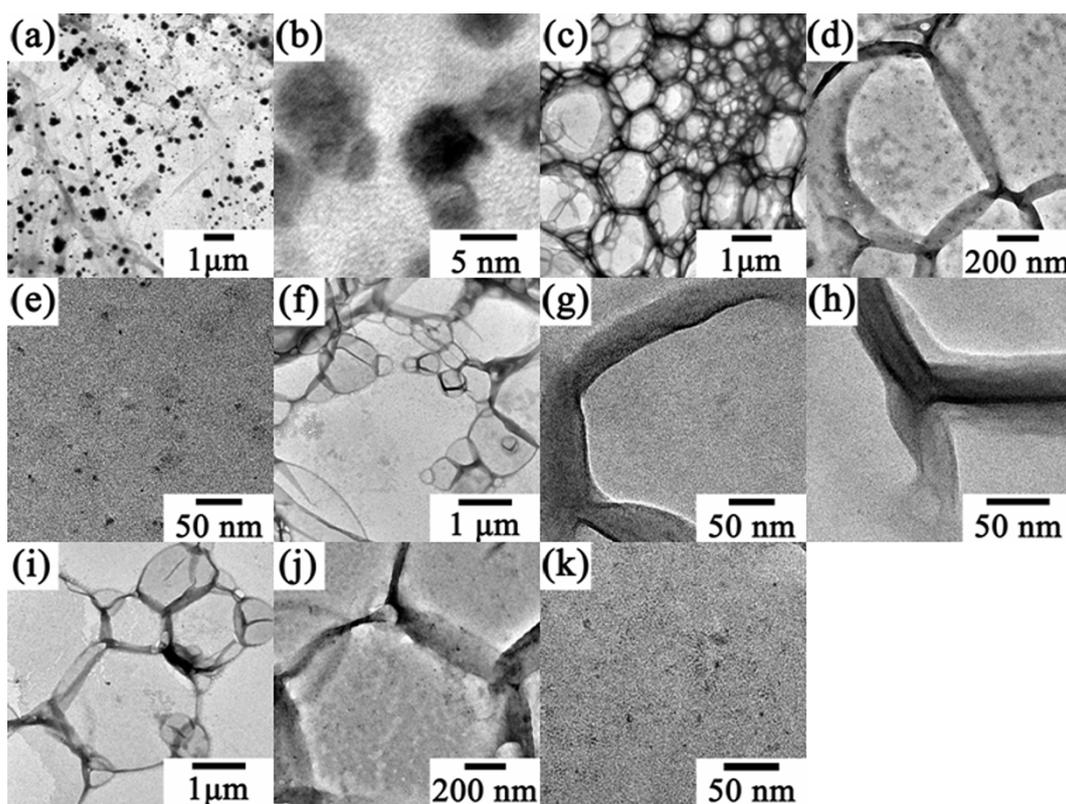


Fig. S4 TEM micrographs of composite thin films of PI-b-P2VP/Au formed at the crosslinked polymer chloroform solution/ $\text{HAuCl}_4$  aqueous solution interface. The concentration of PI-b-P2VP was  $0.2 \text{ mg mL}^{-1}$ , and the concentrations of  $\text{HAuCl}_4$  were  $1 \times 10^{-3}$  (a, b),  $2 \times 10^{-4}$  (c-h),  $2 \times 10^{-4} \text{ mol L}^{-1}$ ; after treatment with  $\text{KBH}_4$  aqueous solution (i-k).

