Electric Supplement Information

A facile method for the construction of stable polymer-inorganic nanoparticle composite multilayers



E. S. I. Fig. 1. TEM images of Fe₃O₄ NPs. The diameters of the nanoparticles are 5-10 nm.



E. S. I. Fig. 2. The UV-vis spectra involved in the process of determination of the amount of DAS loaded into the $(PAH/Fe_3O_4 NPs)_7PAH$ multilayers. (a) UV-vis spectra of the composite multilayers before and after the loading of DAS, and the spectra for the multilayers after elution of DAS. (b) UV-vis spectra of the eluent containing DAS.



E. S. I. Fig. 3. (a) TEM images of Au NPs. (b) Counting from (a), the size distribution of Au NPs is shown as the histogram of frequency versus particle size. The average diameters of the nanoparticles are around 17 nm.



E. S. I. Fig. 4. Absorption spectra of the multilayers of $(PAH/Au NPs)_7PAH$ before (1) and after(2) experiencing the agitating circumstance, which is ultrasonication in aqueous solution of DMF and $ZnCl_2$ (H₂O: DMF: $ZnCl_2=$ 3:5:2 w/w/w) for 30 min.



E. S. I. Fig. 5. UV-vis spectra to follow the infiltration of DAS into the composite multilayers (PAH/Au NPs)₇PAH. The inset plots the absorbance at 340 nm which is characteristic to DAS a function of time, and indicates that the infiltration reaches equilibrium within 10 min.



E. S. I. Fig. 6. The UV-vis spectra involved in the process of determination of the amount of DAS loaded into the (PAH/Au NPs)₇PAH multilayers. (a) UV-vis spectra of the composite multilayers before and after the loading of DAS, and the spectra for the multilayers after elution of DAS. (b) UV-vis spectra of the eluent containing DAS.



E. S. I. Fig. 7. UV-vis spectra of the multilayers after the infiltration of DAS under the irradiation of UV light. The absorption band at around 340 nm decreased rapidly, indicating that the photochemical reaction completed within 5 s.



E. S. I. Fig. 8. Tapping-mode AFM images show the surface morphologies of the composite multilayers. (a) $(PAH/Au NPs)_7PAH$ multilayers; (b) $(PAH/Au NPs)_7PAH$ multilayers infiltrated with DAS and (c) photochemically induced cross-linked multilayers. The images a-c each display an area of $5 \times 5 \mu m$.



E. S. I. Fig. 9. UV-visible spectra of the photo crosslinked $(PAH/Fe_3O_4)_{7.5}$ multilayers before (black line) and after (red line) immersion in aqueous solutions of (a) NaOH (pH=13), (b) HCl (pH=1) and (c) NaCl (1 M) for 30 min, respectively. The residual amount of the multilayers after basic, acidic and salty erosion is 90.34%, 95.43%, and 97.18%, correspondingly.



E. S. I. Fig. 10. UV-visible curves (bottom up) of (PAH/Fe₃O₄ NPs)₈ multilayer after stepwise adsorption of DAS (5 mg/mL, pH=3.8) with increasing immersion time. The inset is the absorbance of the multilayer at 340 nm versus the corresponding absorbing time.

To clarify the point that the infiltration of DAS should not only be related to the outmost layer PAH, but also to the inside PAH, we carried out the kinetics of DAS loading process into the multilayer of $(PAH/Fe_3O_4 NPs)_8$, which had Fe_3O_4 nanoparticles as its outmost layer. We immersed this film into identical DAS solution (5 mg/mL, pH=3.8) with different time and traced the absorbance of DAS at 340 nm after each immersion. The UV-visible spectra for the adsorption of DAS and the absorbance at 340 nm versus loading time were obtained as Fig. S10. From the inset of Fig. S10, we can observe that the loading of DAS reaches a equilibrium after 1 h, which is slower than the adsorption when PAH is the outmost layer (10 min); the saturated absorbance at 340 nm is 0.304, which is lower than the saturated value of 0.312 when PAH is outmost. This phenomenon is rationalized that the nanoparticles stabilized with negative charged species may somewhat prevent the loading of the negative DAS molecules. However, due to the porous and loose structure of the multilayer, DAS still could be loaded into the film.