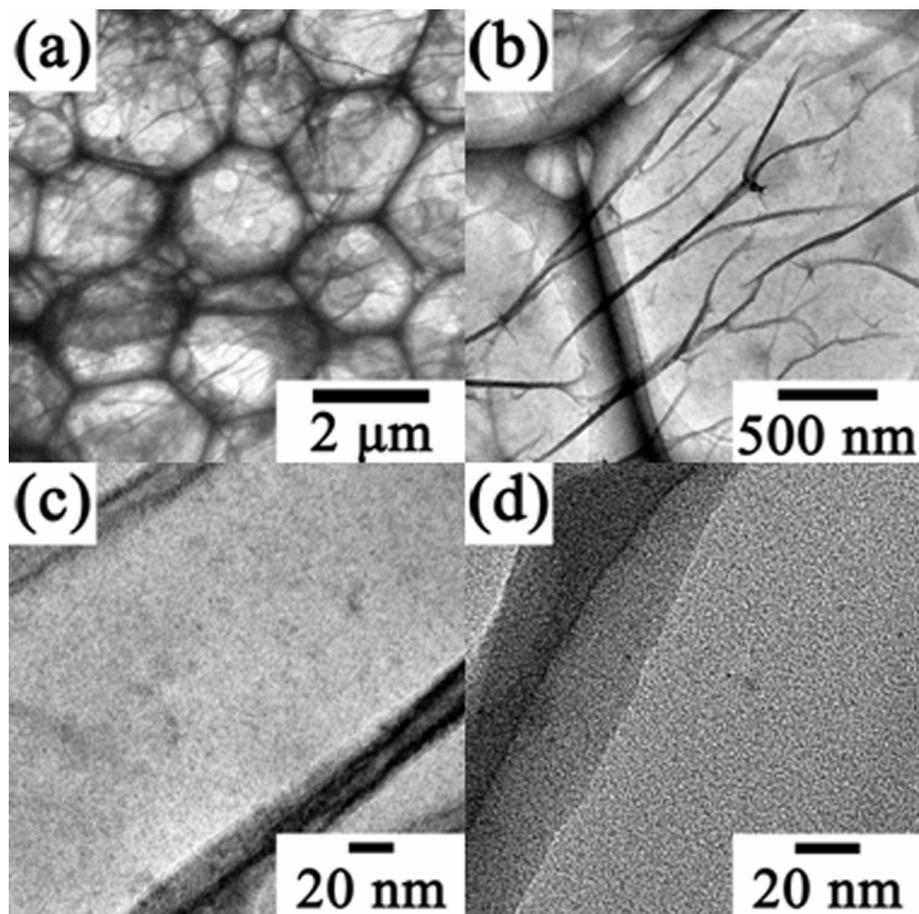


Fig. S5 TEM micrographs of the PI-b-P2VP/Pt composite thin film that formed at the crosslinked polymer chloroform solution/ $\text{H}_2\text{PtCl}_6$  aqueous solution interface. The concentrations of PI-b-P2VP and  $\text{H}_2\text{PtCl}_6$  were  $0.2 \text{ mg mL}^{-1}$  and  $1 \times 10^{-3} \text{ mol L}^{-1}$ , respectively.

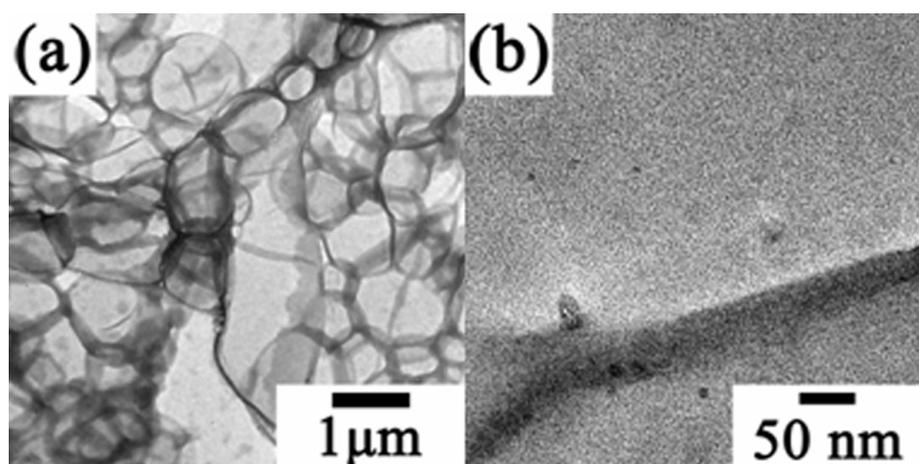


Fig. S6 TEM micrographs of the PI-b-P2VP/Eu formed composite thin film formed at the crosslinked polymer chloroform solution/ $\text{Eu}(\text{NO}_3)_3$  aqueous solution interface. The concentrations of PI-b-P2VP and  $\text{Eu}(\text{NO}_3)_3$  were  $0.2 \text{ mg mL}^{-1}$  and  $1 \times 10^{-3} \text{ mol L}^{-1}$ , respectively.

Fig. S3 shows the TEM micrographs of the composite thin films of PI-b-P2VP/Ag. At first, we used an  $\text{AgNO}_3$  aqueous solution with a concentration of  $1 \times 10^{-2} \text{ mol L}^{-1}$ . The whole film was covered by Ag nanoparticle aggregates, as shown in Fig. S3(a) and (b), and the microstructure formed by the polymer was unclear. When the concentration of the  $\text{AgNO}_3$  aqueous solution was reduced to  $1 \times 10^{-3} \text{ mol L}^{-1}$ , it can be seen that a foam film composed of microcapsules formed (Fig. S3(c-e)). The walls of some of the microcapsules are decorated with nanoparticle aggregates (Fig. S3(c) and (e)), and the walls of some microcapsules are blank without any aggregates (Fig. S3(d)). This indicates that the nanoparticles are not embedded in the polymer matrices; instead, they cover and adhere to the surface of the polymer foam structure. After treatment with the  $\text{KBH}_4$  aqueous solution, silver particles were generated (Fig. S3(f) and (g)). In addition, it can be seen clearly from Fig. 1 and Fig. S3 that the foam structure formed by the pre-crosslinked polymer obviously differs from the honeycomb structure formed by PI-b-P2VP, indicating the great effects of crosslinking of the polymer on the film formation process and structure.

The TEM micrographs of the crosslinked PI-b-P2VP/Au composite films are shown in Fig. S4. When the concentration of the  $\text{HAuCl}_4$  aqueous solution was  $1 \times 10^{-3} \text{ mol L}^{-1}$ , there were many big particles on the film surface and the foam structure of the film appeared indistinct (Fig. S4(a) and (b)). Upon reduction of the concentration to  $2 \times 10^{-4} \text{ mol L}^{-1}$ , a foam structure formed (Fig. S4(c) and (f)). From the high-magnification images one can see that the walls of some of the microcapsules are decorated with nanoparticles (Fig. S4(d) and (e)), while the walls of other microcapsules do not have any visible clusters at all (Fig. S4(g) and (h)). The morphology and structure of the PI-b-P2VP/Au film are similar to those of the PI-b-P2VP/Ag film. These results provide us with a hint that the film formation seems independent of the inorganic species in the aqueous solution. In this case the foam structure of the film was preserved and some nanoparticles were generated after treatment with  $\text{KBH}_4$  aqueous solution (Fig. S4(i-k)), indicating the stability of the film.

We have also used  $\text{H}_2\text{PtCl}_6$  and  $\text{Eu}(\text{NO}_3)_3$  aqueous solutions at a concentration of  $1 \times 10^{-3} \text{ mol L}^{-1}$  as the aqueous phase to fabricate composite films with the pre-crosslinked PI-b-P2VP chloroform solution. A foam film composed of a large amount of microcapsules with diameters from several hundreds of nanometers to several micrometers formed when an

aqueous solution of  $\text{H}_2\text{PtCl}_6$  was used (Fig. S5), and a multi-layer foam structure formed when an aqueous solution of  $\text{Eu}(\text{NO}_3)_3$  was used (Fig. S6). Although some small particles can be distinguished in the high-magnification images of these two films, we were unable to detect Pt or Eu in the EDS spectra. These results show that neither Pt nor Eu existed in the films, indicating that the formation of the foam film is independent from the inorganic species. These results also confirm that the Au and Ag nanoparticles actually adhered to the surface of the foam film, because  $\text{Ag}^+$  and  $\text{AuCl}_4^-$  are easily reduced by small amounts of alcohol, the residual  $\text{S}_2\text{Cl}_2$  in the chloroform solution and by other species.